Infrared Absorption Spectra of 5-Cyanopent-1-ene adsorbed on Y-Type Zeolites

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The i.r. absorption spectra of 5-cyanopent-1-ene on a decationated Y-zeolite and on a sodium-Y zeolite have been compared. It is shown that both functional groups at either end of the alkene-nitrile interact with the H-Y surface. From the absence of absorption bands at 3080 and 1642 cm^{-1} from the spectrum of the adsorbed molecule on H-Y it is concluded that adsorption is accompanied by loss of the alkene bond. New bands which appear at 2400 and 2900 cm^{-1} with a shift of the 2250—2280 cm^{-1} ν(C≡N) vibration upon adsorption suggest some hydrogen-bonding interaction between the nitrile group and surface hydroxy-groups.

In the case of the sodium-Y surface, where zeolite surface hydroxy-groups are not observable in the 3500—3700 cm^{-1} spectral region, the spectrum of adsorbed 5-cyanopent-1-ene strongly resembles the spectrum of the compound in the form of a neat film.

THE preceding paper[1] reporting the i.r. absorption spectra of cyclopentanone oxime and cyclohexanone oxime during their Beckmann rearrangement on a decationated zeolite surface showed no evidence for the formation of nitrile. Venuto and Landis,[2] however, have shown that olefinic nitriles can be produced as by-products of the rearrangement and that the selectivity towards amide or nitrile is dependent upon the nature of the zeolite employed as the catalyst.

The separation of the two functional groups at each end of the carbon chain in 5-cyanopent-1-ene, the suggested by-product from the rearrangement of cyclohexanone oxime, will be sufficiently remote for them to be considered independently from the point of view of their interaction with the surface. A study of the characteristic i.r. absorption bands due to ν(C≡N) and ν(C=C) of the molecule in the adsorbed condition should provide data which indicate how the molecule is held at the surface and the part played by catalyst modification on selectivity.

EXPERIMENTAL

Materials.—5-Cyanopent-1-ene was prepared by the method of La Forge *et al.*[3] 5-Bromopent-1-ene (9·5 g) and potassium cyanide (5 g) were stirred (2 h) in ethylene glycol (25 ml) at 100 °C. The brown solution was diluted with water (50 ml) and the nitrile extracted into ether (3 × 30 ml). The ether extracts were combined, dried ($MgSO_4$), and the ether was removed *in vacuo*. The residue was distilled to yield 5·2 g (86%) of 5-cyanopent-1-ene, b.p. 44—48 °C at 7·5 Torr (lit.,[3] 54—59 °C at 16 Torr), n_D^{25} 1·4270 (lit.,[3] n_D^{25} 1·4268), $\nu_{max.}$ (film) 3080 ($H_2C=$), 2940 (CH_{asym}), 2880 (CH_{sym}), 2250 (C≡N), 1642 (C=C), 1442, 1428, 1420 δ(CH), 1000, and 927 cm^{-1}; *m/e* 55 (100), 41 (62), 28 (46), 39 (30), and 95 (5); τ 8·13 (m, 3-, 4-, and 5-H_2), 4·94 (m, 1-H_2), and 4·25 (m, 2-H).

Catalysts.—The decationated zeolite catalyst H-Y and the Na-Y form have been described.[1]

Apparatus and Procedure.—The exposure time for admitting 5-cyanopent-1-ene from the dosing bulb to the i.r. gas cell was 3 min; otherwise the technique for obtaining the i.r. spectra was similar to that described.[1] The ^1H n.m.r. spectrum was recorded with a Perkin-Elmer R10 instrument at 14,000 G and 60 MHz with tetramethylsilane as internal standard. The mass spectrum was taken on our AEI MS9 instrument and i.r. absorption spectra recorded on a Perkin-Elmer 457 grating spectrometer.

Band assignments for 5-cyanopent-1-ene

Neat film		Absorbed on H-Y [a]	
Wavenumber/cm^{-1}	Assignment	Wavenumber/cm^{-1}	Assignment
1420(sh)		1423	
1428	δ(CH_2)		δ(CH_2)
1442		1442	
1642	ν(C=C)	1642br	
2250	ν(C≡N)	2280	ν(C≡N)
		2400	Overtone of OH [b] bending vibration
2880	ν($CH_{2\,sym}$)	2880	ν($CH_{2\,sym}$)
		2900	Hydrogen bonding interaction with surface OH groups [b]
2940	ν($CH_{2\,asym}$)	2940	ν($CH_{2\,asym}$)
3080	ν(=CH)		

[a] After evacuation for one h at room temperature. δ = Bend; ν = stretch. [b] Ref. 4.

RESULTS AND DISCUSSION

*Adsorption of 5-Cyanopent-*1*-ene on H-Y Zeolite*.—When 5-cyanopent-1-ene is adsorbed on H-Y zeolite and the excess removed by evacuation at room temperature (Figure 1), the interaction between the alkene nitrile and the surface is seen to involve the surface 3640 cm^{-1} hydroxy-band. The most striking difference between the spectrum of 5-cyanopent-1-ene and that of 5-cyanopent-1-ene adsorbed on H-Y is the absence of the ν(CH=) band at 3080, and the broadening of the ν(C=C) band at 1642 cm^{-1} (Figure 1, B). Evacuation for 1 h at room temperature completely removes the sharp band at 1642 cm^{-1} (Figure 1, C) and only the broad band remains. This implies that excess of weakly held alkene nitrile is desorbed by this treatment.

A further feature of adsorbed 5-cyanopent-1-ene is the shift of the ν(C≡N) absorption band 2250 cm^{-1} to 2280 cm^{-1} and the appearance of two new broad bands centred near 2400 and 2900 cm^{-1}. Angell and Howell[4] reported similar bands on adsorption of acetonitrile on H-Y. These authors adopted a deuteriation procedure in an attempt to determine the origin of these bands.

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[1] J. D. Butler and T. C. Poles, *J.C.S. Perkin II*, preceding paper.

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

[3] F. B. La Forge, N. Green, and W. A. Gersdorff, *J. Amer. Chem. Soc.*, 1948, **70**, 3707.

[4] C. L. Angell and M. V. Howell, *J. Phys. Chem.*, 1969, **73**, 2551.

They concluded that both bands were due to vibrations involving surface hydrogen atoms. They suggested that the 2900 cm^{-1} band be assigned to a hydrogen-bonding interaction between the surface hydroxy- and the nitrile group of the adsorbed nitrile and that the 2400 cm^{-1} band is an overtone of the hydroxy-group bending vibration. Since these bands appear in Figure 1, D after the sample has been heated to 120 °C this surface hydrogen-bonded nitrile group interaction must re-form when the sample cools to room temperature before the spectrum is taken. There is no reason to suppose that the olefinic double bond does not remain firmly anchored to the surface during this heat treatment.

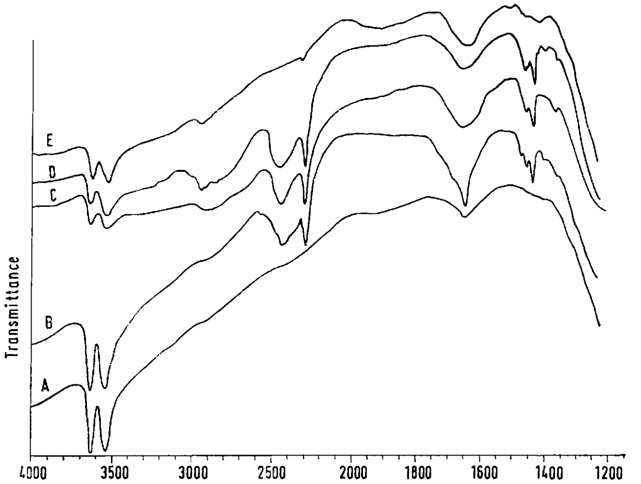

FIGURE 1 I.r. absorption spectrum of 5-cyanopent-1-ene adsorbed on H-Y in the range 1200—4000 cm^{-1}; A, H-Y spectrum at room temperature; B, after exposure to 5-cyano-pent-1-ene at room temperature for 3 min; C, after evacuation at room temperature; D, after heating to 120 °C *in vacuo*; E, after heating to 250 °C *in vacuo*

Adsorption of 5-Cyanopent-1-ene on Na-Y Zeolite.—The spectrum of 5-cyanopent-1-ene on Na-Y zeolite is shown in Figure 2. The absorption bands in Figure 2, C and D, correspond closely to those present in liquid 5-cyanopent-1-ene. They clearly show the 3080 cm^{-1} band indicating that in this case the olefinic double bond is preserved in the molecule in the adsorbed state. The bands at 2260 and 1634 cm^{-1}, due to ν(C≡N) and ν(C=C) vibrations respectively, are sharp. Further, they are only slightly shifted from those of the pure compound.

These results are in agreement with those found by Eberly[5] who has studied the i.r. spectrum of hex-1-ene adsorbed on Na-Y. By measuring the absorbance ratio ν(C=C) : δ(CH) he showed that the extent of preservation of double-bond character in the adsorbed condition was dependent on the nature 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 suggested was an electrostatic attraction between the cation and the polarized π-electrons around the double bond. The extent of such a polarization would naturally depend on the field strength around the cation.

Although the spectra in Figure 2 are very similar to that of liquid 5-cyanopent-1-ene it is apparent that the compound is relatively strongly adsorbed on Na-Y. Even after prolonged heating *in vacuo* at 250 °C (Figure 2, E) the nitrile absorption band at 2260 cm^{-1} is still present. After similar treatment the decationated zeolite had considerably less residual nitrile adsorbed on the surface.

On this evidence it appears probable that on Na-Y zeolite the interaction of the nitrile group with the surface is greater than that of the olefinic group whereas, on the decationated zeolite, where surface hydroxy-groups can participate, the double-bond character of the adsorbate disappears on adsorption. This suggests that the olefinic group is more strongly adsorbed than the nitrile group, particularly if the nitrile group surface interaction involves hydrogen-bonded species of the type envisaged by Angell and Howell.[4]

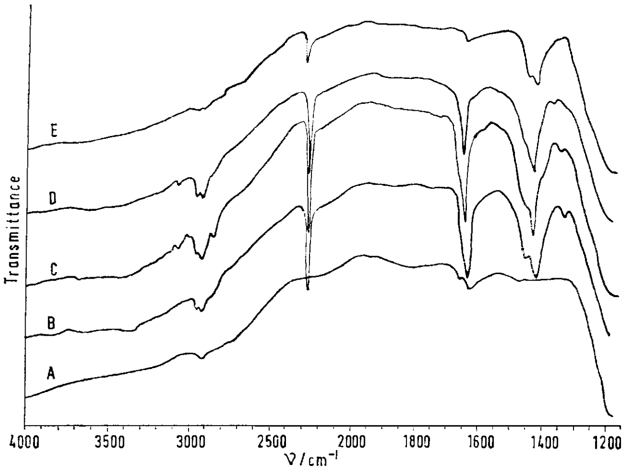

FIGURE 2 I.r. absorption spectrum of 5-cyanopent-1-ene adsorbed on Na-Y in the range 1200—4000 cm^{-1}; A, Na-Y spectrum at room temperature; B, after exposure to 5-cyano-pent-1-ene at room temperature for 2 min; C, after evacuation at room temperature; D, after heating to 120 °C *in vacuo*; E, after heating to 250 °C *in vacuo*

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