STUDIES OF SOME CATALYTIC PROPERTIES OF ZEOLITES

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SUMMARY

The use of Y-type zeolites as catalysts for the vapour phase Beckmann rearrangement of alicyclic oximes has been investigated, particularly for the conversion of cyclopentanone oxime to 2-piperidone. The rearrangements of cyclopentanone oxime and cyclohexanone oxime were studied spectroscopically, and the conversion of cyclopentanone oxime studied further using a flow system. The active sites for the Beckmann rearrangement have been identified as surface hydroxyl groups located at specific sites within the zeolitic lattice. The most efficient catalysts for the rearrangement, therefore, are the decationated or hydrogen zeolites. The interaction of cyclohexanone oxime with zeolites containing no surface hydroxyl groups has also been studied, and the nature of the interaction inferred. The formation of an alkene-nitrile on this catalyst is indicated by the infrared spectra obtained.

Using a flow system, the rearrangement of cyclopentanone oxime to 2-piperidone was studied as a function of the catalyst, temperature, solvent and carrier, and the results of the spectroscopic studies were confirmed and extended. The formation of 2-piperidone has been shown to be a function of catalyst acidity, and the reaction on zeolites containing no surface hydroxyl groups was shown to result in the formation of an alkene-nitrile. The formation of the latter is a function of the electrostatic potential of the zeolitic cation. Cyclopentanone, which is formed in small amounts for all catalysts studied, probably results from hydrolysis of the oxime by residual zeolitic water.

The reason for the short catalyst lifetimes for the rearrangement of cyclopentanone oxime to 2-piperidone is formation of carbon on the catalyst surface. This results from decomposition of the rearrangement product, which is strongly held on the surface. It is predicted that decationated zeolites should be efficient catalysts for the rearrangement of oximes which are stable, and which produce stable products.

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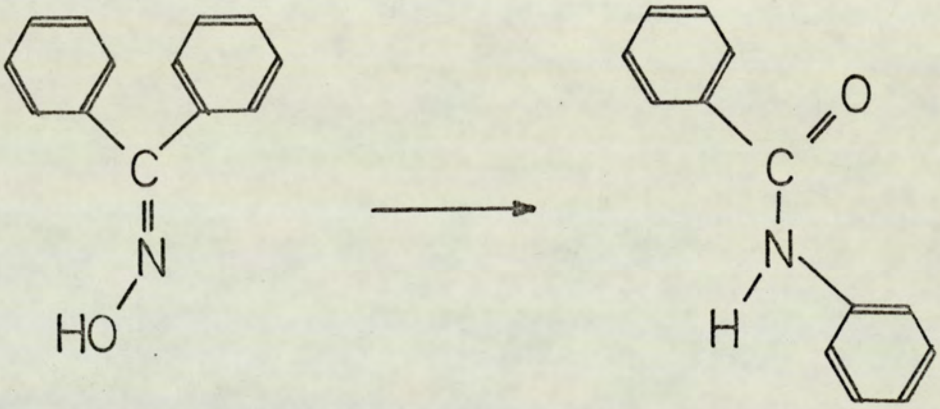
CHAPTER 1

INTRODUCTION

1.1. Reason for the present study and organization of the work.

In 1886 Ernst Otto Beckmann first discovered that benzophenone oxime (I) reacts vigorously with phosphorus pentachloride to form benzanilide (II). The rearrangement of oximes to substituted amides was later named by Victor Meyer as the Beckmann rearrangement. Many reagents have been found to catalyze the conversion, and the mechanism of the homogeneously catalyzed reaction has been the subject of much research. (See section 1.2).



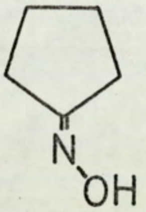
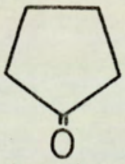
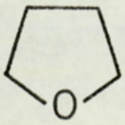
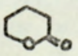
I   II

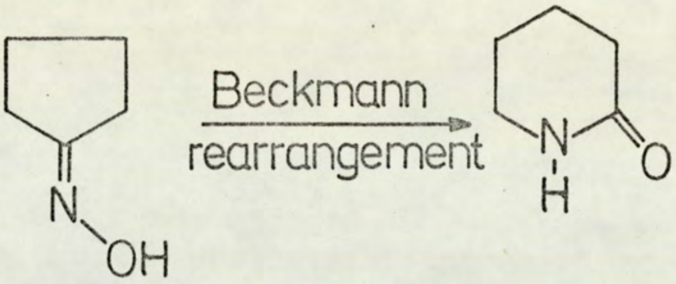
One of the most commonly employed catalysts for the Beckmann rearrangement of ketoximes is concentrated sulphuric acid, however, such rearrangements are often highly exothermic, and precautions must be taken to keep them under control. Usually only small amounts of oxime are rearranged at a time, or the oxime is added to the acid at such a rate that just enough heat is evolved to keep the reaction mixture at the required temperature. The major drawback of the sulphuric acid catalyzed reaction however, from an economic standpoint, is that the product is obtained in admixtures with acid. If only small quantities of acid were required to catalyze the rearrangement, this would not be a serious problem, but since the acid is normally also employed as the reaction solvent, neutralization requires large quantities of base. The neutralization stage must proceed slowly, and the reaction vessel must be held in an ice-salt mixture, otherwise the increase in temperature due to the heat of neutralization causes hydrolysis of the amide. Many of the homogeneous reactions catalyzed by other reagents, while giving good yields of amide, suffer from similar difficulties. Some of them employ the use of autoclaves, whilst others are time consuming.

The advantages of a heterogeneously catalyzed reaction are twofold. Firstly, since the reaction can be performed using an organic solvent rather than in acid solution, no neutralization of the reaction medium is necessary. Secondly, the rearrangement can be brought about continuously, using a flow system. Solid catalysts can usually be regenerated, and the organic solvent can be reused. The principal disadvantage of heterogeneous catalysis of this reaction has been the formation of unwanted by-products, particularly alkene-nitriles from the rearrangement of alicyclic oximes. Nearly all studies of the heterogeneously catalyzed reaction have been made on the rearrangement of cyclohexanone oxime to ϵ-caprolactam (1,2,3), since the latter is an important intermediate in the polymer industry. ϵ-Caprolactam is usually prepared industrially by the sulphuric acid catalyzed conversion of cyclohexanone oxime, but recently it has been reported that this rearrangement can be effected by crystalline aluminosilicate catalysts (4).

In recent years there have been many studies directed towards the synthesis of the pyridine and piperidine ring and their derivatives. This work has gained momentum recently due to the advent of North-Sea gas, and the run down of town-gas plants. Thus many of the by-products of town-gas manufacture must now be sought from other sources. Pyridine and piperidine derivatives are among this class of compounds. One of the most useful of the piperidine derivatives with regard to further synthesis (5) is 2-piperidone (IV). There have been many studies directed at the synthesis of 2-piperidone (Table 1), mostly employing the Beckmann rearrangement of cyclopentanone oxime (III). Whilst often producing 2-piperidone in high yields, these homogeneous preparations usually suffer the disadvantages outlined above.

TABLE 1: PREPARATIONS OF 2-PIPERIDONE

REACTANT	CONDITIONS	YIELD	REF.
(1) 	(1) H_2SO_4 80 - 90%	50-98	eg. 6
	(2) Polyphosphoric acid, 10 min. at 130°	74	7
	(3) HF at R.T. - product contaminated with HF salts	74	8
	(4) $SOCl_2$ in $CHCl_3$ at -5°, temp. slowly to 38°	32	9
	(5) Br_2/liquid SO_2, R.T. 1hr.	37	10
(2) 	+HN_3 in polyphosphoric acid (15 fold X's) - heat several hrs. (Schmidt reaction)	78	11
(3) $NC(CH_2)_4NH_2$	+H_2O at 150° - 180°, 4hr. autoclave	94	12
(4) $Cl(CH_2)_4COOH$	+liq. NH_3 autoclave 10hr. 250°	93	13
(5) $Cl(CH_2)_4CN$	+H_2O+NH_3, 2hr. 180° autoclave	83	14
(6) $Cl(CH_2)_4COCl$	(i) +NH_3 → $Cl(CH_2)_4CONH_2$ (ii) NaOEt	82	15
(7) 	(i) $CH_3COCl/ZnCl_2$ 30 - 78° 2 hr. → $Cl(CH_2)_4OAc$ (75%) (ii) +NaCN in THF, autoclave 100°, 3hr. $NC(CH_2)_4OAc$ (iii) +H_2SO_4 100 - 120°, 6 - 7hr. →  (90-95%) (iv) liquid NH_3, autoclave 280 - 310° 6hr. → 2-Piperidone (81%)	~55	16



III IV

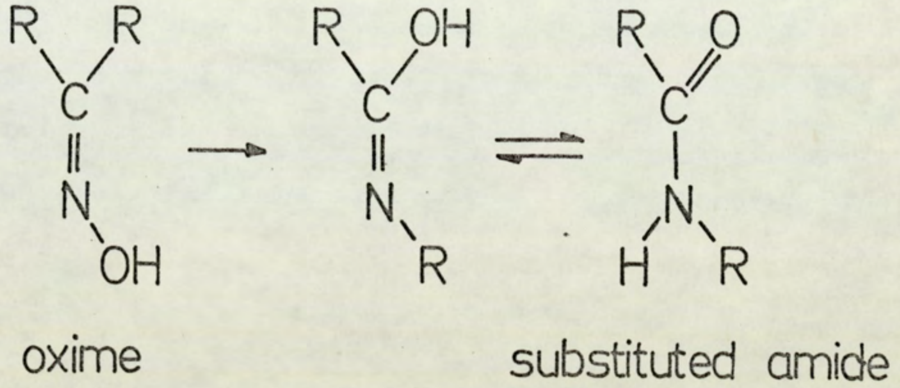
The work reported in this thesis is an evaluation of the use of crystalline aluminisilicates as catalysts for the vapour phase Beckmann rearrangement, particularly for the conversion of cyclopentanone oxime to 2-piperidone. The rearrangement of both cyclopentanone oxime and cyclohexanone oxime is studied spectroscopically, and the rearrangement of cyclopentanone oxime is further studied in a flow system. The results of the spectroscopic studies are presented in Chapter 2, and then a study of the rearrangement of cyclopentanone oxime over various catalysts is reported in Chapter 3. The effects of varying the conditions of reaction for the rearrangement of the five-membered ring oxime on decationated zeolites are presented in Chapter 4, and catalyst lifetime studies and poisoning are discussed in Chapters 5 and 6 respectively.

1.2. The homogeneously catalyzed Beckmann rearrangement.

The literature concerning the homogeneously catalyzed Beckmann rearrangement is voluminous and has been reviewed several times (17,18,19). Unfortunately, of the hundreds of publications dealing with the rearrangement, only a few are of a quantitative nature, and since the reaction was discovered progress in the elucidation of its mechanism has been slow. A brief summary of the principal aspects of the reaction is presented in this section. Such information is essential to enable comparison between the homogeneously catalyzed and heterogeneously catalyzed reactions.

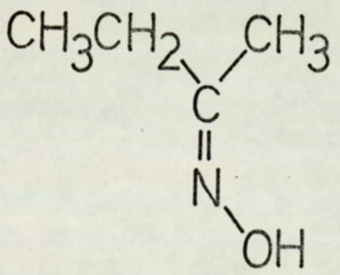
1.2.1. Rearrangement of acyclic ketoximes.

In general terms the rearrangement involves the migration of one of the oxime substituents to the nitrogen atom, and the transfer of the hydroxyl group from nitrogen to carbon:



1.2.1.1. Stereochemistry.

Since asymmetric ketoximes can exist in two stereochemically distinct forms, there is a need for a convention by which the two isomers can be distinguished. The most commonly accepted convention is the one by which the configuration is referred to as syn- or anti- when the hydroxyl group is cis or trans respectively to the first group named.

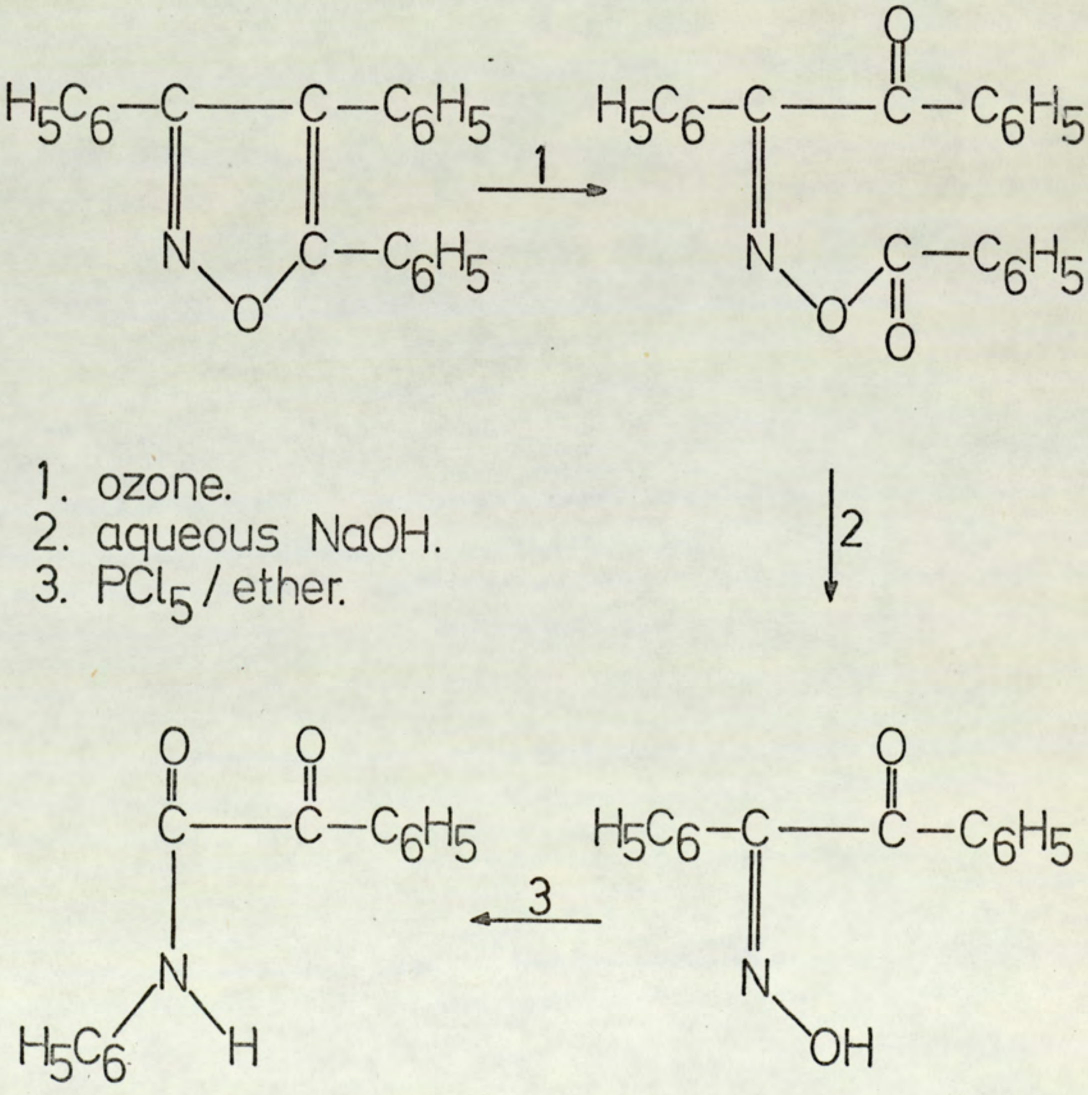


syn-methyl ethyl ketoxime

Depending upon which group migrates to the nitrogen, two possible amides can be formed from the rearrangement of asymmetric ketoximes. The reaction was shown to be stereospecific and independent of migratory aptitudes by Beckmann et al, (20,21) who isolated the two stereoisomeric benzil monoximes, and rearranged them seperately to form two different amides. Beckmann assumed that the migrating group was the one which was syn- in the original oxime, and up to about 1923 many oxime configurations were assigned on this basis.

In 1921 Meissenheimer (22) succeeded in preparing an oxime of known configuration, and was able to show, by identifying its rearrangement product, that the reaction had proceeded with anti- migration. From 3,4,5-triphenylisoxazole (V) Meissenheimer prepared a benzil monoxime with the structure (VI), which he rearranged to form benzoyl formanilide (VII). This amide was the opposite one to that expected on the basis of Beckmann's assumption. Later work indicated that no isomerization of the carbon-nitrogen

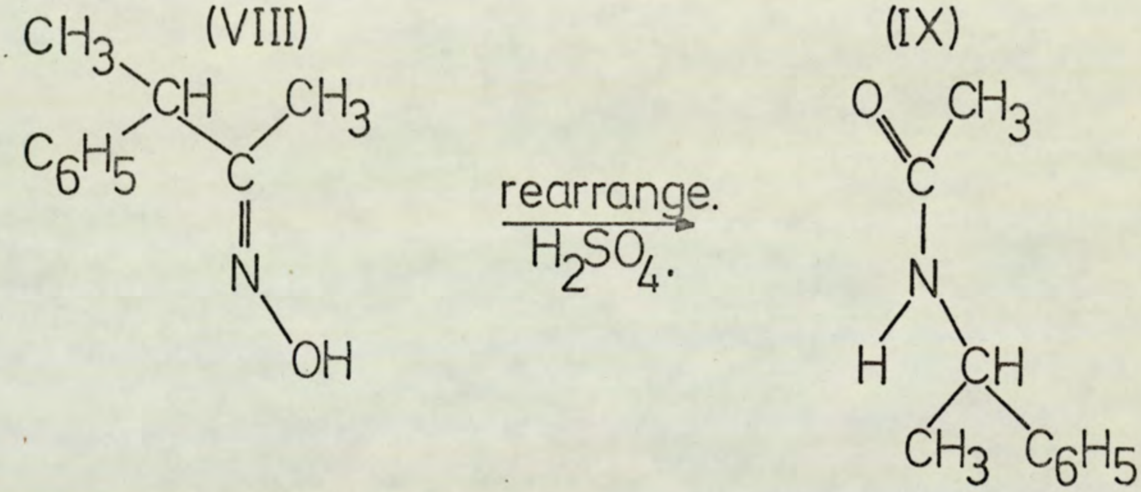
(V)



(VII) (VI)

bond occurred during ozonolysis (23), so substantiating Meissenheimer's demonstration of anti-migration. In all subsequent studies in which the structure of the oxime has been unequivocally determined, the amide obtained by rearrangement has been that resulting from anti-migration.

Migration of the oxime substituent was shown to be intramolecular by the use of optically active migrating groups (24,25). When (+)α- phenylethyl methyl ketoxime (VIII) is treated with sulphuric acid, N -α- phenylethyl acetamide (IX) is obtained in 99.6% optical purity, showing that at no time has the migrating group become detached from the rearranging molecule.

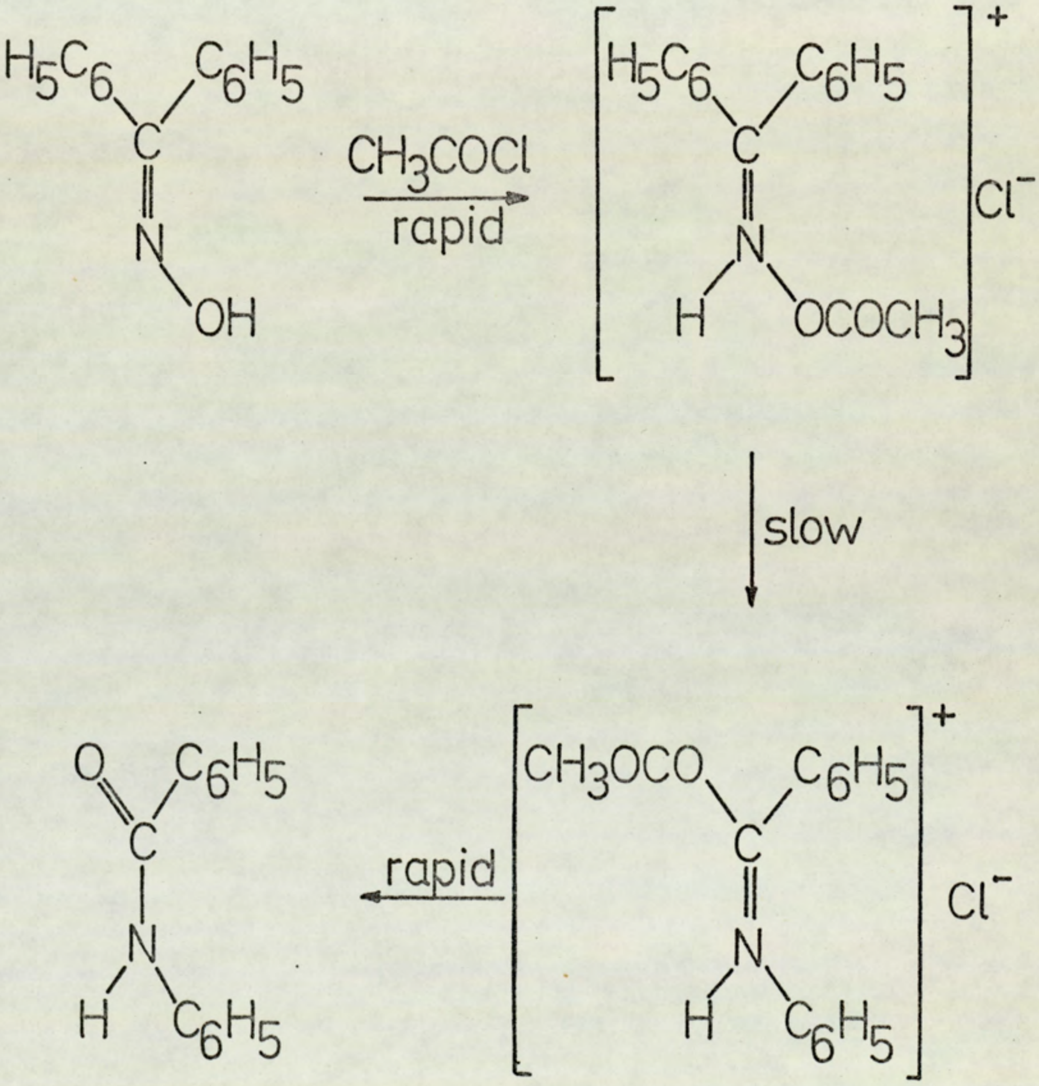

(VIII)
(IX)

The entire process, however, is not intramolecular. When benzophenone oxime is rearranged with phosphorous pentachloride in the presence of ^{18}O enriched water, the resulting benzanilide is found to contain the heavy isotope in the same concentration as the water in which it was formed (26). Since ^{18}O is known not to exchange with benzanilide under similar conditions (27), it is evident that at some stage during the transformation, the hydroxyl group must have been separated from the rest of the molecule.

1.2.1.2. Intermediates.

The diversity of reagents which are capable of catalyzing the Beckmann rearrangement suggests that no single intermediate is involved in the reaction. Much work has been reported, notably by Kuhara and Chapman, on the nature of the intermediates in the reaction, using specific catalysts. For example, while studying the catalytic effect of acid chlorides, Kuhara concluded that it is the ester of the oxime, and not the oxime itself which undergoes rearrangement. Certain esters, for example the benzenesulphonyl ester of benzophenone oxime, rearrange spontaneously (28), even in alkaline solution, whereas others, such as the acetate, require the presence of hydrogen chloride to bring about the rearrangement. Kuhara suggested that the mechanism of the rearrangement of benzophenone oxime (X), catalyzed by acetyl chloride is as follows:

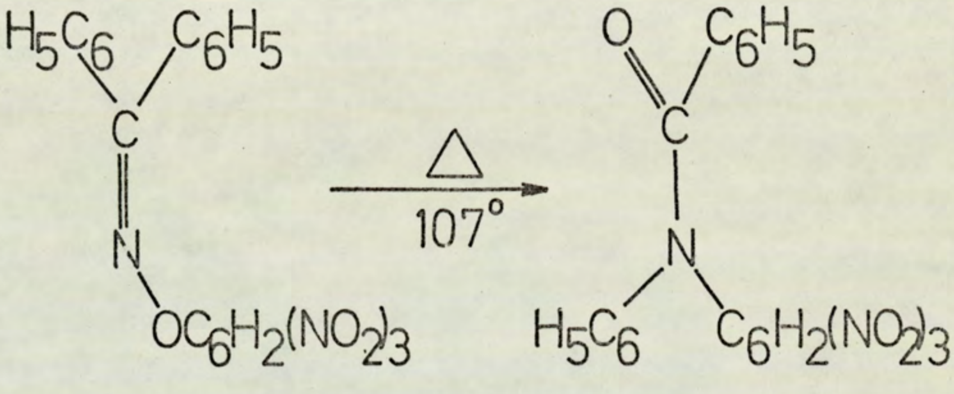
(X)



(XI)

When a series of acid chlorides was used to catalyze the reaction, the rate of production of benzanilide (XI) was found to depend upon the strength of the acid corresponding to the catalyst acyl group. In solution the rearrangement follows a unimolecular course at temperatures as low as 40°C, and the rate increases dramatically with the dielectric constant of the solvent.

Chapman (29), seeking to substantiate Kuhara's claims, succeeded in isolating benzophenone oxime picryl ether (XII), which rearranged almost explosively at its melting point into benz-N-picrylanilide (XIII).

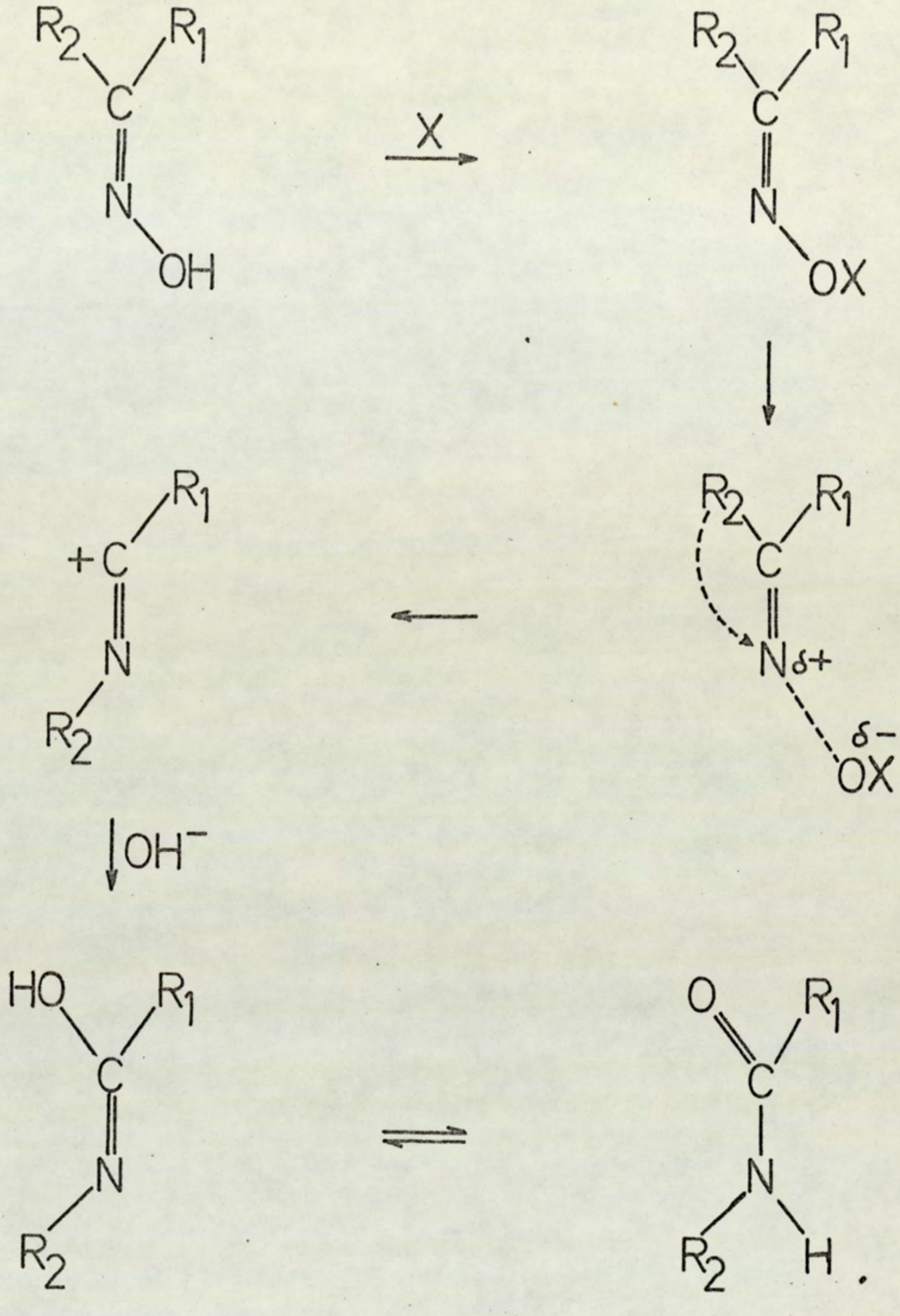


(XII) (XIII)

This work confirmed Kuhara's view that at least under certain conditions, the rearrangement involves the formation of an ester of the type R_2C=NOX. If the group OX is sufficiently electron attracting the transformation then takes place spontaneously to produce the amide RCONHR.

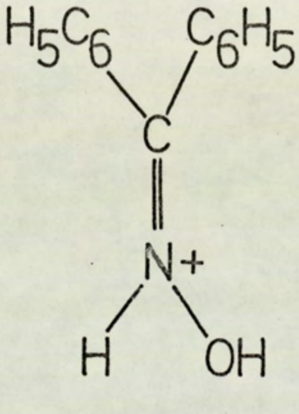
Electron attracting substituents in group R were shown to decrease the rate of reaction, and the converse was shown to be true when electron donating groups were substituted into R (30).

These results have indicated that the rate determining step in the transformation is the fission of the N-O bond of the intermediate ester or ether. The overall rate of reaction is governed, therefore, by the factors which facilitate this fission. The mechanism of the rearrangement under conditions expected to lead to esterification is thought to be represented by the scheme:

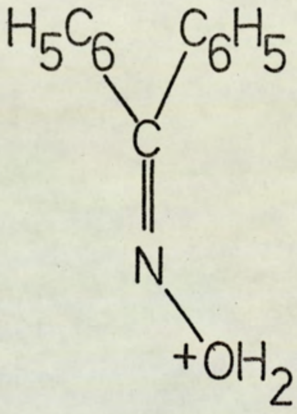


It has not yet been firmly established whether the fission of the N-O bond and the migration of the alkyl group are simultaneous or consecutive. The results of studies on isotope effects using ^{14}C in the migrating group have been ambiguous (31). A study has been reported (32) of the rates of reaction of a series of alkyl methyl ketoximes as a function of steric bulkiness of the migrating group. The rate was found to depend upon the size of the substituent, apparently supporting the simultaneous mechanism. Also in support of this mechanism is the fact that electron donating substituents in the migrating group increase the rate of rearrangement (30).

When the reaction is carried out in the presence of an acid, the first step in the rearrangement is thought to be proton donation to the oxime. The proton coordinates preferentially with the nitrogen of the oxime to form the relatively stable immonium ion (XIV), rather than with the oxygen to give a reactive oxonium (XV) (33).

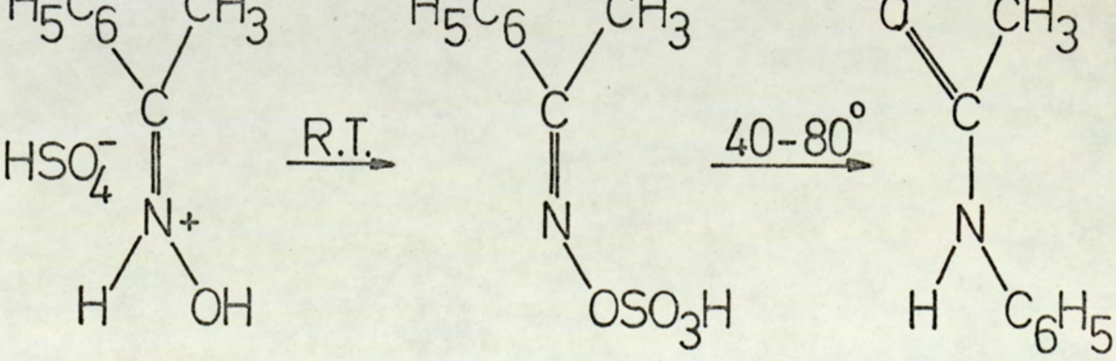


(XIV)



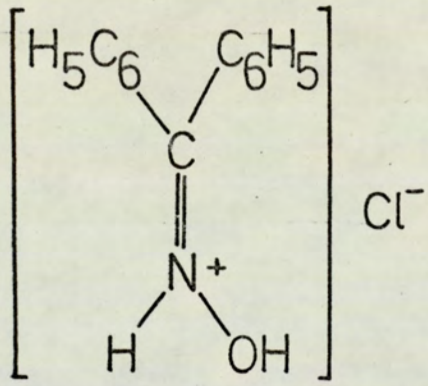
(XV)

For example when sulphuric acid is used to catalyze the reaction, an immonium hydrogen sulphate (XVI) is initially formed. This readily converts to the O-sulphonic ester (XVII), which undergoes the Beckmann rearrangement at relatively low temperatures (34).

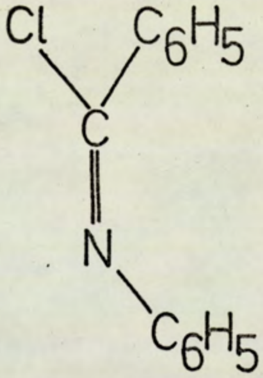


(XVI) (XVII)

When the reaction is catalyzed by hydrogen chloride, a more complicated mechanism is thought to be involved. An immonium chloride (XVIII) is initially formed, and this only rearranges at 125 - 150°C (35,36). Under these conditions evidence has been provided (37) for the formation of an imidochloride (XIX), which can form an ester-like compound with the oxime, and so catalyze the rearrangement. A similar intermediate is involved when phosphorus pentachloride is used as catalyst, under these conditions the imidochloride has been isolated and its configuration determined (38). N-Chloro compounds have been shown not to rearrange (39,40).



(XVIII)

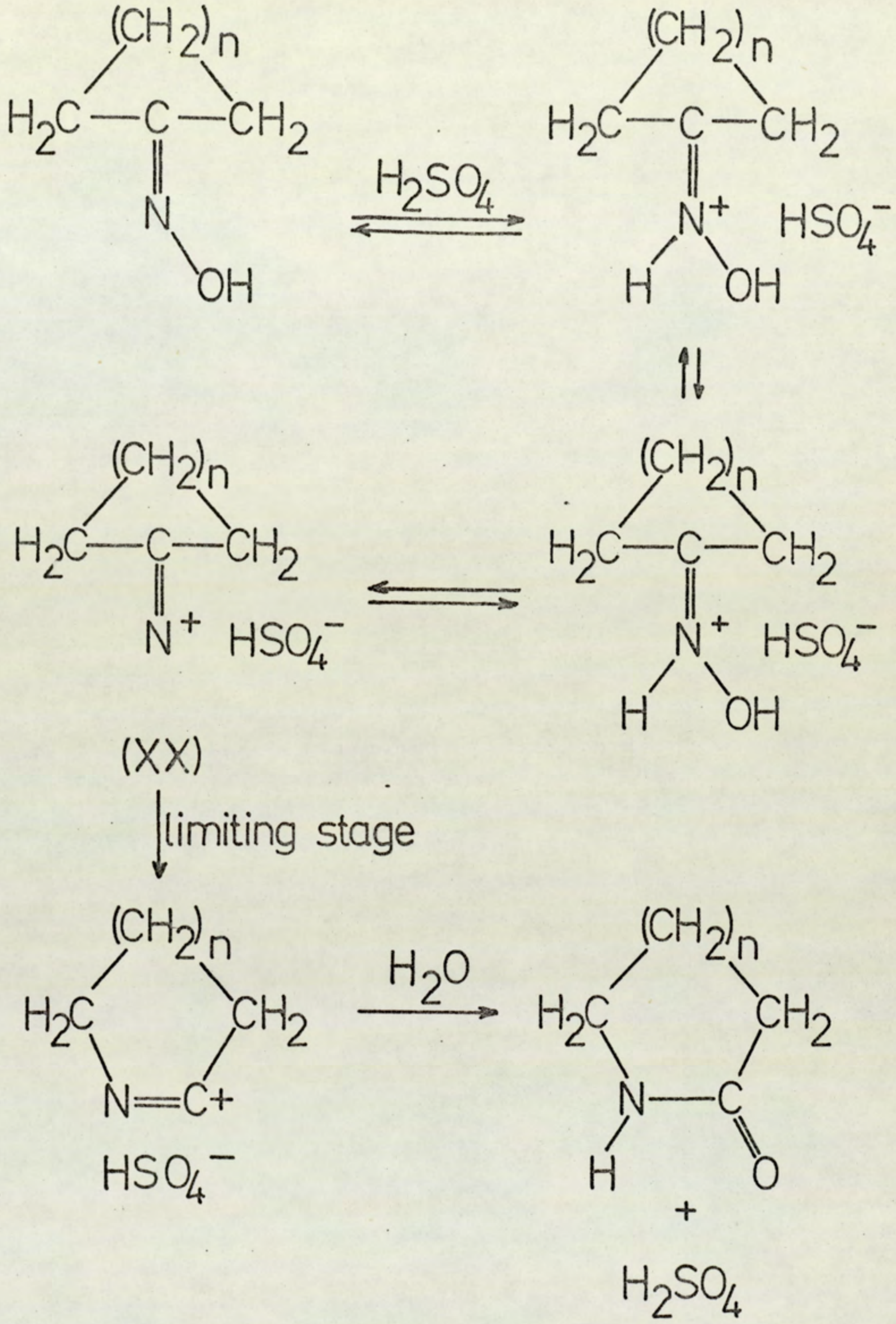


(XIX)

1.2.2. Rearrangement of alicyclic ketoximes.

A recent review by Vinnik and Zarakhani (41) has summarized the literature concerned with the Beckmann rearrangement of alicyclic ketoximes catalyzed by sulphuric acid and oleum. Very little work of a quantitative nature has been reported on similar rearrangements using other catalysts.

The review reveals that the postulated mechanism for the rearrangement of alicyclic ketoximes agrees essentially with that proposed by Kuhara and Chapman for the rearrangement of acyclic ketoximes in non-aqueous solutions. The reactive form is again thought to be the ester of the oxime and acid.



The limiting stage in this scheme can be either the dissociation of the N-O bond, or the rupture of the ring carbon-carbon bond in the dehydrated ion pair (XX). Arguing that (XX) could be in equilibrium with its products of dissociation, Vinnik and Zarakhani suggested that the limiting stage is the rupture of the carbon-carbon bond.

If compound (XX) does dissociate prior to the rate determining step, then one would not expect the reaction to be stereospecific. Hildebrand et al (42) obtained only one product from the rearrangement of 2-alkyl cyclanone oximes, however if dissociation had occurred the dissimilarity between the migratory aptitudes of the $-CH_2$ - and -CHR - substituents could possibly explain the stereospecificity observed. No studies have been reported in which both isomers of a substituted alicyclic oxime have been isolated and rearranged individually. Only in this way could the rearrangement of alicyclic ketoximes be shown to be stereospecific.

Although many publications have dealt with the mechanism of the Beckmann rearrangement, there are still several aspects of the transformation which are not fully understood. Perhaps the slow rate of progress since Beckmann first reported the reaction in 1886, has been due to the great diversity of conditions under which the reaction has been studied and reported.

1.3. The structure and properties of zeolites.

The literature concerning zeolites is summarized in this section, particular attention being given to those aspects of their structure and properties which relate to the present study.

Zeolites were so named as early as the mid eighteenth century, but really only began to gain importance as adsorbents as a result of Professor Barrer's work, which began in the late 1930's. Zeolites or molecular sieves as they are now often called, are crystalline aluminosilicates having the general formula $M_v\ (AlO_2)_x\ (SiO_2)_y \cdot zH_2O$. When the zeolite is prepared, M is usually sodium, and in this case v is equal to x. However, the sodium can be replaced easily and reversibly by many other cations, including ammonium ions. If it is replaced by a divalent atom, v becomes equal to x/2. Water can be removed from the sieves by heating. Molecules whose size allows them ingress into the pores of the zeolite may then be adsorbed. Zeolites have thus gained importance as a result of their drying properties, their selective adsorption properties and their ability to act as catalysts in many organic and some inorganic systems. Many zeolites occur naturally, but these, and some which do not occur in nature, may be synthesized on both a laboratory and an industrial scale. Several reviews have appeared within the last decade dealing with both the structure and properties of zeolites (43,44,45,46,47).

One of the advantages of using zeolites in catalytic studies is that, for the first time, they provide a catalyst which has a relatively well defined crystallographic structure. Substances like alumina and silica have proved difficult to characterize structurally, expecially when impregnated. This is often due to surface migration which can result in conglomerations of atoms.

There are several classes of zeolites, but the one which has proved to be most useful and the most versatile is faujasite. The three most utilized forms of faujasite are the A-, X-. and Y-types. The fundamental structural units of these zeolites are SiO_4^{4-} and AlO_4^{5-} tetrahedra, the extra negative charge on the aluminium tetrahedron being responsible for the relationship between v and x mentioned above. These units are linked together via shared oxygen bridges to form 4,6,8,12 and 18 membered rings, which join together to give a variety of structures. The unit containing six four membered rings and eight six membered rings is the sodalite unit, and these units join together via shared hexagonal and square faces, to form sodalite (Figure 1). Very few molecules can enter this structure, since the diameter of the six membered rings is only 2.2Å.

Type-A faujasite is obtained when sodalite units are joined by their square faces via four bridging oxygen atoms (Figure 2). The large cage enclosed by eight sodalite units is called the α-cage or supercavity, and the diameter of the eight rings of oxygen through which this supercavity is entered by molecules being adsorbed is 4.2 Å. Depending upon the operating temperature, this zeolite can selectively adsorb oxygen over nitrogen, ethane over propane, and propylene over propane (48). When the sodium ions in a type-A zeolite are exchanged with calcium ions, the effective pore diameter increases to 5Å (48). The crystal structure and positions of cations in these zeolites have been correlated with their adsorptive properties (49,50). The Si/Al ratio of type-A zeolite is one.

Types-X and -Y faujasite have the same framework but different Si/Al ratios (1.25 and between 1.5 - 3.0 respectively). They are formed when sodalite units are joined together by their hexagonal faces with six bridging oxygen atoms (Figure 3). The α-cages in the structure of sodium -X and sodium -Y have a critical entry pore diameter of about 9Å. The crystal structure of type-X zeolite has been studied by Broussard and Shoemaker (51), and by Olson (52). Dempsey and Olson (53) have shown how the population of cation sites varies with the water content of the zeolite. The cation positions in a cerium exchanged X zeolite

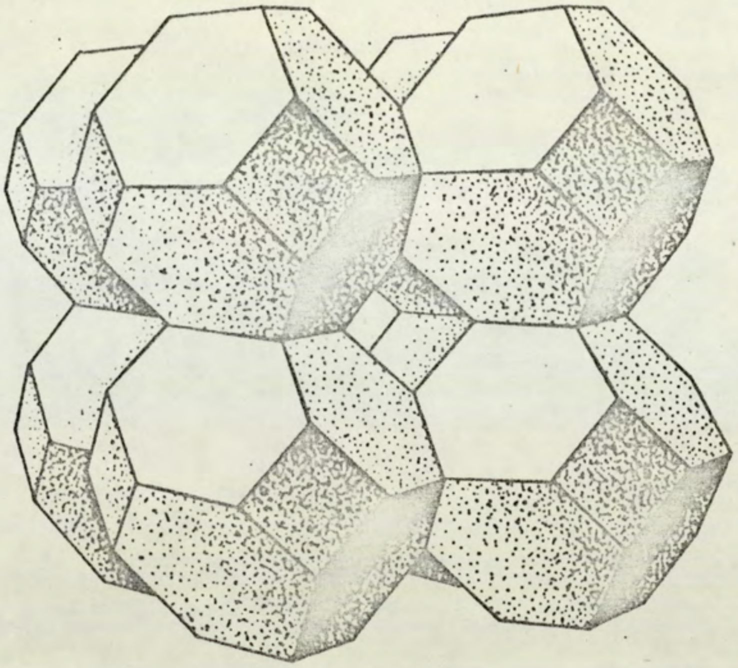


FIG. 1, sodalite.

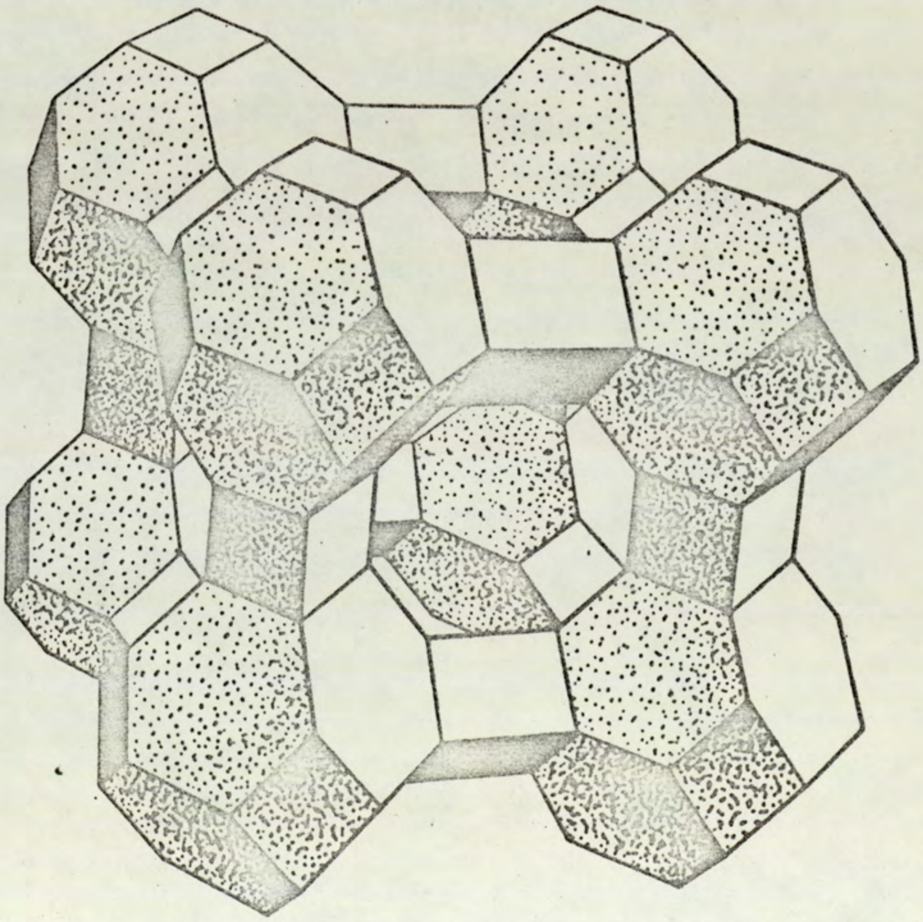


FIG. 2, type-A faujasite.

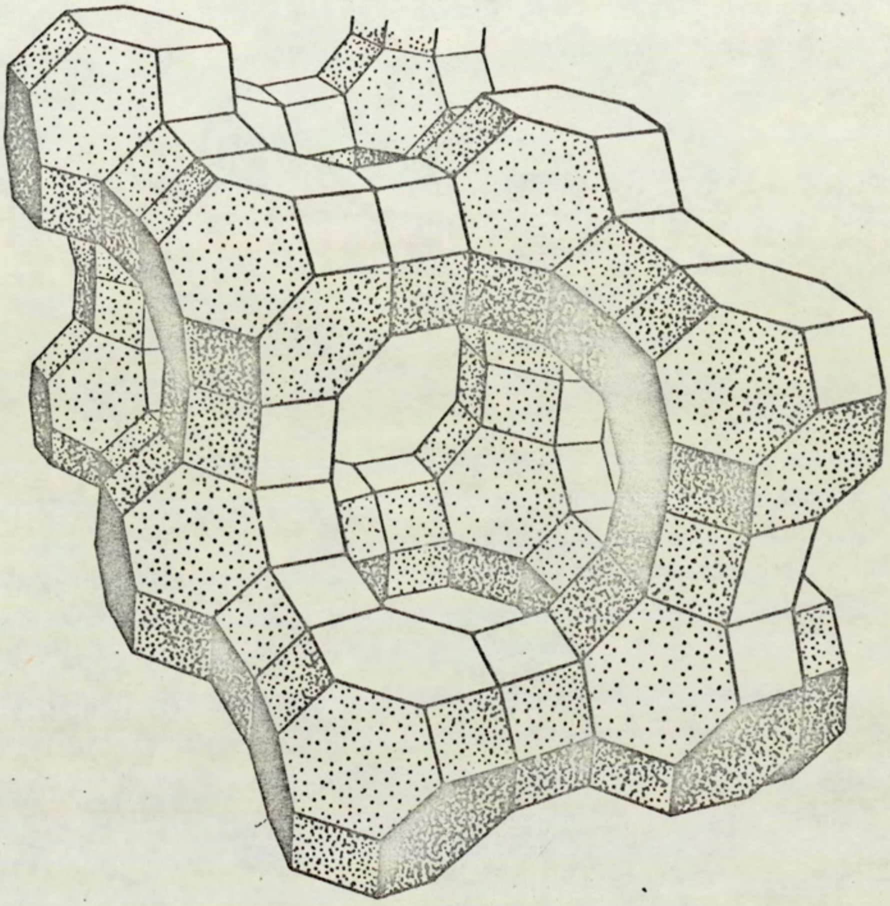


FIG.3, type-X & -Y faujasites.

have been reported by Hunter and Scherzer (54).

Since type-Y faujasites have been used principally in the present work, the structure of this zeolite will be discussed in some detail. Breck (44) has reported that the cations in a Y-type zeolite occupy three different crystallographic positions. Site I is in the centre of the hexagonal prism, site II on the six membered oxygen rings, and site III on the walls of the channels (Figure 4). Cations in both the SII and SIII positions project into the supercavity. The distribution of cations between these sites for a Y-type zeolite was reported by Breck as being:

site	I	II	III
number of cations	16	32	8.

A more rigorous treatment of the cation positions was reported by Eulenberger et al (55), who determined the crystal structure of dehydrated sodium-Y, and its potassium and silver homologues, using three dimensional fourier syntheses. The cation positions determined by these workers are illustrated in Figure 5 and schematically in Figure 6. They reported eight cations in the SI sites, thirty in the SII sites and nineteen in the SI' sites, which are situated on the inside of the sodalite cage, on the opposite side of the six membered oxygen rings to the SI sites. A further site, SII', is situated inside the sodalite unit opposite site SII. The distribution of cations between these sites has led to some controversy, and is apparently dependent upon the amount of water present in the sieves. It has been shown by Sherry (56) that the last sixteen sodium ions are more difficult to exchange with monovalent ions that the others, and it is likely that these are the cations located in the hexagonal prisms. Pure sodium-Y contains no structural hydroxyl groups, and is non-acidic (57).

When the sodium ions in sodium-Y are replaced by divalent cations, the latter have a strong preference for SI sites (58), and most of these must be exchanged before divalent cations

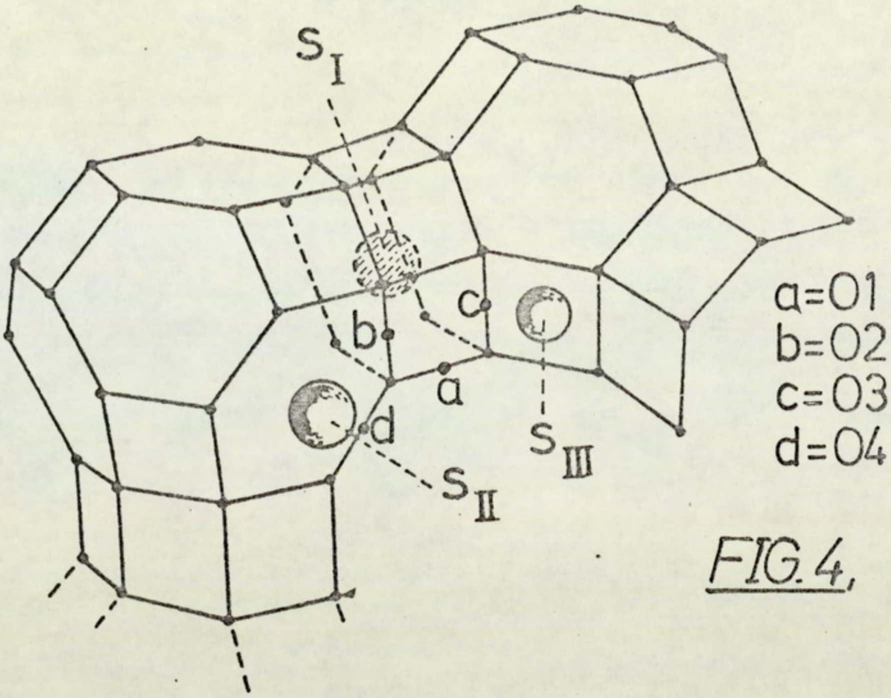


FIG.4,

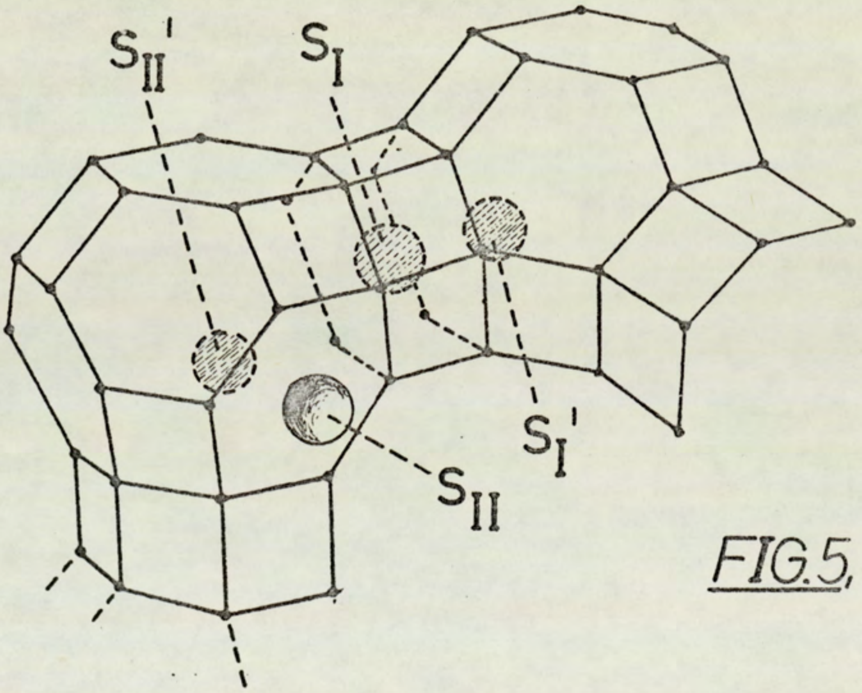


FIG.5,

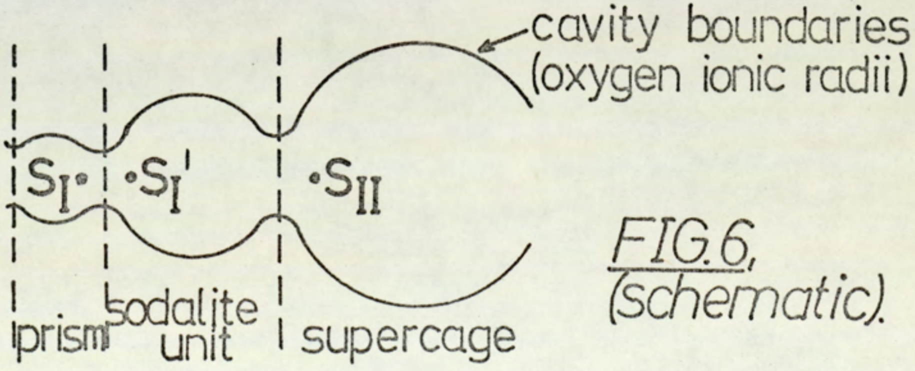


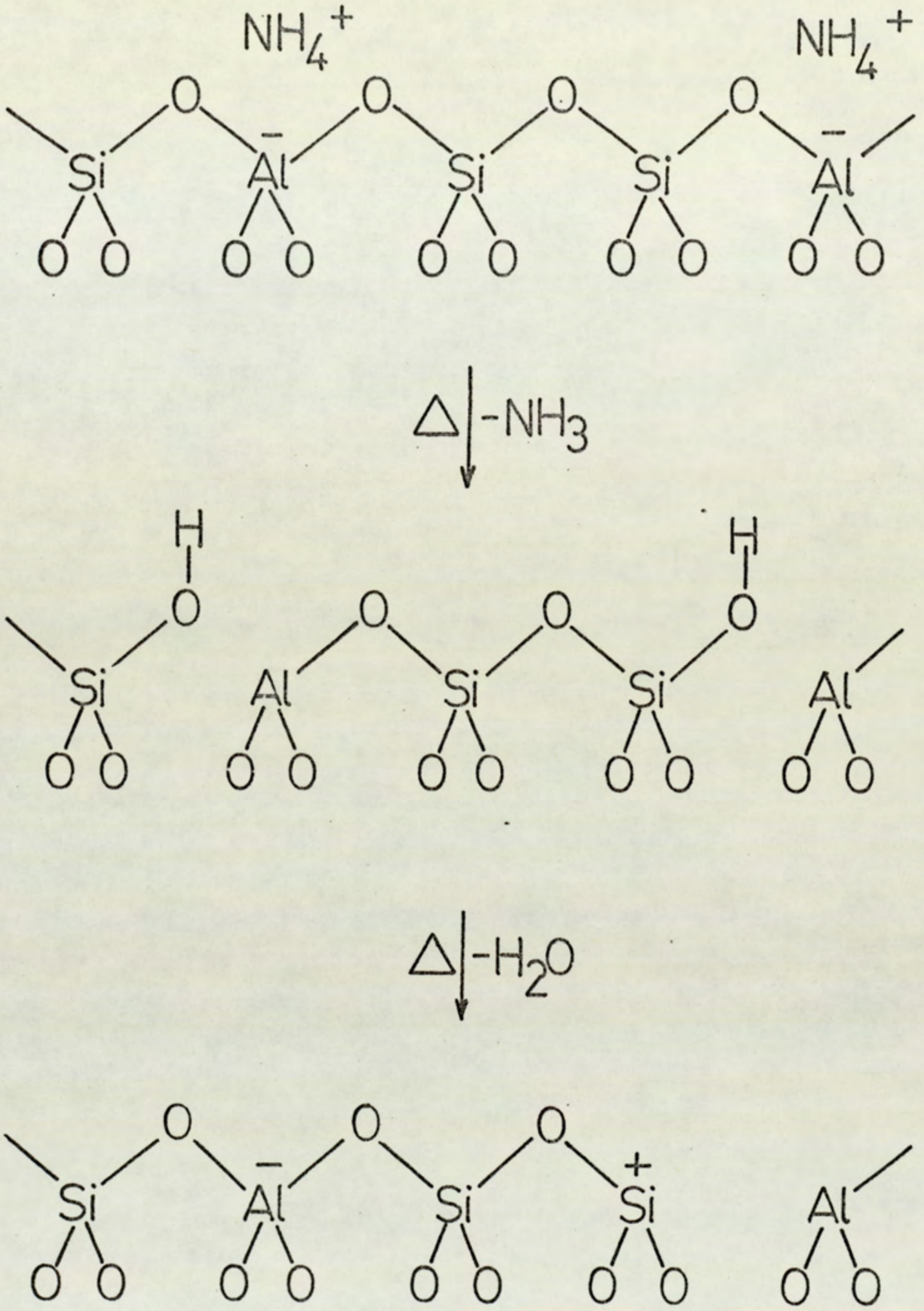
FIG.6,
(schematic).

cation positions in Y-type faujasite.

are exchanged into the catalytically active SII sites. It has been shown that about 45% of the original sodium ions in sodium-Y must be replaced by calcium ions before a substantial change in catalytic activity is observed. The reason for the SI site preference exhibited by divalent cations is thought to be that in the SII positions the cations have only three-fold oxygen ion coordination, whereas in the centre of two puckered six-oxygen rings, the SI sites, they can coordinate with six oxygen ions.

When the sodium ions in sodium-Y are exchanged with ammonium ions, and the zeolite calcined to about 450°, the ammonium ions decompose, and the protons liberated interact with the lattice oxygens to form surface hydroxyl groups (59). The product is hydrogen-Y or decationated-Y. The presence of structural hydroxyl groups on hydrogen-Y was confirmed by a study of the amount of hydrogen that it contains (60). This was measured by deuterium exchange, which indicated that hydrogen-Y (80% exchanged) contains about 2.5×10^{21} hydroxyl groups per gram of catalyst, after it has been activated to about 440°. This figure agrees well with the number of decationated sites calculated from the difference between the sodium and aluminium content of the lattice. Using infrared spectroscopy three different hydroxyl groups have been identified. These absorb near 3740, 3640 and 3540 cm^{-1} and have been assigned to hydroxyl groups located at different crystallographic positions within the zeolite lattice. The 3740 cm^{-1} band is usually weak, and is thought to represent Si - OH groups terminating the lattice, or amorphous impurities present in the structure. Many reports have dealt with the nature of the hydroxyl groups which absorb at 3640 and 3540 cm^{-1}. Much of the infrared work on zeolited has been summarized by Yates (61).

Ward (59) studied the adsorption of pyridine on hydrogen -Y and showed that the hydroxyl groups behave as Bronsted acid sites, if the calcination temperature is below 475°. If ammonium -Y (XXI) is heated above 475° then the bronsted acid form of hydrogen-Y (XXII) is converted to the Lewis acid form (XXIII). It was also shown that Bronsted acidity is responsible for the catalytic activity resulting in the conversion of cumene to propylene and benzene. Only the hydroxyl group at 3640 cm^{-1} was seen to interact with pyridine, however the 3540 cm^{-1} hydroxyl



(XXI)

(XXII)

(XXIII)

group hydrogen bonded with excess pyridine. On the basis of this work, Ward suggested that the bands at 3540 and 3640 cm^{-1} correspond to hydroxyl groups with different acidities, both of which are accessible to molecules inside the supercavity. Hughes and White (62) showed that the 3540 cm^{-1} band interacts with strong bases, such as piperidine and ammonia, and again concluded that both hydroxyl groups are situated in the supercavity. Other workers (63,64) have concluded that the 3540 cm^{-1} band represents hydroxyl groups situated in the hexagonal prisms, mainly on the basis of the non-interaction of this band with various adsorbed molecules. An interesting paper by Hansford and Ward (65) has related the intensity of the two hydroxyl bands to the degree of ion exchange of the zeolite. These authors found that the intensity of the 3640 cm^{-1} hydroxyl band increases almost linearly with the extent of decationation, whereas that of the 3540 cm^{-1} is low until the lattice contains about 5% sodium by weight, when the band intensity begins to increase rapidly. They concluded that the 3640 cm^{-1} band represents the most accessible hydroxyl groups, probably those located in the SII and SIII sites in the hydrated lattice. These authors also concluded that the 3540 cm^{-1} band corresponds to the removal of sodium ions from the SI sites, which are only removed at high levels of decationation. If the 3540 cm^{-1} band does correspond to the removal of these cations, and is therefore situated inside the hexagonal prisms, then the interaction of these hydroxyl groups with strong bases must be explained. Hansford and Ward suggested that the attraction associated with strong bases could be sufficient to remove the proton from the surface hydroxyl group. Also, it is known that delocalization of the hydrogen atoms can occur at elevated temperatures, and they may become free to migrate into the supercavity (66,67).

An X-ray study of hydrogen-Y by Olson and Dempsey (68) in which the positions of the protons were inferred from the Si (Al)-O distances, indicated that the 3640 cm^{-1} band arises from a proton attached to an O1 oxygen atom, and the 3540 cm^{-1} band from a proton attached to an O3 oxygen atom (Figure 4). These authors point out that most of the previous observations are consistent with this model, including those of Hansford and Ward (69).

In conclusion, it is not yet known with any degree of certainty where the hydroxyl groups responsible for the 3640 and 3540 cm^{-1} bands in the spectrum of hydrogen-Y are located. It seems probable from the available evidence that the 3640 cm^{-1} groups are accessible to molecules inside the supercavity, whereas the 3540 cm^{-1} groups are not, and the latter only interact with strong bases, or at elevated temperatures.

Surface hydroxyl groups are also present for certain cation containing zeolites. Although they have been reported for alkali-metal-Y type zeolites (70), it now appears that these materials do not contain hydroxyl groups, and are non-acidic (57).

Y-Type sieves containing alkaline earth cations do contain structural hydroxyl groups however, and are Bronsted acids if calcined below 500° (57). The hydroxyl groups on these zeolites are thought to arise as a result of the large electrostatic fields set up by the cations, which are able to dissociate water molecules to form M-OH and a surface hydroxyl group.

Many reactions have been reported to be catalyzed by various molecular sieves. For example, shape selective reactions (71,72,73), Friedel-Crafts alkylation (74), dehydrohalogenation (75), carbonyl condensation reactions (76), and the Beckmann rearrangement (4) have been found to be catalyzed. The exact nature of the active sites for each of these reactions has not been determined. The factors which effect the catalytic activity of zeolites were discussed by Venuto and Landis (46), but since then much infrared work has been published, and the importance of surface hydroxyl groups has been demonstrated, particularly for decationated zeolites (57,59,65).

The incorporation of a small amount of a noble metal into the lattice of hydrogen-Y has been shown to improve its catalytic activity for many reactions (77,78,79,80). Turkevich and Ohno (81) discussed this promoting effect, and suggested that the presence of a metal such as palladium favours the formation of Bronsted acid sites, and represses their conversion to Lewis acid sites. It has been shown (82) that each metal atom introduced into the lattice is equally effective until an optimum value of about 0.5% by weight is present, when any further addition causes little change in catalytic activity. This suggests that the metal atoms are highly dispersed within the zeolite lattice, and are perhaps present as individual atoms. An X-ray adsorption edge study by Lewis (83), however, has indicated that in a calcium-Y catalyst containing 0.5% by weight platinum, the latter is present in two sizes, and is probably not atomically dispersed. The promoting effect of noble metals, therefore, is not fully understood.

CHAPTER 2

INFRARED STUDIES ON THE HETEROGENEOUSLY CATALYZED BECKMANN REARRANGEMENT

2.1. Band assignments.

In order to obtain the maximum benefit from infrared studies of reactions on surfaces, it is essential to know the positions and origins of infrared bands which are characteristic of the reactant, possible intermediates and products. This knowledge can best be attained by studying the infrared spectra of these and related compounds as a function of their physical state, concentration and isotope exchange. Using these techniques the bands in the spectra of cyclopentanone oxime, cyclohexanone oxime, their monohydrochlorides, and the lactams and nitriles formed by their rearrangement have been given the following assignments. The spectra are presented in Appendix 1.

2.1.1. Cyclopentanone oxime and cyclohexanone oxime (Spectra 1 & 2).

The band assignments are listed in Table 2. The bands at 1290, 1450, 2870 and 2960 cm^{-1} for cyclopentanone oxime, and those at 1250, 1310, 1340, 1450, 2850 and 2930 cm^{-1} for cyclohexanone oxime are assigned by comparison of the spectra of these compounds with those of substituted cyclopentanes and cyclohexanes reported and interpreted by Szymanski (84). The hydroxyl bands for cyclohexanone oxime at 1235, 1365, 1480 and 3598 cm^{-1} have been assigned by Kimura et al (85), who studied changes in the spectra of cyclohexanone oxime and cyclohexanone oxime - d as a function of concentration. The assignments are consistent with the differences obtained in the present work between the spectra of cyclohexanone oxime recorded as a potassium bromide disc and that recorded as a solution in carbon tetrachloride (Spectrum 2). The corresponding assignments for cyclopentanone oxime are based on similar differences (Spectrum 1). The stretching vibrations of the C═N bond result in absorption bands at 1690 cm^{-1} for cyclopentanone oxime and 1662 cm^{-1} for cyclohexanone oxime. These assignments have been reported several times, for example by Bellamy (86) and Saito et al (87).

The bands at 1428 and 1435 cm^{-1} for the two oximes have not previously been discussed or assigned. They appear in the region of the spectrum where bending vibrations of carbon-hydrogen bonds are normally observed. Although one cannot assign the bands to any specific vibration, it is possible to partly explain their

TABLE 2: BAND ASSIGNMENTS FOR CYCLOPENTANONE AND CYCLOHEXANONE OXIMES

Frequency (cm^{-1})		Band assignment (i)
Cyclopentanone oxime	Cyclohexanone oxime	
	1250 , 1310 , 1340	$\delta'(CH_2)_{C6}$ RING
1290		$\omega(CH_2)_{C5}$ RING
1350	1235 , 1365	$\delta(OH)_{FREE}$
1428	1435	SEE TEXT
1450	1450	$\delta(CH_2)$
1470	1480	$\delta(OH)_{ASSOC.}$
1690	1662	$\nu(C = N)$
2870	2850	$\nu(CH)_{SYM.}$
2960	2930	$\nu(CH)_{ASYM.}$
3600	3598	$\nu(OH)_{FREE}$

(i) δ' = deformation; ω = wag; δ = bend; ν = stretch. These symbols are those used by Szymanski (84).

origin by studying the spectra of related compounds. Cyclopentane exhibits only one band in this region, at 1450 cm^{-1} corresponding to $\delta(CH_2)$; methyl cyclopentane and n-propyl cyclopentane exhibit bands at 1461 and 1462 cm^{-1} respectively (88). The spectra of these alkyl substituted cyclopentanes however, are complicated in this region by the presence of the $\delta(CH)_{ASYM.}$ absorption. Both cyclopentanol and bromocyclopentane exhibit two bands in this region, at 1440 and 1450 cm^{-1} for the alcohol, and at 1429 and 1449 cm^{-1} for the bromo compound (89). It appears that in the spectra of substituted cyclopentanes, the $\delta(CH)$ band is split, and while all the compounds show a band near 1450 cm^{-1}, the frequency of the other band is some function of the substituent. It is also noticeable that the intensity of the variable frequency band increases as its frequency decreases. In Figure 7 the position of the variable frequency band is plotted against the Taft polar (inductive) constant σ^*, for the appropriate substituent (90). The latter represents the electron attracting ability of the substituent. For substituents whose σ^* values are available, the position of the variable frequency band is shown in Figure 7 to be a function of the electron attracting ability of the substituent. Taft polar constants for the keto group (1408 and 1450 cm^{-1}) and oxime group (1428 and 1450 cm^{-1}) are unfortunately not available. It is known however, (91), that the electron attracting ability of the keto group is greater than that of the $=NR$ group, and so the values of 1408 cm^{-1} for cyclopentanone and 1428 cm^{-1} for cyclopentanone oxime are qualitatively consistent with the relationship indicated in Figure 7.

For the six membered ring series a similar relationship is not so noticeable. The variable frequency band usually only appears as a shoulder on the side of the 1450 cm^{-1} band for the larger ring system. Although the relationship illustrated in Figure 7 for a series of cyclopentanes cannot be tested for a series of cyclohexanes, qualitatively a similar tendency is indicated.

Similar relationships have previously been reported (92), for example O'Sullivan and Sadler (93) have shown the existence of a linear relationship between σ^* values and the carbonyl stretching frequency for a series of compounds of the type $RCOCH_3$.

Although no specific assignment can be made for the bands absorbing at 1428 cm^{-1} for cyclopentanone oxime and 1435 cm^{-1} for

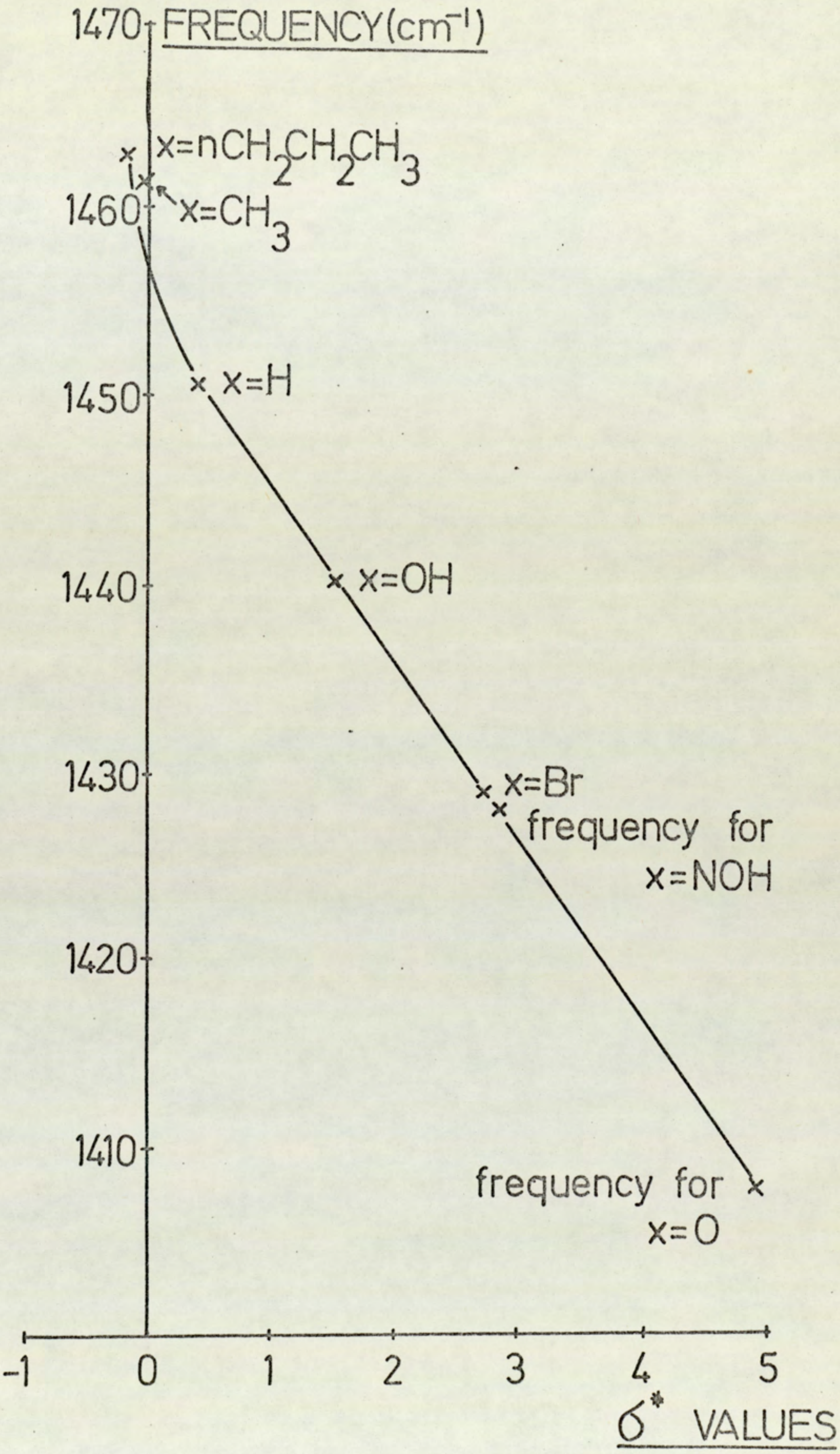


FIG. 7, variation of band frequency with inductive strength of substituent for cyclo-C_5H_9X.

cyclohexanone oxime, therefore, the position of these bands is clearly a function of the electron attracting ability of the ring substituent. Further evidence for this conclusion is presented in the next section, where the presence of a positive change on the ring substituent is seen to greatly effect the position of the bands in question.

2.1.2. Cyclopentanone oxime -HCl and cyclohexanone oxime -HCl (Spectra 3 & 4).

Since the surface of decationated zeolites is known to be highly acidic, it is possible that oximes are protonated upon adsorption. It is necessary, therefore, to be aware of the change which occur in the infrared spectra of cyclopentanone oxime and cyclohexanone oxime, when these compounds are protonated. This can best be achieved by a study of the spectra of the respective oxime hydrochlorides.

It has generally been concluded that when an oxime hydrochloride is formed, the proton becomes attached to the nitrogen atom of the oxime, rather than to the oxygen atom (94). There are several differences between the spectra of the hydrochloride salts and those of the parent oximes, and the bands characteristic of the protonated oximes are reported in Table 3, together with their assignments.

TABLE 3: BAND ASSIGNMENTS FOR CYCLOPENTANONE OXIME -HCl AND CYCLOHEXANONE OXIME -HCl.

Frequency (cm^{-1})		Band Assignment
Cyclopentanone oxime -HCl	Cyclohexanone oxime -HCl	
1394	1430	SEE TEXT
1720 & 1740	1700	$\nu(C=\overset{+}{N})$
2500 - 2900	2640	$\nu(\overset{+}{N}-H)$

The band which is observed at 1428 cm^{-1} for cyclopentanone oxime has a greater intensity in the spectrum of its hydrochloride derivative, and is shifted to 1394 cm^{-1} (Spectrum 3). Since the presence of a positive charge on the ring substituent will greatly increase its electron attracting ability, this shift provides further evidence for the relationship illustrated in Figure 7. The $\nu(C=N)$ band for cyclopentanone oxime at 1690 cm^{-1} has been replaced in the spectrum of its hydrochloride derivative by a band with peaks at 1720 cm^{-1} and 1740 cm^{-1}. This fairly broad band was reported by Saito and Nukada (87), and corresponds to a $\nu(C=\overset{+}{N})$ vibration. These authors have also reported a band at 2600 cm^{-1} for cyclopentanone oxime hydrochloride, and assigned it to $\nu(\overset{+}{N}-H)$. In the present work this vibration gave rise to a broad band between 2500 and 2900 cm^{-1}. The $\delta(OH)_{ASSOC.}$ band is present at 1470 cm^{-1} in the spectrum of cyclopentanone oxime hydrochloride, and this observation together with the change in frequency of the $\nu(C=N)$ band is good evidence for nitrogen protonation.

The spectrum of cyclohexanone oxime hydrochloride in a nujol mull has been reported by Saito (95), who assigned a band at 1696 cm^{-1} to a $\nu(C=\overset{+}{N})$ vibration, and a broad band centred near 2645 cm^{-1} to $\nu(\overset{+}{N}-H)$. In the present study the spectrum of cyclohexanone oxime hydrochloride was obtained both as a nujol mull, and as a potassium bromide disc. The nujol mull spectrum was identical to that reported by Saito. The spectrum of cyclohexanone oxime hydrochloride in the form of a potassium bromide disc (Spectrum 4) shows a few small differences from the nujol mull spectrum. The $\nu(C=\overset{+}{N})$ band is observed at 1700 cm^{-1}, instead of at 1696 cm^{-1}, and the oxime $\delta(OH)_{ASSOC.}$ band at 1480 cm^{-1}, which is not apparent in the nujol mull spectrum, is broadened to 1450 - 1500 cm^{-1} in the KBr disc spectrum. The broad $\nu(\overset{+}{N}-H)$ band which is observed near 2645 cm^{-1} in the mull spectrum, absorbs in the KBr disc spectrum at 2640 cm^{-1}.

The band which absorbs at 1435 cm^{-1} for cyclohexanone oxime is shifted down to 1430 cm^{-1} when the hydrochloride is formed. This shift is consistent with the presence of a positive charge on the ring substituent, and corresponds to the shift of the 1428 cm^{-1} band upon protonation of cyclopentanone oxime. Again, the spectrum of cyclohexanone oxime hydrochloride is consistent with nitrogen protonation. This is in agreement with the findings of Saito et al (87,95,96), who also concluded that when an oxime monohydrochloride is formed, the proton becomes attached to the nitrogen atom.

Evidence for nitrogen protonation of oximes does not come only from infrared spectroscopy. Saito and Nukada (87) have also studied the differences in NMR signals of cyclohexanone oxime and its hydrochloride, and found that the separation of syn- and anti- shifts for the α-methylene protons in cyclohexanone oxime is eliminated when the hydrochloride is formed. The authors concluded that the separation of signals for the oxime is due to interaction of the α-methylene protons with the lone pair on the nitrogen atom, and so the loss of separation for the hydrochloride salt indicates interaction of the nitrogen lone pair of electrons with the proton.

2.1.3. 2-Piperidone and ε-caprolactam (Spectra 5 & 6).

Surprisingly few reports have dealt with the interpretation of these spectra and so, partly due to their complexity, it has been impossible to assign several of the bands. The bands, together with some probable assignments are reported in Table 4.

The carbon-hydrogen stretching bands at 2860 and 2930 cm^{-1} for ε-caprolactam were assigned by Hall and Zbinden (97), who also assigned the δ'(CH) vibrations of the two lactams (98). The carbonyl stretching bands at 1650 and 1655 cm^{-1} have often been assigned, for example by Hall and Zbinden (97). The bands at 1550 and 1540 cm^{-1} for the two lactams result from the NH bending vibrations, and those at 1310 and 1314 cm^{-1} are believed to have a ν(CN) character (99). Horak and Gut (100) have reported a characteristic absorption band for lactams between 1490 and 1510 cm^{-1}, and assigned it to the scissoring deformation vibration of the methylene group next to the NH group. The band at 1495 cm^{-1} for 2-piperidone can tentatively be given this assignment. A study of the spectra of substituted cyclohexanes reported by Szymanski (84), reveals that a deformation vibration of the methylene groups in a six membered ring produces characteristic absorption bands near 1260 and 1350 cm^{-1}. These bands were observed in the spectrum of cyclohexanone oxime. Although 2-piperidone does not contain a six membered carbon ring, it is noticeable that its spectrum exhibits bands at 1270 and 1353 cm^{-1} which may result from a vibration of the methylene groups in the ring, similar to that observed for cyclohexane derivatives.

2.1.4. ε-Caprolactam hydrochloride (Spectrum 7).

Katritsky and Jones (101) have reported that the principal evidence in support of nitrogen protonation of amides comes from vibrational spectra. Bands thought to correspond to

TABLE 4: BAND ASSIGNMENTS FOR 2-PIPERIDONE AND ϵ-CAPROLACTAM

Frequency (cm^{-1})		Band
2-Piperidone	ϵ-Caprolactam	assignment
	1257	-
1270		$\delta'(CH_2)$ 6-MEMB. RING
	1290	-
1310	1314	$\nu(CN)$
1328		-
	1332	-
	1350	-
1353		$\delta'(CH_2)$ 6-MEMB. RING
	1365	-
1410		-
	1414	-
1448 & 1470	1438 & 1480	$\delta'(CH)$
1495		$(CH_2)_{SCISSOR}$
1550	1540	$\delta(NH)$
1650	1655	$\nu(CO)$
2870	2860	$\nu(CH)_{SYM.}$
2950	2930	$\nu(CH)_{ASYM.}$

$\nu(\overset{+}{N}H)$ vibrations have been observed (102) in the region 2000 - 2400 cm^{-1}, and it has also been suggested (103) that the change in the position of the carbonyl stretching frequency upon salt formation is consistent with nitrogen protonation. In the spectrum of ϵ-caprolactam hydrochloride (Table 5), the broad band centred near 2300 cm^{-1} is consistent with a $\overset{+}{N}H$ stretching mode. The bending vibration of this group (104) is only observed as a shoulder on the low frequency side of the carbonyl stretching band, at about 1550 cm^{-1}.

TABLE 5: BAND ASSIGNMENTS FOR ϵ-CAPROLACTAM HYDROCHLORIDE.

Frequency (cm^{-1})	Band Assignment
1550	$\delta(\overset{+}{N}H_2)$
2300	$\nu(\overset{+}{N}H)$

2.1.5. 4-Cyanobut-1-ene and 5-cyanopent-1-ene (Spectra 8 & 9).

The spectra of these compounds exhibit only a few peaks, all of which can be readily assigned (Table 6). These assignments

TABLE 6: BAND ASSIGNMENTS FOR 4-CYANOBUT-1-ENE AND 5-CYANOPENT-1-ENE.

Frequency (cm^{-1})		Band Assignment
4-Cyanobut-1-ene	5-Cyanopent-1-ene	
1420	1420 (Shoulder)	$\delta(CH_2)$
1428	1428	
1445	1442	
1642	1642	$\nu(C=C)$
2250	2250	$\nu(C\equiv N)$
2860	2880	$\nu(CH)_{CHAIN-SYM.}$
2930	2940	$\nu(CH)_{CHAIN-ASYM.}$
2980		
3080	3080	$\nu(=CH)$

are consistent with those given by Bellamy (86).

2.2. Reaction on a decationated zeolite.

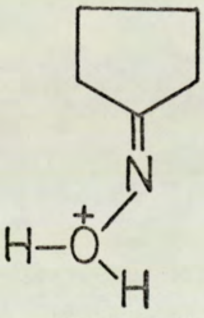
2.2.1. Cyclopentanone oxime on hydrogen-Y (Spectra 10 & 11).

The spectrum of hydrogen-Y obtained in the present work is essentially the same as that reported by many authors (see section 1.3 and Spectra 10a and 11a). The 3740 cm^{-1} band is not present, but hydroxyl bands are observed at 3640cm^{-1} and 3540 cm^{-1}. The origin of these bands was discussed in section 1.3. A small, fairly constant absorption was obtained for all zeolite samples near 1640 cm^{-1}, and is due to a small amount of water remaining in the sieve after the activation procedure.

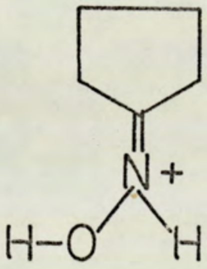
When cyclopentanone oxime is adsorbed onto hydrogen-Y at room temperature, and the excess removed by evacuation, the oxime is seen to interact with the surface hydroxyl group which absorbs at 3640 cm^{-1} (Spectrum 10c). In the region below 1800 cm^{-1} the principal changes in the spectrum of cyclopentanone oxime as a result of adsorption, are the loss of the ν(C=N) band at 1690 cm^{-1}, and the increase in intensity and shift of the 1428 cm^{-1} band to 1410 cm^{-1} (Spectrum 11c). The position and intensity of the latter band was shown in section 2.1.1.to be a function of the ability of the ring substituent to attract electrons. The decrease in intensity of the 3640 cm^{-1} surface hydroxyl band on addition of cyclopentanone oxime, and the shift to a lower frequency of the oxime 1428 cm^{-1} band, strongly suggests that proton donation has occurred from the surface hydroxyl group to the adsorbed molecule. The resulting positive charge on the oxime ring substituent increases its electron attracting ability, which is reflected in the shift of the oxime 1428 cm^{-1} band. The absence of the oxime ν(C=N) band at 1690 cm^{-1} in the spectrum of the adsorbed species indicates that the proton has become attached to the nitrogen atom of the oxime.

If protonation of the oxime nitrogen atom has occurred upon adsorption, then the spectrum of the adsorbed species (Spectrum 11c) should be comparable to that of cyclopentanone oxime hydrochloride (Spectrum 3). The two spectra do show many similarities, such as the replacement of the oxime ν(C=N) band at 1690 cm^{-1} with a broad, weaker band near 1720 cm^{-1}, and the presence of a broad strong band between 2500 cm^{-1} and 2900 cm^{-1}, corresponding to a $\nu(\overset{+}{N}-H)$ vibration. The principal difference between the spectrum of cyclopentanone oxime hydrochloride and that of cyclopentanone oxime adsorbed on hydrogen-Y, is the position of the oxime 1428 cm^{-1} band. The position of this band is a function of the electron attracting ability of the ring substituent, and is shifted from 1428 cm^{-1} to 1394 cm^{-1} upon formation of the oxime hydrochloride. In the spectrum of the adsorbed species, however, this band is only shifted to 1410 cm^{-1}, indicating that the electron attracting ability of the ring substituent in the adsorbed species is less than that in cyclopentanone oxime hydrochloride.

The shift of the oxime 1428 cm^{-1} band to 1410 cm^{-1} and not to 1394 cm^{-1}, can be explained in two possible ways. Firstly it could be argued that upon adsorption the oxime is protonated on the oxygen atom to form an oxonium ion (XXIV), rather than on the nitrogen atom to form an immonium ion (XXV). The positive charge would thus be further from the ring, and the electron attracting ability of the ring substituent would be less than for nitrogen protonation. One could also attempt to justify oxygen protonation by suggesting that the 1720 cm^{-1} shoulder is due to a $\delta(\overset{+}{O}H_2)_{ASYM}$ vibration, and that the broad band between 2500 and 2900 cm^{-1} is due to $\nu(\overset{+}{O}H)$. Studies on the $H_3\overset{+}{O}$ species have suggested that such vibrations do absorb in these regions (105,106). However, oxygen protonation cannot explain the considerable change which has occurred in the ν(C=N) band upon adsorption. Since most of the spectrum of the adsorbed species is very similar to that of cyclopentanone oxime hydrochloride, and since considerable evidence has been presented for nitrogen protonation of the latter, one must conclude that oxygen protonation upon adsorption is very unlikely.



(XXIV)



(XXV)

The second way in which it is possible to explain the shift of the oxime 1428 cm^{-1} band to 1410 cm^{-1} upon adsorption, and not to its hydrochloride value of 1394 cm^{-1}, is by partial charge delocalization between the protonated species and the zeolite lattice. This type of interaction is illustrated in Figure 8. In the interaction indicated the proton is shared between the surface and the adsorbed species. For the surface species shown, the electron attracting ability of the ring substituent is intermediate between that in cyclopentanone oxime and that in cyclopentanone oxime hydrochloride, and this is consistent with the shift of the oxime 1428 cm^{-1} band to 1410 cm^{-1}. The change in frequency for example of the ν(C=N) band, upon nitrogen protonation of the oxime, is due to both the change in electron distribution within the carbon nitrogen double bond, and the presence of an extra atom attached to the nitrogen.

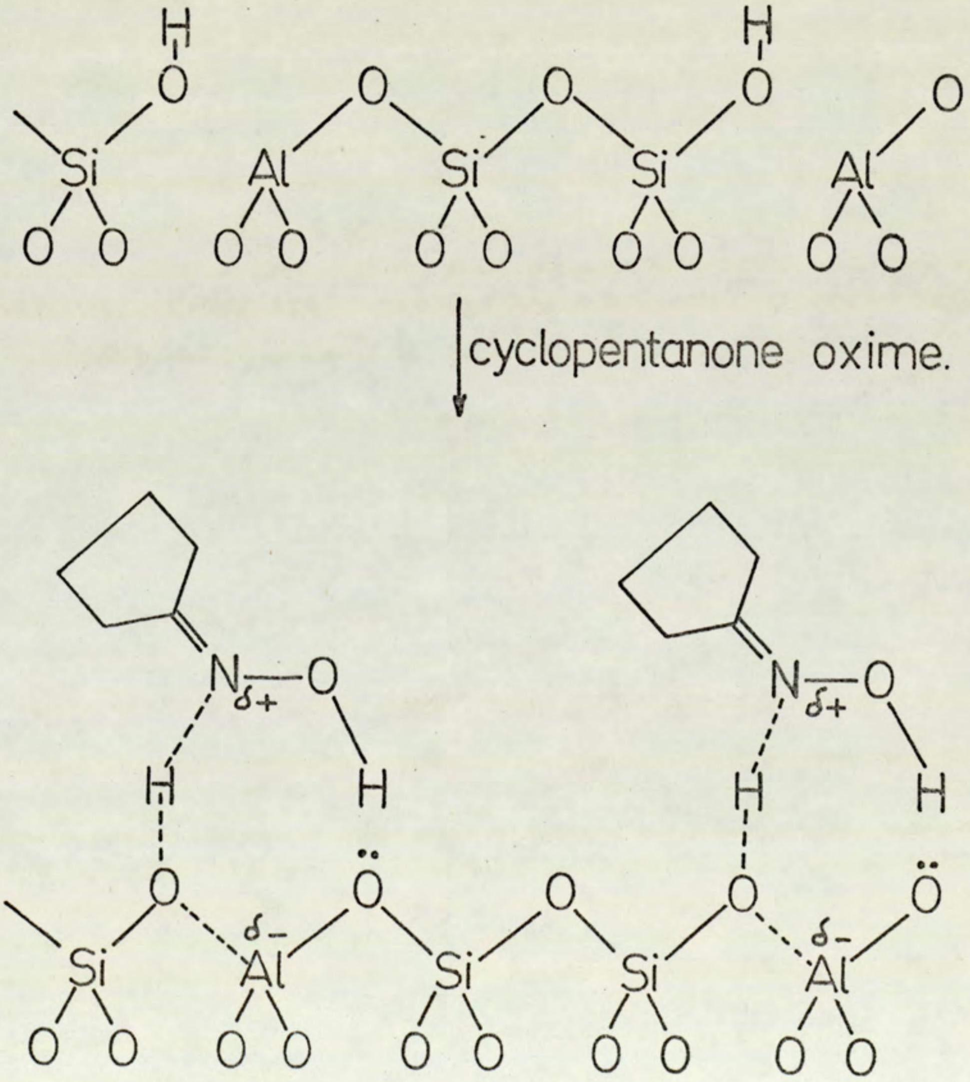


FIG.8, interaction of cyclopentanone oxime with HY.

If partial charge delocalization occurs for the surface species, the electron distribution within some of the bonds will be slightly different from that in cyclopentanone oxime hydrochloride, but the masses of the atoms attached to the carbon and nitrogen will be similar for both systems. Therefore, one would not expect partial charge delocalization to greatly alter the positions of most of the absorption bands from those in the spectrum of cyclopentanone oxime hydrochloride. The only band that will absorb at a different frequency for the surface species illustrated in Figure 8 and the oxime hydrochloride, is the oxime 1428 cm^{-1} band, which is specifically a function of the electron attracting ability of the ring substituent.

The presence of the $\omega(CH_2)_{C_5\ RING}$ band at 1290 cm^{-1} after adsorption of cyclopentanone oxime onto hydrogen-Y indicates the retention of the five membered carbon ring. It is also noticeable that the spectrum of the adsorbed species exhibits a broad band between 1480 and 1510 cm^{-1}. This band probably corresponds to the 1470 cm^{-1} band in the spectrum of the parent oxime, which arises from a bending vibration of an associated hydroxyl group. The presence of this band corresponds to the absence of a free hydroxyl absorption at 1350 cm^{-1}. The shift and broadening of the band in the spectrum of the adsorbed species, relative to the 1470 cm^{-1} band in the spectra of cyclopentanone oxime and its hydrochloride, suggests that it is not due simply to associated cyclopentanone oxime molecules. It probably results from an interaction of the oxime hydroxyl group hydrogen with a lattice oxygen, as illustrated in Figure 8. The adsorbed species illustrated in Figure 8, therefore, is consistent with the spectrum of the surface species (Spectrum 11c).

A remarkable change has taken place in the spectrum of the adsorbed species after the hydrogen-Y disc has been heated to 120° (Spectra 10d and 11d). Rearrangement has obviously taken place as illustrated by the presence of the carbonyl stretching band at 1650 cm^{-1}, and the general resemblance of the spectrum to that of 2-piperidone (Spectrum 5). The broad band between 2500 and 2900 cm^{-1}, due to $\nu(\overset{+}{N}-H)$, has disappeared, and the absence of a 1290 cm^{-1} band shows that most of the five membered ring compound has reacted. However, the shoulder at about 1710 cm^{-1}, and the relative intensity of the 1410 cm^{-1} band in Spectrum 11d compared to its intensity in the spectrum of 2-piperidone, suggests that some oxime is still present on the surface. There are several other differences between Spectrum 11d and that of 2-piperidone. Firstly the band at 1470 cm^{-1} is missing for the adsorbed species. This band has been assigned to a δ(CH) vibration (98). It is very unlikely that any carbon-hydrogen bonds are ruptured during the adsorption or reaction sequence, and the absence of this band probably reflects a difference in the relative positions of the methylene groups, for the adsorbed lactam and the parent lactam. Another band absent in Spectrum 11d is that due to ν(CN) which absorbs at 1310 cm^{-1} for 2-piperidone. The absence of this band suggests the absence of an amide carbon-nitrogen bond in the adsorbed molecule. The rearranged product is still interacting with the 3640 cm^{-1} hydroxyl group, and is presumably therefore protonated. The absence of a $\nu(\overset{+}{N}\text{-H})$ band in the region 2000-2400 cm^{-1} indicates that the proton may be associated with the carbonyl oxygen atom. The structure of the adsorbed lactam will be discussed in greater detail in section 2.3.2.

The spectrum of the adsorbed species does not change appreciably when the zeolite disc is heated for one hour at 250° (Spectra 10e and 11e). The most apparent change is the complete absence of cyclopentanone oxime at 250°, as shown by the loss of the shoulder at 1710 cm^{-1}, and the decrease in relative intensity of the 1410 cm^{-1} band to a value comparable to that in the spectrum of 2-piperidone (Spectrum 5). The rearranged product on the surface is apparently still protonated, since the surface hydroxyl band at 3640 cm^{-1} has not regained any of its original intensity. The ν(CN) band at 1310 cm^{-1} has gained intensity, indicating partial reformation of the amide carbon-nitrogen bond.

Heating the zeolite disc at 350° for one hour does not change the position of the bands due to the adsorbed species, but greatly reduces their intensity. Obviously desorption of the rearranged product has taken place to a considerable extent at 350°, and this has also resulted in the restoration of the 3640 cm^{-1} hydroxyl band to near its original intensity.

2.2.2. Cyclohexanone oxime on hydrogen-Y (Spectra 12 & 13).

The spectrum of cyclohexanone oxime adsorbed onto hydrogen-Y at room temperature (Spectra 12b and 13b) shows the same characteristic features as that of cyclopentanone oxime on hydrogen-Y. Again the oxime interacts with the 3640 cm^{-1} hydroxyl group, and the rest of the spectrum indicates that proton donation has occurred from the zeolite surface to the nitrogen atom of the oxime. Thus the oxime 1435 cm^{-1} band is shifted to 1430 cm^{-1}, and bands have appeared centred near 1700 cm^{-1} and about 2700 cm^{-1}, corresponding to $\nu(C=\overset{+}{N})$ and $\nu(\overset{+}{N}-H)$ respectively. The 1310 cm^{-1} band is still present for the adsorbed species, showing the retention of a six membered ring system, and as for cyclopentanone oxime on hydrogen-Y, the $\delta(OH)_{ASSOC.}$ band is broadened from 1480 cm^{-1} to 1450-1500 cm^{-1}, indicating interaction of the oxime hydroxyl group with the lattice. The latter band was also broadened to 1450-1500 cm^{-1} in the spectrum of cyclohexanone oxime hydrochloride recorded as a potassium bromide disc (Spectrum 4), and this similarity again emphasises the likeness of the oxime surface species to its hydrochloride. The surface species indicated by these observations is illustrated in Figure 9. Since the variation in frequency of the oxime 1435 cm^{-1} band with the electron attracting

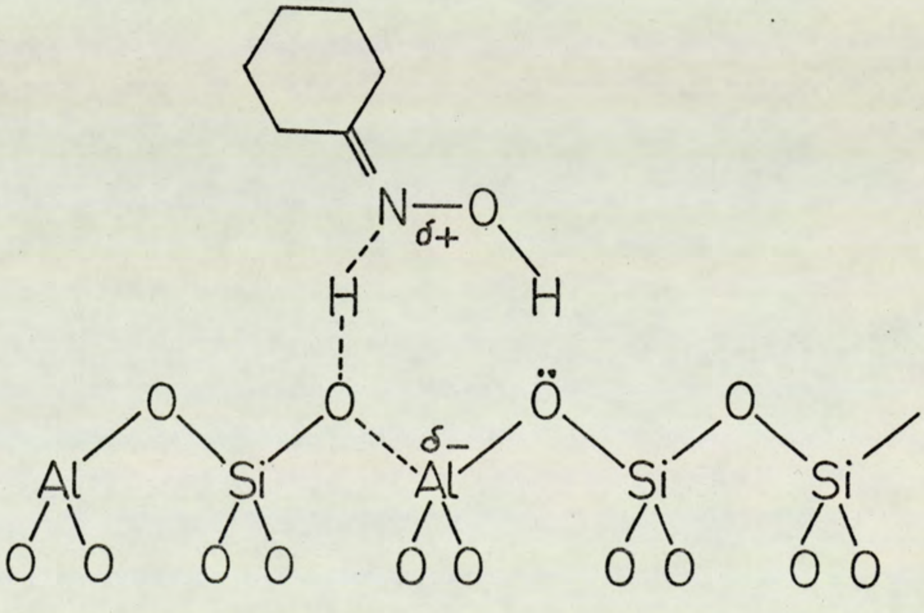


FIG.9, interaction of cyclohexanone oxime with HY.

ability of the ring substituent, is not so great as for the five membered ring oxime, it is not possible to estimate the extent of charge delocalization between the surface and the oxime nitrogen atom for this system.

After the zeolite disc has been heated at 120° for one hour, the intense carbonyl stretching band at 1640 cm^{-1} in Spectrum 13d suggests that considerable rearrangement of cyclohexanone oxime has occurred. The group of bands centred at 1450 cm^{-1} and the shoulder at 1690 cm^{-1}, the latter corresponding to $\nu(C=\overset{+}{N})$, indicate however that some unreacted oxime is still present on the surface. It is interesting to note that apart from the oxime bands, the rest of the spectrum more closely resembles that of 2-piperidone (Spectrum 5), than that of ϵ-caprolactam (Spectrum 6). Thus, bands are observed at 1335, 1360, 1410, 1450 and 1500 cm^{-1}, the relative intensities of which are comparable to those in the spectrum of 2-piperidone.

After heating to 250° all the oxime has disappeared, and Spectrum 13e resembles both those of cyclopentanone oxime on hydrogen-Y heated to 250° (Spectrum 11e), and that of 2-piperidone (Spectrum 5). The amide $\nu(CN)$ absorption at 1314 cm^{-1} in Spectrum 13e is not very pronounced, indicating, in comparison with spectra of cyclopentanone oxime on hydrogen-Y as a function of temperature, that this bond may be just starting to form at 250°. The corresponding band is completely absent at 120° when the five membered ring oxime is rearranged, but since some oxime is still present at this temperature, and since also the spectrum of cyclohexanone oxime itself exhibits a band at 1310 cm^{-1}, it is not possible to say whether the amide $\nu(CN)$ band at 1314 cm^{-1} is completely absent when the six membered ring oxime on hydrogen-Y is heated to 120°.

The reduction in intensity of the absorption bands in the 1200-1800 cm^{-1} region on increasing the temperature of the zeolite disc from 250° to 350°, shows that appreciable desorption has occurred at the higher temperature. This is confirmed by the partial restoration of the 3640 cm^{-1} surface hydroxyl band.

The structure of the adsorbed lactam will be discussed in greater detail in section 2.3.2.

2.3. Spectra of products adsorbed onto a decationated zeolite from the vapour phase.

It is of interest to determine whether the product of reaction, lactam in this case, is held on the surface in the same way as it would be if it had been adsorbed directly from the vapour phase. Also, since no bands have been observed which are characteristic of alkene-nitrile, it is important to determine whether the characteristic bands reported in section 2.1.5. are present when the nitrile is adsorbed onto hydrogen-Y. Both of these objectives can be accomplished by studying the spectra of the respective products adsorbed on hydrogen-Y.

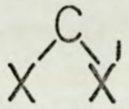
2.3.1. 2-Piperidone on hydrogen-Y (Spectra 14 & 15).

Upon adsorption of 2-piperidone onto hydrogen-Y, the intensity of the 3640 cm^{-1} surface hydroxyl band decreases relative to that of the 3540 cm^{-1} surface hydroxyl band. In the region 1200-1800 cm^{-1}, the spectrum of the adsorbed species (Spectrum 15c) is very similar to that of 2-piperidone formed on the zeolite surface by rearrangement of cyclopentanone oxime (Spectrum 11d). The ν(C-N) band at 1310 cm^{-1} is again absent until a temperature of about 250° is reached, and above 120° the spectra as a function of temperature closely resemble the pattern observed for the product of reaction of cyclopentanone oxime. From this experiment one may conclude that the product of rearrangement of cyclopentanone oxime is held on the surface in an identical manner to 2-piperidone which has been adsorbed from the vapour phase.

2.3.2. ϵ-Caprolactam on hydrogen-Y (Spectra 16 & 17).

From a study of the spectrum of ϵ-caprolactam adsorbed on hydrogen-Y (Spectrum 16b) it is apparent that this lactam also interacts with the 3640 cm^{-1} surface hydroxyl group, even though the intensity of the latter decreases only slightly. Since no quantitative spectroscopic studies were undertaken, it is not known how much lactam was adsorbed on the zeolite, and undoubtedly the small change in intensity of the 3640 cm^{-1} band is due to a relatively low surface coverage. This limitation of the technique also applies to the spectra of 2-piperidone on hydrogen-Y, and probably results from the fact that the lactam in the infrared cell sample bulb dimerizes (107), and therefore has a lower vapour pressure in the infrared cell than would the corresponding oxime under otherwise identical conditions.

It was postulated in the interpretation of Spectrum 13d (cyclohexanone oxime on hydrogen-Y heated to 120°) that the group of bands centred near 1450 cm^{-1} is due to unreacted cyclohexanone oxime. Since this group of bands is also observed in the spectrum of ϵ-caprolactam adsorbed from the vapour phase onto hydrogen-Y (Spectrum 17d), this interpretation now appears to require some modification. Part of the group of bands in Spectrum 13d undoubtedly does represent unreacted cyclohexanone oxime. This is indicated by the shoulder at 1690 cm^{-1} corresponding to a $\nu(C=\overset{+}{N})$ vibration, and by comparison with the cyclopentanone oxime - 2-piperidone system, where the spectra are slightly less complicated and the presence of unreacted oxime at 120° can be readily seen. The part of these bands in Spectrum 13d which is not due to unreacted oxime, and the whole of the group of bands centred at 1450 cm^{-1} in Spectrum 17d, however, require further explanation. This group of bands for adsorbed ε-caprolactam, whether the latter is produced from cyclohexanone oxime or adsorbed directly from the vapour phase, is only observed at temperatures below 250°. It has been stated previously that up to about 250° no evidence has been obtained for the presence of an amide carbon-nitrogen band in the adsorbed lactam. At this temperature, however, the $\nu(C-N)$ band near 1310 cm^{-1} begins to gain intensity, and some desorption occurs. The apparent absence of an amide carbon-nitrogen band below 250° can be shown to be consistent with both the general resemblance of the spectrum of ε-caprolactam on the surface to that of 2-piperidone on the surface, and the presence of the group of bands near 1450 cm^{-1} for adsorbed ε-caprolactam, by the following argument.

The differences in the region 1200-1800 cm^{-1} between the standard spectra of 2-piperidone (Spectrum 5) and ε-caprolactam (Spectrum 6) are due partly to the difference in strain of the two ring systems. An example of this dependence of infrared bands upon steric factors was given by Cook (108), whose work indicated the existence of a linear relationship between the carbonyl stretching frequency and the  angle for several cyclic carbonyl compounds. The degree of strain in 2-piperidone and ε-caprolactam has been calculated by Kachinskaya et al (109,110). These authors estimated the degree of strain by subtracting the calculated heat of combustion of the compounds, based on the incremental heats of combustion for each methylene group and the CONH group, from the experimental heat of combustion. The value obtained obviously depends upon which value is taken for the heat of combustion per methylene group. If the increment for the methylene groups in the lactam is taken to be the same as that in alkanes, then values of 2.2 and 3.8 kcal/mole are obtained for the degree of strain in 2-piperidone and ε-caprolactam respectively.

Similarly, if the methylene increment for cyclohexane is taken, values of 3.4 and 5.4 kcal/mole have been calculated. Obviously these calculations involve too many approximations to provide quantitative results, but they clearly show that there is less strain in 2-piperidone than in ϵ-caprolactam. This difference in strain will undoubtedly be reflected in the infrared spectra of the two compounds, and anything which reduces this difference in strain will tend to make their spectra more similar. The similarity between the spectrum of ϵ-caprolactam on hydrogen-Y and the spectrum of 2-piperidone on hydrogen-Y (for example Spectra 13d and 11d) suggests, therefore, that the extra strain has been removed from the seven membered ring upon adsorption. This similarity in spectra, and the apparent absence of an amide carbon-nitrogen bond in the adsorbed lactams, suggest that the latter are adsorbed as open-chain compounds. Ring opening would obviously involve the rupture of the amide carbon-nitrogen bond, since the carbon-nitrogen bond energy is smaller than that of a carbon-carbon bond, and the extra electron drain associated with the carbonyl group weakens the amide carbon-nitrogen linkage relative to the other carbon-nitrogen bond. Thus the interaction of 2-piperidone with the surface of hydrogen-Y is probably similar to that represented in Figure 10. As in the case of the oxime adsorbed on hydrogen-Y it is possible that some charge delocalization

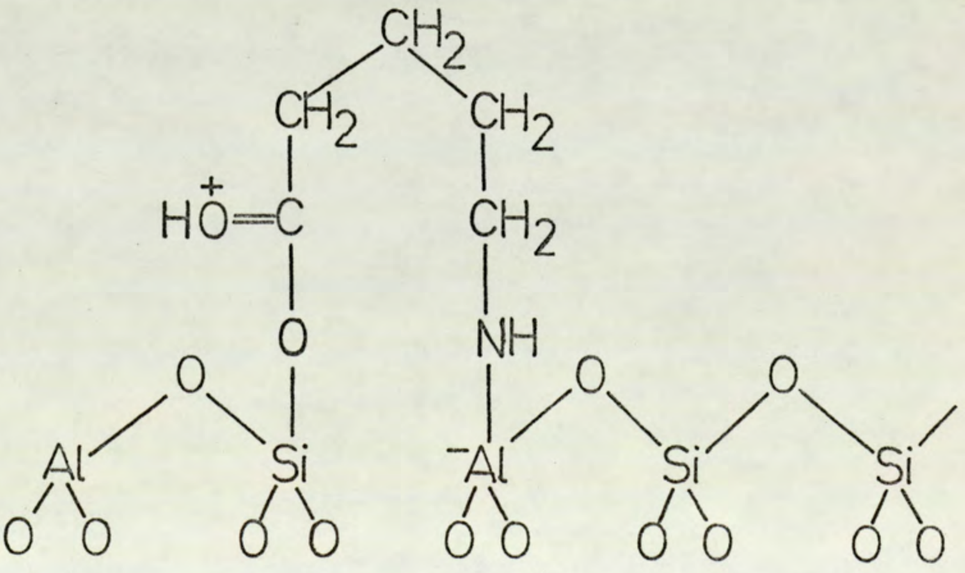


FIG.10, interaction of 2-piperidone with HY.

occurs between the adsorbed lactam and the surface.

The bond-rupture theory can also explain the group of bands in the 1450 cm^{-1} region which are observed for ε-caprolactam on hydrogen-Y (Spectra 17b and 17d), but not for 2-piperidone on hydrogen-Y (Spectra 15c and 15d). The bands in this region result from bending vibrations of carbon-hydrogen bonds, and the position and broadness of these bands are a function of the positions of the methylene groups relative to each other and the extent of interaction between them. When the ε-caprolactam ring is ruptured upon adsorption, the carbon chain produced has one more methylene group than the carbon chain associated with the adsorption of the 2-piperidone ring. More movement of the methylene groups, relative to each other, will therefore be possible for adsorbed ε-caprolactam, and this will result in an increased complexity of the band system near 1450 cm^{-1}.

The rest of the spectrum of ε-caprolactam on hydrogen-Y suggests that when this molecule is adsorbed onto the surface from the vapour phase (Spectrum 17d), it is held in the same way as it would be if it were formed by rearrangement of cyclohexanone oxime (Spectrum 13d). This similarity in spectra is also apparent at higher temperatures.

2.3.3. 5-Cyanopent-1-ene on hydrogen-Y (Spectra 18,19 & 20).

As previously noted, the spectroscopic study of the reactions of both cyclopentanone oxime and cyclohexanone oxime on hydrogen-Y has provided no evidence for alkene-nitrile formation. It is necessary, therefore, to study the adsorption of a corresponding alkene-nitrile, to see whether the characteristic absorption bands such as those due to $\nu(C \equiv N)$ and $\nu(C=C)$ are present for the surface species. For this purpose 5-cyanopent-1-ene was adsorbed onto hydrogen-Y and its spectrum studied as a function of temperature.

The adsorption of a substance like 5-cyanopent-1-ene onto hydrogen-Y is interesting because it has a different functional group at each end of a carbon chain and the two functional groups are sufficiently separated by methylene groups to be considered individually. It is possible that one end will become attached to the surface preferentially, or that either will be attached or finally that both ends will be attached.

The adsorption of olefins has been reported by Eberly (64), who studied the spectra of hex-1-ene and other low molecular weight olefins on a series of Y-type zeolites. This study showed that when hex-1-ene is adsorbed onto hydrogen-Y, it loses its double bond character as evidenced by the loss of the ν(C=C) and ν(CH=) absorption bands. This olefin interacts with the zeolitic 3640 cm^{-1} hydroxyl band, and the original intensity of the latter is only restored after evacuation at 427°. Although the exact nature of the alkene-surface interaction was not postulated by Eberly, a fairly strong adsorption is indicated. The spectra of nitriles adsorbed on decationated Y-type zeolites have been reported by Angell and Howell (111). These authors studied the adsorption of acetonitrile, acetonitrile-d_3 and benzonitrile on a series of Y-type zeolites, and found that for decationated zeolites the adsorption of acetonitrile resulted in complete disappearance of the zeolite 3640 cm^{-1} hydroxyl group. However, this band was completely restored by evacuation at room temperature, and at the same time the bands due to adsorbed nitrile were considerably reduced in intensity. There was no splitting of the ν(C≡N) bands, although they were shifted to slightly higher frequencies. Acetonitrile on hydrogen-Y also exhibited new, fairly broad bands centred near 2900 cm^{-1} and 2400 cm^{-1}. When the deuterated compound was adsorbed onto the same zeolite, the same bands were observed. When the surface hydroxyl groups of the zeolite were deuterated, however, the two bands were shifted down to 2300 cm^{-1} and about 1850 cm^{-1}. It appears that both of these bands are due to vibrations involving surface hydrogen atoms. It was postulated by Angell and Howell that the 2900 cm^{-1} band is due to a hydrogen bonding interaction of the nitrile with the surface hydroxyl groups, and that the 2400 cm^{-1} band is an overtone of the OH bending vibration.

When 5-cyanopent-1-ene is adsorbed onto hydrogen-Y and the excess removed by evacuation at room temperature (Spectrum 18c), the interaction between the alkene-nitrile and the surface is seen to involve the surface 3640 cm^{-1} hydroxyl group. The most obvious difference between the spectrum of 5-cyanopent-1-ene (Spectrum 9), and that of 5-cyanopent-1-ene adsorbed onto hydrogen -Y is the absence in the latter of both the ν (C=C) band at 1642 cm^{-1} (Spectrum 20c), and the ν(=CH) band at 3080 cm^{-1} (Spectrum 18c). Both of these bands are sharp and fairly intense in the spectrum of the parent compound, and although they are present for the surface species when hydrogen-Y is subjected to the vapour of the alkene-nitrile for three minutes (Spectra 18b and 20b), they are completely removed by evacuation at room temperature. It appears, therefore, that the bands at 1642 and 3080 cm^{-1} in Spectra 20b and 18b are due to excess hydrogen bonded material, which is removed by evacuation. One must conclude from this result that when 5-cyanopent-1-ene is adsorbed onto hydrogen-Y at room temperature, it completely loses its double bond character. This finding is in agreement with that of Eberly (64), who derived the same conclusion for the adsorption of hex-1-ene on hydrogen-Y.

Another immediately noticeable feature about Spectrum 19c is that the $\nu(C\equiv N)$ band, which absorbs at 2250 cm^{-1} for 5-cyanopent-1-ene, is shifted to 2280 cm^{-1}, and at the same time new broad bands are observed centred near 2400 cm^{-1} and 2900 cm^{-1}. These features correspond to the characteristic changes reported by Angell and Howell (111) for the adsorption of acetonitrile on hydrogen-Y. The assignments for these bands are not known with any degree of certainty, but they are thought to be due to a hydrogen bonded interaction between the nitrile function and the surface hydrogen atom. The similarity between Spectrum 19c and that of acetonitrile on hydrogen-Y in the range 2000-3000 cm^{-1} reported by Angell and Howell, is good evidence that the nitrile end of 5-cyanopent-1-ene interacts with the surface of hydrogen-Y in an identical manner to that of acetonitrile. It is apparent from the results of Angell and Howell, that the interaction is of a fairly weak nature, and as suggested by these authors, probably involves hydrogen bonding.

The other bands in the spectrum of 5-cyanopent-1-ene adsorbed on hydrogen-Y (Spectrum 20c) are those due to $\delta(CH_2)$. These are changed from the three bands at 1420, 1428 and 1442 cm^{-1} in the spectrum of liquid 5-cyanopent-1-ene, to the two bands at 1423 and 1442 cm^{-1} for the adsorbed species. This alteration presumably reflects the loss of some freedom of movement of the methylene groups for the surface species.

When 5-cyanopent-1-ene is adsorbed onto hydrogen-Y at room temperature, the alkene end of the molecule interacts strongly with the surface, while the nitrile end interacts only weakly. The type of interaction suggested is illustrated in Figure 11. The alkene-surface interaction probably involves the surface proton and the pi-electrons of the carbon-carbon double bond. With this end of the molecule anchored, the nitrile end is free to interact, presumably via hydrogen bonding, with an adjacent surface hydroxyl group.

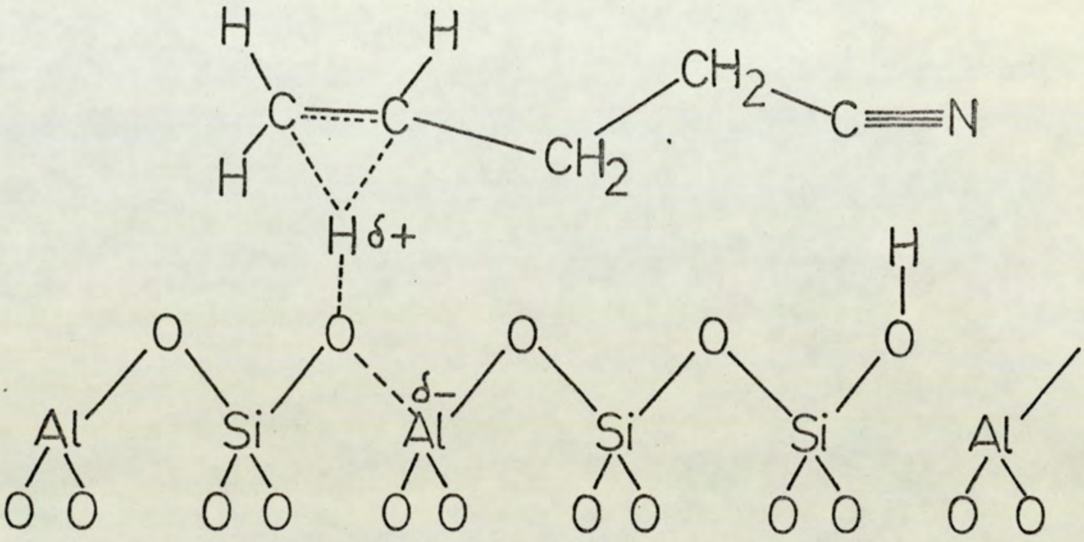


FIG.11, interaction of 5-cyanopent-1-ene with HY.

After the zeolite disc dosed with 5-cyanopent-1-ene has been heated at 120° for one hour, the spectrum of the surface (Spectra 18d, 19d and 20d) shows no changes from that obtained after evacuation at room temperature (Spectra 19c and 20c). Heating the disc to 250°, however, results in considerable desorption of the alkene-nitrile, and restoration of the surface 3640 cm^{-1} band (Spectrum 18e).

From this experiment one can conclude that if a reasonable quantity of a nitrile function had been formed on the surface of hydrogen-Y by the reaction of either cyclopentanone oxime or cyclohexanone oxime, under the conditions of the spectroscopic studies, it would have been observable. The region 2000-2500 cm^{-1} is clear for both of the oximes and lactams studied, and so it should have been possible to detect a C≡N group by its characteristic absorptions in this region. Since the alkene-nitriles are not held on the surface as strongly as the lactams, however, it is possible that at the temperatures at which these compounds are formed, they desorb quickly, and so are not observed under the conditions of the spectroscopic studies.

2.4 Reaction on a non-decationated zeolite.

Having studied the rearrangement of both cyclopentanone oxime and cyclohexanone oxime on hydrogen-Y, and the interaction of both reactants and products with surface hydroxyl groups, it is next necessary to study the reaction on a catalyst which does not have any surface hydroxyl groups. By studying the reaction on, for example, an alkali metal-Y type zeolite, it should be possible to determine whether or not acidic hydroxyl groups are essential for the Beckmann rearrangement to take place. For this reason the reaction of cyclohexanone oxime on sodium-Y was studied spectroscopically.

2.4.1. Cyclohexanone oxime on sodium-Y (Spectra 21 and 22).

When cyclohexanone oxime is adsorbed onto sodium-Y at room temperature (Spectra 21b and 22b), the spectrum of the adsorbed species is very similar to that of the pure oxime. Bands are observed at 1250, 1310, 1350, 1440, 1450, 1657, 2860 and 2940 cm^{-1}, all of which are close to their values in the spectrum of cyclohexanone oxime (Spectrum 2). At room temperature a band is also present at 1485 cm^{-1}, corresponding to $\delta(OH)_{ASSOC.}$. After the zeolite disc has been heated at 120° for one hour the spectrum is similar to that observed at room temperature (Spectra 21d and 22d). The loss of the 1485 cm^{-1} band, and a decrease in intensity of the $\nu(C{=}N)$ band near 1660 cm^{-1} at the higher temperature, are the only differences between the two spectra. It appears that when all the hydrogen bonded material has been removed at 120°, the spectrum of the adsorbed species exhibits neither a free nor an associated hydroxyl group. The absence of either of these bands is the only major difference between the spectrum of the adsorbed species and that of cyclohexanone oxime. The interaction between the oxime and the surface, therefore, must involve the oxime hydroxyl group. and must result in a shift of the $\delta(OH)$ band to a position where it cannot be observed. The interaction could be similar to that illustrated in Figure 12, and probably results from an ion-dipole attraction between the oxygen lone pair and the zeolite cation.

Several changes take place when the zeolite disc is heated to 250° (Spectrum 22e). A strong, fairly sharp band has appeared at 1630 cm^{-1} and the pattern has changed in the 1400-1500 cm^{-1} region. Also, the fairly strong $\delta'(CH_2)_{C6\ RING}$ bands at 1250 and 1310 cm^{-1} in the spectrum of cyclohexanone oxime have disappeared, suggesting that ring opening has occurred. Apart from a few small shifts, Spectrum 22e in the region 1300-1500 cm^{-1} is very similar to that of 5-cyanopent-1-ene (Spectrum 9).

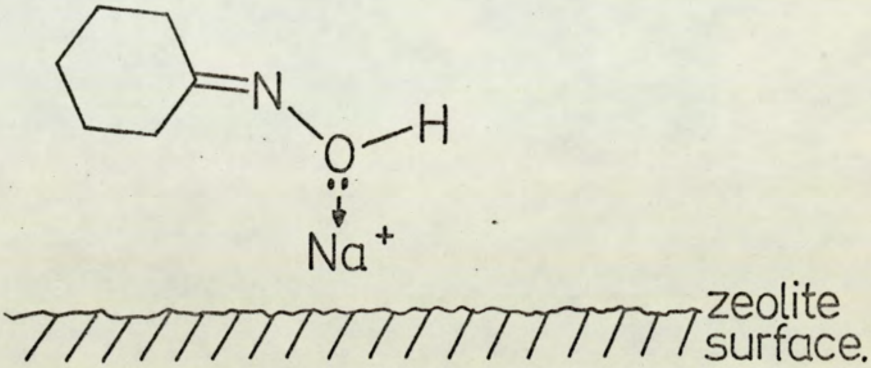


FIG.12, interaction of cyclohexanone oxime with sodium-Y.

The band at 1630 cm^{-1} also appears in the spectrum of the latter, at a slightly higher frequency, corresponding to ν(C=C). However, the ν(=CH) band at 3080 cm^{-1}, corresponding to the ν(C=C) band at 1642 cm^{-1} is absent in Spectrum 21e. There is also no evidence for the formation of a C≡N function in the 2250 cm^{-1} region. At 350° the spectrum is similar to that at 250°, except that a considerable amount of the organic material has desorbed (Spectra 21f and 22f).

If dehydration of the oxime has taken place to form the alkene-nitrile, then the absence of a ν(C≡N) band can only be explained by postulating that this function is not formed until desorption occurs, and that the nitrile, when formed, is held on the surface via a $-\underset{\text{surface}}{\mathrm{C}{=\!=}\mathrm{N}}$ interaction. This is supported by the fact that the ν(C=N) band near 1660 cm^{-1} is present even at 250°. The non-formation of the C≡N function prior to desorption, indicates that even if any alkene-nitrile had been formed on hydrogen-Y, it probably would not have been detected spectroscopically. No evidence was obtained for the formation of a lactam on sodium-Y.

After heating to 350° a broad band appears in the 1660 cm^{-1} region. This band is obtained at the end of all the heating procedures. A band in this region has been observed for cokes formed by the exposure of organic material to silica-alumina surfaces (112).

2.4.2. ε-Caprolactam on sodium-Y.

A most interesting observation was made when sodium-Y was exposed to ε-caprolactam vapour. Although the sample bulb isolation tap was open for a total of thirty minutes, very little evidence was observed in the spectrum of the surface for any adsorbed material. Only slight bumps were observed in the 2800-3000 cm^{-1} region. This is surprising, since a reasonable amount of this lactam was adsorbed onto hydrogen-Y after the sample bulb isolation tap had been opened for only nine minutes (Spectrum 17b) under identical conditions. In the latter case the lactam was seen to interact with the surface hydroxyl groups upon adsorption, and so it appears that in the absence of these sites, adsorption takes place very much more slowly than in their presence. These surface hydroxyl groups are therefore responsible for the strong adsorption of lactams, which are still present on hydrogen-Y after one hours evacuation at 350° (Spectra 15f and 17f).

2.4.3. 5-Cyanopent-1-ene on sodium-Y (Spectra 23,24 and 25).

The interaction of alkenes with alkali metal-Y type zeolites has been studied by Eberly (64). This author showed that the spectrum of hex-1-ene adsorbed onto sodium-Y was similar to that of liquid hex-1-ene. The $\nu(C{=}C)$ band, which absorbs at 1642 cm^{-1} for hex-1-ene, was shifted slightly to 1650 cm^{-1}, and the amount of double bond character, as measured by the absorbance ratio $\nu(C{=}C)/\delta(CH)$, was shown to be a function of the zeolite cation. For calcium, magnesium and cadmium-Y there was increasing loss of double bond character, but for the alkali metal-Y type zeolites there was very little loss. The type of interaction indicated is an electrostatic attraction between the cation and the polarized pi-electron cloud around the double bond. The extent of such a polarization would obviously depend upon the field strength around the cation.

Angell and Howell (111) studied the adsorption of acetonitrile on sodium-Y and reported a small shift of the $\nu(C{\equiv}N)$ band to higher frequencies upon adsorption. This shift was shown to be cation dependent and the authors concluded that adsorption occurs on the cations. Presumably, the interaction is similar to that proposed above for alkenes and the zeolite surface.

When 5-cyanopent-1-ene is adsorbed onto sodium-Y and the excess removed by evacuation (Spectra 23,24c and 25c), the spectrum of the adsorbed species is seen to be similar to that of the parent compound. The $\nu(C\equiv N)$ band is shifted only slightly from 2250 cm^{-1} to 2260 cm^{-1}, and the $\nu(C=C)$ is also shifted, from 1642 cm^{-1} to about 1634 cm^{-1}. These two observations suggest that under the conditions of this spectroscopic study, both ends of the molecule can interact with the zeolite surface independently of each other. This is presumably either due to the functional groups being sufficiently separated by methylene groups to interact with different cations on the zeolite surface (Figure 13a), or the molecule being able to coil itself around so that both ends can interact with the same cation (Figure 13b). The spectrum of 5-cyanopent-1-ene on

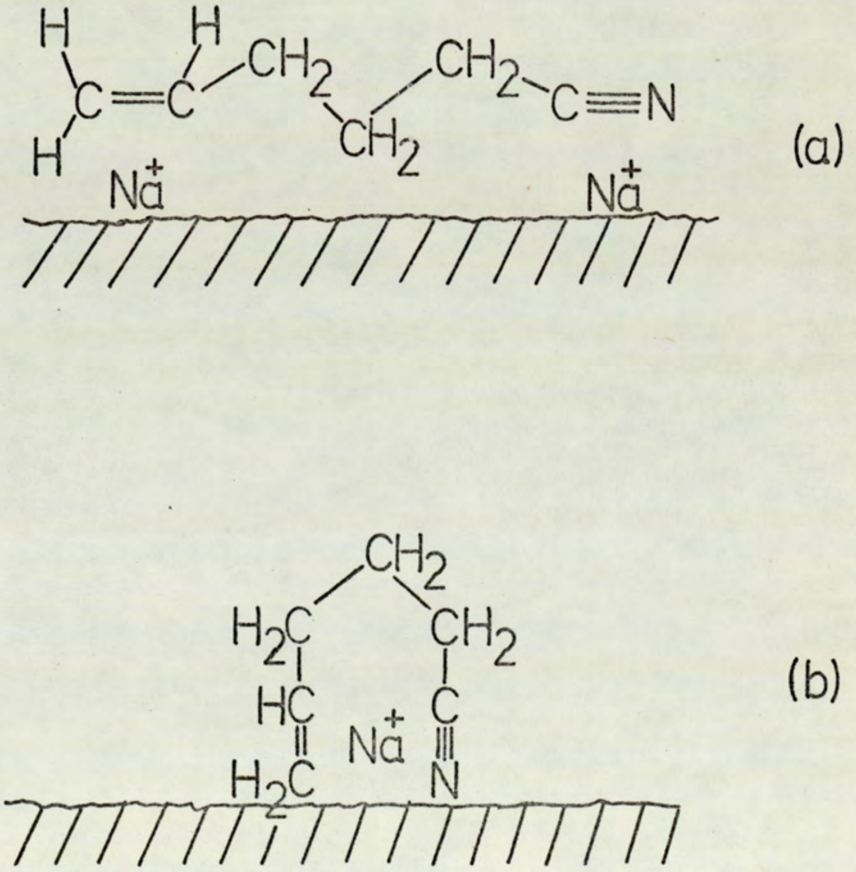


FIG.13, interaction of 5-cyanopent-1-ene with sodium-Y sodium-Y does not change noticeably with temperature, but after evacuating at 250° (Spectra 23e,24e and 25e) for one hour, considerable desorption has occurred.

2.5. Conclusions from spectroscopic studies.

Upon adsorption of either cyclopentanone oxime or cyclohexanone oxime onto hydrogen-Y at room temperature, the proton of the surface hydroxyl group which absorbs at 3640 cm^{-1} is donated to the nitrogen atom of the oxime. Some delocalization of charge occurs, however, between the protonated species and the surface, and the surface species are those illustrated in Figures 8 and 9. The oximes rearrange at the relatively low temperature of 120°, to produce surface bridge structures like that illustrated in Figure 10. These products desorb, via formation of an amide C-N bond, at higher temperatures. Under the conditions of this spectroscopic study, no evidence was obtained for the formation of alkene-nitriles on hydrogen-Y.

A possible mechanism for the surface rearrangement on hydrogen-Y is illustrated schematically in Figure 14. Species XXVI and XXVIII are those detected spectroscopically. If species XXVIII is that present on the surface after rearrangement, as seems very probable from the spectra obtained, then the oxime C=N bond must be ruptured during the reaction sequence. The rupture of the oxime C=N bond, formation of the new C-N bond, and the transfer of the hydroxyl group is probably synchronous, passing through the type of intermediate shown (species XXVII). Obviously this rearrangement would occur far to rapidly for any intermediate to be detected spectroscopically, and one would only expect to observe the protonated oxime, and the protonated product of rearrangement.

If the mechanism presented in Figure 14 is correct, then the Beckmann rearrangement catalyzed by decationated aluminosilicates should be stereospecifically trans. Landis and Venuto (4) studied the rearrangement of acetophenone oxime, and found that the ratio of acetanilide formed to N-methylbenzamide formed was 19:1. Thus the phenyl group which is trans to the hydroxyl group in acetophenone, had migrated preferentially. This experiment did not show the reaction to be stereospecifically trans, however, because the phenyl group has a greater migratory aptitude that the methyl group and so would migrate preferentially even if the reaction was not stereospecifically trans. It is not known, therefore, with any

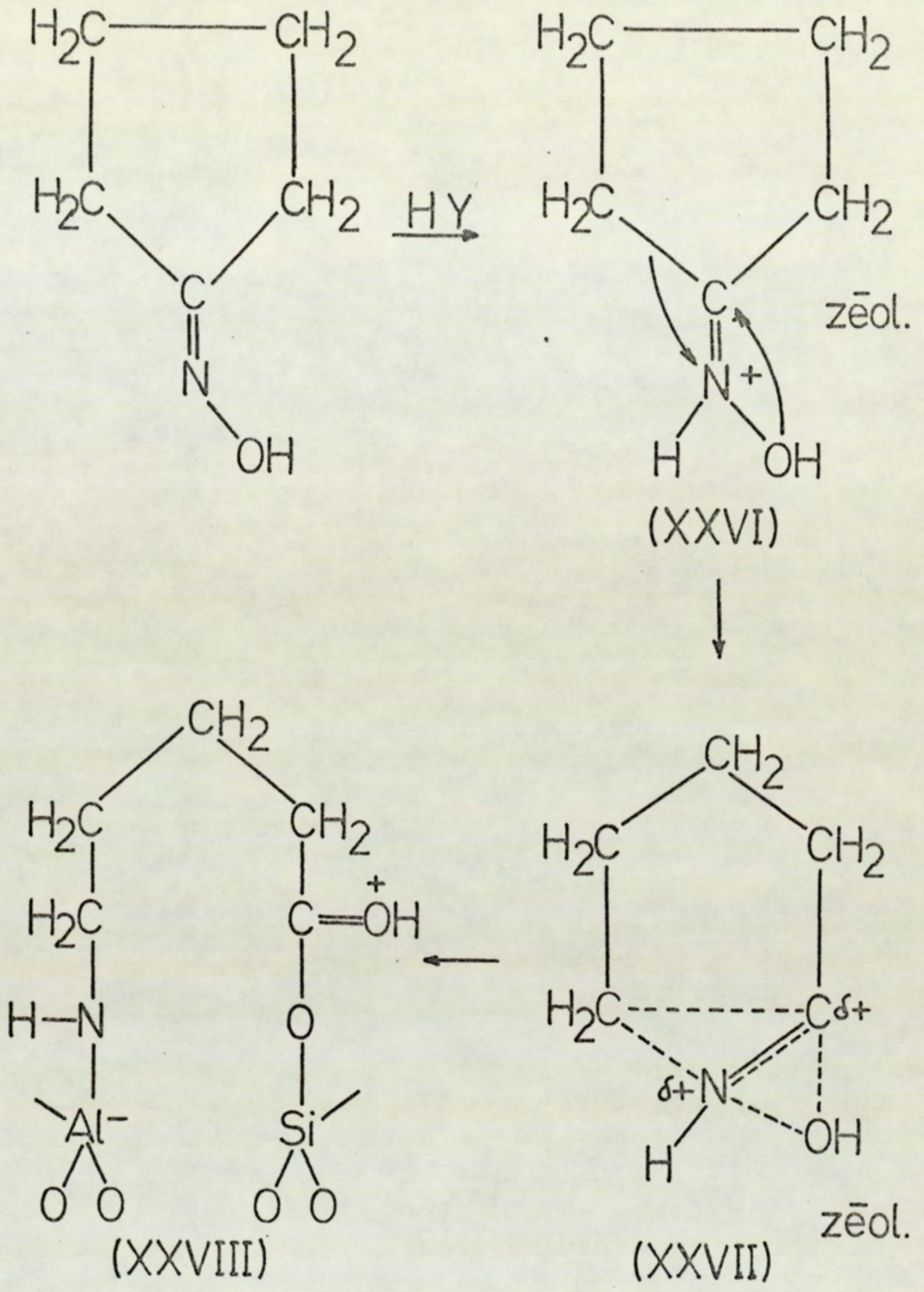


FIG.14,mechanism of surface rearrangement of cyclopentanone oxime.

certainty if the surface reaction is stereospecifically trans.

On sodium-Y the oximes are held via a cation-dipole interaction of the type indicated in Figure 12. There is no evidence for lactam formation on this catalyst, however, some evidence has been obtained for the formation of an alkene-nitrile. If an alkene-nitrile is formed by the reaction of either cyclopentanone oxime or cyclohexanone oxime on sodium-Y, then the C≡N function is not formed until desorption occurs. It is also apparent from these results that even if alkene-nitrile is formed by the reaction of alicyclic oximes on hydrogen-Y, it is probably not detectable by infrared spectroscopy. The characteristic ν(C≡N) absorption is apparently not formed until desorption occurs, and the ν(C=C) band in the 1640 cm^{-1} region is hidden by the intense ν(C=O) absorption of the lactam.

These studies have shown that the surface hydroxyl groups which absorb at 3640 cm^{-1} in the spectrum of hydrogen-Y are the active sites for the Beckmann rearrangement, and are also responsible for the strong adsorption of the product lactam. The spectroscopic studies have also indicated that the product selectivity can be changed by using either an alkali metal-Y type zeolite or a decationated Y-type zeolite.

CHAPTER 3

CONVERSION OF CYCLOPENTANONE OXIME OVER VARIOUS CATALYSTS

Some of the results and conclusions presented in Chapter 2 of this thesis can be tested by studying the heterogeneously catalyzed Beckmann rearrangement of alicyclic oximes using a flow system. Using such a system it is possible also to study the effect of catalyst variation, temperature, solvent, carrier, flow rate and catalyst poisoning, as well as obtaining a more quantitative measure of conversion and selectivity than was possible under the conditions of the spectroscopic study. The results of these studies, particularly on the conversion of cyclopentanone oxime to 2-piperidone, are reported in this and subsequent chapters.

In Table 7 are reported the results of passing cyclopentanone oxime over various catalysts at 340°. The oxime was fed in the form of a 30% solution in benzene, the flow rate being identical for each catalyst. Explanations of the estimation of reaction times, and the definitions of selectivities are given in the experimental section (Chapter 8).

The most noticeable general features of the results reported in Table 7 are the low recoveries of the three named products, and the relatively short catalyst lifetimes. For none of the catalysts studied is the sum of the selectivities for 2-piperidone, 4-cyanobut-1-ene and cyclopentanone greater than 35%.

In spite of the low selectivities, it can be seen that the decationated zeolites hydrogen-Y and hydrogen-Pd-Y give most 2-piperidone, but the other catalysts which are known to possess hydroxyl groups, lanthanum-Y and calcium-Y (see section 1.3), also result in the formation of some 2-piperidone. This finding is in agreement with the results of the spectroscopic study, where it was shown that acidic surface hydroxyl groups are responsible for the Beckmann rearrangement of cyclopentanone oxime to 2-piperidone. The non-acidic alkali metal zeolites give no 2-piperidone since their lattices contain no structural hydroxyl groups (see section 1.3). The principal product of reaction over these catalysts is 4-cyanobut-1-ene, and this is also in agreement with the conclusions from Chapter 2 of this thesis, where evidence was presented for the formation of alkene-nitriles on sodium-Y, and the way in which this product is adsorbed on the catalyst was discussed.

TABLE 7: CONVERSION OF CYCLOPENTANONE OXIME OVER VARIOUS CATALYSTS

Catalyst	Atmosphere (40ml/min.)	Reaction time (min.)	% Oxime Conv.	Selectivity for 2-piperidone formation	Selectivity for 4-cyanobut-1-ene formation	Selectivity for cyclopentanone formation
Hydrogen-Y	N_2	90	58	9.5	7.9	4.0
Hydrogen-Pd-Y	N_2	120	70	14.1	7.8	0.5
Lanthanum-Y	N_2	240	85	4.5	10.8	1.3
Calcium-Y	N_2	240	83	3.6	10.1	6.3
Lithium-Y	H_2	240	76	0	25.5	5.7
Sodium-Y	H_2	240	70	0	24.3	4.9
Potassium-Y	H_2	240	83	0	20.8	3.0
Caesium-Y	H_2	240	80	0	14.3	6.8
Sodium-Pd-Y	H_2	240	74	0	23.5	2.8
Sodium-A	H_2	120	31	0	13.8	15.8
Pd/Al_2O_3	N_2	120	100	1.7	21.5	0.5

340°, LHSV = 1.0, 30% solutions in benzene, 12.75g anhydrous catalyst weight.

It is interesting to compare the results of using sodium-Y and sodium-A, since the effective pore diameter of the latter, 4.2 Å, is close to the molecular dimensions of cyclopentanone oxime. Catalin models indicate that cyclopentanone oxime molecules have dimensions of approximately 7.5 Å by 5.5 Å. The effective pore diameter of sodium-Y is about 9 Å, and cyclopentanone oxime should be able to penetrate the pore system of this catalyst fairly easily. Over a two hour period the oxime conversion over sodium-A is only 31%, whereas for sodium-Y the conversion is 70% over a four hour period. While neither catalyst exhibits any activity for 2-piperidone formation, there is a considerable difference in the production of 4-cyanobut-1-ene on both catalysts. This difference is shown graphically in Figure 15, which gives the 4-cyanobut-1-ene production as a function of time. Only a small, fairly constant amount of 4-cyanobut-1-ene is detected in the effluent stream from sodium-A. Whether this alkene-nitrile formation is due to a slow diffusion of cyclopentanone oxime into the catalyst pore system, followed by reaction, or due to reaction on the external surface of the catalyst is not known. The low conversion and selectivities associated with the reaction of cyclopentanone oxime over sodium-A is consistent with the small pore diameter of this catalyst, and emphasizes the importance of the pore diameter for sieving reactions, and also the importance of the internal surface for catalytic reactions.

The oxime conversion, catalyst lifetime and selectivity for 2-piperidone formation is higher for hydrogen-Pd-Y than for hydrogen-Y. The palladium zeolite contained only 0.5% by weight of the transition metal, corresponding to an average of one palladium atom per eleven catalyst supercavities. It has previously been suggested that the incorporation of a small amount of palladium into a decationated zeolite aids the formation of Bronsted acid sites, and represses their conversion to Lewis acid sites (see section 1.3). Since Bronsted acid sites have been shown to be essential for the formation of 2-piperidone, it is to be expected that the use of a small amount of palladium in a decationated zeolite would be advantageous for the Beckmann rearrangement of oximes. The difference in the lactam formation for the two catalysts is shown in Figure 16, and is quite considerable, illustrating the advantageous effect of palladium on the ability of hydrogen-Y to function as a catalyst for the

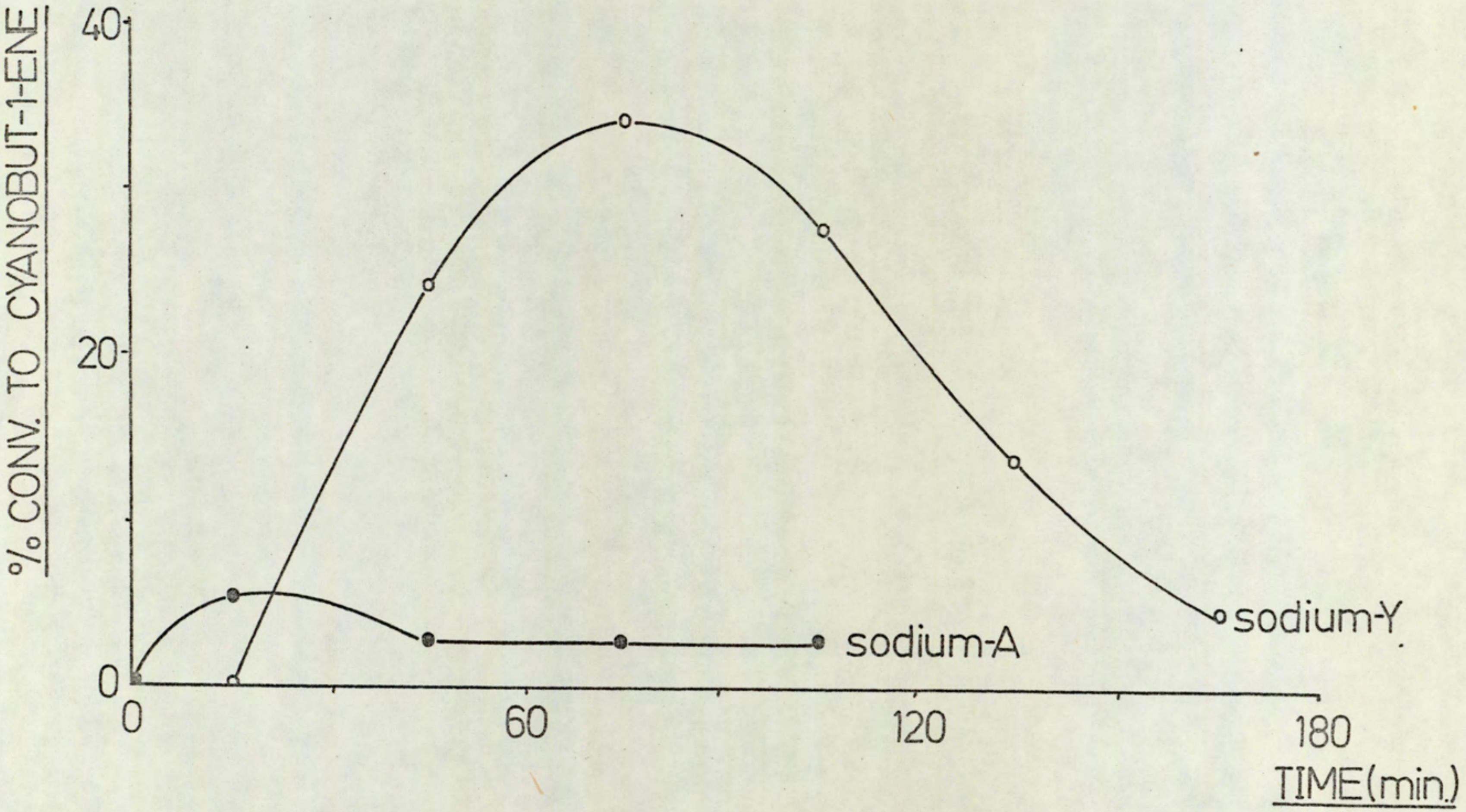


FIG. 15, comparison of 4-cyanobut-1-ene formation on sodium-A and sodium-Y

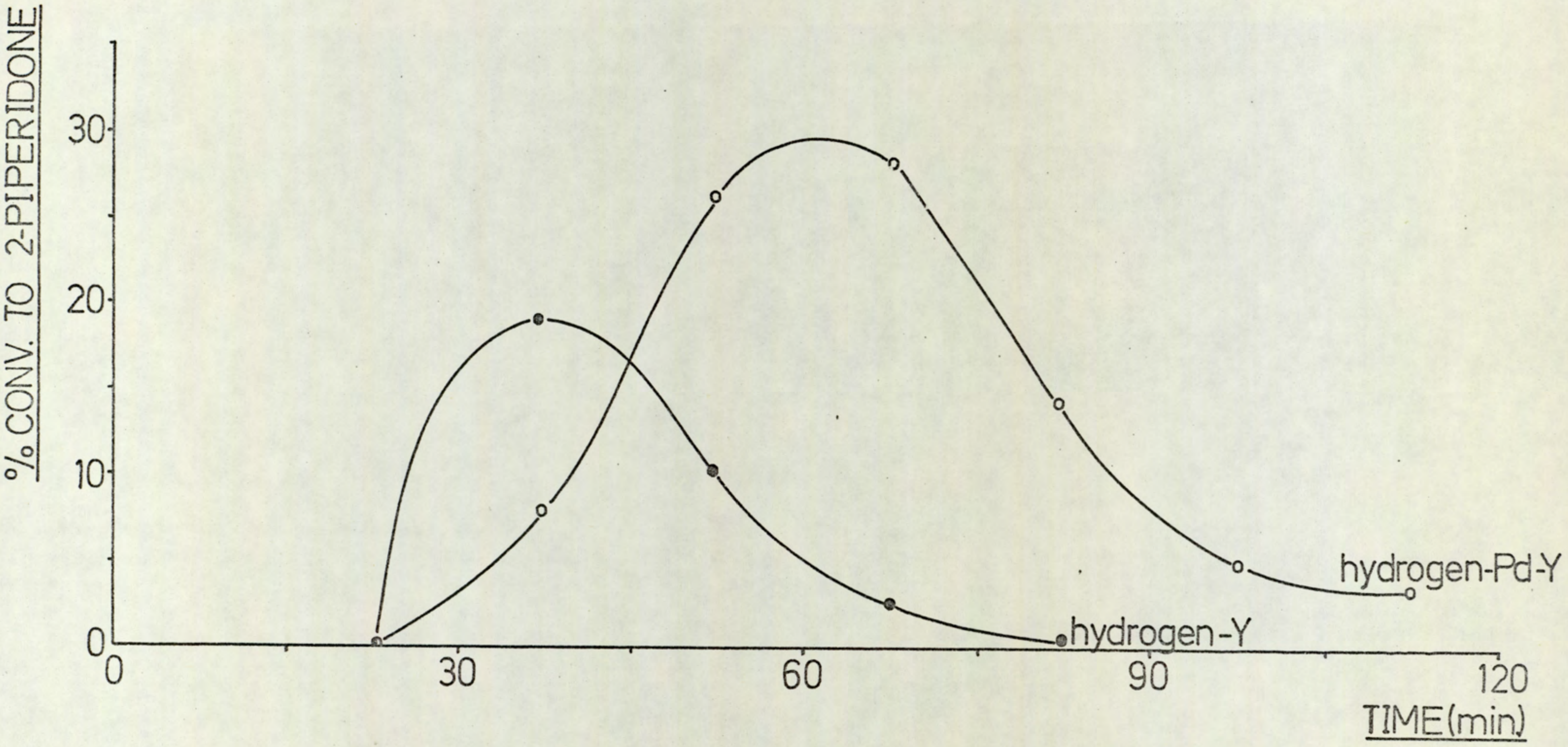


FIG. 16, comparison of 2-piperidone formation on hydrogen-Y and hydrogen-Pd-Y

Beckmann rearrangement of cyclopentanone oxime to 2-piperidone.

The spectroscopic study reported earlier, indicated that the formation of 4-cyanobut-1-ene from cyclopentanone oxime is associated with the zeolite cations. Since the amount of palladium in hydrogen-Pd-Y corresponds to only about 1% of the total number of cations, one would not expect there to be any difference between the amount of alkene-nitrile formed on hydrogen-Y and that formed on hydrogen-Pd-Y. The figures for the 4-cyanobut-1-ene selectivities for the two catalysts reported in Table 7 are almost identical, and in Figure 17 the concentration profiles from the reactor are shown to be comparable. The same effect is shown in Figure 18, where the alkene-nitrile plots for sodium-Y and sodium-Pd-Y are shown. The large effect of palladium on 2-piperidone formation, and its small effect on alkene-nitrile formation are consistent, therefore, with the facts that 2-piperidone formation is associated with surface hydroxyl groups, and that 4-cyanobut-1-ene formation is associated with the zeolite cations.

It has been conclusively shown that acidic surface hydroxyl groups are responsible for the Beckmann rearrangement of alicyclic oximes. A relationship should exist, therefore, between the quantity of 2-piperidone formed on each catalyst, and the Bronsted acidity of that catalyst. There are two ways of obtaining catalysts with acidities varying between that of hydrogen-Y and that of sodium-Y. The first is to produce samples of hydrogen-Y with varying degrees of decationation. The second method is to use zeolites containing different cations. As reported in section 1.3., the electrostatic field associated with certain cations is sufficient to produce dissociation of water molecules, and form surface hydroxyl groups. By using zeolites containing these cations, therefore, one can vary the degree of dissociation of water molecules, and so vary the Bronsted acidity of the catalyst. Ward (57,113) has reported relative values for the Bronsted acidities of certain cation containing and decationated zeolites. Ward estimated these acidities by studying the adsorption of pyridine spectroscopically, and measuring the ratio of the 1545 cm^{-1} band of adsorbed pyridine, which is known to be caused by adsorption onto a Bronsted acid site, to the sample mass. Since an estimation of the relative acidities of hydrogen-Y, rare earth-Y, calcium-Y and sodium-Y are available, these were used as catalysts of varying acidities. It must be remembered that since

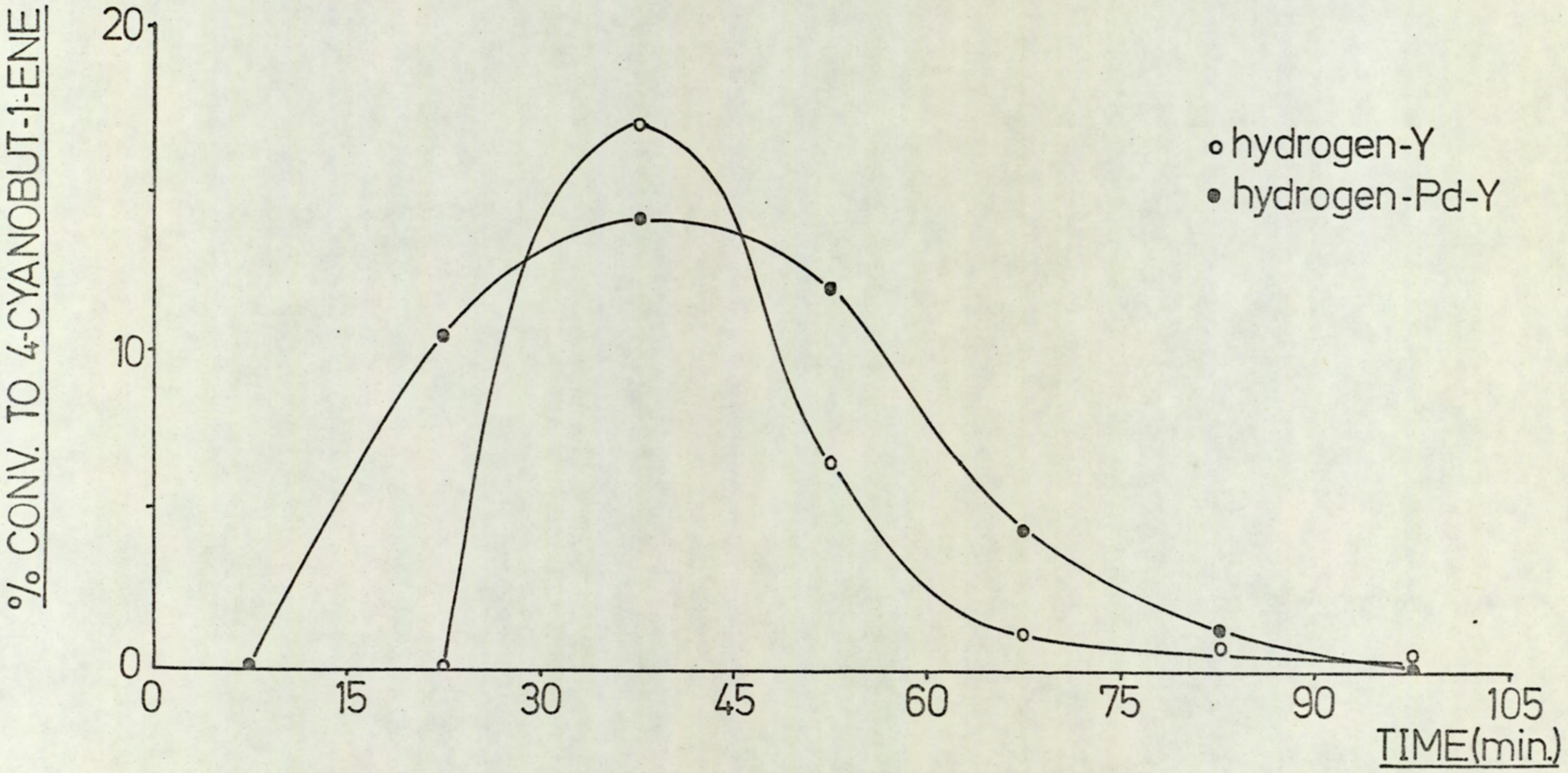


FIG. 17, comparison of 4-cyanobut-1-ene formation on hydrogen-Y and hydrogen-Pd-Y.

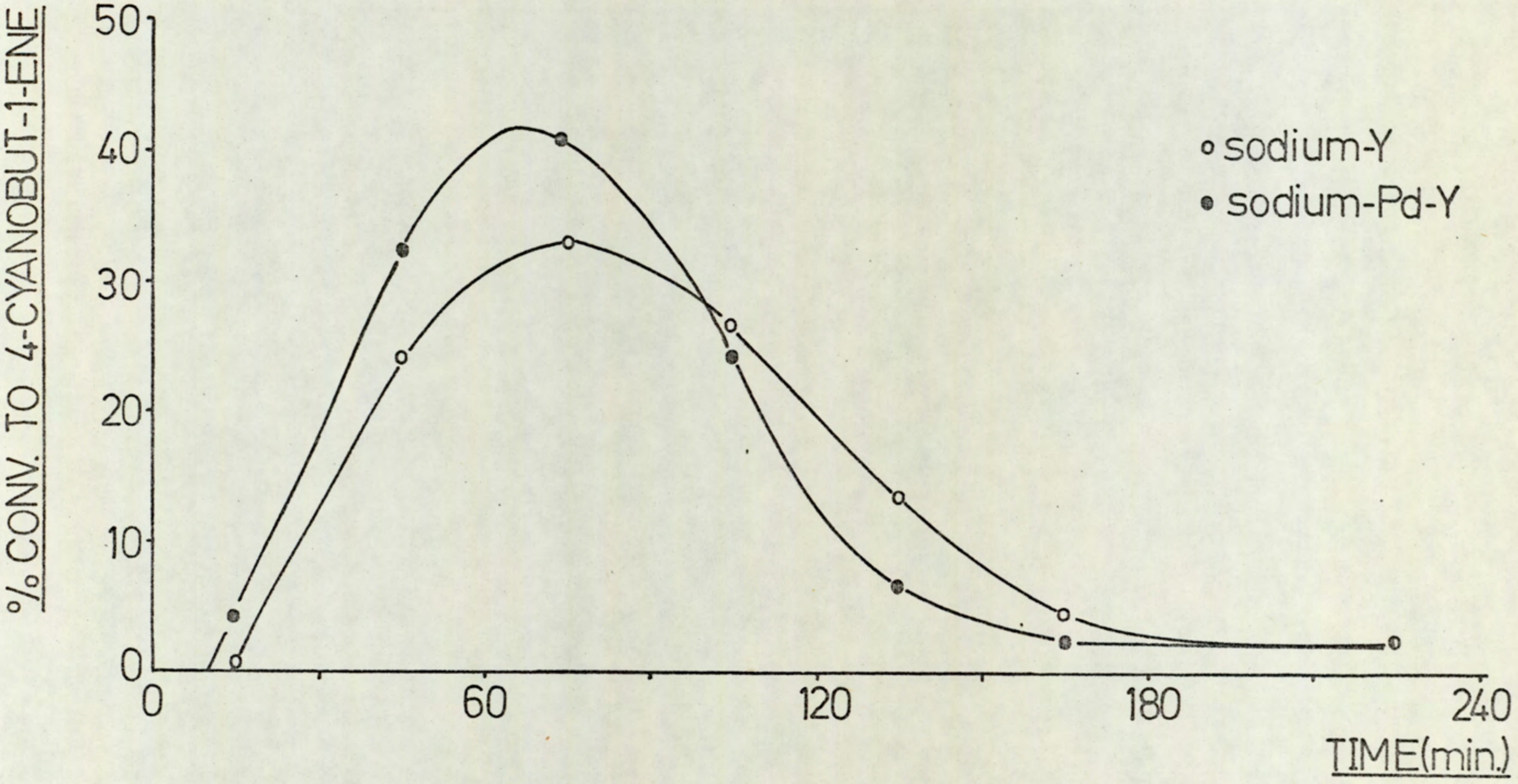


FIG. 18, comparison of 4-cyanobut-1-ene formation on sodium-Y and sodium-Pd-Y.

the formation of alkene-nitriles is associated with the zeolite cations, any relationship between acidity and 2-piperidone formation on these catalysts, will be effected by the varying amounts of alkene-nitrile formed. Other complicating factors associated with this variation are the differences in oxime conversion and catalyst lifetimes for the various catalysts, and the low recoveries. It is apparent that any quantitative interpretations relating acidity to 2-piperidone formation are impossible for a flow system. The acidities determined by Ward and the selectivities for 2-piperidone formation are reported in Table 8. Although the selectivities are calculated over different catalyst

TABLE 8: VARIATION IN 2-PIPERIDONE FORMATION WITH CATALYST ACIDITY

Catalyst	Acidity	Selectivity for 2-piperidone
Hydrogen-Y	15.8	9.4
Lanthanum-Y	11.3	4.5
Calcium-Y	4.3	3.6
Sodium-Y	0	0

lifetimes (see Table 7), qualitatively it can be seen that the order of increasing selectivity for 2-piperidone formation is the same as the order of increasing acidity of the catalyst. This correlation, although only qualitative, is consistent with the conclusions drawn from the spectroscopic studies, and shows that Bronsted acid surface hydroxyl groups are responsible for the Beckmann rearrangement, not only on decationated zeolites, but also on zeolites whose cations have sufficient electrostatic potential to cause dissociation of water molecules, and hence formation of surface hydroxyl groups.

It has been suggested that the formation of an alkene-nitrile from a cyclic oxime occurs on or near the zeolitic cations. It is possible to confirm this theory by studying the formation of an alkene-nitrile on a series of alkali-metal zeolites. In this case any relationship is not complicated by competing reactions, since these catalysts do not contain surface hydroxyl groups, and so no 2-piperidone is formed. The series of zeolites lithium-Y, sodium-Y, potassium-Y and caesium-Y was used to study the variation of alkene-nitrile formation with the zeolitic cation. In Figure 19 the selectivity for 4-cyanobut-1-ene formation is plotted against the electrostatic potential of the zeolitic cation. In Figure 20 the selectivity is plotted as a function of the ionic radius of the cation (57). It is apparent from Figures 19 and 20 that the formation of 4-cyanobut-1-ene from cyclopentanone oxime is a function of the electrostatic potential of the zeolitic cation, being greater for the smaller cations than for the larger ones. This conclusion is in accord with the results of the spectroscopic study reported earlier. In these studies evidence was presented for the formation of an alkene function when cyclopentanone oxime is reacted with sodium-Y. No evidence was obtained for the formation of a nitrile function on this catalyst, however, indicating that the C≡N bond is only formed when desorption occurs.

The difference in alkene-nitrile formation for sodium-Y, and for a hydrogen-Y catalyst in hydrogen, is shown in Figure 21. No 2-piperidone is formed over sodium-Y, since this catalyst contains no surface hydroxyl groups, but the fact that 4-cyanobut-1-ene is formed by reaction of cyclopentanone oxime over hydrogen-Y is consistent with the residual sodium in the decationated zeolite. The latter has about 10% of its total cations as sodium ions. The work of Hansford and Ward reported in section 1.3, suggests that most of the remaining sodium ions are situated in the S_I sites of the zeolite lattice, and are not accessible to molecules inside the catalyst supercavities. Some of the sodium ions will presumably be accessible, however, and these can account for the alkene-nitrile produced on hydrogen-Y. The fact that no alkene-nitrile formation was detected during the spectroscopic studies on hydrogen-Y is probably due to the relatively low concentration of accessible sodium ions in the lattice, and the non-formation of the C≡N function until desorption occurs.

The formation of cyclopentanone over the various catalysts for which results are reported in Table 7, is difficult to correlate with any property of the zeolite samples. Quite a high selectivity for the ketone is obtained from sodium-A, but the oxime conversion is correspondingly low, due to the small pore diameter of the catalyst. This result suggests that the ketone

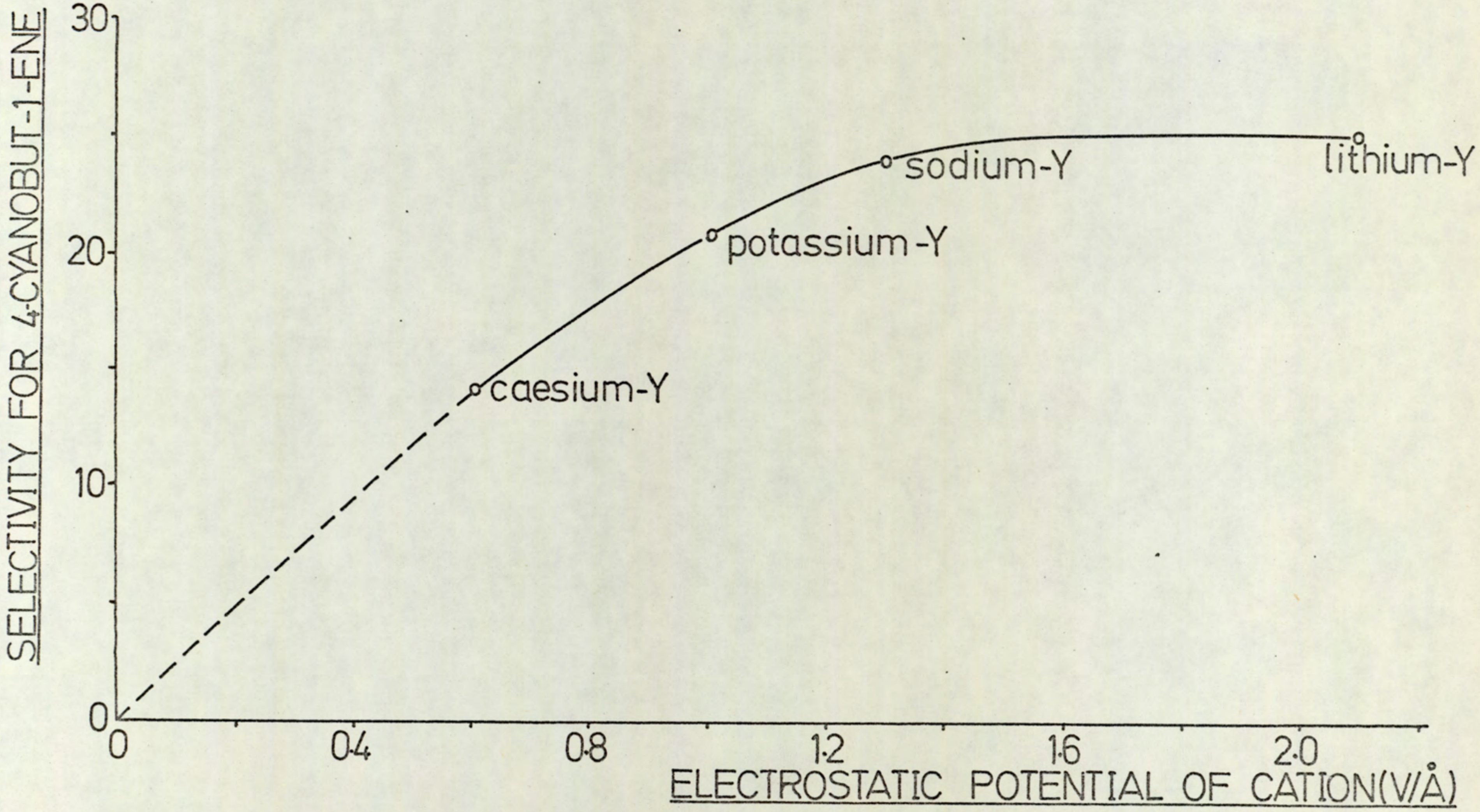


FIG. 19, variation of 4-cyanobut-1-ene selectivity with electrostatic potential of zeolite cation.

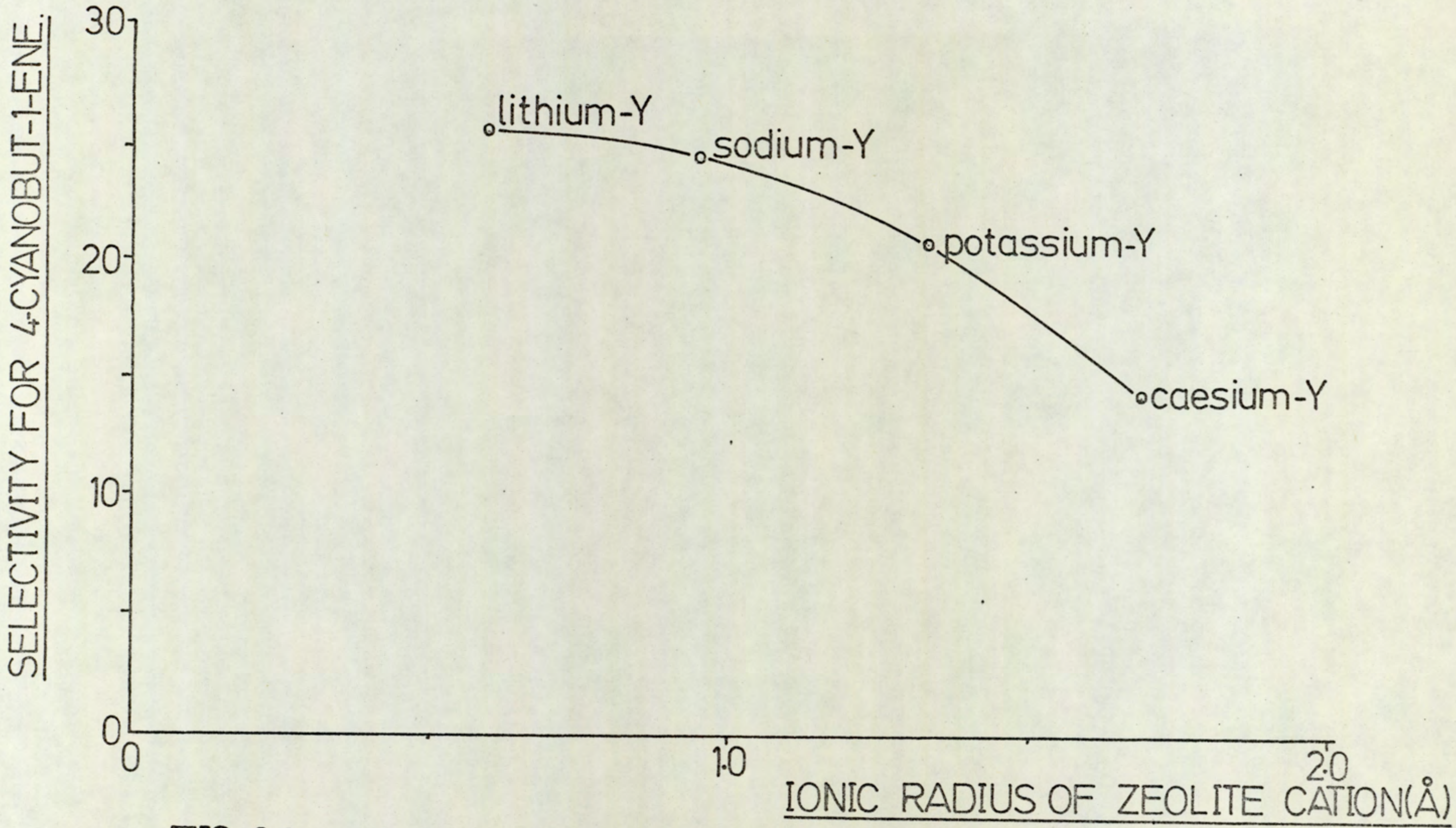


FIG. 20, variation of 4-cyanobut-1-ene selectivity with ionic radius of zeolite cation.

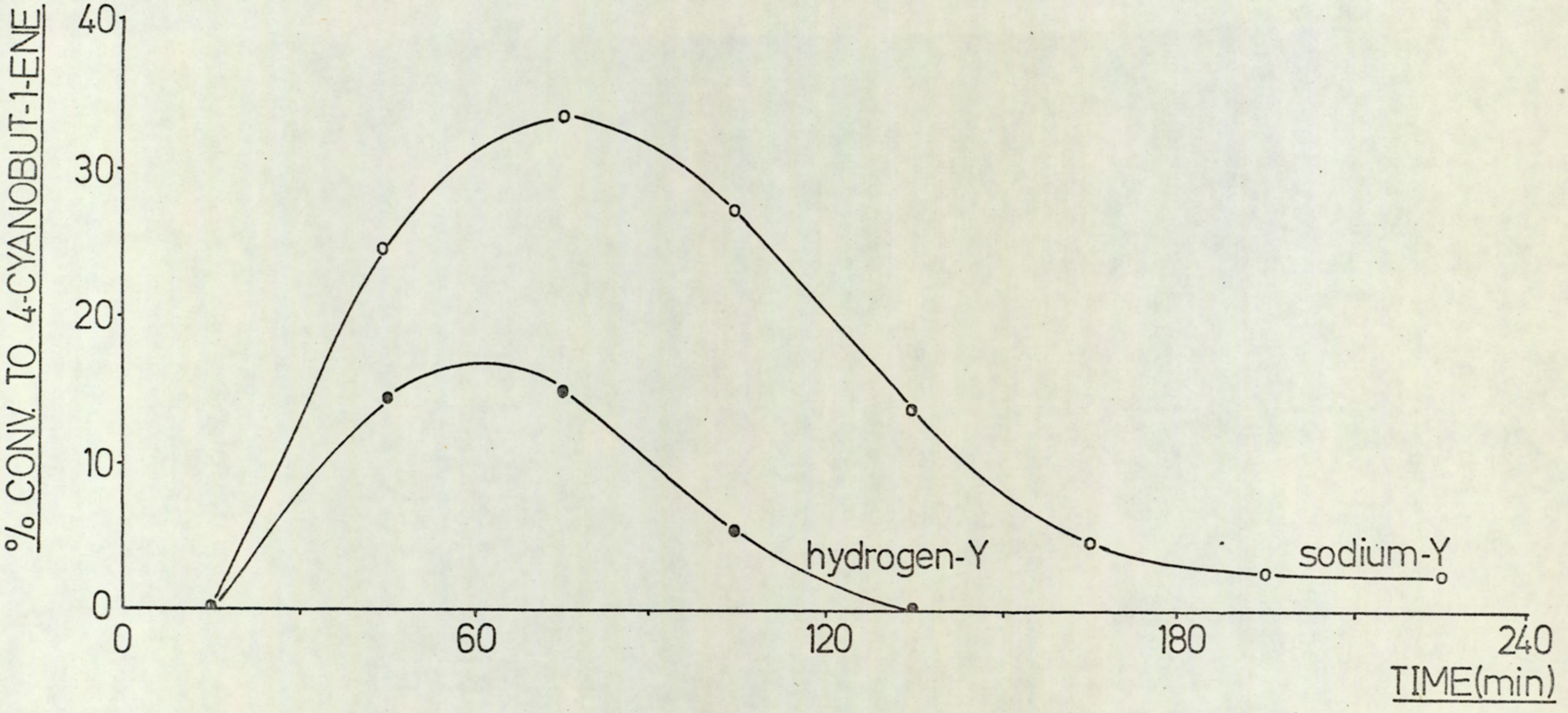


FIG. 21, comparison of 4-cyanobut-1-ene formation on hydrogen-Y and sodium-Y may possibly be formed on the external surface of the sieves. A typical profile of products from a decationated zeolite as a function of time is shown in Figure 22. (The reaction profile, as typified in Figure 22, will be discussed in greater detail in section 4.1). Cyclopentanone is only eluted from the catalyst bed after nearly one hour of reaction on hydrogen-Y. This was also found to be the case for all the zeolite samples reported in Table 7, except for sodium-A, and this finding is difficult to correlate with the formation of cyclopentanone on the external surface of the zeolites. A more feasible explanation of the formation of cyclopentanone is that the oxime is hydrolysed by residual water in the zeolite lattice. The late elution of the ketone from the catalyst bed is probably due to a chromatographic effect within the zeolite pores. Further support for this postulation is provided in section 4.3, where the use of an aqueous solvent is shown to be associated with an increase in the formation of cyclopentanone.

To summarize, the results reported in Table 7 confirm the conclusions drawn from the spectroscopic studies of Chapter 2. The rearrangement of cyclopentanone oxime to 2-piperidone is catalyzed by the Bronsted acid surface hydroxyl groups which absorb at 3640 cm^{-1}. The formation of 4-cyanobut-1-ene is associated with the exchangeable cation in the zeolite lattice, and is a function of its electrostatic potential. Having confirmed the findings of the spectroscopic study, the flow system was used to study the effect of varying the conditions of the rearrangement of cyclopentanone oxime upon its conversion. This work is discussed in the next chapter.

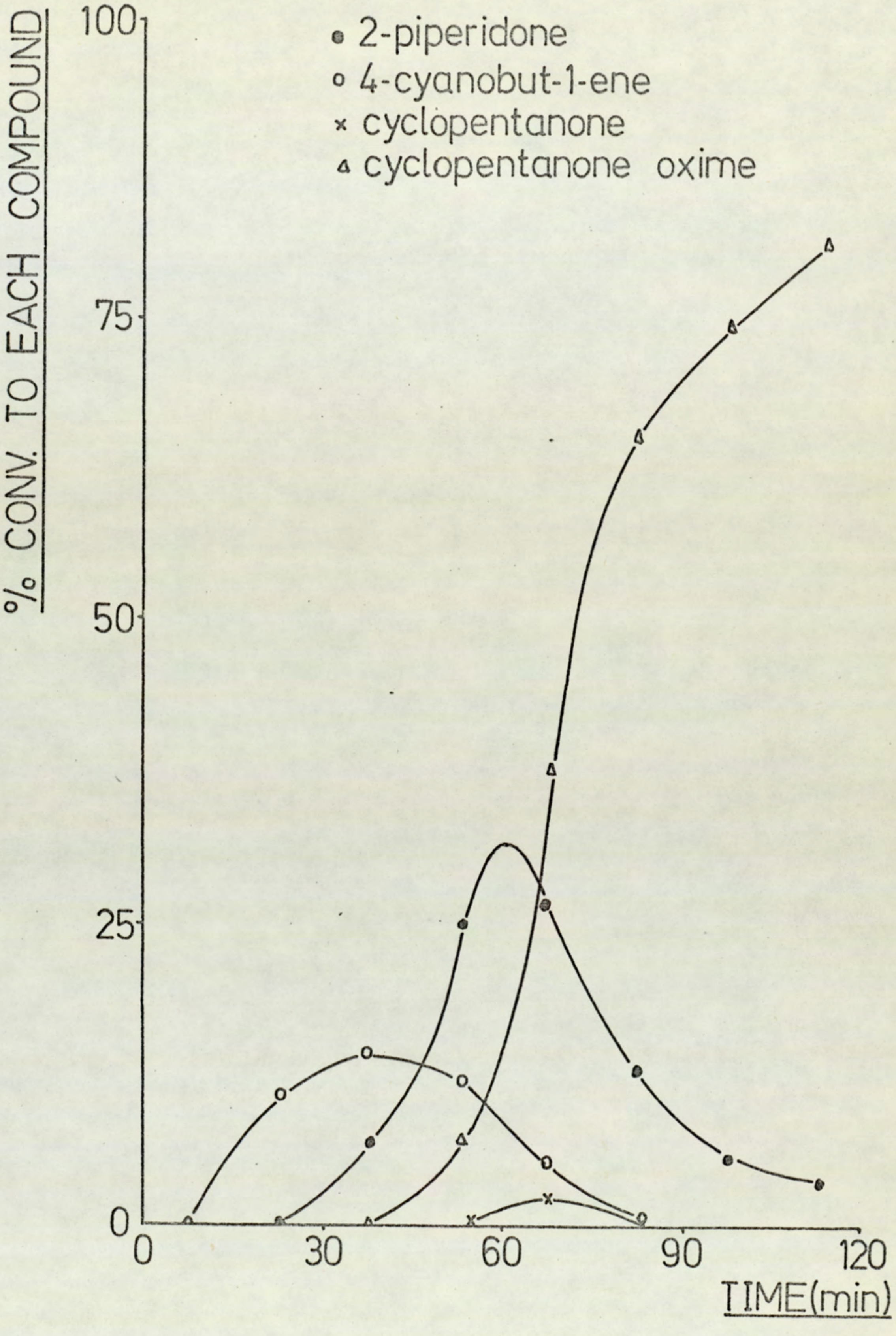


FIG.22, typical reaction profile from a decationated zeolite

CHAPTER 4

FURTHER STUDIES ON THE REARRANGEMENT OF CYCLOPENTANONE OXIME OVER DECATIONATED ZEOLITES.

4.1. Hold-up of organic material.

When a solution of cyclopentanone oxime in benzene is passed over a decationated zeolite at 340°, the order of appearance of products in the collection trap is invariably the same. There is virtually no hold-up of benzene, and in all cases the order of appearance of the other compounds is 4-cyanobut-1-ene, 2-piperidone, cyclopentanone oxime and cyclopentanone. A typical reaction profile is shown in Figure 22 (hydrogen-Pd-Y, 340°, N_2 carrier, solvent benzene, LHSV 1.0). For other solvents the order is sometimes slightly different, but in all cases 2-piperidone is detected before unreacted cyclopentanone oxime.

The amount of cyclopentanone oxime fed to the catalyst from the start of a run until the time when 2-piperidone is first detected in the collection trap, can be easily estimated from a knowledge of the oxime feed rate, and extrapolation of the lactam concentration versus time curve to zero concentration. Not all of this oxime will be retained by the catalyst, since some of it will react to form 4-cyanobut-1-ene, which is detected before 2-piperidone. The weight of alkene-nitrile detected during the period stated can be obtained from the analysis of the reactor effluent, and so the weight of cyclopentanone oxime which has appeared as 4-cyanobut-1-ene over this period can be calculated. This weight of oxime can be subtracted from the weight fed over the same period, and so one can obtain an estimate of the quantity of cyclopentanone oxime actually adsorbed on the catalyst at the time when 2-piperidone is first detected in the collection trap.

In order to take the catalyst weight into account and convert the weights of oxime into more fundamental values, the latter were divided by the number of supercavities present in the given weight of catalyst. Taking the unit cell composition of sodium-Y zeolite as $Na_{56}\ (AlO_2)_{56}\ (SiO_2)_{136}$, and that of hydrogen-Y containing 1% of sodium as $Na_5H_{51}\ (AlO_2)_{56}\ (SiO_2)_{136}$, the latter will have a formula weight of 11,630. One unit cell contains eight supercavities, and so there are 4.14×10^{20} supercavities per gram of anhydrous hydrogen-Y. For the same catalyst containing 0.5% by weight palladium, the formula weight is 11,691, and the number of supercavities per gram is 4.13×10^{20}. For one gram of either catalyst, therefore, one molecule of cyclopentanone oxime per supercavity corresponds to an oxime weight of 0.068 gram. Using this figure the number of cyclopentanone oxime molecules present per supercavity of catalyst, when 2-piperidone is first eluted from the catalyst bed can be calculated. Several of these values are reported in Table 9.

The number of molecules held per supercavity for a benzene solvent and nitrogen carrier is fairly constant at about 3-3½. This figure is almost independent of the quantity of catalyst and the strength of the feed solution. For an aqueous solvent the hold-up is halved; also the use of a hydrogen carrier slightly reduces the amount of cyclopentanone oxime retained by the catalyst over the relevent period.

The consistency of the hold-up for the experiments in which a benzene solvent and nitrogen carrier were used, suggests that the figure of about 3-3½ molecules of cyclopentanone oxime per supercavity may correspond to near saturation of the catalyst. If this is so, then this value should be comparable to literature values for the saturation capacities of Y-type sieves, for molecules of similar size, shape and polarity. The saturation capacity of the decationated zeolite should be fairly independent of whether the adsorbed species is cyclopentanone oxime, 2-piperidone or the open-ring surface species detected during the spectroscopic studies, since all are reasonably similar in size, shape and polarity. Catalin models indicate that cyclopentanone oxime is similar in size to cyclohexane and toluene. Literature values (43) for the number of guest molecules tolerated in each supercavity of type-Y zeolite are 4.1 for cyclohexane and 4.6 for toluene. Comparison of these values with those reported for a benzene solvent in Table 9 suggests that at the beginning of the catalytic reaction, all the cyclopentanone oxime feed is tenaciously adsorbed, and the product of its rearrangement, 2-piperidone, is only detected in the effluent stream when the catalyst is almost saturated with organic material.

It was reported in Chapter 2, as a result of spectroscopic studies, that an open-chain intermediate is present on the catalyst surface after rearrangement of cyclopentanone oxime has occurred. This intermediate is formed at relatively low temperatures (approximately 100°), and is difficult to desorb from the catalyst surface, interacting strongly with the surface hydroxyl groups which absorb at 3640 cm^{-1}. At 340°, therefore, the temperature at which the results reported in Table 9 were obtained, it is probable

TABLE 9: HOLD-UP OF CYCLOPENTANONE OXIME ON DECATIONATED ZEOLITES

Catalyst	Anhydrous Catalyst Weight(g)	Solvent	Solution Strength w/w %	L.H.S.V. of oxime Solution	Carrier (40ml/min.)	Av. no. of cyclo-C_5H_9ON molecules held/supercavity
Hydrogen-Y	12.75	benzene	30	1.0	N_2	3.3
Hydrogen-Pd-Y	12.75	benzene	30	1.0	N_2	3.4
Hydrogen-Pd-Y	18.70	benzene	30	0.7	N_2	3.0
Hydrogen-Pd-Y	25.50	benzene	30	0.5	N_2	2.9
Hydrogen-Pd-Y	12.75	benzene	10	1.5	N_2	3.4
Hydrogen-Pd-Y	12.75	benzene	30	1.0	H_2	2.8
Hydrogen-Pd-Y	12.75	water(i)	10	1.5	N_2	1.5

(i) 90 vol. H_2O : 2 vol. glacial acetic acid to aid solubility,

340°.

that when 2-piperidone is first eluted from the catalyst bed, the open-chain intermediate is the predominant surface species, all of the cyclopentanone oxime having rearranged either on, or very shortly after adsorption. Also, when a 25% solution of 2-piperidone in benzene is passed over hydrogen-Y, the hold-up corresponds to 3.4 lactam molecules per catalyst supercavity. This figure compares favourably with those reported in Table 9. Since it was reported in Chapter 2 that 2-piperidone adsorbed from the vapour phase is held on the surface of hydrogen-Y as the same open-chain compound that is produced by rearrangement of cyclopentanone oxime, the agreement of hold-up values for a feed of cyclopentanone oxime, and one of 2-piperidone, is good evidence that the open-chain intermediate is the predominant surface species during the hold-up period. Further evidence for this conclusion was provided when a catalyst saturated with reactant was extracted using an organic solvent and only 2-piperidone was obtained; no unreacted oxime was detected.

Since the open-ring intermediate is interacting strongly with the hydroxyl groups which absorb at 3640 cm^{-1}, it is interesting to calculate what fraction of the available active hydroxyl groups are occupied by the surface intermediate at near saturation of the catalyst. The deuterium exchange work of Uytterhoeven et al (60) indicates that for an 80% decationated Y-type sieve, activated at 440^{o}, there are about 2.5×10^{21} hydroxyl groups per gram of catalyst. For a 90% decationated sample there will be $2.5 \times 10^{21} \times 9/8$ or 2.8×10^{21} hydroxyl groups. Although the peak areas of the 3540 cm^{-1} and 3640 cm^{-1} cannot be quantitatively measured, since they are not completely resolved (for example Spectrum 10a), it is possible to estimate their relative areas. The ratio area of 3640 cm^{-1} band / (area of 3540 cm^{-1} band + area of 3640 cm^{-1} band) for the sample of hydrogen-Y used in the present work is approximately 0.3. The number of hydroxyl groups absorbing at 3640 cm^{-1} therefore is $2.8 \times 10^{21} \times 0.3 = 8.4 \times 10^{20}$. This corresponds to $8.4 \times 10^{20}/4.14 \times 10^{20}$ or 2.0 hydroxyl groups in each catalyst supercavity which absorb at 3640 cm^{-1}. This figure is less than those reported in Table 9, suggesting that perhaps when the catalyst is saturated, not all of the adsorbed molecules are directly associated with an acidic hydroxyl group. The approximations and estimations involved in arriving at the figures discussed above obviously do not allow this conclusion to be rigidly drawn, but it is apparent that at saturation of the catalyst, all of the 3640 cm^{-1} surface hydroxyl groups are being utilized. Possibly the discrepancy between the value of 2.0 hydroxyl groups per catalyst supercavity, and those reported in Table 9 for a benzene solvent, is due to alkene-nitrile formation, which does not involve acidic hydroxyl groups.

It is shown in Table 9 that the use of an aqueous solvent is associated with a reduced hold-up on the catalyst, and this is also found for other solvents. The dependence of hold-up upon the solvent is discussed in greater detail in section 4.3. For the benzene-nitrogen system the hold-ups reported in Table 9 at 340°, are fairly independent of temperature over the range studied (225-360°).

4.2. Effect of temperature.

Due to the low recoveries of nitrogeneous material and short catalyst lifetimes reported for a temperature of 340° in Chapter 3, the rearrangement of cyclopentanone oxime over decationated zeolites was studied over a limited temperature range, in order to see if substantial extensions of catalyst lifetime are obtained below 340°. The results are summarized in Table 10. The results for hydrogen-Y are the same at 300° as they are at 340°. For hydrogen-Pd-Y, however, variations in 2-piperidone selectivity are obtained. The highest selectivity for 2-piperidone formation is obtained at a temperature of 300°, and there is a decreasing lactam selectivity as the temperature is raised to 360°. The catalyst lifetime is constant over the temperature range studied. At 225° a 69% conversion of oxime is obtained, but the selectivities for the named products are low. Probably little decomposition occurs on the catalyst at this relatively low temperature, and so the catalyst is probably saturated with organic material after two hours. This conversion is misleading, therefore, since the saturation of the catalyst alone accounts for an oxime conversion of 46% over a two hour period. This applies for all the results reported in Table 10, if the catalyst lifetime is only two hours, the maximum total selectivity for 2-piperidone, 4-cyanobut-1-ene and cyclopentanone, neglecting decomposition, and assuming the catalyst to be saturated at the end of the reaction, is only 54%. If the catalyst is not saturated at the end of the reaction, then the number of molecules decomposed per supercavity, in order to reduce the catalyst activity to zero, also places a severe limitation on the

TABLE 10: EFFECT OF TEMPERATURE ON THE REARRANGEMENT OF CYCLOPENTANONE OXIME (i) OVER DECATIONATED ZEOLITES

Catalyst(ii)	Temperature °C	Reaction time (min.)	Oxime Conversion %	Selectivity for 2-piperidone %	Selectivity for 4-cyanobut-1-ene %	Selecivity for cyclopentanone %
Hydrogen-Y	300	90	57	9.4	8.2	6.8
Hydrogen-Y	340	90	58	9.5	7.9	4.0
Hydrogen-Pd-Y	225	120	69	6.0	4.5	0.3
Hydrogen-Pd-Y	300	120	64	25.7	9.9	1.0
Hydrogen-Pd-Y	320	120	59	20.2	8.6	0.8
Hydrogen-Pd-Y	340	120	70	14.1	7.8	0.5
Hydrogen-Pd-Y	360	120	69	10.3	8.1	0.7

(i) 30% w/w solutions in benzene, LHSV 1.0, carrier N_2 40 ml. min.$^{-1}$,

(ii) 12.75g anhydrous weight.

maximum obtainable total selectivity, for the three named products. It is obvious, therefore, that in order for the recovery of nitrogeneous material to become a reasonable percentage, the catalyst lifetime must be extended.

The oxime conversions reported in Table 10 for hydrogen -Pd-Y are fairly constant, but above 300°, the selectivity for 2-piperidone formation decreases with increasing temperature. The predominant surface species at 340° has been shown to be the open-chain lactam species, so it appears that the reduction in 2-piperidone selectivity on increasing the temperature, is due to an increase in the rate of decomposition of this species. The spectroscopic study presented in Chapter 2 indicated that desorption of 2-piperidone from the surface does not occur easily, it is clear, therefore, that in order to increase the catalyst lifetime substantially it is necessary to use conditions which favour the removal of the product from the surface. In subsequent studies involving the variation of solvent and carrier, therefore, a temperature of 340° was used. This is a slightly higher temperature than was found to give a maximum 2-piperidone selectivity for the reaction on hydrogen-Pd-Y, but it was hoped that its use would aid the removal of product from the catalyst surface, perhaps at the expense of some product decomposition.

The selectivity for 4-cyanobut-1-ene formation is fairly constant over the range 300-340° for hydrogen-Y, and between 300 and 360° for hydrogen-Pd-Y. The selectivity for cyclopentanone formation is erratic, supporting the suggestion presented in Chapter 3, that this compound is formed by hydrolysis of cyclopentanone oxime by residual zeolitic water.

4.3. Effect of solvent.

The results of using different solvents for the Beckmann rearrangement of cyclopentanone oxime are reported in Table 11. There is a considerable improvement of selectivity for 2-piperidone formation on going down the table, and this is coupled with a marked increase in the catalyst lifetime. For the same changes in solvent however, the selectivity for 4-cyanobut-1-ene formation is almost constant, and except for an aqueous solution the production of cyclopentanone is unaffected by the change.

The difference in 2-piperidone formation for a benzene solvent and an aqueous solvent is illustrated in Figure 23. The curves for the other solvents reported in Table 11 are intermediate between the profiles for benzene and water. The steady improvement

TABLE 11: EFFECT OF SOLVENT ON THE REARRANGEMENT OF CYCLOPENTANONE OXIME (i) OVER DECATIONATED ZEOLITES

Solvent (ii)	Reaction time (min.)	Oxime conversion %	2-piperidone selectivity %	4-cyanobut-1-ene selectivity %	cyclopentanone selectivity %
Benzene	150	94	4.4	4.8	1.0
Cyclohexane	150	79	12.3	5.4	1.1
Flourobenzene	200	95	12.6	4.5	3.1
Methyl cyanide	330	92	17.1	4.3	2.9
Water (iii)	>360	97	20.8	3.4	8.4

(i) Catalyst 12.75g hydrogen-Pd-Y, 340°, carrier N_2 40 ml. min.$^{-1}$,

(ii) Solutions 10% w/w in named solvent, LHSV 1.5,

(iii) 45 vol. H_2O : 1 vol. glacial acetic acid to aid solubility.

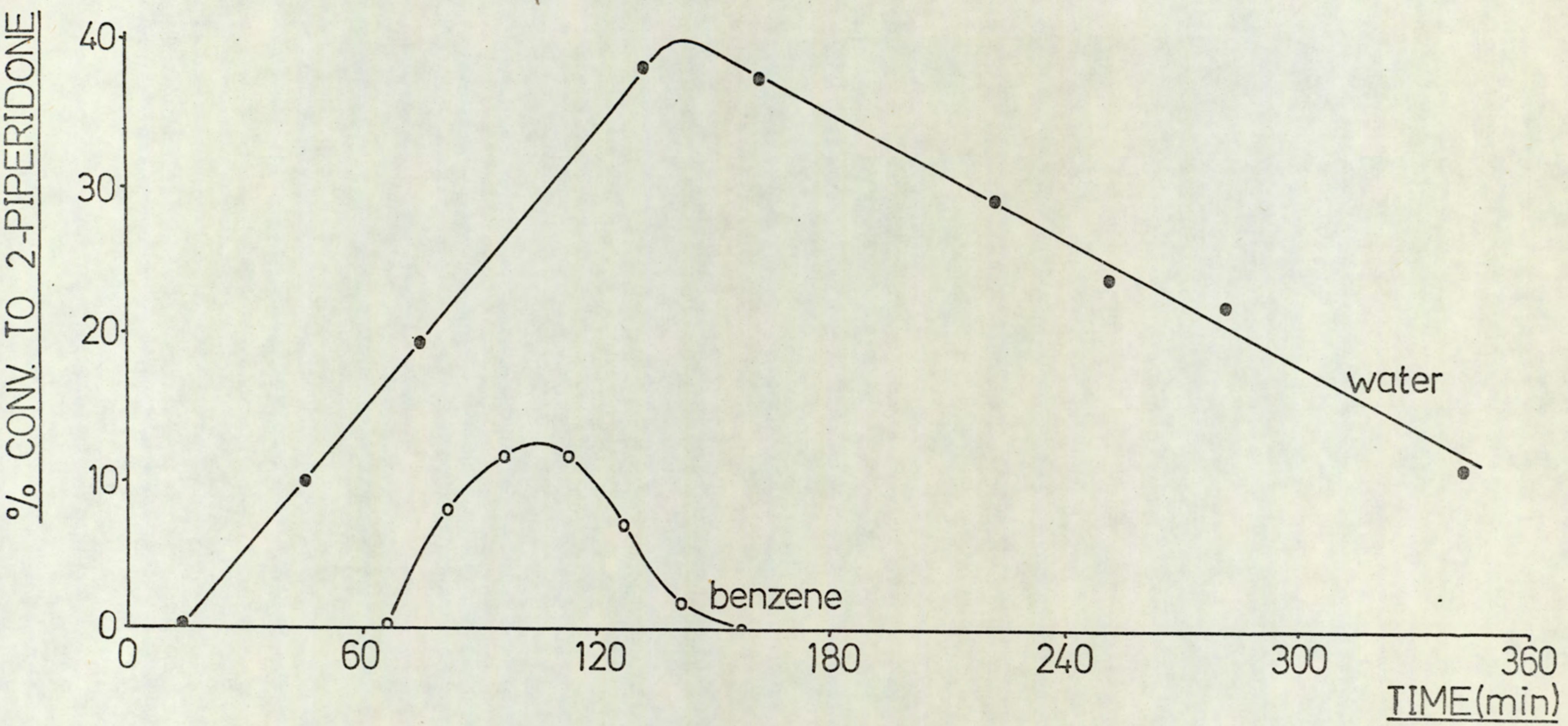


FIG. 23, comparison of 2-piperidone formation for a benzene and an aqueous solvent.

in 2-piperidone selectivity and catalyst lifetime on going down Table 11, is difficult to correlate with any chemical or physical property of the solvents. For example, the order of increasing dipole moments of the solvents is cyclohexane, benzene, fluorobenzene, water, methyl cyanide, and the order of increasing molecular size is water, methyl cyanide, benzene, fluorobenzene and cyclohexane. It is noticeable, however, from the 2-piperidone reaction profiles, that an increase in 2-piperidone formation and catalyst lifetime is associated with a reduced hold-up of lactam on the catalyst. This relationship is shown in Figure 24, where the hold-up is plotted against the 2-piperidone selectivity for each solvent. Figure 24 shows that the selectivity for 2-piperidone formation is very sensitive to changes in hold-up on the catalyst surface. The most efficient solvents for removing 2-piperidone from the surface are also those which extend the catalyst lifetime, and increase the selectivity for 2-piperidone formation. This result is consistent with the suggestion made in section 4.2., that the short catalyst lifetime associated with the use of a benzene solvent is due to decomposition of 2-piperidone, or the open-chain surface detected in the spectroscopic study, on the catalyst surface. Benzene is not efficient in removing 2-piperidone from the catalyst, as was indicated in section 4.1., where it was shown that the catalyst supercavities must be almost saturated with organic material before lactam is eluted from the catalyst bed. The product of rearrangement is therefore on the surface for a long time, and its decomposition could result in surface poisoning. If the open-chain compound is not stable on the catalyst surface, then at a given temperature, the rate of fouling of the catalyst will depend upon the average length of time that the intermediate is on the surface.

The order of effectiveness of the solvents in removing the product from the surface, as shown in Figure 24, is not fully understood. It appears that in general the more polar solvents are those which give the highest selectivity for lactam formation. If solvent polarity is the only governing factor, however, the results of using cyclohexane should be comparable to those using benzene, and the positions of water and methyl cyanide in Figure 24 should be reversed. It is unlikely that any single property of the solvents is correlatable with their order of effectiveness for the Beckmann rearrangement of cyclopentanone oxime. Probably the interaction between the solvent vapour and the adsorbed

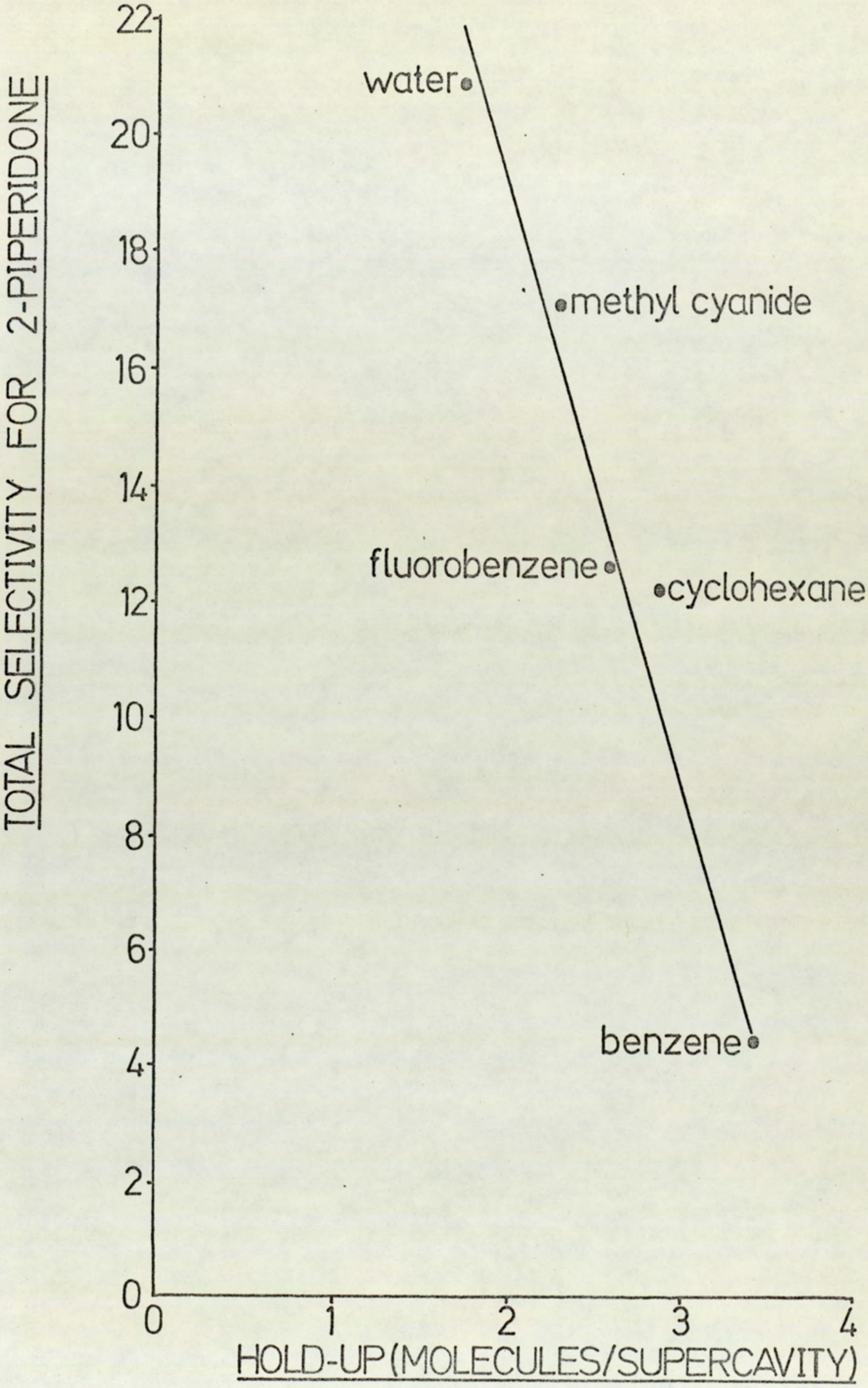


FIG. 24, variation of 2 piperidone selectivity with catalyst hold-up.

species is a complex one, and factors such as solvent stability and polarizability are involved.

A study of the effect of solvent upon the heterogeneously catalyzed Beckmann rearrangement of cyclopentanone oxime, has provided evidence that the short catalyst lifetimes reported previously (Chapter 3), are due primarily to the decomposition of rearranged product on the catalyst surface. Further evidence for this proposal is provided in Chapter 6, where a study of product stabilities is reported. The effect has also indicated one way in which an increased catalyst lifetime can be obtained, namely by using a polar solvent, such as water.

The small effect of solvent upon the selectivity for 4-cyanobut-1-ene production is consistent with the fact that this is the compound first detected in the collection trap. It is fairly easily desorbed from the catalyst surface, therefore, and its removal from the catalyst bed is almost unaffected by changes in the solvent.

The selectivity for cyclopentanone formation is higher for an aqueous solvent that for any other reported in Table 11. It has been suggested earlier (Chapter 3) that perhaps this compound is formed by hydrolysis of the oxime, and the results of using an aqueous solvent support this suggestion. Indeed, when a 10% solution of cyclopentanone oxime in water was passed through the reactor tube at 340°, in the absence of a catalyst, a 22% conversion of oxime occurred over a two hour period, and the selectivity for cyclopentanone formation was 51%. 4-Cyanobut-1-ene or 2-piperidone were not detected in the product from this experiment. The ketone produced from the reaction of cyclopentanone oxime in a non-aqueous solvent presumably results from hydrolysis of the oxime by residual water present inside the catalyst supercavities. This would account for the variations in ketone formation for the various catalysts, since the amount produced would depend upon the extent of drying of the catalyst samples.

4.4. Effect of carrier.

The results of varying the carrier gas for the rearrangement of cyclopentanone oxime over decationated zeolites are reported in Table 12. The use of a hydrogen carrier is seen to extend the catalyst lifetime relative to that for a nitrogen carrier, for both hydrogen-Y and hydrogen-Pd-Y. The use of a strongly basic carrier such as ammonia is associated with

TABLE 12: EFFECT OF CARRIER UPON THE REARRANGEMENT OF CYCLOPENTANONE OXIME (i) OVER DECATIONATED ZEOLITES

Catalyst (ii)	Carrier (40ml/min.)	Reaction time (min.)	Oxime conversion %	2-piperidone selectivity %	4-cyanobut-1-ene selectivity %	cyclopentanone selectivity %
Hydrogen-Y	nitrogen	90	57	9.4	7.7	3.8
Hydrogen-Y	hydrogen	180	60	10.9	10.6	2.4
Hydrogen-Y	ammonia	240	18	0	2.1	11.3
Hydrogen-Pd-Y	nitrogen	120	70	14.1	7.8	0.5
Hydrogen-Pd-Y	hydrogen	120	85	22.6	14.9	3.4

(i) 30% w/w solutions in benzene, LHSV 1.0,

(ii) 12.75g anhydrous weight,

340°.

low conversions of oxime and a complete poisoning for 2-piperidone formation.

The differences in 2-piperidone formation for a nitrogen and hydrogen carrier over hydrogen-Y and hydrogen-Pd-Y are illustrated in Figures 25 and 26 respectively. These figures show that for both zeolite samples the catalyst lifetime is doubled when a hydrogen carrier is used. The use of such a carrier appears to result in a stretching of the 2-piperidone concentration profile, without altering the maximum selectivity for lactam formation. It has been reported by Eberly (64) that the surface hydroxyl groups of hydrogen-Y can be almost quantitatively converted to OD groups by exposure of the hydrogen zeolite to deuterium gas at 427°. Exchange can also occur between vapour phase hydrogen and the surface hydroxyl groups, and during any reaction involving these groups, the presence of hydrogen will obviously aid their regeneration and repress their conversion to Lewis acid sites. The use of a hydrogen carrier, therefore, is expected to extend the catalyst lifetime for such reactions. The increased selectivites for 2-piperidone formation reported in Table 12 are consistent with a prolonged effectiveness of the surface hydroxyl groups in the presence of hydrogen. The curves shown in Figures 25 and 26 are also consistent with this concept, and show that although 2-piperidone is released more slowly from the surface in the presence of a hydrogen carrier, about twice as much lactam is formed in the presence of this carrier that in the presence of nitrogen.

It was concluded from the variation of solvent experiments (section 4.3) that poisoning of the catalyst surface is due primarily to decomposition of the open-chain surface species. The selectivity for 2-piperidone formation was shown to be a sensitive function of the hold-up of organic material. Since the catalyst lifetime is doubled by the use of a hydrogen carrier, without any substantial change in hold-up of organic material, there must be some factor involved other than the regeneration of surface hydroxyl groups by hydrogen. If this were the only factor involved, then presumably decomposition of the surface species would occur at a comparable rate for both a nitrogen and hydrogen carrier, and the build up of coke or polymeric material on the surface would have a comparable effect on 4-cyanobut-1-ene formation for both carriers. 4-Cyanobut-1-ene formation is extended in a comparable manner to 2-piperidone formation, when hydrogen is employed as carrier, as is reflected in the selectivities reported in Table 12.

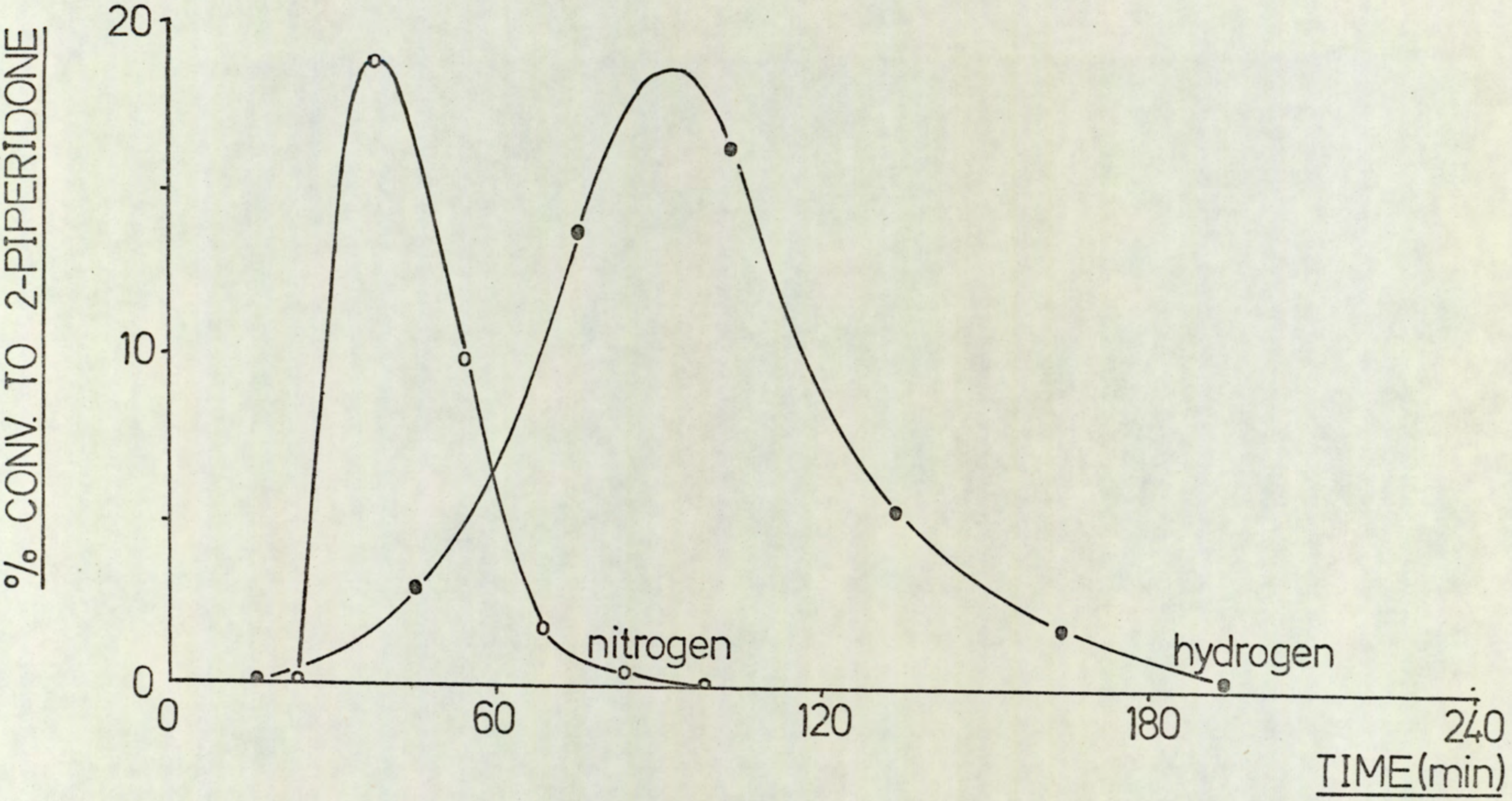


FIG. 25, comparison of 2-piperidone formation for a nitrogen and hydrogen carrier on hydrogen-Y

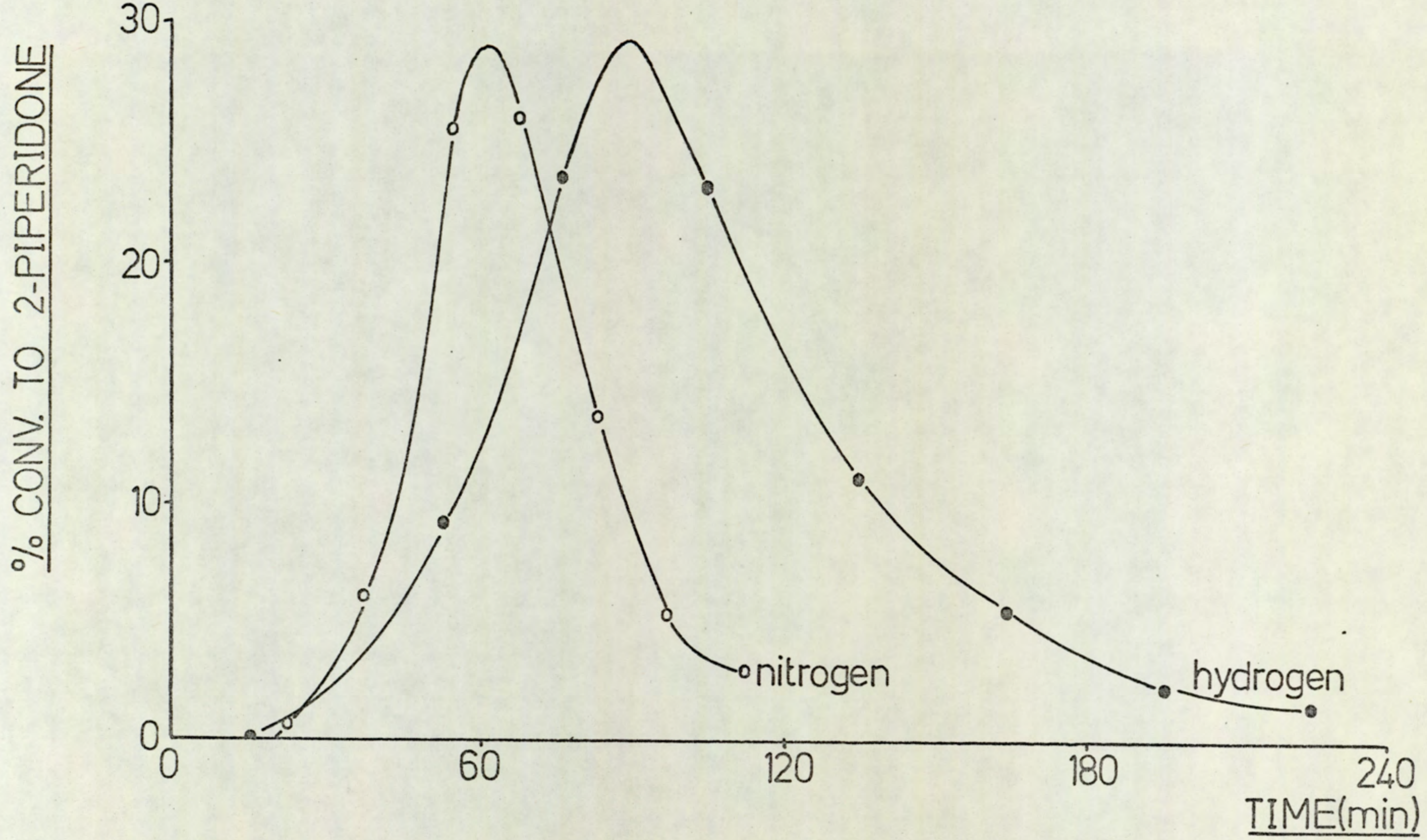


FIG. 26, comparison of 2-piperidone formation for a nitrogen and hydrogen carrier on hydrogen-Pd-Y

Decomposition of the surface species must be repressed in a reducing atmosphere, resulting in a general extension of catalyst lifetime. This stabilization effect is probably more important than the regenerative effect of hydrogen on the surface hydroxyl groups, otherwise the effect of hydrogen upon the formation of 2-piperidone would be much greater that its effect upon 4-cyanobut-1-ene formation. The reason for the increased stability of the surface intermediate in the presence of a reducing atmosphere is not known.

The inconsistency of the results for cyclopentanone formation is in agreement with remarks made earlier, where it was suggested that this compound results from hydrolysis of the oxime by residual water in the zeolite.

The use of ammonia as carrier completely poisons the catalyst surface for 2-piperidone formation, and so results in a low conversion of cyclopentanone oxime. Since ammonia is a strong base, and the active sites for 2-piperidone formation are acidic, it is not surprising that ammonia preferentially interacts with the surface hydroxyl groups, so poisoning the catalyst for lactam formation. It is slightly surprising, however, that the same carrier results in a reduced conversion of cyclopentanone oxime to 4-cyanobut-1-ene. The formation of the latter is a function of the zeolite cations, and so it is more difficult to explain why ammonia inhibits this reaction, than it was for the inhibition of lactam formation. Ward (57) has shown, however, that pyridine can coordinate to zeolite cations, and so it is probable that ammonia has a similar tendency. If this is the case then it explains why the presence of ammonia poisons the surface completely for 2-piperidone formation, and partially for 4-cyanobut-1-ene formation.

CHAPTER 5

CATALYST LIFETIME STUDIES

5.1. Attempts to improve catalyst lifetime.

The results of varying the solvent, reported in section 4.3., show clearly that the solvents which are capable of extending the catalyst lifetime for the rearrangement of cyclopentanone oxime, are those which are efficient in removing the product of rearrangement from the surface; of the solvents studied water is most efficient in this respect. It was considered worthwhile, therefore, to study the rearrangement in an aqueous solvent further. Since the results of the present study have suggested that product decomposition may be the principal cause of catalyst poisoning, the rearrangement in an aqueous solvent was studied at 220° and 280°. It was hoped that the use of a temperature lower than 340° would result in less product decomposition, and that the use of an aqueous solvent would aid the removal of products from the catalyst, even at comparatively low temperatures. The results of these studied are reported in Table 13. The amounts of 4-cyanobut-1-ene and cyclopentanone formed are almost independent of temperature for an aqueous solvent. The fact that a constant amount of ketone is formed when a large excess of water is present is further evidence that this compound is formed by hydrolysis of the oxime.

At 220° no 2-piperidone is formed, the principal product being cyclopentanone. At 280° the selectivity for 2-piperidone formation is 10.5%, but the ketone is still the predominant product. The catalyst lifetime at both of these temperatures is only 180 minutes, however a substantial increase in both catalyst lifetime and lactam selectivity is observed when the temperature is raised to 340°. The oxime conversion is doubled on increasing the reaction temperature from 220° to 340°.

In Chapter 2 it is shown that the Beckmann rearrangement of cyclopentanone oxime occurs at temperatures as low as 120°. The fact that no 2-piperidone is detected from the reaction of cyclopentanone oxime at 220°, using an aqueous solvent, is due, therefore, to the inability of the surface intermediate to desorb. Apparently the use of an aqueous solvent, which is known to be effective for removing the product from the surface at 340°, is not able to do so at 220°. At 280° the results suggest that the

TABLE 13: EFFECT OF TEMPERATURE ON THE REARRANGEMENT OF CYCLOPENTANONE OXIME OVER A DECATIONATED ZEOLITE(i), USING AN AQUEOUS SOLVENT(ii)

Temperature °C	Reaction time (min.)	Oxime conversion %	2-piperidone selectivity %	4-cyanobut-1-ene selectivity %	cyclopentanone selectivity %
220	180	51	0	7.2	16.8
280	180	69	10.5	6.5	15.1
340	>360	97	20.8	3.4	8.4

(i) 12.75g hydrogen-Pd-Y, carrier N_2 40 ml. min.$^{-1}$,

(ii) 10% w/w oxime in 45 vol. H_2O : 1 vol. glacial acetic acid to aid solubility, LHSV 1.5.

product is being removed from the surface, but not at a sufficient rate to produce an extension of the catalyst lifetime. It is apparent that even in the presence of an aqueous solvent, a temperature of about 340° is required for reasonably efficient removal of the product from the catalyst surface.

Since lowering the temperature is not effective in extending the catalyst lifetime beyond about six hours for an aqueous solvent, the reaction at 340° was repeated using a hydrogen carrier. The results are reported in Table 14. The catalyst lifetime is indeed extended by the use of a hydrogen carrier, however other changes accompany this extension. The hold-up time for this reaction corresponds to 13 oxime molecules per supercavity. This figure was found to be reproducible. The catalyst supercavities cannot possibly tolerate this amount of reactant, so it is apparent that considerable decomposition occurs when the reactant first contacts the catalyst. This hold-up period was accompanied by a corresponding increase in the gas flow rate from the reactor. After the hold-up period, 2-piperidone starts to be eluted from the catalyst bed, and the amount eluted increases with time. After nine hours on stream the conversion to 2-piperidone is still increasing, being about 40% of the oxime feed over the period 8½ - 9 hours. No oxime was detected in the collection trap over the entire period of this experiment.

The results indicate that the catalyst is so active for the rearrangement of cyclopentanone oxime in an aqueous solvent, and using a hydrogen carrier that initially all of the feed is decomposed, resulting in an increased gas flow from the reactor. After the activity of the catalyst has subsided somewhat, it becomes efficient in producing 2-piperidone, providing the longest catalyst lifetime encountered in the present study. Undoubtedly over a period of longer study, the 2-piperidone selectivity would increase, and surpass that obtained using a nitrogen carrier.

5.2. Comparison of the rearrangement of cyclopentanone oxime with that of cyclohexanone oxime on decationated zeolites.

The rearrangement of cyclohexanone oxime over zeolites has been reported by Landis an Venuto (4). These authors reported that at a temperature of 380°, the lifetime of hydrogen-Y for this system is in excess of twenty hours. Due to the great difference in this catalyst lifetime, and that encountered for

TABLE 14: EFFECT OF CARRIER UPON THE REARRANGEMENT OF CYCLOPENTANONE OXIME OVER A DECATIONATED ZEOLITE(i), USING AN AQUEOUS SOLVENT(ii)

Carrier(iii)	Reaction time (min.)	Oxime conversion %	2-piperidone selectivity %	4-cyanobut-1-ene selectivity %	cyclopentanone selectivity %
N_2	>360	97	20.8	3.4	8.4
H_2	>540	100	12.8	3.7	6.5

(i) 12.75g hydrogen-Pd-Y,

(ii) 10% w/w oxime in 45 vol. H_2O : 1 vol. glacial acetic acid to aid solubility, LHSV 1.5,

(iii) 40 ml/min.

cyclopentanone oxime in the present study, it was decided to study the rearrangement of cyclohexanone oxime under the same conditions as were used for the rearrangement of the five membered ring oxime. For the reaction of both oximes over hydrogen-Y at 340°, the results are reported in Table 15. The lactam concentration curves for the two systems are shown in Figure 27. Although the catalyst lifetime for the rearrangement of cyclohexanone oxime is not as long as that reported by Landis and Venuto, it is considerably longer than that observed for the rearrangement of cyclopentanone oxime.

It is apparent that the rate of poisoning of the catalyst surface is much more rapid for the reaction of cyclopentanone oxime than for the reaction of cyclohexanone oxime. Any theory advanced concerning the nature of the surface poisoning must take this difference into account.

The difference between the two oxime systems is in contrast to the findings for the homogeneously catalyzed reaction. Studies of the latter have indicated that both oximes give similar yields of amide (19).

TABLE 15: COMPARISON OF THE REARRANGEMENTS OF CYCLOPENTANONE OXIME AND CYCLOHEXANONE OXIME OVER A DECATIONATED ZEOLITE(i)

Reactant(ii)	Reaction time (min.)	Oxime conversion %	lactam selectivity %	alkene-nitrile selectivity %	ketone selectivity %
Cyclopentanone oxime	90	58	9.5	7.9	4.0
Cyclohexanone oxime	330	84	37.5	3.2	2.6

(i) 12.75g hydrogen-Y, 340°, carrier N_2- 40ml min^{-1},

(ii) 30% w/w solutions in benzene, LHSV 1.0.

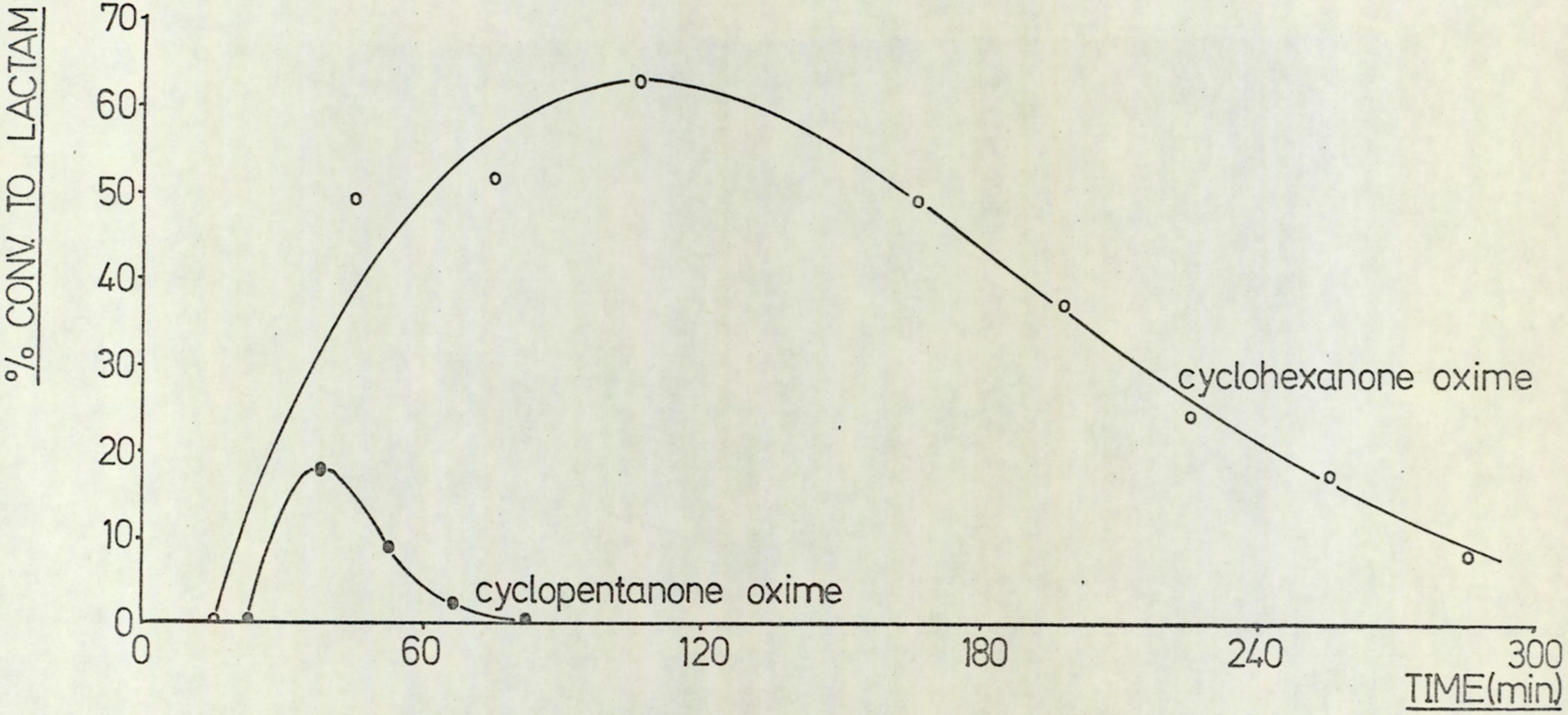


FIG. 27, comparison of lactam formation from cyclopentanone oxime and cyclohexanone oxime over hydrogen-Y.

CHAPTER 6

POISONING OF DECATIONATED ZEOLITES DURING THE BECKMANN REARRANGEMENT OF CYCLOPENTANONE OXIME

In Chapter 3 it is shown that when a solution of cyclopentanone oxime in benzene is fed to zeolites containing surface hydroxyl groups, the active lifetime of the catalyst is very short, and the selectivities for 2-piperidone, 4-cyanobut-1-ene and cyclopentanone formation are low. Poisoning of the catalyst surface is therefore rapid for this reaction system. Several aspects of surface poisoning have been presented in various chapters, and these points are now summarized, with particular attention to the poisoning of decationated zeolites for the Beckmann rearrangement.

(i) Spectroscopic studies indicate that when cyclopentanone oxime has rearranged on the catalyst surface to an open-chain intermediate, which it does at a relatively low temperature, the intermediate is strongly held by the surface, and is difficult to desorb. The predominant surface species at temperatures above about 150°, therefore, is the open-chain intermediate (Chapter 2).

(ii) The hold-up of organic material on a decationated catalyst also indicates a reluctance for desorption of reaction products. When benzene is employed as solvent, calculation indicates that the catalyst supercavities are almost completely saturated with organic material before desorption occurs (section 4.1.). The facts that a solution of 2-piperidone in benzene exhibits the same hold-up as a solution of cyclopentanone oxime in benzene, and that 2-piperidone is adsorbed in the same way as the product of reaction of cyclopentanone oxime, are further evidence that the open-chain adsorbed species is the predominant surface compound at temperatures in excess of about 150°. If the vapour phase reaction is stopped after one hour, and the contents of the catalyst supercavities soxhlet extracted into an organic solvent, then only 2-piperidone is detected.

(iii) During a study of the variation of temperature of reaction, it was observed that the catalyst lifetime is not extended by the use of lower temperatures, but that the selectivity for 2-piperidone formation is increased. The increase in selectivity at lower temperatures, probably reflects the greater percentage of converted oxime which reaches the collection trap as 2-piperidone, rather than an increase in the amount of 2-piperidone formed on the surface. It appears that although the open-chain surface species is more stable at lower temperatures, this extra stability is offset by the decreased tendency for desorption, and hence the catalyst lifetime is not extended (section 4.2.).

(iv) A sensitive dependence has been shown to exist between the hold-up of organic material on the catalyst surface, and the selectivity for 2-piperidone formation, for a series of different solvents (section 4.3.). It appears that the rate of poisoning of the catalyst surface is dependent upon the length of time that the product is adsorbed. This finding indicates that decomposition of the open-chain surface species is the principal cause of catalyst poisoning.

(v) The use of a hydrogen carrier has been shown to result in an increased stability of the surface intermediate (section 4.4.).

(vi) Attempts to improve the catalyst lifetime by employing a solvent which aids desorption (H_2O), and a comparatively low temperature (220° and 280°) were unsuccessful. Even in the presence of such a solvent desorption of 2-piperidone is difficult at these temperatures (section 5.1.).

(vii) The catalyst lifetime for the rearrangement of cyclohexanone oxime is considerably longer than that for the rearrangement of cyclopentanone oxime (section 5.2.). Since it has been shown spectroscopically that the surface intermediate for both rearrangements are similar in structure (Chapter 2), the results summarized above suggest that there is a considerable difference in the thermal stabilities of the two products of rearrangement, when adsorbed on decationated zeolites.

The surface poisoning was shown not to be due to thermal decomposition of either cyclopentanone oxime in benzene, by passing a 30% solution of the former in the latter through the reaction tube, which was packed with glass beads and maintained at 340°. The recovery of benzene over a two hour period (using a nitrogen carrier) was 98%, and that of the oxime was 92%. In a similar experiment, but in the presence of hydrogen-Y, the recovery of 4-cyanobut-1-ene was 85% over a two hour period (including extraction of the catalyst), also the catalyst did not blacken appreciably over this period, and no isomerization products were detected.

In order to test the conclusions drawn from the results reported above, it is necessary to compare the thermal stabilities of 2-piperidone and ϵ-caprolactam adsorbed on a decationated zeolite. It is not possible to determine directly the thermal stabilities of the surface species, but it is reasonable to assume that they are comparable to those of the lactams formed upon their desorption. Passing a solution of either lactam over a decationated zeolite is not a very good way of estimating its thermal stability, since the amount of lactam held by the catalyst would introduce appreciable errors in the percentage recovery. The best way of comparing the thermal stabilities of the two lactams, is simply by passing them down a reactor, which has been packed with glass beads, and is maintained at 340°. If there is an appreciable difference in the lactam recoveries from the two experiments, then this difference will also be apparent in the presence of the catalyst, especially since adsorption will result in the lactams spending a greater time at elevated temperatures, than they would by simply passing down a tube packed with glass beads. When a 25% solution of ϵ-caprolactam in benzene was passed through the reactor (340°, 12.75g glass beads, 20ml feed, duration one hour, 40ml/min N_2), the recovery of lactam was found to be 80% of the feed. When the same experiment was performed using 2-piperidone, the recovery of the latter was only 41%. The low thermal stability of 2-piperidone at 340° is surprising since related compounds are often prepared at elevated temperatures. The reason for the difference in stability of the two lactams is not known, no reference to thermal stability measurements for these two compounds could be found. It is known, however, that 2-piperidone hydrolyzes faster than ϵ-caprolactam in aqueous potassium hydroxide, in the temperature range 30°-90°, and that for a series of lactams studied 2-piperidone was the most reactive (114). Although the conditions of these hydrolysis experiments are far removed from those in a vapour phase catalytic reactor, the results show that 2-piperidone is more reactive than ϵ-caprolactam, and this difference is probably reflected in their relative rates of decomposition at elevated temperatures. The low recovery of 2-piperidone from the thermal stability experiment obviously fully explains the low catalyst lifetimes reported for the rearrangement of cyclopentanone oxime, and the low selectivities for 2-piperidone formation.

6.1. Nature of catalyst poison.

Some experiments were performed to determine the nature and extent of the poisoning on the catalyst surface, when its activity for the Beckmann rearrangement has fallen to zero. Two types of surface poisoning are possible from the decomposition of the surface species, these are polymeric material trapped inside the catalyst supercavities, and carbon deposits on the surface. Judging by the black colour of a spent catalyst, carbon deposits are the principal cause of activity decline, and this conclusion is supported by an elemental analysis of the surface poison. Such an analysis indicated that about 93% of the poison consisted of carbon (after a 30% solution of cyclopentanone oxime in benzene, LHSV 1.0 has been passed over 12.75g hydrogen-Y at 340^{o}, N_2 40 ml/min^{-1}, for two hours).

Thermogravimetric studies also indicate that the catalyst poison is principally carbon. The weight loss of a used catalyst, as a function of temperature occurs in two stages (Figure 28). The first region of weight loss is between the temperatures 60^{o} and 250^{o}, and corresponds to the loss of water from the catalyst. Unused catalysts show only this stage of weight loss, however the weight loss is so large, that for the heating programme employed, the sample was still losing weight at a temperature of 300^{o} (Figure 28). The second region of weight loss, shown only by used catalysts, is between the temperatures of 300^{o} and 650^{o}. The weight loss of samples in this temperature range corresponds to the oxidation of coke from the catalyst surface. If the thermogram is obtained for a used sample which is supported in a stream of nitrogen, only small weight losses are observed in this region, and if the catalyst is allowed to cool to room temperature in the stream of nitrogen, it is still black when removed from the surface. The small weight loss (~1%) in this region, when the thermogram is obtained when the sample in

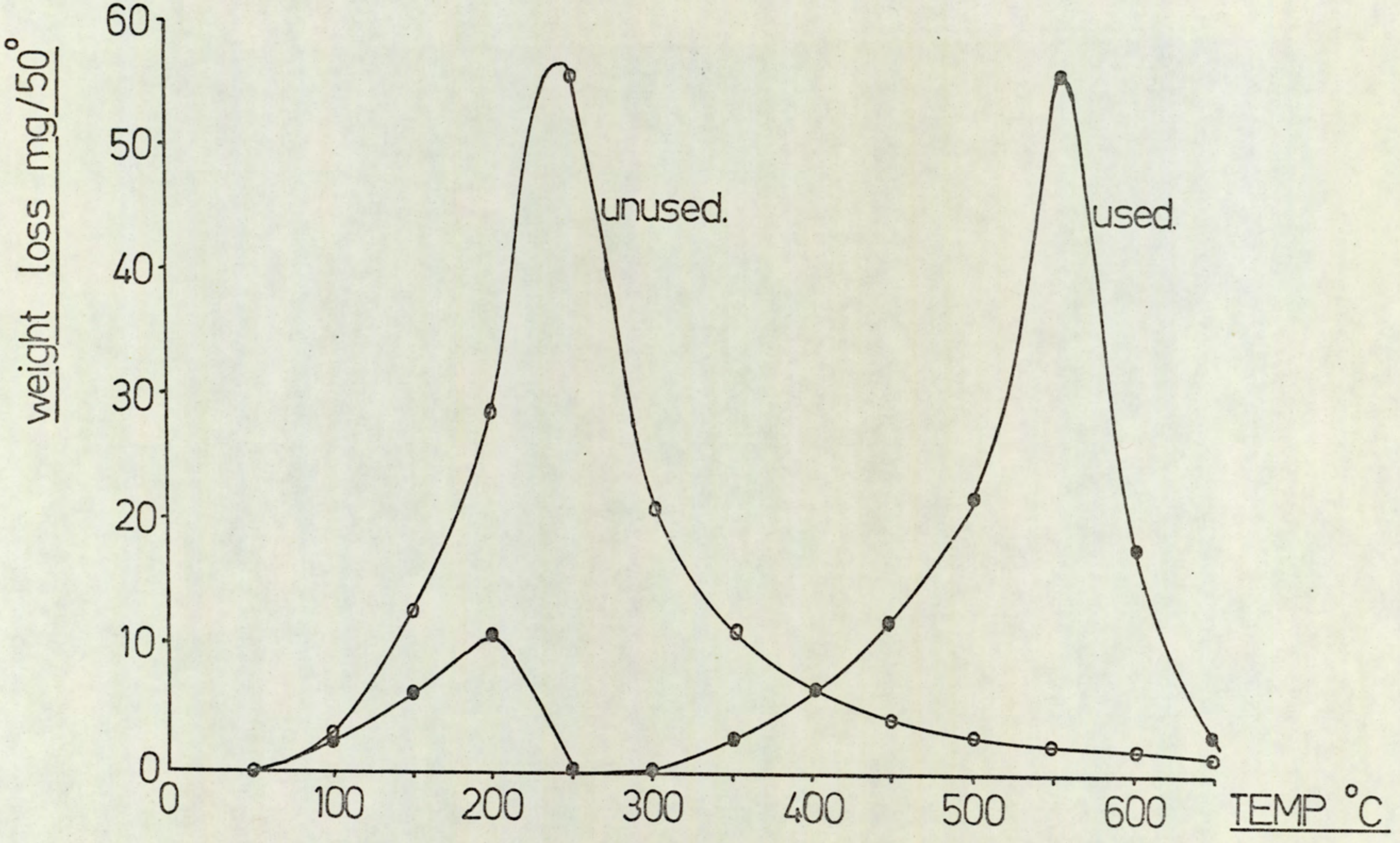


FIG.28, thermogravimetric analysis of used & unused catalysts.

an inert atmosphere, is probably due to 'boiling off' of organic material from the catalyst surface. This small percentage is qualitatively consistent with the elemental analyses given above.

The percentage total coke is defined as

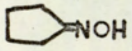
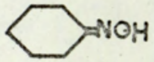
$$\frac{\text{final anhydrous wt} - \text{initial anhydrous wt}}{\text{initial anhydrous wt}} \times 100$$

The catalyst weights, before and after reaction, were corrected to anhydrous values using the percentage water determined by thermogravimetric analysis. Thermogravimetric analysis indicated that after calcination both hydrogen-Y, and hydrogen-Pd-Y pick up water from the atmosphere corresponding to approximately 15% of their final hydrated weight. This figure was used in all cases to calculate the anhydrous weight of the catalyst in the reactor. A similar analysis of the used catalysts gave an indication of their water contents after reaction; this was usually about 2%. Some total coke contents of catalysts are reported in Table 16.

It is immediately noticeable from the results reported in Table 16, that there is a considerable difference between the weight increase of hydrogen-Y due to reaction, and that of hydrogen-Pd-Y due to reaction, when both are used under identical conditions. When the reaction was catalyzed by hydrogen-Pd-Y, analysis of the gas effluent from the reactor showed the presence of large quantities of hydrogen. No hydrogen was detected in the effluent stream when the catalyst was hydrogen-Y. Prior calibration of the gas chromatograph for hydrogen (Porapak-Q 40^{o}; 75ml/min^{-1} N$_2$; katharometer current 100mA; 10ml gas loop;) allowed a quantitative measure of the amount of hydrogen eluted from the reactor, as a function of time. The results of such an analysis are shown in Figure 29. The total amounts of hydrogen detected in the reactor effluent from several experiments are reported in Table 17.

Hydrogen was detected in the effluent from hydrogen-Pd-Y even if the latter had not been heated in hydrogen before use. This rules out the possibility of the hydrogen being adsorbed by palladium during the pre-reaction treatment, and then being desorbed as a result of adsorption of organic material. If, as seems probable, the hydrogen results from dehydrogenation of either solvent or reactant, then one can estimate the catalyst weight

TABLE 16: TOTAL COKE CONTENTS OF DECATIONATED CATALYSTS

Reactant	Catalyst(i)	Temp. °C	Solvent	Solution Strength %	LHSV	Carrier 40 ml/min.	Reaction time (min.)	Total % coke
	HY	300	C_6H_6	30	1.0	N_2	120	8
"	HY	340	C_6H_6	30	1.0	N_2	120	9
"	HPdY	225	C_6H_6	30	1.0	N_2	120	21
"	HPdY	300	C_6H_6	30	1.0	N_2	120	19
"	HPdY	320	C_6H_6	30	1.0	N_2	120	15
"	HPdY	340	C_6H_6	30	1.0	N_2	120	16
"	HPdY	360	C_6H_6	30	1.0	N_2	120	12
"	HPdY	340	C_6H_6	30	1.0	N_2	300	20
"	HPdY	340	C_6H_6	10	1.5	N_2	120	17
"	HPdY	340	H_2O	10	1.5	N_2	360	16
None	HPdY	340	C_6H_6	-	1.0	N_2	120	7
None	HY	340	C_6H_6	-	1.0	N_2	120	3
	HY	340	C_6H_6	30	1.0	N_2	480	9

(i) 12.75g anhydrous wt.

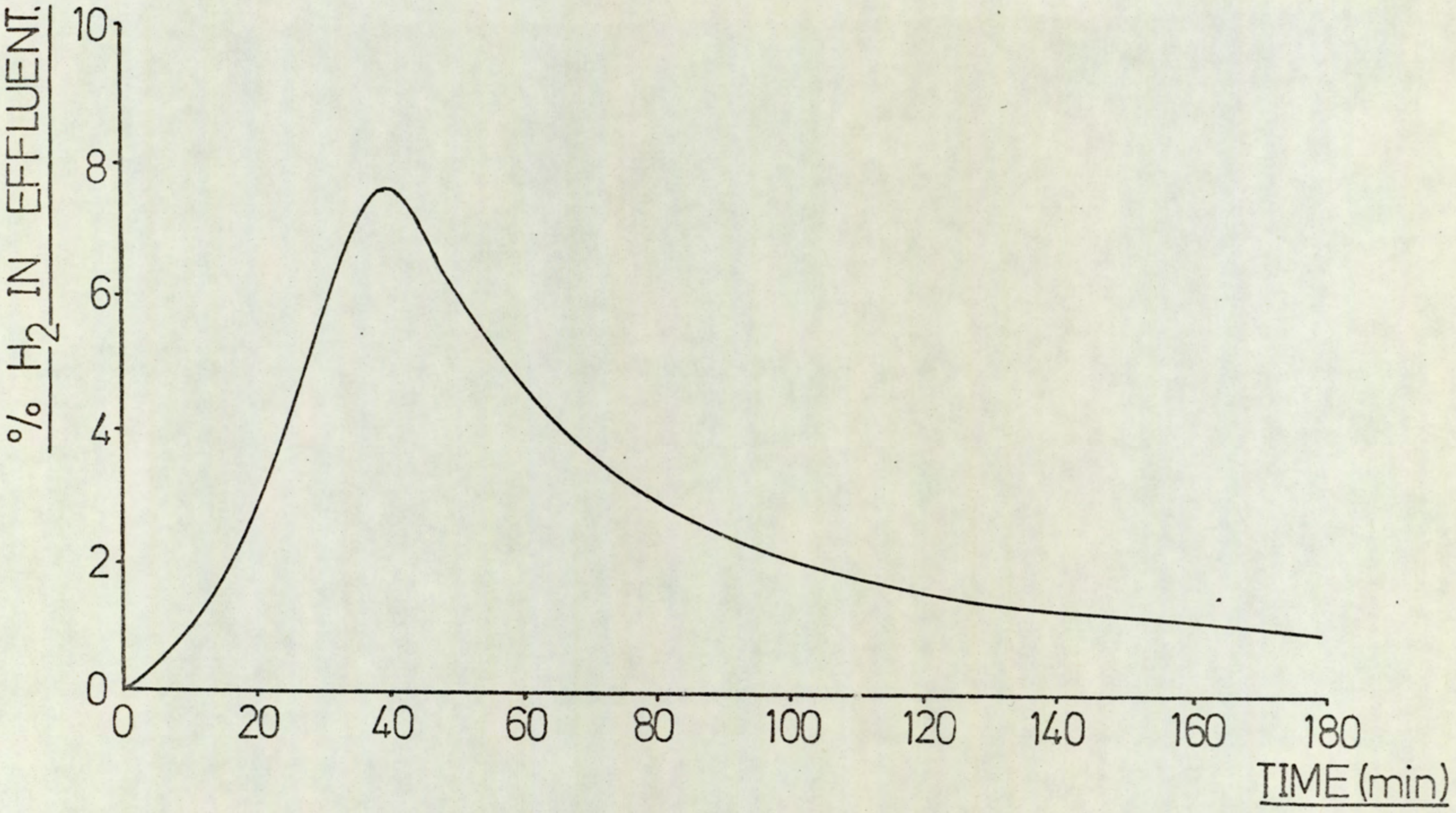


FIG. 29, typical hydrogen analysis from a H-Pd-Y reaction.

TABLE 17: HYDROGEN EFFLUENT ANALYSES FROM HYDROGEN-PD-Y

	Feed	Anhydrous catalyst Wt. (g)	Total volume of H_2 at NTP (ml)
(i)	30% cyclopentanone oxime - benzene	12.75	509
(ii)	30% cyclopentanone oxime - benzene	25.5	1080
(iii)	10% cyclopentanone oxime - benzene	12.75	616
(iv)	10% cyclopentanone oxime - cyclohexane	12.75	1360
(v)	10% cyclopentanone oxime - H_2O	12.75	676
(vi)	benzene	12.75	290
(vii)	H_2O	12.75	0
(viii)	CO_2	12.75	0

(i) carrier N_2 - 40ml/min

increase, due to carbon deposition, as a result of this reaction. For instance, the 290 ml. of hydrogen evolved when benzene alone is passed over hydrogen-Pd-Y, corresponds to a deposition of 0.31g carbon, or a 2.4% weight increase. The catalyst weight increase due to dehydrogenation of benzene, accounts for much of the discrepancy between the weight increases of hydrogen-Y and hydrogen-Pd-Y when benzene is fed to both catalysts. (Table 16). Calculations for a solution of oxime in benzene are not so easy. It is evident from the results reported in Table 17, that such a solution produces much more effluent stream hydrogen than does just benzene. It is apparent, therefore, that perhaps due to its extra polarity, cyclopentanone oxime is more easily dehydrogenated by hydrogen-Pd-Y than is benzene. This conclusion is supported by the results plotted in Figure 30, which show that when the catalyst can no longer dehydrogenate benzene, it still has the ability to dehydrogenate cyclopentanone oxime. When trying to calculate catalyst weight increases corresponding to the volumes of hydrogen reported in Table 17, therefore, it is difficult to know what to take for the ratio of moles of carbon deposited to moles of hydrogen evolved. This ratio lies somewhere between 1 for benzene and 5/9 for cyclopentanone oxime. Calculations based on the 509 ml of hydrogen evolved when a 30% solution of cyclopentanone oxime in benzene is passed over 12.75g of hydrogen-Pd-Y indicate that the catalyst weight increase due to dehydrogenation should be 4.3% for a carbon to hydrogen ratio of 1, and 2.4% for a ratio of 5/9. The difference in catalyst weight increase under these conditions, between hydrogen-Y an hydrogen-Pd-Y is 7% (Table 16), and so it is apparent that dehydrogenation can account for part, but not all, of this discrepancy. If all of the 509 ml of hydrogen detected came from cyclopentanone oxime during a normal two hour run, dehydrogenation would only account for an 8% conversion of the oxime feed.

It is also apparent from the results of Table 16, that when the catalyst activity has fallen to zero, the catalyst weight increase is about the same for several experiments. Thus the passage of a 30% solution of cyclopentanone oxime in benzene, with a nitrogen carrier (16%), the same solution with a hydrogen carrier (20%), a 10% solution of cyclopentanone oxime in benzene (17%) and a 10% solution of cyclopentanone oxime in water (16%), both in nitrogen, all cause a similar weight increase for hydrogen -Pd-Y at 340°, although the catalyst lifetimes are not the same

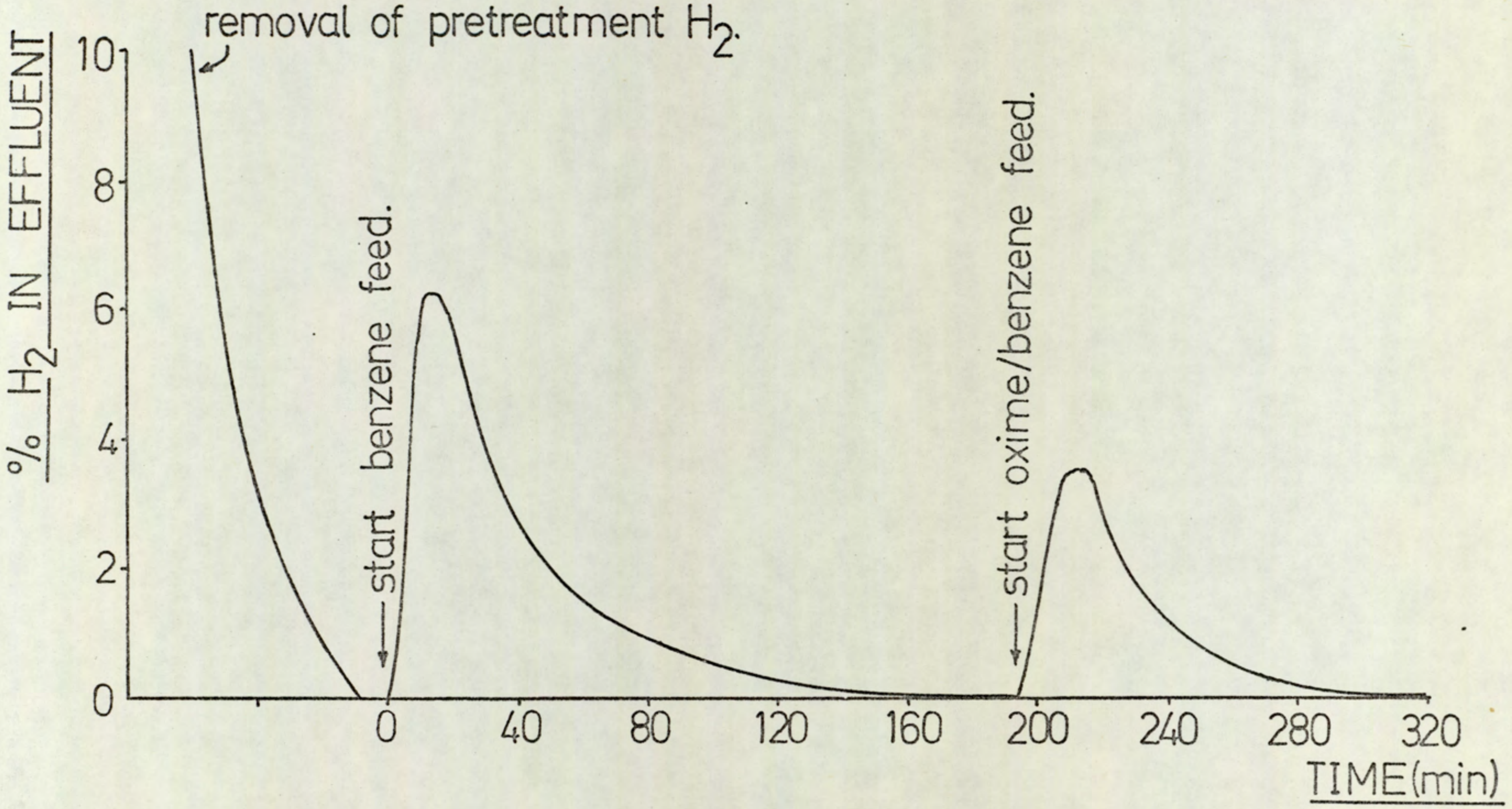


FIG. 30, dehydrogenation of benzene and cyclopentanone oxime by H-Pd-Y in each case. Also, solutions of cyclopentanone oxime in benzene and cyclohexanone oxime in benzene cause identical weight increases for hydrogen-Y, although the catalyst lifetimes are about 120 and 480 minutes respectively. Since elemental analysis of the catalyst poison showed it to be principally carbon, this result indicates that for a constant weight of a given catalyst, the amount of deposited carbon required to reduce its activity to zero is fairly constant. Although this carbon is probably not distributed evenly over the catalyst bed, it is nevertheless interesting to estimate how many carbon layers, on average, are present on the catalyst, when its weight has increased by say 9%. Hydrogen-Y containing 1.1% sodium has a surface area of approximately 860 m^2g^{-1} (115), and assuming a carbon-carbon distance of 1.4 Å (116), the number of carbon atoms per monolayer is given by

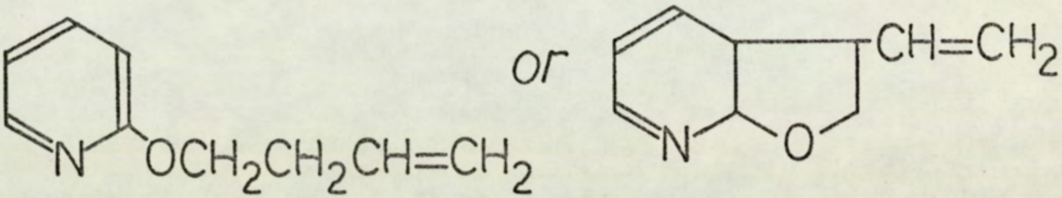
$$\frac{860 \times 10^{20}}{\pi \times (0.7)^2} = \underline{5.6 \times 10^{22}}$$

A catalyst weight increase of 9% on 12.75g, assuming it to be due solely to carbon requires

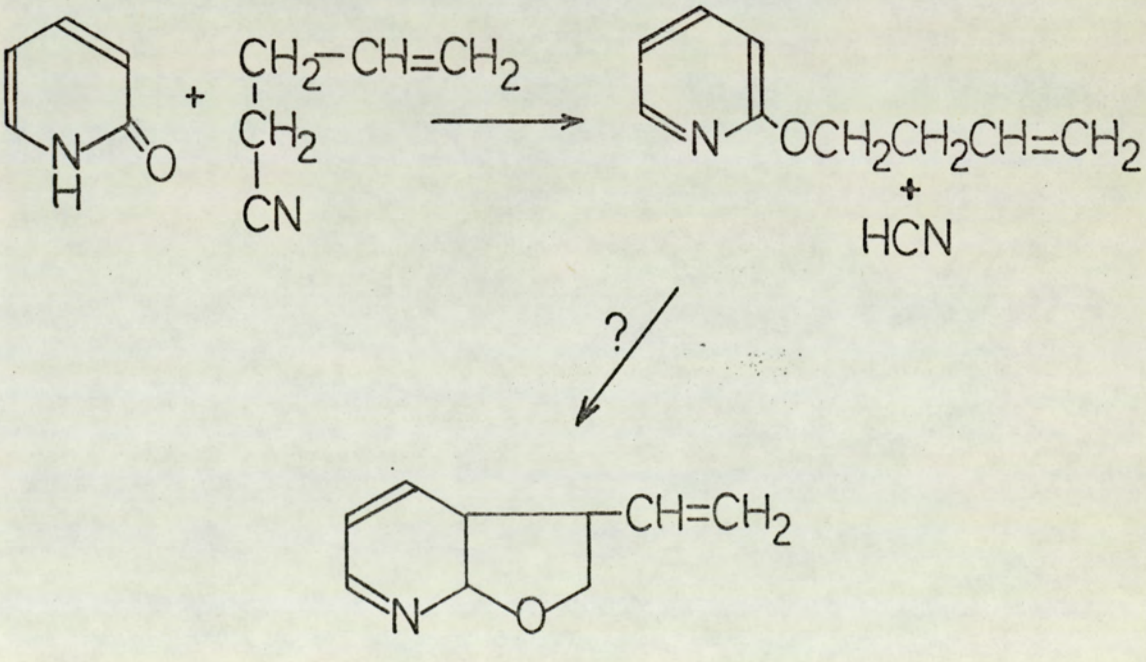
$$\frac{12.75 \times 9 \times 6.023 \times 10^{23}}{12 \times 100} \qquad \underline{5.77 \times 10^{22} \text{ molecules of carbon.}}$$

Hence when the activity of hydrogen-Y for the Beckmann rearrangement has fallen to zero, the catalyst surface is on average, coated with a monolayer of carbon. The 17% weight increase for hydrogen-Pd-Y corresponds to an average of two layers of carbon atoms.

Although the organic material on the catalyst surface after a reaction only accounts for a small fraction of the total poison, soxhlet extraction of several spent catalysts showed that the same compound was extracted from each. This extraction procedure did not restore any activity to the catalyst, which also exhibited no hold-up of organic material, when re-tested with a 30% solution of cyclopentanone oxime in benzene. The compound, which extracted from hydrogen-Pd-Y only, for both a hydrogen and nitrogen carrier, and benzene and water solvents, after the catalyst activity had fallen to zero, could not be isolated, but its structure could be tentatively assigned on the basis of infrared and mass spectral information (section 8.6). The extract appears to be a polymeric material containing the unit



and is presumably formed by condensation of a dehydrogenated form of 2-piperidone, with 4-cyanobut-1-ene, with the loss of hydrogen cyanide according to the equation



Hydrogen cyanide was detected in the gas effluent from the reactor. The extraction of this compound from hydrogen-Pd-Y is consistent with the dehydrogenation which is known to occur on this catalyst, and since no dehydrogenation was detected for hydrogen-Y, it is not surprising that the compound was not extracted from this catalyst. No further attempts were made to completely identify the extract, since both elemental analysis and thermogravimetric analysis indicated that the amount of organic material was small. Also no organic material was extracted from hydrogen-Y, even though its active lifetime was less than that of hydrogen-Pd-Y under identical conditions.

CHAPTER 7

CONCLUSIONS AND CRITICAL APPRAISAL OF RESEARCH

7.1. Conclusions from the present work.

Some aspects of the surface mechanism of the vapour phase Beckmann rearrangement of cyclopentanone oxime and cyclohexanone oxime catalyzed by zeolites have been elucidated, particularly by the use of infrared spectroscopy. The active sites for the Beckmann rearrangement have been identified as acidic surface hydroxyl groups, and hence the most active catalyst for the production of 2-piperidone and ε-caprolactam are decationated zeolites. On such a catalyst the oxime is adsorbed as a protonated species, a proton being transferred from the surface hydroxyl group which absorbs at 3640 cm^{-1} to the nitrogen atom of the oxime. Some delocalization of charge occurs between the protonated species and the surface. The oxime rearranges at relatively low temperatures (~120°) to form a protonated open-chain surface intermediate. The detection of the open-chain intermediate was made possible by a concurrent spectroscopic study of the rearrangements of cyclopentanone oxime to 2-piperidone, and that of cyclohexanone oxime to ε-caprolactam. The open-chain intermediate desorbs, via the formation of the amide C-N bond, at higher temperatures, to produce the lactam. If the latter is adsorbed from the vapour phase onto hydrogen-Y, it is held in the form of the same open-chain surface species. The mechanism suggested for the surface Beckmann rearrangement is shown in Figure 14. According to this mechanism the surface rearrangement is stereospecific. It is not known, however, if either the heterogeneously catalyzed rearrangement or the homogeneously catalyzed rearrangement of cyclic oximes proceeds stereospecifically.

The reaction of alicyclic oximes on sodium-Y does not produce lactams, but instead results in the formation of alkenenitriles. When these compounds are prepared on the surface from an oxime, the C≡N function is apparently not formed until desorption occurs, and remains on the surface as a C=N group. When 5-cyanopent-1-ene is adsorbed onto sodium-Y from the vapour phase, however, the C≡N function remains intact.

The above results were confirmed and extended by a study of the reaction of cyclopentanone oxime over various catalysts using a flow system. Zeolites containing cations whose electrostatic fields are sufficient to produce dissociation of water molecules, and formation of surface hydroxyl groups, also result in some conversion of cyclopentanone oxime to 2-piperidone. The amount of 2-piperidone formed is a function of the catalyst acidity. Also, the incorporation of a small amount of palladium into a decationated zeolite has been shown to result in increased activity for the Beckmann rearrangement. A similar incorporation into an alkali metal containing zeolite produces little change in its ability to catalyze alkene-nitrile formation.

The formation of alkene-nitrile has been shown to be a function of the electrostatic field associated with the zeolitic cation, being greatest for the small cations with large electrostatic fields. The alkene-nitrile is not held on the surface as strongly as is 2-piperidone, and is the product first detected in the collection trap in the flow experiments.

The formation of cyclopentanone is not correlatable with any property of the catalysts, but considerable evidence has been obtained which suggests that it is formed by hydrolysis of cyclopentanone oxime. Thus, the amount of ketone is increased when an aqueous solvent is employed, and it is formed even in the absence of a catalyst for this solvent.

Calculations based on the experimentally observed hold-up of organic material on decationated zeolites, suggests that for a benzene solvent, all the surface hydroxyl groups are interacting with the adsorbed molecules when 2-piperidone is first detected in the catalyst effluent stream. Calculations also indicates that for this solvent the catalyst supercavities are saturated with nitrogenous material at the end of the hold-up period. For other solvents the hold-up of organic material is reduced. Considerable evidence has been presented which suggests that the principal surface species during the reaction period is the open-chain intermediate.

A study of the reaction of cyclopentanone oxime over various catalysts has revealed that both catalyst lifetimes and the total selectivities for 2-piperidone, 4-cyanobut-1-ene, and cyclopentanone are very low at 340°, for a benzene solvent and a nitrogen carrier. Using a flow system, the effects of varying temperature, solvent an carrier were studied for decationated zeolites, in order to determine ways in which these results could be improved.

Variation of the temperature of reaction produces no change in the catalyst lifetimes of either hydrogen-Y or hydrogen-Pd-Y for the production of 2-piperidone. At lower temperatures (300°), however, the selectivity for 2-piperidone formation is slightly higher than that obtained at 340°, for hydrogen-Pd-Y. Some interesting results have been presented concerning the effect of solvent upon the heterogeneously catalyzed Beckmann rearrangement of cyclopentanone oxime. For the homogeneously catalyzed rearrangement, the reaction rate increases with the polarity of the solvent. It was not possible to determine the rate of either the surface reaction or the overall reaction for the heterogeneous process, due to the substantial hold-up of organic material on the catalyst surface. It has been shown, however, that the active lifetime of the catalyst, and hence the amount of 2-piperidone formed, are highly dependent upon the nature of the solvent. A relationship has been shown to exist between the selectivity for 2-piperidone formation and the efficiency of the solvent in removing the product of rearrangement from the catalyst surface. Of the solvents studied, water is the most efficient in this respect. The formation of 4-cyanobut-1-ene is almost independent of the solvent. The use of a hydrogen carrier has been shown to extend the active lifetime of a decationated zeolite, relative to that observed when a nitrogen carrier is employed. The use of hydrogen as carrier results in a general extension of the catalyst lifetime, not just the useful lifetime of the surface hydroxyl group. Thus the formation of alkene-nitrile, which is associated with the residual zeolitic cations for hydrogen-Y, is also extended when this carrier is used. It is apparent that the surface intermediate is more stable in a reducing atmosphere than in nitrogen.

Attempts to improve the catalyst lifetime by the use of an aqueous solvent and temperatures below 340° were unsuccessful; even in the presence of water, the product of rearrangement is reluctant to desorb below about 340°. The longest catalyst lifetime obtained in the present study was associated with the use of an aqueous solvent, and a hydrogen carrier. However, this system produced an extremely large hold-up of organic material on the catalyst.

Comparison of the heterogeneously catalyzed rearrangement of cyclopentanone oxime and cyclohexanone oxime revealed a considerable difference in the lifetime of a hydrogen-Y catalyst for the conversion of these two oximes. This difference has been shown to be due to an unexpected difference in the thermal stabilities of their rearrangement products, 2-piperidone and ε-caprolactam. It has also been shown that poisoning of the catalyst for the rearrangement of cyclopentanone oxime is due principally to carbon formation from the decomposition of the surface intermediate. Only small amounts of organic material were detected on spent catalysts, and on average a monolayer of carbon is present on the surface of hydrogen-Y after a reaction. For hydrogen-Pd-Y, dehydrogenation of both oxime and the organic solvent occurs, and although the catalyst lifetime is longer for this catalyst than for hydrogen-Y, an average of two layers of carbon are present after reaction. The catalyst weight increase as a result of reaction is similar for several reaction conditions, suggesting that for a constant weight of a given catalyst, a constant amount of carbon reduces its activity to zero.

Further exploratory experiments on the vapour phase rearrangement of cyclopentanone oxime under reduced pressure, and the effects of increasing the oxime feed rate to the catalyst, indicated that the catalyst lifetime could not be increased under these conditions.

It is obvious, from the results presented in the thesis, that due to its low thermal stability, 2-piperidone cannot be economically produced at elevated temperatures from the rearrangement of cyclopentanone oxime. Decationated zeolites are efficient in catalyzing the rearrangement at comparatively low temperatures, however, and further studies are warranted on the use of decationated zeolites to catalyze the rearrangement of cyclopentanone oxime, followed by soxhlet extraction of the product from the catalyst using an organic solvent.

On a more general basis, decationated zeolites have been shown to effectively catalyze the Beckmann rearrangement of oximes, and should be efficient for systems in which both the oxime and its rearrangement product are thermally stable. The active sites for the rearrangement have been identified, and the effects of varying the conditions of reaction for the cyclopentanone oxime - 2-piperidone system reported. Using this information it should be possible to easily optimise the conditions of rearrangement of other oximes. Further study is also warranted on the use of cation containing zeolites for the production of alkene-nitriles from cyclic oximes.

7.2. Critical appraisal of present research.

The principal disappointment from the present study was that the system did not lend itself to kinetic studies. Due to the considerable hold-up of organic material, and the short catalyst lifetimes, only overall conversions and selectivities were obtainable. It is perhaps unfortunate in this respect, that the product of the studied reaction was unexpectedly thermally unstable.

Unfortunately, time did not allow study of the use of catalyst extraction techniques coupled with catalysis by zeolites, for the Beckmann rearrangement of cyclopentanone oxime. It would have been interesting in addition, to perform further experiments on the reaction using an aqueous solvent and a hydrogen carrier. It was also disappointing that after having overcome the practical difficulties of obtaining infrared spectra of surface species, time did not allow the use of this technique to study the stereochemical aspects of the surface reaction.

CHAPTER 8

EXPERIMENTAL

8.1. Spectroscopic studies.

8.1.1. Apparatus.

The infrared cell was similar in design to that used by Parry (117), and is shown in Figure 31. It was made from 1¾" diameter pyrex glass, and consisted essentially of two halves. The upper half of the cell was wound with nichrome wore, and was fitted with a thermocouple well. The lower half of the cell was similar in design to a conventional gas cell, and was fitted with sodium chloride plates. One of these plates was permanently sealed in position with glyptal, the other was sealed to the cell by a rubber 'O' ring, and was held in position by a brass coupling. An aluminium holder was used to support the zeolite disc, the holder being free to slide along a glass rod to facilitate transfer from one part of the cell to the other.

The cell could be attached to a conventional vacuum system, vacua of 10^{-5} torr being maintained in the dynamic system. Dosing of the zeolite disc was achieved by means of the sample bulb, which could be isolated from the cell.

Spectra were recorded using a Perkin-Elmer 457 grating spectrophotometer . The position of the cell in the sample beam was reproducible and the reference beam was suitably attenuated. Spectra were recorded over the range 4000 - 1200 cm^{-1} using a scan speed of 400 cm^{-1} $minute^{-1}$, and a normal slit programme. Using this programme the spectral slit width was approximately 2 cm^{-1} over the range 3000 - 1200 cm^{-1}, and rose to 7 cm^{-1} at 4000 cm^{-1}. The gain setting for the instrument was 92.5 at 2500 cm^{-1}.

8.1.2. Technique.

The dosing material was placed in the sample bulb, which was then attached to a vacuum line. With the sample bulb surrounded by an acetone/dry-ice mixture, the space above the dosing material was evacuated. After evacuation, the sample bulb was isolated and attached to the infrared cell. Between 0.03 and 0.07g of the zeolite was pressed at 20,000 p.s.i. to form the zeolite disc. X-ray analysis showed that neither this pressing procedure nor the subsequent treatment caused any collapse of the zeolitic lattice. All the zeolite discs had a diameter of 2.5cm, corresponding to 'thicknesses' of between 5 and 10 mg cm^{-2}. The disc was supported in the aluminium holder which was placed on the

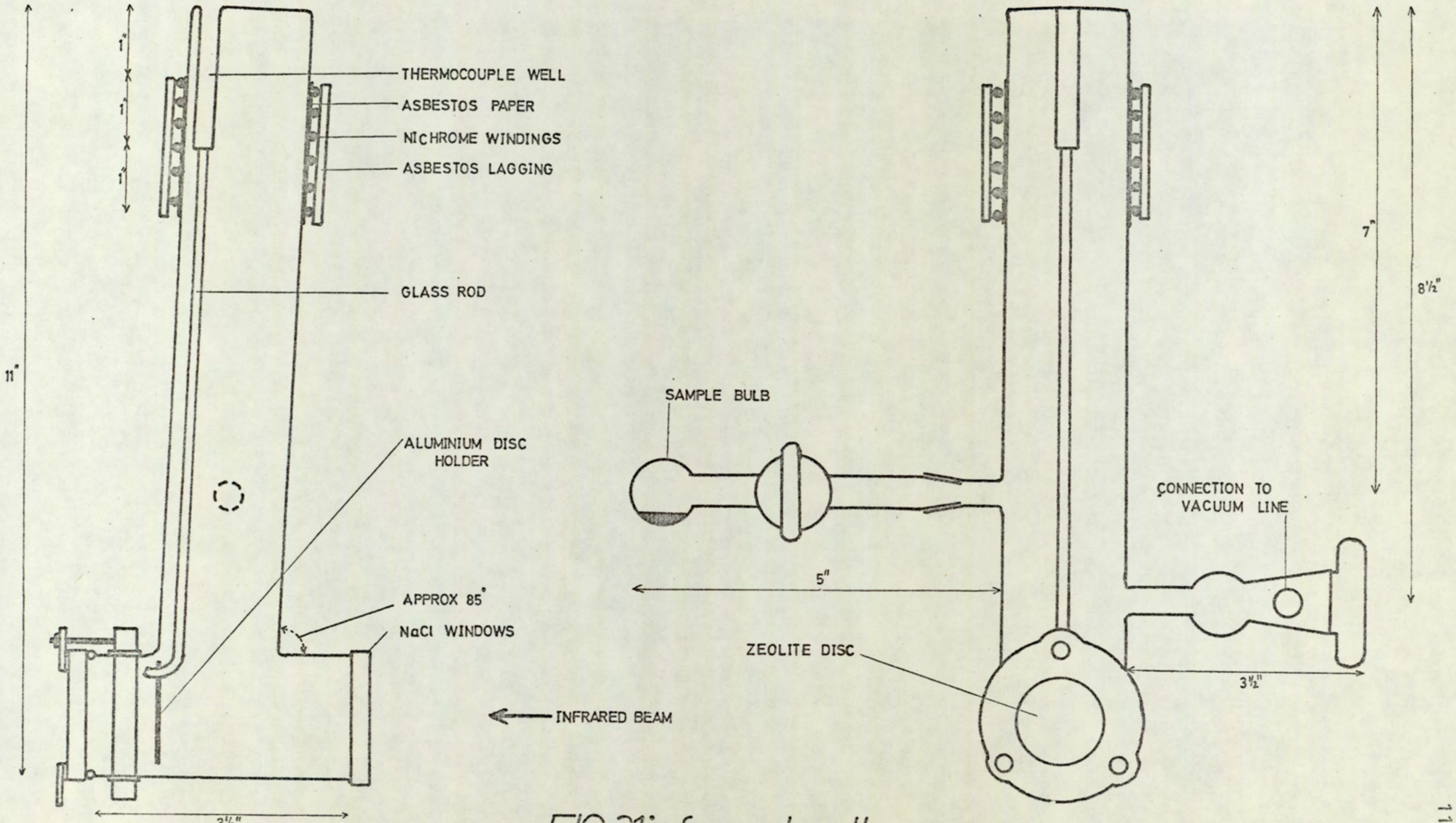


FIG.31,infrared cell.

SCALE- HALF FULL SIZE

glass rod inside the cell, and the latter tilted so that the holder ran along the glass rod and rested on the thermocouple well at the furnace end of the cell. After the rubber 'O' ring and removable sodium chloride plate was put in position and supported there by the brass coupling, the cell was attached to a vacuum line and evacuated to about 10^{-3} torr. Asbestos tape was wound round the furnace end of the cell, and the temperature of the disc raised to 120°. Pumping was continued at this temperature until a vacuum of 10^{-5} torr was obtained. The temperature of the disc was successively raised to 250° and 380° being held at each of these temperatures until a vacuum of 10^{-5} torr was attained, and then pumped at 380° for a further four hours. At the end of this heating procedure the cell was isolated and the disc allowed to cool to room temperature. The cell was removed from the vacuum line and tilted to that the disc holder ran along the glass rod to the bottom end of the cell. The latter was then positioned in the spectrophotometer, with the disc in the centre of the sample beam, and a spectrum obtained of the zeolite surface. Before attenuation the zeolite disc transmitted about 10% of the incident radiation.

The tap isolating the dosing material from the disc was then opened, the time of dosing depending upon the dosing material. These times are reported with the appropriate spectra. After the dosing period the cell was isolated from the dosing material, and the system left for 15 minutes to equilibrate. A spectrum of the surface and reactant was then obtained. In the absence of a zeolite disc a blank determination after the dosing material had been admitted to the cell, revealed no peaks due to organic material which had adhered to the cell windows. The cell was again attached to the vacuum line, and evacuated for one hour at room temperature before another spectrum of the surface was recorded. The temperature of the zeolite disc was raised to 120° and maintained for one hour, while the cell was continuously pumped. At the end of this period the cell was isolated and the disc allowed to cool to room temperature before its spectrum was recorded. This procedure was repeated with the disc being heated to 250°, and then to 350°, the heating period being one hour at each temperature. Using this technique spectra were obtained of the catalyst surface, and of the reactant-surface interaction at room temperature, and after heating to 120°, 250°, and 350°.

8.2. Flow experiments.

8.2.1. Apparatus and Technique.

The apparatus used in the flow experiments is shown in Figure 32.

The reactant, in a suitable solvent, was placed in the burette and pumped at a known rate to the top of the reactor, where a carburettor arrangement ensured a fairly uniform flow of reactant to the catalyst bed. A carrier gas forced the reactant and solvent through a vapourizer maintained at 220°, and into the catalytic reaction vessel. The catalyst bed was maintained at constant temperature (±5°) by an Ether Transitrol control, whose sensing thermocouple was in the centre of the bed. The products of the catalytic reaction were then carried to a trapping system consisting of a water condenser, and two dry-ice traps. The condensed products fell to a collection trap, where they were removed at regular intervals for analysis. The flow rate of the effluent gas was measured by a soap bubble meter.

8.2.2. Analysis.

Reaction products which collected in the receiver were withdrawn at regular intervals during a run (usually 15 minutes). To the weighed samples was added a known amount of n-propyl alcohol, which was used as an internal standard. The product analysis was performed using a Pye Series 104 Chromatograph. Cyclopentanone oxime, cyclohexanone oxime, 2-piperidone and ε-caprolactam were determined using a porapak-Q column (4.5mm x 1.5m) operating at 214° with helium as carrier gas (75ml min^{-1}). 3μl aliquots were injected, and the katharometer current was 195mA. Cyclopentanone and 4-cyanobut-1-ene, which were not resolved on this column, were determined separately using a column packed with 20% silicon oil on firebrick. The temperature of operation was 60°, the helium flow rate 30ml min^{-1}, and the katharometer current 200mA. Cyclohexanone and 5-cyanopent-1-ene were determined on the same column, using a temperature of 80°, a helium flow rate of 30ml min^{-1}, and a katharometer current of 200mA. n-Propyl alcohol was used as internal standard for both columns.

For analyses of samples in aqueous solution severe tailing was observed when using the silicon oil column, and the analyses of cyclopentanone and 4-cyanobut-1-ene were made after extraction of the aqueous solutions with diethyl ether. Calibrations were

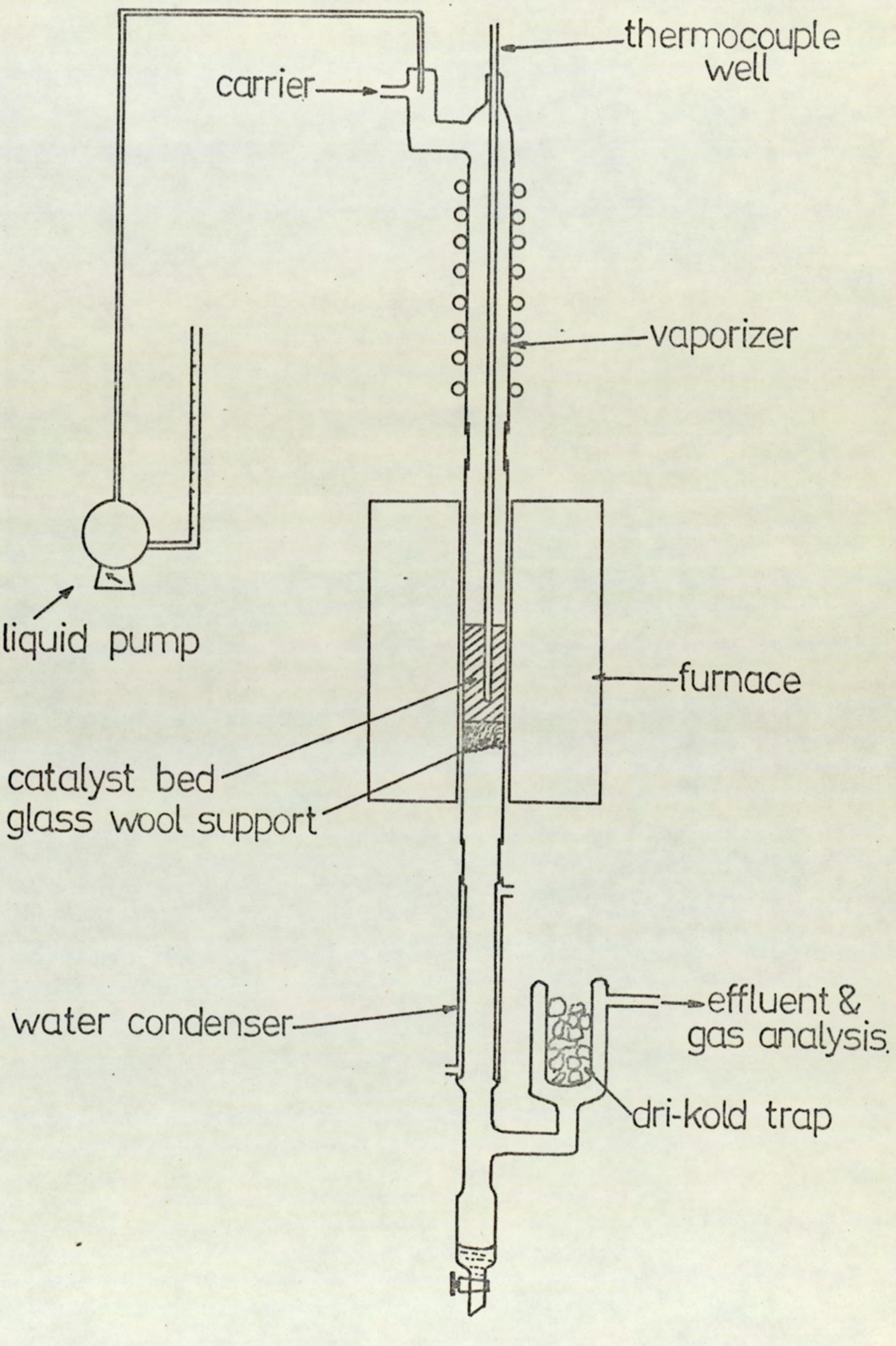


FIG.32, flow apparatus.

performed in order to take into account the distribution of the various compounds between the two solvents, and a few standard mixtures were prepared to check the reliability of the technique.

Analyses of the gas effluent from the reactor were performed using a porapak-Q column operating at either 40° or 100°, the helium flow rate was 75ml min^{-1} and the katharometer bridge current was 195mA.

Prior calibrations allowed the peak heights of the various products to be corrected, via the peak height of the internal standard, to weights of the individual compounds. These weights were usually expressed as the fraction of the converted feed going to the appropriate product, for each sample. Due to the short catalyst lifetimes, and the hold-up of organic material, it was decided that for each catalyst the conversion and selectivities are best calculated over the entire period of reaction; that is from when the reactant is first fed to the catalyst, to when the catalyst activity for the production of 2-piperidone, 4-cyanobut-1-ene and cyclopentanone becomes negligible. The conversion and selectivities are defined as follows:

$$\text{conversion} = \frac{\text{(weight of reactant fed - weight of reactant collected in samples)}}{\text{weight of reactant fed}} \times 100$$

$$\text{selectivity} = \frac{\text{weight of named product formed}}{\text{weight of reactant converted}} \times 100$$

the values reported were calculated over the entire period of catalyst activity. The conversion and selectivity was also calculated for each sample period (usually 15 minutes), and these values used to construct reaction profile curves, of which several are reproduced in the text. Liquid hourly space velocity (LHSV) is defined as the volume of solution fed per volume of catalyst bed per hour ($\text{VsVc}^{-1}\text{hr}^{-1}$). All catalyst weights are based on the anhydrous form, and all temperatures are given in degrees Celsius.

8.3. Catalysts.

8.3.1. Hydrogen-Y.

(i) The hydrogen-Y used in the flow experiments was prepared by passing a 10% solution of ammonium chloride through a column of sodium-Y (Linde SK40 powder, lot no. 1450-351) held at 78°, until a sodium level of 1.0% (anhydrous) was obtained (72hr). The resulting ammonium-Y was thoroughly washed, and dried in air at 120° for 2 hours. To this solid was added 0.5% by weight graphite and 0.5% by weight Sterotex, and the mixture pelleted before calcination at 450° for 24 hours to convert the ammonium-Y to hydrogen-Y.

(ii) The hydrogen-Y used in the spectroscopic studies was prepared by the method of Eberly (64). 36g sodium-Y (Linde SK40 powder, lot no. 1450-351) was treated with 67g ammonium nitrate in 600ml water for 2 hours at 70°. The zeolite was filtered and the procedure repeated to give a total of five treatments. After the final filtration the ammonium-Y was thoroughly washed, and dried at 120° for 2 hours. (Ward (59) has shown that decomposition of NH_4^+ ions does not occur below 200°). Analysis showed the anhydrous ammonium-Y to contain 1.1% sodium, corresponding to 90% exchange of ammonium ions for sodium ions.

8.3.2. Hydrogen-palladium-Y.

This catalyst was obtained as pellets (3/16" x 3/16"), and was used as supplied (Linde SK100, lot no. 13340-58). A Linde publication gives the following analysis for this catalyst; SiO_2=74.0±0.5 wt.%; Al_2O_3=25.0±0.5%; Na_2O=1.5±0.5%; Pd=0.5±0.02%; surface area $>500 m^2/g$.

8.3.3. Sodium-palladium-Y.

0.6g palladium chloride (BDH laboratory reagent) in 125ml water, 0.4g sodium chloride and 15g sodium-Y (Linde SK40 powder, lot no. 1450-351) were stirred for 1 hour at 25°. The suspension was filtered and washed with water, ethyl alcohol and ether. The product was dried at 120° for 2 hours, and pelleted before calcination at 420° for 24 hours.

8.3.4. Sodium-Y.

Apart from those described above, all the other zeolite catalysts were prepared from sodium-Y which was synthesized in the laboratory by the following method (118). A mixture of 142g sodium silicate (Hopkin and Williams), 20g sodium aluminate (BDH Technical grade), and 4100ml water was stirred at 100° for 19 hours. The precipitate was separated from the mother liquor by filtration, and thoroughly washed. The white crystalline solid was dried at 120° for 2 hours to give 56g sodium-Y. The latter was identified by X-ray spectroscopy, the following values being obtained.

hkl	d_{hkl}	estimated intensity	d_{hkl} reported (118)	reported intensity	hkl reported (118)
1.29	14.3	VS	14.3-14.4	VS	111
2.02	8.78	M	8.73-8.80	M	220
2.42	7.34	M	7.45-7.50	M	311
3.12	5.72	S	5.67-5.71	S	311
3.74	4.77	M	4.75-5.08	M	333,511
4.10	4.36	M	4.37-4.79	M	440
4.74	3.77	S	3.77-3.93	S	620
5.38	3.33	S	3.30-3.33	S	642
5.62	3.20	M	3.22-3.24	W	553,731
5.90	3.04	W	3.02-3.04	W	733
6.16	2.91	S	2.91-2.93	S	660,822
6.46	2.65	M	2.63-2.65	M	664
7.54	2.38	M	2.38-2.39	M	666,10,20
8.04	2.27	W	2.22-2.24	VW	775,11,11
10.76	1.705	W	1.70-1.71	W	997,11,93

8.3.5. Lanthanum-Y.

The method of preparation was that described by Plank et al (119). 25g sodium-Y (preparation 8.3.4.) was stirred at 90° with 50ml of a 10% solution of lanthanum chloride ($LaCl_3.7H_2O$ - BDH laboratory reagent, not less than 98%) for 2 hours. At the end of this period the zeolite was isolated by filtration. This procedure was repeated to give a total of eight treatments. After the final exchange the filtered zeolite was thoroughly washed with distilled water, dried at 120° for 2 hours, pelleted and calcined at 420° for 24 hours. X-ray analysis showed the sample to be highly crystalline. Analysis showed the lanthanum-Y to contain 1.15% residual sodium, corresponding to 89% exchange of lanthanum for sodium.

8.3.6. Lithium-Y, potassium-Y, caesium-Y and calcium-Y.

The same method of preparation was used for all these catalysts. 27g sodium-Y (preparation 8.3.4.) was stirred with 600ml of a 10% solution of the appropriate metal chloride, at

80° for 2 hours. The zeolite was separated by filtration, and the process repeated to give a total of five contacts. After the final filtration, the zeolite was washed with distilled water until the filtrate had a pH of 7. The zeolite was then dried at 120° for 2 hours, and pelleted before calcination at 420° for 24 hours. X-ray analysis showed all the samples to be highly crystalline. The sodium analyses were as follows:-

Zeolite	% Na (anhydrous)	% exchange
Na^+	10.6	-
Li^+	1.6	85
K^+	0.5	95
Cs^+	1.9	82
Ca^{++}	1.0	91

8.3.7. Sodium-A.

Sodium-A was BDH laboratory reagent molecular sieve 4A powder, it was pelleted and calcined at 420° for 24 hours before use.

8.3.8. Palladium-alumina.

γ-Alumina impregnated with 0.5% palladium was obtained from Harshaw Chemical Company as pellets (3/16" x 3/16").

Before use all the catalysts were heated in a stream of hydrogen at 400° for 2 hours. Catalysts were regenerated after each run by heating in air at 420°, for about 12 hours.

8.4. Organic reagents.

8.4.1. Cyclopentanone oxime.

This compound was prepared in batches using the following quantities. 238g cyclopentanone (BDH laboratory grade, not less than 99%) was added slowly to 166g hydroxylamine hydrochloride in 600ml water. The solution was stirred at room temperature and made alkaline with ammonium carbonate (199g). The oxime which precipitated was filtered off, the weight of crude oxime being about 250g (80%). The oxime was recrystallized from 60/80° petroleum ether to give white prisms mp. 56.5 (Lit. (120) 56.5°).

8.4.2. Cyclohexanone oxime.

The method employed was that described in 8.4.1. using

272g cyclohexanone (BDH laboratory reagent, not less than 99%). After recrystallization from 60/80° petroleum ether, the oxime melted at 88-89° (lit. (120) 89-90°).

8.4.3. 4-Cyanobut-1-ene.

The method of LaForge et al (121) was used. 25.8g 4-bromobut-1-ene (Koch Light-pure), 15g potassium cyanide and 75ml ethylene glycol were stirred at 100° for 2 hours. The brown solution was diluted with 150ml water, and the nitrile extracted into ether (4 x 50ml). The ethereal extracts were combined, washed and dried over $MgSO_4$. The ether was taken off on a water bath and the residue distilled to give 4-cyanobut-1-ene (8.0g, 52%); b.p. 34-36°/7 torr (lit. (122) 146-147°); $n_D^{19.5}=1.4225$ (lit. (122) $n_D^{19.5}=1.4233$); I.R. ν_{max} 3080(HC=), 2930(CH_2), 2250 (C≡N), 1642(C=C), 1445, 1005, 930 cm^{-1}; m/e 41(100), 39(29), 81 (27), 55(24), 28(24); τ 7.63[m,C(3)H_2, C(4)H_2], 4.87[m,C(1)H_2], 4.18[m,C(2)H].

8.4.4. 5-Cyanopent-1-ene.

This alkene-nitrile was also prepared by the method of LaForge et al (121). 9.5g 5-bromopent-1-ene (Koch Light-pure), 5g potassium cyanide and 25ml ethylene glycol were stirred at 100° for 2 hours. The brown solution was diluted with 50ml water, and the nitrile extracted into ether (3 x 30ml). The ethereal extracts were combined, washed and dried over $MgSO_4$. The ether was removed using a water bath, and the residue distilled to give 5-cyanopent-1-ene (5.2g,86%); b.p. 44-48°/7.5 torr (lit. (121) 54-59°/16 torr); $n_D^{25}=1.4270$ (lit. (121) $n_D^{25}=1.4268$); I.R. ν_{max} 3080(HC=), 2940(CH_2), 2250(C≡N), 1642(C=C), 1428, 1000, 927 cm^{-1}; m/e 55(100), 41(62), 28(46), 39(30), 95(5); τ 8.13[m,C(3)H_2, C(4)H_2, C(5)H_2], 4.94[m,C(1)H_2], 4.25[m,C(2)H].

8.4.5. 2-Piperidone.

2-piperidone was obtained from Phase Separations Ltd., and was 95% pure by vpc. (porapak-Q, 20% silicon oil on firebrick).

8.4.6. ϵ-Caprolactam.

This lactam was BDH laboratory reagent, and was 95% pure by vpc. (porapak-Q, 20% silicon oil on firebrick) m.p. 67-69° (lit. (120) 68-70°).

8.4.7. Cyclopentanone oxime -HCl, cyclohexanone oxime -HCl and ϵ-caprolactam -HCl.

These hydrochlorides were precipitated as white crystalline solids by bubbling HCl gas through a 10% solution of the oxime or lactam in CCl_4. The precipitates were filtered, and dried by pressing between filter paper. Due to the deliquescent nature of the oxime hydrochlorides, it was not possible to determine their melting point accurately. The infrared spectrum of cyclohexanone oxime -HCl was identical to that reported by Saito (95), and that of cyclopentanone oxime -HCl exhibited bands at the same frequencies as those reported by Saito and Nukada (87). ε-Caprolactam -HCl m.p. 115-157° (Lit. (123) 157-158°).

8.4.8. Solvents.

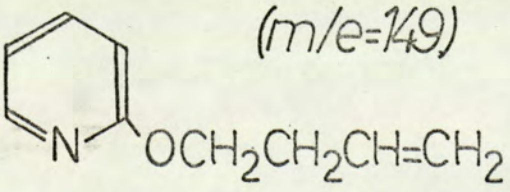
Benzene and cyclohexane were redistilled, the former being stored over sodium. Fluorobenzene was BDH laboratory reagent grade, and methyl cyanide was Fisons laboratory reagent, both were pure by glc., n-propyl alcohol was Fisons laboratory reagent grade, and was 95% pure by glc.

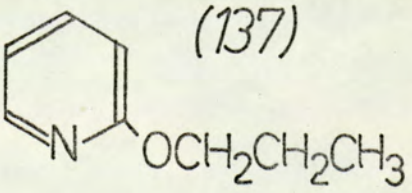
8.5. Identification of reaction products.

Products from the reaction of cyclopentanone oxime in the flow apparatus were identified by peak enrichment on both porapak-Q and silicon oil columns at various temperatures. The product mixture was also fractionally distilled, and the individual components identified by their boiling points, and by comparison of their infrared spectra with those of the pure compounds. Apart from unreacted oxime, 2-piperidone, 4-cyanobut-1-ene, and cyclopentanone, small quantities of acetonitrile and acrylonitrile were detected in the effluent from the reaction of cyclopentanone oxime over decationated zeolites. The products of reaction of cyclohexanone oxime were identified by peak enrichment on porapak-Q and silicon oil columns.

8.6. Analysis of catalyst extract (see Chapter 6).

The extraction of several used catalysts with an organic solvent (CCl_4 and benzene, extraction time 5 hours), and then evaporation of the solvent, produced the same catalyst extract. The extract had infrared maxima at 805, 1000, 1080, 1255, 1460, 2860, 2930, 2960 (small), and 3020 (small). The mass spectrum of the extract is given in Figure 33. The proposed assignments for the most intense lines in the spectrum are as follows:





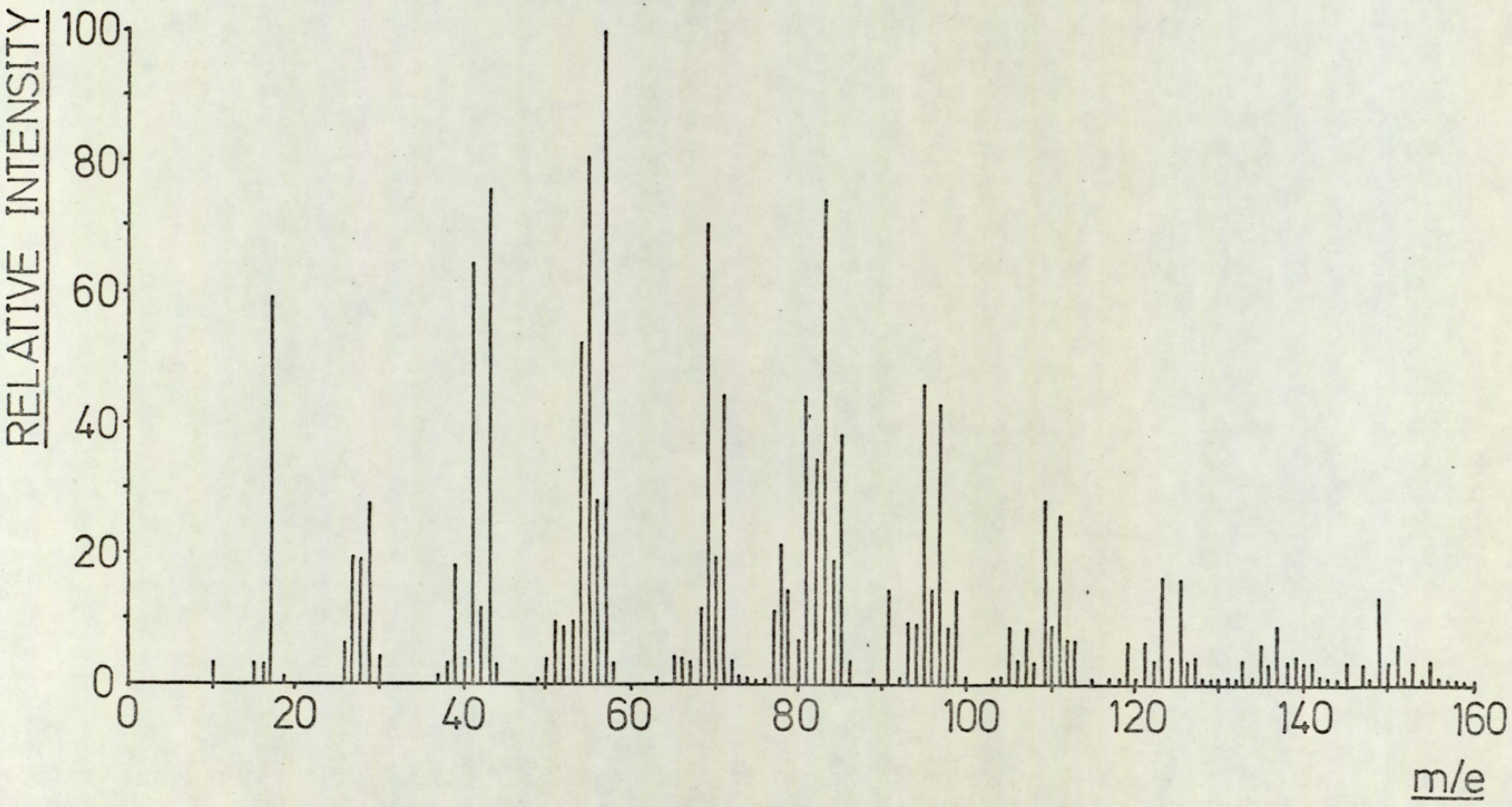
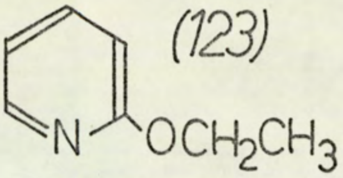
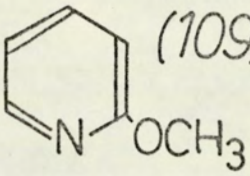


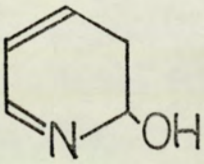
FIG. 33, mass spectrum of catalyst extract.



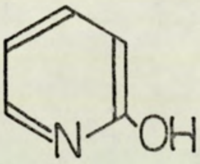
(123)



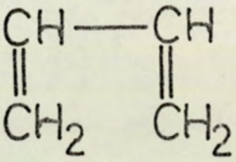
(109)



(97)



(95)



$CH_2=CH-CH=CH_2$

(54)

8.7. X-Ray analyses.

Powder photographs were obtained using a Solus-Schall X-ray generator and a Phillips tube and camera. Cu-Kα radiation was used and the exposure time was usually about 3 hours. All the zeolites used were highly crystalline. For hydrogen-Y and hydrogen-Pd-Y analyses were also obtained after a run, and after regeneration of the catalyst. All samples were crystalline. Catalysts which had been used and reactivated several times exhibited slightly diffuse lines in their X-ray spectra, but were still crystalline.

8.8. Sodium analyses.

The sodium content of zeolites was determined by flame photometry. One gram of the sample was weighed out accurately into a crucible, and 20ml concentrated hydrochloric acid added. The crucible was covered by a watchglass and heated on a hot plate in a fume cupboard for 5 hours, the acid being replenished as necessary. At the end of this period the crucible was allowed to cool, and its contents transferred to a 25ml volumetric flask, and made up to the mark with concentrated hydrochloric acid. The contents of this flask were transferred to a 250ml flask, and made up to the mark with distilled water. Standard solutions of sodium chloride were prepared, having the same pH as the diluted extracts, and the percentage of sodium in the latter was determined, after appropriate dilutions, using and Eel flame photometer. Several control experiments showed that no sodium was detected in the absence of the zeolite, and that all the sodium was extracted from the zeolite by this procedure (124). Using this technique the amount of sodium in one gram of hydrated zeolite could be determined. The percentage of water in the zeolite was found by thermogravimetric analyses, and so the percentage sodium in one gram of anhydrous zeolite could be calculated. These are the figures reported for the various catalyst.

8.9. Acidity measurements.

The method employed was that described by Benesi (125). 0.1g of activated catalyst (the acidities of hydrogen-Y and hydrogen-Pd-Y only were tested) was dried at 120° for 12 hours and then transferred to a desiccator. 10ml of benzene was dried over 13X molecular sieve, and a small amount of anthraquinone was recrystallized from benzene. A 0.1% solution of anthraquinone in benzene was prepared, and four drops of this added to 0.1g catalyst in 4ml benzene. A definite yellow colour appeared on the catalyst surface, indicating an acid strength for each of these catalysts, equivalent to that of at least 90% by weight sulphuric acid (PKa$<$-8.2).

8.10. Thermogravimetric analyses.

A Stanton automatic thermo-recording balance was used. This technique was used to determine the percentage of water in catalysts, and for studying catalyst weight losses as a function of temperature in air, and in an inert atmosphere.

8.11. I.R., N.M.R., and mass spectra.

Infrared spectra were recorded using either a Perkin-Elmer 237 or 457 spectrophotometer, and ^{1}H n.m.r. spectra with a Perkin-Elmer R10 instrument at 14,000 gauss and 60 Mc sec^{-1} with tetramethylsilane as internal standard. Mass spectrometric analyses were performed on the A.E.I. MS 9 instrument.

ACKNOWLEDGEMENTS

I would like to acknowledge all the help which I received both during my three years research, and in the preparation of this thesis. I am particularly indebted to Dr. J. D. Butler, without whom this work would not have been possible. Through many stimulating discussions, Dr. Butler provided constant encouragement and many valuable comments.

My thanks are also due to the many people at Aston University who either provided spectra of submitted samples, or allowed me valuable instrument time, and to the Science Research Council for financial support during the period of research. Finally, I acknowledge with gratitude the patience of my wife Janet, in typing both the draft and final form of this thesis.

APPENDIX 1: INFRARED SPECTRA

Designation for Spectra 10 - 25

(a) Catalyst surface after activation.

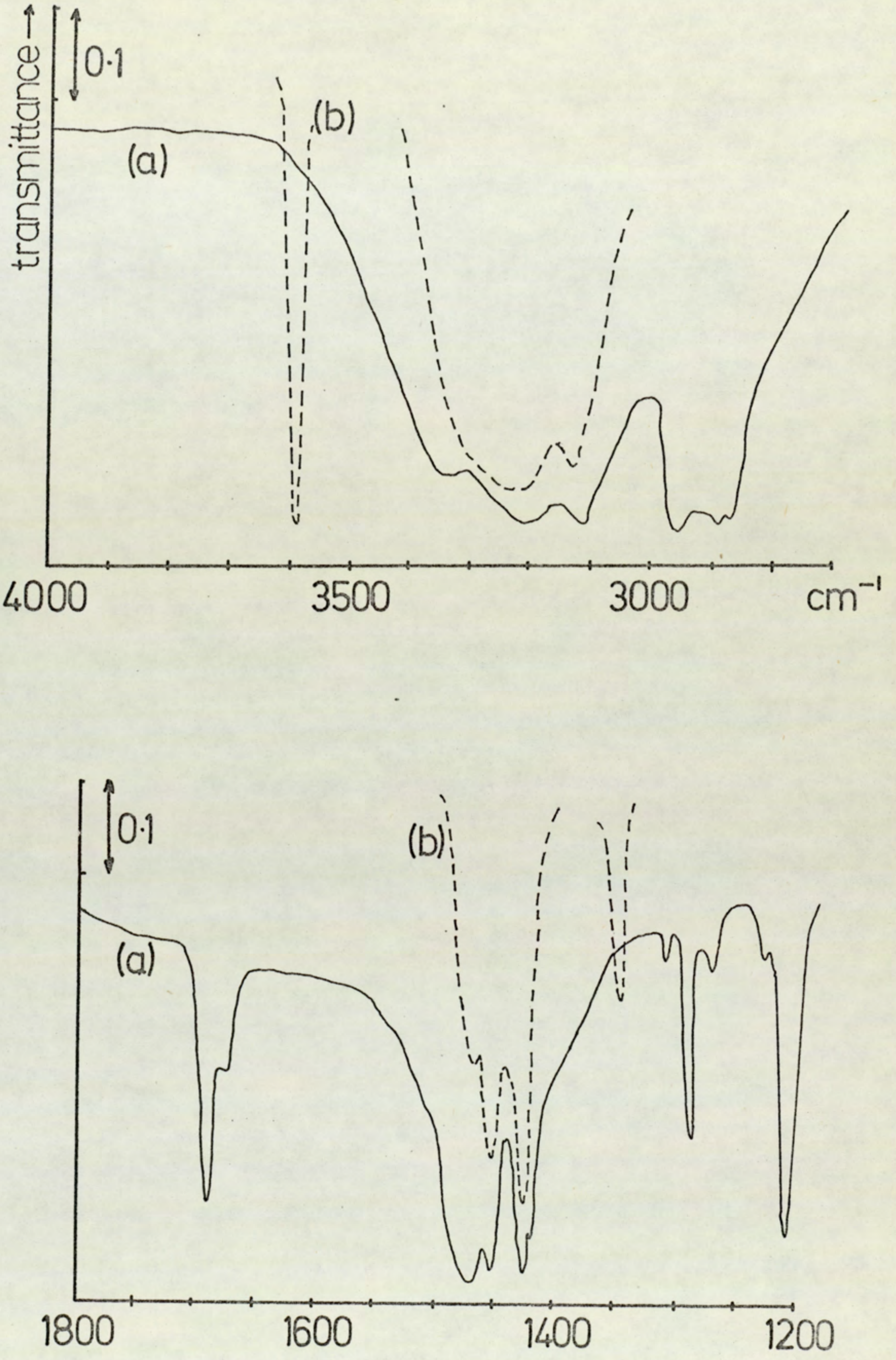
(b) Catalyst surface after dosing for stated period.

(c) Catalyst surface after dosing and evacuation for one hour at room temperature. In some experiments this step was omitted.

(d) Catalyst surface after dosing and evacuation for one hour at 120°C.

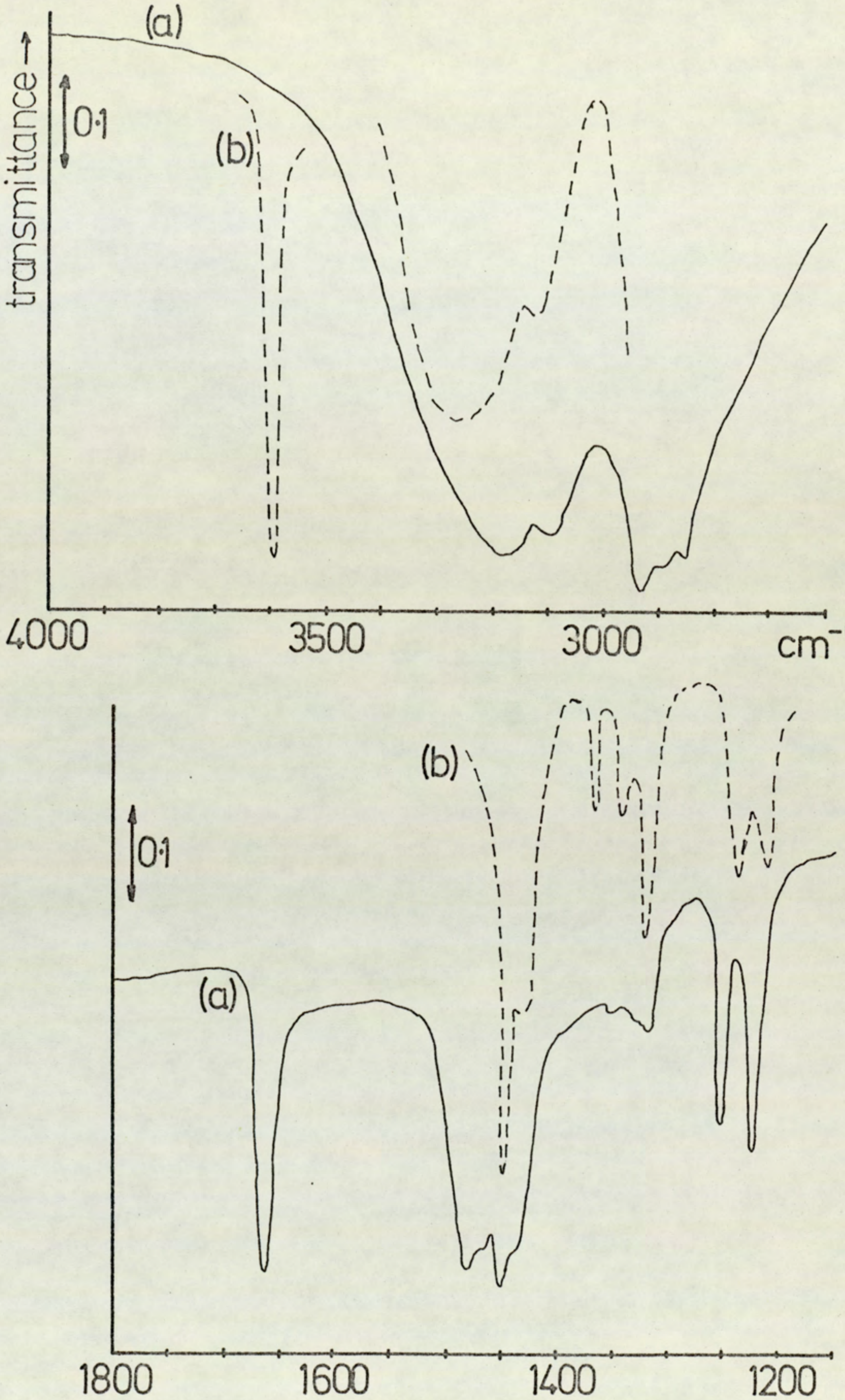
(e) Catalyst surface after dosing and evacuation for one hour at 250°C.

(f) Catalyst surface after dosing and evacuation for one hour at 350°.



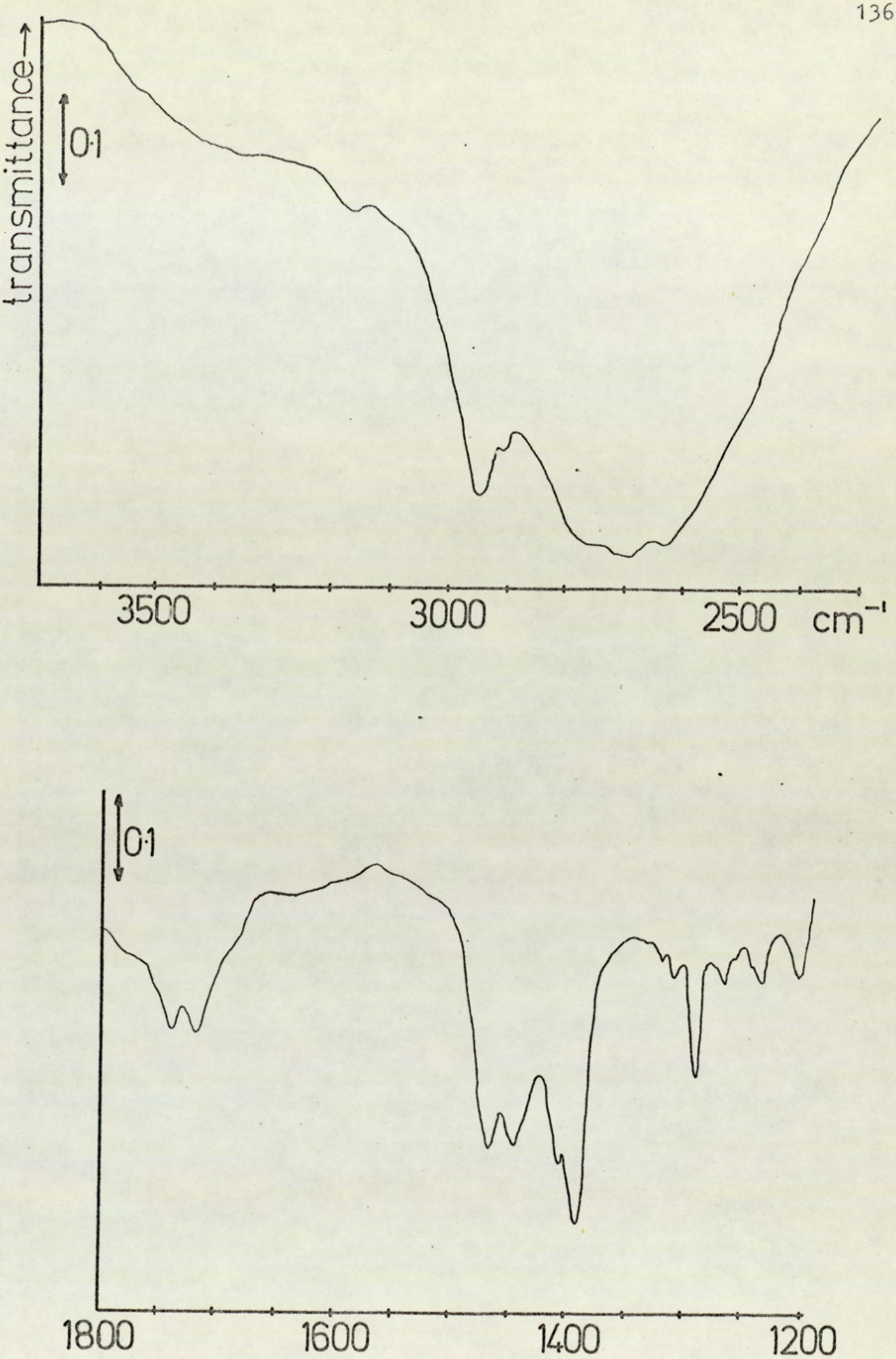
SPECTRUM 1,-Cyclopentanone oxime.

(a) KBr disc, (b) 10% soln. in CCl_4.

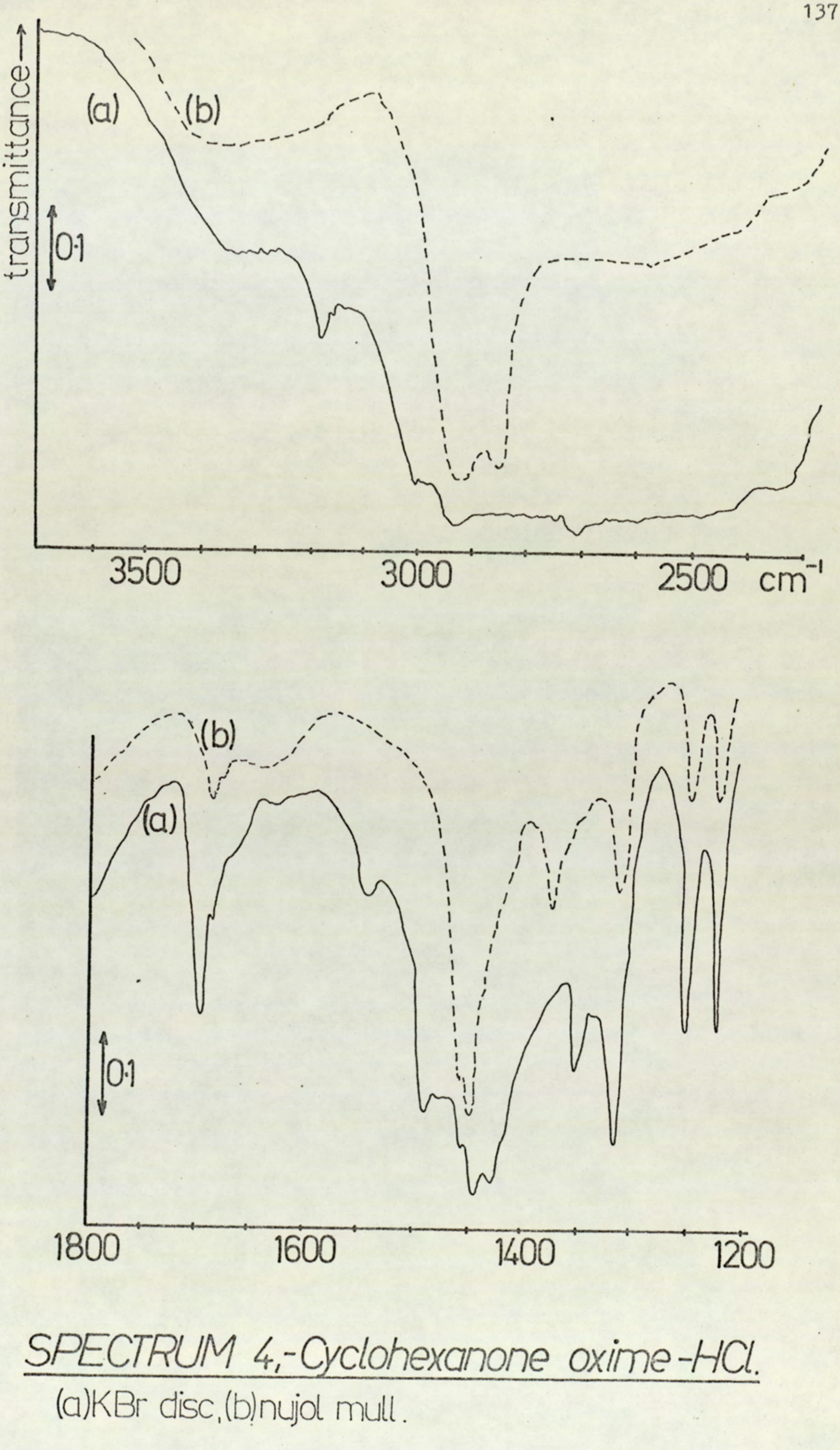


SPECTRUM 2,-Cyclohexanone oxime.

(a)KBr disc, (b)10% soln. in CCl_4.

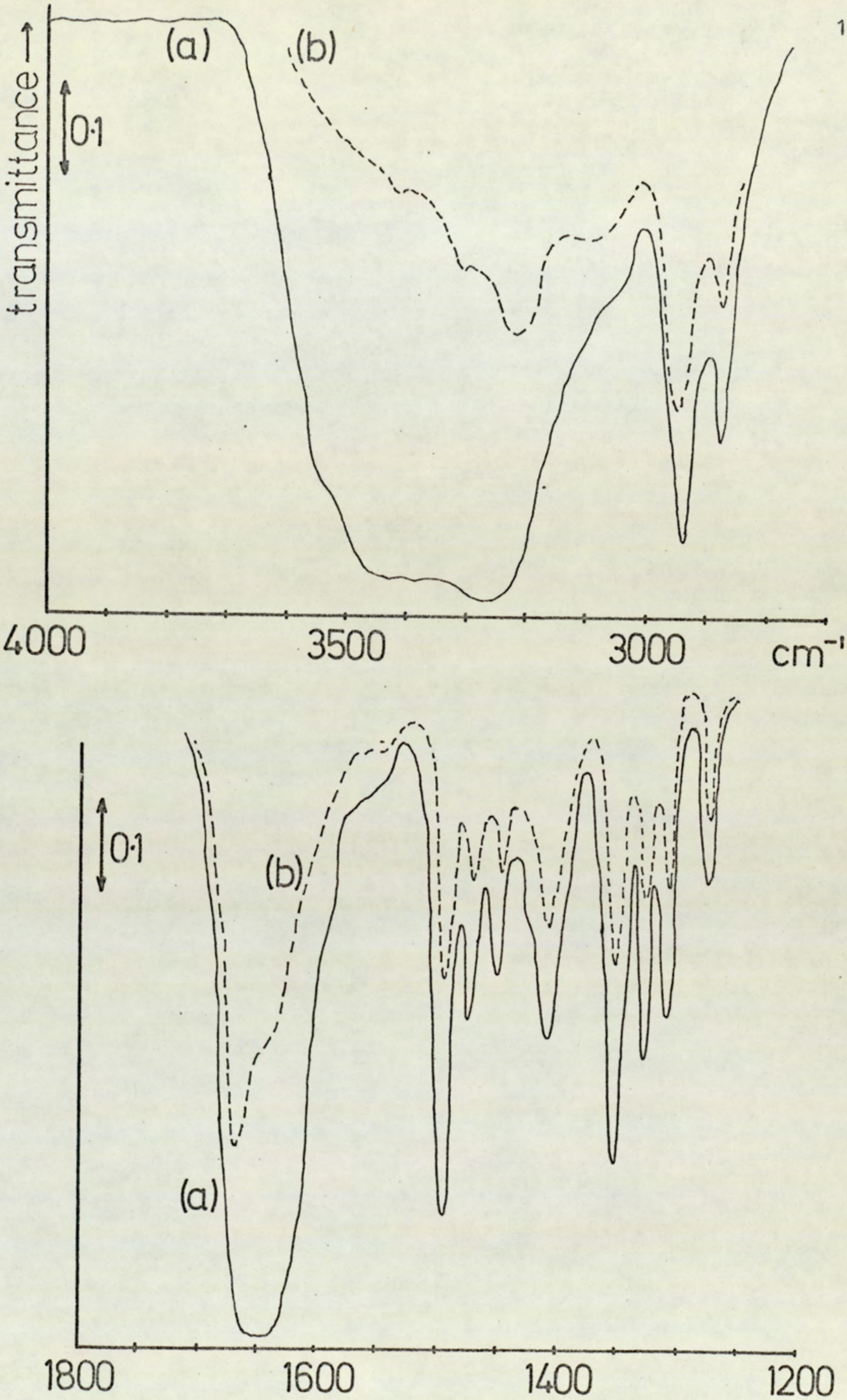


SPECTRUM 3,-Cyclopentanone oxime-HCl.
(KBr).



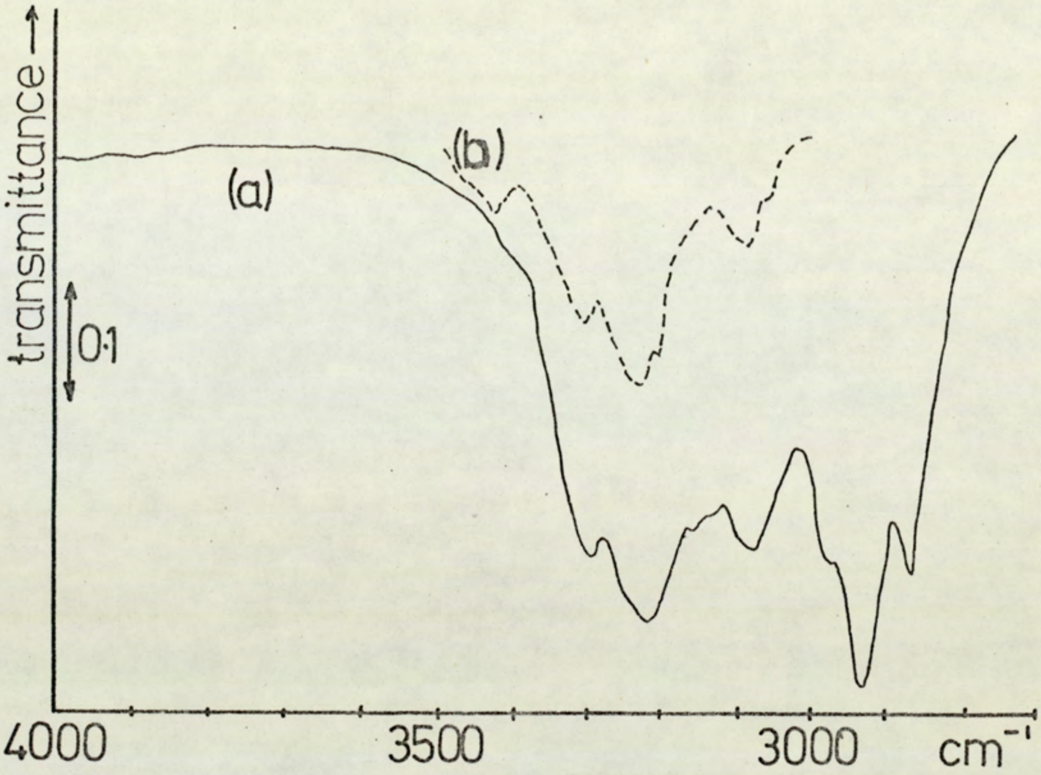
SPECTRUM 4,-Cyclohexanone oxime-HCl.

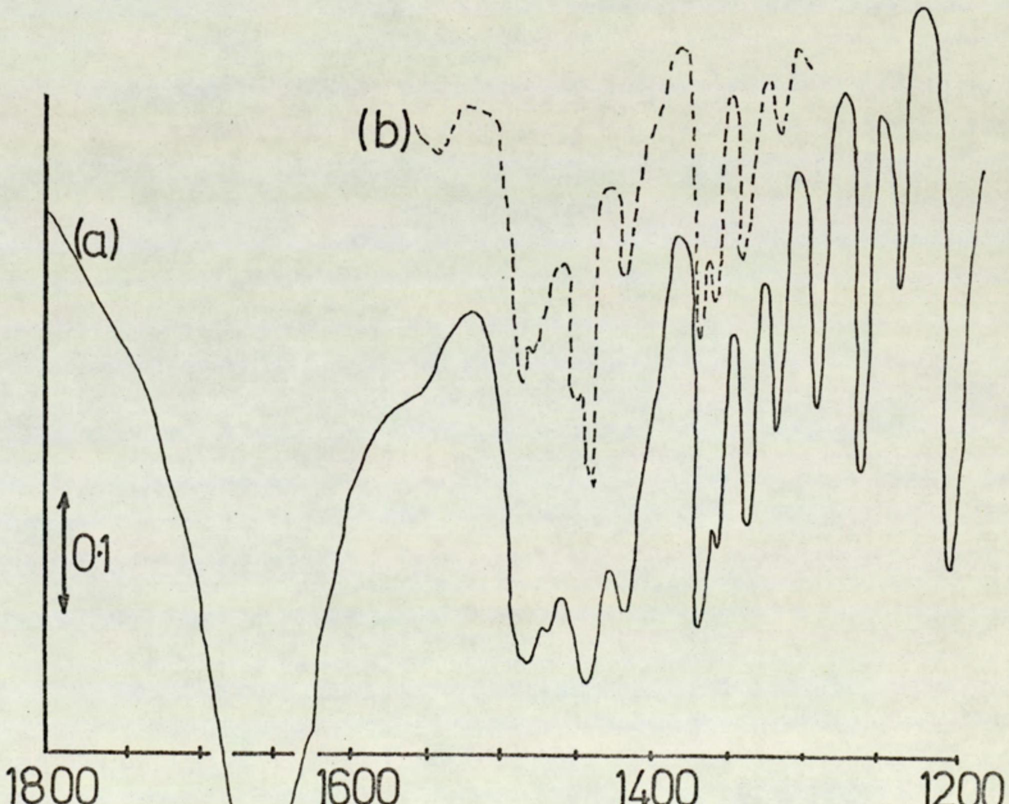
(a)KBr disc,(b)nujol mull.



SPECTRUM 5,- 2-Piperidone.

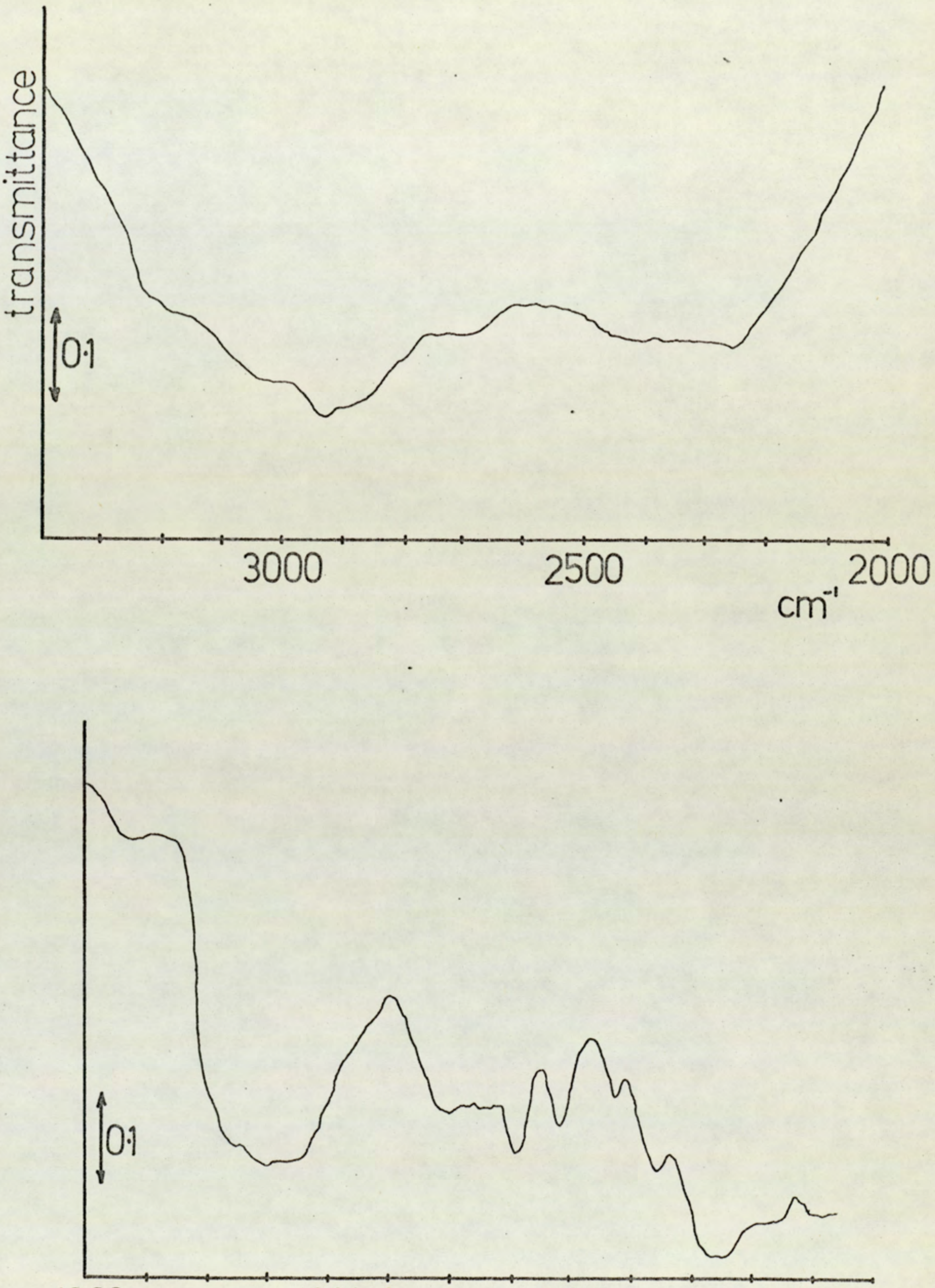
(a)neat film,(b)10% soln in CCl_4.





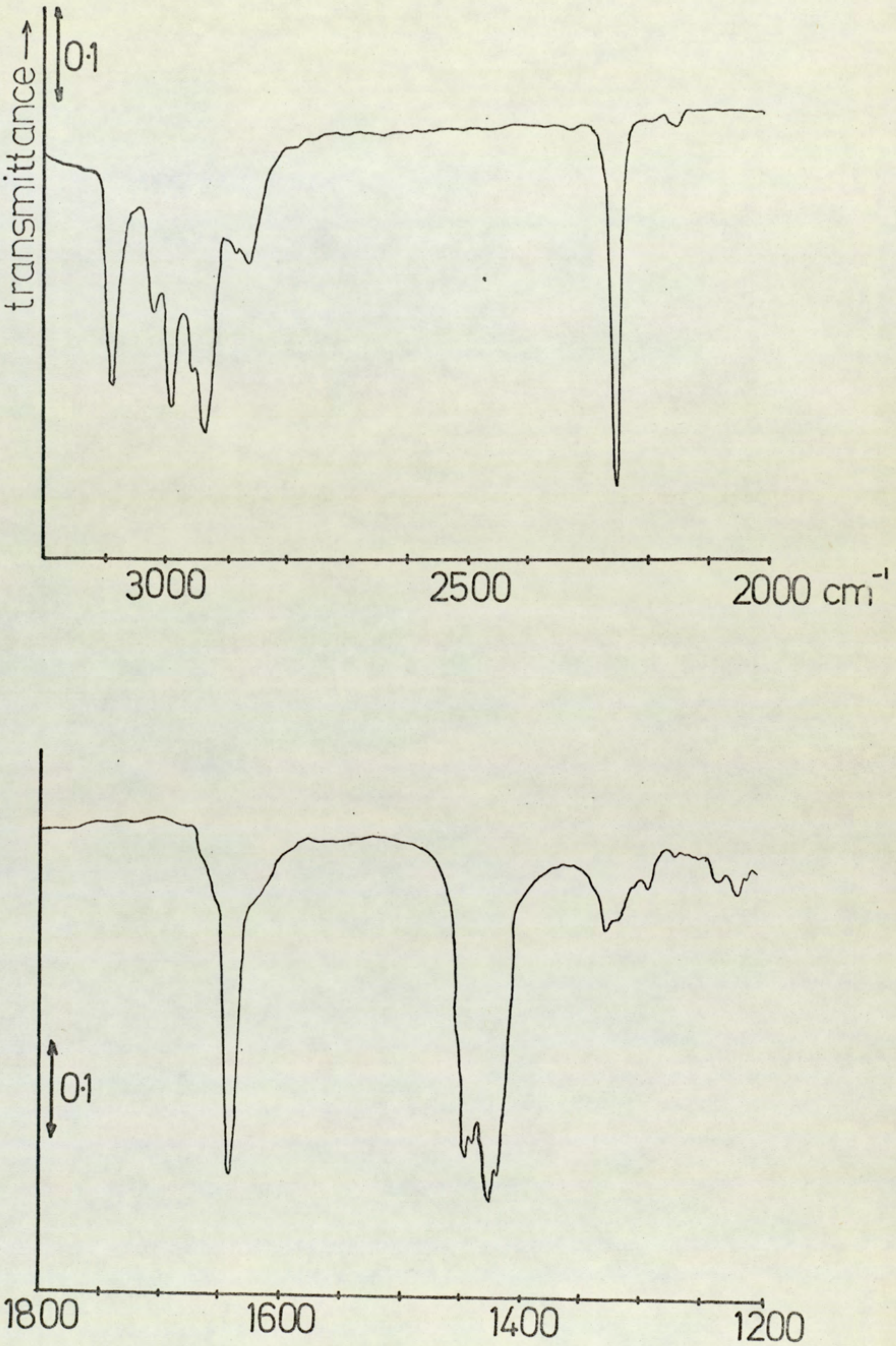
<u>*SPECTRUM 6,- ϵ-Caprolactam.*</u>

(a)KBr disc,(b)10% soln in CCl_4.

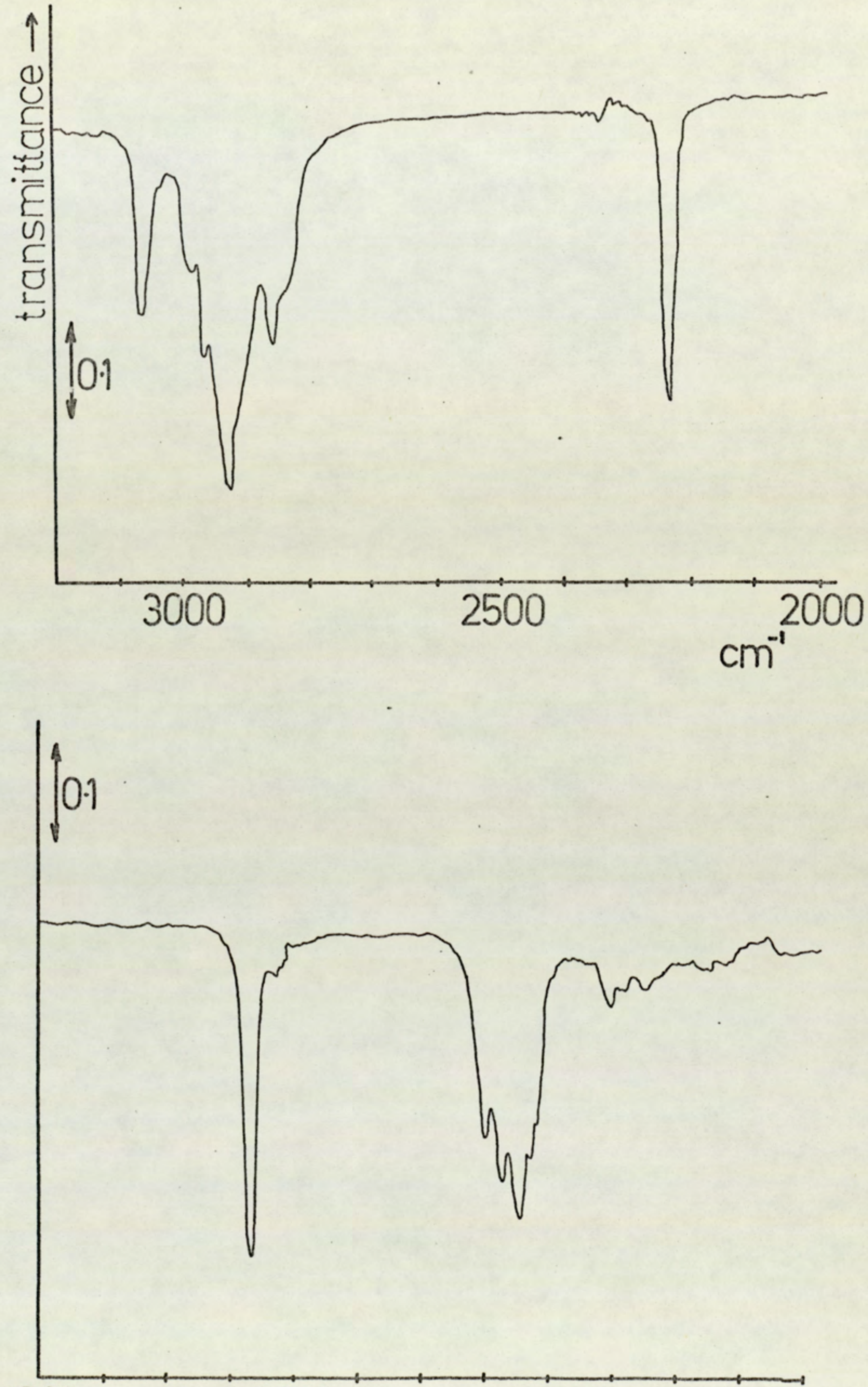


SPECTRUM 7,- ε·Caprolactam-HCl.

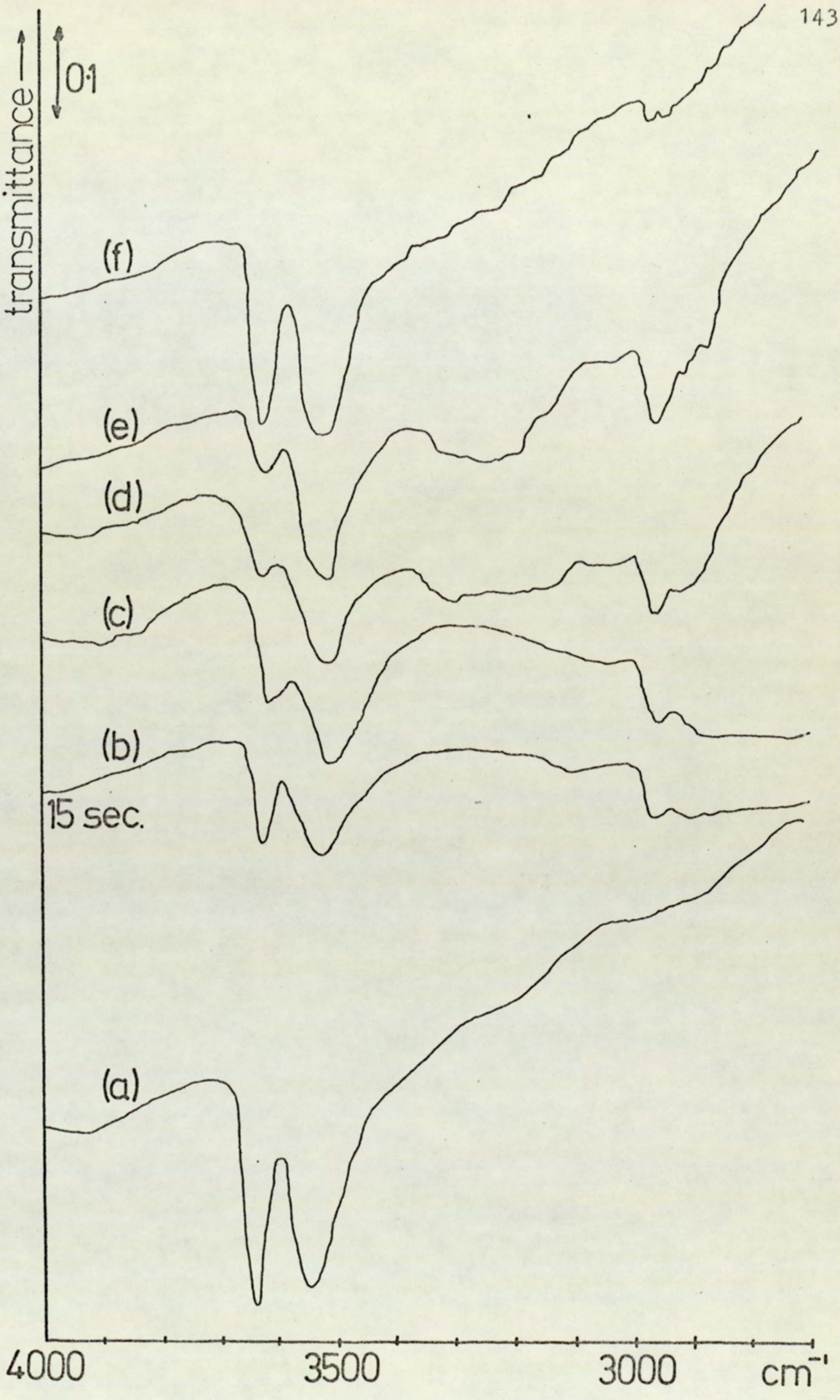
(KBr)



SPECTRUM 8,- 4-Cyanobut-1-ene.
(neat film).

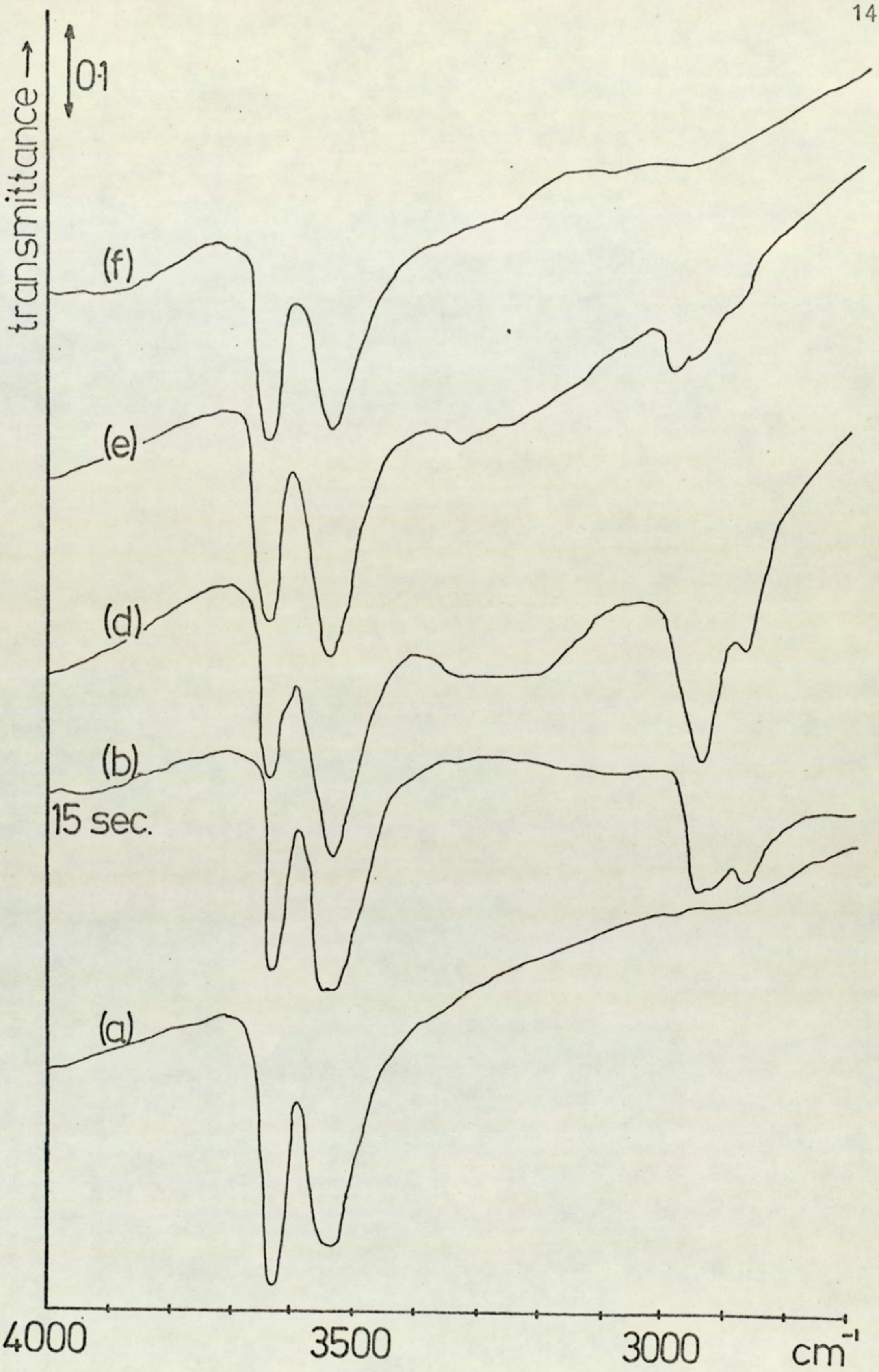


SPECTRUM 9;- 5-Cyanopent-1-ene.
(neat film)

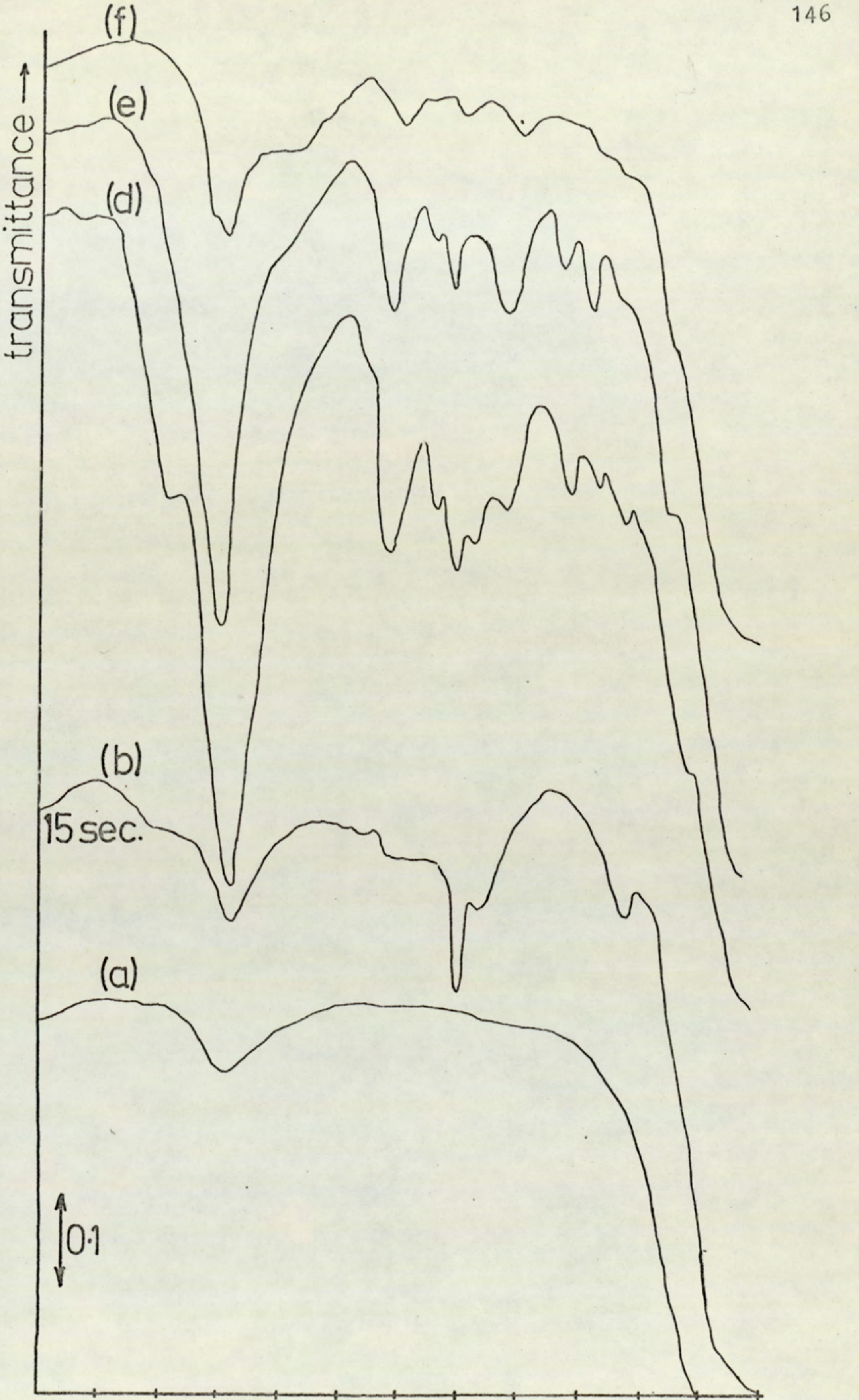


SPECTRUM 10.-Cyclopentanone oxime - HY.

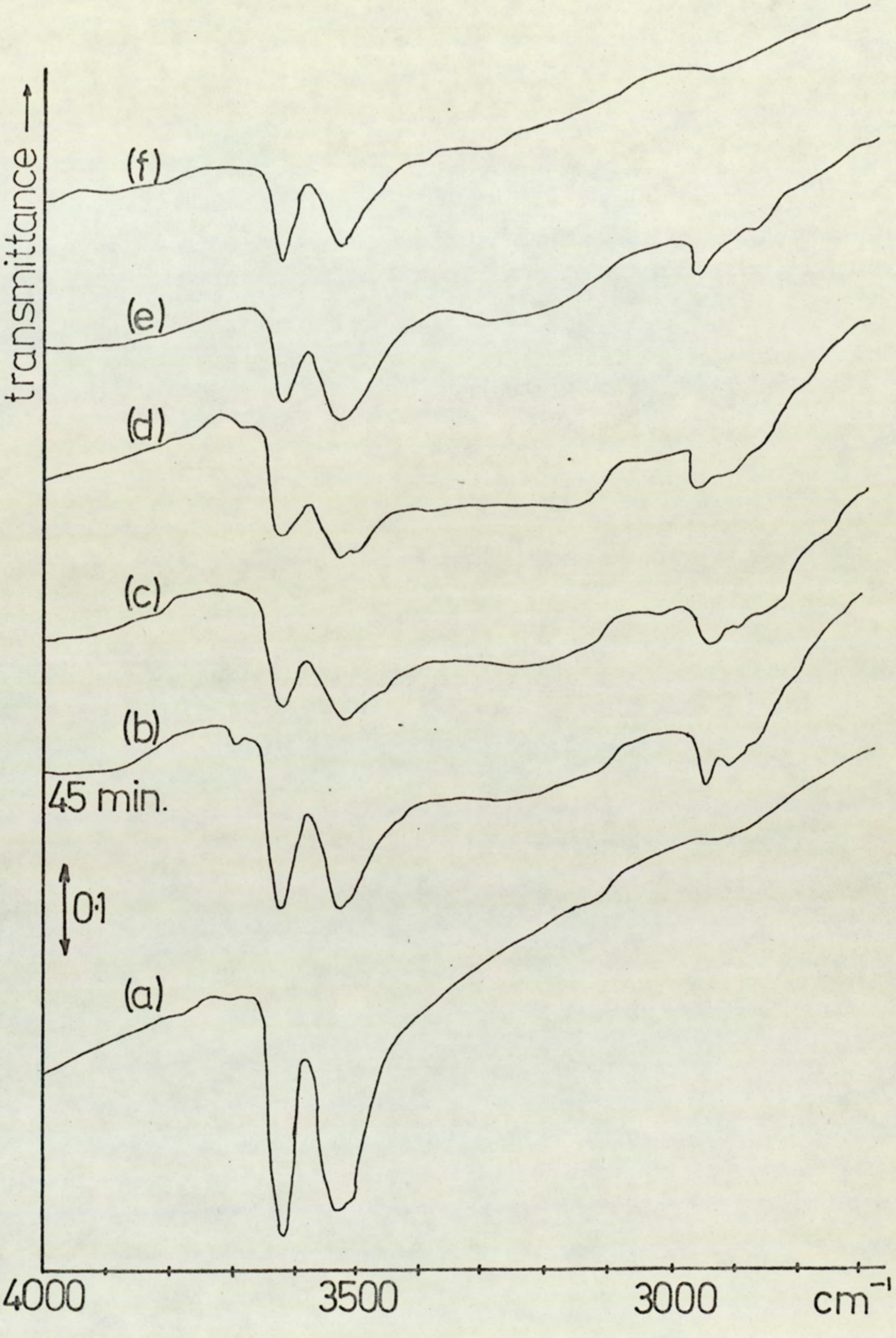
SPECTRUM 11,-Cyclopentanone oxime-HY.



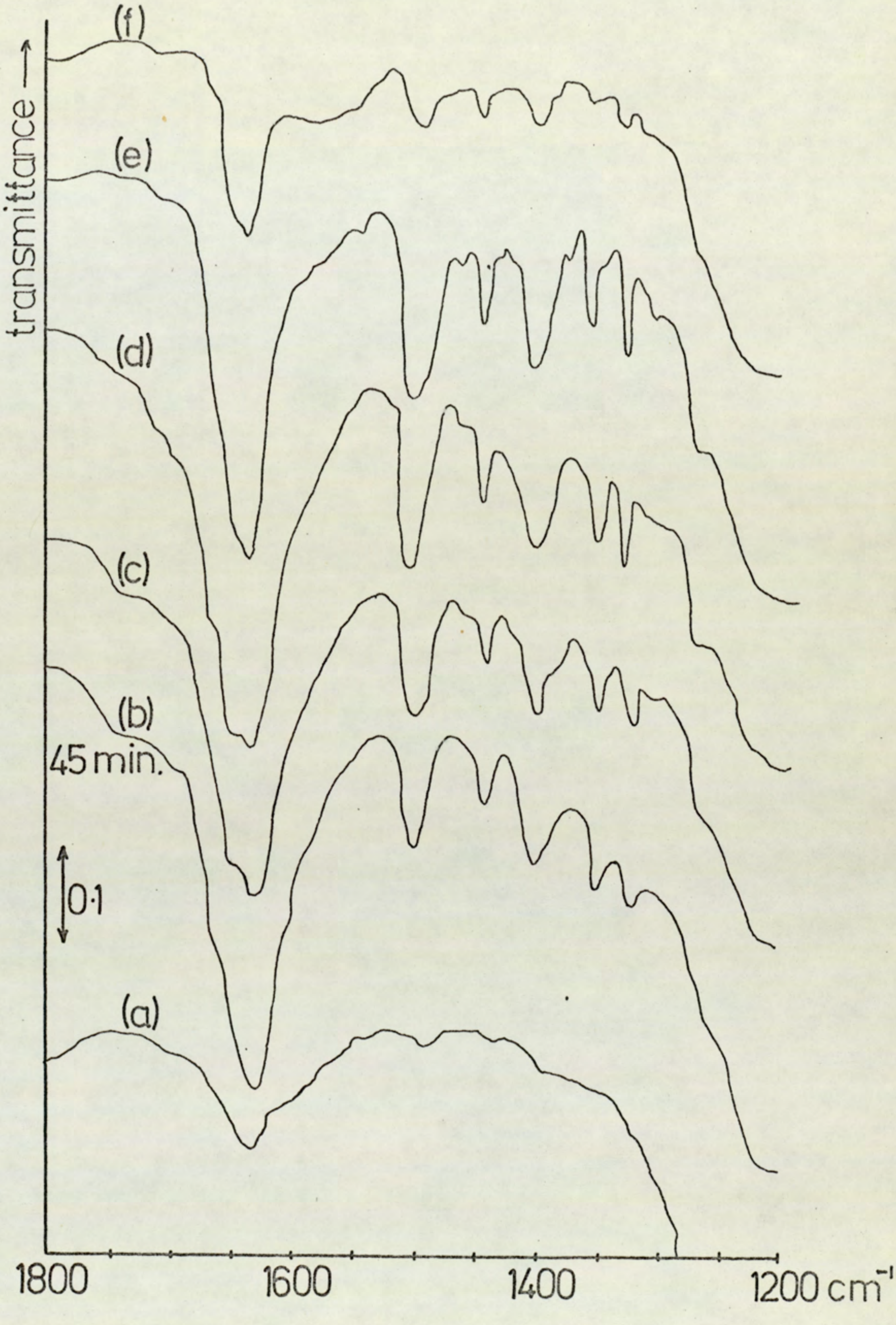
SPECTRUM 12,-Cyclohexanone oxime-HY.



SPECTRUM 13,-Cyclohexanone oxime-HY.



SPECTRUM 14,-2-Piperidone-HY.



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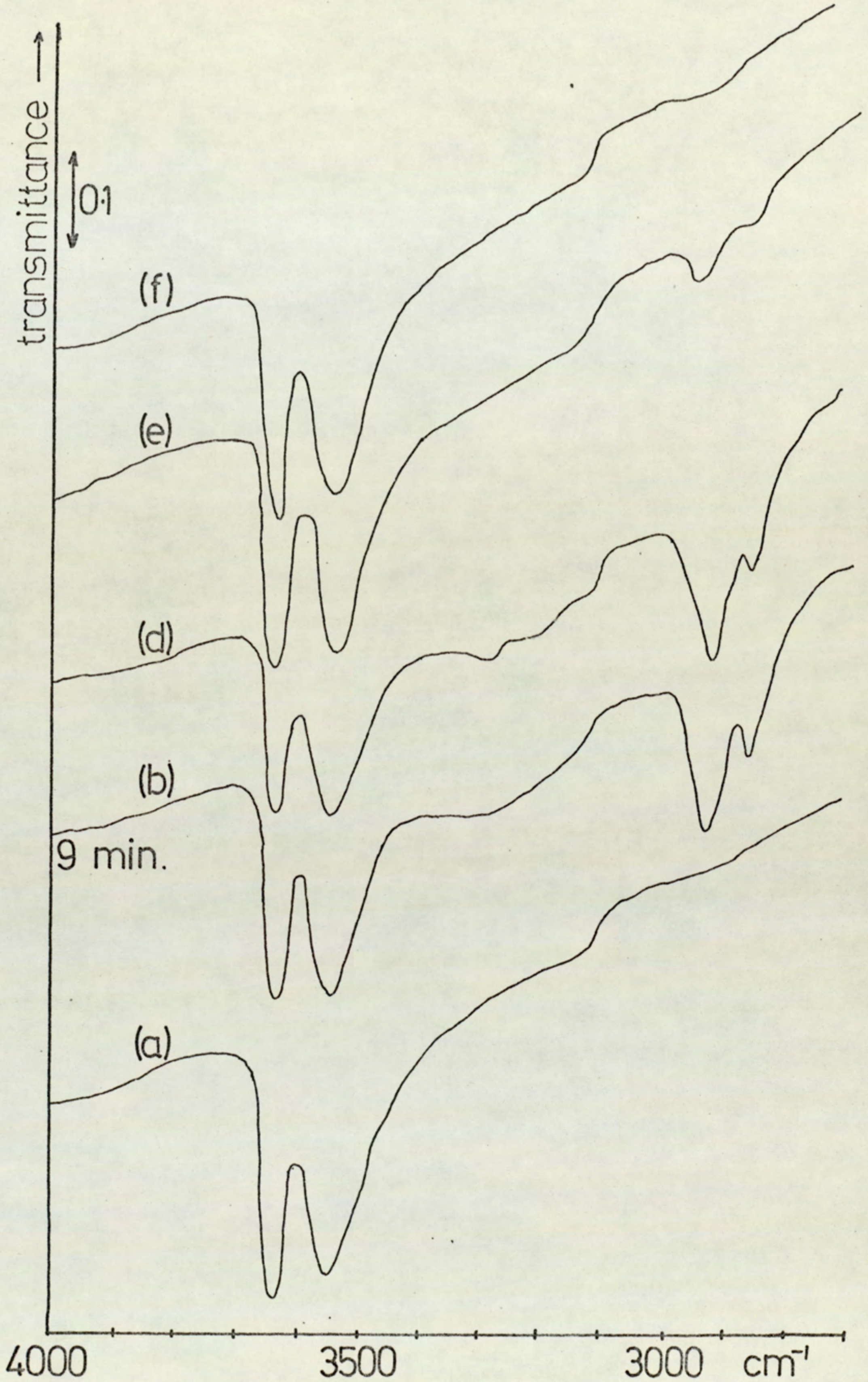
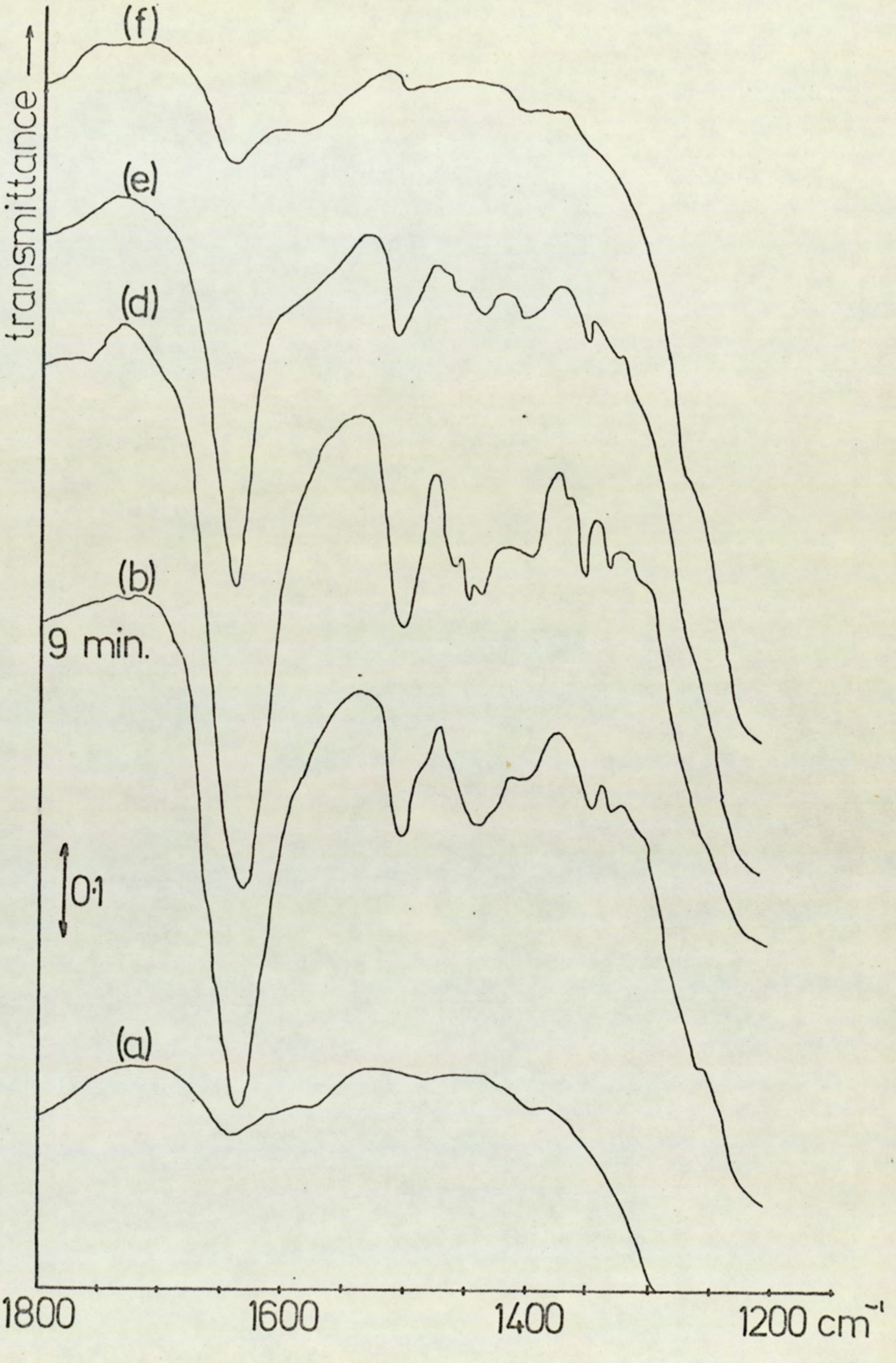
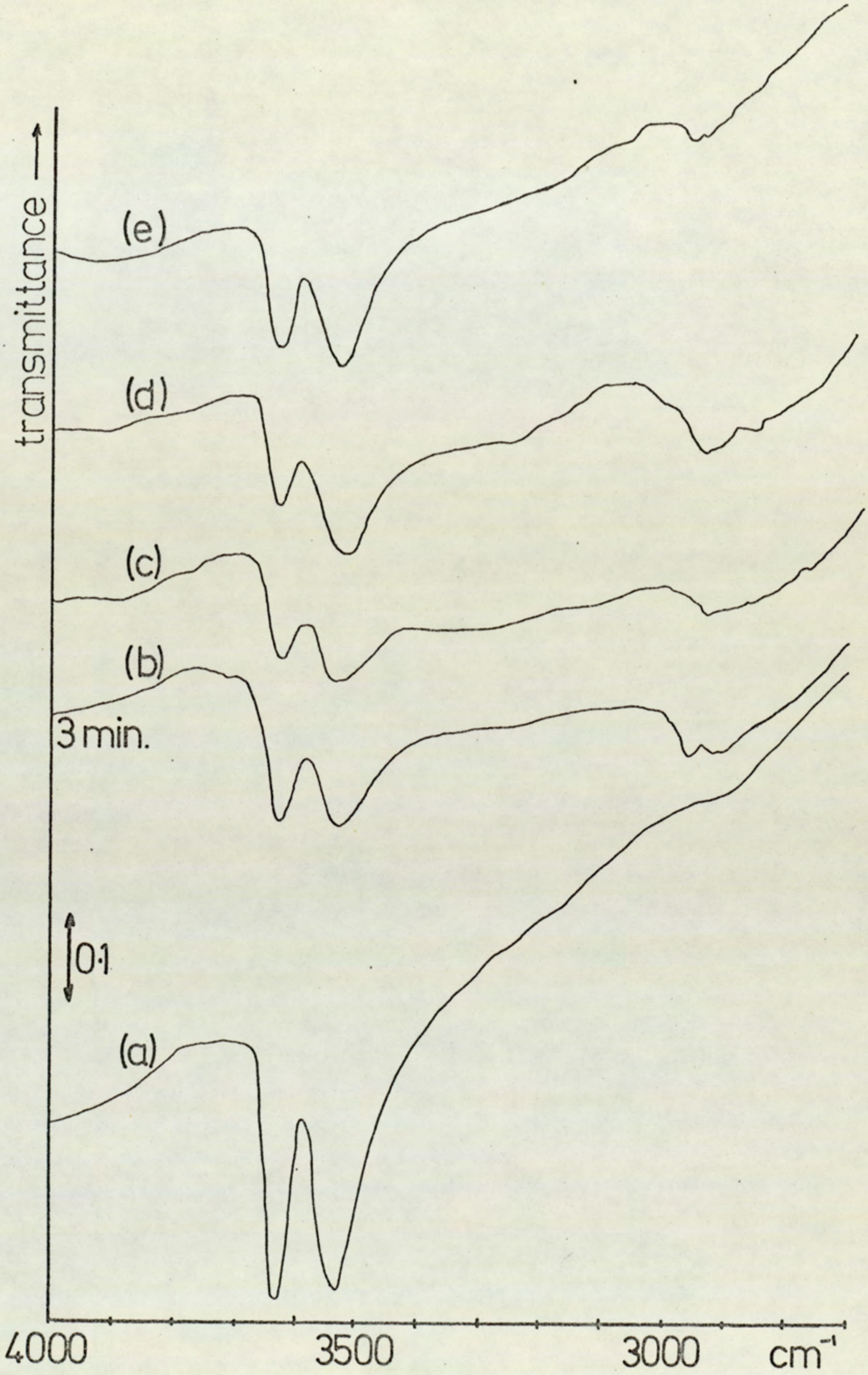


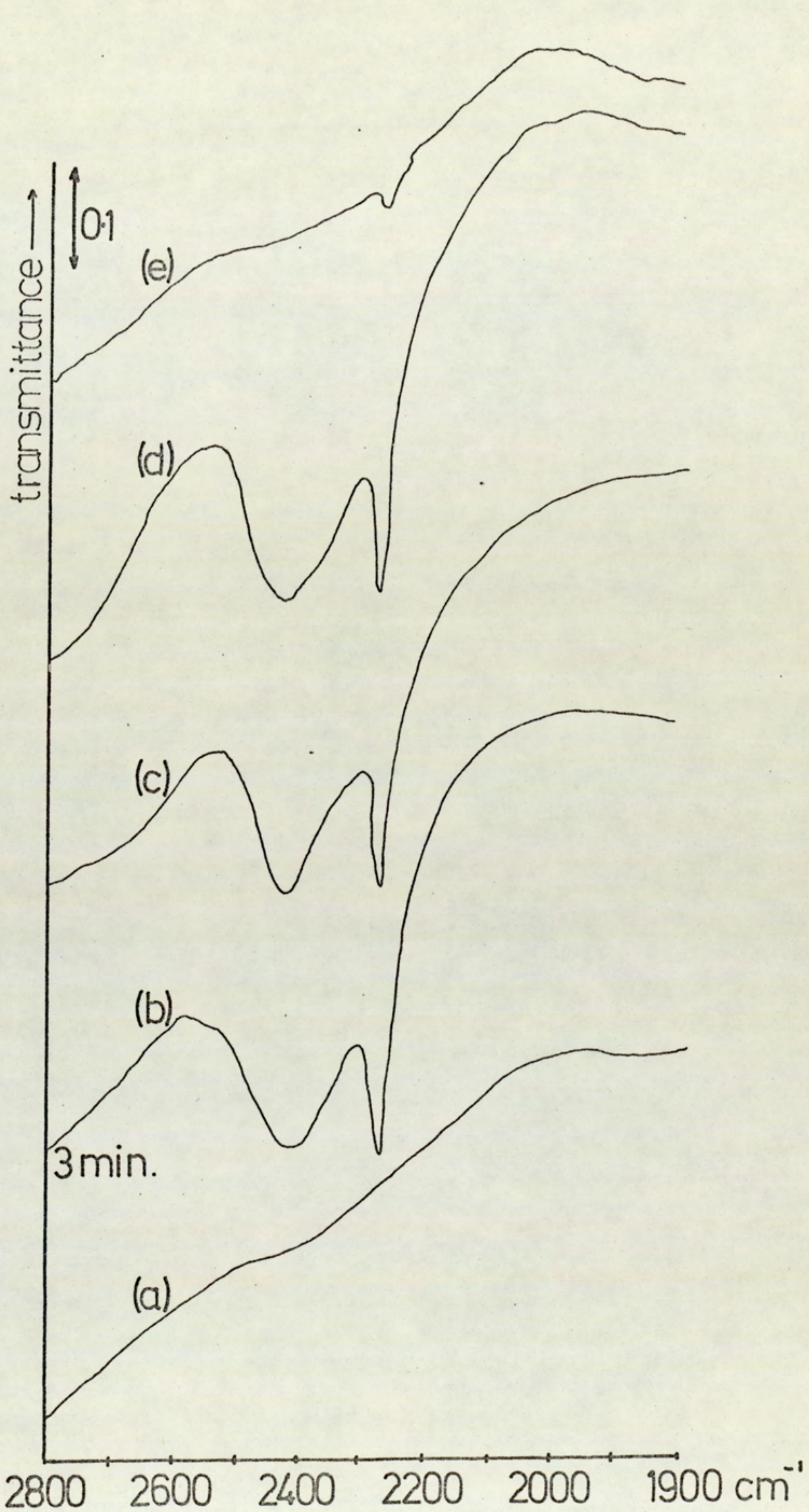
SPECTRUM 16,- ϵ-Caprolactam-HY.



SPECTRUM 17,- ϵ-Caprolactam - HY.



SPECTRUM 18;- 5-Cyanopent-1-ene-HY.



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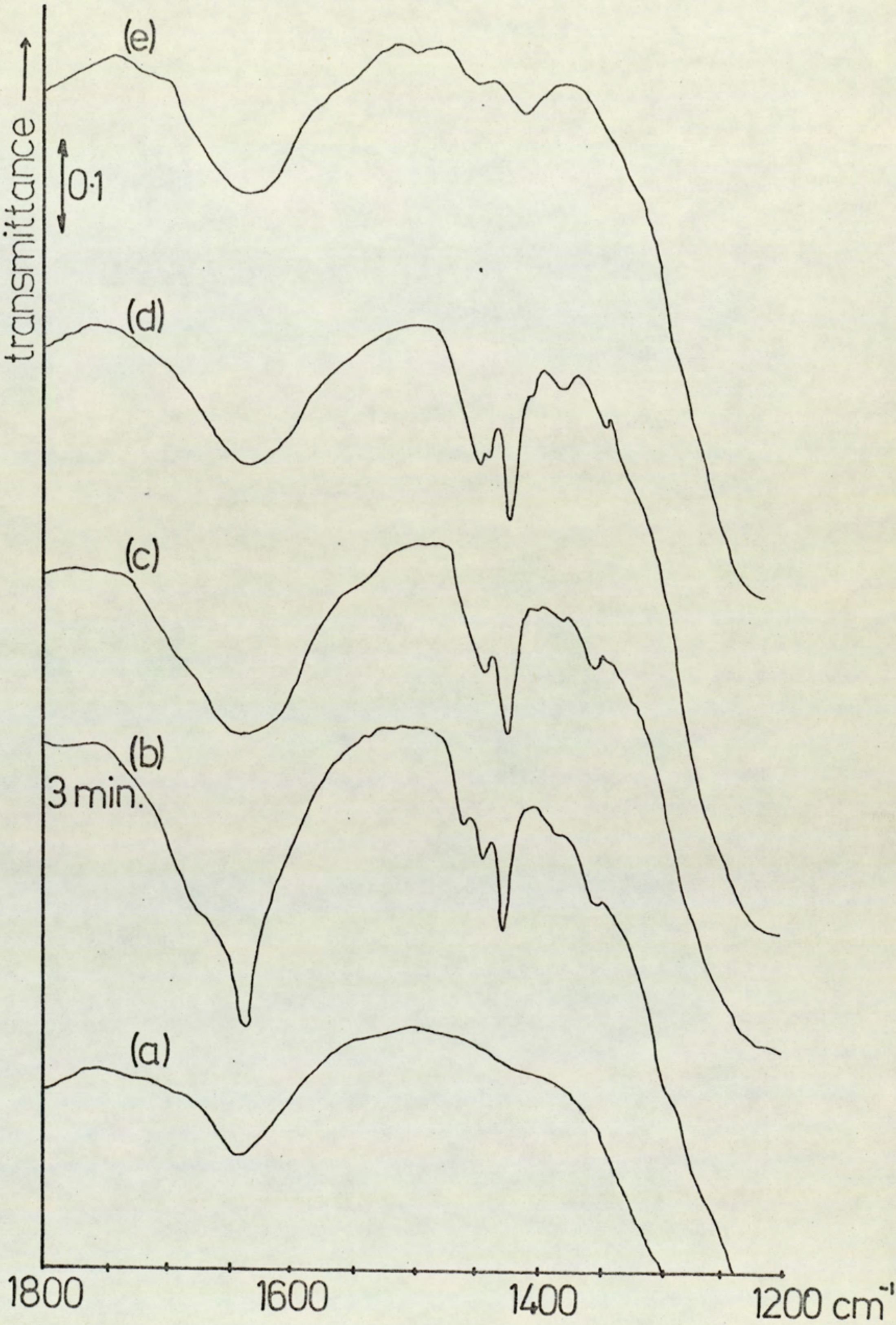
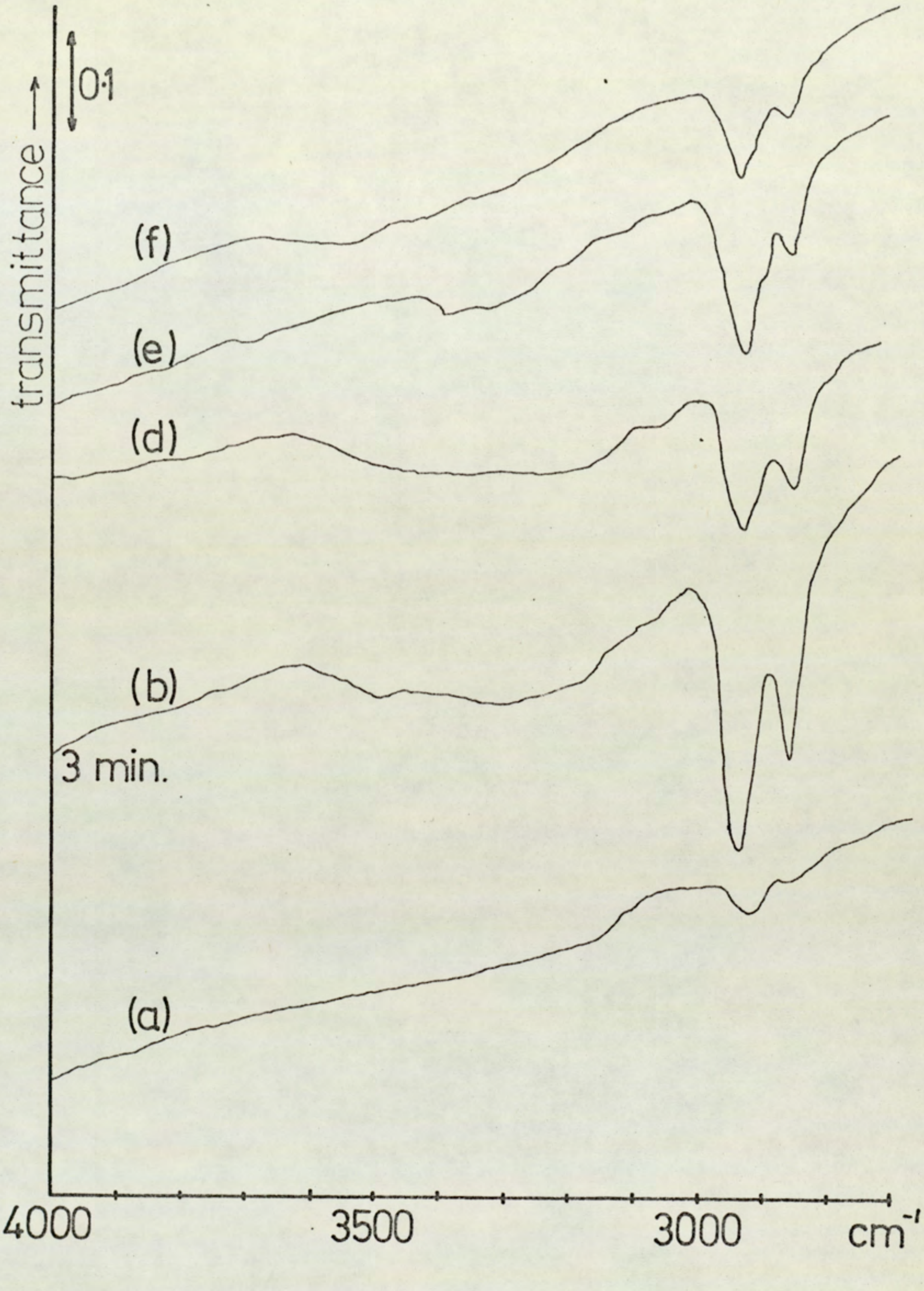
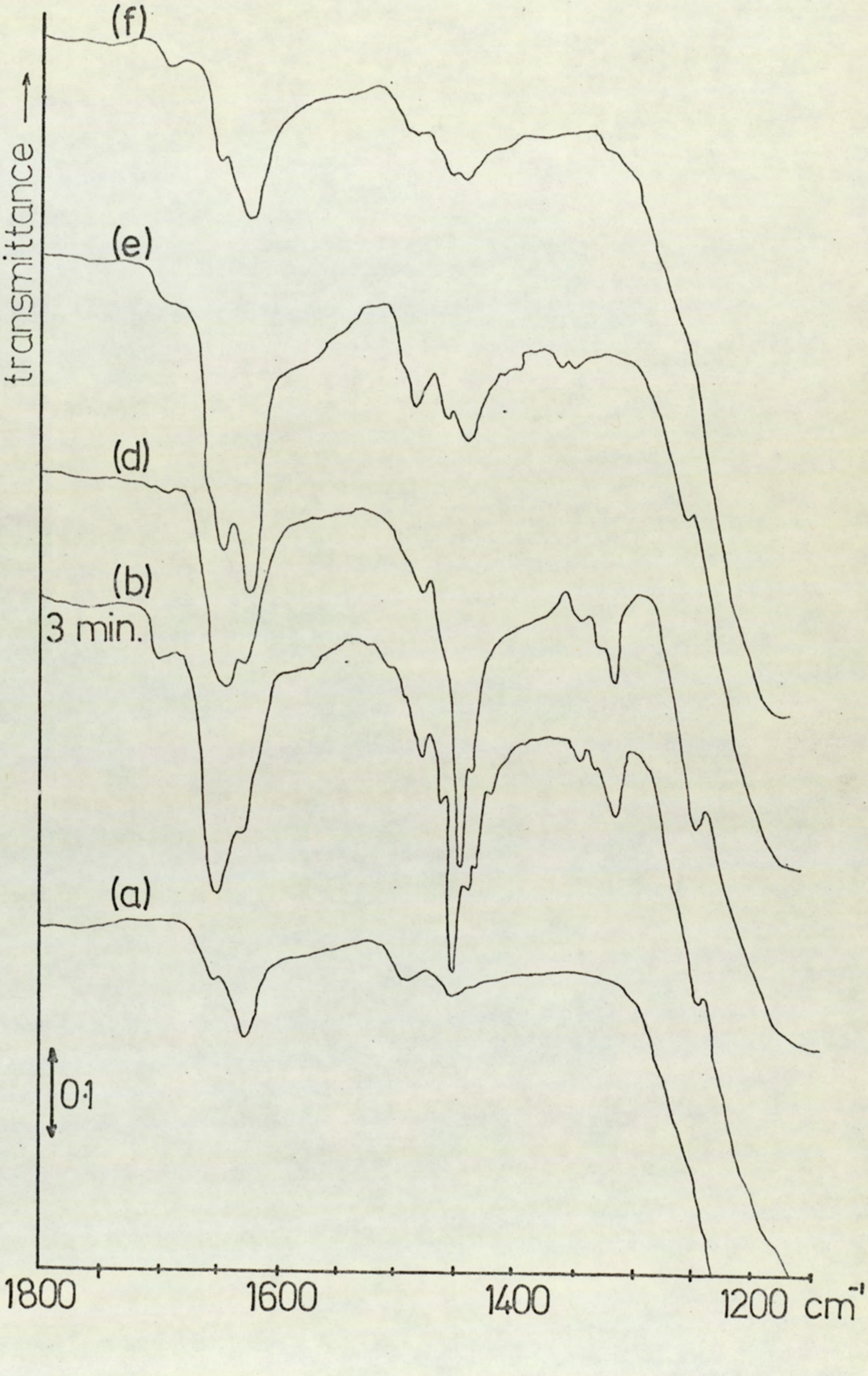


SPECTRUM 20,-5-Cyanopent-1-ene-HY.



SPECTRUM 21,-Cyclohexanone oxime-NaY



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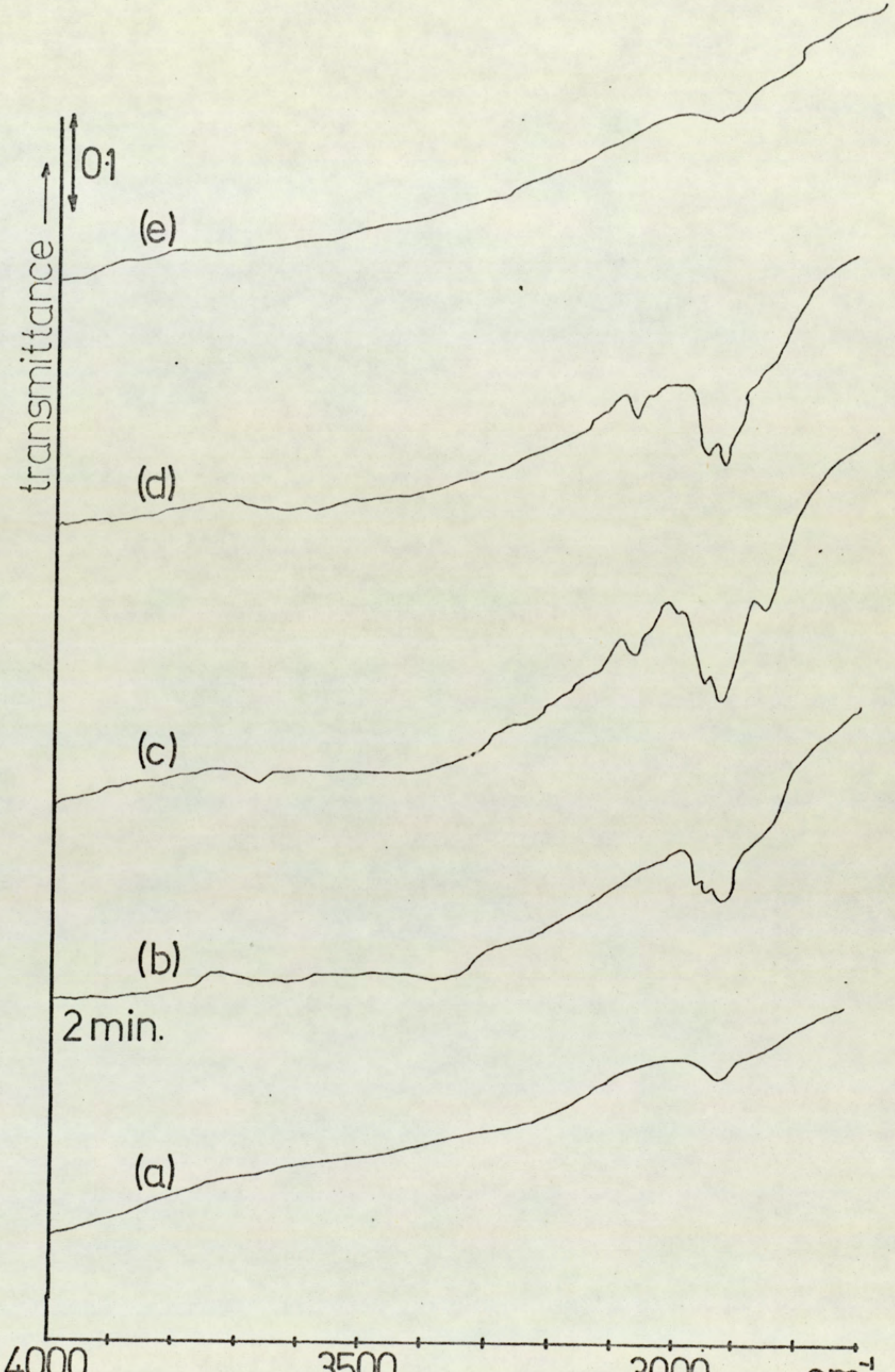
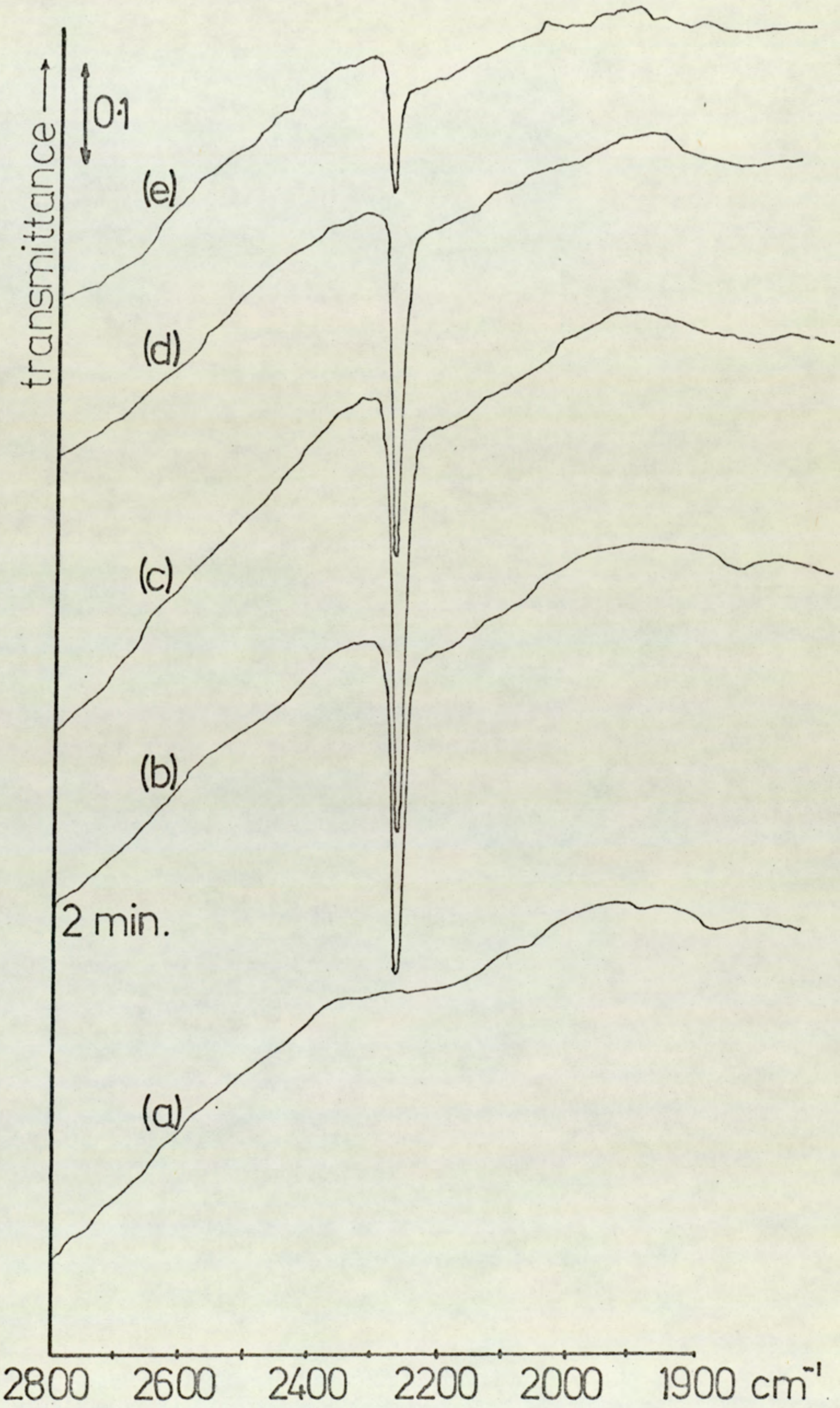


SPECTRUM 23,-5-Cyanopent-1-ene-NaY.



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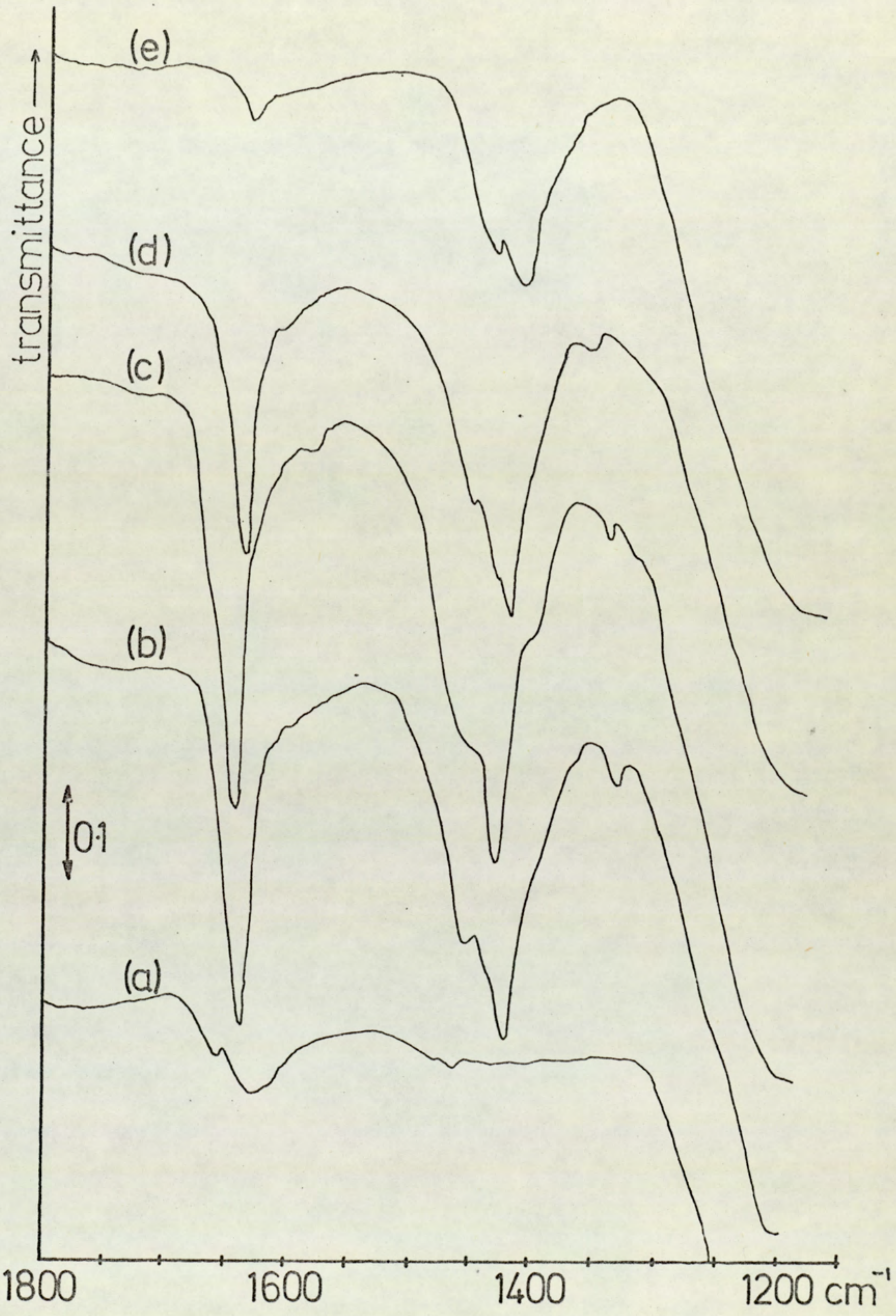

SPECTRUM 25,-5-Cyanopent-1-ene-NaY

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