Infrared Study of the Beckmann Rearrangement catalysed by Decationated Zeolite

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The Beckmann rearrangement of cyclopentanone oxime and cyclohexanone oxime to 2-piperidone and ε-caprolactam, respectively, has been studied by i.r. absorption at a catalysing decationated zeolite surface. By comparison of the spectra of the parent oximes, oxime hydrochlorides, lactams, and lactam hydrochlorides with the oxime–zeolite system it has been possible to show that reaction is initiated by the transfer of a proton from one of the hydroxy-groups associated with the zeolite lattice. The spectra also reveal that rearrangement is substantially complete at 120 °C but that the product is strongly adsorbed at the zeolite surface. This feature of the reaction probably accounts for the limited life of the catalyst which is characteristic of the process.

VENUTO and LANDIS[1] have shown that it is possible to carry out the Beckmann rearrangement of acetone oxime to *N*-methylacetamide and cyclohexanone oxime to caprolactam by heterogeneous catalytic methods using crystalline aluminosilicates as catalysts. The decationated form of the zeolite gave higher total conversions of oxime with higher selectivity for amide formation than the sodium or rare-earth forms. Based on this evidence they concluded that initial adsorption at an acidic site occurred at the catalyst surface and that this was followed by an intramolecular migration of a group *anti* to the departing hydroxy-function. The electron-deficient nitrogen atom formed by partial ionization of the oxygen–nitrogen bond results ultimately in imine formation which then rearranges to the amide.

Using i.r. absorption spectra of oximes adsorbed on zeolite surfaces we have been able to follow the changes that occur upon adsorption and rearrangement. The acidic sites of the decationated zeolite are believed to be surface hydroxy-groups which give characteristic OH stretching vibrations around 3750, 3690, 3650, and 3530 cm^{-1}.[2-4] Since the strong band at 3650 cm^{-1} disappears when the surface is exposed to pyridine vapour with a corresponding synchronous appearance of the pyridinium ion band at 1540 cm^{-1}, the phenomenon has been used as evidence that this surface hydroxy-group represents a Brønsted acid site.

We now give evidence that the hydroxy-group responsible for the 3650 cm^{-1} absorption band also participates in the adsorption and rearrangement of oximes adsorbed on zeolites.

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[1] P. B. Venuto and P. S. Landis, *J. Catalysis*, 1966, **6**, 245.

[2] J. B. Uytterhoeven, L. G. Christner, and W. K. Hall, *J. Phys. Chem.*, 1965, **69**, 2117.

[3] T. R. Hughes and H. M. White, *J. Phys. Chem.*, 1967, **71**, 2192.

[4] D. H. Olsen and E. Dempsey, *J. Catalysis*, 1969, **13**, 221.

EXPERIMENTAL

Apparatus.—The i.r. cell, similar to that used by Parry,[5] was made from Pyrex tube 9 cm in diameter wound at one end with Nichrome ribbon for electrical heating and fitted with a thermocouple well. The end of the cell remote from the Nichrome windings was similar in design to a conventional i.r. gas cell fitted with detachable sodium chloride plate windows. The sodium chloride windows were sealed to Pyrex through rubber O ring seals and brass screw-threaded couplings.

An aluminium holder was used to support the zeolite samples and act as a carriage for the transfer of the holder and sample along a glass rod positioned inside the cell.

Spectra were recorded on 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} at a scan speed of 400 cm^{-1} min^{-1} with a normal slit programme.

Procedure.—The oxime was placed in a dosing bulb of 2 ml capacity immersed in an acetone–solid carbon dioxide mixture and the dosing bulb and contents were evacuated to 10^{-3} Torr.

Between 0·03 and 0·07 g of zeolite was compressed at 20,000 lb in^{-2} to form a disc of 5—10 mg cm^{-2} and radius 1·3 cm. The disc was supported in the aluminium holder which was placed on the glass-rod-rail inside the cell. The cell was tilted to position the sample holder at the furnace end of the cell before attachment to the vacuum line and evacuation to at least 10^{-5} Torr. The temperature of the disc was successively raised to 120, 250, and 380 °C, each temperature was held for about 4 h, and the pressure of 10^{-5} Torr was maintained by continuous pumping. After this heating programme the disc was allowed to cool to room temperature and the cell removed from the vacuum line. It was tilted to position the sample disc between the sodium chloride windows and the spectrum recorded. Before attenuation the zeolite disc transmitted *ca.* 10% of the incident radiation.

The tap isolating the dosing bulb from the cell was opened and the oxime contained in the bulb was sublimed on to the zeolite disc. The dosing time depended upon the compound sublimed and these are reported with the appropriate spectra. Spectra were recorded after allowing 15 min for the system to equilibrate. In the absence of the zeolite disc a blank determination after the dosing material had been admitted to the cell revealed that there was no peak due to organic material which had adhered to the cell windows.

The cell was again attached to the vacuum line and evacuated for 1 h at room temperature before the spectrum was recorded. This procedure was repeated at 120, 250, and 350 °C and the spectrum recorded after the sample had cooled to room temperature.

Catalyst.—(*a*) Sodium-Y type zeolite was synthesized by the following method: a mixture of sodium silicate (142 g) and sodium aluminate (20 g) in distilled water (4100 ml) was stirred (19 h) at 100 °C. The precipitate was separated from the mother-liquor by filtration and thoroughly washed with distilled water until the filtrate was neutral. The white crystalline solid was dried (2 h) at 120 °C to give sodium-Y zeolite (56 g). The latter was identified by *X*-ray spectroscopy:[6] $d_{(hkl)}$ 14·3, 8·78, 7·34, 5·72, 4·77, 4·36, 3·77, 3·33, 3·20, 3·04, 2·91, 2·65, 2·38, 2·27, and 1·70.

(*b*) The ammonium-Y form of the zeolite was prepared by exchange by Eberly's method.[7] Sodium-Y zeolite (36 g) was treated with ammonium nitrate (67 g) in distilled water (600 ml) at 70 °C for 2 h. The zeolite was separated by filtration and the procedure repeated to give a total of five treatments. After the final filtration the ammonium-Y zeolite was thoroughly washed and dried (2 h) at 120 °C. Ward[8] has shown that decomposition does not occur below 200 °C. Analysis showed the anhydrous ammonium-Y form to contain 1·1% of sodium, corresponding to 91% exchange of sodium ions by ammonium ions in the zeolite lattice.

TABLE 1

Band assignments for A, cyclopentanone oxime and B, cyclohexanone oxime. Spectra of compounds obtained in potassium bromide disc unless otherwise specified

Wavenumber/cm^{-1}		Band
A	B	assignment[a]
	1250, 1310	$\delta'(CH_2)$ C6 ring
1290		$\omega(CH_2)$ C5 ring
1350	1235, 1365	$\delta(OH)$ free[b]
1428	1435	See text
1450	1450	$\delta(CH_2)$
1470	1480	$\delta(OH)$ assoc.
1690	1662	$\nu(CN)$
2870	2850	$\nu(CH_2)$ sym.
2960	2930	$\nu(CH_2)$ asym.
3600	3598	$\nu(OH)$ free[b]

[a] δ' = deformation (bend, twist, or rock); ω = wag; δ = bend; ν = stretch. These symbols are those used by Szymanski (ref. 14). [b] 10% Solution of oxime in carbon tetrachloride.

TABLE 2

Band assignments for A, cyclopentanone oxime hydrochloride and B, cyclohexanone oxime hydrochloride

Wavenumber/cm^{-1}		Band
A	B	assignment
1394	1430	See text
1720, 1740	1700	$\nu(C{=}N^+)$
2500—2900	2640	$\nu(N^+{-}H)$

Materials.—Cyclopentanone oxime was recrystallized from light petroleum (b.p. 60—80 °C) to give white prisms, m.p. 56·5 °C (lit.,[9] 56·5 °C). Cyclohexanone oxime was recrystallized from light petroleum (b.p. 60—80 °C) to give crystals, m.p. 88—89 °C (lit.,[10] 89—90 °C). 2-Piperidone was obtained from Phase Separations and ε-caprolactam from B.D.H. Their purity was verified by g.l.c. on a column of Chromosorb P impregnated with 20% SE30. The hydrochlorides of cyclopentanone oxime, cyclohexanone oxime, and ε-caprolactam were precipitated as white crystalline solids by bubbling gaseous hydrogen chloride through a 10% solution of the oxime or lactam in carbon tetrachloride. The precipitates were filtered off and dried. Owing to the very deliquescent nature of the oxime hydrochlorides it was impossible to obtain an accurate m.p. The i.r. spectrum of cyclohexanone oxime hydrochloride, however, was identical to that reported by

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[5] E. P. Parry, *J. Catalysis*, 1963, **2**, 371.

[6] C. R. Castor, U.S.P. 3,013,986/1962.

[7] P. E. Eberly, *J. Phys. Chem.*, 1967, **71**, 1717.

[8] J. W. Ward, *J. Catalysis*, 1967, **9**, 225.

[9] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, 4th edn., vol. 2, p. 799.

[10] Ref. 9, p. 785.

Saito[11] and that of cyclopentanone oxime hydrochloride exhibited bands at the same frequencies as those reported by Saito and Nukada[12] (Figure 3). ε-Caprolactam hydrochloride had m.p. 156—157 °C (lit.,[13] 157—158·5 °C).

RESULTS AND DISCUSSION

Band Assignments.—Before observing the effect of adsorption of oximes on the zeolite surface we must appreciate the significance of the characteristic i.r. absorption bands of reactants and products of the rearrangement. Some relevant assignments of absorption bands of oximes, lactams, and their protonated derivatives are summarized before the spectra of adsorbed species on the zeolite surface are considered.

Cyclopentanone oxime and cyclohexanone oxime. The absorption bands of cyclopentanone and cyclohexanone oximes are shown together with some assignments in Table 1.

The bands at 1290, 1450, 2870, and 2960 cm^{-1} for cyclopentanone oxime and those at 1250, 1310, 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.[14] The hydroxy-bands for cyclohexanone oxime at 1235, 1365, 1480, and 3598 cm^{-1} have been assigned by Kimura *et al.*,[15] who studied changes in the spectra of cyclohexanone oxime and deuteriated cyclohexanone oxime 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. The corresponding assignments for cyclopentanone oxime are based on similar differences. The stretching vibration of the C=N bond results 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[16] and Saito *et al.*[12]

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. By comparison of the spectra of methyl- and n-propyl-cyclopentane[17] with cyclopentanol and bromocyclopentane[18] it appears that there are two bands in this spectral region, one near 1450 cm^{-1} and another at a slightly lower frequency. The intensity of this variable-frequency band increases as its frequency decreases. The actual position of this band is determined by the electron-attracting ability of the substituent. This is shown in Figure 1 where the position of the low-frequency band is plotted against the Taft polar (inductive) constant σ^* for various substituents. In the case of a five-membered ring system this is consistent with the assignment of a $\delta(CH_2)$ scissors mode for a CH_2 group adjacent to an electronegative substituent. For the six-membered ring series the relationship is not so obvious. The variable-frequency band usually appears as a shoulder on the side of the 1450 cm^{-1} band for the larger ring system.

Cyclopentanone oxime hydrochloride and cyclohexanone oxime hydrochloride. 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 changes which occur in the i.r. spectra of cyclopentanone oxime and cyclohexanone oxime when these compounds are protonated. 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 the oxygen atom.[19] There are several differences between the spectra of the hydrochloride salts and those of the parent oximes. The bands characteristic of the protonated oximes are reported in Table 2, together with their assignments.

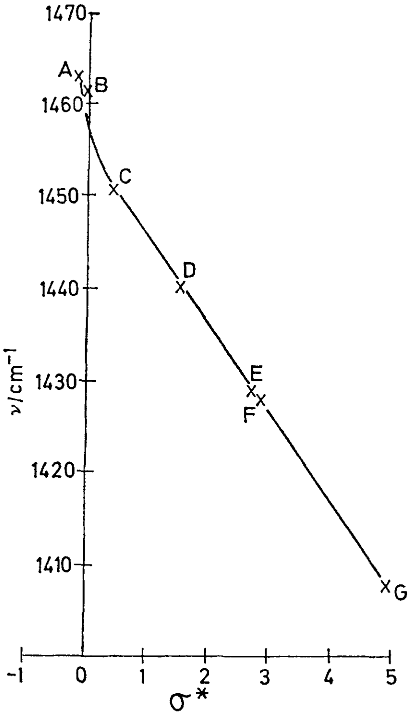

FIGURE 1 Variation in i.r. absorption band frequency with inductive strength of substituent for cyclo-C_5H_9X; A, X = Pr^n; B, X = Me; C, X = H; D, X = OH; E, X = Br; F, frequency for X = NOH; G, frequency for X = O

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[11] H. Saito, *J. Chem. Soc. Japan*, 1964, **85**, 724.

[12] H. Saito and K. Nukada, *J. Mol. Spectroscopy*, 1965, **18**, 1.

[13] M. Rothe, G. Reinish, W. Jaeger, and I. Schopor, *Makrolmol. Chem.*, 1962, **54**, 183.

[14] H. A. Szymanski, 'Interpreted Infrared Spectra,' Plenum Press, New York, 1964, vol. 1.

[15] M. Kimura, Y. Kurada, O. Yamamoto, and M. Kubo, *Bull. Chem. Soc. Japan*, 1961, **34**, 1081.

[16] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1958.

[17] American Petroleum Institute, Research Project 44, Spectra serial No. 15 and 381.

[18] 'Documentation of Molecular Spectroscopy, Spectrum no. 11,385,' Butterworths, London.

[19] C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, 1955, **20**, 1482.

The band observed at 1428 cm^{-1} for cyclopentanone oxime has a greater intensity in the spectrum of its hydrochloride and is shifted to 1394 cm^{-1}. Since the presence of a positive charge on the ring substituent will greatly increase the nucleophilic character, this shift provides further evidence for the relationship illustrated in Figure 1. The ν(C=N) band for cyclopentanone oxime at 1690 cm^{-1} has been replaced in the spectrum of its hydrochloride derivative by bands at 1720 cm^{-1} and 1740 cm^{-1}. This fairly broad band was reported by Saito and Nukada [12] and corresponds to a ν(C=N^+) vibration. These authors also reported a band at 2600 cm^{-1} for cyclopentanone oxime hydrochloride and assigned it to ν(N^+–H). In the present work this vibration gave rise to a broad band between 2500 and 2900 cm^{-1}. The δ(OH) association 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 ν(C=N) band is good evidence of nitrogen protonation.

The spectrum of cyclohexanone oxime hydrochloride shows a band at 1430 cm^{-1}. The shift from 1435 cm^{-1} for the cyclohexanone oxime is again consistent with nitrogen protonation.[11,12,20] Further evidence of nitrogen protonation of oxime has been obtained by Saito and Nukada [12] by studying the differences in n.m.r. signals between cyclohexanone oxime and cyclohexanone oxime hydrochloride. They found that the separation of *syn*- and *anti*-shifts for the α-methylene protons in cyclohexanone oxime is eliminated when the hydrochloride is formed. It was 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. The loss of separation found for the hydrochloride salts indicates interaction of the nitrogen lone-pair electrons with the proton.

2-*Piperidone and* ε-*caprolactam*. Surprisingly few accounts have dealt with the interpretation of the spectra of 2-piperidone and ε-caprolactam. Partly owing to their complexity it has been impossible to assign several of the bands; nevertheless a few of the relevant bands with their probable assignments are reported in Table 3.

The carbon–hydrogen stretching bands at 2860 and 2930 cm^{-1} for ε-caprolactam were assigned by Hall and Zbinden [21] who also assigned the δ(CH) vibration of the two lactams [22] and the carbonyl stretching bands at 1650 and 1655 cm^{-1} (amide I). The weak bands at 1550 and 1540 cm^{-1} (amide II) for the two lactams result from the NH bending vibration and those at 1310 and 1314 cm^{-1} (amide III) are believed to have a ν(CN) character.[23] Horak and Gut [24] have reported a characteristic absorption band for lactams between 1490 and 1510 cm^{-1} and assigned this 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 [14] reveals that a deformation vibration of the methylene groups in a six-membered ring produces characteristic absorption bands at 1260 and 1350 cm^{-1}. These bands were observed in the spectrum of cyclohexanone oxime and although 2-piperidone does not contain a six-membered carbon ring it is noticeable that the 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.

ε-*Caprolactam hydrochloride*. Katritzky and Jones [25] reported that the principal evidence in support of nitrogen protonation of amides comes from vibrational spectra. Bands thought to correspond to $\nu(N^+H_2)$ vibrations have been observed [26] in the 2000—2400 cm^{-1} region and it has also been suggested [27] 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 4) the broad band centred at 2300 cm^{-1} is consistent with an NH^+ stretching mode. The bending vibration of this group [28] is only observed as a shoulder on the low-frequency side of the carbonyl stretching band at *ca.* 1550 cm^{-1}.

TABLE 3

Band assignments for A, 2-piperidone and B, ε-caprolactam

Wavenumber/cm^{-1}		
A	B	Band assignment
1270		$\delta'(CH_2)$ 6-membered ring
1310	1314	ν(CN)
1353		$\delta'(CH_2)$ 6-membered ring
1448, 1470	1438, 1480	δ'(CH)
1495		CH_2 scissor
1550	1540	δ(NH)
1650	1655	ν(CO)
2870	2860	$\nu(CH_2)$ sym.
2950	2930	$\nu(CH_2)$ asym.

TABLE 4

Band assignments for ε-caprolactam hydrochloride

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

Reaction of Oxime catalysed by Hydrogen-Y Zeolite.—*Cyclopentanone oxime on hydrogen-Y zeolite.* The spectrum of hydrogen-Y obtained by the thermal decomposition of ammonium-Y zeolite is shown in Figure 2, A. The characteristic hydroxy-bands appear at 3640 and

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[20] H. Saito, K. Nukada, and M. Ohrio, *Tetrahedron Letters*, 1964, 2124.

[21] H. K. Hall and R. Zbinden, *J. Amer. Chem. Soc.*, 1958, **80**, 6428.

[22] H. K. Hall and R. Zbinden, *J. Amer. Chem. Soc.*, 1960, **82**, 2115.

[23] K. Freudenberg, *Chem. Ber.*, 1956, **89**, 343.

[24] M. Horak and J. Gut, *Coll. Czech. Chem. Comm.*, 1963, **28**, 3392.

[25] A. R. Katritzky and R. A. Y. Jones, *Chem. and Ind.*, 1961, 722.

[26] N. Ogato, *Bull. Chem. Soc. Japan*, 1961, **34**, 248.

[27] F. Klages and E. Zange, *Annalen*, 1957, **607**, 35.

[28] R. A. Heacock and L. Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

3540 cm^{-1} and also a band centred around 1640 cm^{-1} due to water which persists after heating and evacuation of the zeolite sample.

When cyclopentanone oxime is adsorbed on hydrogen-Y at room temperature and the excess removed by evacuation, Figure 2, C shows that interaction has occurred with the surface hydroxy-group characterized by the absorption at 3640 cm^{-1}. 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}. The position and intensity of this band was shown in the previous section to be a function of the ability of the ring substituent to attract electrons. The decrease in intensity of the 3640 cm^{-1} hydroxy-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 hydroxy-group to the adsorbed molecule. The resulting positive charge on the oxime ring substituent thus accounts for the shift in the oxime band from 1428 cm^{-1} to 1410 cm^{-1}. Further, the loss of the 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.

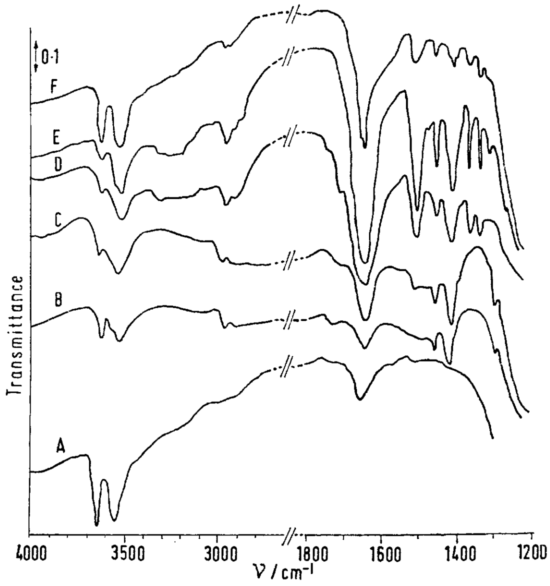

FIGURE 2 I.r. absorption spectrum of cyclopentanone oxime absorbed on H-Y in the range 1200—4000 cm^{-1}; A, H-Y spectrum at room temperature; B, after exposure to cyclopentanone oxime at room temperature for 15 s; C, after evacuation at room temperature; D, after heating to 120 °C *in vacuo*; E, after heating to 250 °C *in vacuo*; F, after heating to 350 °C *in vacuo*

If this supposition is correct then the spectra shown in Figure 2 should be comparable with that of cyclopentanone oxime hydrochloride given in Figure 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, much weaker band near 1720 cm^{-1} and the presence of a broad band between 2500 and 2900 cm^{-1}, corresponding to a $\nu(\mathrm{N^+{-}H})$ vibration, the high-frequency edge of which can be seen in Figure 2, curves B and C. The principal difference between the spectra is that in the oxime hydrochloride the 1428 cm^{-1} band of the oxime has been shifted to 1394 cm^{-1} whereas in the chemisorbed species this band is only shifted to 1410 cm^{-1}. This is probably a reflection of the fact that the electron-attracting ability for the ring substituent in the adsorbed species is less than that in the hydrochloride derivative.

Although it could be considered that the decrease in shift of the 1428 cm^{-1} band of the oxime on adsorption could be attributed to oxygen protonation rather than nitrogen protonation by assuming that the shoulder at 1720 cm^{-1} is due to a $\delta(\mathrm{O^+{-}H_2})_{\mathrm{asym}}$ vibration and that the broad band between 2500 and 2900 cm^{-1} is due to $\nu(\mathrm{O^+{-}H})$.[29,30] This view cannot account for the considerable change that has occurred in the ν(C=N) band upon adsorption. It is more likely that interaction with the surface has produced a partial delocalization of charge as indicated by Figure 4.

The presence of the $\omega(\mathrm{CH_2})$ attributed to a five-membered ring system at 1290 cm^{-1} suggests that this ring system has been retained on adsorption at room temperature. Another feature of the spectrum (Figure 2, C) is that 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

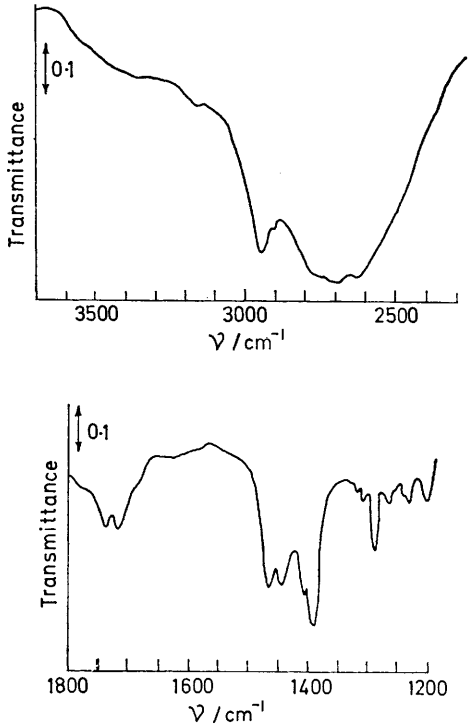

FIGURE 3 I.r. absorption spectrum of cyclopentanone oxime hydrochloride (KBr disc)

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[29] C. C. Ferrisco and D. F. Hornig, *J. Chem. Phys.*, 1955, **23**, 1464.

[30] M. Falk and P. A. Griguere, *Canad. J. Chem.*, 1957, **35**, 1195.

the parent oxime and arises from a bending vibration of an associated hydroxyl group. The presence of this band corresponds to the absence of a free hydroxy-absorption band at 1350 cm^{-1}. The shift and broadening of this band in the adsorbed species relative to 1470 cm^{-1} of cyclopentanone oxime shows that it is not due simply to associated cyclopentanone oxime molecules but probably results from an interaction of the oxime with the hydroxy-group in the zeolite surface as suggested in Figure 4.

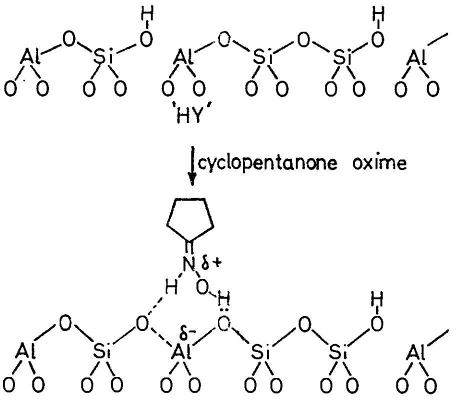

FIGURE 4 Surface interaction of cyclopentanone oxime with decationated zeolite

Figure 2, D reveals that after heating to 120 °C considerable rearrangement has taken place. The development of an adsorbed carbonyl group is apparent from the presence of the carbonyl stretching band at 1650 cm^{-1} and the spectrum has the general resemblance of the spectrum of 2-piperidone. A band characteristic of hydrogen-bonded ν(NH) vibrations has developed in the 3100—3350 cm^{-1} region and the broad band between 2500 and 2900 cm^{-1} due to ν(N$^+$–H) has disappeared together with the 1290 cm^{-1} band due to a five-membered ring system. The shoulder, at 1710 cm^{-1}, however, and the relative intensity of the 1410 cm^{-1} band suggests that some oxime is still present at the surface.

There are several other differences between the spectra shown in Figure 2, D and that of 2-piperidone. First, the band at 1470 cm^{-1} is missing for the adsorbed species. This band has been assigned to a δ′(CH) vibration and since it is unlikely that any carbon–hydrogen bonds are ruptured during the adsorption or reaction sequence 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 from the adsorbed species is that due to ν(CN) (amide III) which absorbs at 1310 cm^{-1} for 2-piperidone, and indicates the absence of an amide carbon–nitrogen bond from the adsorbed molecule. The rearranged product is still interacting with the 3640 cm^{-1} band of the surface hydroxy-group and must, therefore, still be protonated. The absence of a ν(N$^+$–H$_2$) band from the 2000—2400 cm^{-1} supports the view that the proton may now be associated with the carbonyl oxygen atom.

Further heating to 250 °C (Figure 2, E) shows that little change occurs in the adsorbed molecule although at this temperature there is no evidence for cyclopentanone oxime at the surface. The shoulder at 1710 cm^{-1} has disappeared and the ν(CN) band at 1310 cm^{-1} has regained some of its intensity indicating that partial re-formation of the amide carbon–nitrogen bond has taken place. The rearranged product on the surface is apparently still protonated because the surface hydroxy-absorption band at 3640 cm^{-1} has not regained its original intensity. Heating to 350 °C for 1 h (Figure 2, F) does not change the position of any band attributable to the adsorbed molecule but merely weakens the overall intensity. There is a restoration of the 3640 cm^{-1} hydroxy-band intensity to near the original value.

2-Piperidone adsorbed on hydrogen-Y zeolite. The results described in the previous section show that the course of the Beckmann rearrangement at the zeolite surface can be followed from the changes in the i.r. spectra which occur on adsorption and heating. It is likely, however, that these spectra represent surface intermediates and in order to confirm this it is necessary to compare the spectra of the product lactam on the zeolite surface.

Figure 5 shows that upon adsorption of 2-piperidone on hydrogen-Y the intensity of the 3640 cm^{-1} surface hydroxy-band decreases relative to that of the 3540 cm^{-1} surface hydroxy-band. In the region 1200—1800 cm^{-1} the spectra of the adsorbed species is very similar to that of 2-piperidone formed on the zeolite surface by rearrangement of cyclopentanone oxime. The ν(CN) (amide III) band at 1310 cm^{-1} is again absent until the system is heated to 250 °C. From these observations we conclude that the product of rearrangement of

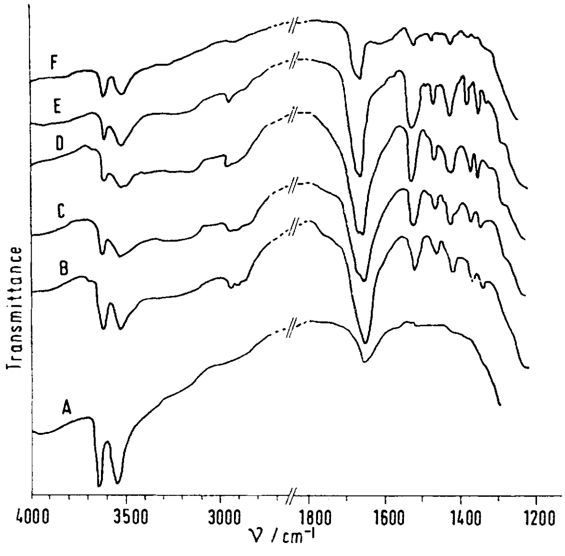

FIGURE 5 I.r. absorption spectrum of 2-piperidone absorbed on H-Y in the range 1200—4000 cm^{-1}; A, H-Y spectrum at room temperature; B, after exposure to 2-piperidone for 45 min at room temperature; C, after evacuation at room temperature; D, after heating at 120 °C *in vacuo*; E, after heating to 250 °C *in vacuo*; F, after heating to 350 °C *in vacuo*

cyclopentanone oxime is held on the surface in an identical manner to 2-piperidone which has been adsorbed from the vapour phase.

Cyclohexanone oxime adsorbed on hydrogen-Y zeolite. The spectrum of cyclohexanone oxime adsorbed on hydrogen-Y at room temperature shows the same general features as that of cyclopentanone oxime on hydrogen-Y. Again the oxime interacts with the 3640 cm^{-1} surface hydroxy-band of the zeolite with resulting shift in the oxime 1435 cm^{-1} band to 1430 cm^{-1} and appearance of bands centred around 1700 and 2700 cm^{-1} corresponding to $\nu(C{=}N^+)$ and $\nu(N^+{-}H)$, respectively. The 1310 cm^{-1} band is still present for the adsorbed molecule showing that the six-membered ring configuration is retained at room temperature. The $\delta(OH)$ association band is broadened from 1480 to 1450—1500 cm^{-1} and is indicative of interaction of oxime hydroxy-groups with the zeolite lattice.

After heating to 120 °C for 1 h an intense carbonyl stretching band at 1640 cm^{-1} develops showing that considerable rearrangement has occurred. The group of bands centred at 1450 cm^{-1} and a shoulder at 1690 cm^{-1} due to $\nu(C{=}N^+)$ suggest that there is some oxime still remaining on the surface. It is noteworthy that apart from the oxime bands the rest of the spectrum more closely resembles that of 2-piperidone than that of ε-caprolactam. Thus bands are observed at 1335, 1360, 1410, 1450, and 1500 cm^{-1}, the relative intensities of which are comparable with those in the spectrum of 2-piperidone. Heating to successively higher temperatures brings about similar changes to those already described for the cyclopentonane oxime–zeolite system.

ε-Caprolactam adsorbed on hydrogen-Y. As in the case of 2-piperidone, ε-caprolactam upon adsorption on hydrogen-Y interacts with the 3640 cm^{-1} surface hydroxy-band, although the decrease in intensity was not so marked in this case. It is not known from our experiments how much lactam was adsorbed on the zeolite but the smaller change in intensity of the 3640 cm^{-1} band undoubtedly reflects the relatively low surface coverage that was achieved by the dosing procedure. A dosing time of 45 min for the lactams must be compared with 15 s for the oximes. This limitation of the technique probably results from the fact that the lactam in the i.r. sample bulb dimerizes.[31] This would account for the lower vapour pressure in the i.r. cell than would obtain for the corresponding oxime under otherwise identical conditions.

Comparison of the spectra of adsorbed ε-caprolactam with that of adsorbed 2-piperidone shown in Figure 5 reveals a closely similar absorption pattern. The lactams themselves, however, show differences in the 1200—1800 cm^{-1} region which are partly attributable to the difference between the two ring systems. The degree of strain in 2-piperidone and ε-caprolactam has been calculated by Kachinskaya[32] who showed that there is less strain in 2-piperidone than in ε-caprolactam. This difference in strain will be reflected in the i.r. spectra of the two compounds[33] and anything which reduces this difference in strain will tend to make their spectra more similar. It appears that in the adsorbed state that the extra strain of the ε-caprolactam has been relieved so that the spectrum conforms more closely to that of 2-piperidone.

This similarity and the apparent absence of an amide carbon–nitrogen bond from the adsorbed lactams suggests that the latter are adsorbed as open-chain compounds. Ring-opening which involves the rupture of the amide carbon–nitrogen bond could result in an intermediate adsorbed species of the type illustrated for 2-piperidone in Figure 6. When the ε-caprolactam ring is ruptured the carbon chain produced has one more methylene group than the carbon chain of the 2-piperidone system. More movement of the methylene groups relative to each other will therefore be possible for ε-caprolactam and this will result in an increased complexity of the band system near 1450 cm^{-1} which has been observed. Evidence already considered supports the view that proton transfer from nitrogen to oxygen occurs as the penultimate stage of the surface reaction. Final proton transfer to the surface from the intermediate with simultaneous re-formation of the carbon–nitrogen bond will complete the ring closure.

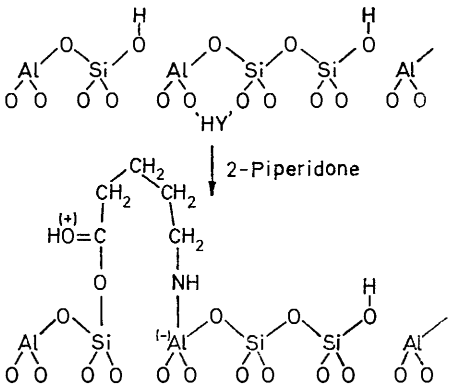

FIGURE 6 Mode of adsorption of 2-piperidone on decationated zeolite surface

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