Infrared Spectra of Some Pyridine Trifluoroacetates in Benzene and Dichloromethane; Effect of Concentration

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The centre of gravity ($\bar{\nu}_H$) of the continuous absorption in the i.r. spectra of three substituted pyridine trifluoroacetates in dry benzene varies by up to 9% over the concentration range 0.07—0.6 M and reflects the dipole interaction of hydrogen bonds with the field from their environment.

Proton transfer reactions between acetic acids and pyridines in solid state,[1] neat liquid,[2] and solvents[3—6] have been widely investigated by means of i.r. spectroscopy. The percentage proton transfer has been obtained from the spectra in the region of the carbonyl, carboxylate, and pyridine ring vibrations.

Gusakova, Denisov *et al.*[4] determined the equilibrium constant (K_{PT}) for the proton transfer reaction of pyridine and dichloroacetic acid in chloroform from the pyridine ring vibrations. The value of K_{PT} varied with concentration; $K_{PT} = 1.2 \pm 0.3$ at 20 °C for solutes up to 0.7 M and then it increased greatly. The increase of K_{PT} with concentration was probably caused by a dipole–dipole association. Formation of complexes *via* a dipole–dipole interaction would affect both intensity and frequency of various i.r. bands and may cause some additional bands which arise from intermolecular simultaneous vibrational transitions.[7]

Previously, one of us[8] determined the equilibrium constants for a dipolar association (K_{DA}) for complexes of some pyridines with trifluoroacetic acid in benzene. Thus it was interesting to investigate the effect of concentration on the whole i.r. spectrum of these complexes. The complexes were obtained as low melting crystals by quantitative neutralization of trifluoroacetic acid with pyridines in diethyl ether at *ca.* −15 °C.[8] Elemental analyses of the compounds were correct.

I.r. spectra were recorded on a Perkin–Elmer 580 spectrophotometer using cells with KBr windows (path length, l = 0.050 and 0.444 mm). Centres of gravity of the reconstructed bands were obtained as $\bar{\nu}_H = \int A(\nu)\nu d\nu / \int A(\nu) d\nu$, where $A = \log_{10} T_{bl}/T$, T_{bl} and T are the transmittance of the solvent alone (base line) and the complex, respectively. In both cells the base line transmittance was a straight line passing through T_{bl} = 0.95 at 4000 cm^{-1} and T_{bl} = 0.99 at 400 cm^{-1}. The integrated intensity was obtained as $B_H = (2.303/c.l)\int A(\nu)d\nu$.

The spectra of the pyridine trifluoroacetates investigated exhibit (Figure 1) a continuous absorption over the broad frequency region from 400 up to 3000 cm^{-1}. Within this range there are usually five overlapping broad absorption bands (A > 2800, B *ca.* 2500, C *ca.* 1900, D *ca.* 1100, and E *ca.* 850 cm^{-1}). All these bands are poorly resolved and exhibit several subpeaks resulting from superposition of sharp bands ascribed to other internal vibrations and to Fermi resonance. Hence, the centre of gravity is used to characterise this complex structure.[5,6] The structure and intensity of bands A—E depend strongly on the proton acceptor properties of the pyridine bases.

Concentration affected both the intensities and absorption centres of bands B—E. The changes observed varied, depending on the presence of ion-pairs ($A^- \cdots HB^+$) or the molecular complex ($AH \cdots B$). The ion-pair is the main species in complexes of 3-Me and 2,4,6-Me_3-derivatives.[6] On increasing the concentration from 0.068 to 0.604 M, the intensity of the bands B and C increased, but the bands D and E decreased, Figure 1(d). The variations of intensity affected the centre of gravity, the magnitude of observed changes of $\bar{\nu}_H$ being proportional to the dipolar association constant (K_{DA}) (Table 1).

The dipolar association constant (K_{DA}) decreases rapidly with an increase in the electric permittivity of the solvent.[9] Thus, one can expect that in dichloromethane (ε = 8.93) the

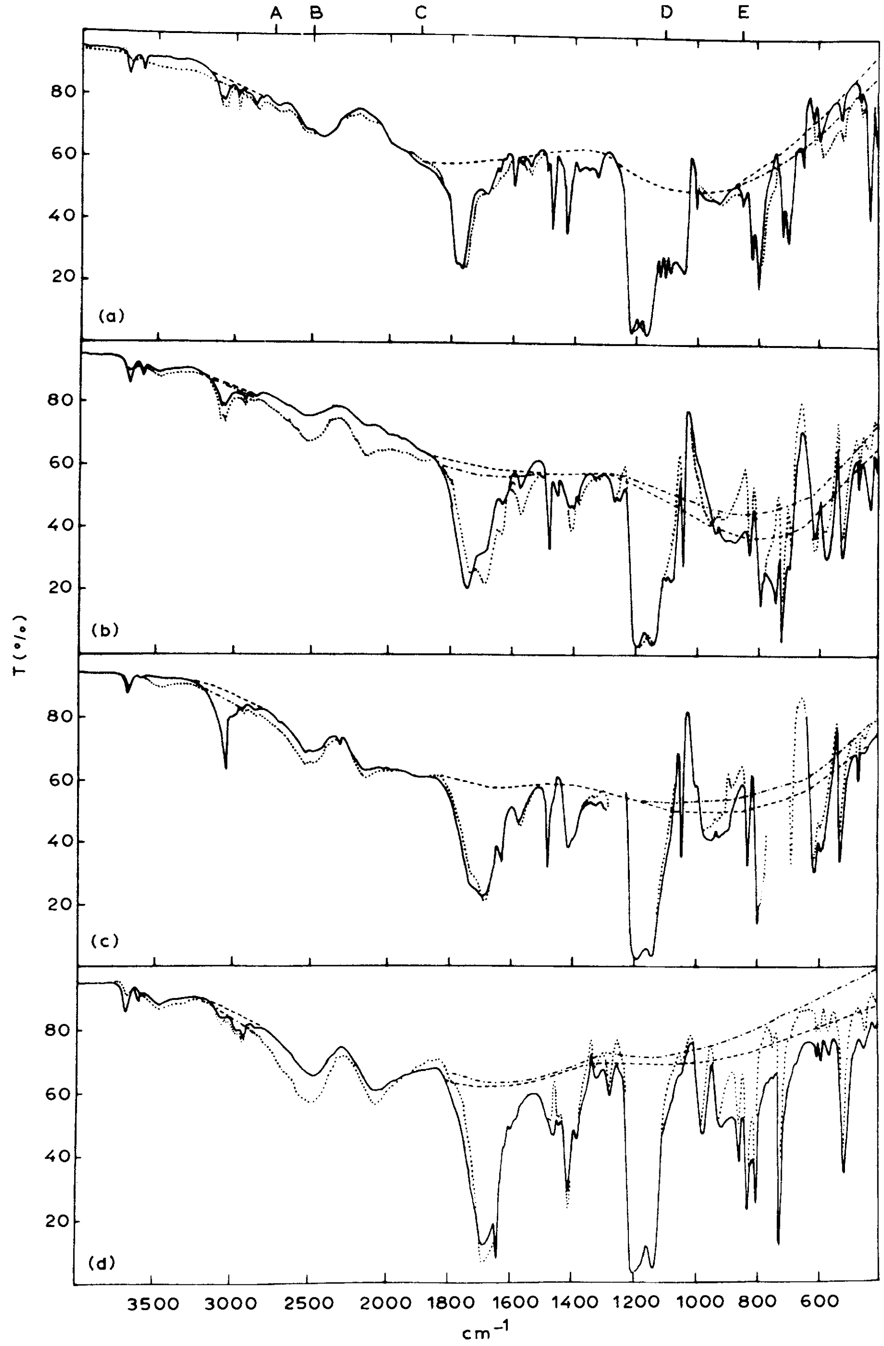

Figure 1. I.r. spectra of complexes of substituted pyridines with trifluoroacetic acid: (a) 3-Br-pyridine (C_6H_6 and C_6D_6); (b) 3-Me-pyridine (C_6H_6 and C_6D_6); (c) 3-Me-pyridine (CH_2Cl_2): (d) 2,4,6-Me$_3$-pyridine (C_6H_6 and C_6D_6); (—— 0.068 M; ···· 0.604 M; --- continuous absorption, 0.068 M; —·— continuous absorption, 0.604 M). The approximate positions of bands A—E are shown above spectrum (a), see text.

changes of intensity caused by concentration should be weaker than those in benzene ($\varepsilon = 2.27$). Indeed, Figure 1(b) and (c) confirm this expectation.

In the case of the complex of 3-Br-pyridine the main species is the molecular complex[6] which is much less polar and the extent of dipolar association is low.[8] Thus the variations of intensity, Figure 1(a), caused by concentration were relatively low. The most pronounced difference was an increase of absorption intensity in the 650—450 cm^{-1} region with an increase in concentration. In dichloromethane the absorption was similar in both spectra.

$$(\Delta\nu - 40)^{\frac{1}{2}} = 9.0\Delta B_H^{\frac{1}{2}} \qquad (1)$$

Odinokov, Iogansen, *et. al.*[5] proposed the linear relationship shown in equation (1) between $\bar{\nu}_H$ and B_H, where: $\Delta B_H^{\frac{1}{2}} = B_{AHB}^{\frac{1}{2}} - B_{AH(free)}^{\frac{1}{2}}$ and: $\Delta\nu = \bar{\nu}_{H(AHB)} - \bar{\nu}_{H(AH\,free)}$. According to equation (1) frequency shift increases more rapidly (*ca.* 80 times) than intensity. The data listed in Table 1 do not follow equation (1).

The variations of $\bar{\nu}_H$ with concentration in the investigated complexes were very similar (with respect to the magnitude and direction) to those caused by solvents.[10] This similarity

Table 1. Effect of concentration on the centres of gravity ($\bar{\nu}_H$, cm^{-1}) and integrated intensity ($B_H \times 10^{-4}$, l mol^{-1} cm^{-2}) of substituted pyridine trifluoroacetates in benzene and dichloromethane.

		C_6H_6/C_6D_6				CH_2Cl_2			
	K_{DA}[a]	0.068 M[b]		0.604 M[c]		0.068 M[b]		0.604 M[c]	
Substituent	kg mol^{-1}	$\bar{\nu}_H$	B_H	$\bar{\nu}_H$	B_H	$\bar{\nu}_H$	B_H	$\bar{\nu}_H$	B_H
3-Br	0.63 ± 0.10	1605	35.0	1623	37.0	1532	38.2	1541	37.4
3-Me	4.69 ± 0.40	1388	40.4	1516	40.1	1514	39.0	1593	38.8
2,4,6-Me$_3$	7.52 ± 0.22	1760	29.5	1923	29.4	1994	27.9	2069	27.6

[a] Ref. 8. [b] Path length l = 0.444 mm. [c] l = 0.050 mm.

suggests that the dipolar association favours proton transfer. Hence, in non-polar solvents, K_{PT} should be dependent on concentration: in benzene both log K_{PT} and log K_{DA} increased linearly with ΔpK_a.[8]

Another interesting feature is the change in the carbonyl–carboxylate region. An increase in concentration considerably increased the absorption of the carboxylate band, Figure 1(b) and (d). In dichloromethane the differences were not so pronounced. Thus the observed alteration of absorption reflects the variations in proton transfer with concentration.

The observed intensity variations of bands B, C, D, and E with concentration are very similar to those predicted by theory[11—13] and are caused by the reaction field of the environment. Thus the effect of concentration can be compared with the effect of solvent since both modulate the reaction field.

Correlations of ΔH with B_H have been observed for more than 250 complexes with hydrogen bonds,[5b] equation (2). The available data for pyridine *N*-oxide trifluoroacetate in benzene show that the enthalpy of dipolar association ($-\Delta H$ 3 kcal mol^{-1})†[14] is much smaller than the enthalpy of hydrogen bond formation ($-\Delta H$ 16 kcal mol^{-1}).[15] Thus, we expect that the effect of concentration on enthalpy should be small and comparable with the standard deviation. The largest variation of B_H with concentration (Table 1) is less than 6%. This corresponds to $\Delta\Delta H$ *ca.* 0.5 kcal mol^{-1}.

$$-\Delta H = 2.9\Delta B_H^{\frac{1}{2}} \qquad (2)$$

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† 1 kcal = 4.18 kJ.

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