Electron Spin Resonance Studies of The Addition of Nitrogen Dioxide to Alkenes

by

SUJANYA JANTARAWARATIT.

A thesis submitted for the degree

of

DOCTOR OF PHILOSOPHY

of

The University of Aston in Birmingham

December, 1980

The work described in this thesis was carried out between 1977 and 1980 at the University of Aston in Birmingham. It has been carried out independently and has not been submitted for any other degree.

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ACKNOWLEDGEMENTS

The author is deeply grateful to her supervisor, Dr. D.A.F. Munday, for the guidance and encouragement given to her throughout the course of the work presented in this thesis.

The facilities made available by the Department of Chemistry which made this work possible are also acknowledged.

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Summary

The addition of solutions of nitrogen dioxide to alkenes has been studied under various reaction conditions. Solutions of low concentration of nitrogen dioxide react with alkyl-substituted alkenes to produce dialkyl nitroxides, and react with α, β -unsaturated carbonyl compounds to produce iminoxy radicals. Most of these reaction mixtures when kept unexposed to air, and light over a period of time showed the decay of nitroxides, and iminoxy radicals, and the formation of acyl nitroxide radicals. Other reaction conditions, for example upon exposure to oxygen, or raising reaction temperature to 100° are found to accelerate the rates of both the formation of acyl nitroxide radicals, and the disappearance of nitroxides, and iminoxy radicals.

The reactions of solutions of high concentration of nitrogen dioxide with alkenes are found to produce mixtures of nitroxides, or iminoxy radicals, together with acyl nitroxide radicals.

The reactions of alkenes with nitric oxide in the presence of a trace of nitrogen dioxide provide the information that vic-nitronitrites may have major role in continuing the reactions of addition of nitrogen dioxide to alkenes to produce acyl nitroxide radicals, and other reaction products.

The effect of substituents of alkenes in deciding the radical products, and the reaction mechanisms are discussed.

Finally, the existence of β-nitroalkyl radicals which are initial radicals formed from addition of nitrogen dioxide to alkenes is confirmed by employing nitrosobenzene as spin trap.

Index Terms :

ESR

nitrogen oxides

alkenes

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Introduction to Reactions of Nitrogen Dioxide with Alkenes

CHAPTER ONE

Introduction to Reactions of Nitrogen Dioxide with Alkenes

1.1 Introduction

The reactions of nitrogen dioxide (NO_2) have been the subject of many previous investigations (J.L.Riebsomer, 1945). The results of numerous investigations have been conflicting and confusing in that the various different products of the addition of nitrogen dioxide to alkenes have been frequently reported. In the past, reactions of nitrogen dioxide were interpreted as ionic reactions. During the 1950s, evidence accumulated in favour of a radical nature of additions of nitrogen dioxide to alkenes and it is now certain that the addition reactions of nitrogen dioxide proceed by radical mechanisms (H.Shechter, and F.Conrad, 1953). In the past eighteen years the electron spin resonance spectroscopy has been applied to study the reaction mechanisms of addition reactions of nitrogen dioxide with alkenes (C.Lagercrantz, and M.Yhland, 1962), and the results have confirmed the free radical nature of nitrogen dioxide in addition reactions. This chapter therefore includes a brief account of our knowledge of chemical and physical properties and also the reaction mechanisms proposed by previous investigators. The details of the previous investigations have been reviewed elsewhere (J.L.Riebsomer, 1945; H.Shechter, and F.Conrad, 1953; P.Gray, and A.D.Yoffe, 1955a and 1955b; H.Shechter, 1964; G.Sosnovsky, 1964; and Y.Rees, and G.H.Williums, 1968).

1.2 Some Physical Properties of Nitrogen Dioxide and Related Oxides of Nitrogen.

Nitrogen dioxide (NO_2) is an odd-electron molecule with seventeen valency electrons and shows high tendency to dimerise and form dinitrogen tetroxide, N_2O_4. At room temperature, nitrogen dioxide is in equilibrium with its dimer, as shown in equation 1.1.

$$2\ NO_2 \rightleftharpoons N_2O_4 \qquad (1.1)$$

The solid (m.p. -11.2°) is colourless and diamagnetic and is assumed to contain only dinitrogen tetroxide. The liquid at the triple-point is yellow, and darkens in colour as the temperature is raised. It is diamagnetic at all temperatures, but the diamagnetism decreases with increasing temperature as more dimeric molecules dissociate. The liquid boils at 21.15°, at which temperature the vapour contains 16.1 % of the monomer and is brown. As the temperature is increased, the proportion of the monomer, and the intensity of the colour, increases; at 150° the vapour is black. At 150° nitrogen dioxide begins to decompose to nitric oxide (NO), which is a colourless gas, and to molecular oxygen and the dissociation is complete at 600°. Impure nitrogen dioxide or dinitrogen tetroxide is often green owing to the presence of dinitrogen trioxide, N_2O_3.

Nitric oxide (NO) is also a paramagnetic molecule, and has eleven valency electrons. Nitric oxide melts at -163.6° and boils at -151.7°. The gas is colourless, but the liquid has been reported as colourless, cobalt blue, and pale straw-green. It shows no marked tendency to dimerise.In the liquid state, nitric oxide exists almost entirely as the dimer, N_2O_2, and is feebly paramagnetic. In the solid state, where association is virtually complete, the dimer is still feebly paramagnetic.

1.3 The Chemical Reactions of Nitrogen Dioxide.

Chemical reactions of nitrogen dioxide have been studied in both the liquid and the gas phases. In the liquid phase and at low temperature, dinitrogen tetroxide is present and is involved in chemical reactions whereas in the gas phase and at high temperature, nitrogen dioxide is principally the species involved in chemical reactions. Kinetic data from studies in both phases suggest that it is the reactions of nitrogen dioxide and not dinitrogen tetroxide.

Since nitrogen dioxide is an odd-electron molecule, a number of its reactions belong to classes typical of free radicals, such as association reactions with radicals including dimerisation, addition to unsaturated systems, hydrogen abstraction, and under appropriate conditions substitution of hydrogen in aromatic nuclei occurs. Other of its reactions such as photolysis, decomposition, reduction, and oxidation are non-radical or owe little character in free radical type reactions. Its reactions with organic compounds have been extensively reviewed (J.L.Riebsomer, 1945; P.Gray, and A.D.Yoffe, 1955a and 1955b; A.V.Topchiev, 1959; and A.I.Titov, 1963).

1.3.1 The Association of Nitrogen Dioxide with Other Radicals

The association of nitrogen dioxide with alkyl radicals and the energetic factors determining the nature of the products have been discussed by P.Gray (1955). When nitrogen dioxide reacts with an alkyl radical, R•, two distinct modes of association are possible, according to whether it combines at a nitrogen or an oxygen atom.

$$R^\bullet + NO_2 \longrightarrow RNO_2 \qquad (1.2)$$

$$R^\bullet + NO_2 \longrightarrow RONO \qquad (1.3)$$

The products are a nitroparaffin and an alkyl nitrite respectively. Although the dissociation energies of those carbon-nitrogen and carbon-oxygen bonds are approximately equal, when the reaction yields a nitrite, the strength of the oxygen-nitrogen bond is frequently so low that the energy released on association is sufficient to break it immediately, yielding an alkoxy-radical and nitric oxide as in equation (1.4), the net effect thus being oxidation of the alkyl radical. Association of

$$R\cdot + NO_2 \longrightarrow [R\text{-}O\text{-}N\text{-}O] \longrightarrow RO\cdot + NO \qquad (1.4)$$

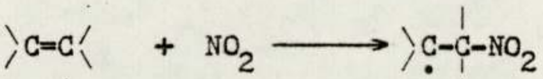
a radical and nitrogen dioxide via the oxygen atom to give a nitrite is more favourable in solution than in the gas phase, since the excessive energy is more easily removed in deactivating collisions with solvent molecules.

As well as with alkyl radicals, nitrogen dioxide also associates with other atoms and radicals, for example the hydrogen atom, fluorine atom, chlorine atom or with hydroxy and alkoxy radicals.

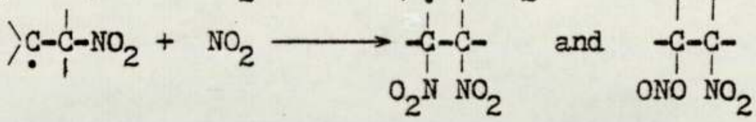
1.3.2 Addition of Nitrogen Dioxide to Unsaturated Compounds

Addition reactions of nitrogen dioxide to simple alkenes were first placed on a firm experimental basis by N.Levy, and C.W.Scaife (1946). Various interpretations of nitrogen dioxide addition reactions have been reported and most evidence favours free radical attack by nitrogen dioxide (H.Shechter, and F.Conrad, 1953).

Addition reactions of nitrogen dioxide to alkenes have been studied in the gaseous phase and in the liquid phase with and without a solvent. The primary products of the reactions are dinitro compounds and nitronitrites in nearly equal proportions. The secondary reactions give rise to other products, such as nitroalkenes, nitronitrates and nitroalcohols and these have all been found in reaction products. In the gas phase at elevated temperature, addition is followed by complete oxidation. In the liquid phase, oxidation is diminished by the presence of solvent and molecular oxygen. Addition of the first nitrogen dioxide molecule always forms nitro compounds, the second nitrogen dioxide may yield either nitro compound or nitrite as shown in equations 1.5 and 1.6.



$$\rangle C{=}C\langle \; + \; NO_2 \longrightarrow \rangle \underset{\bullet}{C}-\overset{|}{\underset{|}{C}}-NO_2 \qquad (1.5)$$



$$\rangle \underset{\bullet}{C}-\overset{|}{\underset{|}{C}}-NO_2 + NO_2 \longrightarrow -\underset{O_2N}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}- \quad \text{and} \quad -\underset{ONO}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}- \qquad (1.6)$$

The studies of reaction products of nitrogen dioxide and unsymmetrically substituted alkenes in various reaction conditions, for example in different solvent systems, varying temperatures or in the presence of oxygen molecule, provides the evidence to deduce reaction mechanisms. Direction of addition is specific in that in formation of nitronitrites, the first nitro group is always attached to the carbon atom containing the larger number of hydrogen atoms, the second nitro group is added to form either C-O-N-O or C-NO_2. With terminal alkene, the addition of the first nitro group occurs exclusively by C-N bond formation at terminal position (H.Shechter, and F.Conrad, 1953). In some cases the addition takes place irrespective of the electronic demands of groups attached to unsaturated system, for example dinitro compounds have been isolated from reaction of fluorinated alkenes and nitrogen dioxide (J.L.Knunyants, and A.V.Fokin, 1956 and 1957). This subject has been reviewed by F.W.Stacey, and J.F.Harris (1963); and H.Shechter (1964). This evidence argues against most addition reactions of nitrogen dioxide to alkenes that nitrogen dioxide is an electrophilic reagent (C.K.Ingold, and E.H.Ingold, 1947).

In 1963, the electron spin resonance spectroscopy was used to study addition reactions of nitrogen dioxide to unsaturated compounds, and stable nitroxides were reported to be reaction products (P.D.Cook et al., 1963; and M.Ebert, and J.Law, 1965). Iminoxy radicals and acyl nitroxide radicals were reported later as the reaction products of addition reactions between nitrogen dioxide and saturated or α,β-unsaturated carbonyl compounds (W.M.Fox et al., 1967). β-Nitroalkyl radicals have been proposed to be initial radical intermediates which lead to several non-radical and radical products. The esr spectra of β-nitroalkyl radicals were observed by R.M.Estefan et al., 1970; and J.R.Rowlands, and E.M.Gause, 1971.

Nitrogen dioxide also adds to acetylenic and aromatic compounds, Numerous of these compounds have been studied and a free radical mechanism is proposed for acetylenic compounds. A mechanism proposed for aromatic compounds is that at elevated temperatures under pressure nitrogen dioxide adds to the ring system and is followed by hydrogen atom abstraction by a second nitrogen dioxide molecule, but the products are formed in very low yield. The mechanism of these reactions have been described by J.L. Riebsomer, 1945; and A.I.Titov, 1949.

1.3.3 Hydrogen Abstraction Reactions

The abstraction of hydrogen from organic molecules by nitrogen dioxide always proceeds via the oxygen atom, with the production of nitrous acid and alkyl radical (equation 1.7).

$$RH + NO_2 \longrightarrow R\cdot + HONO \qquad (1.7)$$

The weaker the R-H bond, the easier the abstraction occurs. It is found that hydrogen abstraction is easiest for tertiary C-H bonds and the hardest for primary C-H bonds. Aldehydic C-H bond of CHO group is considerably weaker than in hydrocarbons. In the reactions of aldehydes with nitrogen dioxide, oxidation occurs at temperature lower than of hydrocarbons. Alkenic and acetylenic C-H bonds are stronger than alkanes and addition reaction takes precedence over hydrogen abstraction.

After hydrogen abstraction the alkyl radical may undergo further reactions. Prominent among these reactions are nitration and oxidation, as described in section 1.3.1; equations 1.2 and 1.4.

Overall the reactions are complex. Their course is dependent on temperature, pressure and catalysts and may involve many different types of individual steps. However, an initial abstraction of a hydrogen atom is able to account satisfactorily for the observed properties in nitration of paraffins, hydrogen abstraction from aldehydes, ethers, alcohols, ketones, acids and other organic compounds (A.E.Rout, 1946; A.D.Yoffe, 1953; and H.B.Hass, and D.E.Hudgin, 1954).

1.3.4 Metathetical Reactions

In this class of reaction, nitrogen dioxide has a role in oxidation-reduction reactions and including decomposition of nitrogen dioxide.

When nitrogen dioxide acts as an oxidising agent, an oxygen atom is transferred from the nitrogen dioxide molecule, as shown in equation 1.8.

$$NO_2 + X \longrightarrow NO + XO \qquad (1.8)$$

where X may be an atom (H,N,O,Na), a radical (C_nH_{2n+1} , C_nF_{2n+1} , CH_3CO, CCl_3), an odd-electron molecule (NO, NO_2,O_2,NO_3) or a normal molecule (CO, SO_2, NOCl). When X is an alkyl radical the process is exothermic. The species RO• is itself very reactive and if R is a secondary or tertiary group the largest alkyl group is split out most readily, leaving a carbonyl compound. The alkyl radical continues to react in the same way, a primary alkoxy radical being formed.

$$R\cdot + NO_2 \longrightarrow RO\cdot + NO \qquad (1.9)$$

when X is an oxygen molecule, its oxidation generates ozone (H.S.Johnston, and H.J.Crosby, 1954).

$$NO_2 + O_2 \longrightarrow NO + O_3 \qquad (1.10)$$

When nitrogen dioxide acts as a reducing agent it gains another oxygen atom. Association and abstraction reactions are included in this type of reaction. The oxidation of nitrogen dioxide by ozone is a rapid reaction. The final product is dinitrogen pentoxide, N_2O_5 (H.S.Johnston, and D.M.Yost, 1949).

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad (1.11)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \qquad (1.12)$$

The decomposition of nitrogen dioxide is an example of oxygen transfer reaction and occurs as in reaction 1.13.

$$2\ NO_2 \longrightarrow 2\ NO + O_2 \qquad (1.13)$$

1.3.5 Photochemistry of Nitrogen Dioxide

Nitrogen dioxide shows absorption in the visible region and as far as λ = 2800 nm in near ultraviolet. The fluorescence spectrum is appreciable at λ = 4360 nm, weak at λ = 4050 nm and virtually zero at λ = 3650 nm. The scheme for fluorescence at wavelengths from 3950 nm to 4360 nm is as following:

absorption $NO_2 + h\nu \longrightarrow NO_2^*$ (1.14)

re-radiation $NO_2^* \longrightarrow NO_2 + h\nu$ (1.15)

quenching $NO_2^* + NO_2 \longrightarrow 2NO_2$ (1.16)

An absorption of radiation and formation of excited nitrogen dioxide is at 6000 nm. This energy of excitation is not enough to dissociate molecule and it is quenched or re-radiated as fluorescence. At shorter wavelengths, 4000 nm the absorption becomes diffuse and fluorescence fades as dissociation begins as following reaction:

$$NO_2 + h\nu \longrightarrow NO + O(^3P) \qquad (1.17)$$

As the wavelength is further diminished and energy of excitation increased, dissociation predominates, the intensity of fluorescence is zero by 3650 nm, absorption is continuous. This leads to the second step:

$$NO_2 + O(^3P) \longrightarrow NO + O_2 \qquad (1.18)$$

The second region of sharp absorption bands near 2596 nm and the second diffuse region near 2459 nm corresponds to dissociation into nitric oxide and an excited oxygen atom.

$$NO_2 + h\nu \longrightarrow NO + O(^1D) \qquad (1.19)$$

1.4 The Previous Studies of the Reactions of Nitrogen Dioxide with Alkenes by Electron Spin Resonance Spectroscopy

Using electron spin resonance spectroscopy to study reactions of nitrogen dioxide with alkenes in liquid phase was first reported by C.Lagercrantz, and M.Yhland in 1962. They observed esr spectra from liquid -photolysed solutions of tetranitromethane in unsaturated and ketonic solvents, and the results were interpreted in terms of formation of charge-transfer complex between the solvent and tetranitromethane and mechanisms of some of the reactions which occurred with nitrogen dioxide, produced by photolysis, were proposed. T.J.Schaafma, and J.Kommandeur (1965) also proposed the formation of charge-transfer complexes from reactions between nitrogen dioxide and aromatic or olefinic solvents. P.D.Cook, and others in 1963; and M.Ebert, and J.Law in 1965 have found that when mixture of nitric oxide and nitrogen dioxide was added to methyl methacrylate at room temperature, a relatively high concentration of radicals was produced and possible structure of this radical has been suggested by J.A.McRae, and M.C.R.Symons, 1966. W.M.Fox, and others, 1967, studies reactions of nitrogen dioxide and a number of saturated and unsaturated carbonyl compounds at room temperature, nitroxide radicals, iminoxy radicals and acyl nitroxide radicals were observed. Interaction of nitrogen dioxide with styrenes and a number of alkenes were also studied by using electron spin resonance spectroscopy, and nitroxide radicals were observed and charge-transfer complexes were thought to be involved (B.H.J.Bielski, and J.M.Gebicki, 1969). The reactions of nitrogen dioxide with styrenes in the presence of nitrosobenzene and the reactions of nitrogen dioxide-nitric oxide mixture with styrenes were also studied, and it was concluded that β-nitroalkyl radicals and vic-nitronitroso compounds were involved in the mechanistic pathways (L.Jonkman et al., 1970, and 1971). When R.M.Estefan et al., 1970; and J.R.Rowland, and E.M.Gause, 1971, studied reactions of nitrogen dioxide with blood and lung components, and also unsaturated lipid components, nitroxide radicals, iminoxy radicals and another radical with hyperfine structure extending over 36 gauss were observed. They proposed that the esr spectrum of the latter radical was the spectrum of the β-nitroalkyl radical, the initial radical intermediate in nitrogen dioxide-alkene reactions.

1.5 Scope of This Present Study

From the brief review of the chemical reactions of nitrogen dioxide with alkenes outlined in sections 1.3 and 1.4, the mechanisms of these reactions seem to be rather complicated and have not yet been completely worked out. The aims of this present work are to study mechanisms of addition reactions of nitrogen dioxide with alkenes by using electron spin resonance spectroscopy. The areas which have been investigated in this study include the interaction between nitrogen dioxide and various alkenes, electron donating-substituted alkenes and electron withdrawing-substituted alkenes. The reactions were carried out in the absence, and in the presence of oxygen, varying reaction temperature, and exposed or unexposed to room daylight or ultraviolet light. Particular attention has been paid to a study of the initial radicals formed which had been proposed to be β-nitroalkyl radicals. These investigations along with those from the previous works may explain some reaction pathways of the reaction studies. The results and discussions are then presented in Chapter Four and Chapter Five.

CHAPTER TWO

Theory of Electron Spin Resonance Spectroscopy

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Theory of Electron Spin Resonance Spectroscopy

2.1 Introduction

Electron spin resonance (esr) spectroscopy means the observation of absorption of electromagnetic radiation caused by the magnetic dipole transitions between spin states of unpaired electrons in a magnetic field. The phenomenon was discovered by E.Zavoiskii in the USSR in 1945, and since then esr has rapidly developed into a most powerful tool of various areas in physics, biology and chemistry. The applications to the study of free radicals were stimulated in the mid-1950s when pioneering work clarified the principles of relating esr patterns to radical structure. Many versatile techniques for the detection of radicals during chemical reactions by esr have been introduced and have made esr a still more valuable method of radical chemistry. The information obtainable from esr spectra of free radicals is contained in

a. the number and positions of the spectral lines,

b. the line widths,

c. the total absorption intensity.

Analysis of the number and positions of the lines leads to the determination of the chemical and steric structure of the radicals and provides insight into the odd-electron distribution, Discussion of the line width may offer additional information on structure as well as on kinetics of reversible radical reactions. The concentration of the radicals is determined from the absorption intensity.

The basic principles and the details of the necessary analyses of esr spectra and many results have been described in a number of books and general reviews (D.J.E.Ingram, 1958; M.Bersohn, and J.C.Baird , 1966; P.W.Atkins and M.C.R.Symons, 1967; P.B.Ayscough, 1967; B.H.J.Bielski, and

and J.M.Gebicki, 1967; A.Carrington, and A.D.McLachlan, 1967; C.P.Poole, 1967, R.S.Alger, 1968; F.Gerson, 1970; J.E.Wertz, and J.R.Bolton, 1972; M.C.R.Symons, 1978; and Landolt Börnstein, 1979). In this chapter we briefly describe basic principles of esr, and the present knowledge of some carbon and nitrogen centred radicals related to our study are also summarised.

2.2 Theoretical Considerations

2.2.1 Resonance Condition

The electron has a non-classical, intrinsic angular momentum called spin. According to the principles of quantum mechanics, only one of the components of the spin in a given direction (z) can be measured accurately apart from its magnitude. The spin is characterised by the quantum number $S = \frac{1}{2}$, its component along the z-axis being characterised by the quantum number $M_s = \pm \frac{1}{2}$. The electron thus has two spin states differing in M_s.

The spin of the electron gives rise to a magnetic moment μ_E, whose z-component μ_E^z can assume only two values corresponding to the spin quantum number $M_s = \pm \frac{1}{2}$. M_s and μ_E^z are related by equation:

$$\mu_E^z = - M_s . g_E . \beta_E = \begin{cases} -(+\frac{1}{2}) g_E \beta_E & \text{for } M_s = +\frac{1}{2} \\ -(-\frac{1}{2}) g_E \beta_E & \text{for } M_s = -\frac{1}{2} \end{cases} \tag{2.1}$$

where β_E is the Bohr magneton, a constant having the value of 9.2733×10^{-21} erg/gauss; g_E is a dimensionless number whose value for free electrons is 2.0023. The g_E value for electrons in atoms or molecules may be different. It is convenient to identify z-axis with the direction of applied magnetic field. The component μ_E^z of the magnetic moment is then responsible for the behaviour of the electron in the magnetic field.

In the absence of an external magnetic field, the two spin states with $M_s = +\frac{1}{2}$ and $M_s = -\frac{1}{2}$ are degenerate. When a magnetic field H is applied along the z-axis, it interacts with magnetic moment μ_E of the electron, and the spin states are no longer degenerate (Zeeman effect). The energy of interaction E is given by the formula

$$E = -\mu_E^z.H = +(M_s g_E \beta_E).H \tag{2.2}$$

and the energy difference between two spin states is

$$E_2 - E_1 = g_E \beta_E H \tag{2.3}$$

where E_1 and E_2 are energy levels of the spin states $M_s = -\frac{1}{2}$ and $M_s = +\frac{1}{2}$ respectively (Fig. 2.1).

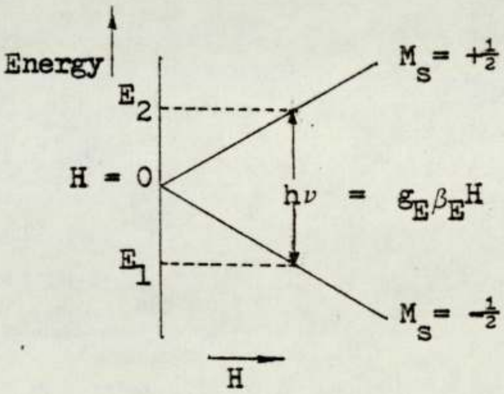


Fig. 2.1 Splitting of the spin levels of an applied magnetic field of intensity H.

Transition from one Zeeman level to the other (i.e. between E_1 and E_2), in which the electron changes its spin state occurs when the system is exposed to an electromagnetic radiation with a resonance frequency ν . This frequency is determined by the resonance condition

$$h\nu = g_E \beta_E H \tag{2.4}$$

where h is Planck's constant (6.624×10^{-27} erg.sec); ν thus depends on

H, and the proportionality constant between them, γ_E, amounts to 2.802 MHz.gauss^{-1}, when g_E= 2.0023.

$$\gamma_E = \frac{\nu}{H} = \frac{g_E \beta_E}{h} \qquad (2.5)$$

To satisfy the resonance condition, one can vary ν and/or H. For technical reasons, the frequency ν is kept constant and the field strength H is varied to bring it to the value at which the resonance condition is fulfilled.

2.2.2 Relaxation Phenomena

The resonance condition $h\nu = g\beta H$ implies that energy has been supplied to electron spins in a lower energy level and has transposed them to a higher energy level. These electron spins must eventually return to the lower state and the time they take to return is known as relaxation time.

Relaxation times comprise two terms, a dipolar spin-spin relaxation time T_2, which is determined by the amount of spin energy shared with other electrons or nuclei, and a spin-lattice relaxation time T_1, which is determined by the rate of sharing spin energy with thermal vibrations of the lattice. T_1 is defined as the time in which an initial excess of energy given to the spins will fall to 1/e or 0.368 of its value. T_1 and T_2 are related to τ by

$$\frac{1}{\tau} = \frac{1}{T_2} + \frac{1}{T_1} \qquad (2.6)$$

where τ is defined by

$$\tau = \pi g(\omega - \omega_o)_{max} \qquad (2.7)$$

in which $g(\omega - \omega_o)$ is the line-shape function.

The magnitude of the spin-lattice relaxation time is controlled by spin-orbit coupling, but since this is a very small parameter in organic radicals this mechanism does not usually contribute to the linewidth of an esr spectrum and T_1 is of the order of seconds. The major contribution to the linewidth of the esr spectrum of an organic radical is the spin-spin relaxation time. This is the reduction of the time spent in a particular spin state because of dipolar interactions with surrounding magnetic particles whether these be electrons or magnetic nuclei.

2.2.3 g-Value

The g-value or spectroscopic splitting factor or Landé factor defined by the equation

$$h\nu = g\beta H$$

is a proportionality constant, relating to the frequency and field at which resonance occur. The g-value for free electron is 2.0023 which resonance occurs at X-band frequencies and with an applied field of some 3300 gauss. This is not generally the case for unpaired electrons in paramagnetic molecules since there may be a contribution to the magnetic moment arising from orbital angular momentum which will be observed as a deviation of the g-value from the free spin value (g_o), and resonance at a field different from 3300 gauss. The g-values of most organic free radicals are within 1 % of the free electron value while those of hydrocarbon free radicals are within 0.1 % of g_o. The deviation of the observed g from g_o has been interpreted as being due to spin-orbit coupling; the spin-orbit coupling parameters for most hetero-atoms are greater than that of the carbon and this explains why those radicals with spin densities localised on, for example oxygen, nitrogen or sulpher atoms have g-values which deviate from g_o more than those of carbon radicals. Since it is possible to measure g-values to very high precision they can be used to give information about the orbital occupied by the unpaired electron and also to identify radicals.

2.2.4 Hyperfine Interactions

2.2.4.1 The Origin of Hyperfine Structure

A well resolved esr signal of a radical in solution may consist of more than a hundred lines. This complexity of the signal, known as its hyperfine structure is determined by the interaction between the unpaired electron and the magnetic nuclei in the radical, for example nuclei with a non-zero spin quantum number I, analogous to the electron spin quantum number S of an electron.

A description of the behaviour of a nucleus in a magnetic field H involves the component of the nuclear magnetic moment μ_N in the direction (z) of the field (μ_N^z). By virtue of

$$\mu_N^z = +M_I g_N \beta_N \qquad (2.8)$$

μ_N^z depends on the spin quantum number M_I. M_I can assume $(2I + 1)$ values, namely $-I$, $(-I+1)$, $(-I+2)$............, $+I$. Among the four most common nuclei in organic compounds, ^{1}H ($I = \frac{1}{2}$, $M_I = \pm \frac{1}{2}$) and ^{14}N ($I = 1$, $M_I = \pm 1$) are magnetic, whereas ^{12}C and ^{16}O are not. The g_N values are dimensionless and characteristic of the type of the nucleus. The nuclear magneton β_N (5.0493×10^{-24} erg/gauss) is smaller than the Bohr magneton β_E by a factor of 1836, which is the ratio between the mass of the proton and that of the electron. The values of μ_N^z are therefore correspondingly smaller than μ_E^z, and provided that $g_N > 0$, they have the same sign as M_I, owing to the positive charge of the nucleus.

In a strong magnetic field H the interaction between the unpaired electron and a magnetic nucleus results in a small perturbation δE to the Zeeman levels E_1 and E_2 of the electron spin, this perturbation being made up of two terms:

$$\delta E = (\delta E)_{aniso} + (\delta E)_{iso} \qquad (2.9)$$

The anisotropic term $(\delta E)_{aniso}$ represents the classical dipole-dipole interaction, which depends on the relative positions of the magnetic moments of the unpaired electron and the nucleus, μ_E and μ_N. In the case of liquids, where the molecular motion continuously changes the relative positions of the magnetic moments, the dipole-dipole interactions average out except for a small residue that depends on the viscosity of the medium. It contributes to the line-width $\Delta\nu$ but not to δE, since the time average $(\delta E)_{aniso}$ is now zero. The hyperfine structure of radicals in solution is therefore due exclusively to the isotropic or direction-independent Fermi contact term $(\delta E)_{iso}$. In a strong magnetic field in the Z-direction, this term can be expressed as

$$(\delta E)_{iso} = - \frac{8\pi}{3}(\mu_E^z \mu_N^z)\rho'(0) \qquad (2.10)$$

where $\rho'(0)$ is the electron spin density at the nucleus. Using equations (2.1) and (2.8) for μ_E^z and μ_N^z, one obtains

$$(\delta E)_{iso} = + \frac{8\pi}{3} g_E \beta_E g_N \beta_N (M_s M_I)\rho'(0) \qquad (2.11)$$

Equation (2.11) shows that, for positive g_N and $\rho'(0)$, the level E_1 and E_2 of the unpaired electron are stabilised when M_s and M_I have the opposite sign, being destabilised when they have the same sign. The diagrams in Fig. 2.2 refer to radicals in which the unpaired electron interacts only with one nucleus having a spin quantum number I of $\frac{1}{2}$ or 1 (for example ^1H or ^{14}N, respectively). The levels E_1 and E_2 of the electron spin states with $M_s = -\frac{1}{2}$ and $M_s = +\frac{1}{2}$ each split into two or three sub-levels corresponding to the two quantum numbers $M_I = -\frac{1}{2}$ and $+\frac{1}{2}$ of the proton or to the three quantum numbers $M_I = -1$, 0, and +1 of the ^{14}N nucleus.

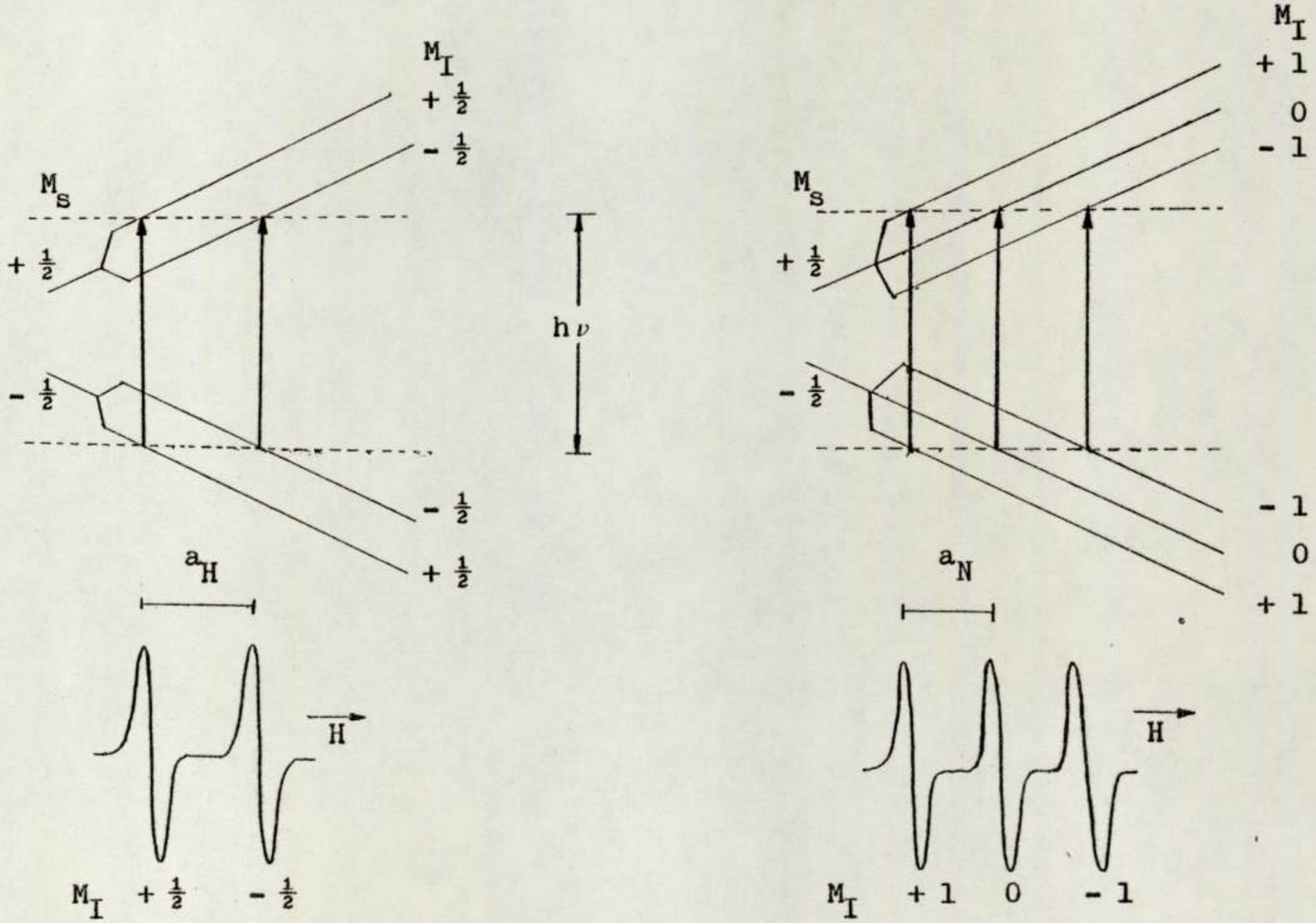


Figure 2.2 Splitting of an esr signal by the hyperfine interaction between the unpaired electron and a nucleus having a spin quantum number $I = \frac{1}{2}$ (left) or $I = 1$ (right). The esr hyperfine components are shown below as first derivatives of absorption intensity with respect to the field strength.

The selection rules

$$M_s = \pm 1, \; M_I = 0 \qquad (2.12)$$

state that only those transitions are allowed which occur between spin states with the same quantum number M_I. Consequently, two hyperfine lines are detected in the spectrum resulting from the interaction of the unpaired electron with a proton, and three hyperfine lines when the electron interacts with ^{14}N as can be seen in Figure 2.2. The separation between the adjacent lines gives the hyperfine coupling constants (hfcs) of the nuclei in question (a_H and a_N in gauss). These are independent of the field and characteristic of the nucleus-electron interaction in the radical.

For a radical containing n equivalent magnetic nuclei, these nuclei have equal coupling constants, and the number of equidistant lines is equal to 2nI + 1. In this case some of the lines appear at the same field strength, and their intensities add. The intensities are given by the expansion coefficients of $(1 + x + x^2 + x^3 + \ldots.)^n$, where the number of symbols within the parentheses is equal to (2I + 1).

2.2.4.2 Hyperfine Splittings and Their Relations to Radical Structure.

2.2.4.2.1 Proton Hyperfine Splitting

It is convenient to distinguish the positions of the coupling nuclei with respect to their relation to the electron-bearing carbon as $\alpha, \beta, \gamma, \delta$, and so on. Thus in the n-butyl radical we denote the nuclei as in the structure formula

$$\cdot C^{\alpha}H_2^{\alpha} - C^{\beta}H_2^{\beta} - C^{\gamma}H_2^{\gamma} - C^{\delta}H_3^{\delta}$$

Isotropic hyperfine splittings of protons arise through a net spin population of the hydrogen 1s orbitals. If this spin population were 1, the resulting parameter would be 507 G; therefore

$$a_H = 507.\rho_H \qquad (2.13)$$

Proton coupling constants seldom exceed values of 50 G; that is, ρ_H is mostly lower than 10 %. The mechanisms leading to spin populations in 1s orbitals are different for the different types of protons.

Table 2.1 gives the hyperfine splittings and g factors of a number of radicals, many of which have α and β protons.

Often, one distinguishes between π- and σ-type radicals. In π radicals the unpaired electron occupies essentially carbon $2p_z(\pi)$ orbitals, the axes of which are perpendicular to the axes of the carbon-substituent bonds. In σ-type radicals the electron occupies a sp^3 or sp^2 hybrid orbital of carbon and the angles between the axis of these orbitals and the bond axes are 109° or 120°. While many radicals may be of intermediate structure, phenyl and formyl radicals are probably good examples for σ-type radicals (120°), whereas methyl very probably is a typical π radical (90°).

The α-proton hyperfine parameter (a_α) of methyl is -23.04 at -188° C. Because of symmetry there can be no direct participation of the hydrogen 1s orbitals in the molecular orbital of the odd electron. The nonzero value of hyperfine coupling constant is therefore explained by a higher order effect, called spin polarisation of the C-H bonding orbitals. This generates a net spin population in the hydrogen 1s orbitals of opposite sign to that in the carbon $2p_z$ orbital and simultaneously a net spin population in the carbon sp^2 hybrid of like sign to that in the carbon $2p_z$ orbital. Because of the inversion of sign of spin populations, the hyperfine coupling constant of the hydrogen is negative. To a very good approximation, the spin population of the hydrogen 1s orbital is proportional to the spin population of the carbon $2p_z$ orbital. Therefore, for α protons in planar radicals with conjugated π systems one may write

$$a_{H\alpha} = 507.\rho_H = Q.\rho_\pi \qquad (2.14)$$

where ρ_π is the spin population of the carbon $2p_z$ orbital and Q is a proportionality constant. From the methyl α splitting ($\rho_\pi = 1$) the value Q = -23 G follows. Relation (2.14) has found wide application in the interpretation of coupling constants of in-plane protons of conjugated π radicals as well of neutral species like allyl, cyclohexadienyl, or benzyl and of aromatic radical ions. A transfer of Q from one class of radicals to another will hold only if the involved orbitals are very similar. On the basis of a comparison of experimental splittings with the results of INDO calculations on a large variety of radicals, a value of Q = -22 G has been suggested to be most appropriate (J.A.Pople et al., 1968).

The hyperfine interactions of β protons with the odd electron are nearly isotropic. The isotropic splitting parameter of β protons may be larger than that of α protons, as is seen from the values given in Table 2.1 for ethyl, isopropyl, and tert-butyl radicals. The corresponding spin population in the 1s hydrogen orbitals results from a hyperconjugative delocalisation of the odd electron into these orbitals. This mechanism can operate for planar radical site at C_α only if the β-hydrogens are not located in the nodal plane of the α-carbon $2p_z$ orbital. This explains why the value of $a_{H\beta}$ depends on the angle θ between the $2p_z$ axis at C_α and the plane containing C_α, C_β, and H_β. For radicals in solution, the analysis of the β-coupling is not straightforward since there is often hindered internal rotation about the $C_\alpha - C_\beta$ bond and also leads to angular dependence.

$$a_{H\beta} = (B_o + B_2\cos^2\theta)\rho_i^\pi \qquad (2.15)$$

The quantity θ is the azimuthal angle between the axis of the p orbital and the CH bond; B_o is sometimes considered to be the spin-polarisation term, and B_2 is the hyperconjugative term. The values of these parameters are generally of the order of 0 to 6 gauss for B_o and 50 to 60 gauss for B_2. These parameters are uncertain, but for many applications the value of B_o can be assumed to be zero.

Hyperfine splitting by γ and δ protons in alkyl radicals is generally of the order of 1 gauss or less and often resolved only in solution spectra. They are temperature dependent, which indicates a sort of hyperconjugative mechanism for the coupling modulated by internal rotation. For cyclic radicals larger splittings have been obtained for the remote protons.

2.2.4.2.2 Hyperfine Splitting by other nuclei.

Hyperfine splitting by other nuclei, for example ^{13}C, ^{14}N, ^{15}N, or ^{17}O, if they are part of a planar π-radical skeleton, their isotropic hyperfine coupling constants obey a Karplus-Fraenkel relation (2.16) (M.Karplus, and G.K.Fraenkel, 1961). For trigonal ^{13}C radical, one obtains

$$a_C = (S^C + \Sigma Q^C_{CX}) \rho^C_\pi + \Sigma Q^C_{XC} \rho^X_\pi \qquad (2.16)$$

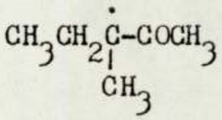
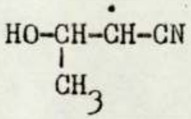
where ρ^C_π is the spin population of the $2p_z$ orbital of the considered carbon, and the ρ^X_π are the spin populations of the corresponding orbitals of the three neighbouring atoms X of this carbon. The coupling arises through spin polarisation mechanisms, as outlined for α protons. The positive terms Q^C_{CX} denote the spin polarisation of the C-X σ bond by electron interactions at the considered carbon; the negative terms Q^C_{XC} denote the corresponding contributions from interactions at atoms X. The term S^C represents a spin polarisation of the carbon 1s shell. The parameters S^C and Q^C have been determined empirically and for planar π radicals the values $S^C = -12.7$ G, $Q^C_{CH} = +19.5$ G, $Q^C_{CC'} = 14.5$ G and $Q^C_{C'C} = -13.9$ G

Table 2.1

Isotropic Hyperfine Splittings and g Factors of Some Alkyl Radicals

Radical	g-value	a(H α) (gauss)	Other Splittings(gauss)	Reference
$\cdot CH_3$	2.00255	23.04	-	R.W.Fessenden, and other, 1963
$\cdot CH_2CH_3$	2.00260	22.38	$3H(\beta)$: 26.87	"
$\cdot CH(CH_3)_2$	2.00260	22.11	$6H(\beta)$: 24.68	"
$\cdot C(CH_3)_3$	2.00260		22.72	"
$\cdot CH(CH_3)OH$	2.00323	15.37		R.Livingston, and other, 1966
$(CH_3)_2\dot{C}\text{-}NO_2$			$6H(\beta)$: 19.8 N : 3.9	G.A.Russell, and other, 1967
$(CH_3)_2\dot{C}\text{-}CH_2NH_3^+$			$2H(CH_2)$: 5.8 $6H(CH_3)$: 24.1 N : 9.4	H.Taniguchi et al., 1968
$(CH_3)_2\dot{C}\text{-}COCH_3$	2.0040		$3H(\beta,1)$: 20.34 $3H(\beta,2)$: 18.93 $H(\gamma)$: 1.33	H.Paul, and other, 1973; H.Itzel, and other, 1976

Table 2.1 (continued)

Radical	g-value	a(H α) (gauss)	Other Splittings(gauss)	Reference
$(CH_3)_2\dot{C}CHO$	2.0045		$3H(CH_3,1)$: 21.1	T.Foster et al., 1974
			$3H(CH_3,2)$: 18.0	
			H : 3.0	
 $CH_3CH_2\dot{C}(CH_3)\text{-}COCH_3$	2.00422		$2H(\beta,CH_2)$: 9.5	D.M.Camaioni et al.,
			$3H(\beta,CH_3)$: 19.7	1973
			$3H(\gamma,CH_3)$: 0.7	
$(COOH)_2CH\text{-}\dot{C}HCOOH$		20.9	$H(\beta)$: 15.2	W.T.Dixon et al., 1974
$CH_3CH(COOH)\dot{C}H\text{-}COOH$		20.8	$H(\beta)$: 13.5	W.T.Dixon et al., 1974
			$3H(\gamma,CH_3)$: 0.6	
 $HO\text{-}CH(CH_3)\text{-}\dot{C}H\text{-}CN$	2.00291	19.51	$H(\beta)$: 22.77	P.Smith et al., 1975
			$3H(\gamma,CH_3)$: 0.57	
			N : 3.51	

(trigonal hybridisation of C') are commonly accepted. The relation(2.16) is semiempirical, and the constants Q^C may change from system to system. Similar relationships hold for other heteroatoms. Nevertheless, the Karplus-Fraenkel treatment often allows reasonable estimates of coupling constants or of spin population distributions.

There are some indications that alkyl radicals with α-amino or alkylamino groups may be nonplanar at the radical site in which case relation (2.16) breaks down. Coupling constants of nitrogen nuclei substituted at β-carbon atoms have been treated by assuming the validity of an expression like (2.15) and values of $B_0^N \approx 0$, $B_2^N \approx 7$ G were suggested (H.Paul, and H.Fischer, 1969).

2.3 The Present Knowledge of Some Free Radicals Related to This Study.

2.3.1 Transient Free Radicals.

Many of the radicals which are of interest in organic chemistry are transient in the sense that they react with each other with great efficiency and little or no activation energy if they come to close spatial contact. Therefore their rates of disappearance are governed by the rates of approach, that is, by the diffusional motion within the medium. This allows a prediction on the radical concentration to be expected during a typical reaction, for example

$$K \xrightarrow{k_1} 2R\cdot \qquad (2.17)$$

$$R\cdot + S \xrightarrow{k_2} R'\cdot \qquad (2.18)$$

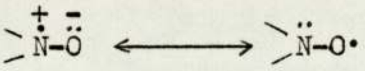
$$2R'\cdot \xrightarrow{k_3} P \qquad (2.19)$$

Esr can detect radical concentrations as low as predicted only in very special cases (for instance, if the signal is one sharp resonance line) and under most circumstances the recording of good quality spectra requires concentrations above 5×10^{-7} M. Therefore, often special techniques have to be applied to study the radicals of interest. Either the rate of radical production has to be enhanced drastically or the rate for radical disappearance has to be diminished. The latter approach corresponds to the use of highly viscous media, or to trapping the radicals in solids, or to converting reactive primary radicals R• by reaction with suitable substrates S into unreactive species R'• with low k_3 (spin trapping) so that these species can be conveniently observed. The former approach is employed in the various techniques for rapid generation of radicals in solution and within the cavities of esr spectrometers, while the spectra are observed, for example radiochemical, photochemical, mixed-flow, and thermolysis techniques.

Transient free radicals in this study are β-nitroalkyl radicals which we detect by employing spin trapping and mixed-flow techniques. The details of these two techniques have been discussed elsewhere (E.G.Janzen, and B.J.Blackburn, 1969; S.Forshult et al., 1969; G.R.Chalfont et al., 1968; I.H.Leaver, and G.C.Ramsay, 1969; E.G.Janzen, 1971; I.Yamazaki et al., 1959; E.Saito, and B.H.J.Bielski, 1961; B.H.J.Bielski, 1962; and W.T.Dixon, and R.O.C.Norman, 1962 and 1963).

2.3.2 Nitroxide Radicals

Nitroxide radicals are compounds containing the $>$N-O group, which has one unpaired electron. The structure of this fragment can be conceived as a superposition of two resonance structures:

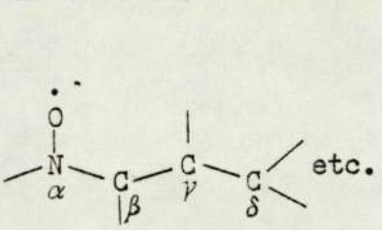


$$>\overset{+}{\dot{N}}-\overset{-}{\ddot{O}} \longleftrightarrow >\ddot{N}-O\cdot$$

The fundamental chemical and physical properties of stable nitroxides were established over the last 20 years largely through the pioneering research of E.G.Rozantsev in the USSR, and A.Rassat in France and their collaborators. Several books and reviews summarise the many contributions of these and other investigators in this area. (A.R.Forrester, 1968; E.G.Janzen, 1971; E.G.Rozantsev et al., 1971; and J.F.W. Keana, 1978).

The esr spectrum of the nitroxide function consists of three lines, or group of three lines, due to the nitrogen hyperfine splitting (I_N= 1). The nitrogen hyperfine splitting constant (a_N) varies substantially with the nature of the one or two substituents attached to nitrogen. Table 2.2 gives the range of a_N values expected from different types of nitroxides for the nitroxide of unknown structure is being identified. Steric or remote powerful electronic effects may cause the a_N value to increase or decrease to values outside these limits. Solvent is also important, polar and protic solvents cause an increase in a_N probably because of an enhanced contribution of the dipolar resonance form in high dielectric or hydrogen bonding solvents (E.G.Janzen, 1971). The a_N values in Table 2.2 are those expected using solvent in the polarity range benzene to chloroform. g-Values are of less diagnostic value than a_N values when considered by themselves but when used with a_N values they provide complementary evidence of structure.

Nuclei with spin attached directly to nitrogen or one, two or even three (carbon) atoms removed from the nitroxide function show further hyperfine splitting. From the esr point of view, the following position nomenclature has evolved:

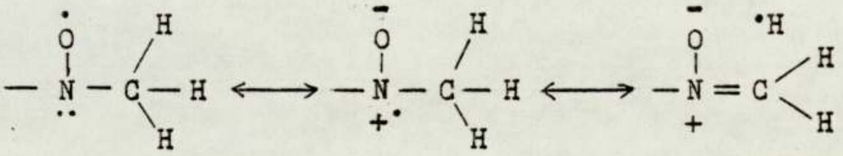


Hydrogen attached directly to nitrogen (α -position) gives large hyperfine splitting. Hyperfine splitting from hydrogens in the β -position have a strong well understood angular dependence. The mechanism of β -hydrogen hyperfine coupling is most readily ascribed to hyperconjugation, for example in methyl-substituted nitroxides.

Table 2.2

Summary Table of ESR Parameters of Nitroxide Radicals

nitroxide radical	structure	a_N value (gauss)	g-value
alkyl alkoxy	RN(O•)OR	24.0...29.0	2.0054..2.0060
dialkyl	R_2NO•	14.0...15.5	2.0059..2.0065
aryl alkoxy	aryl-N(O•)R	13.0...15.5	2.0046..2.0054
monoalkyl	RNHO•	12.3...13.3	2.0060..2.0065
alkyl aryl	RN(O•)-aryl	10.5...12.5	2.0056..2.0064
diaryl	(aryl)$_2$NO•	9.0...10.5	2.0055..2.0063
monoaryl	aryl-NHO•	8.5....9.5	2.0060
alkyl acyl	RN(O•)COR	6.5....8.5	2.0065..2.0075
aryl acyl	aryl-N(O•)CO-aryl	7.0....8.0	2.0060..2.0070

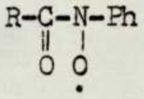


The magnitude of this coupling depends both on the spin density on nitrogen and on the dihedral angle between the p-orbital on nitrogen and the C-H bond of the methyl group.

The equation $a_H = 26 \cos^2\theta$ which is derived from the relation (2.15) when $B_o \approx 0$, $B_2\rho_N = 26$ is used to calculate the dihedral angle for the β-hydrogen in alkyl nitroxides and thus obtain the conformation of the group attached (G.Chapelet-Letourneux et al., 1968). E.G.Janzen (1971), and A.Rassat (1971) have summarised some of the configulational aspects of nitroxide radicals as determined by esr.

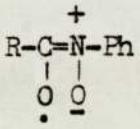
Splitting from more remote hydrogens also varies as a function of angle, but this angular dependence is not as well understood. The a_H values are usually fairly small or non-existant, typical values for $|a_{H\gamma}|$ are approximately 0.4 gauss or less (F.W.King, 1976). Table 2.3 represents a_N and a_H of some nitroxides which include methyl-, methylene-, and methine-substituted nitroxides.

Acyl nitroxides have the rather low a_N values, for example phenyl acetyl nitroxide and phenyl benzoyl nitroxide have a_N values of 7.18 and 7.55 G respectively indicating a large contribution of form (2-Ib) to the hybrid. In addition there is very little interaction of the unpaired electron with the protons of the acyl group. (see Table 2.4).



$\mathrm{R{-}\underset{\overset{\|}{O}}{C}{-}\underset{\overset{|}{O^{\bullet}}}{N}{-}Ph}$

(2-Ia)



$\mathrm{R{-}\underset{\overset{|}{O^{\bullet}}}{C}{=}\overset{+}{\underset{\overset{|}{O^{-}}}{N}}{-}Ph}$

(2-Ib)

Structure of nitroxide function based on esr and X-ray data is believed to be essentially planar with the unpaired electron to the extent of at least 80-90 % in a N-O π^* orbital. Deviations from pure sp^2 hybridisation are observed in the case of fluoro and alkoxy nitroxides. The calculated a_N for an unpaired electron in a nitrogen 2s-orbital is 552 G (P.W.Atkins, and M.C.R.Symons, 1967). The a_N of 13-15 G found for aliphatic nitroxides is a relatively small fraction of this, a condition which strongly suggests a planar nitroxide structure with unpaired electron occupying a π-orbital on the nitrogen and oxygen atom.

Stable nitroxide radicals are polar, deeply coloured solids or liquids; an exception is bis- [tri-fluoromethyl] -nitroxide which is a gas under ordinary conditions. All nitroxides except the latter show no tendency to dimerise at O-N centre at room temperature. Certain nitroxides form inclusion compounds with hydrocarbons (E.G.Rozantsev,

Table 2.3

Isotropic Hyperfine Splittings and g Factors of Some Nitroxide Radicals

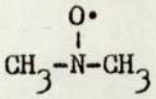
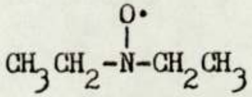
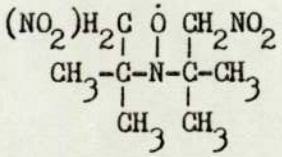
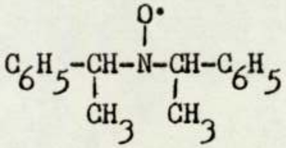
Radical	g-value	a_N (gauss)	Other Splitting(gauss)	Reference
 $CH_3-\overset{O\cdot}{\overset{\vert}{N}}-CH_3$	2.0060	15.90	$6H(CH_3)$: 13.48	C.Darnez, and other, 1972
 $CH_3CH_2-\overset{O\cdot}{\overset{\vert}{N}}-CH_2CH_3$		15.5	$4H(CH_2)$: 10.6	G.M.Coppinger, and other, 1961
$\left[(CH_3)_2CH\right]_2N-O\cdot$		16.0	$2H(CH)$: 4.7	G.M.Coppinger, and other, 1961
$\left[\text{tert-But}\right]_2N-O\cdot$		15.2		H.Lemaire et al.,1962
 $CH_3-\underset{CH_3}{\overset{(NO_2)H_2C}{C}}-\overset{\dot{O}}{N}-\underset{CH_3}{\overset{CH_2NO_2}{C}}-CH_3$		14.8	$4H(CH_2NO_2)$: 0.54	J.Pfab, 1977
 $C_6H_5-\underset{CH_3}{CH}-\overset{O\cdot}{\overset{\vert}{N}}-\underset{CH_3}{CH}-C_6H_5$		15.1	$2H(CH)$: 9.4	Th.A.J.W.Wajer et al., 1967; A.Mackor et al., 1967b

Table 2.3 (continued)

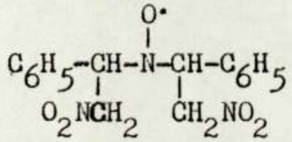
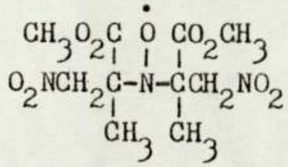
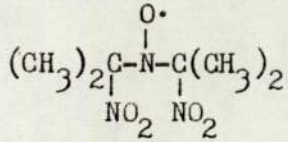
Radical	g-value	a_N (gauss)	Other Splittings(gauss)	Reference
 $C_6H_5\text{-}CH(CH_2NO_2)\text{-}N(O^{\bullet})\text{-}CH(CH_2NO_2)\text{-}C_6H_5$	2.00592	Stereoisomer I: 14.9 Stereoisomer II: 14.5	$2H(CH_2)$: 0.5, 0.21 2H(CH) : 11.4 2H(CH) : 6.6	L.Jonkman et al., 1971; L.Jonkman et al., 1970; B.H.J.Bielski, and other, 1969
 $O_2NCH_2C(CH_3O_2C)(CH_3)\text{-}N(\dot{O})\text{-}C(CO_2CH_3)(CH_3)CH_2NO_2$	2.0065	14.5	2H : 0.3	W.M.Fox et al., 1967; L.Jonkman et al., 1971
 $(CH_3)_2C(NO_2)\text{-}N(O^{\bullet})\text{-}C(NO_2)(CH_3)_2$		10.4	$2N(NO_2)$: 5.2	T.A.B.M. Bolsman, and other, 1973; A.H.M.Kayen et al., 1976

Table 2.4

Isotropic Hyperfine Splittings and g Factors of Some Acyl Nitroxide Radicals

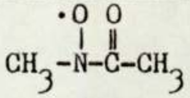
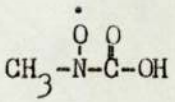
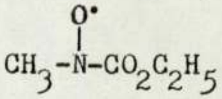
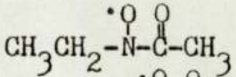
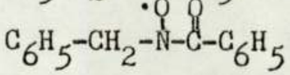
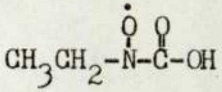
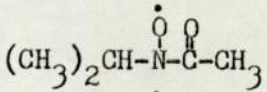
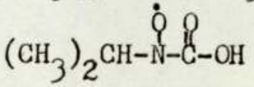
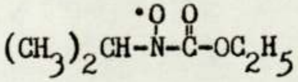
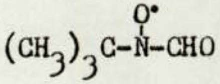
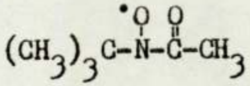
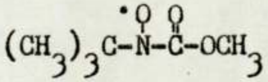
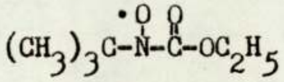
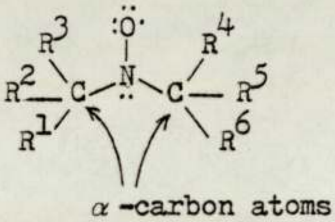
Radical	g-value	a_N (gauss)	Other Splitting(gauss)	Reference
 $CH_3-\overset{\cdot O}{\overset{\mid}{N}}-\overset{O}{\overset{\|}{C}}-CH_3$	2.00651	6.9	$3H(CH_3)$: 8.1	P.Tordo et al., 1972a; P.Tordo et al., 1972b
 $CH_3-\overset{\overset{\bullet}{O}}{N}-\overset{O}{C}-OH$	2.0060	10.80	$3H(CH_3)$: 11.30	D.J.Edge, and other, 1970
 $CH_3-\overset{O^{\bullet}}{\overset{\mid}{N}}-CO_2C_2H_5$		9.1	$3H(CH_3)$: 10.1 $2H(CH_2)$: 1.0	C.J.W.Gutch, and other, 1965
 $CH_3CH_2-\overset{\cdot O}{N}-\overset{O}{C}-CH_3$		6.9	$2H(CH_2)$: 6.1	P.Tordo et al., 1972b
 $C_6H_5-CH_2-\overset{\cdot O}{N}-\overset{O}{C}-C_6H_5$	2.00692	7.5	$2H(CH_2)$: 4.9	A.Mackor et al., 1968
 $CH_3CH_2-\overset{\overset{\bullet}{O}}{N}-\overset{O}{C}-OH$	2.0060	11.155	$2H(CH_2)$: 7.905	D.J.Edge, and other, 1970
 $(CH_3)_2CH-\overset{\overset{\bullet}{O}}{N}-\overset{O}{C}-CH_3$		6.9	$1H(CH)$: 2.3	P.Tordo et al., 1972b
 $(CH_3)_2CH-\overset{\overset{\bullet}{O}}{N}-\overset{O}{C}-OH$	2.0060	11.205	$1H(CH)$: 3.405	D.J.Edge, and Other, 1970

Table 2.4 (continued)

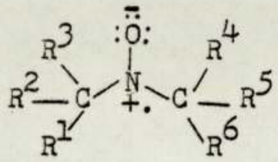
Radical	g-value	a_N(gauss)	Other Splittings(gauss)	Reference
 $(CH_3)_2CH-\overset{\cdot O}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-OC_2H_5$		9.0	1H(CH) : 2.9	A.M.Vasserman et al., 1969
 $(CH_3)_3C-\overset{O^{\cdot}}{\overset{\vert}{N}}-CHO$		7.0	H(CHO) : 1.4	R.G.Gasanov et al.,1976; H.G.Aurich et al.,1975; C.M.Camaggi et al.,1972; E.G.Janzen et al.,1973
 $(CH_3)_3C-\overset{\cdot O}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.0068	8.0		A.Mackor et al., 1968
 $(CH_3)_3C-\overset{\cdot O}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-OCH_3$	2.00712	8.2	$3H(CH_3)$: 0.45	C.M.Camaggi et al., 1972; R.J.Holman, and other, 1971a and 1971b; R.G.Gasanov et al., 1976
 $(CH_3)_3C-\overset{\cdot O}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-OC_2H_5$		8.0		A.Mackor et al., 1968

1966).

Most of the stable nitroxide free radicals are secondary amine N-oxides of the general structure (2-II) in which there are no hydrogens

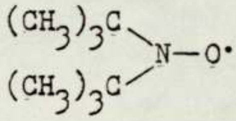


(2-IIa)

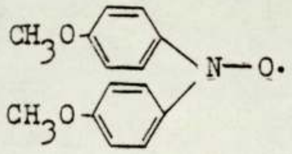


(2-IIb)

attached to the α -carbon atoms, for example di-tert-butyl nitroxide (2-III) and 4,4'-dimethoxyphenyl nitroxide (2-IV) are stable in the sense that they can be isolated and stored indefinitely. However the vast majority of organic nitroxides are unstable since they react with each other through some other centre of the molecule. For example, diphenyl nitroxide in solution decomposes over the course of several days to diphenylamine and N-phenyl-p-benzoquinone-N-oxide.



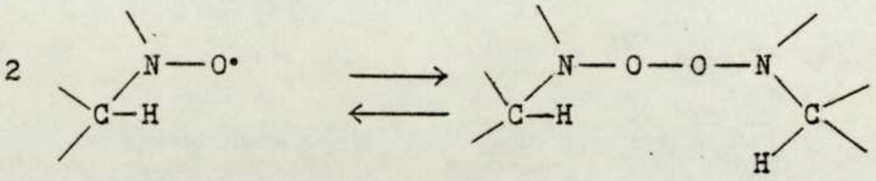
(2-III)



(2-IV)

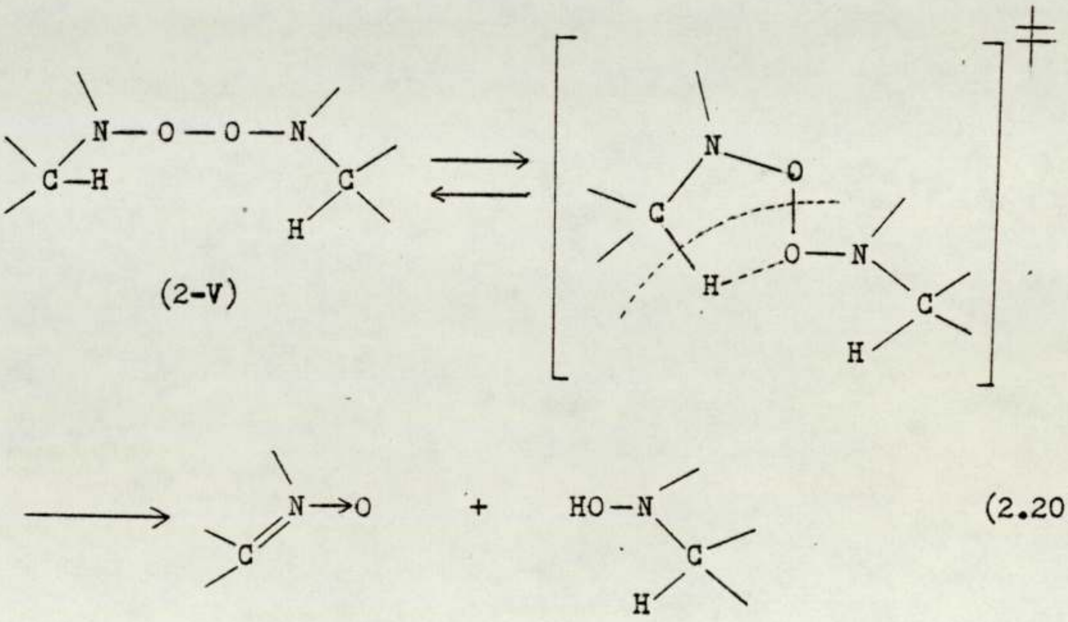
Dialkyl nitroxides other than di-tert-butyl nitroxide are much less stable than diaryl nitroxides.

When one or more hydrogen atoms are attached to the α -carbon atoms of the nitroxide group, the radicals typically undergo a disproportionation reaction (D.F.Bowman et al., 1971; J.Martinie-Hombrouck, and A.Rassat, 1974) producing a nitrone (2-VI) and a N-hydroxyamine (2-VII), either or both of which may undergo further reaction. The rate of the disproportionation reaction strongly depends on the degree of substitution of the α-carbon atoms and on the solvent (D.F.Bowman et al., 1971). The following scheme for the decomposition has been proposed by D.F.Bowman et al., 1971; and G.D.Mendenhall et al., 1974. The structure of the dimer (2-V) must be regarded as uncertain (G.D.Mendenhall, and K.U.Ingold, 1973).



(2.19)

(2-V)

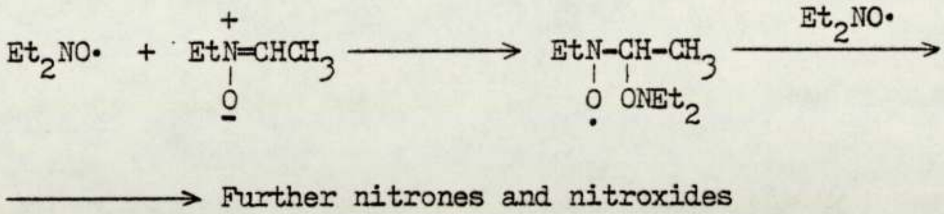


(2-V)

(2.20)

(2-VI) (2-VII)

In addition, the nitrone appears to act as a trap for nitroxide radicals so that the esr signal during the decay of high concentrations of nitroxide changes continuously. A whole series of nitroxides could be formed, for example:



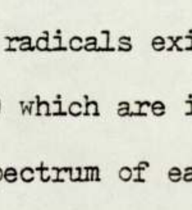
$$\mathrm{Et_2NO\cdot} + \mathrm{Et}\underset{\underset{\underset{-}{O}}{|}}{\overset{+}{\mathrm{N}}}{=}\mathrm{CHCH_3} \longrightarrow \mathrm{Et}\underset{\underset{\underset{\cdot}{O}}{|}}{\mathrm{N}}-\underset{\underset{\mathrm{ONEt_2}}{|}}{\mathrm{CH}}-\mathrm{CH_3} \xrightarrow{\mathrm{Et_2NO\cdot}} \qquad (2.21)$$

$$\longrightarrow \text{Further nitrones and nitroxides}$$

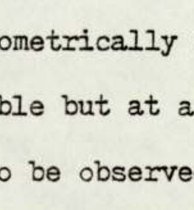
The rate constant for nitroxide decay gradually decreases during a decay presumably because of the increasing stability of the more hindered nitroxides that are formed by this reaction sequence (K.Adamic et al., 1971).

2.3.3 Iminoxy Radicals

Iminoxy radicals have been characterised as σ radicals. The unpaired electron is contained in an orbital which is derived from a p-orbital on oxygen and the nonbonding sp^2 orbital on nitrogen and which lies in the nodal plane of the molecular C-N π bond, as represented by the contribution of the canonical structures (2-VIIIa) and (2-VIIIb). Nearly 50 % of the spin density is associated with the nitrogen nucleus (M.C.R.Symons, 1963, and 1965) the nitrogen hyperfine splitting constant is about 30 gauss.

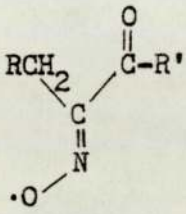


(2-VIIIa)



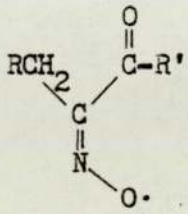
(2-VIIIb)

Iminoxy radicals exist in two geometrically isomeric forms, (2-IXa) and (2-IXb) which are interconvertible but at a sufficiently low rate for the spectrum of each radical to be observed. We shall use the term cis- when the mentioned group is on the same side with iminoxy oxygen and trans- when the mentioned group is on the opposite side to the iminoxy oxygen. The terms E- and Z- will be used throughout the discussions in Chapter Four in which these terms correspond to the nomenclature of iminoxy radicals in Landolt-Börnstein, 1979.



E-isomer

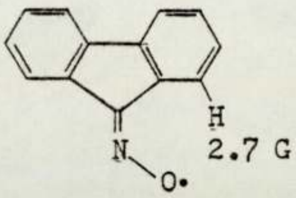
(2-IXa)



Z-isomer

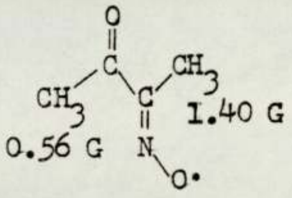
(2-IXb)

The esr spectra of iminoxy radicals have been discussed in detail by numerous authors (J.R.Thomas, 1964; B.C.Gilbert et al., 1964; H.Lemaire, and A.Rassat, 1964; M.Bethoux et al., 1964; W.M.Fox, and W.A.Waters, 1965; B.C.Gilbert, and R.O.C.Norman, 1966a, 1966b, 1967a, 1967b, and 1968; and J.W.Lown, 1966). The hyperfine splitting patterns for protons or nuclei in iminoxy radicals show two types of effect, one is a long-range interaction which is greatest when the proton, the iminoxy group and the intervening atoms are coplanar. In particular, the interaction is larger when the nuclei are on the same side of the double bond as the oxygen atom. Nuclei such as protons which are five or six bonds removed from the iminoxy oxygen also show interaction, which is greatest when the H-C_n and =N-O• fragments are coplanar. The other effect is a shorter range interaction that appears to occur directly across space, for example in the case of radical (2-X), the iminoxy oxygen and the proton lie closely together so that there is possibly a direct overlap of the orbital containing the unpaired electron and the hydrogen 1s orbital, and it may be that some at least of the spin density at the proton arises from this overlap, and the remainder arising by transmission through the bonding framework. (R.O.C.Norman, and B.C.Gilbert, 1967; and J.L.Brokenshire et al., 1972).

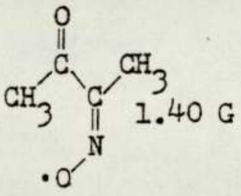


(2-X)

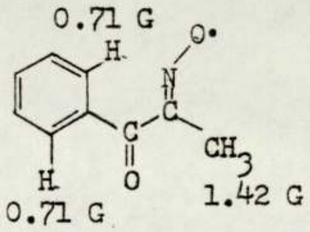
For carbonyl-containing iminoxy radicals, the attenuation for transmission of spin density across carbonyl may be greater than that across methylene when a particular geometry is involved, the carbonyl group can aid the transmission of spin density by increasing the stability of coplanar conformations, for example (2-XI) and (2-XIII) which are effective for spin transmission, are more heavily populated than (2-XII) and (2-XIV) respectively.



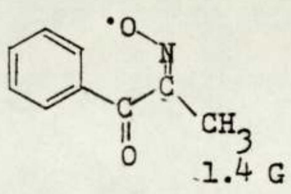
(2-XI)



(2-XII)



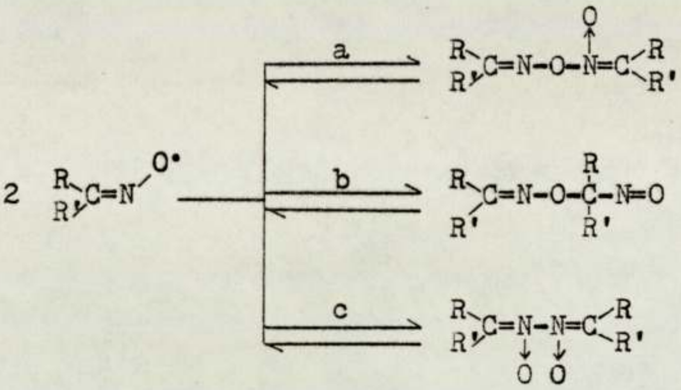
(2-XIII)



(2-XIV)

The N-hfsc and H-hfsc of some iminoxy radicals are shown in Table 2.5.

Iminoxy radicals can dimerise by N-N, N-O, and O-C coupling and rather complex mixtures of products are produced because of the instability of some of the iminoxy radical dimers. With unhindered dialkyl iminoxy radicals the equilibrium favours the radicals or else is only slowly established and decay is second order (J.L.Brokenshire et al., 1972). The principle self-reactions of the majority of iminoxy radicals are shown in following diagram.



(2.22)

<u>Table 2.5</u>

Isotropic Hyperfine Splittings and g Factors of Some Iminoxy Radicals

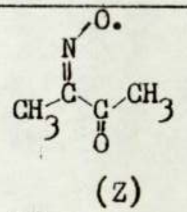
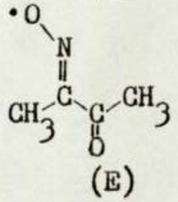
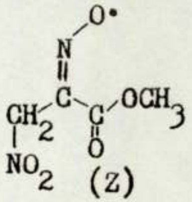
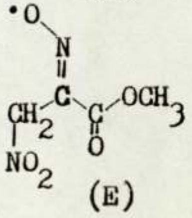
Radical	g-value	a_N(gauss)	Other Splittings(gauss)	Reference
 (Z)	2.0047	28.40	$3H(4,CH_3)$: 1.40	B.C.Gilbert, and other, 1969; R.O.C.Norman, and other, 1967
 (E)	2.0049	31.3	$3H(1,CH_3)$: 1.40 $3H(4,CH_3)$: 0.55	B.C.Gilbert, and other, 1969; R.O.C.Norman, and other, 1967; W.M.Fox et al., 1967
 (Z)	2.0045	30.2		W.M.Fox et al., 1967
 (E)	2.0045	34.5	$N(NO_2)$: 0.6	W.M.Fox et al., 1967

Table 2.5 (continued)

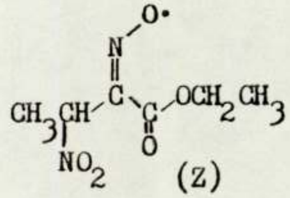
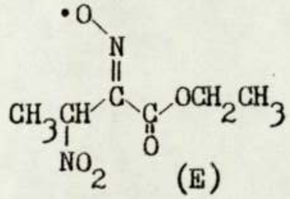
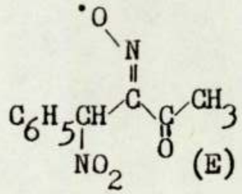
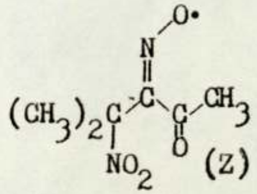
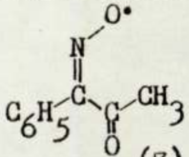
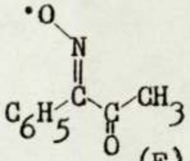
Radical	g-value	a_N(gauss)	Other Splittings(gauss)	Reference
 (Z)	2.0045	29.7		W.M.Fox et al., 1967
 (E)	2.0045	33.8	H(CH) : 4.4 3H(CH_3) : 1.4 N(NO_2) : 0.4	W.M.Fox et al., 1967
 (E)	2.0051	30.7	H(CH) : 2.7	W.M.Fox et al., 1967
 (Z)	2.0043	30.3	further hyperfine splittings	W.M.Fox et al., 1967

Table 2.5 (continued)

Radical	g-value	a_N(gauss)	Other Splittings(gauss)	Reference
 (Z)	2.0051	29.4	$3H(CH_3)$: 0.38 3H(2,6) : 0.38	B.C.Gilbert et al., 1971 W.M.Fox et al., 1967
 (E)	2.0048	31.6	$3H(CH_3)$: 0.75 3H(2,6) : 1.30	B.C.Gilbert et al., 1971; W.M.Fox et al., 1967

CHAPTER THREE

Experimental

CHAPTER THREE

EXPERIMENTAL

3.1 Materials

3.1.1 Alkenes Investigated

Most alkenes readily available commercially were purchased, in the purest form available. They were redistilled or recrystallised before use. Gaseous alkenes were used without further purification.

3.1.1.1 Alkenes with di-alkyl, tri-alkyl or halogen substituents.

The following materials were purchased:

Compound	Supplier
cis-2-butene	BDH Chemicals Ltd.
trans-2-butene	"
2-methyl-2-butene	"
cyclohexene	"
oleic acid (9-octadecenoic acid)	"
methyl oleate (9-octadecenoic acid, methyl ester)	"
1,2-dichloroethylene	Fisons
tetrachloroethylene	"

3.1.1.2 Terminal alkenes with alkyl, aryl or halogen substituents.

The following alkenes were purchased:

Compound	Supplier
iso-butene	BDH Chemicals Ltd.
2-methyl-1-butene	Koch-Light lab. Ltd.
1-decene	"
ethyl vinyl ether	"
allyl chloride (3-chloropropene)	BDH Chemicals Ltd.

Compound	Supplier
3-butenoic acid	Koch-Light lab. Ltd.
styrene (phenylethylene)	BIP Chemicals Ltd.
p-methoxystyrene (4-methoxyphenylethylene)	Koch-Light lab. Ltd.
α -methylstyrene (1-methyl-1-phenylethylene)	BDH Chemicals Ltd.
hexachloropropene	Koch-Light lab. Ltd.
hexachloro-1,3-butadiene	"

3.1.1.3 Alkenes with carbonyl, alkyl carbonyl or halogen substituents.

The following alkenes were purchased:

Compound	Supplier
acrylic acid (propenoic acid)	BDH Chemicals Ltd.
3-butene-2-one	Koch-Light lab. Ltd.
acraldehyde (propenal)	Aldrich Chemical Co.Ltd.
methacrolein (2-methylpropenal, α -methylacraldehyde)	"
methacryloyl chloride (2-methylpropenyl chloride)	"
methyl methacrylate (monomer) (2-methylpropenoic acid,methyl ester)	BDH Chemicals Ltd.
crotonic acid (2-butenoic acid)	Hopkin & Williams Ltd.
ethyl crotonate (2-butenoic acid, ethyl ester)	Fisons
methyl crotonate (2-butenoic acid, methyl ester)	Fisons
crotonaldehyde (2-butenal)	Hopkin & Williams Ltd.

Compound	Supplier
hexachloro-2-butenoic acid	Koch-Light lab. Ltd.
3-pentene-2-one	Aldrich Chemical Co.Ltd.
tiglic acid (2-methyl-2-butenoic acid)	Koch-Light lab.Ltd.
3,3-dimethylacrylic acid (3-methyl-2-butenoic acid)	"
mesityl oxide (4-methyl-3-pentene-2-one)	Hopkin and Williams Ltd.
maleic acid (cis-ethylene-1,2-dicarboxylic acid)	Fisons

The following alkenes were prepared using the methods described by A.I.Vogel (1978):

fumaric acid	(trans-ethylene-1,2-dicarboxylic acid)
dimethyl maleate	(cis-ethylene-1,2-dicarboxylic acid, dimethyl ester)
dimethyl fumarate	(trans-ethylene-1,2-dicarboxylic acid, dimethyl ester).

3.1.1.4 Alkenes with aryl or aryl carbonyl substituents.

The alkenes purchased were:

Compound	Supplier
cis-stilbene (cis-1,2-diphenylethylene)	Koch-Light lab.Ltd.
trans-stilbene (trans-1,2-diphenylethylene)	"
cinnamaldehyde (trans-3-phenylpropenal)	BDH Chemicals Ltd.
cinnamic acid (trans-3-phenylpropenoic acid)	Hopkin and Williams Ltd.
benzalacetone (4-phenyl-3-butene-2-one)	"

Compound	Supplier
cinnamyl alcohol (3-phenyl-2-propene-1-ol)	BDH Chemicals Ltd.
α-methylcinnamaldehyde (2-methyl-3-phenylpropenal)	Aldrich Chemical Co.Ltd.

The following alkenes were prepared using the methods described by A.I.Vogel (1978):

benzalacetophenone	(1,3-diphenyl-2-propene-2-one, or chalcone)
dibenzalacetone	(1,5-diphenyl-1,4-pentadiene-3-one or dibenzilideneacetone)

3.1.2 Nitrogen dioxide (NO_2) and nitric oxide (NO).

Nitrogen dioxide and nitric oxide were purchased from BDH Chemicals Ltd. They were purified before use by the methods described in sections 3.2.1 and 3.2.2.

3.1.3 Nitrosobenzene

Nitrosobenzene was prepared by the method described by G.H.Coleman, C.M.McCloskey, and F.A.Stuart (1955). Recrystallised product was white solid, m.p.= 64-67° and was kept in a closed container at 0°.

3.1.4 Phenyl N-tert-butyl nitrone (PBN).

Phenyl N-tert-butyl nitrone was purchased from Lancaster Synthesis Ltd., and it was used without further purification.

3.1.5 1,4-Dioxan

Solvent which was used throughout this work was 1,4-dioxan. It was purified by the method described by A.I.Vogel, 1978.

3.2 Methods

3.2.1 Solutions of NO_2 in 1,4-Dioxan

NO_2 gas was bubbled through 1,4-dioxan until the solution became dark brown and this solution was used as "solution of high concentration of NO_2". In practice, this solution was further diluted with a small quantity of 1,4-dioxan if it gave a violent reaction with alkenes or to prevent the reaction from overoxidised by NO_2.

"Solution of low concentration of NO_2" was prepared by diluting the "solution of high concentration of NO_2" with 1,4-dioxan to the concentration which upon gradually mixed to solution of alkene resulted in only one type of radical product and high esr spectral intensities were observed.

Both solutions of low and high concentrations of NO_2 were bubbled with oxygen to oxidise lower oxides of nitrogen, for example NO to NO_2 and they were deoxygenated by bubbling nitrogen through the solutions before mixing with the alkene solutions.

3.2.2 Solution of NO in 1,4-dioxan in the presence of a trace of NO_2.

NO from cylinder was purified by passing through KOH solution and two cold traps, one containing solid carbon dioxide and a second containing a solid carbon dioxide and acetone mixture. The gas was then bubbled through 1,4-dioxan solution until a saturated solution was obtained. This solution was used together with a drop of solution of low concentration of NO_2 (from section 3.2.1) to mix with alkene solutions in the experiments on the reactions of NO in the presence of a trace of NO_2 with alkenes.

3.2.3 Solutions of Alkenes

Solutions of gaseous alkenes, for example cis-2-butene, trans-2-butene, and iso-butene were prepared by bubbling the gaseous alkene into 1,4-dioxan until saturation occurred.

Solutions of liquid alkenes were prepared by mixing equal quantities of liquid alkene and 1,4-dioxan together. Some alkenes, for example ethyl vinyl ether, acrylic acid and acraldehyde were very reactive. The solutions of these alkenes were prepared by adding a drop of alkene to 0.5 ml of 1,4-dioxan.

Solutions of solid alkenes were prepared by dissolving the alkene in 0.5 ml of 1,4-dioxan until a saturated solution was formed. In the case of trans-stilbene, a mixture of n-hexane and 1,4-dioxan (1:1) was used as solvent.

3.2.4 Sample preparation for electron spin resonance spectroscopy.

3.2.4.1 Sample preparation for the study of reactions of NO_2 with alkenes under "ordinary reaction condition".

In most cases, a few drops of NO_2 solution were added to 0.5 ml of solution of alkene at room temperature. A small quantity of this mixture was subsequently transferred into a small capillary tube, both ends were sealed and the mixture was examined for radical products in the cavity of esr spectrometer at room temperature.

Only in the case of cinnamaldehyde, was the sample prepared at ice-salt cooling-bath temperature and the esr measurement carried out at room temperature.

The reactions of both low and high concentrations of NO_2 with alkenes were studied using these reaction condition (see sections 4.5, and 4.6).

3.2.4.2 Sample preparation for the study of reactions of NO_2 with alkenes with the addition of oxygen gas.

The samples were prepared as in the same method as under "ordinary reaction condition" but as soon as both reactants were well mixed, oxygen was bubbled through the solutions for two minutes and the resulting solutions were then sealed in capillary tubes and examined for radical products by esr spectroscopy.

The reactions of both low and high concentrations of NO_2 and alkenes with the addition of oxygen were studied as discussed in section 4.7.

3.2.4.3 Sample preparation for the study of reactions of NO_2 with alkenes at elevated reaction temperature.

The reaction solutions were prepared as in the same method as "ordinary reaction condition" sample preparation, as soon as both reactants were well mixed, the reaction solutions were placed in a boiling water-bath for one minute or until the colour of the solutions changed from green or blue to yellow or colourless and the resulting solutions in sealed capillary tubes were examined for radical products at room temperature. Some alkenes were studied at varying reaction temperatures, for example raising, and lowering the temperatures in the range between room temperature and boiling water-bath temperature, and the esr measurements were carried out at room temperature. Some alkenes solutions were kept in the boiling water-bath until the colour of the solution no longer changed or for about five minutes and then the radical products were examined by esr spectroscopy.

The reactions of NO_2 and alkenes under this reaction condition were discussed in section 4.7.

3.2.4.4 Sample preparation for the study of reactions of NO in the presence of a trace of NO_2 with alkenes.

In all cases, equal quantities of a solution of NO in 1,4-dioxan in the presence of a trace of NO_2 and the solution of the alkene (section 3.2.3) were mixed together and subsequently a small amount of this solution in a sealed capillary tube was examined for radical products.

Another reaction condition used was that of bubbling oxygen through the reaction solution, prepared as described above, for two minutes and then examining the solution for radical products.

The study of reactions of NO in the presence of a trace of NO_2 with alkenes under "ordinary reaction condition", and in addition of oxygen is described in section 4.8.

3.2.4.5 Sample preparation for the study of reaction of NO_2 with alkene upon exposure to ultraviolet light

The sample was prepared as method described in section 3.2.4.1, and it was transferred into a capillary tube, both ends were sealed. This capillary tube containing sample was continuously exposed to ultraviolet light in an ultra-violet exposure carbinet for a period of time as required and radical products were examined by esr spectroscopy (see section 4.9)

3.2.4.6 Sample preparation for the study of reaction of NO_2 with alkenes in the presence of spin trap.

Two spin traps, nitrosobenzene and phenyl N-tert-butyl nitrone were used in this experiment. When nitrosobenzene was used as spin trap, the sample was prepared by the addition of a few drops of the solution of low concentration of NO_2 at the same time adding a few drops of nitrosobenzene solution to the alkene solution and thoroughly mixing the lot. Solution of nitrosobenzene was prepared by dissolving a few crystals of nitrosobenzene in 0.3 ml of 1,4-dioxan. When phenyl N-tert-butyl nitrone was used as spin trap, the sample was prepared by dissolving a few crystals of phenyl N-tert-butyl nitrone in 0.5 ml of alkene solution and then a few drops of the solution of low concentration of NO_2 was added. The resulting solutions were transferred and kept in sealed capillary tubes and examined for radical products in esr cavity (see Chapter Five).

3.2.4.7 Sample preparation for the study of reactions of NO_2 with alkenes by using continuous flow technique.

The saturated alkene solution and the solution of low concentration of NO_2 were placed in separate containers, and flowed through a mixing chamber by gravitational force and then the mixed solution entered the esr cavity. The fastest flow rate of an apparatus in this study was 0.60 ml/sec, but other flow rates were able to be obtained. The radical products were examined at the position at which both reactants just mixed and then entered a quartz flat cell in esr cavity (see sections 5.2 and 5.4). The mixing cell is described in section 3.3.2.

3.3 Instruments

3.3.1 Ultra-violet exposure carbinet

The source of ultra-violet light used were 24 'Actinic' lamps and 8 'sunlamps' which were symmetrically arranged on a 3:1 basis in the ultra-violet carbinet. The samples placed in this carbinet were rotated to exposed to all light wavelengths.

3.3.2 Mixing cell

The mixing cell which was used in this study was based on the mixing cell of D.G.Borg (1964). Two reactants flowed from separate containers to the arms of mixing cell and mixed at the point at which the mixed solution could enter the quartz flat compartment of mixing cell within the shortest time. The quartz flat compartment was fixed in esr cavity. Figure 3.1 shows the mixing cell which was used in this study.

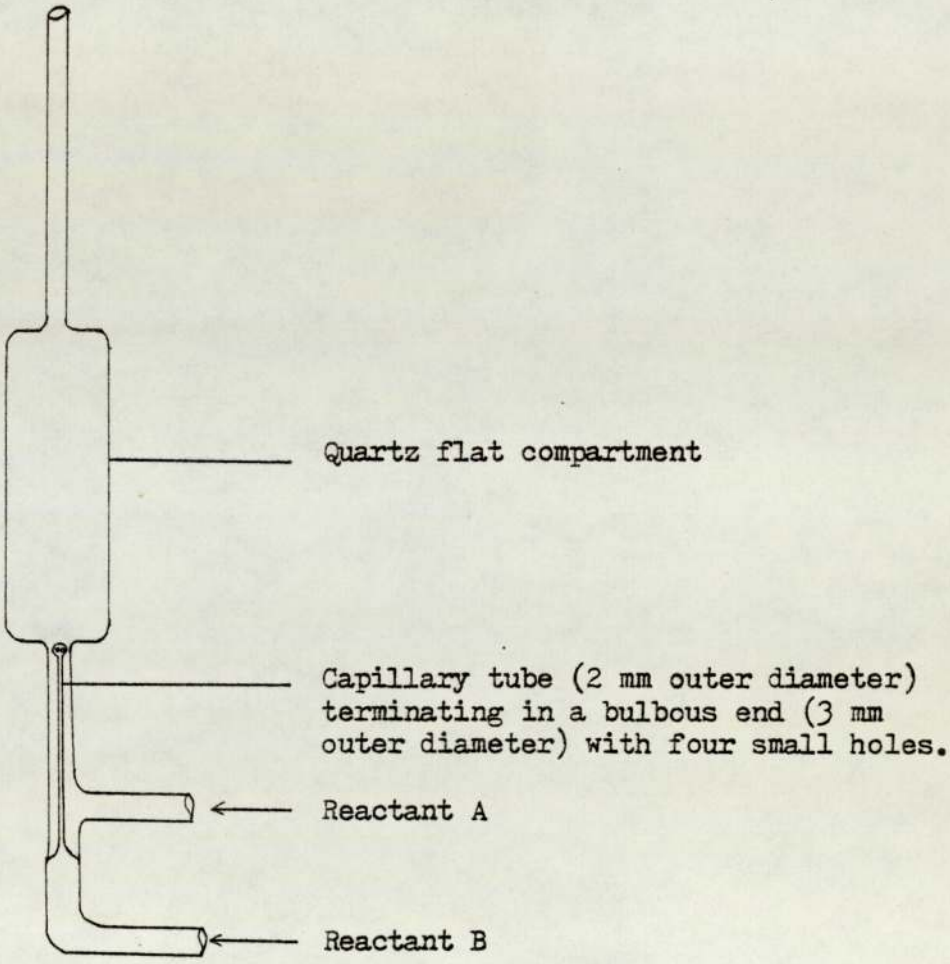


Figure 3.1 Mixed-flow cell

3.3.3 The Electron Spin Resonance Spectrometer

3.3.3.1 A Description of the Instrument

The electron spin resonance spectrometer used in this work was a commercially available one, the 'JEOL-PE 1' manufactured by Jeol Ltd., Japan. This is an instrument using high frequency modulation and phase sensitive detection. This is also known as homodyne detection, and involves modulating the magnetic field at high frequency, usually 100 kHz, with an amplitude small compared with the line width, and then sweeping slowly through the resonant condition.

A block diagram of the apparatus is given in Figure 3.2.

Energy is fed into the hybrid tee bridge from the klystron and is split equally between the side arms, one arm feeds energy to the resonant cavity, the other arm carries components which reflect back a resonance wave, adjustable in amplitude and phase. These two reflected waves are detected in the fourth arm of the tee. In the off-resonant condition, the reference wave is adjusted to give a reflection equal in amplitude and opposite in phase to the reflection from the sample and cavity, and therefore cancels, with zero power being transmitted to the crystal detector in the fourth arm. At resonance, an off-balance signal is detected.

A modulation coil is mounted inside the cavity. It modulates the steady magnetic field of the sample at the modulation frequency. Any absorption or dispersion due to resonance in the specimen changes the reflection coefficient unbalances the bridge. The crystal detects the resulting high frequency signal (100 kHz), which passes through a low noise pre-amplifier and a narrow band amplifier to a phase sensitive detector, which is also fed with a reference signal that is adjustable in phase relative to the modulation. The high frequency modulator supplies

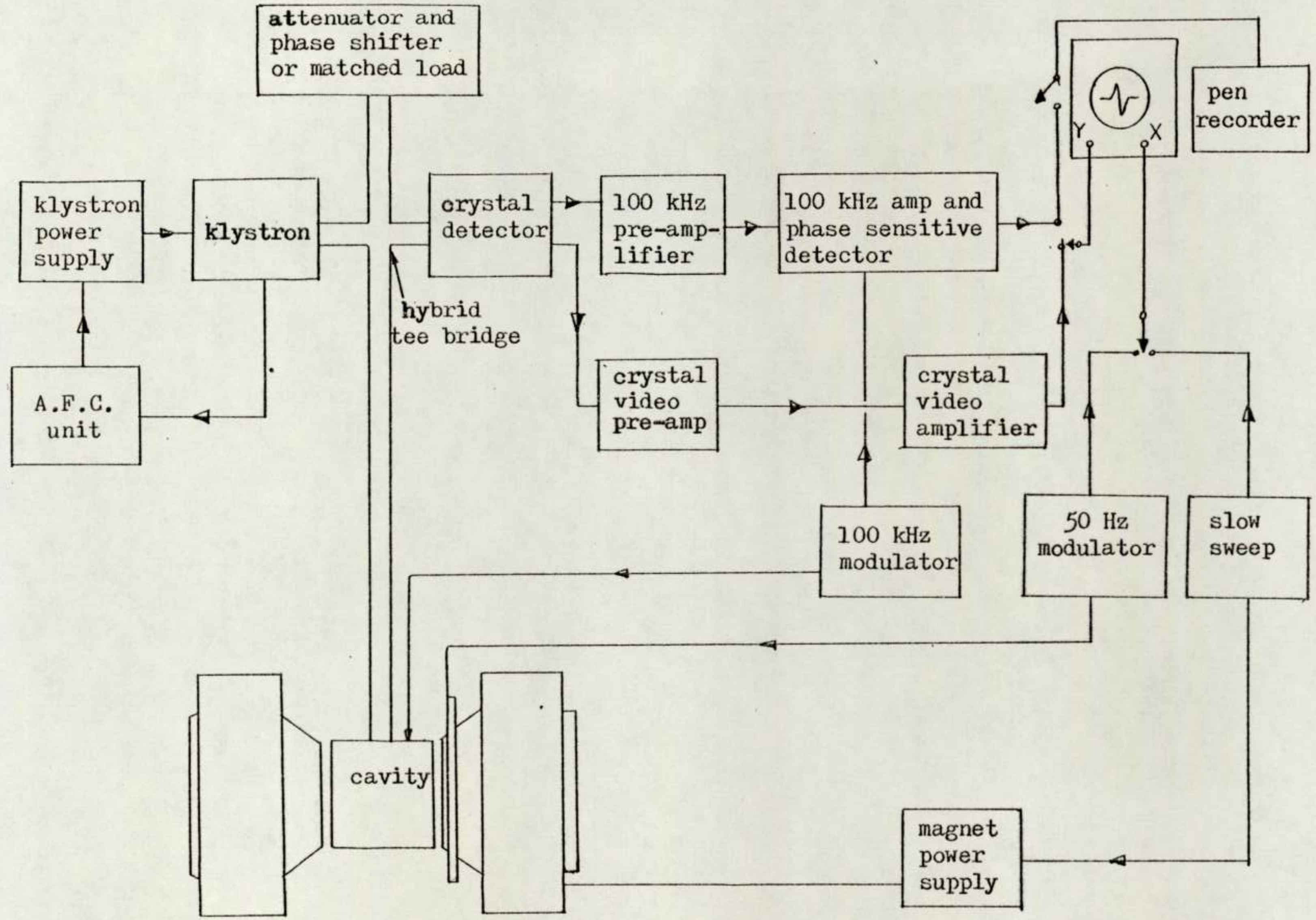


Figure 3.2 Block diagram of high frequency modulation spectrometer.

the modulation coils and also reference output for the phase sensitive detector.

Automatic frequency control is an incorporated feature of the machine, allowing the klystron frequency to be locked to the resonant frequency of the sample cavity.

The esr signal may be displayed on a cathode-ray oscilloscope, or by a pen recorder.

All the work was carried out using X-band radiation, approximately 9400 MHz frequency, and the field intensity according to this frequency band is 3360 gauss.

3.3.3.2 Cavity

TE 011 mode (cylindrical) was used throughout this work. The magnetic and electric field configulation is shown in Figure 3.3. The maximum magnetic field is along the central vertical axis, and the sample should be positioned at the centre of the cavity. In addition, the greater the sample quantity placed in the cavity, the greater the effective volume subject to the magnetic field, hence the stronger the signal.

3.3.3.3 Spectrometer Operation

The instrument was set up as instructed by manufacturers.

The frequency of the Klystron and the natural resonance frequency of the sample cavity were adjusted to be the same, and the Klystron frequency was then locked to the sample cavity frequency by an AFC unit. Changes in sample cavity frequency were then followed by the klystron, the instrument remaining 'on tune' (assuming changes in sample cavity frequency were small). This enabled the spectrometer to be used for several hours without retuning. Samples were often changes without necessitating more than very minor adjustment of the spectrometer, enabling comparisons between different samples to be carried out.

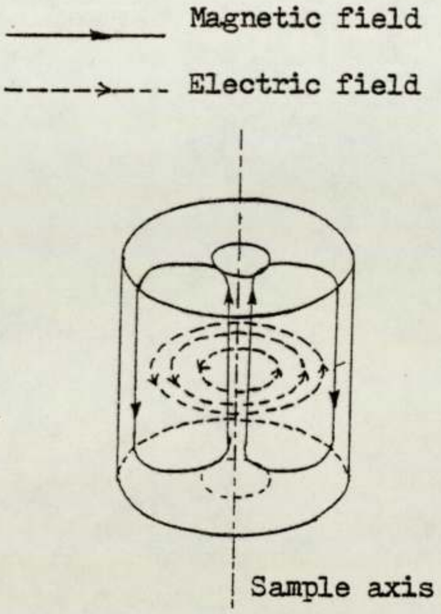


Figure 3.3 Cylindrical TE 011 resonant cavity and the electric and magnetic fields of the standing wave.

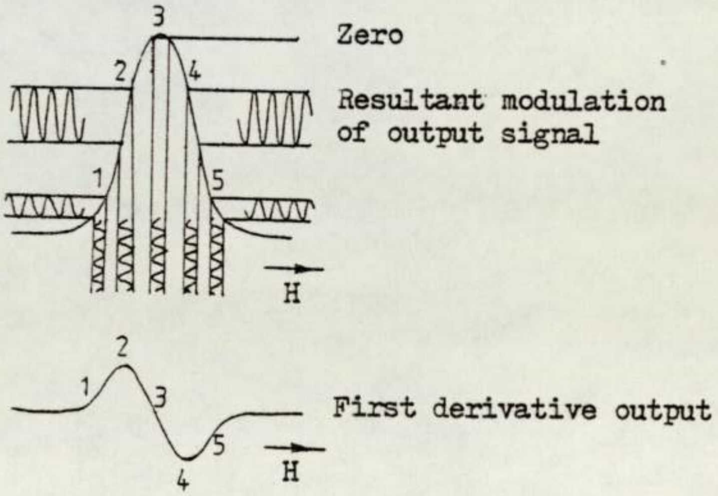


Figure 3.4 First derivative output, obtained when the amplitude of the high frequency modulation is small compared to the line width.

The absorption of microwave energy was detected using phase-sensitive detection with a 100 kHz modulation current, and the first derivative signal thus obtained displayed on an oscilloscope. The magnitude of the modulation current, and thus the amplitude of the modulation field, was made small enough to minimise lack of resolution by modulation current broadening, and the scan speed and the amplitude set to display the signal. A permanent recording was made by a chart recorder.

3.3.3.4 Use of Derivative of Absorption

The amount of the supplied microwave power absorbed by the sample is only a small fraction, necessitating amplification of the signal. If the dc output from the microwave detector were amplified, it would be difficult to detect the small change in the dc level the absorption would make. If, instead, a small oscillating magnetic field is superimposed onto the large applied field, a process referred to as modulation of the applied field, this small field alternately adds to and abstracts from the large field, H_o.

As the resultant $H_o + H_{modulation}$ swings up and down, the dc output also increases and decreases. This therefore supplies an ac signal which may be amplified, and is not a small alteration of a large signal level, but is zero when the sample is not absorbing microwave power. This process is illustrated diagramatically in Figure 3.4.

3.3.3.5 Measurement of g-values and hyperfine splitting constants

The g-value or spectroscopic splitting constant of a paramagnetic species is defined by the equation

$$h\nu = g\beta H \qquad (3.1)$$

where h and β are known constants, and it is usual for practical reasons, to hold ν constant and sweep the magnetic field over the resonance positions. Thus,

$$gH = \frac{h\nu}{\beta} = \text{constant} \qquad (3.2)$$

Thus, if the frequency ν and the magnetic field H are measured, g may be calculated. It was, however, not possible to read the frequency accurately. The g-values were therefore calculated relative to a standard.

The standard chosen was Mn^{++} containing in MgO which gives six lines esr spectrum, the g-value of the fourth line counted from the low magnetic field side is $g_1 = 1.981$. In the JES-UCX-2 Cavity Resonator, this value remains constant for cavity resonance frequencies between 9200 ~ 9400 MHz. Furthermore, the distant between the third and the fourth lines is 86.9 gauss.

Assume that the following measured sample and esr standard signals were recorded simultaneously and the data as shown in Figure 3.5 was obtained.

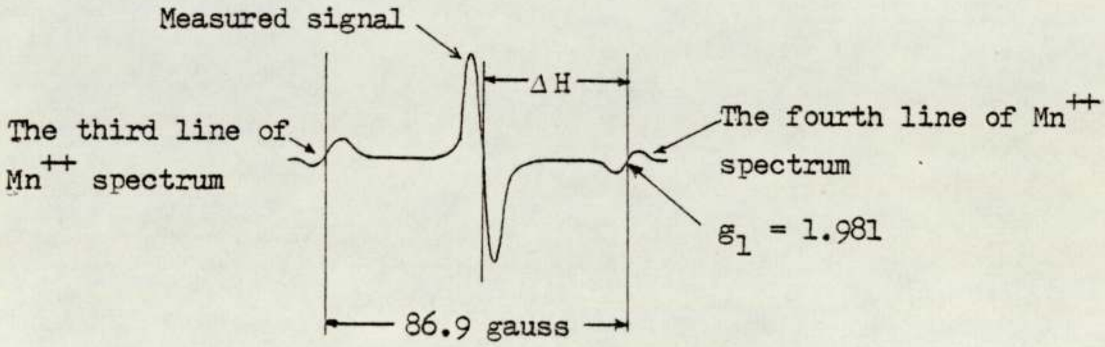


Figure 3.5

From the diagram
$$g = \frac{g_1 H_1}{H_1 - \Delta H} \qquad (3.3)$$

where g is the g-value of the unknown sample

g_1 is the g-value of the fourth line of Mn^{++} spectrum (1.981 at 9300 MHz)

H_1 is the value of the field at the fourth line of Mn^{++} spectrum and ΔH is the field deviation of the unknown peak and the fourth line of Mn^{++} spectrum.

Thus, the g-value can be obtained easily without measuring the microwave frequency. In this case, if the measured sample spectrum appears in a magnetic field higher than that of the fourth line, it will be necessary to make ΔH negative.

Using proportional calculation compares to the distant between the third and the fourth lines of Mn^{++} spectrum, hyperfine splitting are easily determined from the recorded spectra.

CHAPTER FOUR

The Addition of Nitrogen Dioxide to Alkenes

Results and Discussion

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The Addition of Nitrogen Dioxide to Alkenes

Results and Discussion

Results

Alkenes which were studied in this work were classified into four groups by the characteristics of substituents on a single double bond as following:

1. Alkenes with dialkyl-, trialkyl-, or halogen substituents.
2. Terminal alkenes with alkyl-, aryl-, or halogen substituents.
3. Alkenes with carbonyl-, alkyl carbonyl-, or halogenyl carbonyl- substituents.
4. Alkenes with aryl-, or aryl carbonyl substituents.

The difference in substituents and also in reaction conditions lead to the production of different radical products. Reactions of low concentration of NO_2 with alkenes at room temperature and 1,4-dioxan as solvent were studied and the radical products were detected by esr spectroscopy within few minutes in freshly prepared solutions. The esr spectra showed that alkyl nitroxides, a_N = 13-15 G, or iminoxy radicals, a_N = 29-32 G were formed. In reactions in which there was a high concentration of NO_2 with alkenes, the radical products which we detected, apart from alkyl nitroxides, and iminoxy radicals, were radicals with N-hyperfine splitting of about 7 G which was the characteristic of acyl nitroxides were also observed.

In the study of the reactions of both low and high concentrations of NO_2 with alkenes with the addition of oxygen at room temperature or when the reaction was carried out at an elevated temperature (at boiling water-bath temperature) and with 1,4-dioxan as solvent, we found that the main radical products were acyl nitroxides. Although there were some alkenes which did not produce acyl nitroxides under these conditions, the esr spectra showed a change in radical concentrations compared to that produced by 'ordinary' condition.

In order to understand the reaction mechanisms of radical formation, we also studied the reactions of NO in the presence of a trace of NO_2 with alkenes. The radical products were alkyl nitroxides and/or iminoxy radicals produced in high yields compared to the radical products observed from the reactions of NO_2 with alkenes. At high concentration of NO, or with the addition of oxygen, or at elevated reaction temperature, acyl nitroxides were never detected.

Consideration was also given to the involvement of atmospheric oxygen and room daylight in the reactions of NO_2 with alkenes. We studied the reactions of both low and high concentrations of NO_2 with iso-butene in which the reaction mixtures were kept exposed or unexposed to room daylight or to atmospheric oxygen (air). The radical products were detected at different times for two months. The esr spectra showed a decrease in alkyl nitroxide concentration and increase in acyl nitroxide concentration dependent on reaction time, and also at different reaction rates according to the oxygen concentration present in the reaction mixture. We found that there was no difference in radical products and their concentrations on exposure or unexposure to room daylight.

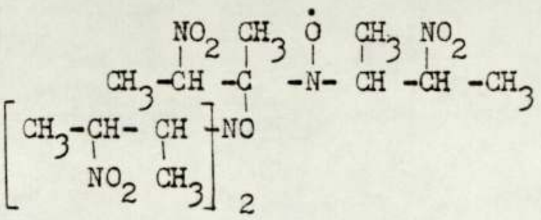
The results from all experiments will be described in detail as following.

4.1 Alkenes with dialkyl-, trialkyl-, or halogen substituents.

Alkenes which were classified into this group were cis-2-butene, trans-2-butene, 2-methyl-2-butene, cyclohexene, oleic acid, methyl oleate, dichloroethylene, and tetrachloroethylene. Radical products which we observed from these alkenes were alkyl nitroxides, and acyl nitroxides.

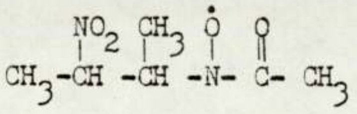
4.1.1 cis-2-Butene, and trans-2-Butene

Blue solutions of low concentration of NO_2, and cis-2-butene or trans-2-butene in 1,4-dioxan yielded radicals which had esr spectra which were typical of alkyl nitroxides, i.e. 3 doublets a_N = 13.167 G (1:1:1), $a_{H(CH)}$ = 1.756 G (1:1), and a_N = 13.268 G (1:1:1), $a_{H(CH)}$ = 1.749 G (1:1) from cis-2-butene, and trans-2-butene respectively (Figure 4.1). We suggest structure (4-I) for these alkyl nitroxides. When similar reactions were carried out but elevated reaction temperature or with the addition of oxygen then resulted yellow solutions, and only acyl nitroxide (4-II), 3 doublets esr spectra a_N = 7.618 G (1:1:1), $a_{H(CH)}$ = 2.12 G (1:1), and a_N = 7.683 G (1:1:1), $a_{H(CH)}$ = 2.048 G (1:1) were detected from cis-,and trans-2- butenes respectively.



$$\mathrm{CH_3{-}\overset{NO_2}{\overset{|}{CH}}{-}\overset{CH_3}{\overset{|}{\underset{\left[CH_3{-}\underset{NO_2}{\underset{|}{CH}}{-}\underset{CH_3}{\underset{|}{CH}}\right]_2 NO}{\underset{|}{C}}}}{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}{-}\overset{CH_3}{\overset{|}{CH}}{-}\overset{NO_2}{\overset{|}{CH}}{-}CH_3}$$

(4-I)



$$\mathrm{CH_3{-}\overset{NO_2}{\overset{|}{CH}}{-}\overset{CH_3}{\overset{|}{CH}}{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

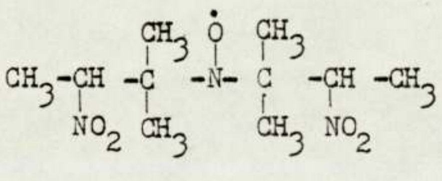
(4-II)

At high concentration of NO_2, and cis-2-butene or trans-2-butene, the yellow solutions which resulted, contained alkyl nitroxide (4-I) and acyl nitroxide (4-II) (Figure 4.2), but only acyl nitroxide (4-II) was observed when the same reaction mixtures were studied at elevated reaction temperature or with the addition of oxygen gas (Figure 4.3).

In the study of the reaction of NO with cis-2-butene, and trans-2-butene in the presence of a trace of NO_2 in 1,4-dioxan solution, at room temperature or at elevated reaction temperatrue, with or without the addition of oxygen, and also with an excess amount of NO, only alkyl nitroxide (4-I) was detected. This radical was observed in high yield under 'ordinary' reaction condition and its spectral intensities were increased at elevated reaction temperatures.

4.1.2 2-Methyl-2-butene

The blue solution of low concentration of NO_2, and 2-methyl-2-butene in 1,4-dioxan gave 3 lines esr spectrum of alkyl nitroxide (4-III), a_N = 14.147 G (1:1:1). A higher intensity spectrum of this radical was observed when reaction temperature was increased and a lower intensity spectrum of the same radical was obtained when the reaction temperature was prolong increased where acyl nitroxide (4-IV), a_N = 7.804 G (1:1:1) was also observed in low yield. Addition of oxygen to the reaction mixture, resulted in decreased spectral intensities of alkyl nitroxide (4-III).



$$CH_3-\underset{NO_2}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\dot{O}}{N}-\overset{CH_3}{\underset{CH_3}{C}}-\underset{NO_2}{CH}-CH_3$$

(4-III)

Figure 4.1 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with cis-2-butene, at room temperature.

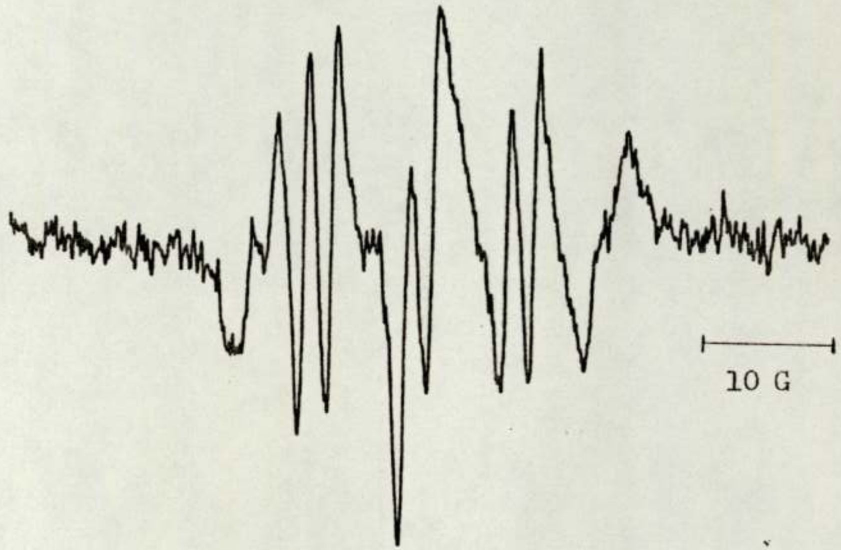


Figure 4.2 Electron spin resonance spectrum of radicals formed by reaction of high concentration of NO_2 with cis-2-butene, at room temperature.

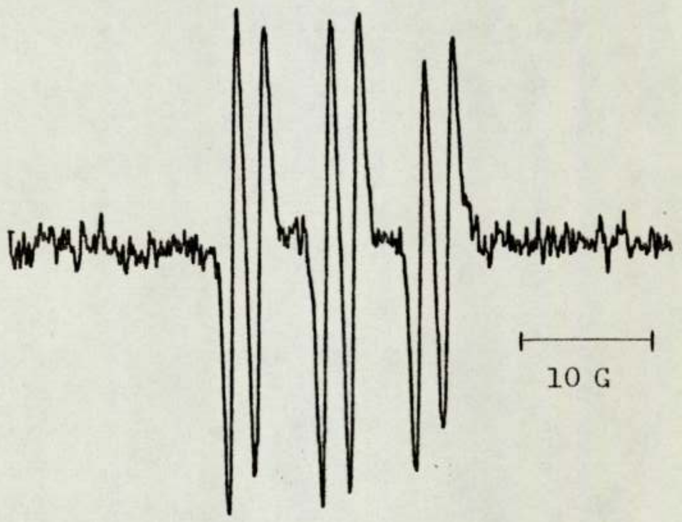
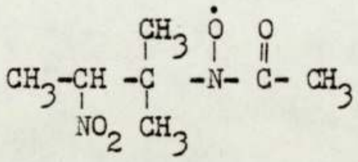


Figure 4.3 Electron spin resonance spectrum of radicals formed by reaction of high concentration of NO_2 with cis-2-butene, with addition of oxygen.



$CH_3-CH(NO_2)-C(CH_3)_2-N(\dot{O})-C(=O)-CH_3$

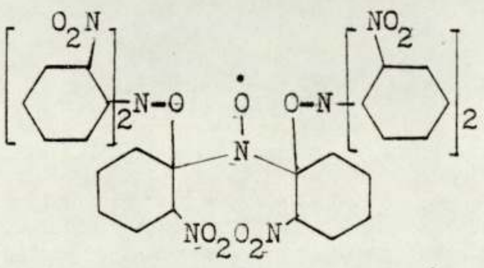
(4-IV)

At high concentration of NO_2, and 2-methyl-2-butene, the main radical product detected was alkyl nitroxide (4-III) and acyl nitroxide (4-IV) was found only in traces.

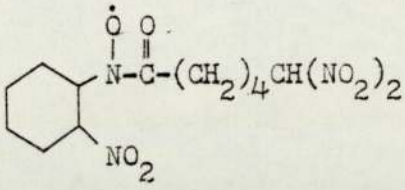
In the reaction of NO, and 2-methyl-2-butene in the presence of a trace of NO_2 in 1,4-dioxan , only alkyl nitroxide (4-III) was observed in high yield especially at elevated reaction temperature.

4.1.3 Cyclohexene

The yellow solution of low concentration of NO_2, and cyclohexene yielded alkyl nitroxide (4-V), its esr spectrum showed 3 lines with a_N = 12.374 G (1:1:1) and was stable for a few hours in this reaction mixture. The reaction of high concentration of NO_2 and cyclohexene resulted in acyl nitroxide (4-VI) in low yield, the weak 3 lines esr spectrum showed a_N = 6.705 G (1:1:1).



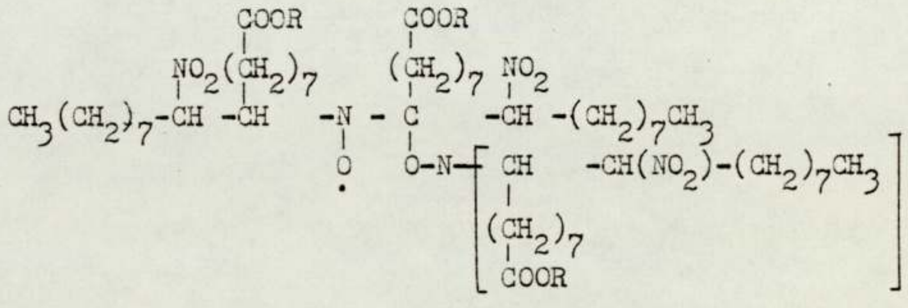
(4-V)



(4-VI)

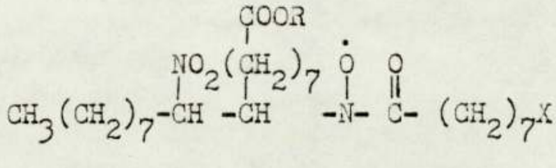
4.1.4 Oleic acid, and Methyl oleate

Alkyl nitroxide (4-VIIa), or (4-VIIb) was obtained from the reactions of low concentration of NO_2, and oleic acid or its methyl ester in 1,4-dioxan solution. Their esr epectra showed 3 doublets with a_N = 14.952 G, $a_{H(CH)}$ = 2.06 G for nitroxide (4-VIIa), and a_N = 14.759 G, $a_{H(CH)}$ = 2.11 G for nitroxide (4-VIIb). When the reaction temperature was increased, alkyl nitroxide (4-VIIa) or (4-VIIb), and acyl nitroxide (4-VIIIa) a_N = 6.713 G, or (4-VIIIb) a_N = 6.78 G were detected.



(4-VIIa) R = H

(4-VIIb) R = CH_3



$CH_3(CH_2)_7-CH(NO_2)-CH((CH_2)_7COOR)-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_7X$

X = COOR, or CH_3

(4-VIIIa) R = H

(4-VIIIb) R = CH_3

At high concentration of NO_2, and oleic acid or methyl oleate in 1,4-dioxan solution, only acyl nitroxide (4-VIIIa) or (4-VIIIb) was obtained.

4.1.5 Dichloroethylene, and Tetrachloroethylene

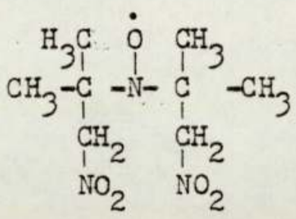
Reactions of dichloroethylene, and tetrachloroethylene with NO_2 at both low, and high concentrations were studied at room temperature or at elevated reaction temperature, with or without the addition of oxygen, the resulted reaction mixtures did not generate any detectable radical product.

4.2 Terminal alkenes with alkyl-, aryl-, or halogen substituents.

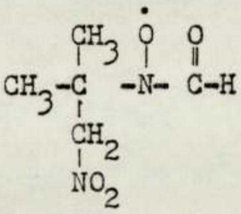
Compounds which were classified into this group were iso-butene, 2-methyl-1-butene, 1-decene, ethyl vinyl ether, allyl chloride, 3-butenoic acid, styrene, p-methoxystyrene, α-methylstyrene, hexachloropropene, and hexachloro-1,3-butadiene. Radical products observed from this group were alkyl nitroxides, and acyl nitroxides.

4.2.1 iso-Butene

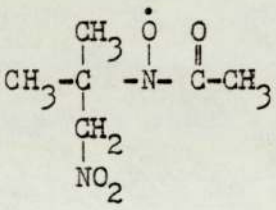
The blue solution of low concentration of NO_2, and iso-butene in 1,4-dioxan yielded alkyl nitroxide whose esr spectrum showed 3 quintets with $a_N = 14.695$ G (1:1:1), $a_{4H(\gamma CH_2)} = 0.561$ G (1:4:6:4:1) which is suggested to be the alkyl nitroxide (4-IX). Its esr spectra is shown in Figure 4.4. Reaction of high concentration of NO_2, and iso-butene resulted in a yellow solution whose esr spectrum showed broad 3 lines of the alkyl nitroxide (4-IX), and 3 doublets of acyl nitroxide (4-X), $a_N = 7.126$ G (1:1:1), and $a_{H(-CHO)} = 1.397$ G (1:1), and is shown in Figure 4.5. Reaction of low concentration of NO_2, and iso-butene with the addition of oxygen gave colourless solution which esr spectrum showed 3 doublets of acyl nitroxide (4-X) as radical product (Figure 4.6).



(4-IX)



(4-X)



(4-XI)

The solution of low concentration of NO_2, and iso-butene was studied at elevated reaction temperature, and produced acyl nitroxide (4-XI), 3 lines, $a_N = 7.665$ G (1:1:1) as main radical product, and acyl nitroxide (4- X) as a minor radical product (Figure 4.7).

The high concentration of NO_2, and iso-butene reaction with addition of oxygen produced only acyl nitroxide (4-X) or when this solution was carried out at elevated reaction temperature only acyl nitroxide (4-XI) was detected.

The study of the reaction of an excess of NO with iso-butene in the presence of a trace of NO_2 in 1,4-dioxan, at room temperature or at elevated reaction temperature, with or without the addition of oxygen, only alkyl nitroxide (4-IX) was detected.

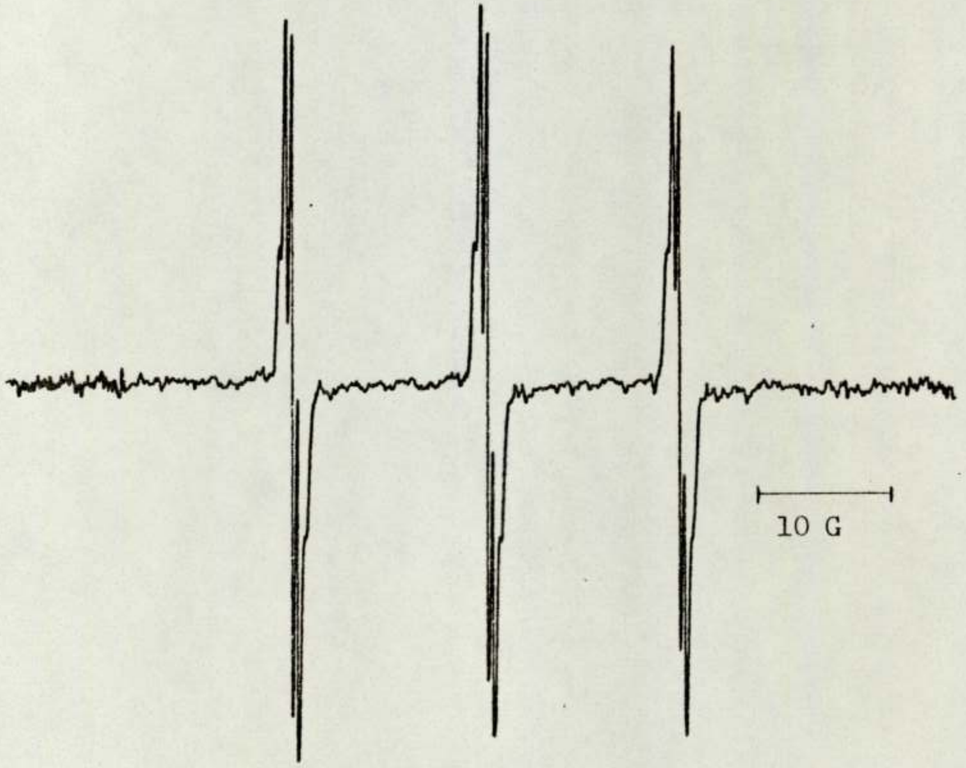


Figure 4.4 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with iso-butene, at room temperature.

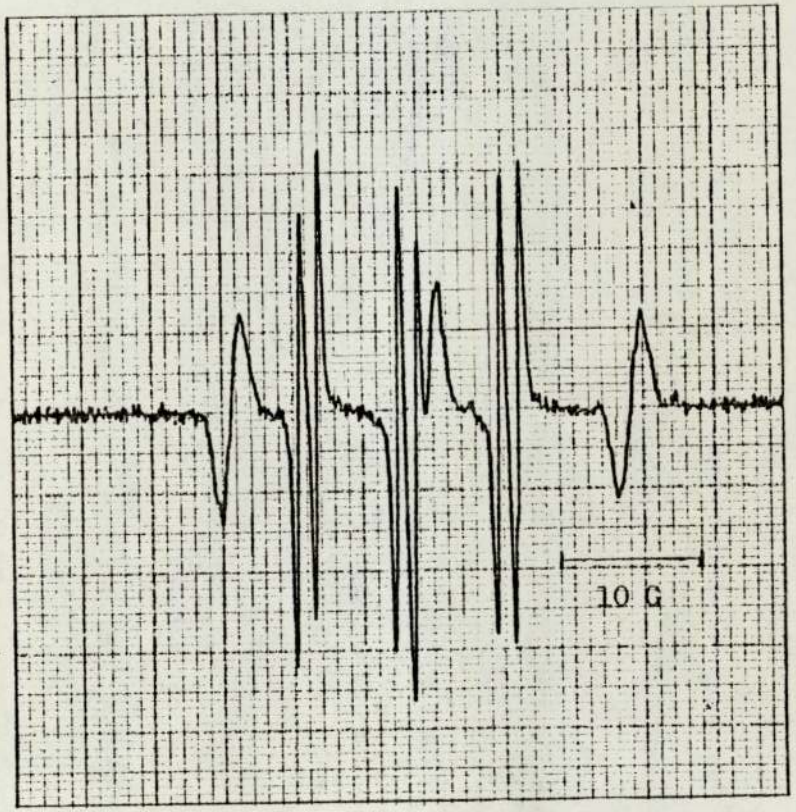


Figure 4.5 Electron spin resonance spectrum of radicals formed by reaction of high concentration of NO_2 with iso-butene, at room temperature.

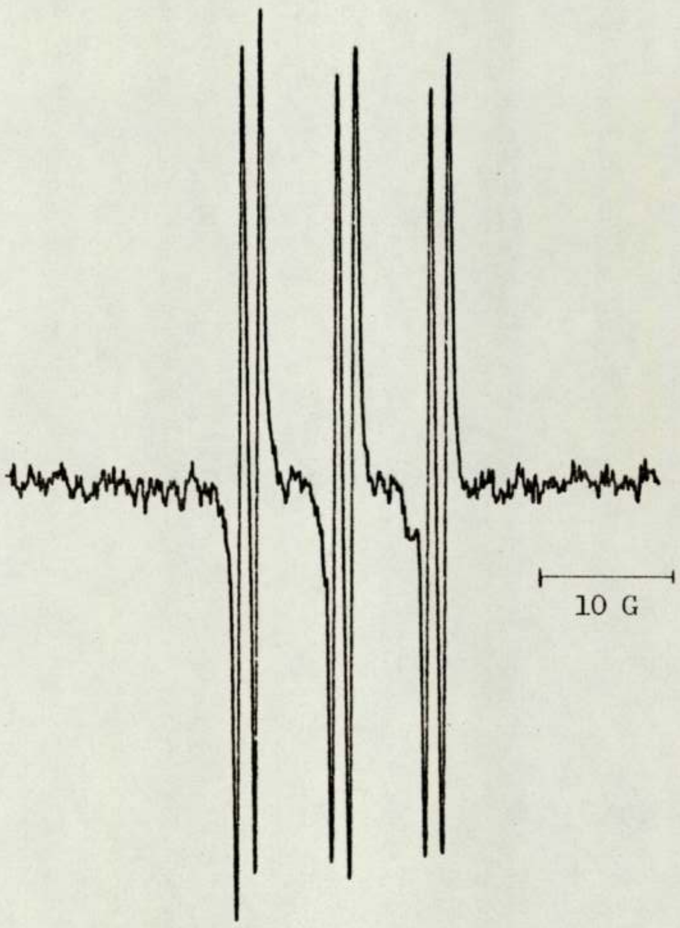


Figure 4.6 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with iso-butene, with addition of oxygen.

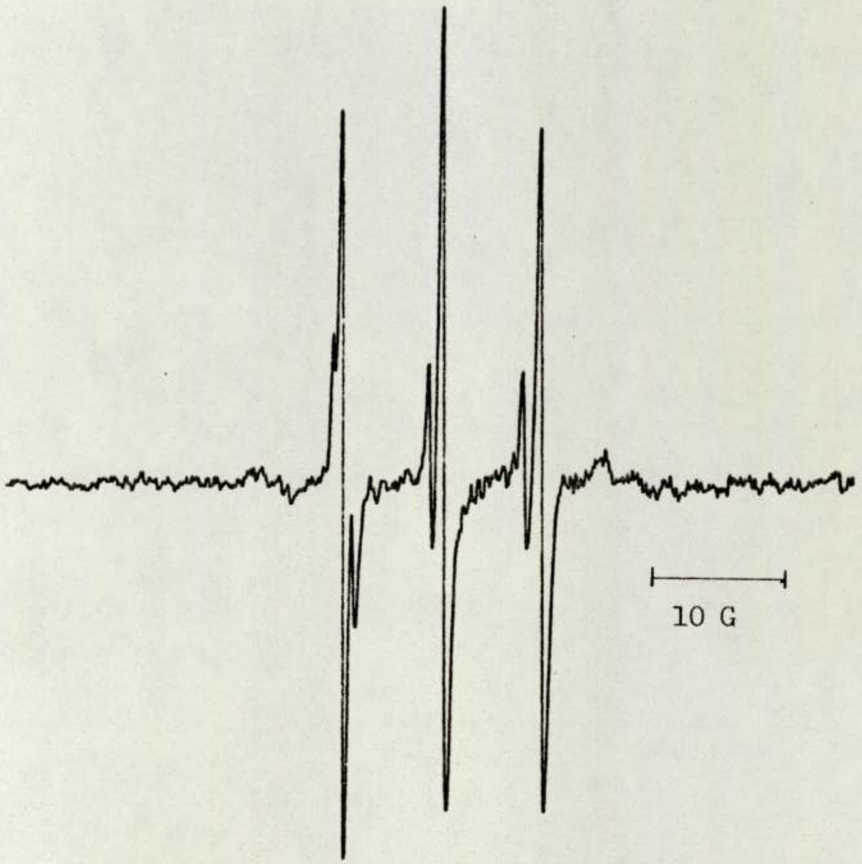


Figure 4.7 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with iso-butene, at elevated temperature.

The solution of low concentration of NO_2, and iso-butene in 1,4-dioxan was studied to determine the stability of alkyl nitroxide (4-IX) and the formation and stability of acyl nitroxide (4-X), and the results are now described.

The solution of low concentration of NO_2, and iso-butene in 1,4-dioxan containing alkyl nitroxide (4-IX) when kept in a sealed tube in the absence of oxygen and unexposed to room daylight, slowly produced acyl nitroxide (4-X) which we observed together with alkyl nitroxide (4-IX) in equal amounts at the fifth week of the reaction time. We also observed the same result when the reaction mixture was kept in sealed tube in the absence of oxygen but exposed to room daylight.

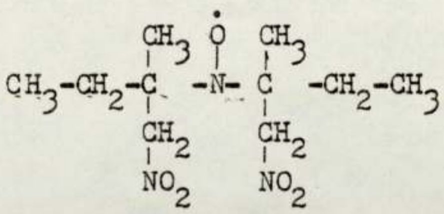
When the reaction mixture which contained only alkyl nitroxide (4-IX) was exposed to air and room daylight, the acyl nitroxide (4-X) was slowly produced and observed as the main radical product within 24 hours.

When the reaction mixture with addition of oxygen was prepared in which acyl nitroxide (4-X) was present, and kept in sealed tube, we found that the acyl nitroxide (4-X) was stable for more than five weeks.

When the reaction mixture containing alkyl nitroxide (4-IX) was kept in sealed tube, and exposed to ultraviolet light for four days, we found that the concentration of this radical increased, and no other radical product was observed.

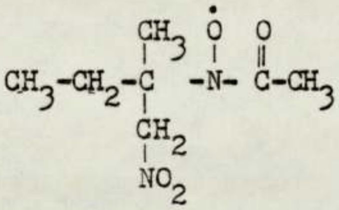
4.2.2 2-methyl-1-butene

Alkyl nitroxide (4-XII), acyl nitroxide (4-XIII), and acyl nitroxide (4-XIV) were observed from reactions of NO_2, and 2-methyl-1-butene which was carried out with the same experimental procedure as in the study of reactions of NO_2, and iso-butene in which alkyl nitroxide (4-IX), acyl nitroxide (4-X), and acyl nitroxide (4-XI) were produced .



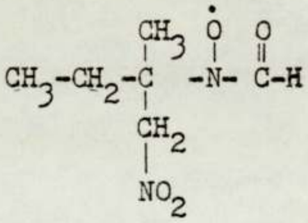
$CH_3-CH_2-C(CH_3)(CH_2NO_2)-N(\dot{O})-C(CH_3)(CH_2NO_2)-CH_2-CH_3$

(4-XII)



$CH_3-CH_2-C(CH_3)(CH_2NO_2)-N(\dot{O})-C(=O)-CH_3$

(4-XIII)



$CH_3-CH_2-C(CH_3)(CH_2NO_2)-N(\dot{O})-C(=O)-H$

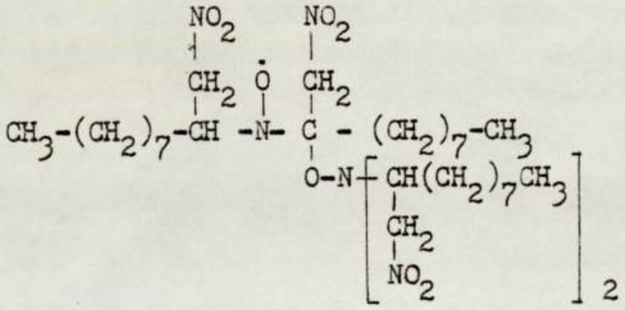
(4-XIV)

A solution of low concentration of NO_2, and 2-methyl-1-butene was initially blue and turned green when the temperature was raised to 100° and there resulted an increase in spectral intensities of alkyl nitroxide (4-XII), and acyl nitroxide (4-XIII). Acyl nitroxide (4-XIV) was formed in low concentration from reaction with addition of oxygen. Esr spectra of alkyl nitroxide (4-XII), and acyl nitroxide (4-XIII) showed only simple 3 lines with $a_N = 14.623$ G (1:1:1), and $a_N = 7.126$ G respectively, and no H-hyperfine splitting was detected. The 3 doublets esr spectrum of acyl nitroxide (4-XIV) showed $a_N = 7.405$ G. (1:1:1), and $a_{H(CH)} = 1.677$ G (1:1).

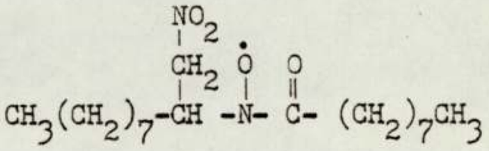
The reaction of NO with 2-methyl-1-butene resulted in alkyl nitroxide formation (4-XII), and the yield was increased when the reaction was carried out at elevated reaction temperature.

4.2.3 1-Decene

The solution of low concentration of NO_2, and 1-decene produced alkyl nitroxide (4-XV) for which only a 3 lines esr spectrum was observed, a_N = 13.547 G (1:1:1). With high concentration of NO_2, and 1-decene, only acyl nitroxide (4-XVI), for which esr spectrum showed 3 lines , a_N = 7.153 G (1:1:1), was detected. Both alkyl nitroxide (4-XV), and acyl nitroxide (4-XVI) were not stable in these reaction mixtures since the esr spectra became weak and were not observed after twelve hours.



(4-XV)

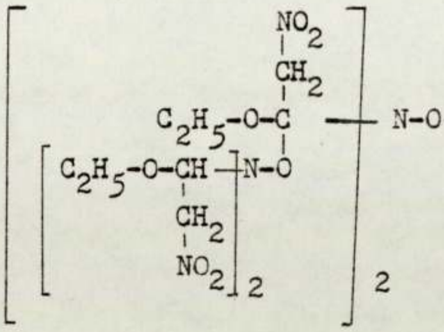


$CH_3(CH_2)_7-\overset{\overset{NO_2}{|}}{\overset{CH_2}{\overset{|}{CH}}}-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH_3$

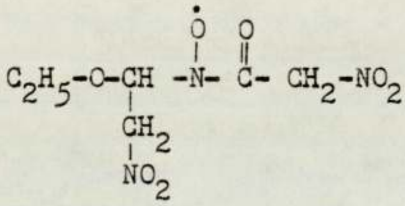
(4-XVI)

4.2.4 Ethyl vinyl ether

Since ethyl vinyl ether reacted with NO_2 in solution violently, only very low concentration of NO_2 was used for study with this alkene. The yellow solution of very low concentration of NO_2 and very low concentration of ethyl vinyl ether yielded an alkyl nitroxide (4-XVII), a_N = 13.603 G (1:1:1), and acyl nitroxide (4-XVIII), a_N = 7.132 G (1:1:1). These two radicals were not detectable after an hour.



(4-XVII)

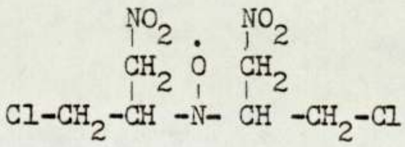


$C_2H_5\text{-}O\text{-}CH(CH_2NO_2)\text{-}N(\dot{O})\text{-}C(=O)\text{-}CH_2\text{-}NO_2$

(4-XVIII)

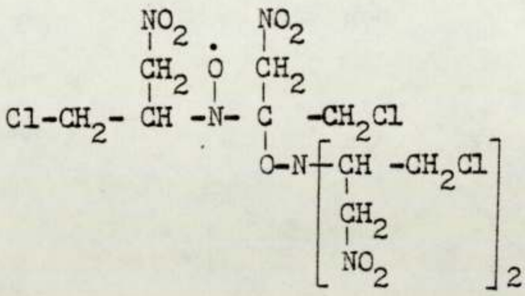
4.2.5 Allyl chloride

The green solution of low concentration of NO_2, and allyl chloride was observed to produce an alkyl nitroxide (4-XIX) whose esr spectrum showed 3 triplets with $a_N = 13.282$ G (1:1:1), $a_{2H(\beta CH)} = 4.239$ G (1:2:1). The same reaction solution, when oxygen was added went colourless and its esr spectrum showed only broad 3 lines of alkyl nitroxide (4-XIX). When the reaction was studied at elevated reaction temperature, the solution went dark green and the main radical product was alkyl nitroxide (4-XX), whose esr spectrum showed 3 doublets $a_N = 13.095$ G (1:1:1), $a_{H(CH)} = 3.274$ G (1:1) and acyl nitroxide (4-XXI), 3 doublets esr spectrum $a_N = 7.642$ G (1:1:1), $a_{H(CH)} = 2.530$ G (1:1) was also obtained.

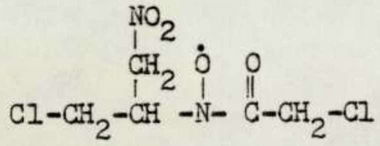


$Cl\text{-}CH_2\text{-}CH(CH_2NO_2)\text{-}N(\dot{O})\text{-}CH(CH_2NO_2)\text{-}CH_2\text{-}Cl$

(4-XIX)



(4-XX)



$\mathrm{Cl{-}CH_2{-}CH(CH_2NO_2){-}N(\dot{O}){-}C(=O){-}CH_2{-}Cl}$

(4-XXI)

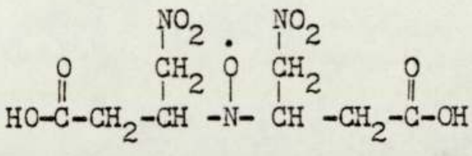
When the reaction mixture was held at the elevated temperature for prolonged period, only the broad 3 lines of alkyl nitroxide (4-XX) was obtained.

With high concentrations of NO_2 and allyl chloride, two spectra of alkyl nitroxide (4-XX) and acyl nitroxide (4-XXI) were detected. The addition of oxygen broadened the esr spectral lines, and an elevated reaction temperature yielded only alkyl nitroxide (4-XX) in low concentration.

The reaction of NO with allyl chloride in 1,4-dioxan in the presence of a trace of NO_2 produced alkyl nitroxide (4-XIX) in high yield.

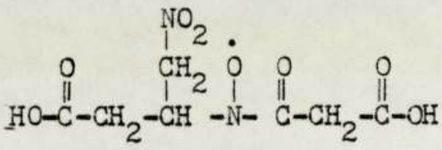
4.2.6 3-Butenoic acid

The bluish green solution of low concentration of NO_2, and 3-butenoic acid yielded alkyl nitroxide (4-XXII), the esr spectrum of which showed 3 triplets $a_N = 13.766$ G (1:1:1), $a_{2H(\beta CH)} = 4.225$ G (1:2:1). On the addition of oxygen, the spectral intensities of alkyl nitroxide (4-XXII) were increased and acyl nitroxide (4-XXIII) was detected, $a_N = 7.355$ G (1:1:1), $a_{H(CH)} = 2.179$ G (1:1). At elevated reaction temperature, only acyl nitroxide (4-XXIII) was produced.



$$HO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{\overset{NO_2}{|}}{\overset{CH_2}{\overset{|}{CH}}}-\overset{\overset{\cdot}{O}}{\overset{|}{N}}-\overset{\overset{NO_2}{|}}{\overset{CH_2}{\overset{|}{CH}}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(4-XXII)



$$HO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{\overset{NO_2}{|}}{\overset{CH_2}{\overset{|}{CH}}}-\overset{\overset{\cdot}{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

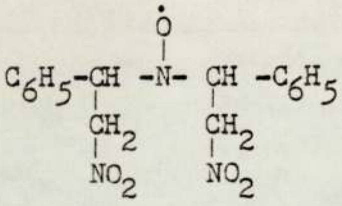
(4-XXIII)

At high concentration of NO_2 and 3-butenoic acid reaction, the radical product was acyl nitroxide (4-XXIII) showing 3 doublets in the esr spectrum. On addition of oxygen, the same radical was observed with each line of 3 doublets further split into another 5 hyperfine lines, and its splitting constant was 0.341 G. When the reaction mixture was studied at elevated temperature, this acyl nitroxide (4-XXIII) was observed with decreased spectral intensities.

The reaction of NO with 3-butenoic acid in 1,4-dioxan in the presence of a trace of NO_2 gave alkyl nitroxide (4-XXII) in high yield, and under any reaction condition tried, acyl nitroxide (4-XXIII) was never detected.

4.2.7 Styrene

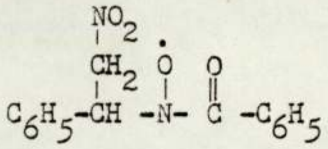
The reaction of low concentration of NO_2 in 1,4-dioxan with styrene resulted in a green solution which contained two stereoisomers of alkyl nitroxide, (4-XXIVa) and (4-XXIVb), their esr spectra showed two sets of 3 triplets superimposed with the same g-values and N-hyperfine splitting constants which were 2.00685, and 14.755 G respectively. The H-hyperfine splitting of the one stereoisomer was 11.715 G (2H, 1:2:1), and the other stereoisomer gave $a_{2H(\beta CH)} = 6.377$ G (1:2:1). These radicals could be observed for 2-3 hours at room temperature and they could be detected in high intensity spectrum when this solution was carried out at boiling water-bath temperature. We found that the spectrum intensities were increased or decreased when the reaction mixture were increased or decreased in reaction temperature. When the reaction mixture was studied with the addition of oxygen, the esr spectrum showed the broadened lines of two sets of 3 triplets with decreased in spectral intensities of alkyl nitroxides (4-XXIVa, and 4-XXIVb).



$C_6H_5-CH(CH_2NO_2)-N(\dot{O})-CH(CH_2NO_2)-C_6H_5$

(4-XXIV)

The yellow solution of high concentration of NO_2, and styrene in 1,4-dioxan solution gave acyl nitroxide (4-XXV), its esr spectrum showed 3 doublets, $a_N = 8.129$ G (1:1:1), $a_{H(CH)} = 3.784$ G (1:1). The higher spectral intensities was obtained when increased the reaction temperature, and the lower spectral intensities was obtained from the reaction mixture with the addition of oxygen.



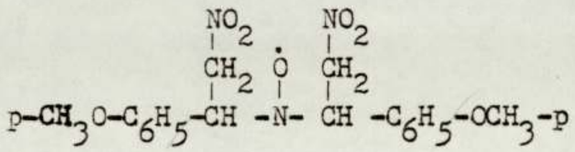
$C_6H_5-CH(CH_2NO_2)-N(\dot{O})-C(=O)-C_6H_5$

(4-XXV)

The reaction of NO with styrene in 1,4-dioxan in the presence of a trace of NO_2 produced only two stereoisomers of alkyl nitroxide (4-XXIVa) and (4-XXIVb) in good yield. Acyl nitroxide (4-XXV) was not observed in any reaction condition which was carried out in the same reaction procedure as in the reactions of NO_2, and styrene.

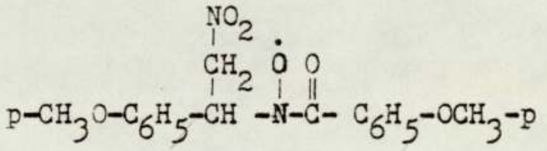
4.2.8 p-Methoxystyrene

p-Methoxystyrene was studied in the same reaction procedure as in the study of styrene, and similar results were obtained. The two stereoisomers of alkyl nitroxide, (4-XXVIa) and (4-XXVIb), $a_N = 14.917$ G (1:1:1), $a_{2H(\beta CH)} = 12.113$ G (1:2:1), and $a_{2H(\beta CH)} = 6.671$ G (1:2:1) were detected from low concentration of NO_2 and p-methoxystyrene solution, and from reaction of NO with p-methoxystyrene in the presence of a trace of NO_2. Acyl nitroxide (4-XXVII), $a_N = 7.427$ G (1:1:1), $a_{H(CH)} = 3.268$ G (1:1) was obtained from reaction of high concentration of NO_2, and p-methoxystyrene in 1,4-dioxan solution.



$$p\text{-}CH_3O\text{-}C_6H_5\text{-}\overset{\overset{NO_2}{|}}{\overset{CH_2}{|}}{CH}\text{-}\overset{\dot{O}}{\overset{|}{N}}\text{-}\overset{\overset{NO_2}{|}}{\overset{CH_2}{|}}{CH}\text{-}C_6H_5\text{-}OCH_3\text{-}p$$

(4-XXVI)



$$p\text{-}CH_3O\text{-}C_6H_5\text{-}\overset{\overset{NO_2}{|}}{\overset{CH_2}{|}}{CH}\text{-}\overset{\dot{O}}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5\text{-}OCH_3\text{-}p$$

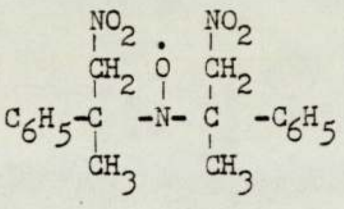
(4-XXVII)

The reaction mixture of low concentration of NO_2, and p-methoxystyrene with the addition of oxygen, the solution turned yellow and the esr spectrum showed line broadening effect. The same reaction mixture when studied at elevated reaction temperature, the solution went dark green, and with increase in alkyl nitroxides concentrations.

The reaction of high concentration of NO_2, and p-methoxystyrene always resulted in yellow solution, with the addition of oxygen or raising the reaction temperature led to decrease in spectral intensities.

4.2.9 α-Methylstyrene

The bluish green coloured solution were obtained from both low and high concentrations of NO_2 with α-methylstyrene in 1,4-dioxan. The esr spectrum showed 3 lines of alkyl nitroxide (4-XXVIII), a_N = 14.91G (1:1:1). Upon raising the reaction temperature or with the addition of oxygen into the reaction mixture, this alkyl nitroxide (4-XXVIII) was still obtained in which the latter case the high spectral intensities were observed.



$C_6H_5-C(CH_3)(CH_2NO_2)-N(\dot{O})-C(CH_3)(CH_2NO_2)-C_6H_5$

(4-XXVIII)

The reaction of NO with α-methylstyrene in the presence of a trace of NO_2 also gave alkyl nitroxide (4-XXVIII).

Acyl nitroxide radical was not observed from the study of this alkene.

4.2.10 Hexachloropropene, and Hexachloro-1,3-butadiene

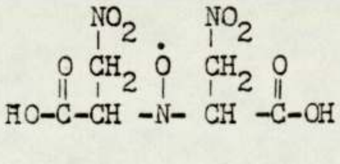
The reactions of NO_2, and hexachloropropene or hexachloro-1,3-butadiene were studied with the same reaction conditions as used in the previous experiments, no esr spectrum was observed nor was any seen from experiments with these two alkenes with NO and a trace of NO_2.

4.3 Alkenes with carbonyl-, alkyl carbonyl-, or halogenyl carbonyl substituents.

Alkenes which were studied and classified into this group were acrylic acid, 3-butene-2-one, acraldehyde, methacrolein, methacryloyl chloride, methyl methacrylate, crotonic acid, ethyl crotonate, methyl crotonate, crotonaldehyde, hexachlorobutenoic acid, 3-pentene-2-one, tiglic acid, 3,3-dimethylacrylic acid, mesityl oxide, maleic acid, dimethyl maleate, fumaric acid, and dimethyl fumarate. The radical products observed from these alkenes were alkyl nitroxides, acyl nitroxides, and iminoxy radicals as described in detail below.

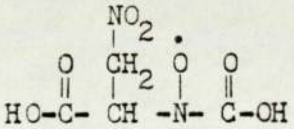
4.3.1 Acrylic acid

Acrylic acid produced an alkyl nitroxide (4-XXIX) from the reaction mixture of low concentration of NO_2 and acrylic acid in 1.4-dioxan. The esr spectrum showed 3 triplets splitting a_N = 12.615 G (1:1:1), $a_{2H(CH)}$ = 3.647 G (1:2:1), and could be detected for 30 minutes. With high concentrations of NO_2, and acrylic acid in 1,4-dioxan the reaction gave a yellowish green solution containing three radical products which were alkyl nitroxide(4-XXIX), acyl nitroxide (4-XXX), and iminoxy radical (4-XXXI), and their esr spectra showed 3 triplets, 3 doublets. and 3 triplets respectively. The N-hyperfine splitting constant of acyl nitroxide (4-XXX) was 7.637 G (1:1:1), and H-hyperfine splitting constant was 3.16 G (1:1), and for iminoxy radical (4-XXXI), a_N = 29.493 G (1:1:1) and $a_{N(NO_2)}$ = 2.897 G (1:1:1), and no further hyperfine splitting due to hydrogen atom was detected.



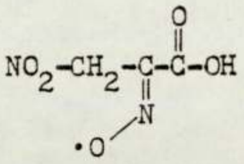
$HO\text{-}C(=O)\text{-}CH(CH_2NO_2)\text{-}N(\dot{O})\text{-}CH(CH_2NO_2)\text{-}C(=O)\text{-}OH$

(4-XXIX)



$HO\text{-}C(=O)\text{-}CH(CH_2NO_2)\text{-}N(\dot{O})\text{-}C(=O)\text{-}OH$

(4-XXX)



$NO_2-CH_2-C(=N-O^\bullet)-C(=O)-OH$

E-isomer

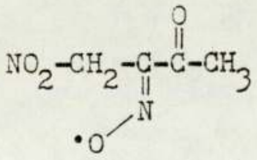
(4-XXXI)

These three radical products could be detected for 30 minutes, therefore other reaction conditions were not able to be studied.

The reaction of NO, and acrylic acid was studied in the presence of a trace of NO_2 and 1,4-dioxan as solvent, the radical product was alkyl nitroxide (4-XXIX).

4.3.2 3-Butene-2-one

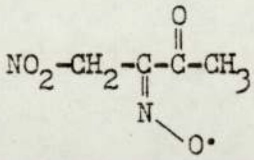
The green solution of low concentration of NO_2, and 3-butene-2-one resulted in two isomers of iminoxy radical (4-XXXIIa) and (4-XXXIIb) which were E-, and Z- isomers respectively. The esr parameters for iminoxy radical (4-XXXIIa) were $a_N = 31.124$ G (1:1:1), $a_{H(CH_2)} = 2.203$ G (1:1), $a_{H(CH_2)} = 1.01$ G (1:1), and $a_{N(NO_2)} = 0.459$ G. (1:1:1), and for iminoxy radical (4-XXXIIb) was $a_N = 28.09$ G (1:1:1) with the further splitting which was not clear. The intensities of the spectra revealed that E-isomer of iminoxy radical (4-XXXIIa) was the main radical product, and Z-isomer of iminoxy radical (4-XXXIIb) was found as trace radical product. These two radicals could be detected in this reaction mixture for 2 hours at room temperature, and when the solution went yellow, no radical product was detected.



$NO_2-CH_2-C(=N-O^\bullet)-C(=O)-CH_3$

E-isomer

(4-XXXIIa)

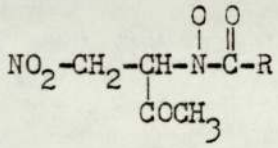


$$NO_2\text{-}CH_2\text{-}\underset{\underset{\displaystyle N\diagdown O\cdot}{\|}}{C}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3$$

Z-isomer

(4-XXXIIb)

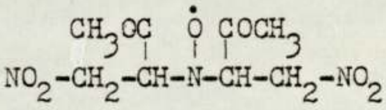
The solution of high concentration of NO_2, and 3-butene-2-one, resulted in two isomers of iminoxy radical (4-XXXIIa) and (4-XXXIIb), acyl nitroxide (4-XXXIII), and alkyl nitroxide (4-XXXIV). The esr spectrum of acyl nitroxide (4-XXXIII) showed 3 doublets $a_N = 6.839$ G (1:1:1), $a_{H(CH)} = 0.884$ G (1;1), and the esr spectrum of alkyl nitroxide (4-XXXIV) showed 3 triplets $a_N = 13.62$ G (1:1:1), $a_{2H(\beta CH)} = 3.849$ G (1:2:1).



$$NO_2\text{-}CH_2\text{-}\underset{\underset{\displaystyle COCH_3}{|}}{CH}\text{-}\overset{\overset{\displaystyle \dot{O}}{|}}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R$$

$R = CH_3$, or CH_2NO_2

(4-XXXIII)



$$NO_2\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3OC}{|}}{CH}\text{-}\overset{\overset{\displaystyle \dot{O}}{|}}{N}\text{-}\overset{\overset{\displaystyle COCH_3}{|}}{CH}\text{-}CH_2\text{-}NO_2$$

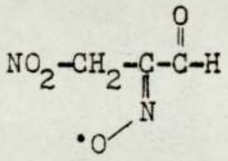
(4-XXXIV)

In experiments involving addition of oxygen, the detected esr spectra showed the better resolution of hyperfine lines of iminoxy radicals, the broadened esr lines of alkyl nitroxide, and the decrease in acyl nitroxide radical concentration. When the reaction was studied at elevated reaction temperature, the esr spectrum did not show the presence of any radical.

In the reaction of NO, and 3-butene-2-one in the presence of a trace of NO_2, the main radical product was alkyl nitroxide (4-XXXIV), and the iminoxy radicals (4-XXXIIa) and (4-XXXIIb) were found as minor radical products.

4.3.3 Acraldehyde

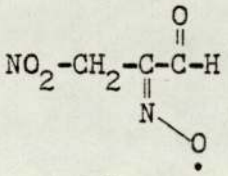
The reaction of low concentration of NO_2, and acraldehyde resulted in green solution which went yellow within a few seconds. The esr spectrum showed two isomers of iminoxy radical were produced as main radical products: E-isomer(4-XXXVa), $a_N = 30.917$ G (1:1:1), $a_{N(NO_2)} = a_{2H(CH_2)} = 1.182$ G (1:3:4:3:1), and Z-isomer (4-XXXVb), $a_N = 29.558$ G (1:1:1), $a_{H(-CHO)} = 14.188$ G (1:1), $a_{2H(CH_2)} = 0.887$ G (1:2:1), and the esr spectrum also showed 3 doublets of acyl nitroxide (4-XXXVI), $a_N = 7.389$ G (1:1:1), $a_{H(CH)} = 2.069$ G (1:1) as minor radical product (Figure 4.8).



$NO_2{-}CH_2{-}C({=}N{-}O^{\bullet}){-}C({=}O){-}H$

E-isomer

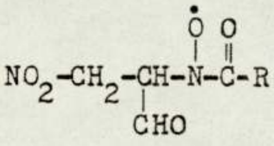
(4-XXXVa)



$NO_2{-}CH_2{-}C({=}N{-}O^{\bullet}){-}C({=}O){-}H$

Z-isomer

(4-XXXVb)



$NO_2{-}CH_2{-}CH(CHO){-}N(O^{\bullet}){-}C({=}O){-}R$

$R = -CH{=}CH_2$ for (4-XXXVIa)
$= -H$ for (4-XXXVIb)

(4-XXXVI)

The reaction with high concentration of NO_2, and acraldehyde also resulted in the same radical products as obtained from the reaction

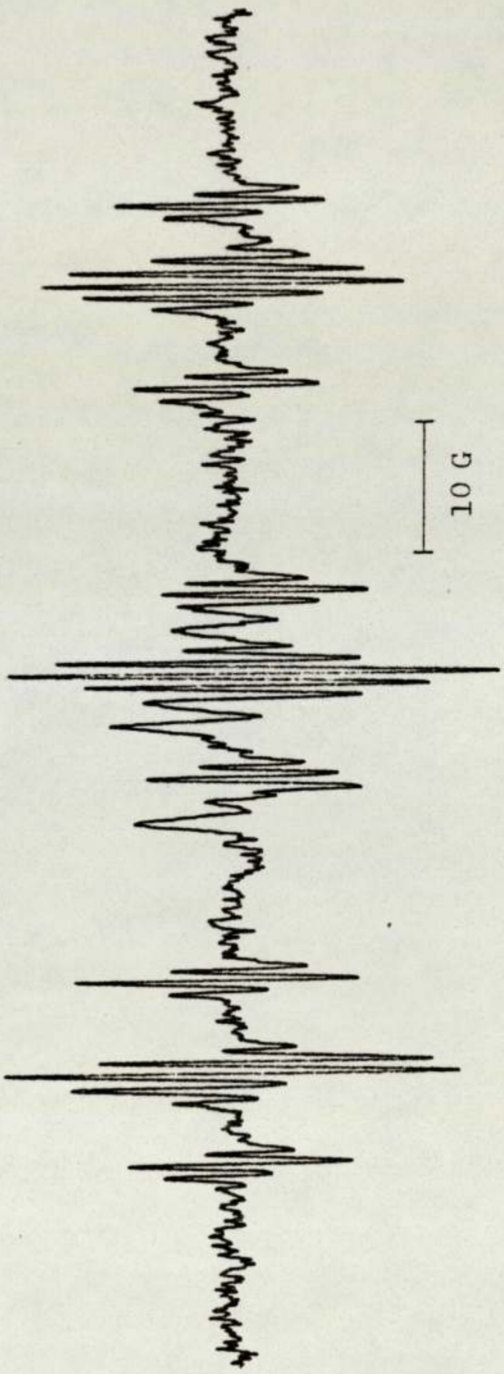


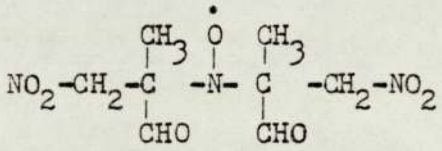
Figure 4.8 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with acraldehyde, at room temperature.

of low concentration of NO_2 and acraldehyde. These radicals were stable in this reaction mixture for few hours.

When the reaction of NO_2 and acraldehyde was studied in the presence of oxygen or at elevated reaction temperatures, the resulting yellow solution did not show the presence of any radical products.

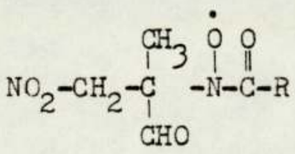
4.3.4 Methacrolein

The bluish green coloured solution of low concentration of NO_2 and methacrolein resulted in alkyl nitroxide (4-XXXVII), the esr spectrum of which showed 3 lines $a_N = 14.53$ G (1:1:1). With oxygen present, the spectral intensities due to alkyl nitroxide (4-XXXVII) was found to be increased, and the esr spectrum showed the presence of acyl nitroxide (4-XXXVIII) as a trace radical product, $a_N = 7.405$ G (1:1:1). When the reaction was studied at elevated temperature, the reaction mixture was colourless and both alkyl nitroxide (4-XXXVII) and acyl nitroxide (4-XXXVIII) were observed but with low spectral intensities.



$$NO_2-CH_2-\overset{CH_3}{\underset{CHO}{C}}-\overset{\overset{\bullet}{O}}{N}-\overset{CH_3}{\underset{CHO}{C}}-CH_2-NO_2$$

(4-XXXVII)



$$NO_2-CH_2-\overset{CH_3}{\underset{CHO}{C}}-\overset{\overset{\bullet}{O}}{N}-\overset{O}{\overset{\|}{C}}-R$$

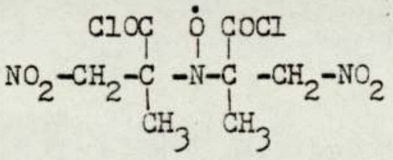
R = CH_3, or CH_2NO_2, or H

(4-XXXVIII)

The reaction of high concentration of NO_2, and methacrolein resulted in green solution which went yellow in few seconds, and the radical products detected were alkyl nitroxide (4-XXXVII), and acyl nitroxide (4-XXXVIII). An increase in spectral intensities of both radicals was observed from the reaction mixture with addition of oxygen and a decrease in spectral intensities of both radicals was observed from the reaction which studied at elevated reaction temperature.

4.3.5 Methacryloyl chloride

The colourless solution of low concentration of NO_2, and methacryloyl chloride produced an alkyl nitroxide (4-XXXIX), its esr spectrum showed 3 lines, $a_N = 13.021$ G (1:1:1), and this alkyl nitroxide was also observed from the reaction with a high concentration of NO_2. When the reaction was studied at high temperature, the solution went green and a poor esr spectrum of alkyl nitroxide (4-XXXIX) was detected. With addition of oxygen, the resulting colourless solution yielded the same alkyl nitroxide (4-XXXIX) and the spectrum intensities were unchanged.

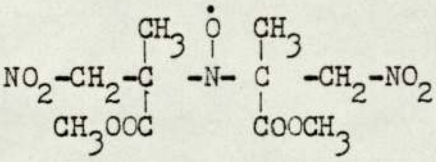


$$NO_2-CH_2-\underset{CH_3}{\overset{ClOC}{C}}-\overset{\dot{O}}{N}-\underset{CH_3}{\overset{COCl}{C}}-CH_2-NO_2$$

(4-XXXIX)

4.3.6 Methyl methacrylate

The blue solution always obtained from reaction mixtures of both low, and high concentrations of NO_2 and methyl methacrylate, resulted in alkyl nitroxide (XL), and its esr spectrum showed 3 lines $a_N = 13.932$ G (1:1:1).



$$NO_2-CH_2-\underset{CH_3OOC}{\overset{CH_3}{C}}-\overset{\dot{O}}{N}-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-NO_2$$

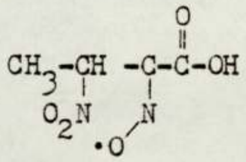
(4-XL)

When the reaction was studied at an elevated temperature, or with the addition of oxygen, the same radical product was formed but the esr spectrum showed an increase in spectral intensities in the former experiment, and was broadened in the latter.

In the reaction of NO with methyl methacrylate in the presence of a trace of NO_2, the same alkyl nitroxide (4-XL) was detected in high yield.

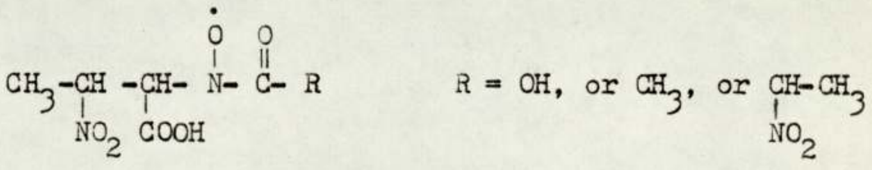
4.3.7 Crotonic acid

The low concentration of NO_2, and crotonic acid in 1,4-dioxan solution resulted in a blue solution which turned yellow in a few seconds, and the radical products were detected by rather good esr spectra after the reaction had proceeded for an hour. The esr spectra showed 3 triplets of E-isomer of iminoxy radical a_N = 29.557 G (1:1:1), $a_{N(NO_2)}$ = 6.497 G (1:1:1) (4-XLIa), and 3 lines esr spectra of acyl nitroxide (4-XLII), a_N = 7.139 G (1:1:1). We found that the longer the reaction time, the higher the concentrations of radical products were obtained. These two radicals were stable in the reaction mixture for few days.



E -isomer

(4-XLIa)



R = OH, or CH_3, or $\underset{NO_2}{CH}-CH_3$

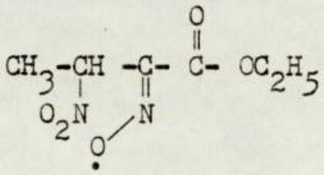
(4-XLII)

When the reaction was studied at elevated reaction temperature, the good esr spectra were observed which E-isomer of iminoxy radical (4-XLIa), and acyl nitroxide (4-XLII) were produced. In the reaction with the addition of oxygen, the same results were observed.

When the reaction was studied at high concentration of NO_2, we got the same results as in the reaction at low concentration of NO_2, and crotonic acid study.

4.3.8 Ethyl crotonate

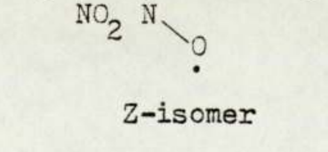
Esr spectra detected from reaction of low concentration of NO_2, and ethyl cretonate in 1,4-dioxan solution were due to two isomers of an iminoxy radical and where partly superimposed. The reaction mixture was blue for the first few minutes and then turned yellow. The E-isomer, iminoxy radical (4-XLIIIa) was the minor radical product, the esr spectrum showed 3 multiplets, $a_N = 33.8$ G (1:1:1) $a_{H(CH)} = 4.45$ G, $a_{3H(CH_3)} = 1.50$ G, $a_{N(NO_2)} = 0.389$ G. The Z-isomer iminoxy radical (4-XLIIIb) was the main radical product and its esr spectrum showed $a_N = 29.755$ G (1:1:1), and other hyperfine lines superimposed by its E-isomer. In the reaction in which oxygen was added, the esr spectrum showed good resolution of hyperfine lines of both isomers of iminoxy radical. With an increase in reaction temperature, the esr spectrum was observed to decrease in its intensities and it disappeared when the reaction was prolonged at increased temperature.



$CH_3-CH(O_2N)-C(=N-\dot{O})-C(=O)-OC_2H_5$

E-isomer

(4-XLIIIa)

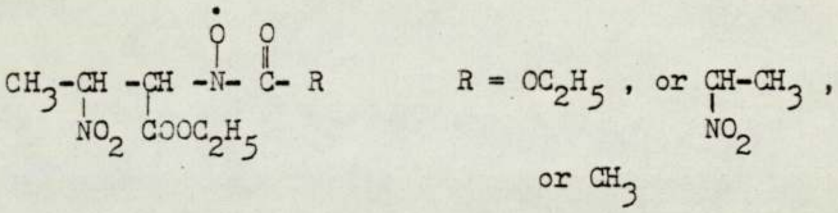


$CH_3-CH(NO_2)-C(=N-\dot{O})-C(=O)-OC_2H_5$

Z-isomer

(4-XLIIIb)

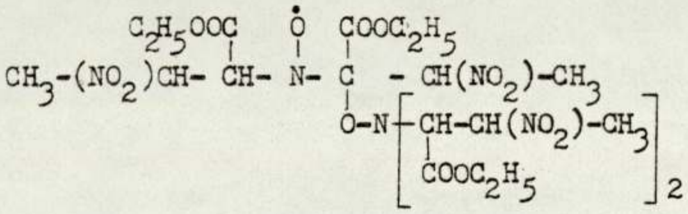
The reaction of high concentration of NO_2, and ethyl crotonate in 1,4-dioxan produced high concentrations of both E-isomer and Z-isomer of iminoxy radical, (4-XLIIIa) and (4-XLIIIb) respectively in which the Z-isomer was the main radical product. From the reaction in which oxygen was added, the esr spectrum showed clear hyperfine lines of both isomers. At elevated reaction temperature, both isomers of the iminoxy radical (4-XLIII) were observed in decreased spectral intensities and acyl nitroxide (4-XLIV) was detected in very low concentration, $a_N \sim 7$ G (1:1:1).



$$CH_3-\underset{NO_2}{CH}-\underset{COOC_2H_5}{CH}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-R \qquad R = OC_2H_5\text{ , or }\underset{NO_2}{CH}-CH_3\text{ , or }CH_3$$

(4-XLIV)

The reaction of NO with ethyl crotonate produced the iminoxy radical of both isomers, (4-XLIIIa) and (4-XLIIIb), and we also observed a 3 doublets esr spectrum of nitroxide (4-XLV) from this reaction mixture, $a_N = 13.383$ G (1:1:1) and $a_{H(CH)} = 3.380$ G (1:1).

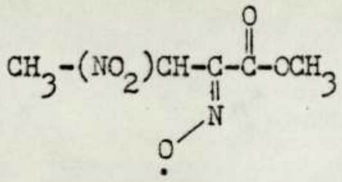


$$CH_3-(NO_2)CH-\overset{C_2H_5OOC}{CH}-\overset{\dot{O}}{N}-\overset{COOC_2H_5}{\underset{O-N\left[\underset{COOC_2H_5}{CH}-CH(NO_2)-CH_3\right]_2}{C}}-CH(NO_2)-CH_3$$

(4-XLV)

4.3.9 Methyl crotonate

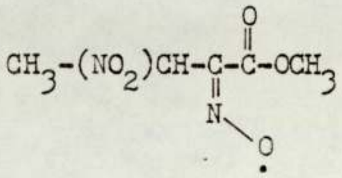
Radical products observed from reactions of NO_2 with methyl crotonate were similar to those obtained from reaction of NO_2 with ethyl crotonate. The E-, and Z-isomers of iminoxy radical, (4-XLVIa) and (4-XLVIb), showed in the esr spectrum of two sets of three multiplets partly superimposed: for E-isomer $a_N = 32.118$ G (1:1:1),$a_{H(CH)} = 4.4$ G, $a_{3H(CH_3)} = 1.50$ G, and $a_{N(NO_2)} = 0.389$ G , and for Z-isomer $a_N = 29.755$ G, and other hyperfine lines superimposed by its E-isomer. The esr spectrum showed that Z-isomer (4-XLVIb) was the main radical product.



$$CH_3-(NO_2)CH-\underset{\overset{\|}{N}\diagdown\dot{O}}{C}-\overset{\overset{O}{\|}}{C}-OCH_3$$

E-isomer

(4-XLVIa)



$$CH_3-(NO_2)CH-\underset{\overset{\|}{N}\diagdown\dot{O}}{C}-\overset{\overset{O}{\|}}{C}-OCH_3$$

Z-isomer

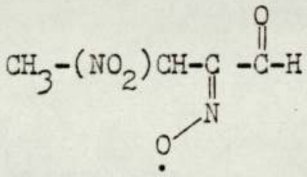
(4-XLVIb)

With added oxygen, the esr spectrum showed the good hyperfine lines and increase in spectral intensities of both isomers of iminoxy radical (4-XLVI). At the elevated reaction temperature, the esr intensity of the spectrum of each of these iminoxy radicals was decreased and finally became zero.

We also observed acyl nitroxide (4-XLIV) from the reaction of high concentration of NO_2 and methyl crotonate in trace amount only when the reaction was carried out at elevated reaction temperature. The Z-isomer of the iminoxy radical (4-XLVIb) was the main radical product from this reaction condition and the E-isomer (4-XLVIa) was observed as minor radical product.

4.3.10 Crotonaldehyde

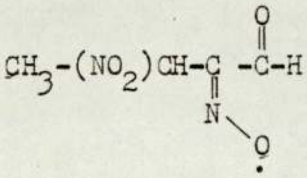
The green solution of low concentration of NO_2 and crotonaldehyde in 1,4-dioxan, turned yellow in few minutes, and contained two isomers of iminoxy radical: E-isomer (4-XLVIIa) $a_N = 30.922$ G (1:1:1), $a_{N(NO_2)} = 6.798$ G (1:1:1), $a_{H(CH)} = 0.822$ G (1:1), and Z-isomer (4-XLVIIb), $a_N = 26.546$ G(1:1:1), $a_{H(-CHO)} = 19.41$ G (1:1), and $a_{N(NO_2)} = 0.87$ G (1:1:1). The latter isomer was found as main radical product, as shown in Figure 4.9. With addition of oxygen, the esr spectral intensities of Z-isomer (4-XLVIIb) was increased, and at an elevated reaction temperature we observed the decrease in concentrations of both isomers of iminoxy radical, and in both cases the E-isomer (4-XLVIIa) slowly disappeared.



$CH_3-(NO_2)CH-\underset{\underset{\dot{O}\diagup N}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$

E-isomer

(4-XLVIIa)



$CH_3-(NO_2)CH-\underset{\underset{N\diagdown\dot{O}}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$

Z-isomer

(4-XLVIIb)

With a high concentration of NO_2 and crotonaldehyde, the solution changed from green to yellow, and we observed the two isomers of iminoxy radical: E-isomer (4-XLVIIa) and Z-isomer (4-XLVIIb), and acyl nitroxide (4-XLVIII) as the radical products. The esr spectrum of acyl nitroxide showed only 3 lines $a_N = 6.984$ G (1:1:1). Figure 4.10 shows that from this reaction mixture, the Z-isomer of iminoxy radical (4-XLVIIb)

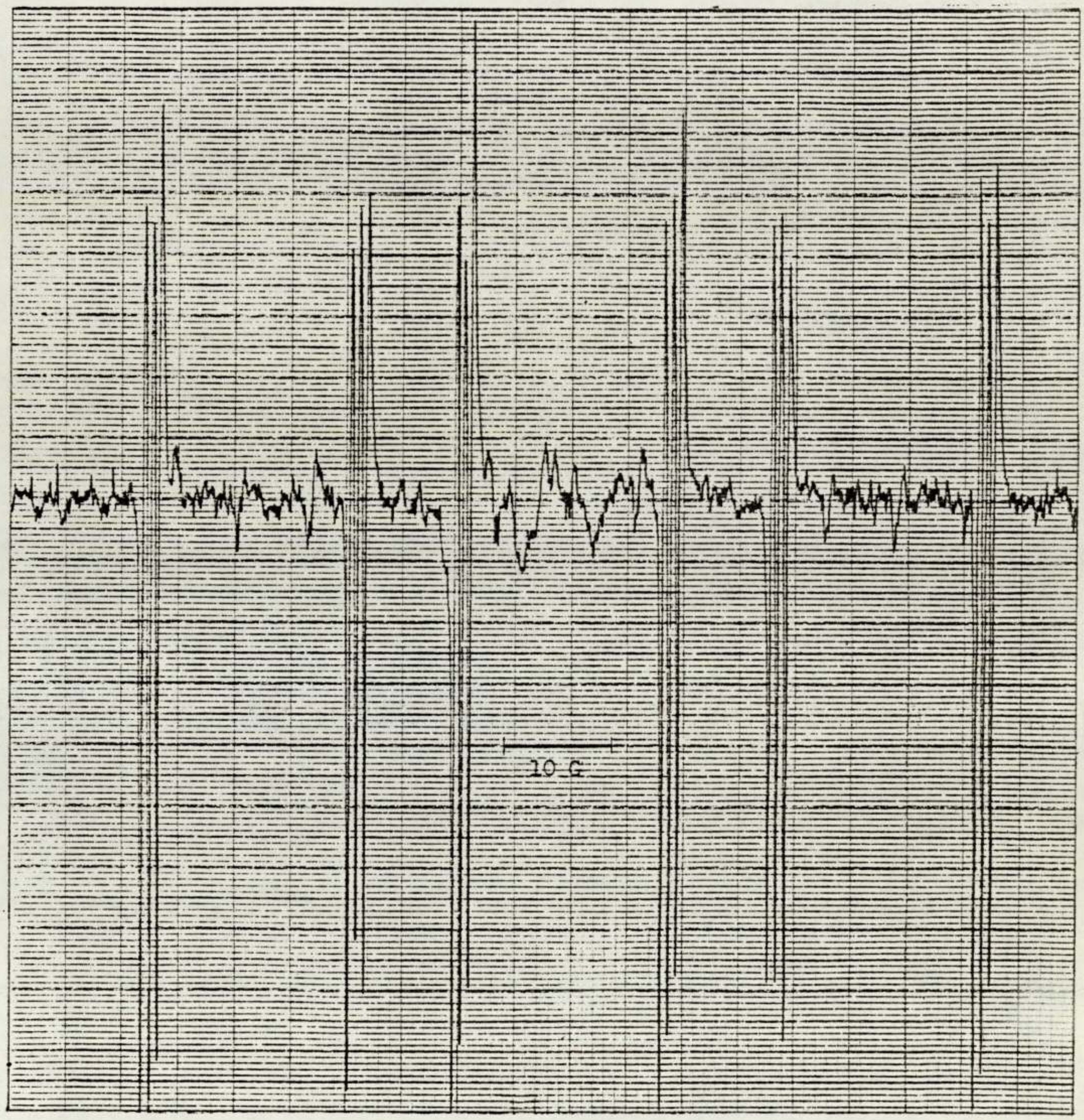


Figure 4.9 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with crotonaldehyde, at room temperature.

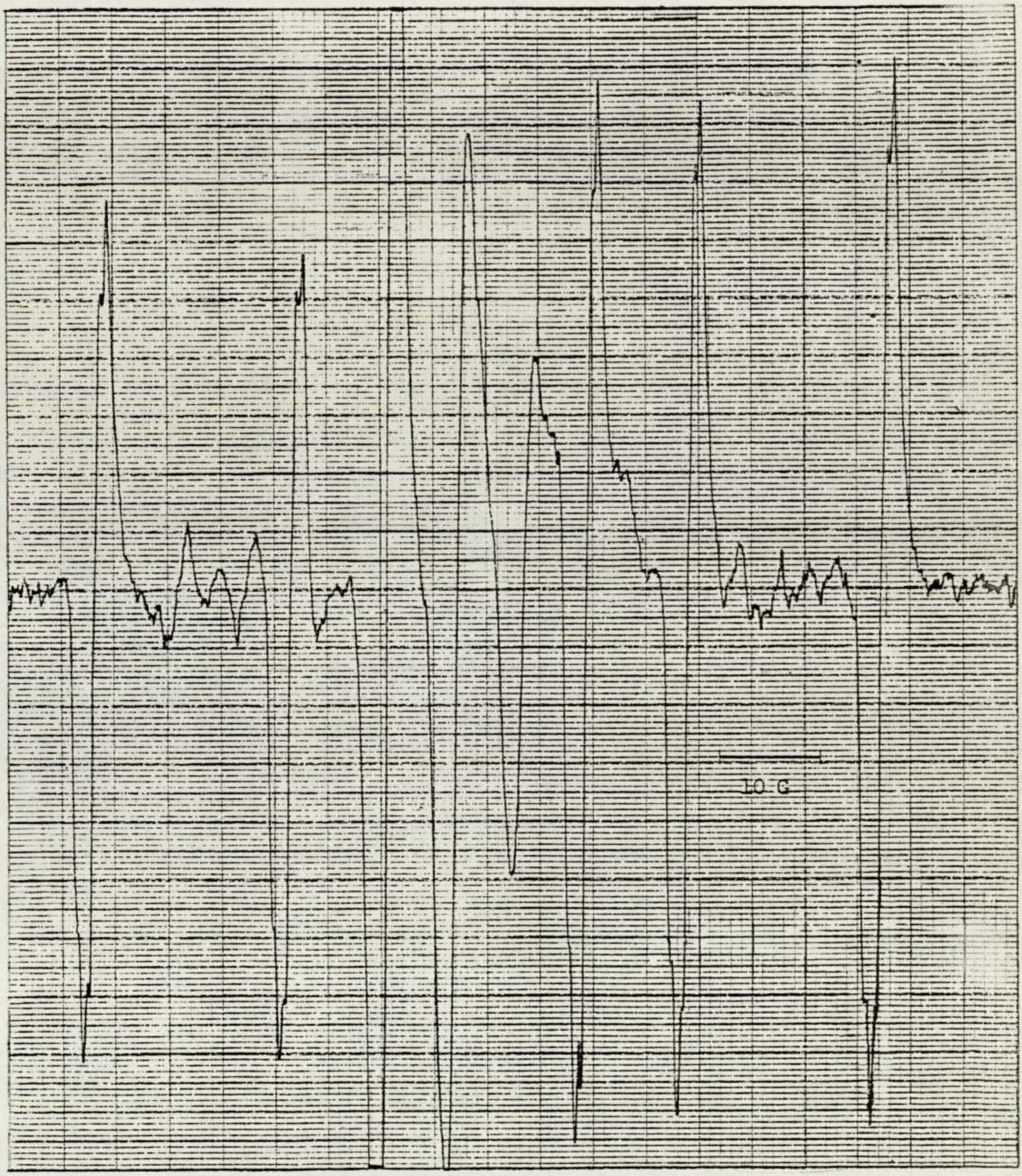
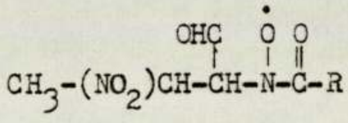


Figure 4.10 Electron spin resonance spectrum of radicals formed by reaction of high concentration of NO_2 with crotonaldehyde, at room temperature.

was the main radical product, acyl nitroxide (4-XLVIII) was found as the minor and E-isomer of iminoxy radical (4-XLVIIa) was a trace radical product which slowly disappeared.



$$CH_3-(NO_2)CH-\overset{OHC}{CH}-\overset{\dot{O}}{N}-\overset{\overset{O}{\|}}{C}-R$$

R = H, or CH_3

(4-XLVIII)

When this reaction was carried out at elevated reaction temperature or with addition of oxygen, the esr spectrum did not show the presence of any radical product.

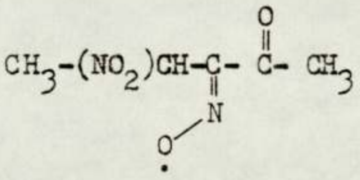
4.3.11 Hexachlorobutenoic acid

The reactions of both low and high concentrations of NO_2 with hexachlorobutenoic acid at room temperature or at elevated reaction temperature or with addition of oxygen, did not produce any stable radical detectable by esr.

4.3.12 3-Pentene-2-one

The reaction of low concentration of NO_2 with 3-pentene-2-one in 1,4-dioxan gave yellowish green solution which turned yellow in few minutes. The esr spectrum showed the presence of two isomers of iminoxy radical: the E-isomer (4-XLIXa) was present in the reaction mixture as minor radical product and it was detected as 3 multiplets $a_N = 33.696$ G (1:1:1), $a_{H(CH)} = 1.276$ G (1:1), $a_{N(NO_2)} = 0.638$ G (1:1:1), and the Z-isomer (4-XLIXb) which was the main radical product and its 3 multiplets esr spectrum showed $a_N = 30.001$ G (1:1:1), $a_{3H(CH_3)} = 1.914$ G (1:1:1), $a_{N(NO_2)} = 0.638$ G (1:1:1). In the reaction at elevated temperature, the esr spectrum of both isomers of iminoxy radical were observed to decrease in intensities and we also observed 3 doublets esr spectrum of nitroxide (4-L) as a trace radical product $a_N = 13.597$ G (1:1:1), $a_{H(CH)} = 2.956$ G

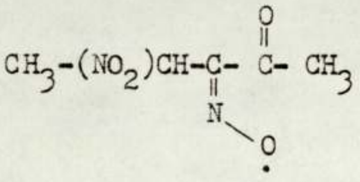
(1:1). Another radical which was formed at elevated reaction temperature was acyl nitroxide (4-LI) detected by its 3 lines esr spectrum, $a_N = 7$ G (1:1:1), $a_{H(CH)} = 1.157$ G (1:1), which showed that it was present in the reaction mixture in almost equal concentrations to the Z-isomer iminoxy radical (4-XLIXb). When the reaction was prolonged at an elevated temperature, the esr spectrum did not show the presence of any radical product. When the reaction was studied with addition of oxygen, the esr spectrum showed good hyperfine splitting of both isomers of iminoxy radical (4-XLIXa) and (4-XLIXb), and the nitroxide (4-L) and acyl nitroxide (4-LI) were observed in equal spectral intensities. Acyl nitroxide (4-LI) produced from the reaction with addition of oxygen was observed in lower concentration than it was in the reaction at elevated reaction temperature.



$CH_3\text{-}(NO_2)CH\text{-}C(=N\text{-}\dot{O})\text{-}C(=O)\text{-}CH_3$

E-isomer

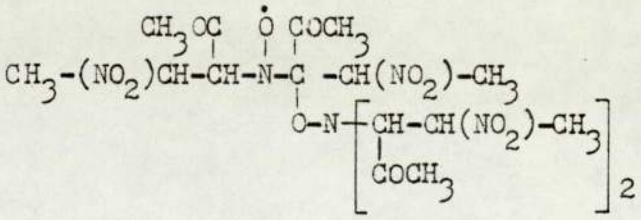
(4-XLIXa)



$CH_3\text{-}(NO_2)CH\text{-}C(=N\text{-}\dot{O})\text{-}C(=O)\text{-}CH_3$

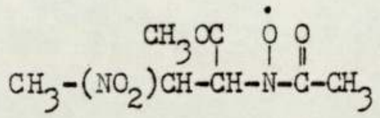
Z-isomer

(4-XLIXb)



$CH_3\text{-}(NO_2)CH\text{-}CH(COCH_3)\text{-}N(\dot{O})\text{-}C(COCH_3)(O\text{-}N[CH(COCH_3)\text{-}CH(NO_2)\text{-}CH_3]_2)\text{-}CH(NO_2)\text{-}CH_3$

(4-L)



$$CH_3\text{-}(NO_2)CH\text{-}\overset{CH_3OC}{\overset{|}{C}H}\text{-}\overset{\dot{O}}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

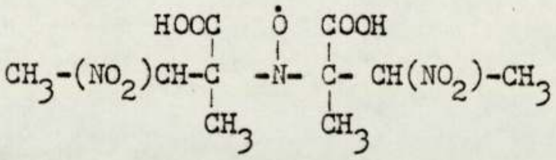
(4-LI)

The reaction of high concentration of NO_2 and 2-pentene-2-one in 1,4-dioxan produced a yellow solution in which two isomers of iminoxy radical (4-XLIXa) and (4-XLIXb) were observed in high yield with the Z-isomer (4-XLIXb) as the main radical product. The nitroxide (4-L) and acyl nitroxide (4-LI) were observed as trace radical products. In the reaction at elevated reaction temperature, the esr spectra of iminoxy radicals (4-XLIXa) and (4-XLIXb) were greatly decreased in intensity and acyl nitroxide (4-LI) was only the trace radical product observed. On addition of oxygen into the reaction mixture, the esr spectra showed the good hyperfine splittings of iminoxy radicals slightly decreased in intensity. The nitroxide (4-L) and acyl nitroxide (4-LI) were also observed as trace radical products.

Iminoxy radicals (4-XLIXa) and (4-XLIXb) were found to be stable in the reaction mixture at room temperature for 24 hours.

4.3.13 Tiglic acid

The initial green solution of a low concentration of NO_2 and tiglic acid in 1,4-dioxan , turned dark blue in few minutes, and contained the nitroxide (4-LII), whose esr spectrum showed 3 lines $a_N = 13.729$ G (1:1:1) and increased in intensity with reaction time. When the reaction time. When the reaction mixture was carried out at elevated temperature, the dark blue solution turned green, and showed increased intensity in the esr spectrum of nitroxide (4-LII). On addition of oxygen, the dark blue solution gave a decrease in the amount of nitroxide (4-LII) since its esr spectrum showed a decrease in spectral intensities.



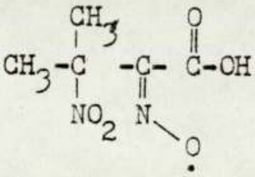
$$\mathrm{CH_3{-}(NO_2)CH{-}\overset{HOOC}{\underset{CH_3}{C}}{-}\overset{\dot{O}}{N}{-}\overset{COOH}{\underset{CH_3}{C}}{-}CH(NO_2){-}CH_3}$$

(4-LII)

The same result was observed when reaction was studied with a high concentration of NO_2 and tiglic acid in 1,4-dioxan which produced a high intensity esr spectrum of nitroxide (4-LII). In the reaction at elevated temperature, a pale green solution was obtained, which did not show the presence of any free radical. In addition of oxygen into the reaction mixture, the solution went blue and only a weak esr spectrum of nitroxide (4-LII) was detected.

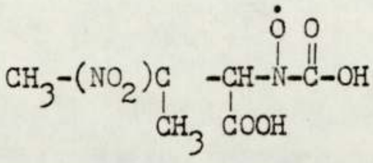
4.3.14 3,3-Dimethylacrylic acid

The pale green solution of a low concentration of NO_2 and 3,3-dimethylacrylic acid in 1,4-dioxan produced the Z-isomer of the iminoxy radical (4-LIII) in low yield which could observed for an hour at room temperature after the reaction had started. Its esr spectrum showed weak 3 lines $a_N = 29.885$ G (1:1:1). Another radical product was acyl nitroxide (4-LIV) whose esr spectrum increased in intensity with reaction time, the spectrum showed 3 doublets $a_N = 7.094$ G (1:1:1) $a_{H(CH)} = 3.695$ G (1:1) and when the longer the reaction time was taken, it became the main radical product. When the reaction was studied with the addition of oxygen after the reaction started, the acyl nitroxide (4-LIV) was observed or when it was carried out at elevated temperature, we detected acyl nitroxide (4-LIV) with increased spectral intensity.



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{NO_2}{C}}{-}\underset{N{-}\dot{O}}{\overset{}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

(4-LIII)



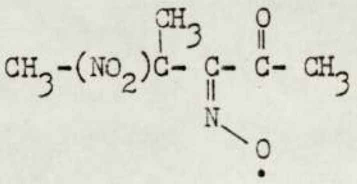
$$CH_3-(NO_2)\underset{\displaystyle CH_3}{C}-\underset{\displaystyle COOH}{CH}-\overset{\displaystyle \dot{O}}{N}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

(4-LIV)

The study of high concentration of NO_2 and 3,3-dimethylacrylic acid in 1,4-dioxan, we observed the same Z-isomer of iminoxy radical (4-LIII) and acyl nitroxide (4-LIV). The solution changed from blue to green and finally to yellow. The esr spectrum showed the Z-isomer of iminoxy radical (4-LIII) as trace radical product and acyl nitroxide (4-LIV) as the final main radical product.

4.3.15 Mesityl oxide

The green solution of the reaction of low concentration of NO_2 and mesityl oxide in 1,4-dioxan produced the Z-isomer of iminoxy radical (4-LV), its 3 multiplets esr spectrum showed $a_N = 30.036$ G (1:1:1), $a_{3H(CH_3)} = 1.750$ G (1:3:3:1) and $a_{N(NO_2)} = 0.680$ G (1:1:1).

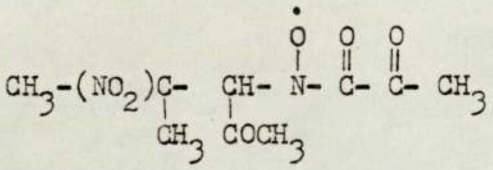


$$CH_3-(NO_2)\overset{\displaystyle CH_3}{C}-\underset{\displaystyle N-\dot{O}}{\underset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

Z-isomer

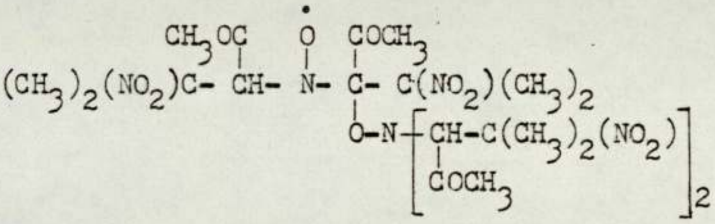
(4-LV)

When the reaction temperature was elevated, we observed that the main radical product was acyl nitroxide (4-LVI), whose esr spectrum showed 3 doublets $a_N = 7.338$ G (1:1:1), $a_{H(CH)} = 1.583$ G (1:1). The esr spectrum also showed the decrease in spectrum intensity of the Z-isomer (4-LV) and we also observed the presence of nitroxide (4-LVII), $a_N = 13.064$ G (1:1:1) $a_{H(CH)} = 2.642$ G (1:1), and another acyl nitroxide (4-LVIII) $a_N = 7.338$ G(1:1:1) $a_{H(CH)} = 4.892$ G (1:1) as trace radical products (Figure 4.11). This reaction mixture was followed over three hours and we found that the longer the reaction time was taken, the acyl nitroxide (4-LVIII) became the main radical product and acyl nitroxide (4-LVI) was found as minor radical product (Figure 4.12). On prolonged reaction at elevated temperature, the solution mixture gave only acyl nitroxide for which only a very weak three lines esr spectrum $a_N \sim 7$ G was detected.



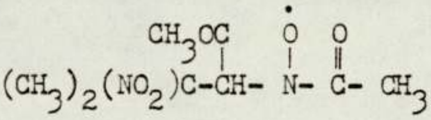
$$CH_3-(NO_2)\underset{CH_3}{C}-\underset{COCH_3}{CH}-\overset{\overset{\bullet}{O}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

(4-LVI)



$$(CH_3)_2(NO_2)C-\overset{CH_3OC}{CH}-\overset{\overset{\bullet}{O}}{N}-\overset{COCH_3}{\underset{O-N\left[\underset{COCH_3}{CH}-C(CH_3)_2(NO_2)\right]_2}{C}}-C(NO_2)(CH_3)_2$$

(4-LVII)



$$(CH_3)_2(NO_2)C-\overset{CH_3OC}{CH}-\overset{\overset{\bullet}{O}}{N}-\overset{\overset{O}{\|}}{C}-CH_3$$

(4-LVIII)

In the reaction mixture of low concentration of NO_2 and mesityl oxide in 1,4-dioxan with addition of oxygen, we observed the acyl nitroxide (4-LVI) as the main radical product and the Z-isomer of iminoxy radical (4-LV) was the minor radical product (Figure 4.13).

The yellow solution of high concentration of NO_2 and mesityl oxide in 1,4-dioxan, produced three radical products with equal esr spectral intensities, these showed the presence of the Z-isomer of iminoxy radical (4-LV), acyl nitroxide (4-LVI) and nitroxide (4-LVII), and we also observed

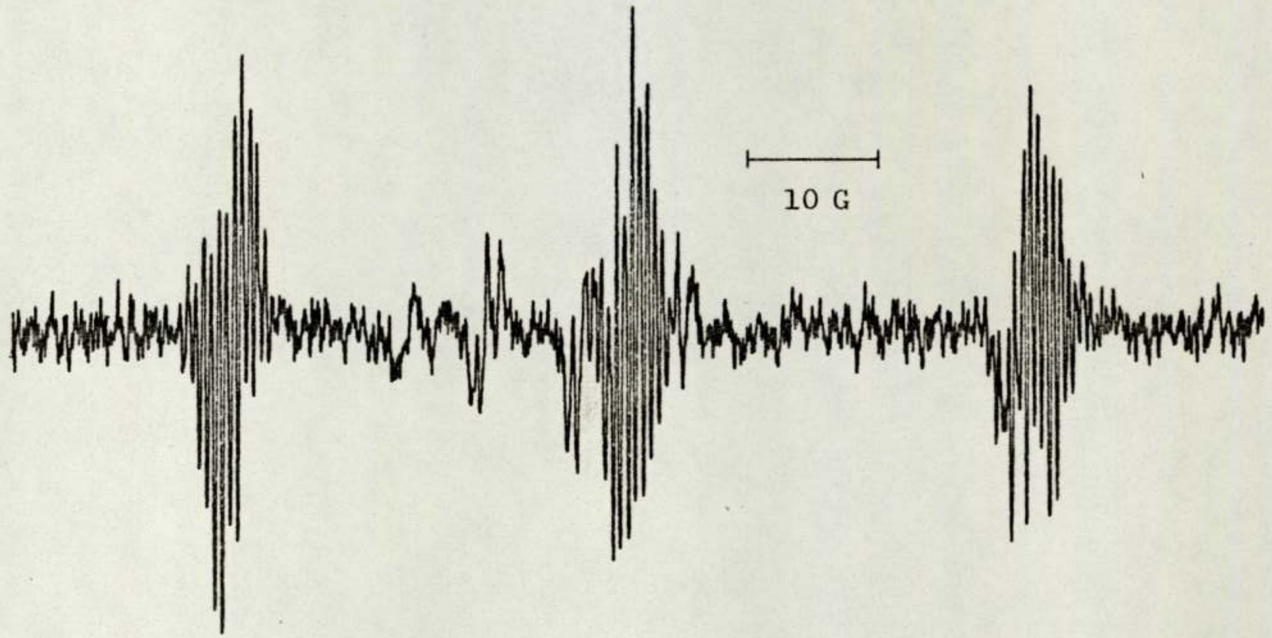


Figure 4.11 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with mesityl oxide, at elevated temperature.

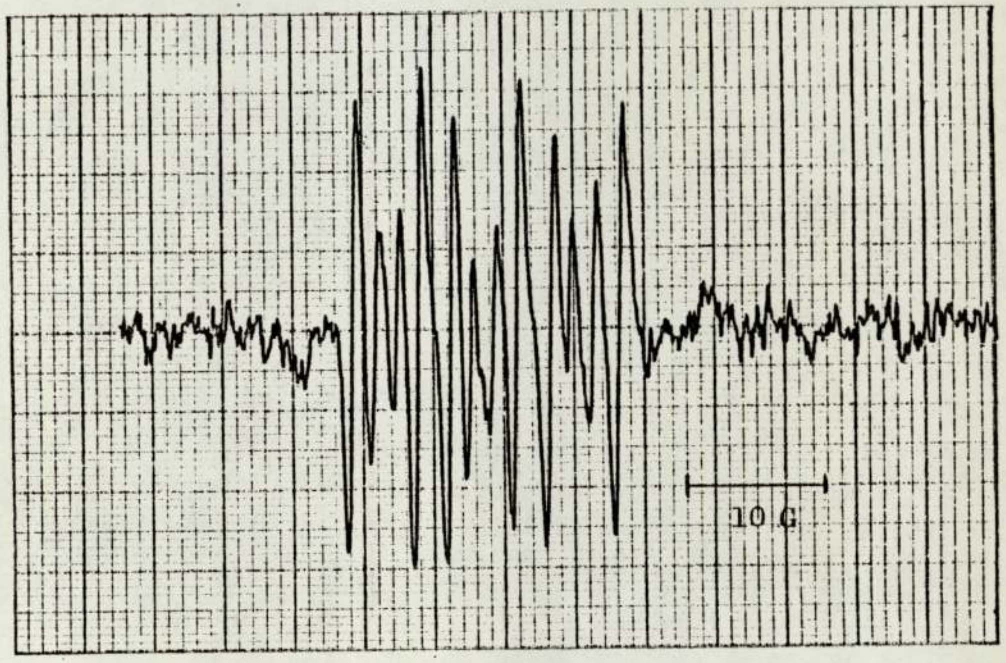


Figure 4.12 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with mesityl oxide, at elevated temperature, detected after the reaction had progressed for three hours.

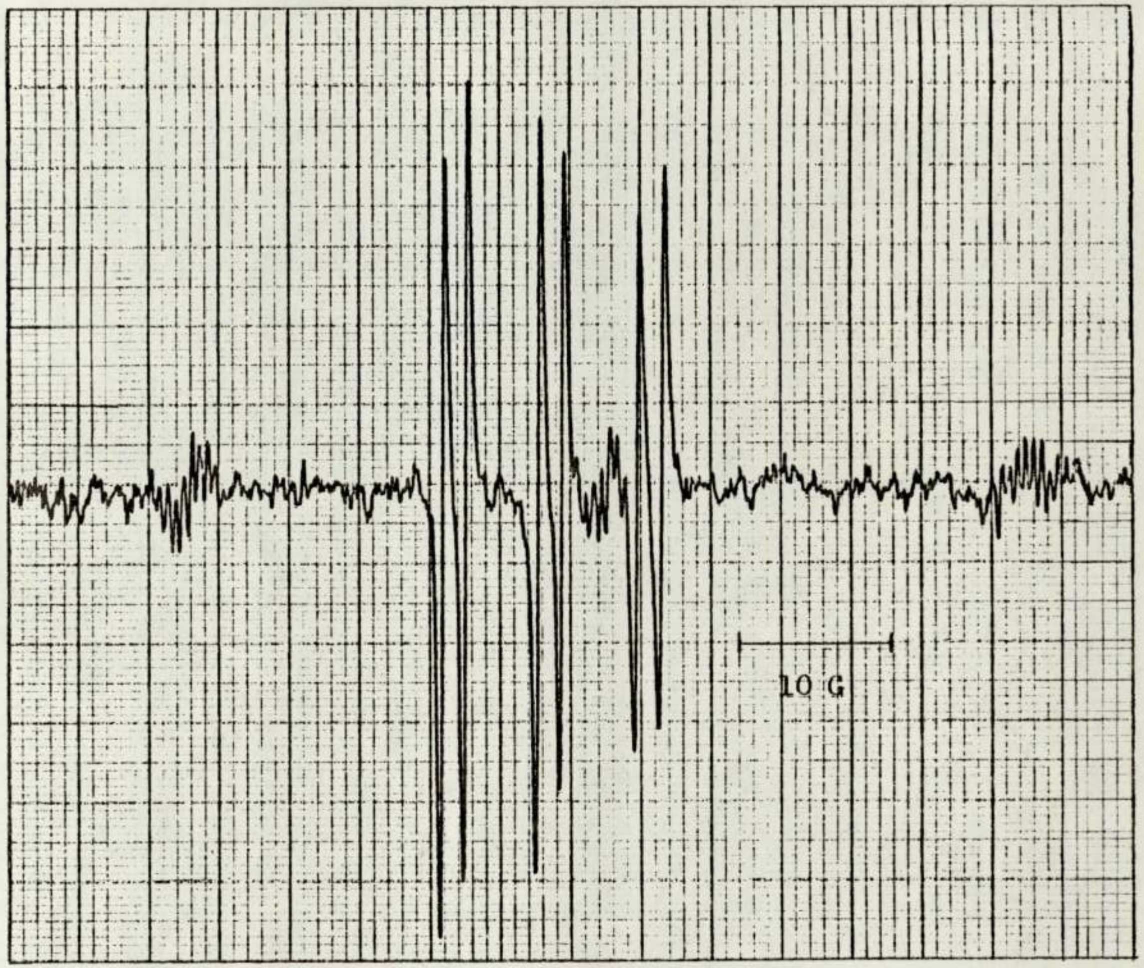


Figure 4.13 Electron spin resonance spectrum of radicals formed by reaction of low concentration of NO_2 with mesityl oxide, with addition of oxygen.

the acyl nitroxide (4-LVIII) in trace amount.

The reaction mixture of low concentration of NO_2 and mesityl oxide slowly produced an acyl nitroxide (4-LVI) when it was kept in sealed tube at room temperature, and within two days it was found to be the only radical product remaining in the reaction mixture.

4.3.16 Maleic acid, Fumaric acid, Dimethyl maleate, and Dimethyl fumarate.

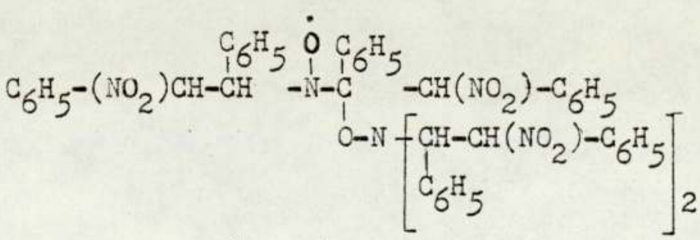
No esr spectrum was detected from the reaction mixtures of both low and high concentrations of NO_2 with these alkenes at room temperature, or at elevated reaction temperature or with addition of oxygen.

4.4 Alkenes with aryl-, or aryl carbonyl substituents.

Alkenes which were studied and classified into this group were cis-stilbene, trans-stilbene, cinnamaldehyde, cinnamic acid, benzalacetone, benzalacetophenone, dibenzalacetone, cinnamyl alcohol, and α-methylcinnamaldehyde. Radical products obtained were nitroxides, iminoxy radicals, and acyl nitroxides.

4.4.1 cis-Stilbene, and trans-Stilbene.

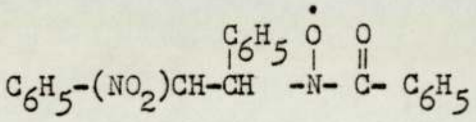
The green solution of the reaction of low concentration of NO_2 and cis-stilbene or trans-stilbene in the mixture of 1,4-dioxan and n-hexane (1:1), produced a nitroxide (4-LIX). The esr spectra showed the 3 doublets $a_N = 14.014$ G (1:1:1), $a_{H(CH)} = 2.817$ G (1:1) for nitroxide from cis-stilbene, and $a_N = 14.107$ G (1:1:1), $a_{H(CH)} = 3.245$ G (1:1) for nitroxide from trans-stilbene. These radicals were stable for a few days.



$$C_6H_5\text{-}(NO_2)CH\text{-}\overset{C_6H_5}{CH}\text{-}\overset{\dot{O}}{N}\text{-}\underset{O\text{-}N\left[\underset{C_6H_5}{CH}\text{-}CH(NO_2)\text{-}C_6H_5\right]_2}{\overset{C_6H_5}{C}}\text{-}CH(NO_2)\text{-}C_6H_5$$

(4-LIX)

With addition of oxygen to the reaction mixture, we observed the 3 broad lines of nitroxide (4-LIX), and when the reaction was carried out at elevated reaction temperature we observed the acyl nitroxide (4-LX) $a_N = 8.290$ G (1:1:1) $a_{H(CH)} = 2.665$ G (1:1) as a radical product.



$$C_6H_5-(NO_2)CH-\overset{C_6H_5}{\overset{|}{CH}}-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-C_6H_5$$

(4-LX)

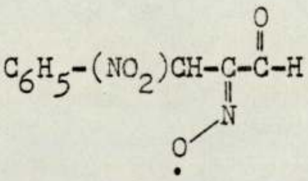
The yellow solution of high concentration of NO_2 and cis-stilbene or trans-stilbene in the mixture of 1,4-dioxan and n-hexane, produced only the acyl nitroxide (4-LX) shown by a three doublets esr spectrum.

4.4.2 Cinnamaldehyde

The green solution of the low concentration of NO_2 and cinnamaldehyde in 1,4-dioxan was prepared at ice-bath temperature, the esr measurements were carried out at room temperature at which the solution became yellow and yielded two isomers of iminoxy radicals: E-isomer (4-LXIa), $a_N = 30.749$ G(1:1:1), $a_{H(CH)} = 2.005$ G (1:1), and Z-isomer (4-LXIb), $a_N = 29.412$ G (1:1:1), $a_{H(-CHO)} = 19.311$ G (1:1), $a_{N(NO_2)} = 0.897$ G (1:1:1) in equal spectral intensities and also produced an acyl nitroxide (4-LXII) as an another main radical product. The esr spectrum of this acyl nitroxide showed 3 doublets $a_N = 8.913$ G (1:1:1), $a_{H(CH)} = 4.456$ G (1:1). When the reaction was carried out at room temperature, the solution was yellow and the esr spectrum did not show the presence of any radical product.

The acyl nitroxide (4-LXII) was observed as the main radical product and its esr spectrum increased in intensity with increased in the reaction time. The E- and Z-isomeric iminoxy radicals (4-LXIa) and (4-LXIb) were present in equal amount as minor radical products in the reaction mixture.

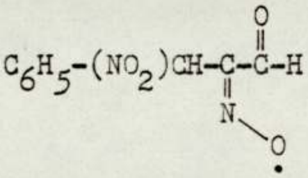
When the reaction was studied with addition of oxygen, we observed the increase in radical concentration of the Z-isomer of iminoxy radical (4-LXIb), but the concentrations of both E-isomer (4-LXIa), and acyl nitroxide (4-LXII) did not change. The esr spectrum was detected again after the reaction had progressed for twenty four hours, and we observed only acyl nitroxide (4-LXII) present in the reaction mixture.



$$C_6H_5-(NO_2)CH-\underset{\underset{\dot{O}\diagup}{\overset{\|}{N}}}{C}-\overset{\overset{O}{\|}}{C}-H$$

E-isomer

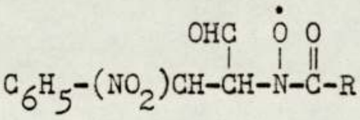
(4-LXIa)



$$C_6H_5-(NO_2)CH-\underset{\underset{\diagdown\dot{O}}{\overset{\|}{N}}}{C}-\overset{\overset{O}{\|}}{C}-H$$

Z-isomer

(4-LXIb)



$$C_6H_5-(NO_2)CH-\overset{OHC}{\overset{|}{C}}H-\overset{\dot{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R$$

R = H, or C_6H_5

(4-LXII)

At elevated reaction temperature, we also observed acyl nitroxide (4-LXII) as a radical product in the reaction mixture which was prepared at ice-bath temperature initially.

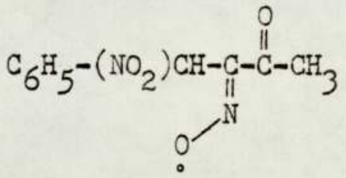
The same results were observed from the reaction of high concentration of NO_2 with cinnamaldehyde, whose E-isomer (4-LXIa), and Z-isomer (4-LXIb) of iminoxy radical, and acyl nitroxide (4-LXII) were detected.

4.4.3 Cinnamic acid

The reaction of both low and high concentrations of NO_2 with cinnamic acid in 1,4-dioxan solution at room temperature, or at elevated reaction temperature, or with addition of oxygen, did not produce any radical product. We also did not observed any radical product when the reaction mixture was prepared at ice-bath temperature.

4.4.4 Benzalacetone

The reaction of low concentration of NO_2 with benzalacetone in 1,4-dioxan, at room temperature did not produce any detectable radical product but when the reaction mixture was carried out at elevated temperature, we observed a three doublets esr spectrum of an iminoxy radical (4-LXIII) $a_N = 31.977$ G (1:1:1) $a_{H(CH)} = 1.717$ G (1:1).



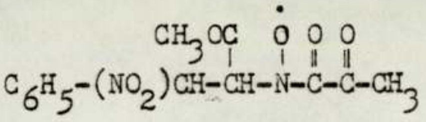
$$C_6H_5\text{-}(NO_2)CH\text{-}\underset{\underset{O^{\bullet}}{\overset{\|}{N}}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$$

E-isomer

(4-LXIII)

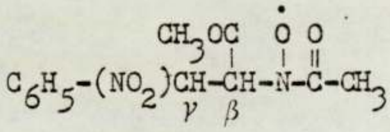
When the reaction was studied at high concentration of NO_2, the green solution slowly changed to yellow and esr spectrum showed 3 lines of acyl nitroxide (4-LXIV) $a_N = 6.5$ G (1:1:1) present in the reaction mixture soon after the reaction started, and we observed that the E-isomer of iminoxy radical (4-LXIII) was slowly formed since its esr spectrum slowly increased in its intensities. With addition of oxygen. these two radicals were detected with the E-isomer (4-LXIII) as the main radical product, and we could also observe the hyperfine lines of acyl nitroxide (4-LXIV) from this reaction condition. The esr spectrum revealed that there were two acyl nitroxides produced from this reaction mixture:

which were acyl nitroxide (4-LXIV) , 3 doublets esr spectrum $a_N = 6.584$ G (1:1:1) $a_{H(CH)} = 1.483$ G (1:1), and acyl nitroxide (4-LXV), three sets of 2 doublets esr spectrum $a_N = 6.525$ G (1:1:1) $a_{H(\beta CH)} = 8.601$ G (1:1) $a_{H(\gamma CH)} = 1.483$ G (1:1).



$C_6H_5\text{-}(NO_2)CH\text{-}\underset{}{CH}(OCCH_3)\text{-}N(\dot{O})\text{-}C(=O)\text{-}C(=O)\text{-}CH_3$

(4-LXIV)



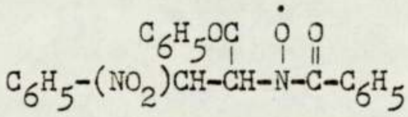
$C_6H_5\text{-}(NO_2)\underset{\gamma}{CH}\text{-}\underset{\beta}{CH}(OCCH_3)\text{-}N(\dot{O})\text{-}C(=O)\text{-}CH_3$

(4-LXV)

When the reaction of high concentration of NO_2 and benzalacetone was studied at elevated reaction temperature, the esr spectrum of E-isomer of iminoxy radical (4-LXIII) disappeared, and the esr spectra of acyl nitroxides (4-LXIV) and (4-LXV) still remained.

4.4.5 Benzalacetophenone

No radical product was observed from reaction of NO_2 and benzalacetophenone in 1,4-dioxan solution when both low and high concentrations of NO_2 were studied at room temperature. When the reaction of high concentration of NO_2 was studied at elevated temperature, the acyl nitroxide (4-LXVI) was produced in low yield. The esr spectrum showed 3 lines $a_N = 8.468$ G (1:1:1).

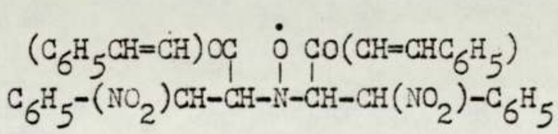


$C_6H_5\text{-}(NO_2)CH\text{-}CH(OCC_6H_5)\text{-}N(\dot{O})\text{-}C(=O)\text{-}C_6H_5$

(4-LXVI)

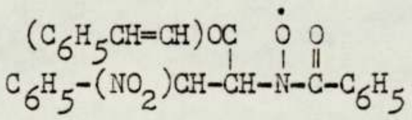
4.4.6 Dibenzalacetone

The solution of low concentration of NO_2 and dibenzalacetone in 1,4-dioxan produced the nitroxide (4-LXVII) the esr spectrum of which showed three triplets $a_N = 12.958$ G (1:1:1) $a_{2H(\beta CH)} = 4.122$ G (1:2:1). The esr spectral intensities increased with reaction time. When the reaction temperature was elevated, the esr spectrum of nitroxide (4-LXVII) disappeared. When the reaction was studied with the addition of oxygen at room temperature, acyl nitroxide (4-LXVIII) was produced, its esr spectrum showed 3 lines $a_N = 7.55$ G (1:1:1) and it was stable for a day. When the reaction mixture, without addition of oxygen, was kept in sealed tube for three hours, the acyl nitroxide (4-LXVIII) was also formed.



$$C_6H_5\text{-}(NO_2)CH\text{-}\overset{(C_6H_5CH=CH)OC}{\overset{|}{C}H}\text{-}\overset{\dot{O}}{\overset{|}{N}}\text{-}\overset{CO(CH=CHC_6H_5)}{\overset{|}{C}H}\text{-}CH(NO_2)\text{-}C_6H_5$$

(4-LXVII)



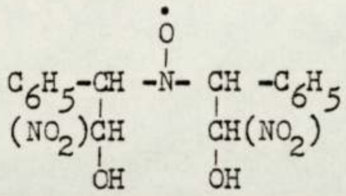
$$C_6H_5\text{-}(NO_2)CH\text{-}\overset{(C_6H_5CH=CH)OC}{\overset{|}{C}H}\text{-}\overset{\dot{O}}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5$$

(4-LXVIII)

When the reaction of high concentration of NO_2 and dibenzalacetone was studied, we observed only acyl nitroxide (4-LXVIII) as the radical product.

4.4.7 Cinnamyl alcohol

The reaction of low concentration of NO_2 , and cinnamyl alcohol in 1,4-dioxan solution produced two stereoisomers of nitroxide, (4-LXIXa) and (4-LXIXb). Their esr parameters were $a_N = 14.656$ G (1:1:1), $a_{2H(\beta CH)} = 4.737$ G(1:2:1), and $a_{2H(\beta CH)} = 1.776$ G (1:2:1).

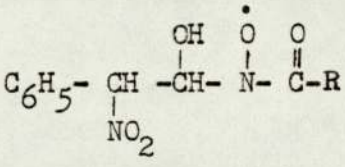


$$C_6H_5\text{-}CH(CH(NO_2)OH)\text{-}N(\dot{O})\text{-}CH(CH(NO_2)OH)\text{-}C_6H_5$$

(4-LXIX)

When this reaction was carried out at elevated reaction temperature, we observed these two nitroxide isomers in high yield. When the reaction mixture was studied with addition of oxygen, the esr spectrum was broadened and showed the presence of these two stereoisomers of nitroxide (4-LXIX) as radical products.

The solution of high concentration of NO_2 and cinnamyl alcohol in 1,4-dioxan produced an acyl nitroxide (4-LXX) in low yield; when the reaction was carried out at elevated temperature, we observed the presence of acyl nitroxide (4-LXX) as the main radical product and nitroxide (4-LXIX) as a trace radical product. The esr spectrum showed the increase in concentration of acyl nitroxide (4-LXX) produced from reaction which was carried out at room temperature. This acyl nitroxide (4-LXX) was also observed in high yield when the reaction was carried out with addition of oxygen as the esr spectrum showed three sets of two doublets $a_N = 7.440$ G (1:1:1) $a_{H(\beta CH)} = 2.678$ G (1:1) $a_{H(\gamma CH)} = 1.190$ G (1:1).



$$C_6H_5\text{-}CH(NO_2)\text{-}CH(OH)\text{-}N(\dot{O})\text{-}C(=O)\text{-}R$$

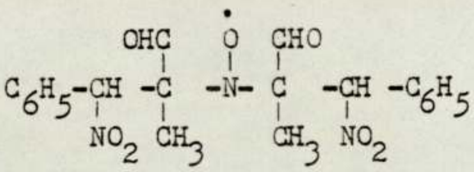
$R = OH$ or C_6H_5

(4-LXX)

4.4.8 α-Methylcinnamaldehyde

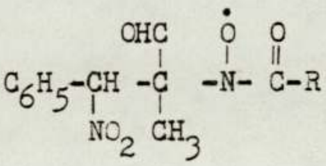
The pale green solution of low concentration of NO_2 and α-methylcinnamaldehyde produced nitroxide (4-LXXI) and acyl nitroxide

(4-LXXII) in equal amounts. The esr spectra showed 3 lines which had $a_N = 13.072$ G (1:1:1) for nitroxide (4-LXXI), and 3 lines which $a_N = 7.427$ G (1:1:1) for acyl nitroxide (4-LXXII). When the reaction was studied at elevated temperature or with addition of oxygen, we observed a broad esr spectra of both radicals , also in equal quantities.



$$C_6H_5-\underset{NO_2}{CH}-\overset{OHC}{\underset{CH_3}{C}}-\overset{\dot{O}}{N}-\overset{CHO}{\underset{CH_3}{C}}-\underset{NO_2}{CH}-C_6H_5$$

(4-LXXI)



$$C_6H_5-\underset{NO_2}{CH}-\overset{OHC}{\underset{CH_3}{C}}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-R$$

R = H, or C_6H_5

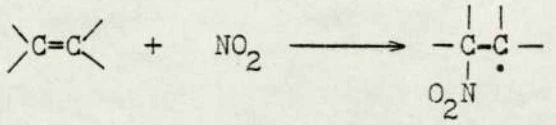
(4-LXXII)

We also observed the same results from the reactions of high concentration of NO_2 , and α-methylcinnamaldehyde.

Discussion

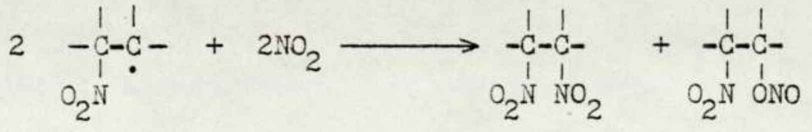
General Introduction to the Addition Reaction of NO_2 with Alkenes.

Mechanism of addition reaction between NO_2, and alkenes is of the free radical type reaction (H.Shechter, and F.Conrad, 1953). The rate of addition is the second-order with respect to NO_2 in the study of reaction of NO_2 at low concentration, and alkenes (R.D.Cadle et al., 1961). Regarding the mechanism of NO_2 and alkenes addition reactions in producing stable free radical products it has been proposed that the first NO_2 always attaches to the carbon atom containing the larger number of hydrogen atoms, this results in a β-nitroalkyl radical which we term the initial free radical intermediate. The second NO_2 then adds to give either C-ONO or C-NO_2, for example the β-nitroalkyl radical gives vic-dinitro and vic-nitronitrite in equal proportion (H.Shechter, 1964). In terminal alkenes, the addition of the first NO_2 occurs exclusively by C-N bond formation at the terminal position (H.Shechter, and F.Conrad, 1953). From our study of radical products in this work , when pure NO_2 is used in reaction studies, we suggest that vic-nitronitrite takes an important role in free radical product formation since it decomposes into ·β-nitroalkoxy radical and nitric oxide (NO), both of which are involved in the formation of further reaction products. Reactions 4.1 to 4.3 represent this part of mechanism.



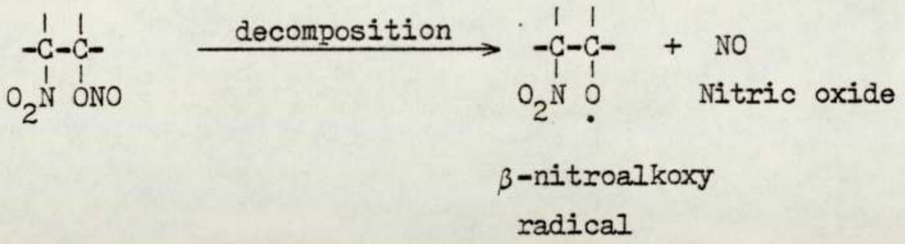
$$\rangle C=C \langle \; + \; NO_2 \longrightarrow -\underset{O_2N}{\overset{|}{C}}-\overset{|}{\dot{C}}- \qquad (4.1)$$

β-nitroalkyl radical
(initial radical intermediate)



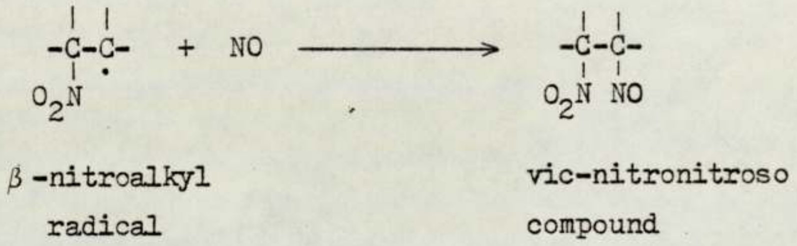
$$2\;-\underset{O_2N}{\overset{|}{C}}-\overset{|}{\dot{C}}- \; + \; 2NO_2 \longrightarrow -\underset{O_2N}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}- \; + \; -\underset{O_2N}{\overset{|}{C}}-\underset{ONO}{\overset{|}{C}}- \qquad (4.2)$$

vic-dinitro compound vic-nitronitrite



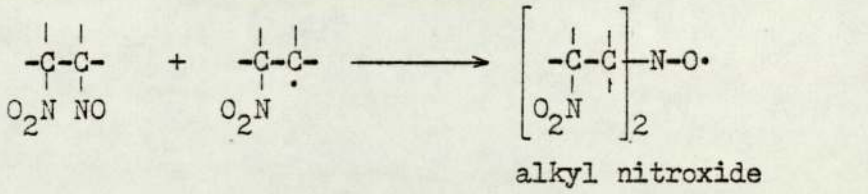
$$\mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}ONO} \xrightarrow{\text{decomposition}} \mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O\cdot} + \mathrm{NO} \qquad (4.3)$$

Nitric oxide which is produced from decomposition of vic-nitronitrite as in reaction 4.3 could add to β-nitroalkyl radical resulting in a vic-nitronitroso compound as shown in reaction 4.4.

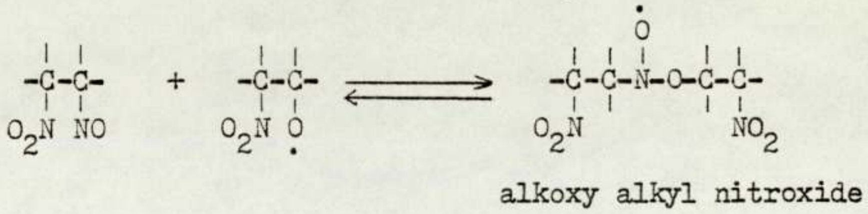


$$\mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{C}{\cdot}} + \mathrm{NO} \longrightarrow \mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}NO} \qquad (4.4)$$

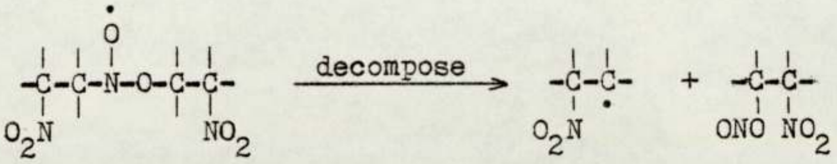
When vic-nitronitroso compound is present in reaction mixture which contains either β-nitroalkyl radical or β-nitroalkoxy radical, it will react with these radicals and give alkyl nitroxide and alkoxy alkyl nitroxide respectively as shown in reactions 4.5 and 4.6. Alkoxy alkyl nitroxide is unstable, it decomposes to alkyl nitrite and alkyl radical or reversibly to nitrosoalkane and alkoxy radical (A.Mackor et al., 1966; Th.A.J.W.Wajer et al., 1967; A.Mackor et al., 1968; and P.J.Cowley, 1969) as shown in reactions 4.6, and 4.7.



$$\mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}NO} + \mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{C}{\cdot}} \longrightarrow \left[\mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}}\right]_2\mathrm{N{-}O\cdot} \qquad (4.5)$$

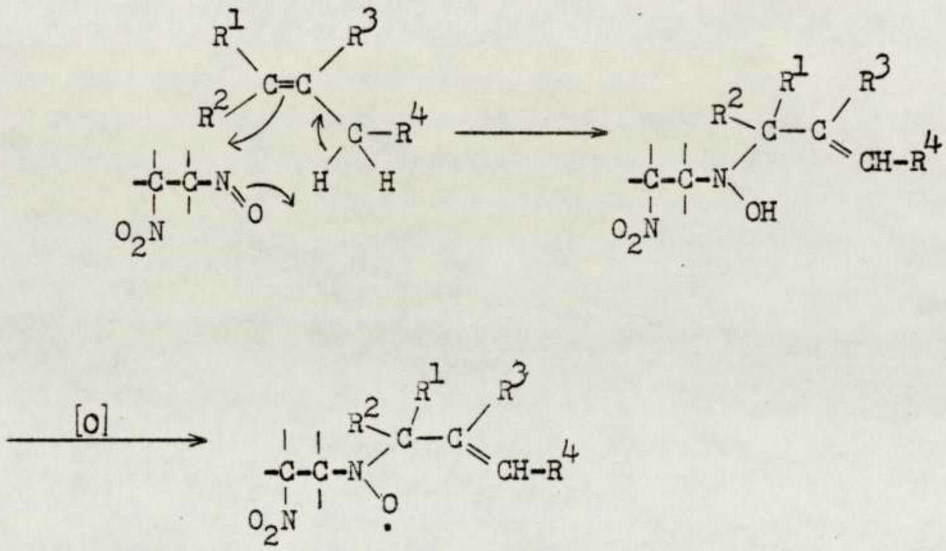


$$\mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}NO} + \mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O\cdot} \rightleftharpoons \mathrm{O_2N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{\overset{\cdot}{O}}{N}{-}O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}NO_2} \qquad (4.6)$$



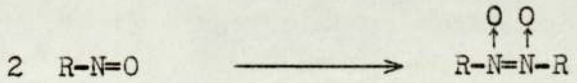
$$\underset{O_2N}{-\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-\overset{\dot{O}}{N}-O-\overset{|}{\underset{|}{C}}-\underset{NO_2}{\overset{|}{\underset{|}{C}}-} \xrightarrow{\text{decompose}} \underset{O_2N}{-\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{\bullet}{C}}- \; + \; \underset{ONO}{-\overset{|}{\underset{|}{C}}}-\underset{NO_2}{\overset{|}{\underset{|}{C}}-} \qquad (4.7)$$

Apart from free radical trapping, nitroso compounds are also able to react with alkyl substituted alkenes and yield hydroxylamine, and are further oxidised by unreacted nitroso compounds or by air and finally yield alkyl nitroxides (A.R.Forrester et al., 1968).

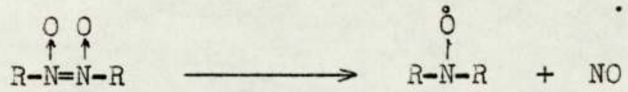


(4.8)

Primary and secondary nitroso compounds dimerise in solution to give nitroso dimers which are unstable, when exposed to air, or at elevated temperatures when they decompose into nitroxide and nitric oxide (A.Mackor et al., 1967a;E.G.Janzen, 1971).



$$2\;R\text{-}N{=}O \longrightarrow R\text{-}\overset{\overset{O}{\uparrow}}{N}{=}\overset{\overset{O}{\uparrow}}{N}\text{-}R \qquad (4.9)$$



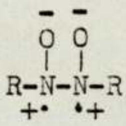
$$R\text{-}\overset{\overset{O}{\uparrow}}{N}{=}\overset{\overset{O}{\uparrow}}{N}\text{-}R \longrightarrow R\text{-}\overset{\overset{\mathring{O}}{\uparrow}}{N}\text{-}R \; + \; NO \qquad (4.10)$$

Nitroso compound are stable only when they contain no α -hydrogen, primary and secondary nitroso compounds undergo nitroso-oxime tautomerisation in which the equilibrium lies far over to the right as in reaction 4.11.

$$(R)_2CH\text{-}N{=}O \rightleftarrows (R)_2C{=}N\text{-}OH \qquad (4.11)$$

Oxime tautomer is able to be oxidised by oxidising agents, such as NO_2 or air, the end products could be both non-radical and free-radical products (A.I.Titov, 1963).

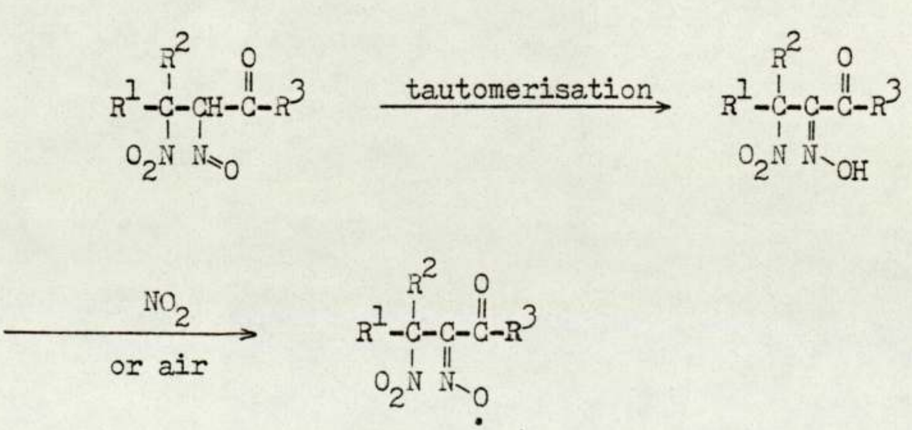
Some nitroso compounds couple to themselves and result in nitroxide biradicals (4-LXXIII) in which there is no interaction between the unpaired electrons (W.Theilacker et al., 1965).



$$R\text{-}\underset{+\bullet}{\overset{\overset{-}{O}}{N}}\text{-}\underset{\bullet+}{\overset{\overset{-}{O}}{N}}\text{-}R$$

(4-LXXIII)

Nitroso-oxime tautomerisation could lead to iminoxy radical formation by oxidation of oxime tautomer . The iminoxy radicals are always observed from the reactions of NO_2 with alkyl carbonyl substituted alkenes, or α, β-unsaturated carbonyl compounds in which there is hydrogen atom available at α-position (J.A.McRae, and M.C.R.Symons, 1966; and W.M.Fox et al., 1967). The mechanism of their formation has been suggested to involve tautomerisation of the vic-nitronitroso compounds into their hydroxyimine tautomers which are further oxidised by NO_2 or air to iminoxy radicals (C.L.Chapman, and D.C.Heckert, 1966).



$$R^1\text{-}\underset{O_2N}{\overset{R^2}{C}}\text{-}\underset{N{=}O}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^3 \xrightarrow{\text{tautomerisation}} R^1\text{-}\underset{O_2N}{\overset{R^2}{C}}\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^3$$

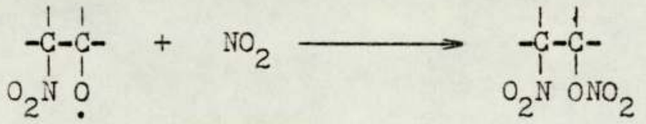
$$\xrightarrow[\text{or air}]{NO_2} R^1\text{-}\underset{O_2N}{\overset{R^2}{C}}\text{-}\underset{\underset{N\text{-}\dot{O}}{\|}}{C}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^3 \qquad (4.12)$$

iminoxy radical

α , β-Unsaturated carbonyl compounds without a hydrogen atom at the α-position do not produce any iminoxy radicals.

4.5 The Study of Reactions of Low Concentration of NO_2 with Alkenes at Room Temperature.

In our reactions of low concentration of NO_2 and alkenes studied in 1,4-dioxan solution, the main radical products are alkyl nitroxides and iminoxy radicals as summarised in Table 4.1. Alkoxy alkyl nitroxide radicals which N-hyperfine splitting constants of about 25-30 gauss, and g-values are slightly different from the values of alkyl nitroxides are not observed in these studies. We suggest that since the β-nitroalkoxy radicals are produced, they undergo further reaction with NO_2 and yield vic-nitronitrates (reaction 4.13), or that they could disproportionate or decompose before they are trapped by vic-nitronitroso compounds, or the alkoxy alkyl nitroxides are formed but decompose to β-nitroalkyl radicals and vic-nitronitrites , or they are formed reversibly (reactions 4.6, and 4.7).



$$\underset{O_2N\ \ \dot{O}}{-\overset{|\ \ |}{C-C}-} + NO_2 \longrightarrow \underset{O_2N\ \ ONO_2}{-\overset{|\ \ |}{C-C}-} \qquad (4\text{-}13)$$

vic-nitroalkoxy radical

vic-nitronitrate

When an excess of alkenes and low concentration of NO_2 are used in the reaction studies, the esr spectra do not show the presence of any nitroxide radicals which might be formed from reaction of nitroso compounds and alkenes as described in reaction 4.8. This is clearly shown in the study of gem-dialkyl alkenes, for example iso-butene, the esr spectrum shows only 3 quintets $a_N = 14.695$ G (1:1:1), and $a_{4H(\gamma CH_2)} = 0.561$ G (1:4:6:4:1). If alkyl nitroxide formed from reaction 4.14 was observed,

<u>Table 4.1</u>

Esr parameters of radical products obtained from reactions of low concentration of NO_2 with alkenes, at room temperature, and 1,4-dioxan as solvent.

<u>1. Alkenes with dialkyl-, trialkyl-, or halogen substituents.</u>

Alkenes	Radical Products	g-value	a_N (gauss)	a_H (gauss)	Spectra
cis-2-butene	nitroxide (4-I)	2.00642	13.167	H(βCH) = 1.756	3 doublets
trans-2-butene	nitroxide (4-I)	2.00668	13.268	H(βCH) = 1.749	3 doublets
2-methyl-2-butene	nitroxide (4-III)	2.00668	14.147	-	3 lines
cyclohexene	nitroxide (4-V)	2.00670	12.374	-	3 lines
oleic acid	nitroxide (4-VIIa)	2.00666	14.952	H(βCH) = 2.06	3 doublets
methyl oleate	nitroxide (4-VIIb)	2.00668	14.759	H(βCH) = 2.11	3 doublets
dichloroethylene	no	-	-	-	-
tetrachloroethylene	no	-	-	-	-

Table 4.1 (continued)

2. Terminal alkenes with alkyl-, aryl-, or halogen substituents.

Alkenes	Radical Products	g-value	a_N (gauss)	a_H (gauss)	Spectra
iso-butene	nitroxide (4-IX)	2.00649	14.695	$4H(\gamma CH_2) = 0.561$	3 quintets
2-methyl-1-butene	nitroxide (4-XII)	2.00654	14.623	-	3 lines
1-decene	nitroxide (4-XV)	2.00726	13.547	-	3 lines
ethyl vinyl ether	nitroxide (4-XVII)	2.00729	13.603	-	3 lines
	acyl nitroxide (4-XVIII)	2.00761	7.132	-	3 lines
allyl chloride	nitroxide (4-XIX)	2.00649	13.282	$2H(\beta CH) = 4.239$	3 triplets
3-butenoic acid	nitroxide (4-XXII)	2.00731	13.766	$2H(\beta CH) = 4.225$	3 triplets
styrene	nitroxides (4-XXIVa),	2.00658	14.755	$2H(\beta CH) = 11.715$	3 triplets
	and (4-XXIVb)			$2H(\beta CH) = 6.377$	3 triplets
p-methoxystyrene	nitroxides (4-XXVIa),	2.00659	14.917	$2H(\beta CH) = 12.113$	3 triplets
	and (4-XXVIb)			$2H(\beta CH) = 6.671$	3 triplets

Table 4.1 (continued)

Alkenes	Radical Products	g-value	a_N (gauss)	a_H (gauss)	Spectra
α -methylstyrene	nitroxide (4-XXVIII)	2.00640	14.91	-	3 lines
hexachloropropene	no	-	-	-	-
hexachloro-1,3-butadiene	no	-	-	-	-

Table 4.1 (continued)

3. Alkenes with carbonyl-, alkyl carbonyl, or halogenyl carbonyl substituents.

Alkenes	Radicals Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
acrylic acid	nitroxide (4-XXIX)	2.00645	12.615	2H(βCH) = 3.647	3 triplets
3-butene-2-one	iminoxy radicals	2.00531			
	E-isomer (4-XXXIIa),		31.124	1H(4CH_2)= 2.203	3×10 lines
	(main product)			1H(4CH_2)= 1.01	
				N(NO_2) = 0.459	
	Z-isomer (4-XXXIIb)		28.09	not clear	3 broad lines
acraldehyde	iminoxy radicals	2.00578			
	E-isomer (4-XXXVa),		30.917	N(NO_2) = 1.182	3×5 lines
				2H(3CH_2)= 1.182	
	Z-isomer (4-XXXVb)		29.558	H(-CHO)= 14.188	6×3 lines
	(main product),			2H(3CH_2)= 0.887	
	acyl nitroxide (4-XXXVIa)	2.00757	7.389	H(βCH) = 2.069	3 doublets
methacrolein	nitroxide(4-XXXVII)	2.00662	14.53	-	3 lines
methacryloyl chloride	nitroxide (4-XXXIX)	2.00679	13.021	-	3 lines

Table 4.1 (continued)

Alkenes	Radical Products	g-value	a_N(gauss)	a_X (gauss)	Spectra
methyl methacrylate	nitroxide (4-XL)	2.00646	13.932	-	3 lines
crotonic acid	iminoxy radical				
	E-isomer (4-XLIa),	2.00580	29.557	$N(NO_2)$ = 6.497	3 triplets
	acyl nitroxide (4-XLII)	2.00823	7.139	-	3 lines
ethyl crotonate	iminoxy radicals	2.00489			2 spectra
	E-isomer (4-XLIIIa),		33.8	H(3CH) = 4.45 $3H(4CH_3)$= 1.50 $N(NO_2)$ = 0.389	superimposed
	Z-isomer (4-XLIIIb) (main product)		29.755		
methyl crotonate	iminoxy radicals	2.00486	32.118		2 spectra
	E-isomer (4-XLVIa),		32.118	H(3CH) = 4.4 $3H(4CH_3)$= 1.50 $N(NO_2)$ = 0.389	superimposed
	Z-isomer (4-XLVIb), (main product)		29.755		

Table 4.1 (continued)

Alkenes	Radical Products	g-values	a_N (gauss)	a_X (gauss)	Spectra
crotonaldehyde	iminoxy radicals	2.00571			
	E-isomer (4-XLVIIa),		30.922	$N(NO_2) = 6.798$	3 triplets
	Z-isomer (4-XLVIIb)		29.546	$H(-CHO) = 19.41$	6X3 lines
	(main product)			$N(NO_2) = 0.87$	
hexachlorobutenoic acid	no	-	-	-	-
3-pentene-2-one	iminoxy radicals	2.00480			
	E-isomer (4-XLIXa),		33.696	$N(NO_2) = 1.276$	3X6 lines
				$H(4CH) = 0.638$	
	Z-isomer (4-XLIXb)		30.001	$3H(1CH_3) = 1.914$	3X12 lines
	(main product)			$N(NO_2) = 0.638$	
tiglic acid	nitroxide (4-LII)	2.00661	13.729	-	3 lines
3,3-dimethylacrylic acid	iminoxy radical				
	Z-isomer (4-LIII),	2.00498	29.885	-	3 lines
	acyl nitroxide (4-LIV)	2.00678	7.094	$H(\beta CH) = 3.695$	3 doublets

<u>Table 4.1</u> (continued)

Alkenes	Radicals Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
mesityl oxide	iminoxy radical Z-isomer (4-LV)	2.00498	30.036	$3H(CH_3)$ = 1.750 $N(NO_2)$ = 0.680	3x12 lines
maleic acid	no	-	-	-	-
fumaric acid	no	-	-	-	-
dimethyl maleate	no	-	-	-	-
dimethyl fumarate	no	-	-	-	-

Table 4.1 (continued)

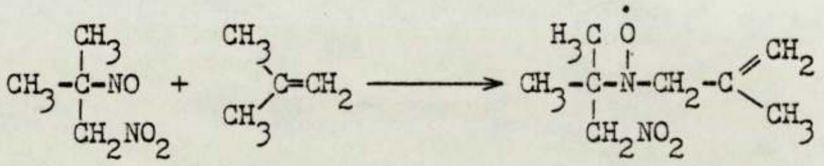
4. Alkenes with aryl-, or aryl carbonyl substituents.

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
cis-stilbene	nitroxide (4-LIX)	2.00743	14.014	H(βCH) = 2.817	3 doublets
trans-stilbene	nitroxide (4-LIX)	2.00755	14.107	H(βCH) = 3.245	3 doublets
cinnamaldehyde	iminoxy radicals	2.00447			
	E-isomer (4-LXIa),		30.749	H(3CH) = 2.005	3 doublets
	Z-isomer (4-LXIb)		29.412	H(-CHO)= 19.311	6X3 lines
	(main product) ,			N(NO_2) = 0.897	
	acyl nitroxide (4-LXII)	2.00663	8.913	H(βCH) = 4.456	3 doublets
cinnamic acid	no	-	-	-	-
benzalacetone	iminoxy radical				
	E-isomer (4-LXIII)	2.00448	31.979	H(4CH) = 1.717	3 doublets
benzalacetophenone	no	-	-	-	-
dibenzalacetone	nitroxide (4-LXVII)	2.00709	12.958	2H(βCH) = 4.122	3 triplets

Table 4.1 (continued)

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
cinnamyl alcohol	nitroxides (4-LXIXa),	2.00618	14.656	2H(βCH) = 4.737	3 triplets
	and (4-LXIXb)			2H(βCH) = 1.776	3 triplets
α-methylcinnamaldehyde	nitroxide (4-LXXI)	2.00663	13.072	-	3 lines
	acyl nitroxide (4-LXXII)	2.00690	7.427	-	3 lines

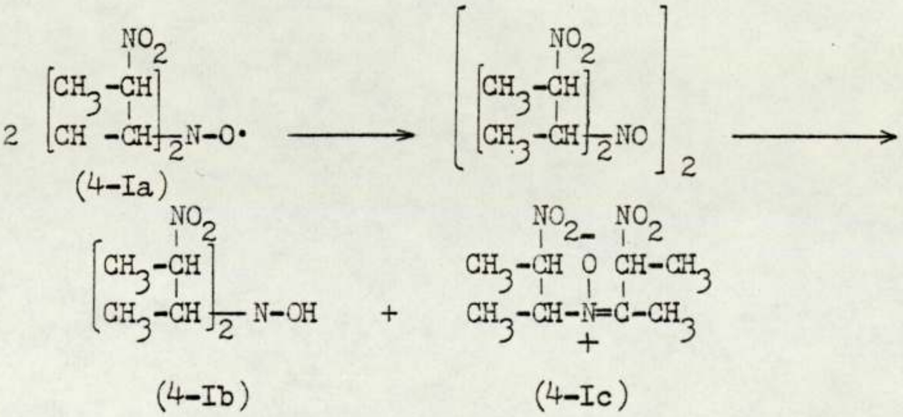
the esr spectrum would show 3 triplets with β H-hyperfine splitting constant = 10.7 G (E.G.Janzen, 1971).



$$CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-NO + \overset{CH_3}{\underset{CH_3}{}}\!\!>C{=}CH_2 \longrightarrow CH_3-\underset{CH_2NO_2}{\overset{H_3C}{C}}-\overset{\overset{\bullet}{O}}{N}-CH_2-C\begin{matrix}{=}CH_2\\ \diagdown CH_3\end{matrix} \qquad (4.14)$$

4.5.1 Alkenes with dialkyl-, trialkyl-, or halogen substituents.

In the study of reactions of cis-, and trans-2-butenes with low concentration of NO_2 in 1,4-dioxan solution at room temperature, we observed that both alkenes yielded alkyl nitroxides the esr spectra of which showed similar 3 doublets, $a_N \approx 13$ G and one hydrogen atom coupling constant $a_H \approx 1.7$ G as shown in Figure 4.1. We suggest that these two alkenes produce the same alkyl nitroxide (4-I), since the previous work observed that NO_2 catalysed cis-trans isomerisation of alkenes before final addition occurred (C.Kelber, and A.Schwarz, 1912; and H.Shechter, 1964). We propose that the initial alkyl nitroxide produced from these reactions is bis-(1-methyl-2-nitro-2-methyl ethyl) nitroxide (4-Ia) which is unstable , it undergoes disproportionation and decomposition which results in the hydroxylamine (4-Ib) and the nitrone (4-Ic), and we suggest that alkyl nitroxide (4-I) is the product of alkyl nitroxide (4-Ia) trapped by nitrone (4-Ic). This reaction mechanism could occur within sample preparation time.

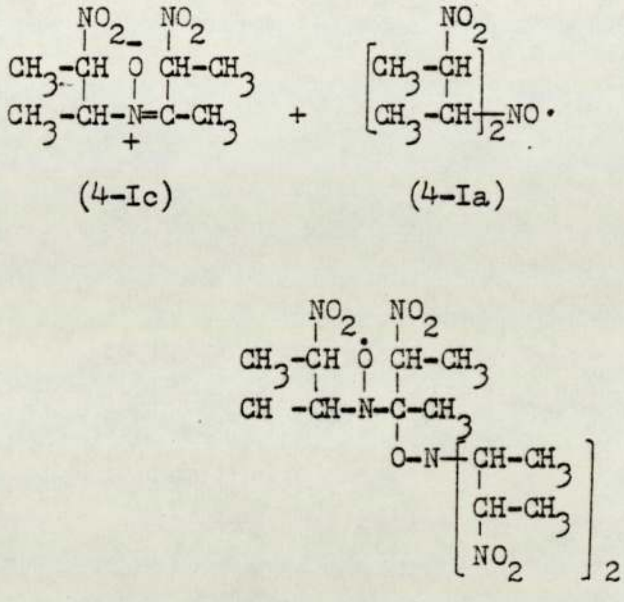


$$2\left[\begin{matrix}CH_3-\overset{NO_2}{CH}\\ CH\ -CH\end{matrix}\right]_2 N-O\bullet \longrightarrow \left[\left[\begin{matrix}CH_3-\overset{NO_2}{CH}\\ CH_3-CH\end{matrix}\right]_2 NO\right]_2 \longrightarrow$$

$$\left[\begin{matrix}CH_3-\overset{NO_2}{CH}\\ CH_3-CH\end{matrix}\right]_2 N-OH \quad + \quad \begin{matrix}CH_3-\overset{NO_2}{CH}\ \ O^-\ \ \overset{NO_2}{CH}-CH_3\\ CH_3-CH-\underset{+}{N}{=}C-CH_3\end{matrix} \qquad (4.15)$$

(4-Ia)

(4-Ib) (4-Ic)



(4-Ic) (4-Ia)

(4-I)

(4.16)

The rate constant for alkyl nitroxide decay gradually decreases during decay, this mechanism has been discussed by K.Adamic et al., 1971 who presumed that it was due to increasing stability of the more hindered nitroxides that are formed in the reaction sequence. The decay of nitroxide (4-I) into nitrone and hydroxylamine derivatives which could lead to further alkyl nitroxide was not observed during the reactions which we studied.

The same results as found for cis-, and trans-2-butenes were observed from reactions of cyclohexene, oleic acid, and methyl oleate with low concentration of NO_2. We suggest that the same reaction mechanism was involved and the alkyl nitroxides (4-V), (4-VIIa), and (4-VIIb) were obtained from the disproportionation and decomposition of the first alkyl nitroxides produced from NO_2 addition reactions.

We observed that alkyl nitroxide (4-III) which was produced from reaction of low concentration of NO_2, and 2-methyl-2-butene was the only alkyl nitroxide product of this reaction. Since this nitroxide has no β -hydrogen atom therefore it could not decay as the mechanism described in reaction 2.21.

Dichloroethylene, and tetrachloroethylene do not yield any stable radical product, although there was a report of a reaction of tetrachloroethylene with NO_2 which produced 1,2-dinitrotetrachloroethylene in high yield in the presence of oxygen at 100° for three hours (Biltz, 1902), but in the reaction condition studied in this work, esr spectroscopy did not show the presence of any free radical.

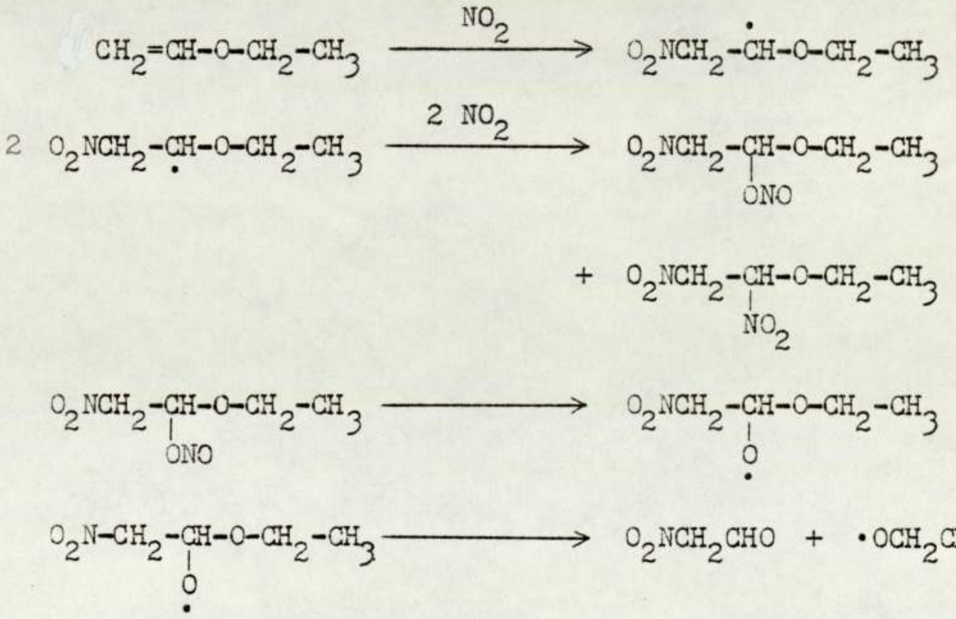
4.5.2 Terminal alkenes with alkyl- , aryl-, or halogen substituents.

Radical products detected from the reactions of low concentration of NO_2 and terminal alkenes are represented in Table 4.1. Nitroxide radicals were observed. We suggest that only the alkyl nitroxides (4-XV), and (4-XVII) produced from 1-decene, and ethyl vinyl ether respectively are products from disproportionation and decomposition of initial alkyl nitroxides formed in the same way as the alkyl nitroxide (4-I) from cis-, and trans-2-butenes. Nitroxide radicals detected from iso-butene (4-IX), 2-methyl-1-butene (4-XII), and α-methylstyrene (4-XVIII) are stable for weeks in their reaction mixtures. We attribute this to the fact that they are nitroxide without hydrogen atom at β-positions. The esr spectrum of alkyl nitroxide (4-IX) shows hyperfine splitting of four protons at γ, γ' positions of about 0.561 G. A similar esr spectrum has been reported for the alkyl nitroxide product from the reaction of N_2O_3 with iso-butene (J.Pfab, 1977), which we suggest that this alkyl nitroxide is the same alkyl nitroxide (4-IX) that we observed in our work.

We also find that nitroxide radicals in which there are hydrogen atoms at β, β' positions do not disproportionate and decompose into hydroxylamines and nitrones, are produced from allyl chloride (4-XIX), 3-butenoic acid (4-XXII), styrene(4-XXIVa and 4-XXIVb), and p-methoxystyrene (4-XXVIa and 4-XXVIb). We suggest that the electron withdrawing groups substituted at β- and β'-positions of nitroxide could stabilise the free electron by delocalisation, we also suggest that dimerisation of nitroxide could occur but the decomposition is not involved.

Reactions of styrene, and p-methoxystyrene with low concentration of NO_2, gave two stereoisomeric nitroxides (4-XXIVa and 4-XXIVb), and (4-XXVIa and 4-XXVIb) respectivly. B.H.J.Bielski, and J.M.Gebicki, 1969; and L.Jonkman et al., 1970 and 1971, have discussed the radical structures but have not related their esr parameters to any proposed structures. The results of our studies were similar to those observed in the previous works.

The mechanism for nitration of aliphatic ethers in the gas phase has been studied and it has been proposed that the fissions of carbon-carbon and carbon-oxygen bonds could occur and yield nitroalkanes and nitroethers which are then oxidised and finally yield aldehydes, ketones, alcohols, and acids (H.B.Hass et al., 1954). Acyl nitroxide which we observed from the addition reaction of ethyl vinyl ether with low concentration of NO_2 possibly follows this mechanism yields nitroacetaldehyde, formaldehyde, nitromethane, and other products. Hydrogen abstraction could occur with nitroacetaldehyde and result in a carbonyl radical which could be trapped by nitroso compounds present in the reaction medium and finally yield an acyl nitroxide (4-XVIII). We suggest the following reaction mechanism for acyl nitroxide (4-XVIII) formation.



$$CH_2{=}CH{-}O{-}CH_2{-}CH_3 \xrightarrow{NO_2} O_2NCH_2{-}\overset{\bullet}{C}H{-}O{-}CH_2{-}CH_3 \qquad (4.17)$$

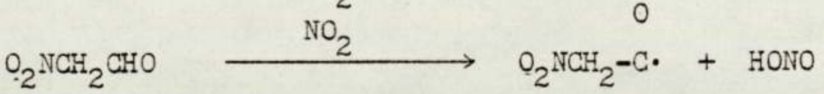
$$2\ O_2NCH_2{-}\underset{\bullet}{C}H{-}O{-}CH_2{-}CH_3 \xrightarrow{2\ NO_2} O_2NCH_2{-}\underset{ONO}{\underset{|}{C}H}{-}O{-}CH_2{-}CH_3 \qquad (4.18)$$

$$+\ O_2NCH_2{-}\underset{NO_2}{\underset{|}{C}H}{-}O{-}CH_2{-}CH_3$$

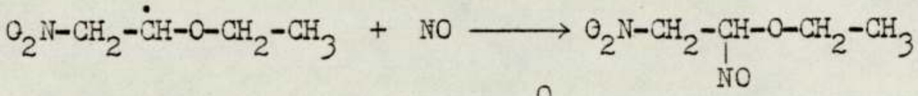
$$O_2NCH_2{-}\underset{ONO}{\underset{|}{C}H}{-}O{-}CH_2{-}CH_3 \longrightarrow O_2NCH_2{-}\underset{\underset{\bullet}{O}}{\underset{|}{C}H}{-}O{-}CH_2{-}CH_3 + NO \quad (4.19)$$

$$O_2N{-}CH_2{-}\underset{\underset{\bullet}{O}}{\underset{|}{C}H}{-}O{-}CH_2{-}CH_3 \longrightarrow O_2NCH_2CHO + {\cdot}OCH_2CH_3 \qquad (4\text{-}20)$$

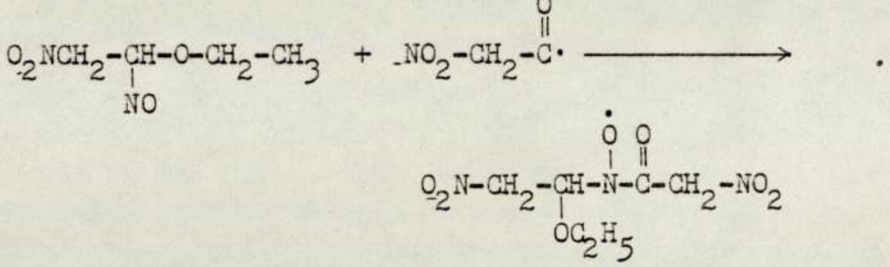
$$\cdot OCH_2-CH_3 \xrightarrow[NO_2]{-CH_2O} CH_3NO_2 + HCHO \qquad (4.21)$$



$$O_2NCH_2CHO \xrightarrow{NO_2} O_2NCH_2-\overset{O}{C}\cdot + HONO \qquad (4.22)$$



$$O_2N-CH_2-\dot{C}H-O-CH_2-CH_3 + NO \longrightarrow O_2N-CH_2-\underset{NO}{\underset{|}{CH}}-O-CH_2-CH_3 \qquad (4.23)$$



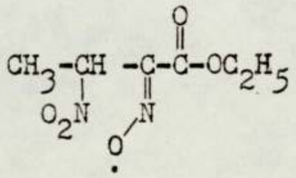
$$O_2NCH_2-\underset{NO}{\underset{|}{CH}}-O-CH_2-CH_3 + NO_2-CH_2-\overset{O}{\overset{\|}{C}}\cdot \longrightarrow O_2N-CH_2-\underset{OC_2H_5}{\underset{|}{CH}}-\overset{\dot{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_2-NO_2 \qquad (4.24)$$

(4-XVIII)

In the study of the reactions of NO_2 with hexachloropropene, and hexachloro-1,3-butadiene, we could not detect any radical products, although conjugated alkenes have been reported to be more reactive than unconjugated alkenes and terminal alkenes in gas phase reactions (A.P. Altshuller, and I.R.Cohen, 1959). We suggest that chlorine atoms which are electron withdrawing decrease the nucleophilicity of alkenes, and NO_2 which is electrophilic does not react with these alkenes or that the rate of reaction is very slow (H.Shechter, 1964).

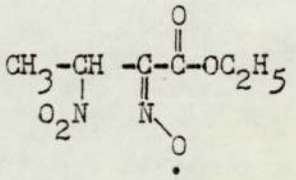
4.5.3 Alkenes with carbonyl-, alkyl carbonyl-, or halogenyl carbonyl-substituents.

The mechanism of the reaction of NO_2 with α, β-unsaturated carbonyl compounds is such that the first NO_2 always adds to the β-carbon position, the second NO_2 adds to α-carbon atom. The radical products which we observed from reactions of NO_2 with α-alkyl- α, β-unsaturated carbonyl compounds are nitroxides. For example we observed a three line esr spectra of nitroxide radicals from methacrolein, methacryloyl chloride, methyl methacrylate, and tiglic acid. Other radical products which we often observe are iminoxy radicals which are produced from reactions of NO_2 with α,β-unsaturated carbonyl compounds in which there is a hydrogen atom present at an α-position. Esr spectra of iminoxy radicals are quite complicated due to long range interaction of the unpaired electron with other nuclei in molecule, and they also show that two isomers, E- and Z-isomers, of iminoxy radicals are produced from each compound. Therefore the two sets of three multiplets are typical of esr spectra for iminoxy radicals detected from these alkenes. For example 3-butene-2-one, acraldehyde, crotonic acid, ethyl crotonate, methyl crotonate, crotonaldehyde, 3-pentene-2-one, 3,3-dimethylacrylic acid, and mesityl oxide produce iminoxy radicals from the reaction studies (Table 4.1). The yield of E-, and Z-isomers are not produced in equal amount, since the esr spectra of iminoxy radicals of ethyl crtonate and methyl crotonate indicate that Z-isomers are produced in higher amount than the E-isomers, and also with



E-isomer

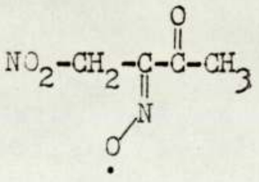
(4-XLIIIa)



Z-isomer

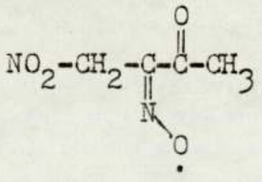
(4-XLIIIb)

the esr spectrum of iminoxy radicals of 3-butene-2-one, the E-isomer (4-XXXIIa) is obtained with much higher spectrum intensity than of Z-isomer (4-XXXIIb), the latter radical is observed only as a trace product.



E-isomer

(4-XXXIIa)



Z-isomer

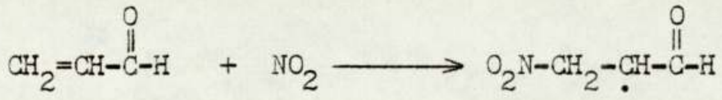
(4-XXXIIb)

Iminoxy radicals which are detected from reactions of NO_2 with α, β-unsaturated aldehydes, for example acraldehyde, and crotonaldehyde are always found to produce the Z-isomers in high yields and their esr spectra show six triplets, as shown in Figures 4.8, and 4.9. E-isomers are observed as a trace or are not detected. Steric hindrance and the ability to form a hydrogen bond between iminoxy group and other nuclei within a molecule determine the stability of each iminoxy isomer produced. E-isomers could be initially formed in high yield, but they interconvert to be the more stable isomer.

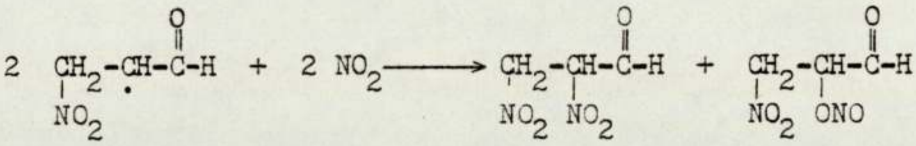
Maleic acid, fumaric acid , and their dimethyl esters and hexachlorobutenoic acid do not yield any radical product under our reaction condition, which we ascribed to them containing electron withdrawing which decrease the reactivities of alkenes.

Although NO_2 can react with carbonyl functional groups, for example NO_2 has been observed to abstract aldehydic hydrogen atom from aldehyde with subsequent loss of a carbonyl group, in gas phase reactions, (S.Jaffe,1971), but in our works in which we studied at low concentration of NO_2 and aldehyde in 1,4-dioxan solution, we would suggest that hydrogen abstraction from aldehydic group could occur but in low amount. The results obtained from the low concentration of NO_2 and acraldehyde, apart from E-, and Z-isomers of iminoxy radical (4-XXXVa) and (4-XXXVb) which were the main addition reaction radical products, the acyl nitroxide (4-XXXVIa) was also produced since it was detected in low concentration. The following reactions are the mechanism which we propose for radical products formation from reaction of NO_2, and acraldehyde in this study.

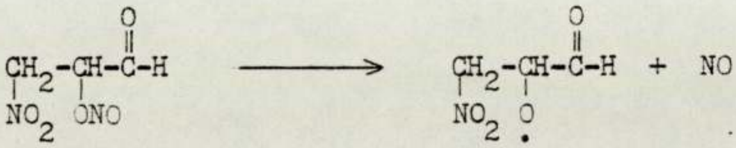
Addition Reaction :



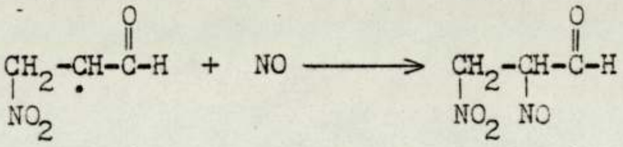
$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H \quad + \quad NO_2 \longrightarrow O_2N{-}CH_2{-}\underset{\bullet}{C}H{-}\overset{\overset{O}{\|}}{C}{-}H \qquad (4.25)$$



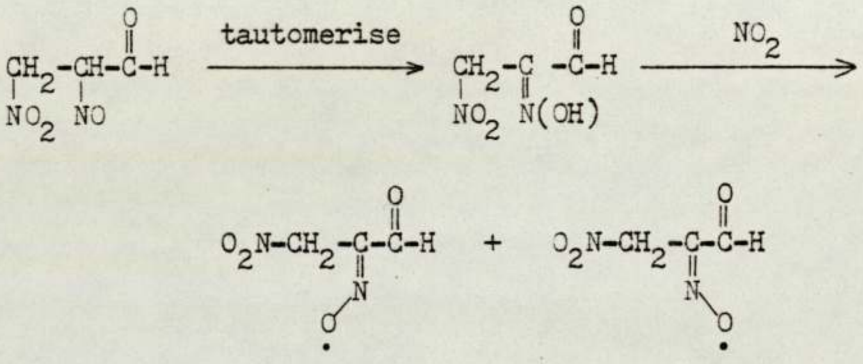
$$2\ \underset{NO_2}{CH_2}-\underset{\bullet}{CH}-\overset{O}{\overset{\|}{C}}-H + 2\ NO_2 \longrightarrow \underset{NO_2}{CH_2}-\underset{NO_2}{CH}-\overset{O}{\overset{\|}{C}}-H + \underset{NO_2}{CH_2}-\underset{ONO}{CH}-\overset{O}{\overset{\|}{C}}-H \qquad (4.26)$$



$$\underset{NO_2}{CH_2}-\underset{ONO}{CH}-\overset{O}{\overset{\|}{C}}-H \longrightarrow \underset{NO_2}{CH_2}-\underset{\dot{O}}{CH}-\overset{O}{\overset{\|}{C}}-H + NO \qquad (4.27)$$



$$\underset{NO_2}{CH_2}-\underset{\bullet}{CH}-\overset{O}{\overset{\|}{C}}-H + NO \longrightarrow \underset{NO_2}{CH_2}-\underset{NO}{CH}-\overset{O}{\overset{\|}{C}}-H \qquad (4.28)$$



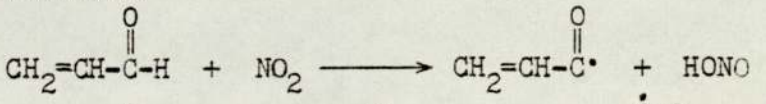
$$\underset{NO_2}{CH_2}-\underset{NO}{CH}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{tautomerise}} \underset{NO_2}{CH_2}-\underset{N(OH)}{\overset{}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NO_2} \qquad (4.29)$$

$$O_2N-CH_2-\underset{\underset{\dot{O}}{N}}{C}-\overset{O}{\overset{\|}{C}}-H + O_2N-CH_2-\underset{\underset{\dot{O}}{N}}{C}-\overset{O}{\overset{\|}{C}}-H$$

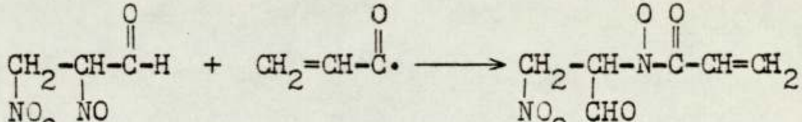
E-isomer Z-isomer

(4-XXXVa) (4-XXXVb)

Hydrogen Abstraction:



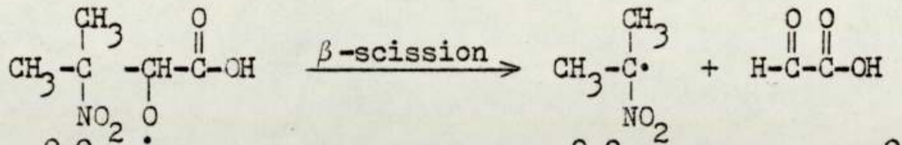
$$CH_2=CH-\overset{O}{\overset{\|}{C}}-H + NO_2 \longrightarrow CH_2=CH-\overset{O}{\overset{\|}{C}}\cdot + HONO \qquad (4.30)$$



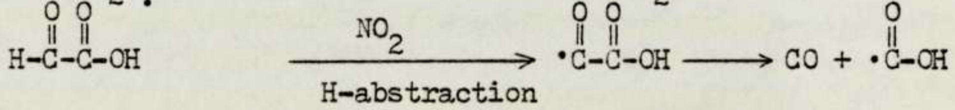
$$\underset{NO_2}{CH_2}-\underset{NO}{CH}-\overset{O}{\overset{\|}{C}}-H + CH_2=CH-\overset{O}{\overset{\|}{C}}\cdot \longrightarrow \underset{NO_2}{CH_2}-\underset{CHO}{CH}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-CH=CH_2 \qquad (4.31)$$

(4-XXXVIa)

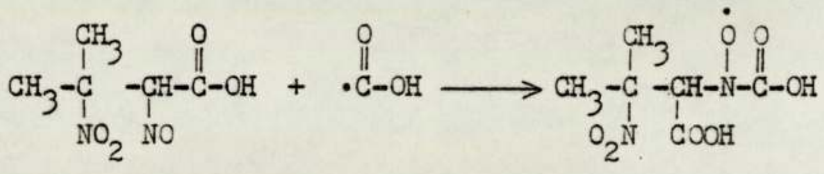
We also observed acyl nitroxides in low yields from the reactions of low concentration of NO_2 with crotonic acid, also with 3,3-dimethylacrylic acid in 1,4-dioxan solution. We would suggest that their formation could involve the β-scission of β-nitroalkoxy radicals. The carboxylic acid groups are not proposed to react with NO_2 since the carboxylic acids are usually found as the end oxidation products of NO_2 and alkenes reactions in gas phase (A.P.Altshuller et al., 1959; and A.I.Titov, 1963). We suggest the following reactions to explain the mechanism of acyl nitroxides formation from these two alkenes.



$$\mathrm{CH_3\text{-}\overset{CH_3}{\underset{NO_2}{C}}\text{-}\underset{\dot{O}}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH} \xrightarrow{\beta\text{-scission}} \mathrm{CH_3\text{-}\overset{CH_3}{\underset{NO_2}{C}}\cdot + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH} \qquad (4.32)$$



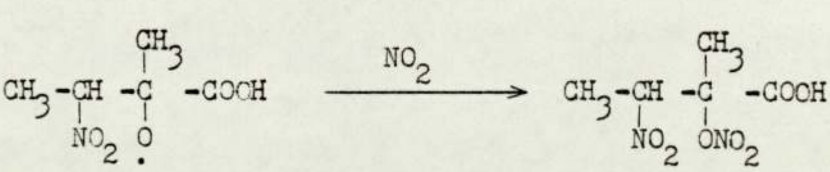
$$\mathrm{H\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH} \xrightarrow[\text{H-abstraction}]{\mathrm{NO_2}} \mathrm{\cdot\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH} \longrightarrow \mathrm{CO + \cdot\overset{O}{\overset{\|}{C}}\text{-}OH} \qquad (4.33)$$



$$\mathrm{CH_3\text{-}\overset{CH_3}{\underset{NO_2}{C}}\text{-}\underset{NO}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + \cdot\overset{O}{\overset{\|}{C}}\text{-}OH} \longrightarrow \mathrm{CH_3\text{-}\overset{CH_3}{\underset{O_2N}{C}}\text{-}\underset{COOH}{CH}\text{-}\overset{\dot{O}}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH} \qquad (4.34)$$

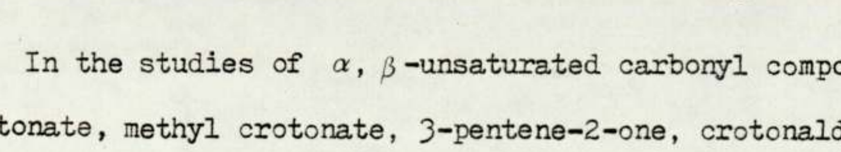
acyl nitroxide (4-LIV)

Radicals which we observed from reactions of low concentration of NO_2 with methacrolein, and tiglic acid were nitroxides (4-XXXVII), and (4-LII) respectively and we could not detect any acyl nitroxide from this reaction. We suggest that the β-nitroalkoxy radicals from these alkenes which are tertiary alkoxy radicals do not undergo β-scission in normal reaction condition as proposed by A.Mackor et al., 1968, and vic-nitronitrates are formed from these radicals.



$$\mathrm{O_2N\text{-}CH_2\text{-}\overset{CH_3}{\underset{\dot{O}}{C}}\text{-}CHO} \xrightarrow{\mathrm{NO_2}} \mathrm{O_2N\text{-}CH_2\text{-}\overset{CH_3}{\underset{ONO_2}{C}}\text{-}CHO} \qquad (4.35)$$

β-nitroalkoxy radical — vic-nitronitrate derivative of methacrolein



$$\mathrm{CH_3\text{-}\underset{NO_2}{CH}\text{-}\overset{CH_3}{\underset{\dot{O}}{C}}\text{-}COOH} \xrightarrow{\mathrm{NO_2}} \mathrm{CH_3\text{-}\underset{NO_2}{CH}\text{-}\overset{CH_3}{\underset{ONO_2}{C}}\text{-}COOH} \qquad (4.36)$$

β-nitroalkoxy radical — vic-nitronitrate derivative of tiglic acid

In the studies of α, β-unsaturated carbonyl compounds, for example ethyl crotonate, methyl crotonate, 3-pentene-2-one, crotonaldehyde, and crotonic acid, in NO_2 addition reactions, from the radical products observed, we could conclude that carbonyl functional group determines the reactivities of alkenes. We observed that the activities decreased from ketone, ester, aldehyde to acid which is the same order of the increasing in strength of electron withdrawing effect. From this reactivity order, we could confirm that in the NO_2 addition reactions, NO_2 acts as an electrophilic agent.

Although α, β-unsaturated esters are reactive in NO_2 addition reactions, we could not obtain any radical product for the vic-diesters alkenes, for example dimethyl maleate, and dimethyl fumarate, From this result we suggest that the addition of the first NO_2 molecule is the rate determining step in which the NO_2 attaches to the position which is higher in electron density and also lower in substitutions.

4.5.4 Alkenes with aryl-, or aryl carbonyl substituents.

The radicals obtained from reactions of low concentration of NO_2 with cis-, or trans-stilbenes were nitroxides. From their three doublets esr spectra we suggest that the nitroxides observed are the result of disproportionation and decomposition of the nitroxide monomers as for alkyl nitroxide (4-I) formation from cis-, and trans-2-butenes, and we also suggest that both cis-, and trans-stilbenes give the same nitroxide (4-LIX) (H.Shechter,1964). These two stibenes are less reactive when compare to cis-, and trans-2-butenes, since the low intensity spectra of nitroxide (4-LIX) were observed.

In the reactions of low concentration of NO_2, and aryl carbonyl alkenes, we suggest that the first NO_2 adds to aryl substituted carbon and the second NO_2 adds to carbonyl substituted carbon, since aryl has less electron withdrawing effect than any carbonyl functional groups. The reactivities of aryl carbonyl alkenes are less than the reactivities of alkyl carbonyl alkenes which we could observe radical products with quite high esr spectral intensities and in less reaction time. We conclude that it is the effect of aryl group which has an electron withdrawing effect leading to a decrease in electron density at reaction centre in the rate determining step. We found this effect in the reactions of low concentration of NO_2 with cinnamaldehyde, α-methylcinnamaldehyde, and benzalacetone in which we observed radical products with low spectral intensities, and we did not observe any radical product from reactions of low concentration of NO_2 with cinnamic acid, and benzalacetophenone.

Dibenzalacetone produced nitroxide (4-LXVII) from its reaction with low concentration of NO_2, we suggest that its vic-nitronitroso derivative does not undergo hydroxyimine tautomerisation because of carbonyl group is stabilised by conjugated system of the molecule, therefore its vic-nitronitroso derivative produces a nitroxide rather than an iminoxy radical.

Radicals obtained from cinnamyl alcohol are two stereoisomers of nitroxide (4-LXIX), and their formations could be by the same mechanism as the nitroxides formation from styrene, and p-methoxystyrene and NO_2 addition reaction.

4.6 The Study of the Reactions of High Concentration of NO_2 with Alkenes in 1,4-Dioxan Solution at Room Temperature.

The roles of NO_2 in the reactions of high concentration of NO_2, and alkenes reported in previous works have not been fully understood. The rate of reactions has been reported to be not in agreement with second-order dependence on concentration of NO_2(T.L.Cottrell, and T.E. Graham, 1953 , and 1954). In these studies we gradually increased the concentration of NO_2 in the reactions of low concentration of NO_2 and alkenes, we observed that the esr spectral intensities of alkyl nitroxides decreased and esr spectra of acyl nitroxides were observed, the yield of nitroxide depending on the concentration of NO_2. In the experiments in which a very high concentration of NO_2 was involved from the beginning of the reaction, we observed acyl nitroxide as the, only, or the main radical product of the reactions studied. From these observations, we suggest that acyl nitroxides are not derived from the decay of alkyl nitroxides and that the alkyl nitroxides may not be produced from the reactions of very high concentration of NO_2, and alkenes.

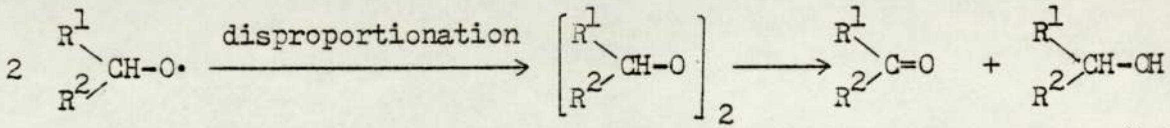
We considered vic-dinitro compounds, and vic-nitronitrites, which are the primary reaction products of addition reaction of NO_2, and alkenes, to be involved in the pathway of producing acyl nitroxides. vic-Nitronitrites which are unstable could undergo decomposition into β -nitroalkoxy radicals and nitric oxide (A.Mackor et al., 1967a). In the reaction medium with the excess of NO_2, β -nitroalkoxy radicals further react with NO_2 and produce vic-nitronitrate or undergo disproportionation, and decomposition, or β -scission which could lead to the formation of several non-radical, and radical products. Nitric oxide also could further react with any radicals in the reaction medium, and nitroso compounds would be among the products obtained. In the reactions of high concentration of NO_2, and alkenes in solution at room temperature, we suggest that β -nitroalkoxy radicals, and nitroso compounds are the main components in producing acyl nitroxides, and the excess amount of NO_2 and the presence of NO in the reaction medium have their roles in extensive oxidation to alkenes.

It has been known that primary ,and secondary alkoxy radicals undergo disproportionation and result in aldehydes or ketones,and alcohols (A.L.Nussbaum, and C.H.Robinson, 1962). Secondary alkoxy radicals also undergo β -C-C scission in which the most stable radicals are split off to leave aldehydes in low yield (P.Kabasakalian et al., 1962; P.Kabasakalian, and E.R.Townley, 1962; and D.Durant, and G.R.McMillan, 1966). Tertiary alkoxy radicals could undergo hydrogen abstraction or radical fragmentation, and they usually do not give rise to the formation of aldehydes. The following reactions represent the disproportionation, decomposition, and radical fragmentation of primary, secondary, and tertiary alkoxy radicals.

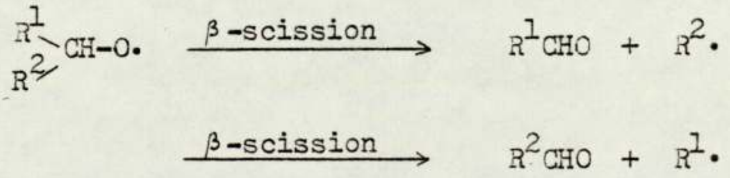
Primary alkoxy radicals:

$$2\ \mathrm{R\text{-}CH_2\text{-}O\cdot}\ \xrightarrow{\text{disproportionation}}\ \left[\mathrm{RCH_2\text{-}O}\right]_2 \longrightarrow \mathrm{RCH_2\text{-}OH} + \mathrm{RCHO} \qquad (4.37)$$

Secondary alkoxy radicals:

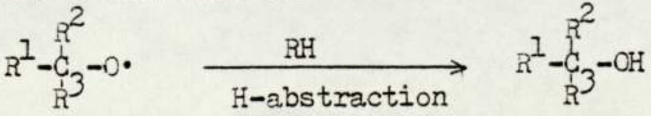


(4.38)

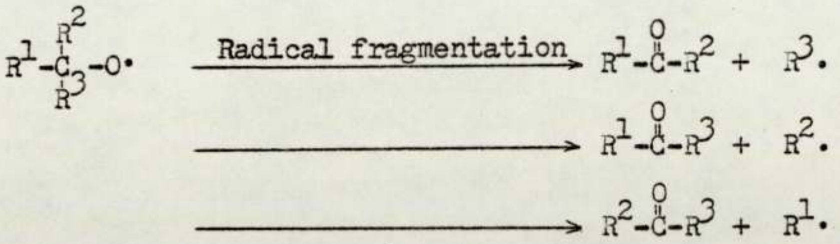


(4.39)

Tertiary alkoxy radicals:



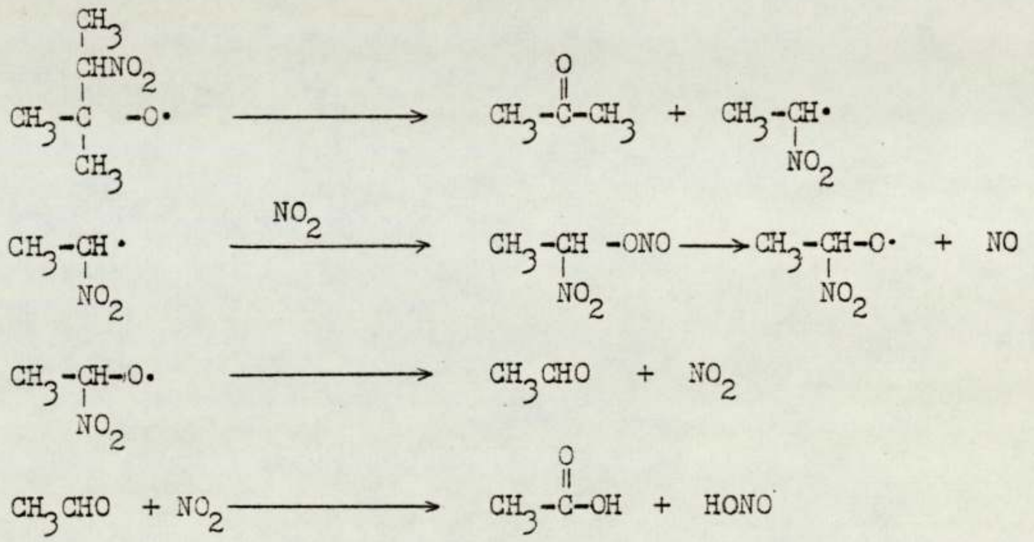
$$\mathrm{R^1\text{-}\overset{R^2}{\underset{R^3}{C}}\text{-}O\cdot}\ \xrightarrow[\text{H-abstraction}]{\mathrm{RH}}\ \mathrm{R^1\text{-}\overset{R^2}{\underset{R^3}{C}}\text{-}OH} \qquad (4.40)$$



$$R^1-\overset{R^2}{\underset{R^3}{C}}-O\cdot \xrightarrow{\text{Radical fragmentation}} R^1-\overset{O}{\overset{\|}{C}}-R^2 + R^3\cdot$$
$$\longrightarrow R^1-\overset{O}{\overset{\|}{C}}-R^3 + R^2\cdot$$
$$\longrightarrow R^2-\overset{O}{\overset{\|}{C}}-R^3 + R^1\cdot$$

(4.41)

The products which were reported from the reaction of NO_2, and 2-methyl-2-butene in the gas phase, were acetone, and acetic acid (A.P. Altshuller et al., 1959). From this result we suggest that the tertiary alkoxy radical was formed and further fragmented into acetone, and nitroalkyl radical which the latter radical could be further oxidised by NO_2, and produced acetic acid.



$$CH_3-\overset{\overset{CH_3}{|}\atop CHNO_2}{\underset{CH_3}{C}}-O\cdot \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\underset{NO_2}{CH}\cdot \qquad (4.42)$$

$$CH_3-\underset{NO_2}{CH}\cdot \xrightarrow{NO_2} CH_3-\underset{NO_2}{CH}-ONO \longrightarrow CH_3-\underset{NO_2}{CH}-O\cdot + NO \qquad (4.43)$$

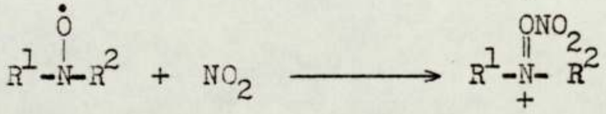
$$CH_3-\underset{NO_2}{CH}-O\cdot \longrightarrow CH_3CHO + NO_2 \qquad (4.44)$$

$$CH_3CHO + NO_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + HONO \qquad (4.45)$$

In our study, the reactions were carried out in solution in which solvent molecules could prevent the extensive oxidation, and we suggest that the reaction sequence proceeds only as far as step 4.44 and aldehydes resulted.

Nitroso compounds have been reported to be oxidised by NO_2 to produce nitro compounds, or their oxime tautomers to react with NO_2 to produce gem-trinitro compounds, pseudo-nitrols, nitrolic acids, nitrile oxides, furoxanes, aldehydes, ketones, and carboxylic acid (A.I.Titov, 1963). The nitroso compounds also could react with NO to give diazo compounds (A.Mackor et al., 1968). In the gas phase study of 2-methyl-2-butene, the vic-nitronitrite, and vic-nitronitroso derivatives were not observed (A.P.Altshuller et al., 1959), and we suggest that they were completely oxidised by NO_2. In our studies, the radicals which we observed were mostly acyl nitroxides, so we suggest that vic-nitronitroso compounds produced from the reactions in solution could undergo not only further reactions with the excess of NO_2 but also be involved in acyl nitroxide formation.

The results which we obtained in our study from the reactions in which we gradually increased the concentration of NO_2, was a decrease in esr spectral intensities of alkyl nitroxides and we suggest that alkyl nitroxides could react with the excess of NO_2 and produce oxoammonium nitrate, and lead to a decreased concentration of alkyl nitroxides in the reaction mixtures (J.A.Nelson et al., 1971, S.Chou et al., 1974), as shown in reaction 4.46.



$$R^1-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-R^2 \; + \; NO_2 \longrightarrow R^1-\underset{+}{\overset{\overset{-}{O}NO_2}{\overset{\|}{N}}}-R^2 \qquad (4.46)$$

The radical products which we observed from the reactions of high concentration of NO_2 and alkenes in 1,4-dioxan solution at room temperature are represented in Table 4.2, and the detail of radical products formation are suggested in the following discussion.

4.6.1 Alkenes with dialkyl-, trialkyl-, or halogen substituents.

In the reaction of high concentration of NO_2 and alkenes in this group, cis-2-butene, trans-2-butene, cyclohexene, oleic acid, and methyl oleate produced acyl nitroxides in good yield but 2-methyl-2-butene produced acyl nitroxide (4-IV) only in low concentration.

Alkoxy radicals generated from the decomposition of vic-nitronitrite derivatives of cis-2-butene, trans-2-butene, cyclohexene, oleic

Table 4.2

Esr parameters of radical products obtained from the reactions of high concentration of NO_2 with alkenes at room temperature , 1,4-dioxan as solvent.

1. Alkenes with dialkyl-, trialkyl-, or halogen substituents.

Alkenes	Radical Products	g-value	a_N(gauss)	a_X (gauss)	Spectra
cis-2-butene	nitroxide (4-I), acyl nitroxide (4-II)	2.00747	7.618	H(βCH) = 2.12	3 doublets
trans-2-butene	nitroxide (4-I), acyl nitroxide (4-II)	2.00748	7.683	H(βCH) = 2.05	3 doublets
2-methyl-2-butene	nitroxide (4-III), acyl nitroxide (4-IV)	2.00704	7.804	-	3 lines
cyclohexene	acyl nitroxide (4-VI)	2.00693	6.705	-	3 lines
oleic acid	acyl nitroxide (4-VIIIa)	2.00715	6.713	-	3 lines
methyl oleate	acyl nitroxide (4-VIIIb)	2.00708	6.78	-	3 lines
dichloroethylene	no	-	-	-	-
tetrachloroethylene	no	-	-	-	-

Table 4.2 (continued)

2. Terminal alkenes with alkyl-, aryl-, or halogen substituents.

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
iso-butene	nitroxide (4-IX),				
	acyl nitroxide (4-X)	2.00757	7.126	H(-CHO) = 1.397	3 doublets
2-methyl-1-butene	nitroxide (4-XII),				
	acyl nitroxide (4-XIII)	2.00738	7.126	-	3 lines
1-decene	acyl nitroxide (4-XVI)	2.00689	7.153	-	3 lines
ethyl vinyl ether	no	-	-	-	-
allyl chloride	nitroxide (4-XIX),	2.00649	13.282	H(βCH) = 4.239	3 doublets
	acyl nitroxide (4-XXI)	2.00802	7.642	H(βCH) = 2.530	3 doublets
3-butenoic acid	acyl nitroxide (4-XXIII)	2.00697	7.355	H(βCH) = 2.179	3 doublets
styrene	acyl nitroxide (4-XXV)	2.00696	8.129	H(βCH) = 3.784	6 lines
p-methoxystyrene	acyl nitroxide (4-XXVII)	2.00771	7.427	H(βCH) = 3.268	6 lines
α -methylstyrene	nitroxide (4-XXVIII)				
hexachloropropene	no	-	-	-	-

Table <u>4.2</u> (continued)

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
hexachloro-1,3-butadiene	no	-	-	-	-

Table 4.2 (continued)

3. Alkenes with carbonyl-, alkyl carbonyl-, or halogenyl carbonyl substituents.

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
acrylic acid	nitroxide (4-XXIX),				
	acyl nitroxide (4-XXX),		7.637	H(βCH) = 3.16	3 doublets
	iminoxy radical				
	E-isomer (4-XXXI)		29.493	N(NO_2) = 2.897	3 triplets
3-butene-2-one	iminoxy radical				
	E-isomer (4-XXXIIa),				
	nitroxide (4-XXXIV)(trace)		13.62	2H(βCH) = 3.849	3 triplets
	acyl nitroxide (4-XXXIII)	2.00743	6.839	H(βCH) = 0.884	3 doublets
acraldehyde	iminoxy radicals				
	E-isomer (4-XXXVa),				
	Z-isomer (4-XXXVb),				
	acyl nitroxide (4-XXXVIb)	2.00757	7.389	H(βCH) = 2.069	3 doublets
methacrolein	nitroxide (4-XXXVII),				
	acyl nitroxide (4-XXXVIII)		7.405	-	3 lines

Table 4.2 (continued)

Alkenes	Radical Products	g-value	a_N(gauss)	a_X (gauss)	Spectra
methacryloyl chloride	nitroxide (4-XXXIX)				
methyl methacrylate	nitroxide (4-XL)				
crotonic acid	iminoxy radical				
	E-isomer (4-XLIa),				
	acyl nitroxide (4-XLII)				
ethyl crotonate	iminoxy radicals				
	E-isomer (4-XLIIIa),				
	Z-isomer (4-XLIIIb)				
	(main product)				
methyl crotonate	iminoxy radicals				
	E-isomer (4-XLVIa),				
	Z-isomer (4-XLVIb)				
	(main product)				
crotonaldehyde	iminoxy radicals				
	E-isomer (4-XLVIIa),				
	Z-isomer (4-XLVIIb),				
	acyl nitroxide (4-XLVIII)		6.984	-	3 lines

Table 4.2 (continued)

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
hexachlorobutenoic acid	no	-	-	-	-
3-pentene-2-one	iminoxy radicals E-isomer (4-XLIXa), Z-isomer (4-XLIXb) (main product),				
	nitroxide (4-L),		13.597	H(βCH) = 2.956	3 doublets
	acyl nitroxide (4-LI)		7.0	H(βCH) = 1.157	3 doublets
tiglic acid	nitroxide (4-LII)				
3,3-dimethylacrylic acid	iminoxy radicals Z-isomer (4-LIII) (trace), acyl nitroxide (4-LIV) (main product)				
mesityl oxide	iminoxy radical Z-isomer (4-LV),				
	nitroxide (4-LVII),		13.064	H(βCH) = 2.642	3 doublets

Table 4.2 (continued)

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
mesityl oxide	acyl nitroxide (4-LVI),	2.00721	7.338	H(βCH) = 1.583	3 doublets
(continued)	acyl nitroxide (4-LVIII)		7.338	H(βCH) = 4.892	3 doublets
maleic acid	no	-	-	-	-
fumaric acid	no	-	-	-	-
dimethyl maleate	no	-	-	-	-
dimethyl fumarate	no	-	-	-	-

Table 4.2 (continued)

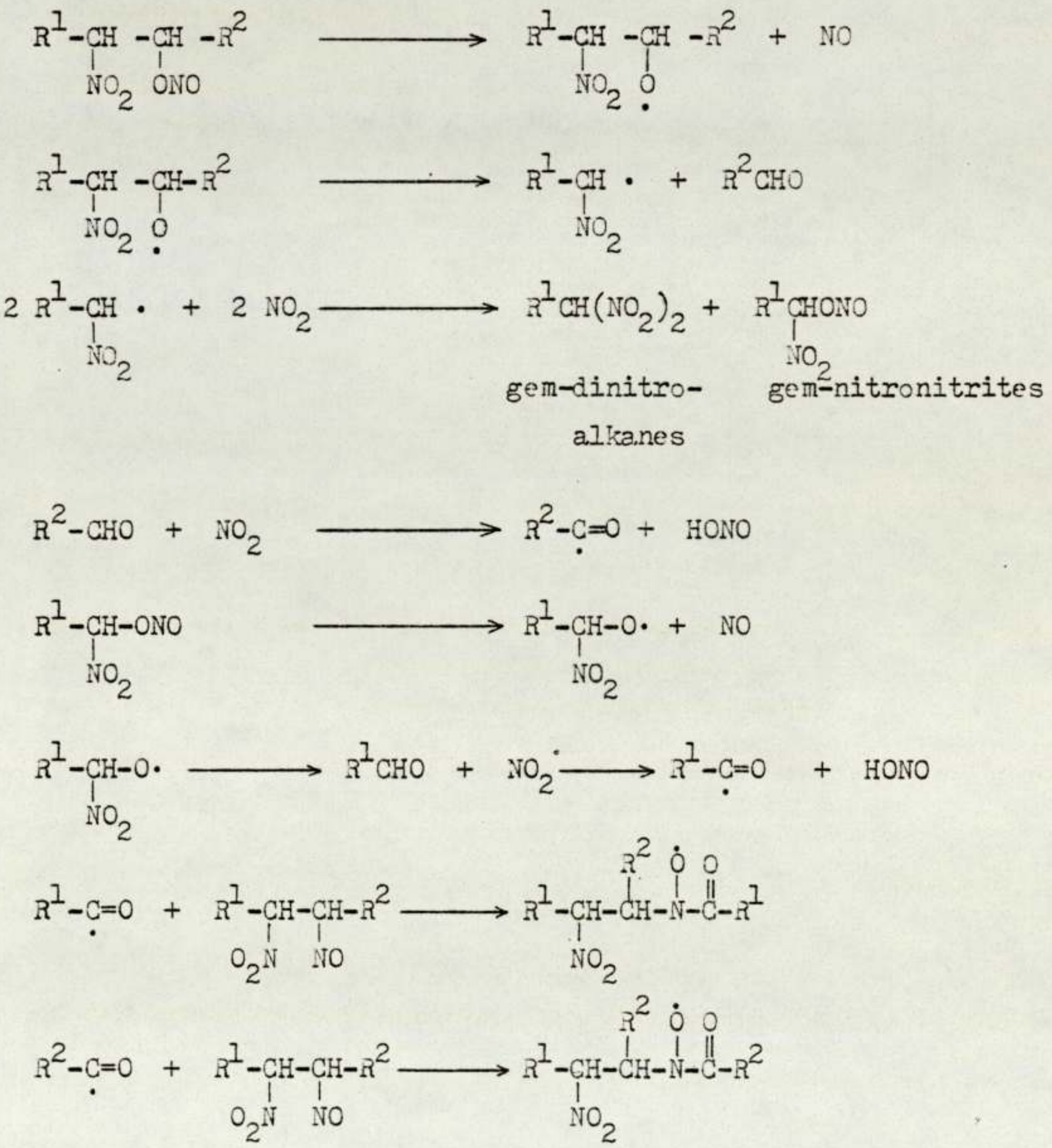
4. Alkenes with aryl-, or aryl carbonyl substituents.

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
cis-2-stilbene	acyl nitroxide (4-LX)	2.00744	8.290	H(βCH) = 2.665	3 doublets
trans-2-stilbene	acyl nitroxide (4-LX)	2.00744	8.290	H(βCH) = 2.665	3 doublets
cinnamaldehyde	iminoxy radicals E-isomer (4-LXIa), Z-isomer (4-LXIb),				
	acyl nitroxide (4-LXII)	2.00663	8.913	H(βCH) = 4.456	3 doublets
cinnamic acid	no	-	-	-	-
benzalacetone	acyl nitroxide (4-LXIV),	2.00820	6.584	H(βCH) = 1.483	3 doublets
	acyl nitroxide (4-LXV)	2.00820	6.525	H(βCH) = 8.601 H(γCH) = 1.483	6 doublets
benzalacetophenone	no	-	-	-	-
dibenzalacetone	acyl nitroxide (4-LXVIII)	2.00694	7.55	-	3 lines

Table 4.2 (continued)

Alkenes	Radical Products	g-value	a_N (gauss)	a_X (gauss)	Spectra
cinnamyl alcohol	acyl nitroxide (4-LXX)	2.00767	7.440	H(βCH) = 2.678 H(γCH) = 1.190	2 sets of 3 doublets
α-methylcinnamaldehyde	nitroxide (4-LXXI),	2.00663	13.072	-	3 lines
	acyl nitroxide (4-LXXII)	2.00690	7.427	-	3 lines

acid and methyl oleate could undergo β-C-C scission and result in formation of aldehydes and α-nitroalkyl radicals which both of them further react with excess of NO_2 in the reaction mixture. Nitrogen dioxide reacts with aldehydes by aldehydic hydrogen abstraction to give carbonyl radicals, and NO_2 could add to α-nitroalkyl radicals to give gem-dinitroalkanes or gem-nitronitrites. In the presence of vic-nitronitroso compounds in the reaction mixture, the carbonyl radicals could be trapped and finally produce acyl nitroxides. We suggest the mechanism of acyl nitroxide formation in this study is by the following reactions:



$$R^1-\underset{NO_2}{\underset{|}{CH}}-\underset{ONO}{\underset{|}{CH}}-R^2 \longrightarrow R^1-\underset{NO_2}{\underset{|}{CH}}-\underset{\dot{O}}{\underset{|}{CH}}-R^2 + NO \qquad (4.3)$$

$$R^1-\underset{NO_2}{\underset{|}{CH}}-\underset{\dot{O}}{\underset{|}{CH}}-R^2 \longrightarrow R^1-\underset{NO_2}{\underset{|}{CH}}\cdot + R^2CHO \qquad (4.47)$$

$$2\,R^1-\underset{NO_2}{\underset{|}{CH}}\cdot + 2\,NO_2 \longrightarrow \underset{\text{gem-dinitro-alkanes}}{R^1CH(NO_2)_2} + \underset{\text{gem-nitronitrites}}{R^1\underset{NO_2}{\underset{|}{C}}HONO} \qquad (4.48)$$

$$R^2-CHO + NO_2 \longrightarrow R^2-\dot{C}=O + HONO \qquad (4.49)$$

$$R^1-\underset{NO_2}{\underset{|}{CH}}-ONO \longrightarrow R^1-\underset{NO_2}{\underset{|}{CH}}-O\cdot + NO \qquad (4.50)$$

$$R^1-\underset{NO_2}{\underset{|}{CH}}-O\cdot \longrightarrow R^1CHO + NO_2^{\cdot} \longrightarrow R^1-\dot{C}=O + HONO \qquad (4.51)$$

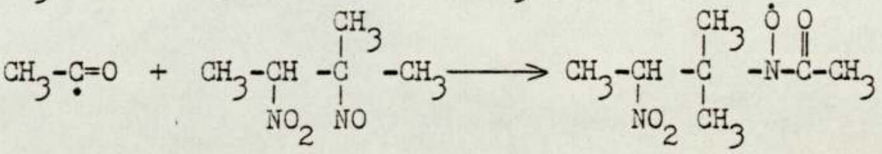
$$R^1-\dot{C}=O + R^1-\underset{O_2N}{\underset{|}{CH}}-\underset{NO}{\underset{|}{CH}}-R^2 \longrightarrow R^1-\underset{NO_2}{\underset{|}{CH}}-\overset{R^2}{\overset{|}{CH}}-\overset{\dot{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R^1 \qquad (4.52)$$

$$R^2-\dot{C}=O + R^1-\underset{O_2N}{\underset{|}{CH}}-\underset{NO}{\underset{|}{CH}}-R^2 \longrightarrow R^1-\underset{NO_2}{\underset{|}{CH}}-\overset{R^2}{\overset{|}{CH}}-\overset{\dot{O}}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R^2 \qquad (4.53)$$

The acyl nitroxides produced from this mechanism in reaction (4.52), and (4.53) could be the same acyl nitroxides when the symmetrically substituted alkenes are studied in NO_2 addition reactions. We suggest that the acyl nitroxides observed from the reactions of cis-2-butene, trans-2-butene, cyclohexene, oleic acid, and methyl oleate with high concentration of NO_2 are produced by this mechanism.

In the reaction of 2-methyl-2-butene with high concentration of NO_2 in solution, we suggest that the β-nitroalkoxy radical derivative, which is a tertiary alkoxy radical,undergoes radical fragmentation, as shown in reactions (4.42), (4.43), and (4.44), and produces acetone and acetaldehyde. In the presence of excess of NO_2, and the vic-nitronitroso derivative in the reaction mixture, the acyl nitroxide (4-IV) could be formed by the following reactions.

$$CH_3CHO + NO_2 \longrightarrow CH_3\text{-}\dot{C}\text{=}O + HONO \qquad (4.54)$$



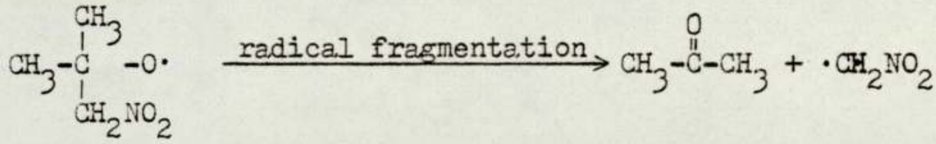
$$CH_3\text{-}\dot{C}\text{=}O + CH_3\text{-}\underset{NO_2}{CH}\text{-}\overset{CH_3}{\underset{NO}{C}}\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{NO_2}{CH}\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}\overset{\dot{O}}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \qquad (4.55)$$

(4-IV)

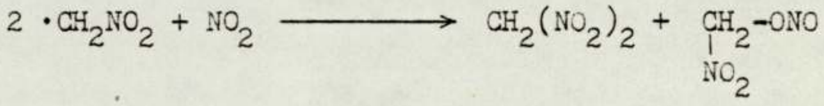
The values of hyperfine splitting constant of hydrogen atoms, which were observed from acyl nitroxides (4-II) from cis-, and trans-2-butenes, are about two gauss which are equal to the value of splitting constant of hydrogen at α-carbon of the known acyl nitroxides (see Table 2.4).The hydrogen splitting constants which we observed from these studies could be the splitting of hydrogen at α-carbon of the postulated acyl nitroxide (4-II). No other hydrogen splitting was observed from acyl nitroxides (4-IV), (4-VI), (4-VIIIa), and (4-VIIIb), probably because of the radicals were produced in low yields and the samples were prepared at high concentrations.

4.6.2 Terminal alkenes with alkyl-, aryl-, or halogen substituents.

We suggest the mechanisms of acyl nitroxide formations of these alkenes to be the same mechanisms as proposed in section 4.6.1. The esr parameters of acyl nitroxides could explain their partial structure and lead to more understanding about the decompositions of β-nitroalkoxy radicals derivatives from each alkenes, for example iso-butene its acyl nitroxide (4-X) showed three doublets in which the hydrogen splitting value is equal to aldehydic hydrogen atom of the known formyl nitroxide radicals (Table 2.4). From this result we suggest that formyl radical is produced in the pathway of decomposition of tertiary β-nitroalkoxy radical derivative of iso-butene. We propose the mechanism of acyl nitroxide (4-X) formation is as follows.

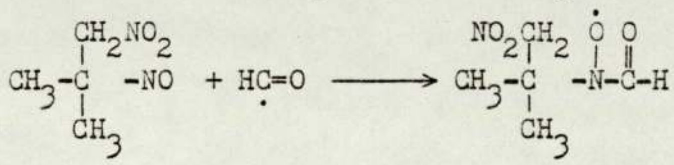


$$\mathrm{CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-O\cdot} \xrightarrow{\text{radical fragmentation}} \mathrm{CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \cdot CH_2NO_2} \quad (4.56)$$



$$2\,\cdot\mathrm{CH_2NO_2 + NO_2 \longrightarrow CH_2(NO_2)_2 + \underset{NO_2}{CH_2}-ONO} \quad (4.57)$$

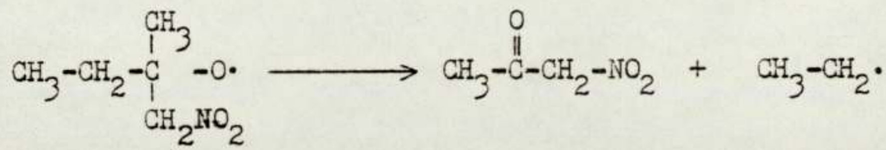
$$\mathrm{NO_2-CH_2-ONO} \longrightarrow \left[\mathrm{NO_2-CH_2O\cdot + NO}\right] \longrightarrow \mathrm{H\underset{\cdot}{C}=O + HONO + NO} \quad (4.58)$$



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_2NO_2}{C}}-NO + H\underset{\cdot}{C}=O \longrightarrow CH_3-\underset{CH_3}{\overset{NO_2CH_2}{C}}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-H} \quad (4.59)$$

acyl nitroxide (4-X)

Acyl nitroxide (4-XIII) detected from reaction of 2-methyl-1-butene and high concentration of NO_2 in 1,4-dioxan, reveals that the decomposition of its β-nitroalkoxy radical derivative produces ethyl radical which could be further oxidised by NO_2 to give the acetyl radical as in the following reactions.



$$CH_3\text{-}CH_2\text{-}\underset{CH_2NO_2}{\overset{CH_3}{C}}\text{-}O\cdot \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}NO_2 + CH_3\text{-}CH_2\cdot$$

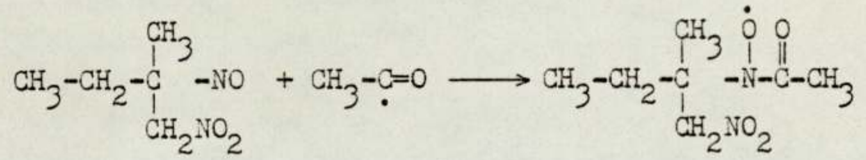
(4.60)

$$2\ CH_3\text{-}CH_2\cdot + 2\ NO_2 \longrightarrow CH_3\text{-}CH_2\text{-}NO_2 + CH_3\text{-}CH_2\text{-}ONO \qquad (4.61)$$

$$CH_3\text{-}CH_2\text{-}ONO \xrightarrow{\text{decompose}} CH_3\text{-}CH_2\text{-}O\cdot + NO \qquad (4.62)$$

$$2\ CH_3\text{-}CH_2\text{-}O\cdot \xrightarrow{\text{disproportionation}} CH_3CHO + CH_3CH_2OH \qquad (4.63)$$

$$CH_3CHO + NO_2 \longrightarrow CH_3\text{-}\underset{\cdot}{C}{=}O + HONO \qquad (4.64)$$



$$CH_3\text{-}CH_2\text{-}\underset{CH_2NO_2}{\overset{CH_3}{C}}\text{-}NO + CH_3\text{-}\underset{\cdot}{C}{=}O \longrightarrow CH_3\text{-}CH_2\text{-}\underset{CH_2NO_2}{\overset{CH_3}{C}}\text{-}\overset{\overset{\cdot}{O}}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

(4.65)

acyl nitroxide (4-XIII)

1-Decene, allyl chloride, 3-butenoic acid, styrene, p-methoxystyrene produce secondary β-nitroalkoxy radicals derivatives from the decomposition of their vic-nitronitrites. The carbonyl radical could be formed by β C-C scissions in which the most stable radicals are split off and we suggest that the bond between "nitro" carbons and "alkoxy"carbons are broken to produce nitromethyl radicals and aldehyde derivatives.

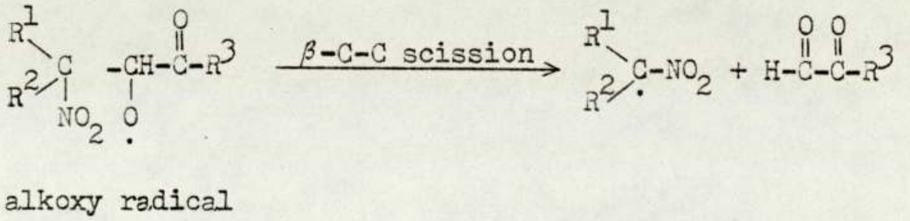
Ethyl vinyl ether did not yield any radical product in the reaction with high concentration of NO_2, we suggest that ethyl vinyl ether underwent complete oxidation to give non-radical products since the reaction started violently and produced a yellow solution.

α- Methylstyrene produced only alkyl nitroxide (4-XVIII) from the reactions with both low and high concentrations of NO_2, we suggest that its vic-nitroalkoxy radical which is a tertiary alkoxy radical, and quite stable, and could undergo further reaction with NO_2 to give vic-nitronitrate, or H-abstraction to produce a vic-nitroalcohol rather than undergo radical fragmentation.

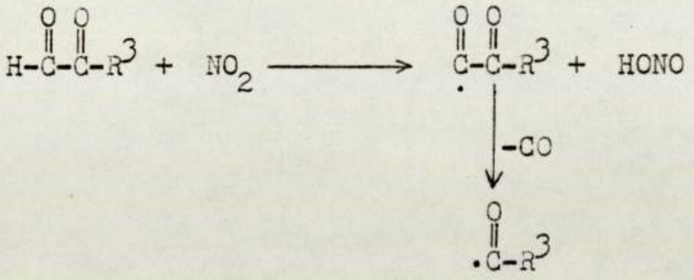
Hexachloropropene, and hexachloro-1,3-butadiene did not produce any detectable radical product from the reactions with high concentration of NO_2 which supports the conclusion of S.Jaffe (1971) that NO_2 is an electrophilic agent and reactive only with nucleophilic alkenes.

4.6.3 Alkenes with carbonyl-, alkyl carbonyl-, or halogenyl carbonyl substituents.

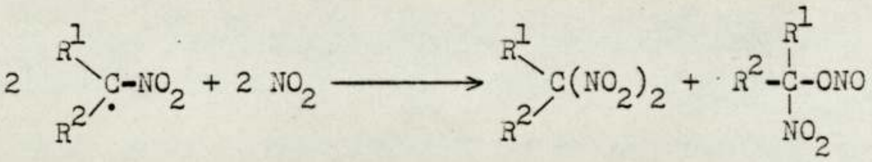
Nitrogen dioxide at high concentration reacts with the alkenes in this group to give a mixture of radical products; nitroxides, iminoxy radicals, and acyl nitroxides. The α,β-unsaturated carbonyl compounds with an α-hydrogen atom, when addition occurs, produce vic-dinitro, and vic-nitronitrite derivatives, the same reaction mechanism as in alkenes in sections 4.6.1, and 4.6.2 could occur i.e., the vic-nitronitrites decompose to β-nitroalkoxy radicals and nitric oxide. The β-nitroalkoxy radicals from these compounds are secondary alkoxy radical type which could disproportionate and decompose to give ketones, and alcohols or undergo β-C-C scission to give lower alkyl radicals and aldehydes. We suggest that the β-C-C scission could occur between "nitro" carbon and "alkoxy" carbon atoms to produce nitroalkyl radicals and aldehyde derivatives which further undergo reaction with excess of NO_2 and that their radical products would lead to acyl nitroxide formation. We suggest that acyl nitroxide produced from reactions of high concentration of NO_2 and acrylic acid, 3-butene-2-one, acraldehyde, crotonic acid, crotonaldehyde, 3-pentene-2-one, 3,3-dimethylacrylic acid, and mesityl oxide occur by the following reaction mechanism.



(4.66)

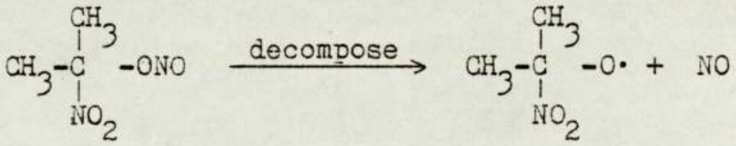


$$\mathrm{H\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^3 + NO_2 \longrightarrow \underset{\cdot}{\overset{O}{\overset{\|}{C}}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^3 + HONO \xrightarrow{-CO} \cdot\overset{O}{\overset{\|}{C}}\text{-}R^3} \qquad (4.67)$$

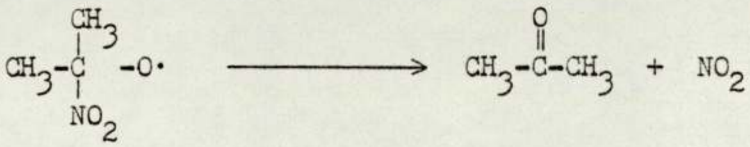


$$\mathrm{2\ (R^1)(R^2)\dot{C}\text{-}NO_2 + 2\ NO_2 \longrightarrow (R^1)(R^2)C(NO_2)_2 + R^2\text{-}\underset{NO_2}{\overset{R^1}{C}}\text{-}ONO} \qquad (4.68)$$

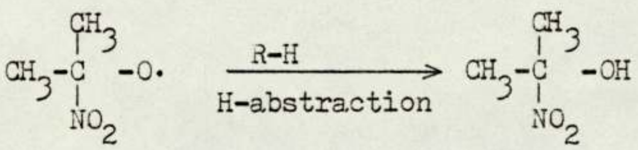
When $R^1 = R^2 = H$ for acrylic acid, 3-butene-2-one, and acraldehyde, their gem-nitronitrites could follow reaction (4.58) to produce formyl radicals; when $R^1 = H$, $R^2 = CH_3$ for crotonic acid, crotonaldehyde, and 3-pentene-2-one, their gem-nitronitrites could follow reaction (4.43) to produce acetyl radicals, and when $R^1 = R^2 = CH_3$ for 3,3-dimethylacrylic acid, and mesityl oxide, their gem-nitronitrites could produce acetone, or gem-nitroalcohols as in reactions (4.69), (4.70), and (4.71), which in this case does not produce carbonyl radical.



$$\mathrm{CH_3\text{-}\underset{NO_2}{\overset{CH_3}{C}}\text{-}ONO \xrightarrow{decompose} CH_3\text{-}\underset{NO_2}{\overset{CH_3}{C}}\text{-}O\cdot + NO} \qquad (4.69)$$

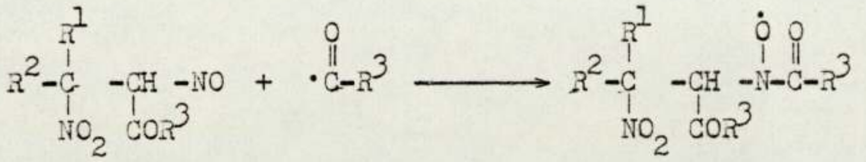


$$\mathrm{CH_3\text{-}\underset{NO_2}{\overset{CH_3}{C}}\text{-}O\cdot \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + NO_2} \qquad (4.70)$$

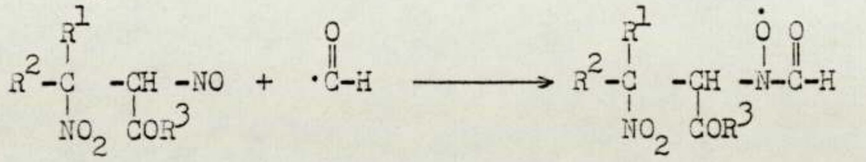


$$\mathrm{CH_3\text{-}\underset{NO_2}{\overset{CH_3}{C}}\text{-}O\cdot \xrightarrow[\text{H-abstraction}]{R\text{-}H} CH_3\text{-}\underset{NO_2}{\overset{CH_3}{C}}\text{-}OH} \qquad (4.71)$$

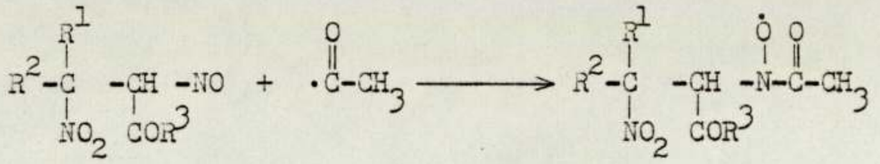
In the presence of vic-nitronitroso compounds in the reaction mixture, we suggest the following acyl nitroxides could be produced.



$$\mathrm{R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{COR^3}{CH}-NO} + \cdot\overset{O}{\overset{\|}{C}}\mathrm{-R^3} \longrightarrow \mathrm{R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{COR^3}{CH}-\overset{\dot{O}}{N}-}\overset{O}{\overset{\|}{C}}\mathrm{-R^3} \tag{4.72}$$



$$\mathrm{R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{COR^3}{CH}-NO} + \cdot\overset{O}{\overset{\|}{C}}\mathrm{-H} \longrightarrow \mathrm{R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{COR^3}{CH}-\overset{\dot{O}}{N}-}\overset{O}{\overset{\|}{C}}\mathrm{-H} \tag{4.73}$$



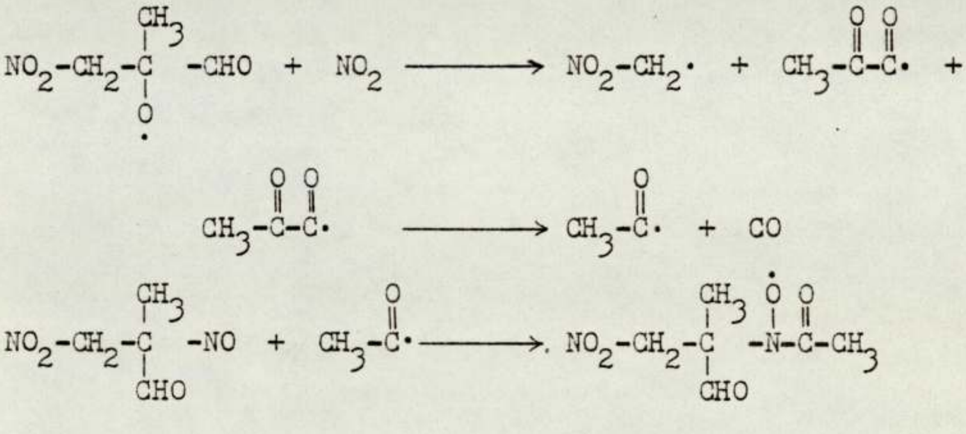
$$\mathrm{R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{COR^3}{CH}-NO} + \cdot\overset{O}{\overset{\|}{C}}\mathrm{-CH_3} \longrightarrow \mathrm{R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{COR^3}{CH}-\overset{\dot{O}}{N}-}\overset{O}{\overset{\|}{C}}\mathrm{-CH_3} \tag{4.74}$$

The acyl nitroxides which we observed from acrylic acid (4-XXX), 3-butene-2-one (4-XXXIII), and acraldehyde (4-XXXVIb),have esr parameters which reveal that R^3 is $-OH$, $-CH_3$, and $-H$ respectively, which are acyl nitroxides formed via reactions (4.67) and (4.72). The acyl nitroxide (4-XXXVI) produced from acraldehyde in this study, we could not tell whether the formyl radical was derived from reactions (4.67), and (4.72) or (4.58), and (4.73), or from both pathways, and we also did not observe acyl nitroxides produced from acrylic acid, and 3-butene-2-one by the pathway in reactions (4.58), and (4.73).

We suggest that the acyl nitroxides which we observed from crotonic acid (4-XLII), crotonaldehyde (4-XLVIII), and 3-pentene-2-one (4-LI), are formed by the pathways as in reactions (4.67), and (4.72), and also by reactions (4.43), and (4.74). Acyl nitroxides (4-XLII), and (4-XLVIII) observed from crotonic acid, and crotonaldehyde respectively, did not show any H-hyperfine splitting lines, so we suggest that they were produced in low yield from the solution of high concentrations of reactants which would affect esr spectrum measurements.

Acyl nitroxides observed from 3,3-dimethylacrylic acid (4-LIV), and mesityl oxide (4-LVI), and (4-LVIII) could be formed via the mechanism as in reaction (4.67),and (4.72) in which it is shown that for the reaction of mesityl oxide the two carbonyl radicals formed in the reaction (4.67) were trapped by the vic-nitronitroso derivative and produced the two acyl nitroxides (4-LVI), and (4-LVIII).

The radicals observed from reactions of high concentration of NO_2 with α,β-unsaturated carbonyl compounds with alkyl substituents at α-carbon, which are methacrolein, methacryloyl chloride, methyl methacrylate, and tiglic acid, were nitroxides. Only methacrolein produced an acyl nitroxide (4-XXXVIII) in low yield as trace radical product from its reaction. We suggest that their β-nitroalkoxy radicals derivatives being of the tertiary alkoxy type, undergo reactions with NO_2 or H-abstraction to produce vic-nitronitrates and vic-nitroalcohols respectively. We suggest that the aldehydic hydrogen atom is involved as in reactions (4.75),(4.76) and (4.77) in the formation of the acyl nitroxide from methacrolein (4-XXXVIII).



$$NO_2\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\bullet}{O}}{C}}\text{-}CHO + NO_2 \longrightarrow NO_2\text{-}CH_2\cdot + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\cdot + HONO \qquad (4.75)$$

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\cdot \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\cdot + CO \qquad (4.76)$$

$$NO_2\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CHO}{C}}\text{-}NO + CH_3\text{-}\overset{O}{\overset{\|}{C}}\cdot \longrightarrow NO_2\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CHO}{C}}\text{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \qquad (4.77)$$

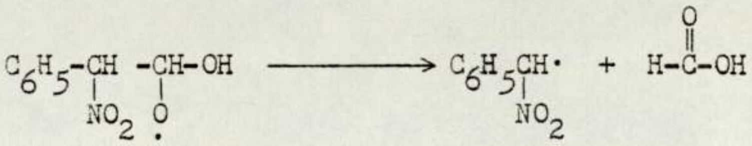
(4-XXXVIII)

The α,β-unsaturated esters, ethyl crotonate, and methyl crotonate, did not produce any acyl nitroxide. From this result we suggest that their vic-nitronitroso derivatives undergo tautomerisation to be hydroxyimines, and further react with the excess NO_2 to produce more iminoxy radicals and that their β-nitroalkoxy radicals could react with excess of NO_2, undergoing H-abstraction , disproportionation, and decomposition, or β-scission.

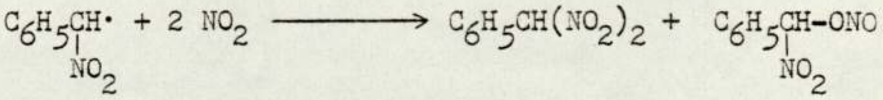
4.6.4 Alkenes with aryl-, or aryl carbonyl substituents.

Acyl nitroxides produced from the reactions of high concentration of NO_2, and alkenes in this group could follow the same mechanisms as suggested for the similar alkenes. For example, cis-stilbene and trans-stilbene could produce acyl nitroxides(4-LX) by the same mechanism as acyl nitroxides(4-II) formation from cis-2-butene, and trans-2-butene; cinnamaldehyde, and α-methylcinnamaldehyde could produce acyl nitroxides (4-LXII), and (4-LXXII) respectively by the same mechanism by which acyl nitroxides (4-XLVIII) and (4-XXXVIII) are formed from crotonaldehyde and methacrolein. Benzalacetone and dibenzalacetone could follow the mechanism suggested for 3-pentene-2-one and produce acyl nitroxides (4-LXIV) and (4-LXV), and (4-LXVIII).

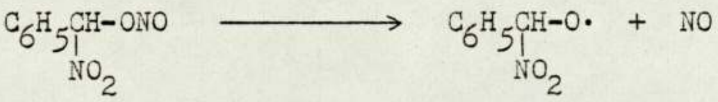
The mechanism which we suggest for acyl nitroxide (4-LXX) formation from cinnamyl alcohol is in the mechanism in which β-C-C scission of β-nitroalkoxy radical derivatives could occur and lead to acyl nitroxide radical formation. The esr spectrum shows the H-hyperfine splitting of protons at β- and γ-carbons. The following reactions describe the acyl nitroxide (4-LXX) formation.



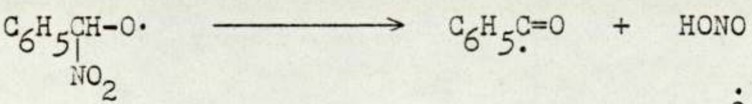
$$\mathrm{C_6H_5{-}\underset{NO_2}{CH}{-}\underset{\dot{O}}{CH}{-}OH \longrightarrow C_6H_5\underset{NO_2}{CH}\cdot + H{-}\overset{\overset{O}{\|}}{C}{-}OH} \qquad (4.78)$$



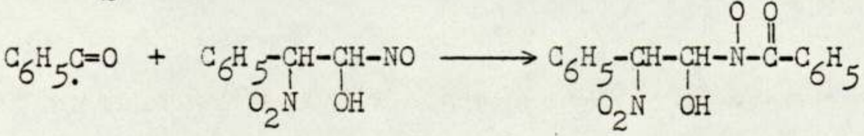
$$\mathrm{C_6H_5\underset{NO_2}{CH}\cdot + 2\,NO_2 \longrightarrow C_6H_5CH(NO_2)_2 + C_6H_5\underset{NO_2}{CH}{-}ONO} \qquad (4.79)$$



$$\mathrm{C_6H_5\underset{NO_2}{CH}{-}ONO \longrightarrow C_6H_5\underset{NO_2}{CH}{-}O\cdot + NO} \qquad (4.80)$$



$$\mathrm{C_6H_5\underset{NO_2}{CH}{-}O\cdot \longrightarrow C_6H_5\dot{C}{=}O + HONO} \qquad (4.81)$$



$$\mathrm{C_6H_5\dot{C}{=}O + C_6H_5{-}\underset{O_2N}{CH}{-}\underset{OH}{CH}{-}NO \longrightarrow C_6H_5{-}\underset{O_2N}{CH}{-}\underset{OH}{CH}{-}\overset{\dot{O}}{N}{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5} \qquad (4.82)$$

Cinnamic acid and benzalacetophenone did not produce any radical product which we suggest is due to the electron withdrawing effect of their substituents decreasing the electron densities at the reaction centres, and making them less reactive in these addition reactions.

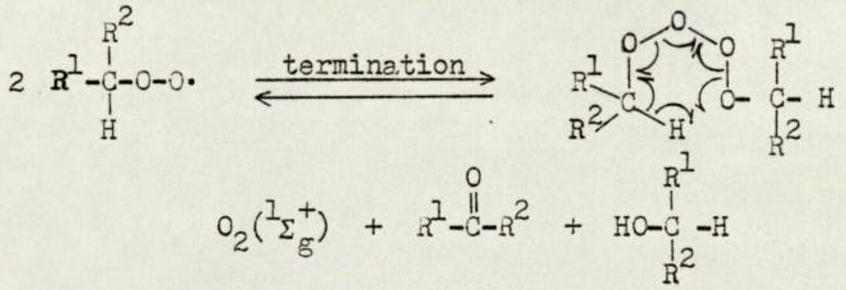
4.7 Reactions of NO_2 with Alkenes in 1,4-Dioxan Solution With Addition of Oxygen or at Elevated Reaction Temperatures.

Acyl nitroxides are always produced in the reactions of low concentrations of NO_2 with alkenes with addition of oxygen or at elevated reaction temperature. The mechanism of their formation could be similar to that of acyl nitroxides formations from the reactions of high concentrations of NO_2 and alkenes in which the carbonyl radicals are formed and trapped by vic-nitronitroso compounds in the reaction medium. We suggest that carbonyl radicals are produced from compounds in the reaction medium which are unstable or sensitive to oxygen or heat. For example, N_2O_4, vic-nitronitrites, vic-nitronitroso monomer and dimers, nitric oxide, nitrones, and hydroxylamines.

At elevated reaction temperatures, the greater the dissociation of N_2O_4 into NO_2 to carry on the reactions with excess alkenes to produce more primary products and to continue reactions with primary products which are already present in the reaction mixture will result in more non-radical, and radical products. vic-Nitronitrites, and vic-nitronitroso dimers will also be more dissociated at elevated temperature and we suggest that their dissociation products could be involved in acyl nitroxides formation.

The addition of oxygen into the reaction mixture after the reactions have been started will affect the reaction product formation. Oxygen could react with NO to produce more NO_2, could oxidise hydroxylamines into nitroxides, and it also adds to alkyl radicals to produce alkyl peroxy radicals and could lead to carbonyl radical formations.

The greater the amount of decomposition of vic-nitronitrites into β-nitroalkoxy radicals and NO at elevated reaction temperatures, the greater the amount of β-nitroalkoxy radicals that could undergo β-C-C scission and the greater the amount of NO_2 produced by the increase in N_2O_4 dissociation, all lead to an increase in acyl nitroxide formation and we suggest the mechanism of acyl nitroxide formation to be the same as that discussed in the reactions of high concentrations of NO_2 with alkenes, in section 4.6. When the reactions are carried out with addition of oxygen at room temperature, vic-nitronitrites also produce β-nitroalkoxy radicals from their decomposition and when β-C-C scission of β-nitroalkoxy radicals occurs, the β-nitroalkyl radicals produced could react with oxygen to give β-nitroalkylperoxy radicals. The mechanism of β-nitroalkylperoxy radicals in termination could follow the mechanism of alkylperoxy radical termination which has been proposed by G.A.Russell, 1957, in which alcohols and aldehydes or ketones are produced from primary or secondary peroxy radicals respectively with evolution of singlet molecular oxygen in which there are no confirmed chemical reactions with organic molecules (J.N. Pitts, Jr., 1971). The mechanism of primary and secondary peroxy radicals termination are described as following.



$$O_2(^1\Sigma_g^+) + R^1-\overset{O}{\overset{\|}{C}}-R^2 + HO-\underset{R^2}{\overset{R^1}{C}}-H$$

(4.83)

The termination step for tertiary alkylperoxy radicals does not involve transannular peroxide formation, their self-reactions produce tertiary alkoxy radicals and triplet ground state molecular oxygen (J.A. Howard, and K.U.Ingold, 1968).

$$2\ \text{tert-}C_4H_9OO\cdot \longrightarrow \text{tert-}C_4H_9OOOOC_4H_9\text{-tert} \longrightarrow 2\ \text{tert-}C_4H_9O\cdot + O_2(^3\Sigma_g^-) \qquad (4.84)$$

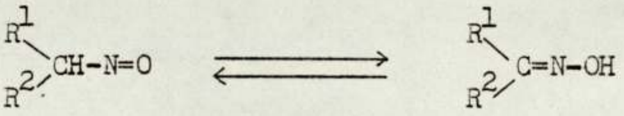
We could conclude that in the reactions of low concentration of NO_2 and alkenes with addition of oxygen, aldehydes and alkoxyl radicals could be involved in acyl nitroxides formation.

Nitroso compounds which are unstable to oxygen and high temperatures are known to exist in monomeric and dimeric forms and they are found to be in equilibrium in solution (A.Mackor et al., 1967a).

$$\underset{\text{colourless}}{(RN{=}O)_2} \rightleftharpoons \underset{\text{blue}}{2\ RN{=}O} \qquad (4.85)$$

Solution of tertiary nitroso dimers are blue owing to considerable dissociation. Solution of primary and secondary nitrosoalkanes contain only traces of the monomer at room temperature and are therefore colourless.

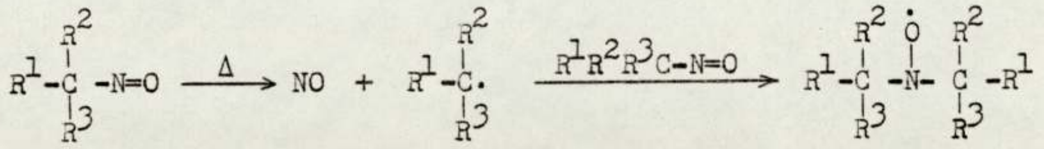
When primary and secondary nitroso monomers are present in low concentration, the oxime structure usually predominates. The mechanism of oxime formation may vary with the solvent which affects the isomerisation



$$R^1R^2CH{-}N{=}O \rightleftharpoons R^1R^2C{=}N{-}OH \qquad (4.86)$$

step (B.G.Gowenlock, and W.Lüttke, 1958). The addition of oxygen or working at elevated reaction temperatures which results in an increase of NO_2 concentration, means that the oximes could react with the excess of NO_2 to give gem-dinitrocompounds (L.F.Fieser, and W.von E.Doering,1946; and A.I.Titov, 1963).

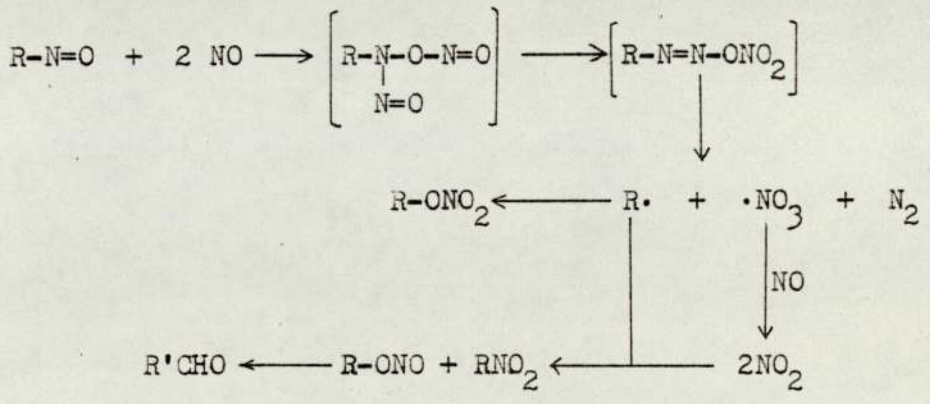
The thermal decomposition of nitroso compounds leads to nitroxide formation. These nitroxides could be produced by homolytic cleavage followed by trapping of the radical formed (E.G.Janzen, 1971).



$$R^1\text{-}\overset{R^2}{\underset{R^3}{C}}\text{-N=O} \xrightarrow{\Delta} NO + R^1\text{-}\overset{R^2}{\underset{R^3}{C}}\cdot \xrightarrow{R^1R^2R^3C\text{-N=O}} R^1\text{-}\overset{R^2}{\underset{R^3}{C}}\text{-}\overset{\dot{O}}{N}\text{-}\overset{R^2}{\underset{R^3}{C}}\text{-}R^1 \quad (4.87)$$

From this nitroxide formation, we suggest that the yield of some nitroxide radicals could be increased by raising the reaction temperature.

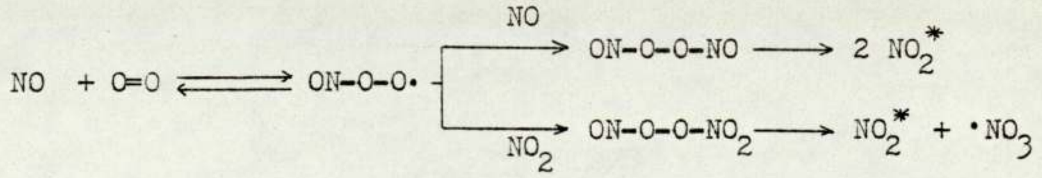
Nitric oxide which is one of the products from the decomposition of nitronitrites, when it is present in the reaction mixture could add to NO_2 to produce N_2O_3 which retards the rate of reaction of NO_2 (A.I.Titov, 1951). Nitric oxide also reacts with nitroso compounds to give diazonitrates which decompose into alkyl radicals, nitrogen, and nitrates (J.F.Brown, Jr., 1957). This mechanism is shown in the following reactions in which nitrocompound, nitrate, aldehyde, and NO_2 are generated.



(4.88)

Aldehyde (R'CHO) is produced, and this mechanism could be involved in acyl nitroxide formation in our reaction studied.

Nitric oxide is oxidised to NO_2 in the presence of oxygen. The mechanism of conversion of NO had been proposed by A.I.Titov, 1941, and 1951, who suggest that active NO_2 and NO_3 were generated as shown in reactions (4.89), and (4.90).



$$NO + O{=}O \rightleftharpoons ON\text{-}O\text{-}O\cdot \xrightarrow{NO} ON\text{-}O\text{-}O\text{-}NO \longrightarrow 2\,NO_2^* \quad (4.89)$$

$$ON\text{-}O\text{-}O\cdot \xrightarrow[NO_2]{} ON\text{-}O\text{-}O\text{-}NO_2 \longrightarrow NO_2^* + \cdot NO_3 \quad (4.90)$$

Another mechanism has been suggested by J.Heicklen, and N. Cohen, 1968, as shown in reaction(4.91).Without oxygen, the conversion of NO

$$2\ NO + O_2 \longrightarrow 2\ NO_2 \qquad (4.91)$$

to NO_2 may occur through disproportionation (G.F. Bloomfield, and G.A. Jeffrey, 1944; and J.D.Park et al., 1961).

We conclude from the studies of reactions both at elevated reaction temperature and with addition of oxygen that NO_2 is increased in its concentration. In the reaction medium, we propose that nitrones are present, as discussed in section 4.5, and we suggest that they could produce acyl nitroxides by reaction with NO_2 (L.V.Okhlobystina et al., 1975, and this work in Chapter five).

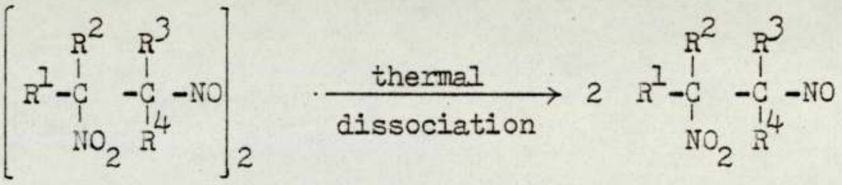
The effects of oxygen, and temperature upon reaction products from the reactions of low concentration of NO_2 and alkenes as already described, lead to an increase in NO_2 concentration and carbonyl compound formation and these are the main components in acyl nitroxides formation suggested in these studies.

The reactions of high concentration of NO_2 and alkenes produce acyl nitroxides as main radical products (section 4.6). When these reactions were studied at elevated reaction temperature or with addition of oxygen, alkyl nitroxides were observed in decreased amount or not at all. Iminoxy radicals were detected but most of them were not stable so we suggest that they underwent self-reactions as in the mechanisms proposed by G.B.Watts, and K.U.Ingold, 1972; and J.L.Brokenshire et al., 1972. The rate of iminoxy radicals disappearance as shown by esr spectroscopy from reactions of high concentration of NO_2 and alkenes is faster than the rate observed from reactions of low concentration of NO_2 and alkenes , this could be due to a greater chance for the iminoxy radicals to undergo dimerisation in the more concentrated solution.

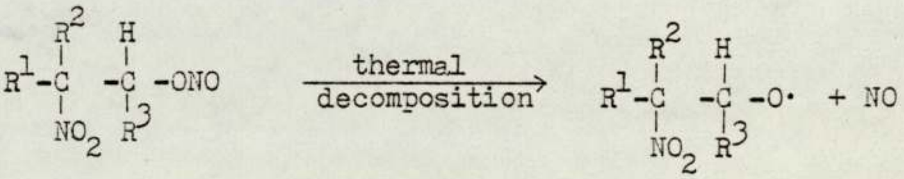
The mechanisms which we suggest for product formation especially the acyl nitroxides formation from the reactions of NO_2 at both low, and high concentrations with alkenes at temperature between 25°- 100°, or with addition of oxygen gas are described as following.

The compounds which we propose to be present in the reaction mixtures of the reactions of low concentrations of NO_2 and alkenes are N_2O_4, NO, nitroso monomers and dimers, alkyl nitroxides, vic-dinitroalkanes, vic-nitronitrites, vic-nitroalcohols, vic-nitronitrate, nitrones, and hydroxylamines. In the reactions studied at elevated reaction temperature, we suggest most of these compounds undergo further reactions as follows:

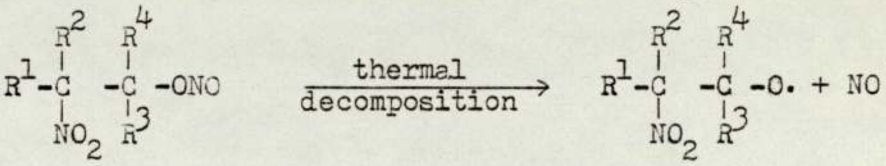
$$N_2O_4 \xrightarrow[\text{dissociation}]{\text{thermal}} 2\ NO_2 \qquad (4.92)$$



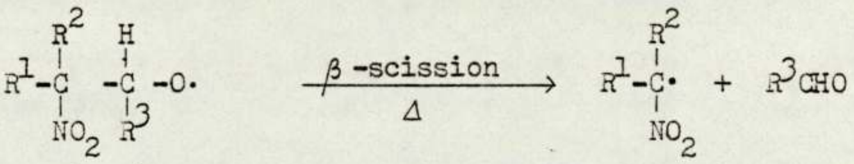
$$\left[R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^4}{\overset{R^3}{C}}\text{-NO}\right]_2 \xrightarrow[\text{dissociation}]{\text{thermal}} 2\ R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^4}{\overset{R^3}{C}}\text{-NO} \qquad (4.93)$$



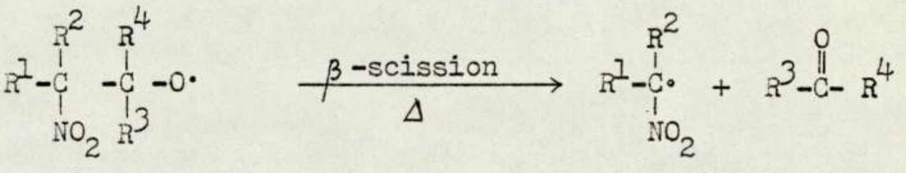
$$R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{H}{C}}\text{-ONO} \xrightarrow[\text{decomposition}]{\text{thermal}} R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{H}{C}}\text{-O}\cdot + NO \qquad (4.94)$$



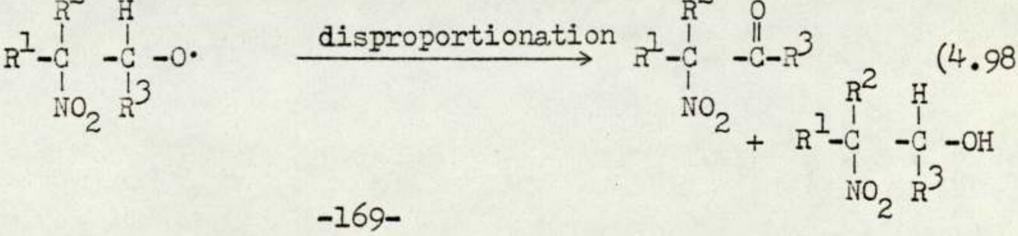
$$R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{R^4}{C}}\text{-ONO} \xrightarrow[\text{decomposition}]{\text{thermal}} R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{R^4}{C}}\text{-O}\cdot + NO \qquad (4.95)$$



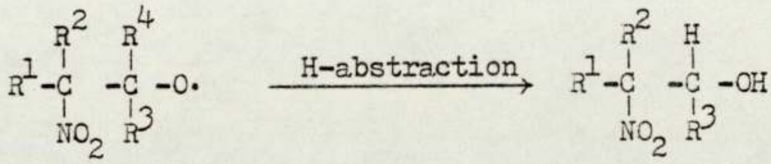
$$R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{H}{C}}\text{-O}\cdot \xrightarrow[\Delta]{\beta\text{-scission}} R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\cdot + R^3CHO \qquad (4.96)$$



$$R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{R^4}{C}}\text{-O}\cdot \xrightarrow[\Delta]{\beta\text{-scission}} R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\cdot + R^3\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^4 \qquad (4.97)$$



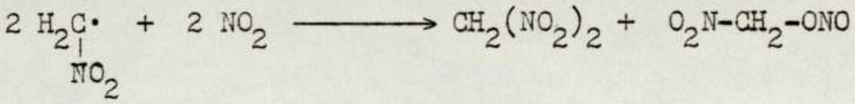
$$R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{H}{C}}\text{-O}\cdot \xrightarrow{\text{disproportionation}} R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^3 + R^1\text{-}\underset{NO_2}{\overset{R^2}{C}}\text{-}\underset{R^3}{\overset{H}{C}}\text{-OH} \qquad (4.98)$$



$$R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^3}{\overset{R^4}{C}}-O\cdot \xrightarrow{\text{H-abstraction}} R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^3}{\overset{H}{C}}-OH \qquad (4.99)$$

We suggest that nitroalkyl radicals are generated from β-scissions of secondary and tertiary nitroalkoxy radicals in these studies (reactions(4.96),and(4.97)),most of them are primary nitroalkyl radicals (R^1 or R^2 = H), and secondary nitroalkyl radicals (R^1 = alkyl, R^2 = H), and few tertiary nitroalkyl radicals (R^1, R^2 = alkyls) which could lead to carbonyl compounds the same way as described in section 4.6. When NO_2 is present in reaction medium, we suggest the following reactions could occur.

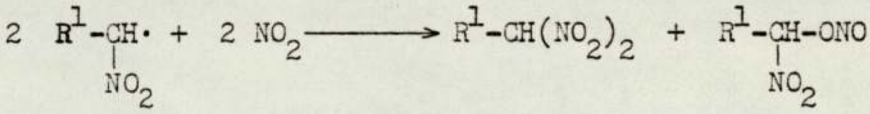
Primary nitroalkyl radical:



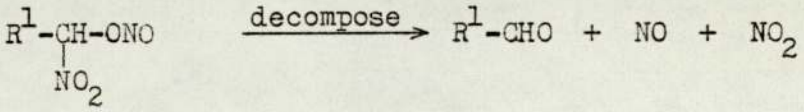
$$2\ \underset{NO_2}{H_2C\cdot} + 2\ NO_2 \longrightarrow CH_2(NO_2)_2 + O_2N-CH_2-ONO \qquad (4.100)$$

$$O_2N-CH_2-ONO \xrightarrow{\text{decompose}} HCHO + NO + HONO \qquad (4.101)$$

Secondary nitroalkyl radical:

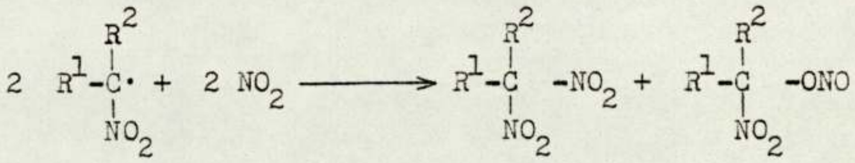


$$2\ R^1-\underset{NO_2}{CH\cdot} + 2\ NO_2 \longrightarrow R^1-CH(NO_2)_2 + R^1-\underset{NO_2}{CH}-ONO \qquad (4.102)$$

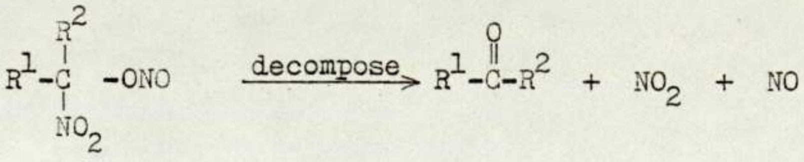


$$R^1-\underset{NO_2}{CH}-ONO \xrightarrow{\text{decompose}} R^1-CHO + NO + NO_2 \qquad (4.103)$$

Tertiary nitroalkyl radical:



$$2\ R^1-\underset{NO_2}{\overset{R^2}{C}}\cdot + 2\ NO_2 \longrightarrow R^1-\underset{NO_2}{\overset{R^2}{C}}-NO_2 + R^1-\underset{NO_2}{\overset{R^2}{C}}-ONO \qquad (4.104)$$



$$R^1-\underset{NO_2}{\overset{R^2}{C}}-ONO \xrightarrow{\text{decompose}} R^1-\overset{O}{\overset{\|}{C}}-R^2 + NO_2 + NO \qquad (4.105)$$

Aldehydes formed in the reactions (4.96),(4.101), and (4.103) further react with NO_2 by aldehydic hydrogen atom abstraction and produce carbonyl radicals (S.Jaffe, 1969).

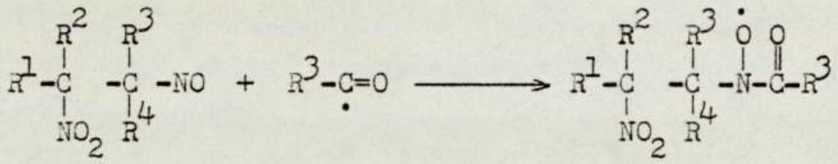
$$R^3CHO + NO_2 \longrightarrow R^3-\underset{\bullet}{C}=O + HONO \qquad (4.106)$$

$$HCHO + NO_2 \longrightarrow H-\underset{\bullet}{C}=O + HONO \qquad (4.107)$$

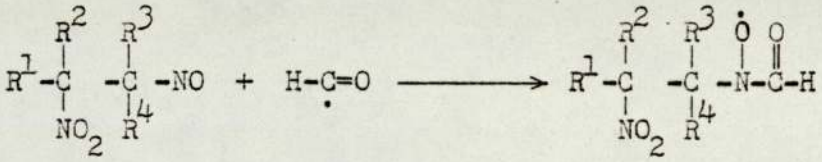
$$R^1CHO + NO_2 \longrightarrow R^1-\underset{\bullet}{C}=O + HONO \qquad (4.108)$$

$$2\ HONO \longrightarrow H_2O + NO + NO_2 \qquad (4.109)$$

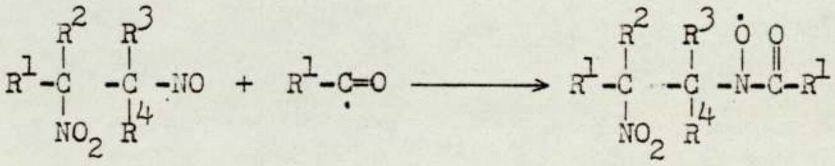
Carbonyl radicals produced from reactions (4.106), (4.107), and (4.108)could be trapped by nitroso compounds in the reaction mixtures, and finally produce acyl nitroxides which are detected as radical products.



$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO + R^3-\underset{\bullet}{C}=O \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-R^3 \qquad (4.110)$$



$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO + H-\underset{\bullet}{C}=O \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-H \qquad (4.111)$$



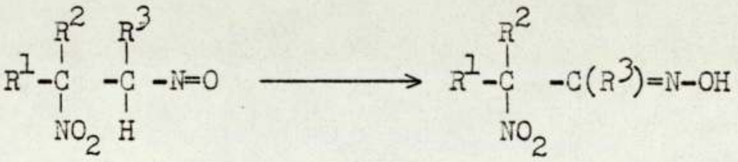
$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO + R^1-\underset{\bullet}{C}=O \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-\overset{\dot{O}}{N}-\overset{O}{\overset{\|}{C}}-R^1 \qquad (4.112)$$

Other reactions could occur in reaction mixtures and lead to variety of products as follows:

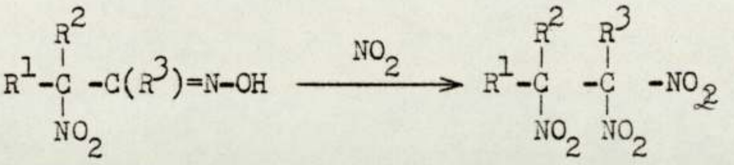
Nitronitroso compounds:

Isomerisation of nitronitroso compounds:

We suggest that isomerisation of nitronitroso compounds could occur in the reactions of low concentration studied.

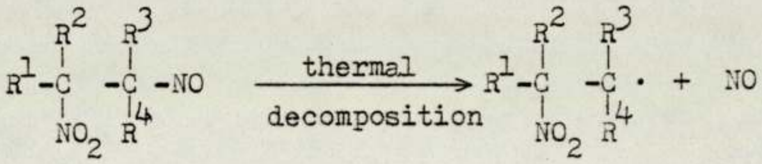


$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{H}{C}}-N=O \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-C(R^3)=N-OH \qquad (4.113)$$

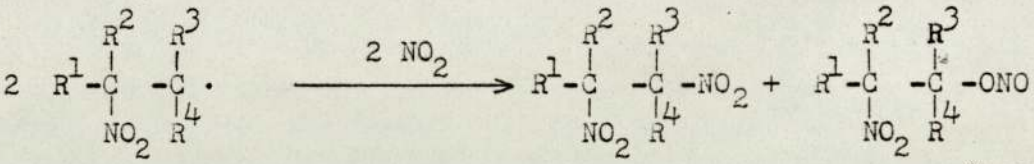


$$R^1-\overset{R^2}{\underset{NO_2}{C}}-C(R^3)=N-OH \xrightarrow{NO_2} R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{NO_2}{C}}-NO_2 \tag{4.114}$$

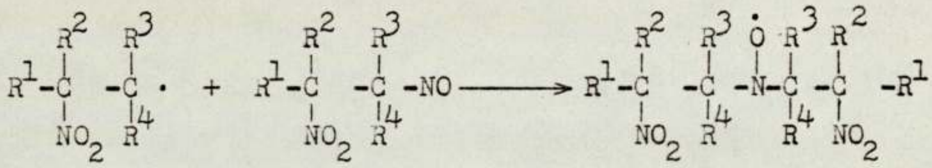
Thermal decomposition:



$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO \xrightarrow[\text{decomposition}]{\text{thermal}} R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}\cdot + NO \tag{4.115}$$

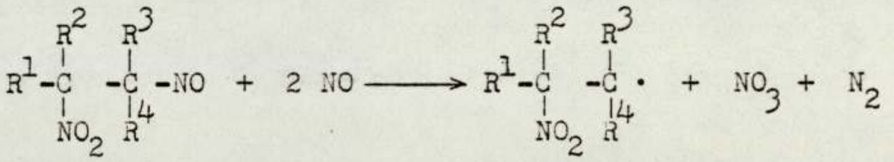


$$2\ R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}\cdot \xrightarrow{2\ NO_2} R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO_2 + R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-ONO \tag{4.116}$$



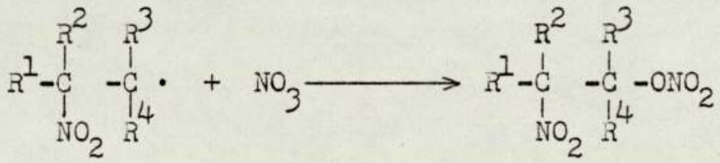
$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}\cdot + R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-\overset{\dot{O}}{N}-\overset{R^3}{\underset{R^4}{C}}-\overset{R^2}{\underset{NO_2}{C}}-R^1 \tag{4.117}$$

Decomposition in the presence of NO:

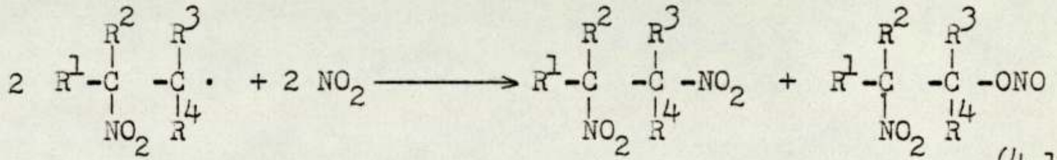


$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO + 2\ NO \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}\cdot + NO_3 + N_2 \tag{4.118}$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \tag{4.119}$$



$$R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}\cdot + NO_3 \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-ONO_2 \tag{4.120}$$

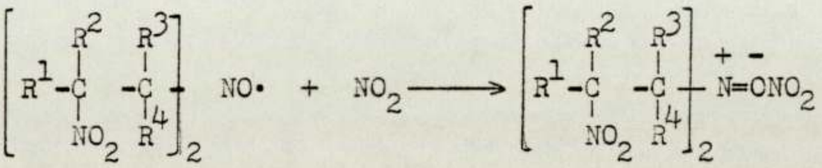


$$2\ R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}\cdot + 2\ NO_2 \longrightarrow R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-NO_2 + R^1-\overset{R^2}{\underset{NO_2}{C}}-\overset{R^3}{\underset{R^4}{C}}-ONO \tag{4.121}$$

vic-Nitronitrites produced from reactions (4.116), and (4.121) are the same compound and could be precursors of acyl nitroxides by the same mechanism as for vic-nitronitrites in reactions (4.94), and (4.95).

Alkyl nitroxides:

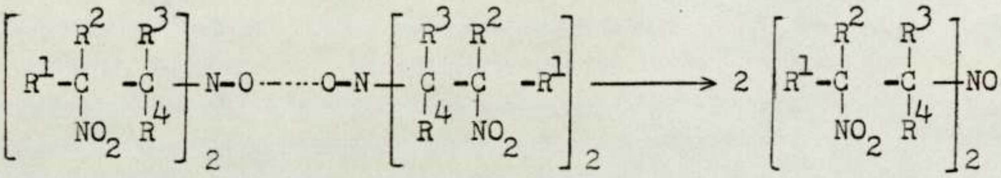
Reaction with NO_2:



$$\left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 NO\cdot + NO_2 \longrightarrow \left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 \overset{+}{N}\overset{-}{=}ONO_2 \quad (4.122)$$

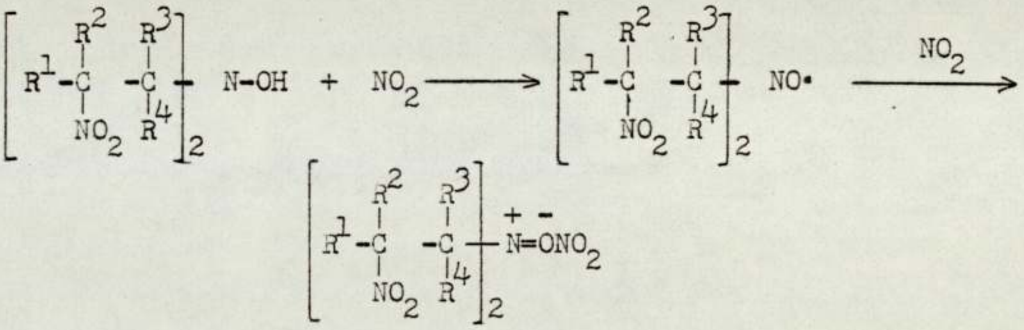
nitrosonium nitrate derivatives

Thermal dissociation of alkyl nitroxide dimers:



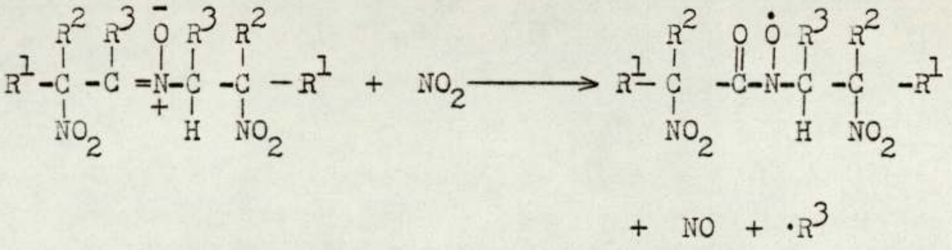
$$\left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 N-O\cdots\cdots O-N\left[\underset{R^4}{\overset{R^3}{C}}-\underset{NO_2}{\overset{R^2}{C}}-R^1\right]_2 \longrightarrow 2\left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 NO\cdot \quad (4.123)$$

Hydroxylamines:



$$\left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 N-OH + NO_2 \longrightarrow \left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 NO\cdot \xrightarrow{NO_2} \quad (4.124)$$
$$\left[R^1-\underset{NO_2}{\overset{R^2}{C}}-\underset{R^4}{\overset{R^3}{C}}\right]_2 \overset{+}{N}\overset{-}{=}ONO_2$$

Nitrones:



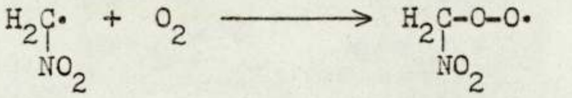
$$R^1-\underset{NO_2}{\overset{R^2}{C}}-\overset{R^3}{C}=\underset{+}{\overset{\overset{-}{O}}{N}}-\underset{H}{\overset{R^3}{C}}-\underset{NO_2}{\overset{R^2}{C}}-R^1 + NO_2 \longrightarrow R^1-\underset{NO_2}{\overset{R^2}{C}}-\overset{O}{\overset{\|}{C}}-\overset{\dot{O}}{N}-\underset{H}{\overset{R^3}{C}}-\underset{NO_2}{\overset{R^2}{C}}-R^1$$
$$+ NO + \cdot R^3 \quad (4.125)$$

Acyl nitroxides produced from reactions (4.110), (4.111), (4.112), and (4.125) are not the same nitroxides, therefore we suggest that esr spectra may show the presence of one or more than one acyl nitroxides spectra from one reaction mixture, or that the esr spectra may be superimposed. We could detect only a simple three lines esr spectrum, $a_N \sim 7-8$ G. Alkyl nitroxides could be presence in the reaction mixture but in different concentration as observed from ordinary reaction condition.

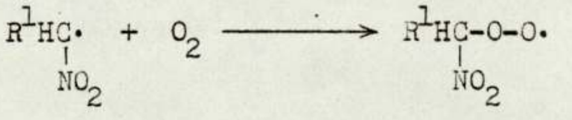
For the experiments in which oxygen is added to the reaction mixtures of the reactions of low concentrations of NO_2 and alkenes, we suggest the following mechanisms which could give the mixture of products including the acyl nitroxides.

$$2\ NO + O_2 \longrightarrow 2\ NO_2 \qquad (4.126)$$

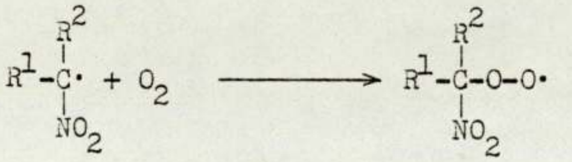
vic-Nitronitrite also decompose as in the same mechanism as vic-nitronitrites decomposition in thermal reaction (reactions (4.94)-(4.99)) to produce aldehydes (R^3-CHO), and nitroalkyl radicals. In the presence of oxygen and NO_2 in reaction medium, primary nitroalkyl ($R^1 = R^2 = H$), secondary nitroalkyl (R^1 = alkyl, R^2 = H), and tertiary nitroalkyl (R^1, R^2 = alkyls) radicals produced from β C-C scissions of β-nitroalkoxy radicals as shown in reactions (4.96), and (4.97) could react with oxygen at a faster rate than they react with NO_2 (S.Jaffee, 1969) and result in primary nitroalkyl peroxy, secondary nitroalkyl peroxy, and tertiary nitroalkyl peroxy radicals respectively in higher yields than gem-dinitroalkanes, and gem-nitronitrite derivatives. The reactions of nitroalkyl radicals with oxygen are described as following:



$$H_2\underset{NO_2}{C}\cdot + O_2 \longrightarrow H_2\underset{NO_2}{C}\text{-}O\text{-}O\cdot \qquad (4.127)$$

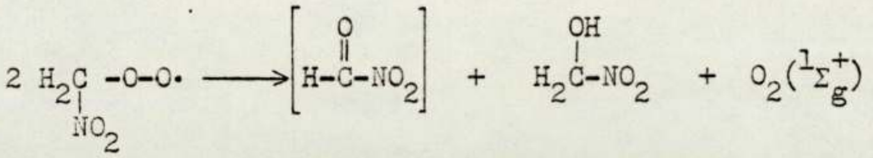


$$R^1H\underset{NO_2}{C}\cdot + O_2 \longrightarrow R^1H\underset{NO_2}{C}\text{-}O\text{-}O\cdot \qquad (4.128)$$

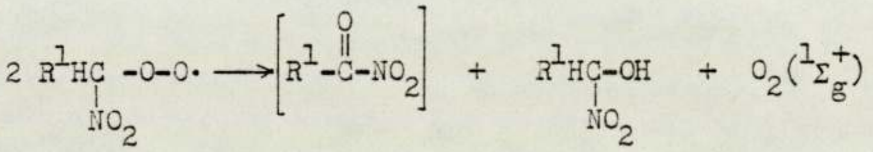


$$R^1\text{-}\overset{R^2}{\underset{NO_2}{C}}\cdot + O_2 \longrightarrow R^1\text{-}\overset{R^2}{\underset{NO_2}{C}}\text{-}O\text{-}O\cdot \qquad (4.129)$$

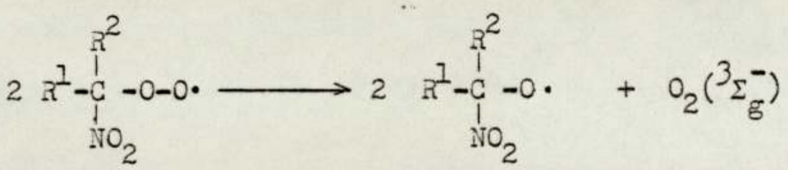
Termination steps of peroxy radicals could occur to give aldehydes, alcohols or ketone (G.A.Russell, 1957; and K.U.Ingold, 1969).



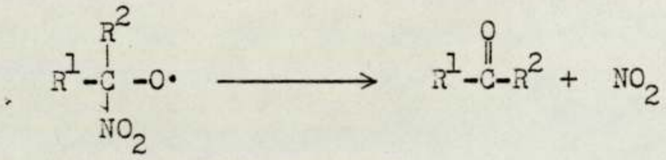
$$2\,H_2\underset{NO_2}{C}-O-O\cdot \longrightarrow \left[H-\overset{O}{\overset{\|}{C}}-NO_2\right] + H_2\overset{OH}{C}-NO_2 + O_2(^1\Sigma_g^+) \qquad (4.130)$$



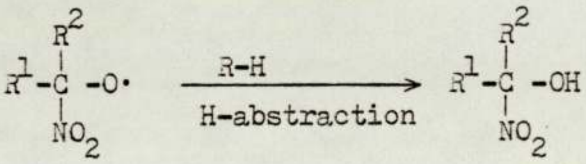
$$2\,R^1H\underset{NO_2}{C}-O-O\cdot \longrightarrow \left[R^1-\overset{O}{\overset{\|}{C}}-NO_2\right] + R^1H\underset{NO_2}{C}-OH + O_2(^1\Sigma_g^+) \qquad (4.131)$$



$$2\,R^1-\overset{R^2}{\underset{NO_2}{C}}-O-O\cdot \longrightarrow 2\,R^1-\overset{R^2}{\underset{NO_2}{C}}-O\cdot + O_2(^3\Sigma_g^-) \qquad (4.132)$$

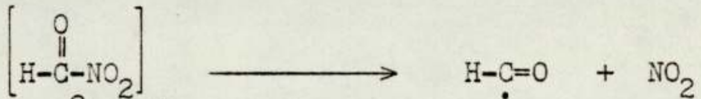


$$R^1-\overset{R^2}{\underset{NO_2}{C}}-O\cdot \longrightarrow R^1-\overset{O}{\overset{\|}{C}}-R^2 + NO_2 \qquad (4.133)$$

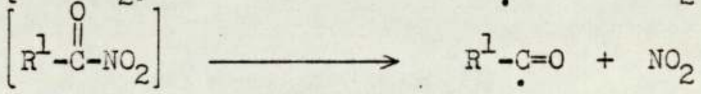


$$R^1-\overset{R^2}{\underset{NO_2}{C}}-O\cdot \xrightarrow[\text{H-abstraction}]{\text{R-H}} R^1-\overset{R^2}{\underset{NO_2}{C}}-OH \qquad (4.134)$$

Nitroaldehyde and nitroketones produced from reactions (4.130), and (4.131) are unstable, they decompose to formyl,and carbonyl radicals respectively and NO_2 as shown in reactions (4.135), and (4.136).



$$\left[H-\overset{O}{\overset{\|}{C}}-NO_2\right] \longrightarrow H-\underset{\bullet}{C}=O + NO_2 \qquad (4.135)$$



$$\left[R^1-\overset{O}{\overset{\|}{C}}-NO_2\right] \longrightarrow R^1-\underset{\bullet}{C}=O + NO_2 \qquad (4.136)$$

We suggest that nitroalkyl radicals also could react with NO_2 by the same reaction mechanism as described in reactions (4.100)-(4.105), and reactions (4.107)-(4.109) which produce formyl radical ($H-\underset{\bullet}{C}=O$), and carbonyl radical ($R^1-\underset{\bullet}{C}=O$).

We suggest that in the reactions of low concentration of NO_2 and alkenes with addition of oxygen, the decomposition of vic-nitronitrites could occur in low quantities which would result in a small amount of carbonyl radicals being present in the reaction mixture. The acyl nitroxides could be formed by reactions of these carbonyl radicals and vic-nitronitroso compounds as in reactions (4.110),(4.111), and (4.112). From the mechanisms suggested, we conclude that the acyl nitroxides produced from the reactions with addition of oxygen should be the same acyl nitroxides produced from the reactions at elevated temperatures.

The decomposition and dissociations of nitrites, nitroso dimers, and N_2O_4 are accelerated by increasing temperature of the reaction solution which would result in an increase in carbonyl compound formation. In the reactions with addition of oxygen, the decomposition, and dissociation of nitrites and N_2O_4 could occur at the rate of decomposition and dissociation at room temperature which result in low concentrations of β-nitroalkoxy radical and NO_2. The amount of NO_2 could be increased by the reaction of NO, and O_2. vic-Nitronitroso compounds tend to be in dimeric form at room temperature, but on the addition of oxygen vic-nitronitroso compounds would produce more nitroxides. The product formation from these reactions show that acyl nitroxides are produced in lower concentration than observed from the reactions studied at elevated reaction temperatures.

Nitroalkyl radicals could undergo reaction with NO which is produced and present in the reaction mixture to produce gem-nitronitroso derivatives. But in the reaction mixture of low concentration of NO_2 and alkenes in addition of oxygen or at elevated reaction temperature, the NO_2 is reproduced and present in solution medium in higher concentration than NO, the possibilities that NO_2 and /or oxygen react with nitroalkyl radicals are more than that NO does. If gem-nitronitroso compounds were produced from reaction of NO and nitroalkyl radicals, they would be in trace amount, and we do not propose that these gem-nitronitroso derivatives are involved in the mechanisms of acyl nitroxides formation.

Other reactions that may occur in reaction mixtures in the studies of low concentration of NO_2 and alkenes with addition of oxygen could be by the same mechanisms as in the studies at elevated reaction temperatures, for example, the isomerisation of secondary nitroso compounds as in reactions (4.113), and (4.114), the decompositions of vic-nitro-nitroso compounds in the presence of NO as in the reactions (4.118)-(4-121) which could increase the concentration of carbonyl compounds in the reaction mixture, the radical reaction of alkyl nitroxides with NO_2 which results in a decrease in alkyl nitroxides concentrations (reaction 4.122), the oxidation of hydroxylamines by NO_2 and oxygen to reproduce nitroxides, and nitrones are oxidised by NO_2 to produce acyl nitroxides as in reaction (4.125).

Radical products observed from these experiments are summarised in Table 4.3. Most alkenes produce acyl nitroxides from the reactions with addition of oxygen or at elevated reaction temperature, for which their formations are suggested by previously described mechanisms. The esr spectra of these acyl nitroxides are three lines or three doublets with $a_N \sim 7\text{-}8$ G which could reveal only the nature of hydrogen atom at β-positions. Their spectra could not explain the complete structure of acyl nitroxides which we suggest to be formed as in the reactions (4.110), (4.111), and (4.112). One or more than one acyl nitroxides may be produced from the reaction of each alkenes . For example, cis-2-butene, trans-2-butene, and 2-methyl-2-butene could produce only one acyl nitroxides which are formed as in the reactions (4.110), and (4.112) for which we suggest the carbonyl moieties are acetyl groups, iso-butene and 2-methyl-1-butene produce two acyl nitroxides and we suggest that they are formyl nitroxides and acetyl nitroxides.

The formyl nitroxides (4-X), and (4-XIV) detected from reactions of NO_2 with iso-butene, and 2-methyl-1-butene respectively with addition of oxygen we suggest are formed as in the reactions (4.110) and (4.111). The formation of acetyl nitroxides(4-XI),and (4-XIII) detected from the

Table 4.3

Effects of oxygen, and reaction temperature upon radical products from the study of the reactions of both low and high concentrations of NO_2 with alkenes, in 1,4-dioxan solution.

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
cis-2-butene	low	O_2, RT	nitroxide (4-I) (intensities decreased), acyl nitroxide(4-II) (main radical product)
	low	100°	acyl nitroxide(4-II)
	high	O_2, RT	acyl nitroxide(4-II)
	high	100°	acyl nitroxide(4-II)
trans-2-butene	low	O_2, RT	nitroxide(4-I) (intensities decreased), acyl nitroxide(4-II) (main product)
	low	100°	acyl nitroxide(4-II)
	high	O_2, RT	acyl nitroxide(4-II)
	high	100°	acyl nitroxide(4-II)
2-methyl-2-butene	low	O_2, RT	nitroxide(4-III) (intensities decreased)
	low	100°	nitroxide(4-III) (intensities increased)
	high	O_2, RT	nitroxide(4-III) (main product), acyl nitroxide(4-IV)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
2-methyl-2-butene (continued)	high	100°	nitroxide(4-III) (main product), acyl nitroxide(4-IV)
iso-butene	low	O_2, RT	acyl nitroxide(4-X),
	low	100°	acyl nitroxide(4-X), acyl nitroxide(4-XI) (main product)
	high	O_2, RT	acyl nitroxide(4-X)
	high	100°	acyl nitroxide(4-XI)
2-methyl-1-butene	low	O_2, RT	nitroxide(4-XII), acyl nitroxide (4-XIII)(main), acyl nitroxide (4-XIV)(trace)
	low	100°	nitroxide(4-XII), (main product, intensities increased), acyl nitroxide (4-XIII)
	high	O_2, RT	nitroxide(4-XII) (main product), acyl nitroxide (4-XIII), acyl nitroxide (4-XIV)(trace)
	high	100°	nitroxide(4-XII), acyl nitroxide (4-XIII) (main radical product)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
Allyl chloride	low	O_2, RT	nitroxide(4-XIX) (broadened lines)
	low	100°	nitroxide(4-XX) (main radical), acyl nitroxide (4-XXI)
	high	O_2, RT	nitroxide(4-XX) (broadened lines), acyl nitroxide (4-XXI)(broadened lines)
	high	100°	acyl nitroxide (broad 3 lines)
3-butenoic acid	low	O_2, RT	nitroxide(4-XXII) (intensities increased), acyl nitroxide (4-XXIII)
	low	100°	acyl nitroxide (4-XXIII)
	high	O_2, RT	acyl nitroxide (4-XXIII)(with further hyperfine lines)
	high	100°	acyl nitroxide (4-XXIII)
styrene	low	O_2, RT	nitroxides(4-XXIVa) and (4-XXIVb) (intensities decreased)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
styrene (continued)	low	100°	nitroxides(4-XXIVa), and (4-XXIVb) (intensities increased)
	high	O_2, RT	acyl nitroxide (4-XXV)
	high	100°	acyl nitroxide (4-XXV)(intensities increased)
p-methoxystyrene	low	O_2, RT	nitroxides(4-XXVIa), and (4-XXVIb)(intensities decreased)
	low	100°	nitroxides(4-XXVIa), and (4-XXVIb)(intensities increased)
	high	O_2, RT	acyl nitroxide (4-XXVII)
	high	100°	acyl nitroxide (4-XXVII)(intensities decreased)
α-methylstyrene	low	O_2, RT	nitroxide(4-XXVIII) (intensities increased)
	low	100°	nitroxide(4-XXVIII) (intensities increased)
	high	O_2, RT	nitroxide(4-XXVIII) (intensities increased)
	high	100°	nitroxide(4-XXVIII) (intensities increased)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
3-butene-2-one	low	O_2, RT	iminoxy radicals E-isomer(4-XXXIIa) (intensities increased and showed (showed better resolution) Z-isomer(4-XXXIIb) (trace)
	low	100°	no
	high	O_2, RT	iminoxy radicals E-isomer(4-XXXIIa), and Z-isomer (4-XXXIIb)(intensities decreased), nitroxide(4-XXXIV), acyl nitroxide (4-XXXIII)(main)
	high	100°	no
acraldehyde	low	O_2, RT	no
	low	100°	no
	high	O_2, RT	no
	high	100°	no
methacrolein	low	O_2, RT	nitroxide(4-XXXVII) (intensities increased), acyl nitroxide (4-XXXVIII)(trace)
	low	100°	nitroxide(4-XXXVII) (trace), acyl nitroxide (4-XXXVIII)(trace)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
methacrolein (continued)	high	O_2, RT	nitroxide(4-XXXVII), and acyl nitroxide (4-XXXVIII)(intensities increased)
	high	100°	nitroxide(4-XXXVII), and acyl nitroxide (4-XXXVIII)(intensities decreased)
methacryloyl chloride	low	O_2, RT	nitroxide(4-XXXIX) (broadened lines)
	low	100°	nitroxide(4-XXXIX) (intensities decreased)
	high	O_2, RT	nitroxide(4-XXXIX) (broadened lines)
	high	100°	nitroxide(4-XXXIX) (intensities decreased)
methyl methacrylate	low	O_2, RT	nitroxide(4-XL) (broadened lines)
	low	100°	nitroxide(4-XL) (intensities increased)
	high	O_2, RT	nitroxide(4-XL) (broadened lines)
	high	100°	nitroxide(4-XL) (intensities increased)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
crotonic acid	low	O_2, RT	iminoxy radical E-isomer(4-XLIa), acyl nitroxide (4-XLII)
	low	100°	iminoxy radical E-isomer(4-XLIa) (intensities increased), acyl nitroxide (4-XLII)
	high	O_2, RT	iminoxy radical E-isomer(4-XLIa), acyl nitroxide (4-XLII)
	high	100°	iminoxy radical E-isomer(4-XLIa) (intensities increased), acyl nitroxide (4-XLII)
ethyl crotonate	low	O_2, RT	iminoxy radicals E-isomer(4-XLIIIa), Z-isomer(4-XLIIIb) (showed better resolution)
	low	100°	iminoxy radicals E-isomer(4-XLIIIa), Z-isomer(4-XLIIIb) (intensities decreased)
	high	O_2, RT	iminoxy radicals E-isomer(4-XLIIIa),

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
ethyl crotonate (continued)			and Z-isomer (4-XLIIIb)(showed better resolution)
	high	100°	iminoxy radicals E-isomer(4-XLIIIa), and Z-isomer (4-XLIIIb)(intensities decreased), acyl nitroxide (4-XLIV)(trace)
methyl crotonate	low	O_2, RT	iminoxy radicals E-isomer(4-XLVIa), and Z-isomer(4-XLVIb) (showed better resolution)
	low	100°	iminoxy radicals E-isomer(4-XLVIa), and Z-isomer(4-XLVIb) (intensities decreased)
	high	O_2, RT	iminoxy radicals E-isomer(4-XLVIa), and Z-isomer(4-XLVIb) (showed better resolution)
	high	100°	iminoxy radicals E-isomer(4-XLVIa), and Z-isomer(4-XLVIb) (intensities decreased), acyl nitroxide(4-XLIV) (trace)
crotonaldehyde	low	O_2, RT	iminoxy radicals E-isomer(4-XLVIIa), Z-isomer(4-XLVIIb) (intensities increased)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
crotonaldehyde (continued)	low	100°	iminoxy radicals E-isomer(4-XLVIIa), and Z-isomer (4-XLVIIb)(intensities decreased)
	high	O_2, RT	no
	high	100°	no
3-pentene-2-one	low	O_2, RT	iminoxy radicals E-isomer(4-XLIXa), and Z-isomer (4-XLIXb)(showed better resolution), nitroxide(4-L), and acyl nitroxide (4-LI)(in equal intensities)
	low	100°	iminoxy radicals E-isomer(4-XLIXa), Z-isomer(4-XLIXb) (main)(both decreased in intensities) nitroxide(4-L) (trace), acyl nitroxide (4-LI)(main)
	high	O_2, RT	iminoxy radicals E-isomer(4-XLIXa), and Z-isomer (4-XLIXb)(showed better resolution), nitroxide(4-L) (trace), acyl nitroxide (4-LI)(trace)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
3-pentene-2-one (continued)	high	100°	iminoxy radicals E-isomer(4-XLIXa), and Z-isomer(4-XLIXb) (intensities increased), acyl nitroxide (4-LI)(trace)
tiglic acid	low	O_2, RT	nitroxide(4-LII) (intensities decreased)
	low	100°	nitroxide(4-LII) (intensities increased)
	high	O_2, RT	nitroxide(4-LII) (weak spectrum)
	high	100°	no
3,3-dimethylacrylic acid	low	O_2, RT	acyl nitroxide (4-LIV)
	low	100°	acyl nitroxide (4-LIV)(intensities increased)
	high	O_2, RT	iminoxy radical Z-isomer(4-LIII) (trace), acyl nitroxide (4-LIV)
	high	100°	acyl nitroxide (4-LIV)
mesityl oxide	low	O_2, RT	acyl nitroxide (4-LVI)(main product), iminoxy radical Z-isomer(4-LV)
	low	100°	acyl nitroxide (4-LVI)(main),

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
mesityl oxide (continued)			iminoxy radical Z-isomer(4-LV) (intensities decreased), nitroxide(4-LVII) (trace), acyl nitroxide (4-LVIII)(trace)
	low	100° (followed reaction)	acyl nitroxide (4-LVIII)(main), acyl nitroxide (4-LVI) (minor)
	low	100° (for prolonged period)	acyl nitroxide (trace)
cis-stilbene	low	O_2, RT	nitroxide(4-LIX) (broad spectrum)
	low	100°	acyl nitroxide(4-LX)
cinnamaldehyde	low	O_2, RT	iminoxy radicals E-isomer(4-LXIa), Z-isomer(4-LXIb) (intensities increased)
	low	100°	acyl nitroxide (4-LXII)
benzalacetone	low	O_2, RT	no
	low	100°	iminoxy radical E-isomer(4-LXIII)
	high	O_2, RT	iminoxy radical E-isomer(4-LXIII) (main product), acyl nitroxide (4-LXIV), acyl nitroxide (4-LXV)

Table 4.3 (continued)

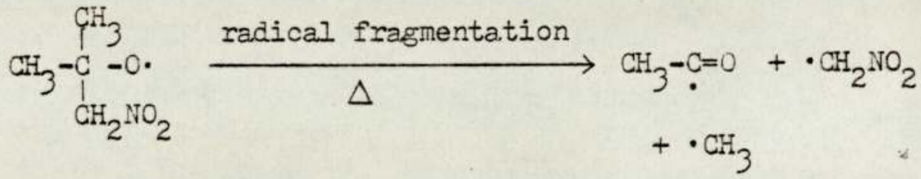
Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
benzalacetone (continued)	high	100°	acyl nitroxide (4-LXIV), acyl nitroxide (4-LXV)
benzalacetophenone	high	100°	acyl nitroxide (4-LXVI)(weak)
dibenzalacetone	low	O_2, RT	acyl nitroxide (4-LXVIII)
	low	100°	no
cinnamyl alcohol	low	O_2, RT	nitroxides(4-LXIXa), and (4-LXIXb) (broadened lines)
	low	100°	nitroxides(4-LXIXa), and(4-LXIXb) (intensities increased)
	high	O_2. RT	acyl nitroxide (4-LXX)(showed better resolution, and intensities increased)
	high	100°	acyl nitroxide (4-LXX)(intensities increased), nitroxides(4-LXIXa), and(4-LXIXb)(trace)
α -methylcinnamaldehyde	low	O_2, RT	nitroxide(4-LXXI) (broadened lines), acyl nitroxide (4-LXXII)(broadened lines)
	low	100°	nitroxide(4-LXXI) (broadened lines), acyl nitroxide (4-LXXII) (broadened lines)

Table 4.3 (continued)

Alkenes	Concentration of NO_2	Reaction Condition	Radical Products
α-methylcinnamaldehyde (continued)	high	O_2, RT	nitroxide(4-LXXI), acyl nitroxide (4-LXXII) (broadened lines)
	high	100°	nitroxide(4-LXXI), acyl nitroxide (4-LXXII) (broadened lines)

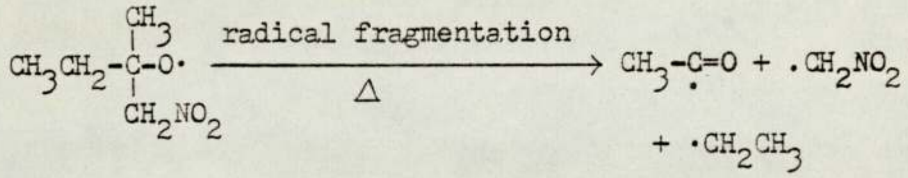
same reactions but at boiling water-bath temperature reveals that acetyl radicals are formed probably during radical fragmentation of tertiary β -nitroalkoxy radical derivatives as following reactions:

Iso-butene:



$$CH_3-\overset{CH_3}{\underset{CH_2NO_2}{C}}-O\cdot \xrightarrow[\Delta]{\text{radical fragmentation}} CH_3-\underset{\cdot}{C}=O + \cdot CH_2NO_2 + \cdot CH_3 \qquad (4.137)$$

2-Methyl-1-butene:



$$CH_3CH_2-\overset{CH_3}{\underset{CH_2NO_2}{C}}-O\cdot \xrightarrow[\Delta]{\text{radical fragmentation}} CH_3-\underset{\cdot}{C}=O + .CH_2NO_2 + \cdot CH_2CH_3 \qquad (4.138)$$

$$2\ CH_3CH_2\cdot + 2\ NO_2 \longrightarrow CH_3CH_2NO_2 + CH_3CH_2ONO \qquad (4.139)$$

$$CH_3CH_2ONO \xrightarrow[\Delta]{\text{decomposition}} CH_3CH_2O\cdot + NO \qquad (4.140)$$

$$CH_3CH_2O\cdot \longrightarrow CH_3\cdot + HCHO \qquad (4.141)$$

We observed formyl nitroxides only from the reactions of iso-butene with NO_2 at both low and high concentrations with addition of oxygen, and from 2-methyl-1-butene with NO_2 at high concentration with addition of oxygen. We did not obtain other formyl nitroxides from the reactions of terminal alkenes for which β -nitroalkoxy radical derivatives are secondary alkoxy radical type, and tertiary alkoxy radical type with aryls or carbonyl substituents, for example allyl chloride, 3-butenoic acid, styrene, p-methoxystyrene, α-methylstyrene, methyl methacrylate. We suggest that the β C-C scission of nitroalkoxy radicals occurs less in the reactions studied with the addition of oxygen and it could occur in the reactions at elevated reaction temperature in which nitromethyl radicals could be produced, but we suggest that nitromethyl radicals may be further oxidised completely to give formic acid (A.P.Altshuller, and I.R.Cohen, 1959).

Aryl substituted terminal alkenes which we studied include styrene, p-methoxystyrene, and α-methylstyrene, we found that these compounds do not produce acyl nitroxides at low concentration of NO_2 reactions with the addition of oxygen or at elevated reaction temperature. In the presence of oxygen, their nitroxide spectra are rather broad which is the broadening effect of oxygen on esr spectra. At elevated reaction temperature, the intensities of their nitroxide spectra increase , and are decreased when the reaction mixtures cool down to room temperature. These findings were also observed by L.Jonkman et al., 1971,who suggested that the concentration of nitroxides increased due to the greater dissociation of nitroso dimers at elevated reaction temperature. But in our studies, we find that raising and lowering of reaction temperatures directly affects the spectral intensities which reflect the increase and decrease in radical concentrations, and we suggest that the nitroxide radicals exist in equilibrium with their dimers in solution as proposed by K.Adamic et al., 1971; and K.U.Ingold, 1975 . We agree that at elevated reaction temperature, the nitroso dimers dissociate into monomers and lead to more nitroxide formation as suggested by L.Jonkman et al., 1971 but in the studies at low concentration and with varying the reaction temperature we would suggest that the increase, and decrease in nitroxide concentration is due to the equilibrium of nitroxide monomers and their dimers as suggested by K.Adamic et al., 1971, and we would not suggest the equilibrium between between nitroso dimers and nitroxide formation could occur in this reaction condition.

The reactions of high concentration of NO_2 with styrene and p-methoxystyrene produce acyl nitroxides (4-XXV) and (4-XXVII), with addition of oxygen or at elevated reaction temperature we also observed these acyl nitroxides and their esr spectral intensities increase when the reaction temperature is increased, we suggest that the increase in reaction temperature would result in an increase in concentrations of oxidation products, and the complete oxidation reactions could occur.

The reactions of high concentration of NO_2 with α-methylstyrene produces only nitroxide (4-XXVIII). When the reaction mixture was studied with addition of oxygen or at elevated reaction temperature, we observed only the increase in spectral intensities of nitroxide(4-XXVIII). We suggest that its β-nitroalkoxy radical derivative is stable to radical fragmentation.

In the reactions of NO_2 with α,β-unsaturated carbonyl compounds in which a hydrogen atom is available at α-position, we always observed iminoxy radicals whose esr spectra showed better resolved hyperfine lines from the reactions with addition of oxygen than those from reactions under "ordinary reaction condition", and most of them were observed to decrease in intensity or disappear when the reaction temperature was increased. For example, 2-butene-2-one, ethyl crotonate, methyl crotonate, crotonaldehyde, and 3-pentene-2-one. We suggest that oxygen could be involved in hydroxyimine oxidation to produce more iminoxy radicals, and the elevated temperature could accelerate the dacay of iminoxy radicals. Acyl nitroxides were also produced which were usually observed from the reaction of low concentration of NO_2 at elevated reaction temperature or with a high concentration of NO_2 with, or without elevating the reaction temperature. The mechanism of acyl nitroxide formation could be the same mechanism as previously described which in β C-C scission occurs. Ethyl crotonate, and methyl crotonate produced acyl nitroxide in trace amount at high concentration of NO_2 and elevated reaction temperature, and we suggest that their β-nitroalkoxy radicals were stable to β C-C scission at this temperature.

The results obtained from reactions of NO_2 with α,β-unsaturated carbonyl compounds with methyl group at α-position were nitroxides, for example methacryloyl chloride, methyl methacrylate, and tiglic acid. Their nitroxides esr spectra were always observed in increased in intensities at elevated reaction temperature, and acyl nitroxides were never produced. These results could be explained as suggested for α-methylstyrene.

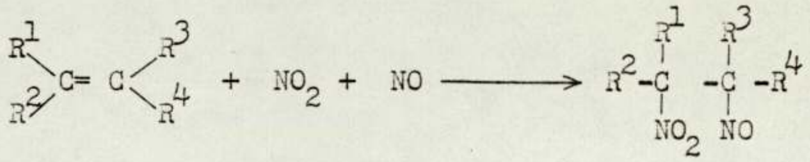
The reactions of NO_2 with aryl, or aryl carbonyl alkenes with addition of oxygen or at elevated reaction temperature also produced acyl nitroxides which we suggest are the same acyl nitroxides as we observed from the reactions of high concentration of NO_2 with these alkenes (section 4.6.4). The results obtained from reaction of benzalacetophenone with high concentration of NO_2 at elevated reaction temperature in which a very low yield of acyl nitroxide (4-LXVI), the only radical product observed from this alkene, and with cinnamic acid which did not produce any detectable radical product from any reaction condition, confirm that the addition reaction of NO_2 to alkenes is an electrophilic addition reaction.

4.8 The Reactions of NO in the Presence of a Trace of NO_2 with Alkenes in 1,4-Dioxan Solution.

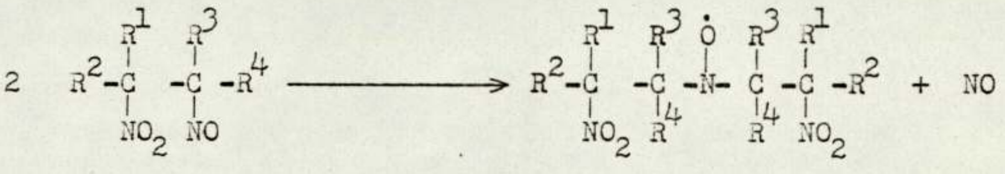
The reactions of NO and NO_2 are similar and have the general characteristic of free radical reactions. For example, the reaction of alkenes with very pure NO has an induction period, and therefore some investigations could not achieve reaction of ethylenic compounds with absolutely pure NO. However, the reaction can be initiated with a trace of NO_2 (J.F.Brown, Jr., 1957).

Many investigators have studied the reactions of NO with alkenes in the presence of a trace of NO_2, they observed nitroxide radicals for which they proposed structures as those observed from the reactions of NO_2 with alkenes (M.Ebert, and J.Law, 1965; J.A.McRae, and M.C.R.Symons, 1966; L.Jonkman et al., 1971; and J. Pfab, 1977). In our studies, we obtained nitroxide radicals from reactions of alkenes with high concentration of NO in the presence of a trace of NO_2, and in order to get more understanding about the mechanism of acyl nitroxide formation, we carried out reactions in which oxygen was added or carried out the reactions at boiling water-bath temperature. The results are shown in Table 4.4.

We found that only alkyl nitroxides and iminoxy radicals were produced in high yield from the reactions of high concentration of NO with alkenes in the presence of a trace of NO_2. With addition of oxygen, we always observed broadened lines in the esr spectra of the same radicals from the freshly prepared solutions, or when the reactions were carried out at boiling water-bath temperature for few minutes, the esr spectra showed a slight increase in the spectral intensities of the same radicals which we observed from the reaction at room temperature. From these results, we conclude that NO_2 initiates the reaction to give β-nitroalkyl radical which further reacts with NO to produce vic-nitronitroso derivative and subsequently results in nitroxide radical. We did not observe any acyl



$$R^1R^2C{=}CR^3R^4 + NO_2 + NO \longrightarrow R^2\text{-}\overset{R^1}{\underset{NO_2}{C}}\text{-}\overset{R^3}{\underset{NO}{C}}\text{-}R^4 \qquad (4.142)$$



$$2\;R^2\text{-}\overset{R^1}{\underset{NO_2}{C}}\text{-}\overset{R^3}{\underset{NO}{C}}\text{-}R^4 \longrightarrow R^2\text{-}\overset{R^1}{\underset{NO_2}{C}}\text{-}\overset{R^3}{\underset{R^4}{C}}\text{-}\overset{\dot{O}}{N}\text{-}\overset{R^3}{\underset{R^4}{C}}\text{-}\overset{R^1}{\underset{NO_2}{C}}\text{-}R^2 + NO \qquad (4.143)$$

nitroxide in freshly prepared solutions from these experiments. We suggest that there is no nitrite derivative present in the reaction solution which has been suggested to be precursor of carbonyl compound (A.Mackor et al., 1967a).These results support our suggestion that acyl nitroxides are produced from reaction of low concentration of NO_2 with alkenes in the reactions with addition of oxygen or studied at water-bath temperature,

Table 4.4

The radical products obtained from reactions of high concentration of NO in the presence of a trace of NO_2 with alkenes, 1,4-dioxan as solvent.

Alkenes	Reaction Conditions	Radical Products
cis-2-butene, and trans-2-butene	RT	nitroxide (4-I)
	RT, O_2	nitroxide (4-I)
	100°	nitroxide (4-I)
2-methyl-2-butene	RT	nitroxide (4-III)
	RT, O_2	nitroxide (4-III)
	100°	nitroxide (4-III)
iso-butene	RT	nitroxide (4-IX)
	RT, O_2	nitroxide (4-IX)
	100°	nitroxide (4-IX)
2-methyl-1-butene	RT	nitroxide (4-XII)
	RT, O_2	nitroxide (4-XII)
	100°	nitroxide (4-XII)
3-butenoic acid	RT	nitroxide (4-XXII)
	RT, O_2	nitroxide (4-XXII)
	100°	nitroxide (4-XXII)
styrene	RT	nitroxides (4-XXIVa), and (4-XXIVb)
	RT, O_2	nitroxides (4-XXIVa), and (4-XXIVb)
	100°	nitroxides (4-XXIVa), and (4-XXIVb)
α -methylstyrene	RT	nitroxide (4-XXVIII)
	RT, O_2	nitroxide (4-XXVIII)
	100°	nitroxide (4-XXVIII)
acrylic acid	RT	nitroxide (4-XXIX)
	RT, O_2	no
	100°	no

Table 4.4 (continued)

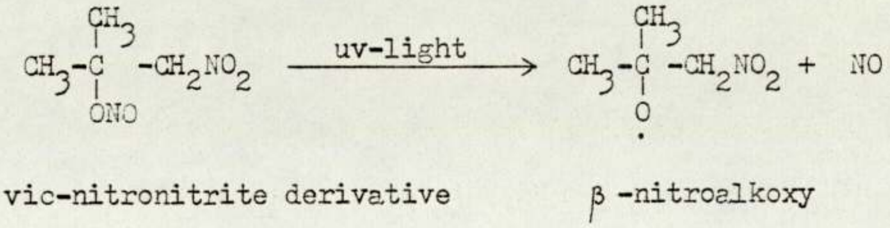
Alkenes	Reaction Conditions	Radical Products
3-butene-2-one	RT	iminoxy radicals (4-XXXIIa), and (4-XXXIIb), nitroxide (4-XXXIV) (main)
	RT, O_2	iminoxy radicals (4-XXXIIa), and (4-XXXIIb), nitroxide (4-XXXIV) (main)
	100°	iminoxy radicals (4-XXXIIa), and (4-XXXIIb), nitroxide (4-XXXIV) (main)
methyl methacrylate	RT	nitroxide (4-XL)
	RT, O_2	nitroxide (4-XL)
	100°	nitroxide (4-XL)
ethyl crotonate	RT	iminoxy radicals (4-XLIIIa), and (4-XLIIIb), nitroxide (4-XLV)
	RT, O_2	iminoxy radicals (4-XLIIIa), and (4-XLIIIb), nitroxide (4-XLV)
	100°	iminoxy radicals (4-XLIIIa), and (4-XLIIIb), nitroxide (4-XLV)

or from the reactions of high concentration of NO_2 with alkenes because of vic-nitronitrite derivatives are produced and they decompose to β-nitroalkoxy radicals which undergo β C-C scission to give carbonyl compounds as we described in sections 4.6, and 4.7.

The addition of oxygen to solutions of high concentration of NO with alkenes in the presence of a trace of NO_2 which were studied in freshly prepared solution did not increase the yield of alkyl nitroxides because of the slow rate of reaction of oxygen and NO to give NO_2 (E.R. Stephens, 1969). The slight increase in the yield of alkyl nitroxides from the solutions which were studied at boiling water-bath temperature could be the result of dissociation of nitroso dimers and thermal decomposition of nitroso compounds to give nitroxide radicals (A.Mackor et al., 1966; Th.A.J.W.Wajer et al., 1967; and A.Mackor et al., 1968). We obtained nitroxides (4-XXXIV), and (4-XLV) from the reactions of NO with 3-butene-2-one, and ethyl crotonate in the presence of a trace of NO_2 in higher yields than their iminoxy radicals (4-XXXIIa), and (4-XXXIIb); (4-XLIIIa), and (4-XLIIIb) for which we suggest that there were high concentrations of vic-nitronitroso derivatives present in the reaction solutions which would dimerise and decompose to give nitroxide radicals (reactions (4.9), and (4.10)) rather than tautomerise to give hydroxyimines and subsequently result in iminoxy radicals (A.I.Titov, 1963).

4.9 The Study of Radical Products from the Reaction of Low Concentration of NO_2 and iso-Butene in 1,4-Dioxan, Under Various Reaction Conditions.

The results which we observed from reactions of low concentration of NO_2 with iso-butene under different reaction conditions, for example, exposed to air, room daylight or ultraviolet light, are shown in Table 4.5. The results reveal that alkyl nitroxide (4-IX) which is one of the radical products is stable for months in the reaction solution in the absence of oxygen, and that acyl nitroxide (4-X) could be formed at a slow reaction rate in the same reaction condition at room temperature, and it is also stable for months. The mechanism of acyl nitroxide formation in this reaction in which the solution was not exposed to air, and room daylight could be as the same mechanism as we suggest for the reaction of high concentration of NO_2 with iso-butene (section 4.6). We have suggested that vic-nitronitrites, which are produced from the reaction of $\dot{N}O_2$ with alkenes, and could lead to carbonyl compound formation, and finally result in acyl nitroxides. In this experiment in which the reaction solution was not exposed to air, we suggest that vic-nitronitrite decomposes to β-nitroalkoxy radical and this latter compound undergoes fragmentation at a slow rate to give acetone and methyl radical. The acyl nitroxide (4-X) is formed by the reaction of NO_2 with methyl radical (as in section 4.6 in which we observed its formation at a slow rate). In the experiment in which the reaction solution was unexposed to air but ultraviolet light and produced alkyl nitroxide (4-IX) in increased yield, we suggest that the decomposition of vic-nitronitrite derivative is accelerated by ultraviolet light to produce β-nitroalkoxy radical which is then trapped by vic-nitronitroso derivative which is present in reaction solution to give alkoxy alkyl nitroxide which further decomposes to give alkyl nitroxide (4-IX) (A.Mackor et al., 1966; Th.A.J.W.Wajer et al., 1967; and A.Mackor et al., 1968).



$$CH_3-\underset{ONO}{\overset{CH_3}{C}}-CH_2NO_2 \xrightarrow{\text{uv-light}} CH_3-\underset{\dot{O}}{\overset{CH_3}{C}}-CH_2NO_2 + NO \qquad (4.144)$$

vic-nitronitrite derivative derivative

β-nitroalkoxy radical

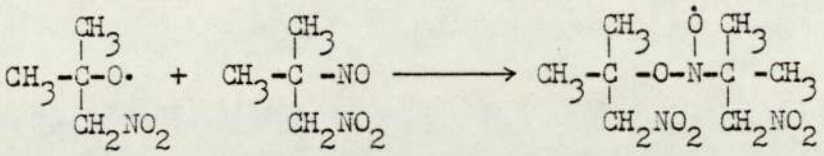
Table 4.5

The study of radical products from the reaction of low concentration of NO_2 and iso-butene in 1,4-dioxan, under various conditions.

Reaction Conditions	Reaction Time	Radical Products
RT, in freshly prepared solution	few minutes	alkyl nitroxide (4-IX)
RT, O_2, in freshly prepared solution	few minutes	alkyl nitroxide (4-IX), acyl nitroxide (4-X) (main)
RT, exposed to air, and room daylight	24 hours	alkyl nitroxide (4-IX), acyl nitroxide (4-X) (main)
RT, unexposed to air, and room daylight	7 days	alkyl nitroxide (4-IX) (main) acyl nitroxide (4-X)
	5 weeks	alkyl nitroxide (4-IX), and acyl nitroxide (4-X) in equal proportion.
	2 months	alkyl nitroxide (4-IX) (intensities decreased) acyl nitroxide (4-X) (main)
RT, unexposed to air, but exposed to room daylight	7 days	alkyl nitroxide (4-IX), (main) acyl nitroxide (4-X)
	5 weeks	alkyl nitroxide (4-IX), and acyl nitroxide (4-X) in equal proportion.
	2 months	alkyl nitroxide (4-IX) (intensities decreased) acyl nitroxide (4-X) (main)

Table 4.5 (continued)

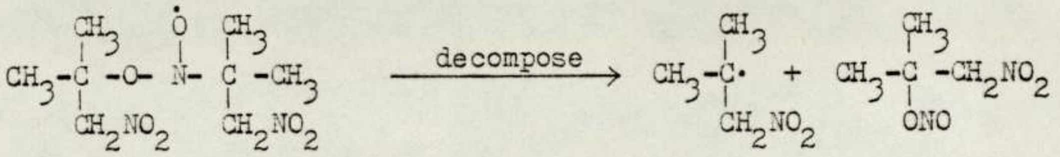
Reaction Conditions	Reaction Time	Radical Products
RT, unexposed to air, but exposed to ultraviolet light	4 days	alkyl nitroxide (4-IX) (intensities increased)



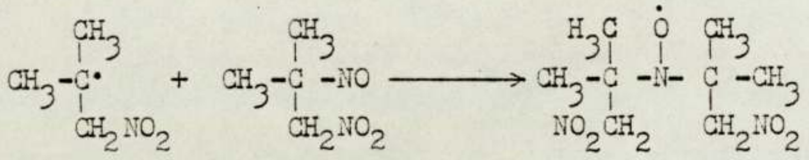
$$CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-O\cdot + CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-NO \longrightarrow CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-O-\overset{\dot{O}}{N}-\underset{CH_2NO_2}{\overset{CH_3}{C}}-CH_3 \qquad (4.145)$$

vic-nitronitroso derivative

alkoxy alkyl nitroxide



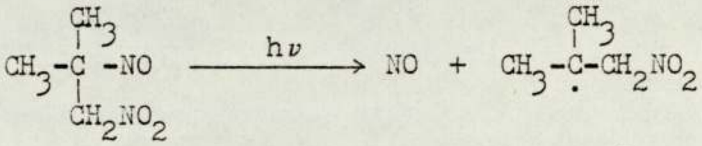
$$CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-O-\overset{\dot{O}}{N}-\underset{CH_2NO_2}{\overset{CH_3}{C}}-CH_3 \xrightarrow{decompose} CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}\cdot + CH_3-\underset{ONO}{\overset{CH_3}{C}}-CH_2NO_2 \qquad (4.146)$$



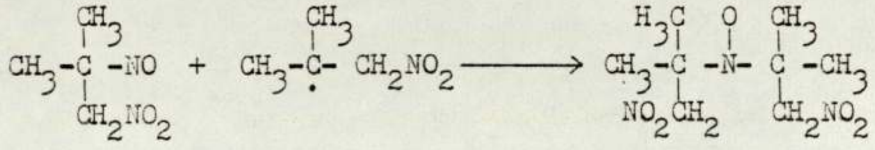
$$CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}\cdot + CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-NO \longrightarrow CH_3-\underset{NO_2CH_2}{\overset{H_3C}{C}}-\overset{\dot{O}}{N}-\underset{CH_2NO_2}{\overset{CH_3}{C}}-CH_3 \qquad (4.147)$$

alkyl nitroxide (4-IX)

The ultraviolet light exposure of this reaction solution also results in decomposition of nitroso compound and leads to nitroxide formation. It is produced by homolytic cleavage followed by trapping of the radical formed (E.G.Janzen ,1971).



$$CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-NO \xrightarrow{h\nu} NO + CH_3-\underset{\cdot}{\overset{CH_3}{C}}-CH_2NO_2 \qquad (4.148)$$



$$CH_3-\underset{CH_2NO_2}{\overset{CH_3}{C}}-NO + CH_3-\underset{\cdot}{\overset{CH_3}{C}}-CH_2NO_2 \longrightarrow CH_3-\underset{NO_2CH_2}{\overset{H_3C}{C}}-\overset{\dot{O}}{N}-\underset{CH_2NO_2}{\overset{CH_3}{C}}-CH_3 \qquad (4.149)$$

alkyl nitroxide (4-IX)

Acyl nitroxide (4-X) was not produced from this reaction condition.

From the result obtained, we could conclude that acyl nitroxide (4-X) could be formed at a slow reaction rate in the reaction of low concentration of NO_2 with iso-butene in the absence of oxygen as in the same mechanism as acyl nitroxide (4-X) formation from the reaction of high concentration of NO_2 with iso-butene. Room daylight, and ultraviolet light are not involved in acyl nitroxide (4-X) formation but oxygen accelerates the rate of formation of this radical.

CHAPTER FIVE

The Detection of Initial Radical Formation

Results and Discussion

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Results

We carried out the reactions of NO_2 with alkenes with two different techniques in order to try to produce evidence for β-nitroalkyl radicals which have been suggested to be initial radical intermediates. The techniques were:

1. Spin trapping method by using nitrosobenzene, and phenyl N-tert-butyl nitrone as spin traps.
2. Mixed-flow method.

The alkenes which we studied in these experiments were the alkenes which could react with NO_2 to give high yields of only one type of radical product, for example they produced only alkyl nitroxide radicals or iminoxy radicals from the reactions of low concentration of NO_2 with alkenes under ordinary reaction condition (see Chapter Four), and we also considered that these alkenes were able to produce β-nitroalkyl radicals which could possibly be detected by the above techniques. These alkenes were cis-2-butene, 2-methyl-2-butene, iso-butene, ethyl crotonate,methyl methacrylate and α-methylstyrene. The results from each experiment are described below.

5.1 Spin Trapping Method

5.1.1 Nitrosobenzene

We observed nitroxide radicals from reactions of low concentration of NO_2 with alkenes and a small amount of nitrosobenzene, for example cis-2-butene, 2-methyl-2-butene, iso-butene, α-methylstyrene, and ethyl crotonate resulted in nitroxides of which their esr parameters are shown in Table 5.1. Solutions of alkenes in 1,4-dioxan in the presence of a small amount of nitrosobenzene also gave esr spectra of nitroxide radicals. Freshly, prepared nitrosobenzene itself in 1,4-dioxan gave no esr spectrum but after one hour this solution gave rise to a nitroxide radical. Nitrosobenzene in the presence of NO_2 resulted in 3 lines esr spectrum of a nitroxide radical. The esr parameters of these radical products are summarised in Table 5.1.

5.1.2 Phenyl N-tert-butyl nitrone (PBN)

The reactions of low concentration of NO_2 with 2-methyl-2-butene, iso-butene, and methyl methacrylate in the presence of a small amount of phenyl N-tert-butyl nitrone gave nitroxide radicals together with 3 lines esr spectrum of acyl nitroxide (5-III). The solution of a small amount of phenyl N-tert-butyl nitrone in the presence of low concentration of NO_2 gave 3 lines esr spectrum of acyl nitroxide (5-III), a_N = 8.078 gauss. The solutions of alkenes in the presence of phenyl N-tert-butyl nitrone did not give rise to any radical product. The results from this experiment are summarised as shown in Table 5.2.

Table 5.1

The esr parameters and proposed radical structures of radical products obtained from reactions of low concentration of NO_2 with alkenes and nitrosobenzene, 1,4-dioxan as solvent.

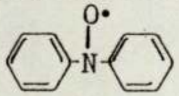
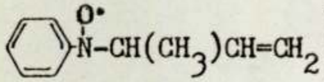
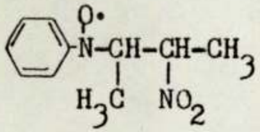
Alkenes	Reaction Condition	g-value	a_N (gauss)	a_H (gauss)	Proposed Radical Structures
-	nitrosobenzene (1 hour in 1,4-dioxan)	2.00671	11.42	$a_{3H(o-,p-)}=3.063$ $a_{2H(m-)}$ not seen	
-	nitrosobenzene, NO_2	2.00662	11.213	-	
cis-2-butene	nitrosobenzene	2.00670	10.93	$a_{4H(o-,p-,\beta)}$ = 3.364 and further small hyperfine lines	
	nitrosobenzene, NO_2	2.00670	10.721	$a_{4H(o-,p-,\beta)}$ = 2.483 $a_{3H(m-,\gamma)}$ = 1.016	

Table 5.1 (continued)

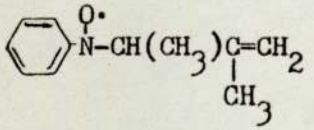
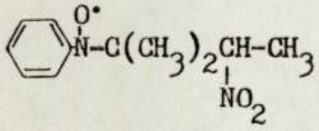
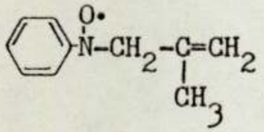
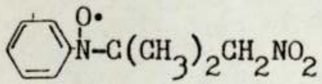
Alkenes	Reaction Condition	g-value	a_N (gauss)	a_H (gauss)	Proposed Radical Structures.
2-methyl-2-butene	nitrosobenzene	2.00602	10.372	broad spectrum, hyperfine lines not clear	
	nitrosobenzene, NO_2	2.00602	10.372	$a_{3H(o-,p-)} = 2.523$ $a_{2H(m-)}$ not clear	
iso-butene	nitrosobenzene	2.00540	11.383	$a_{2H(CH_2)} = 5.83$ $a_{3H(o-,p-)} = 2.776$ $a_{2H(m-)} = 1.111$	
	nitrosobenzene, NO_2	2.00687	11.709	3 broad lines, with further hyperfine lines	

Table <u>5.1</u> (continued)

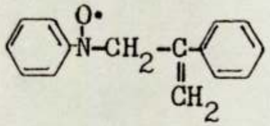
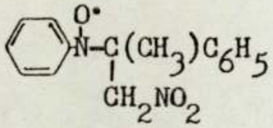
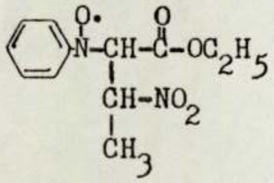
Alkenes	Reaction Conditions	g-value	a_N (gauss)	a_H (gauss)	Proposed Radical Structure
α-methylstyrene	nitrosobenzene	2.00670	10.09	$a_{3H(o-,p-)}=2.579$ $a_{2H(m-)}=0.841$ $a_{2H(\beta H)}=3.644$	
	nitrosobenzene, NO_2	2.00568	11.81	$a_{3H(o-,p-)}=2.249$ $a_{2H(m-)}= 1.125$	
ethyl crotonate	nitrosobenzene	-	-	-	-
	nitrosobenzene, NO_2	2.00670	8.746		

Table 5.2

Radical products obtained from reactions of low concentration of NO_2 with alkenes in the presence of phenyl N-tert-butyl nitrone (PBN) in 1,4-dioxan solution.

Alkenes	Reaction Condition	Radical Products
-	PBN in 1,4 dioxan	no radical product
-	PBN, NO_2	acyl nitroxide(5-III) $g = 2.00755$ $a_N = 8.078$ G.
2-methyl-2-butene	PBN, NO_2	nitroxide (4-III) acyl nitroxide(5-III)
iso-butene	PBN, NO_2	nitroxide (4-IX) acyl nitroxide(5-III)
methyl methacrylate	PBN, NO_2	nitroxide (4-XL) acyl nitroxide(5-III)

5.2 Mixed-Flow Method

The solution of low concentration of NO_2 in 1,4-dioxan and dilute solution of alkene flowed from separate containers by gravitational force at the rate of 0.60, and 0.30 ml/sec respectively through a mixing chamber, the mixed solution then entered the cavity, and the esr spectra were recorded during continuous flow and stop-flow. The alkenes which were studied by this method were cis-2-butene, 2-methyl-2-butene, iso-butene, and α-methylstyrene. The esr measurements from each experiment revealed that no radicals were produced at the flow rate of 0.60 ml/sec, and at the flow rate of 0.30 ml/sec or upon stopping the flow we obtained the esr spectra of nitroxide radicals (4-I), (4-III), (4-IX), and(4-XXVIII) from their corresponding alkenes and we observed the gradual increase in esr spectral intensities of nitroxides upon stopping the flow of the two reactants.

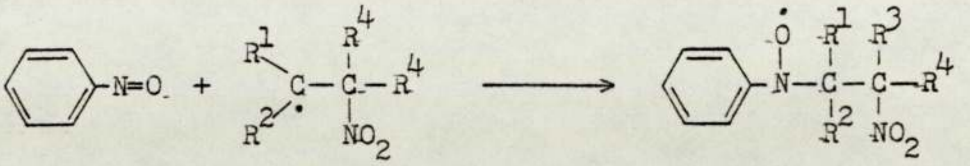
Discussion

Our purpose was to elicit evidence for the presence of β-nitroalkyl radicals which were thought to be initial radical intermediates of the reactions of NO_2 with alkenes by a method of varying the substituents of the alkenes, for example varying the substituents from electron donating to electron withdrawing should lead to a decrease in the rate of formation of the β-nitroalkyl radicals and to a decrease of esr signal intensity as the substituents more electron withdrawing. We have suggested that there are NO_2 and NO present in the reaction solution which could react with β-nitroalkyl radicals as soon as they are produced to give non-radical compounds. In our study to detect β-nitroalkyl radical in solution at room temperature, we carried out the experiments by using the techniques for detecting transient free radicals which were spin trapping and mixed-flow techniques. Another technique which we ignored was frozen method since many previous investigators, for example P.W. Atkins et al., 1962 observed an esr spectrum which showed the radical nature of NO_2 when an experiment was carried out by uv-irradiation of N_2O_4 in ice, and B.H.J.Bielski et al.,1967, reported the esr spectra of nitroxides and iminoxy radicals when NO_2 dissolved in acetone, cyclohexene, cyclopentanone, 1.5-cyclooctadiene, and styrene at low temperature range between -130° to -20°.

5.3 Spin Trapping Method

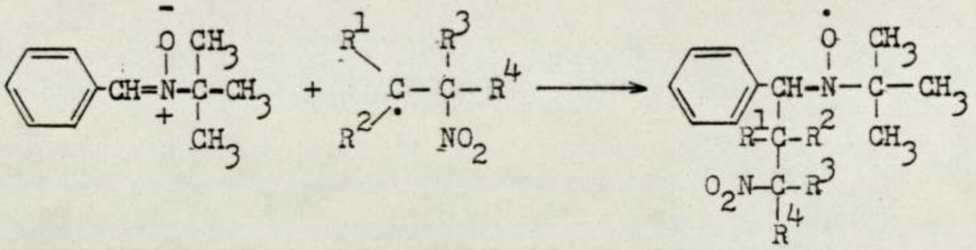
Spin trapping method involves the trapping of a reactive free radical by an addition reaction to produce a more stable radical, detected by esr, whose hyperfine coupling parameters permit identification of the initial radical trapped.

Nitrosobenzene and phenyl N-tert-butyl nitrone were employed as spin traps in our experiments. They added to β-nitroalkyl radicals to produce nitroxide as in equations (5.1), and (5.2).



(5.1)

(5.I)



(5.2)

(5.II)

The esr spectrum of nitroxide (5-I) could reveal the nature of trapped β-nitroalkyl radical but nitroxide (5-II) could only provide the nature of reaction studied but the structure of the trapped radical is difficult to obtain. The results which we observed from reactions of NO_2 with alkenes in the presence of spin traps are discussed in detail as below.

5.3.1 Nitrosobenzene

We observed a 3 lines esr spectrum from the solution of low concentration of NO_2 and nitrosobenzene for which the esr parameter, $a_N = 11.213$ gauss, revealed that it was nitroxide radical. We also observed 3 multiplets esr spectra, $a_N = 11\text{-}12$ gauss, from the solutions of alkenes and nitrosobenzene which showed the presence of nitroxide radicals and we have suggested that they are formed by the mechanism proposed by A.B. Sullivan, 1966 (see reaction 4.8). We conclude that the possibilities that nitroxides produced from the reactions of NO_2 with alkenes in the presence of a small amount of nitrosobenzene could be the two mechanisms just mentioned, together with nitroxides produced from β-nitroalkyl radicals trapped by nitrosobenzene.

The results which we obtained from our experiments revealed that the nitroxides produced from β-nitroalkyl radicals trapped by nitrosobenzene were the only radical products observed from reactions of NO_2 with alkenes and a small amount of nitrosobenzene. Esr spectra detected from these reaction products were different from those detected from reactions of alkenes with nitrosobenzene (Table 5.1), and hyperfine coupling constants of protons of alkyl moiety at β-position of nitroxides revealed the nature of the trapped alkyl radicals, and we assumed the values of β-hydrogen hyperfine coupling constant were in similar to their corresponding primary, secondary, or tertiary alkylaryl nitroxides as shown in Table 5.3. These results (Table 5.1) confirm that β-nitroalkyl radicals are initial radical intermediates of the addition reactions of NO_2 with alkenes.

Table 5.3

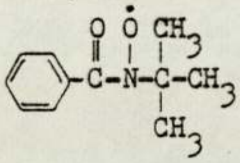
Hyperfine coupling constants (in gauss) of some alkylarylnitroxides, and diarylnitroxides.

Ar	R or Ar	Solvent	a_N (gauss)	$a_{H(o-)}$	$a_{H(m-)}$	$a_{H(p-)}$	$a_{H(R)}$	Reference
C_6H_5	$-CH_3$	-	11.0	2.9	1.0	2.9	10.4	1
C_6H_5	$-CH_2CH_3$	-	11.1	2.9	1.0	2.9	8.3	1
C_6H_5	$-CH(CH_3)_2$	-	11.1	2.8	0.9	2.8	2.8	2
C_6H_5	$-C(CH_3)_3$	Ethylene glycol	13.4	1.9	0.8	1.9	-	3
C_6H_5	C_6H_5	Benzene	10.9	1.97	0.77	1.97	-	4,5

References:
1. G.Chapelet-Letourneux et al., 1965
2. H.Lemaire et al., 1964
3. H.Lemaire et al., 1965
4. J.R.Thomas, 1960
5. J.C.Baird, 1960

5.3.2 Phenyl N-tert-butyl nitrone (PBN)

We found that phenyl N-tert-butyl nitrone reacted with NO_2 to give acyl nitroxide (5-III) of which the esr spectrum showed 3 lines a_N = 8.078 G (Table 5.2) as has been reported by L.V.Okhlobystina et al., 1975.



(5-III)

In the reactions of low concentration of NO_2 with alkenes in the presence of phenyl N-tert-butyl nitrone, we always found that acyl nitroxide (5-III) was produced together with radical products from reactions of low concentration of NO_2 with alkenes. We never observed nitroxides (5-II) whose esr spectra showed 3 doublets , a_N = 14 G, $a_{H(\beta)}$ = 2-3 G, from these reactions of which we propose that the nitroxides (5-II) are the result of β-nitroalkyl radicals trapped by phenyl N-tert-butyl nitrone as in equation (5.2). For example, the reaction of low concentration of NO_2 with iso-butene in the presence of phenyl N-tert-butyl nitrone produced alkyl nitroxide (4-IX) and acyl nitroxide (5-III). The reaction of low concentration of NO_2 with 2-methyl-2-butene in the presence of phenyl N-tert-butyl nitrone produced alkyl nitroxide (4-III) and acyl nitroxide (5-III) without the presence of nitroxide (5-II). A similar result was obtained from the reaction of low concentration of NO_2 with methyl methacrylate in the presence of phenyl N-tert-butyl nitrone (Table 5.2).

From these results, we suggest that both alkenes and phenyl N-tert-butyl nitrone react with NO_2 by their own mechanisms to give nitroxides. Phenyl N-tert-butyl nitrone did not behave as spin trap for β-nitroalkyl radicals because this nitrone could trap only less bulky radicals or resonance stabilised radicals (E.G.Janzen, and B.J.Blackburn, 1969).

5.4 Mixed-Flow Method

The method of generating short-lived free radicals in solution within the cavity of esr spectrometer by fast flow-mixing technique was applied in order to observe β-nitroalkyl radicals in our study. We expected to obtain esr spectra with g-values of about 2.0026 from continuous flow experiments in which solutions of low concentration of NO_2 were mixed with cis-2-butene, 2-methyl-2-butene, iso-butene, and α-methylstyrene.

In our experiment, under flow conditions of approximately 0.60 ml/sec of each reactant, the reaction mixtures did not give rise to any free radical signal. Upon stopping the flow of the reactants, the esr spectra showed a gradual increase in spectral intensities of nitroxide radicals with a_N of about 14 G which we usually observed from reactions carried out by employing ordinary technique. When the reactants were allowed to flow at a rate of approximately 0.30 ml/sec, the reaction mixtures were detected to give rise to the same nitroxide radicals as we obtained from stopping the flow of reactants.

From the result obtained, we suggest that the β-nitroalkyl radicals are slowly generated in a rate determining step in which the first molecule of NO_2 adds to the alkene. The rate of the addition of the second molecule of NO_2 to the initial radical intermediate is faster than the addition reaction of the first NO_2 molecule. When the experiments were carried out at flow rates which were faster than the rate determining step of NO_2 addition reaction, the reactions of NO_2 with alkenes in esr cavity had not started, and when the flow rate was equal or slower than the rate determining step resulted in β-nitroalkyl radicals which further reacted with the second NO_2 molecule rapidly and continued further reactions to produce nitroxides. Upon stopping the flow of the reactants the observed gradual increase in spectral intensities of nitroxides revealed that β-nitroalkyl radicals were slowly produced and further reacted with the second molecule of NO_2. We suggest that β-nitroalkyl radicals were present in the reaction mixtures in esr cavity but in too low concentrations to be detected because these radicals, when they were produced, did not accumulate in the reaction mixtures.

Conclusion

The conclusion of employing spin trapping and mixed-flow techniques to study the initial radical formations from the addition reactions of NO_2 with various alkenes is that we observed the β-nitroalkyl radicals formations by trapping β-nitroalkyl radicals with nitrosobenzene. Using phenyl N-tert-butyl nitrone as spin trap, or using mixed-flow technique fail to confirm the presence of β-nitroalkyl radicals from the reaction studied.

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