Interaction of 2,4,6-Trimethylpyridine with Some Halogenocarboxylic Acids in Benzene and Dichloromethane. Problem of Stoicheiometry

Piotr Barczyński, Zofia Dega-Szafran, and Mirosław Szafran *
Department of Chemistry, A. Mickiewicz University, 60780 Poznań, Poland

The practical molal osmotic coefficients of 2,4,6-trimethylpyridine complexes with dichloroacetic and 2,2-dichloropropionic acid in benzene solutions over the concentration range 0.05—0.5 mol kg^{-1} were determined by vapour pressure osmometry (v.p.o.). The non-ideal behaviour of the investigated systems is interpreted on the basis of the stepwise aggregation model and the association constants are derived. ^{1}H N.m.r. and i.r. spectra are reported for 2,4,6-trimethylpyridine with dichloroacetic, 2,2-dichloropropionic, and trifluoroacetic acids with various acid–base ratios (2:1, 1.33:1, and from 1:1 to 1:10). Both the chemical shift of hydrogen-bonded protons and the continuous absorption in i.r. spectra are affected when an excess of base is added to the equimolar mixture of 2,4,6-trimethylpyridine with dichloroacetic and 2,2-dichloropropionic acids. The results can be rationalized in terms of formation of the following complexes: $B\cdots HA$, $B^+H\cdots A^-$, $(BHA)_n$, and $B^+H(A^-\cdots HA)$. For trifluoroacetic acid the $B^+H(A^-\cdots HA)$ complex is formed only when there is an excess of acid, while for dichloroacetic and 2,2-dichloropropionic acids the equilibrium can be completely shifted to the 1:1 complex only when there is a three-fold excess of base.

Brønsted acid–base interactions in non-basic, non-polar, and aprotic solvents have been discussed in the classic monograph of Davis[1] and several other reviews.[2–5] These demonstrate that such systems must involve a bewildering array of hydrogen-bonded complexes between the neutral species and between the ion pairs produced by protolysis. The structures of these complexes are easy to postulate but often difficult to demonstrate.

Various experimental techniques[1,4] are used in specifying several types of structures which may be in equilibrium with each other and with the monomeric acid (HA) and base (B) over different parts of the normal concentration range of the solution studied (1—10^{-6}M). The simplest and most clearly defined of these species are acid dimers $(HA)_2$,[6] the 1:1 molecular hydrogen-bonded complex between acid and base, $B\cdots HA$, 1:1 hydrogen-bonded ion pairs between conjugates of the original acid–base pair, $B^+H\cdots A^-$, and solvated ions, B^+H and A^-.[1]

Strong evidence may also be cited for the presence of higher aggregates $(BHA)_n$[7–10] and triple ions $(B^+H)_2A^-$ and $B^+H(A^-)_2$.[11,12]

The 1:1 hydrogen-bonded ion pairs interact with an excess of acid or base to form the 2:1 homoconjugate ion pair complex, $B^+H(A^-\cdots HA)$, involving two molecules of acid, and the 1:2 homoconjugate ion pair involving two molecules of base, $(B^+H\cdots B)A^-$.[13–16]

In this paper we report ^{1}H n.m.r., i.r., and vapour pressure osmometry (v.p.o.) data for 2,4,6-trimethylpyridine complexes with dichloroacetic (DCA), 2,2-dichloropropionic (DCP), and trifluoroacetic (TFA) acids in benzene and dichloromethane. The results which we shall present below show that in the solution containing equimolar quantities of DCA or DCP and 2,4,6-trimethylpyridine besides 1:1 complexes [$B\cdots HA$, $B^+H\cdots A^-$, $(B^+H\cdots A^-)_n$] there are also 2:1 complexes [$B^+H(A^-\cdots HA)$].

Experimental

2,4,6-Trimethylpyridine (EGA Chemie) was stored for at least a week over calcium hydride, then distilled and stored over molecular sieves (4 Å). Dichloroacetic acid (Fluka), 2,2-dichloropropionic acid (Alfa Products), and trifluoroacetic acid (Fluka) were refluxed over P_2O_5 (5% w/w) and distilled.

Complexes were prepared by adding stoicheiometric amounts of acids to an ether solution of 2,4,6-trimethylpyridine and cooled in a CO_2–acetone bath. The resulting precipitates were recrystallized from ether and dried over P_2O_5: 2,4,6-trimethylpyridine·$HOOCCHCl_2$, m.p. 68—70 °C; 2,4,6-trimethylpyridine·$HOOCCCl_2CH_3$, m.p. 29—31 °C, the crystals are fairly hygroscopic; 2,4,6-trimethylpyridine·$HOOCCF_3$, m.p. 44—45 °C.

Solvents were purified by standard methods and stored over molecular sieves (4 Å). All solutions were prepared and all transfers of non-aqueous solutions were made in the dry-box.

I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer using cells with KBr windows (0.07, 0.124, 0.227, and 0.45 mm). The centre of gravity of the graphically 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 base line and complex, respectively. The compensation of solvent in the 4 000—1 600 cm^{-1} region and the broad absorption of acids in the 1 600—400 cm^{-1} region were used as a base line.

^{1}H N.m.r. spectra were measured on a Tesla BS 467 spectrometer. All chemical shifts were taken downfield relative to the resonance of the solvents and then converted into δ values by adding 7.17 and 5.3, respectively, for benzene and dichloromethane.

A Knauer vapour pressure osmometer was used. The instrumental calibration procedure and the method of measurements were similar to those described previously.[8] Osmotic coefficients (Φ) were calculated from equation (1) and fitted by a

$$V/k = \Phi m \qquad (1)$$

$$\Phi = 1 + \sum_{i=1}^{q=5} A_i m^i \qquad (2)$$

least-squares method to the orthogonal polynomial of form (2) where V is the measured imbalance (μV) at 27 °C, k is the calibration constant, m is the stoicheiometric solute concentration (mol kg^{-1}), q is the size of the polynomial, and A_i is constant. The stepwise aggregation constant, K_D, was calculated from equation (3); for details see ref. 17.

$$K_D = [m - (\Phi m)]/(\Phi m)^2 \qquad (3)$$

Results and Discussion

Vapour Pressure Osmometry.—The coefficients A_i are given in Table 1 and the osmotic coefficients are shown in Figure 1. A marked lowering of the molal osmotic coefficient with increasing concentration indicates that these complexes undergo self-association in solution. Using the model of successive-step association [equation (3)] the internally consistent equilibrium constants are obtained for both complexes (Table 2). Since self-association is controlled by the dipole moment[8] we are surprised to find relatively large differences of the equilibrium constants between complexes of DCA and DCP. The pK_a value of DCP is unknown. However, the methyl group only slightly decreases proton-donor properties of the carboxylic acid. Thus, the dipole moments and hydrogen-bond strength of complexes of 2,4,6-trimethylpyridine with DCA and DCP should be comparable. Similar values of the chemical shift and the centre of gravity of these complexes (see below) support this point of view. Thus, the bulky effect of the methyl group can be responsible for the observed differences in K_D values. Furthermore, the concentration effect on the continuous absorption in the i.r. spectra of these complexes in benzene is proportional to the values of K_D (see below).

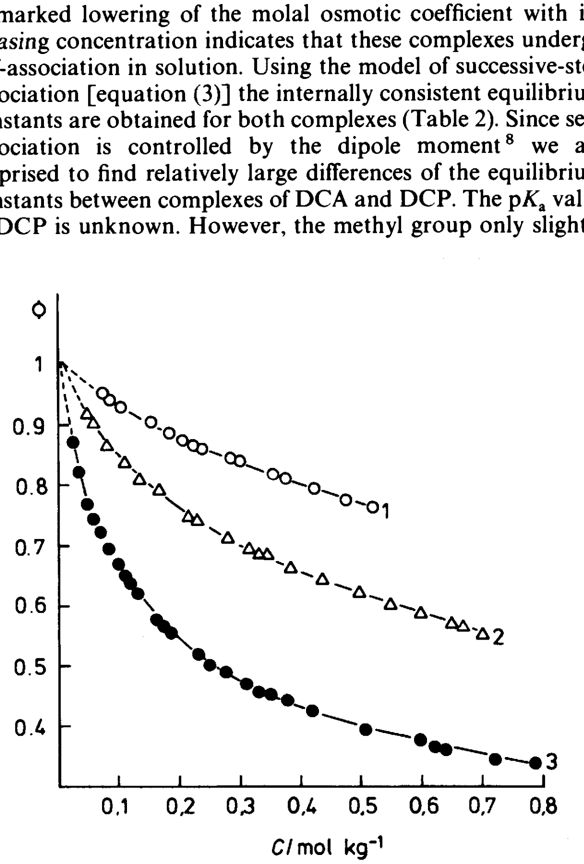


Figure 1. Molal osmotic coefficients of 2,4,6-trimethylpyridine complexes with (1) 2,2-dichloropropionic, (2) dichloroacetic, and (3) trifluoroacetic[9] acids

Table 1. Values of regression coefficients A_i of equation (2) and standard error of estimate S_q for complexes for 2,4,6-trimethylpyridine (TMP) with dichloroacetic (DCA) and 2,2-dichloropropionic (DCP) acids in benzene at 27 °C

	TMP·DCA	TMP·DCP
A_1	−2.053 78	−0.726 81
A_2	6.500 89	0.332 86
A_3	−13.980 21	3.445 32
A_4	15.926 59	−11.151 93
A_5	−7.293 14	10.163 67
10^4S_q	6.49	4.24
No. of points	18	18

^{1}H *N.m.r. Spectra.*—The chemical shift of the hydrogen-bonded protons in the investigated complexes of 2,4,6-trimethylpyridine with DCA and DCP varies with concentration (Table 2, Figure 2), solvent (Table 3 and ref. 17), and acid–base ratio (Figure 3).

As shown in Table 3, addition of an excess of 2,4,6-trimethylpyridine to the 1:1 acid–base mixture caused a downfield shift of the hydrogen-bonded protons. The magnitude of this shift is much larger than that observed for complexes of various pyridines (including weak base *e.g.* 3-cyanopyridine) with trifluoroacetic acid.[17] Our recent measurements for 2,4,6-trimethylpyridine·HOOCCF$_3$ are, within experimental accuracy, similar to the previous ones. One can expect that DCA and

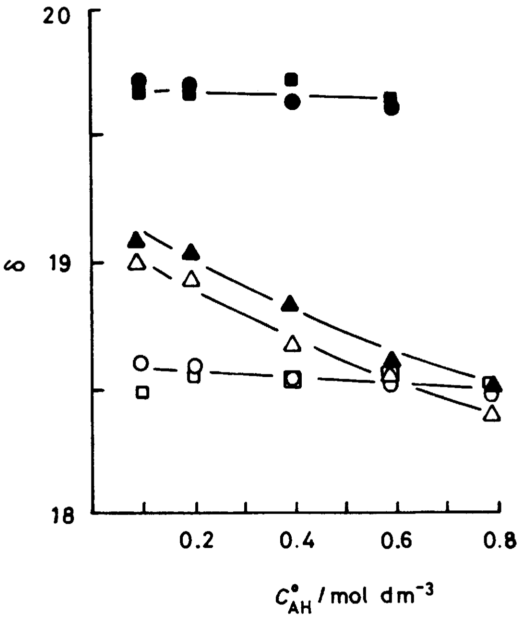


Figure 2. Effect of concentration and excess of base on the chemical shift of complexes of 2,4,6-trimethylpyridine with dichloroacetic (○, ●), 2,2-dichloropropionic (□, ■), and trifluoroacetic (△, ▲) acids in benzene; ○, □, △, $C^\circ_{AH}:C^\circ_B$ = 1:1; ●, ■, ▲, $C^\circ_{AH}:C^\circ_B$ = 1:4

Table 2. Dipolar association constants and chemical shifts of hydrogen-bonded protons in mixtures of 2,4,6-trimethylpyridine with some carboxylic acids in benzene

			C°_{AH}/M				
			Chemical shift				
Acid	K_D/kg mol^{-1}	$C^\circ_{AH}:C^\circ_B$	0.1	0.2	0.4	0.6	0.8
$CHCl_2COOH$	2.06 ± 0.08	1:1	18.61	18.60	18.56	18.53	18.48
		1:4	19.72	19.70	19.65	19.62	
CH_3CCl_2COOH	0.77 ± 0.03	1:1	18.50	18.55	18.56	18.58	18.50
		1:4	19.66	19.66	19.73	19.64	
CF_3COOH	7.52 ± 0.22	1:1	19.01	18.93	18.67	18.53	18.40
		1:4	19.18	19.05	18.83	18.60	18.50

Table 3. The chemical shift of the hydrogen-bonded protons δ_H in mixtures of 2,4,6-trimethylpyridine with some carboxylic acids (C°_{AH} 0.2M)

	$CHCl_2COOH$		CH_3CCl_2COOH	CF_3COOH
$C^{\circ}_{AH}:C^{\circ}_B$	C_6H_6	CH_2Cl_2	C_6H_6	C_6H_6
1:0.6	16.73		16.67	16.23
1:1	18.60	18.43	18.55	18.93
1:2	19.32	18.85	19.38	19.03
1:4	19.70	18.97	19.66	19.05
1:6	19.65	19.00	19.73	19.00
1:8	19.67	19.05	19.70	18.95
1:10	19.67	19.03	19.70	18.93

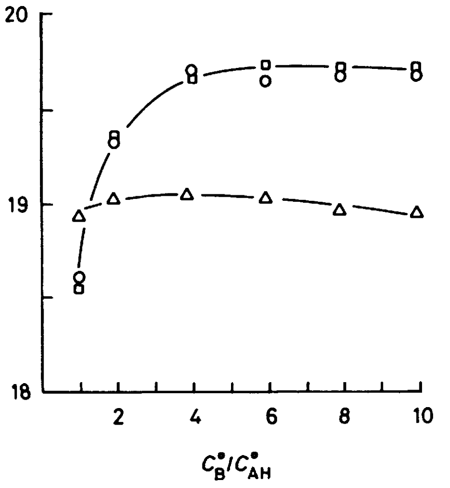


Figure 3. Effect of excess of base on the chemical shift of complexes of 2,4,6-trimethylpyridine with dichloroacetic (○), 2,2-dichloropropionic (□), and trifluoroacetic (△) acids; C°_{AH} 0.2M

DCP would have a lower ability to form $(B^+H\cdots B)A^-$ species than TFA, since they are weaker acids. Thus, the large downfield shift observed on addition of the excess of base to 1:1 complexes of DCA and DCP is, therefore, probably not due to formation of $(B^+H\cdots B)A^-$ or uncomplexed acid. The remaining explanation is formation of $B^+H(A^-\cdots HA)$ species.

Arnett *et al.*[18,19] found that the 1:2 $(B^+H\cdots B)A^-$ complex is not significant in polar (sulpholane) and non-polar (CCl_4) solvents. Enthalpy of the titration of 2,4,6-trimethylpyridine in CCl_4 with 0.5 mole of TFA is slightly greater than that of 1 mole of acid.[9] The formation of the $(B^+H)(AHA)^-$ complex is a more exothermic process.

I.r. Spectra.—The 1:1 and 2:1 acid–base complexes are in some cases distinguished in i.r. spectra.[20–22]

All the spectra investigated exhibit continuous absorption over the frequency region from 3 000 to 400 cm^{-1}. Within this range there are several overlapping absorption bands. All these bands are poorly resolved subpeaks resulting from superposition of sharp bands ascribed to other internal vibrations and to the Fermi resonance. The intensity of these bands strongly depends on the acid–base ratio, solvent, and nature of the acid.

Figure 4 and 5 show the effect of the acid–base ratio on the i.r. spectra. When the concentration of 2,4,6-trimethylpyridine increases, a systematic decrease in intensity of the band in the 2 500 cm^{-1} region is observed. Its centre also shifts to the lower wavenumbers. Simultaneously the intensity of the absorption in the regions 2 000 and 900—400 cm^{-1} increases. The observed variations in the absorption as the amount of 2,4,6-trimethylpyridine increases can be explained by a shift of equilibrium (4) to the 1:1 complex.

$$B^+H(A^-\cdots HA) + B \rightleftharpoons 2\,B^+H\cdots A^- \qquad (4)^*$$

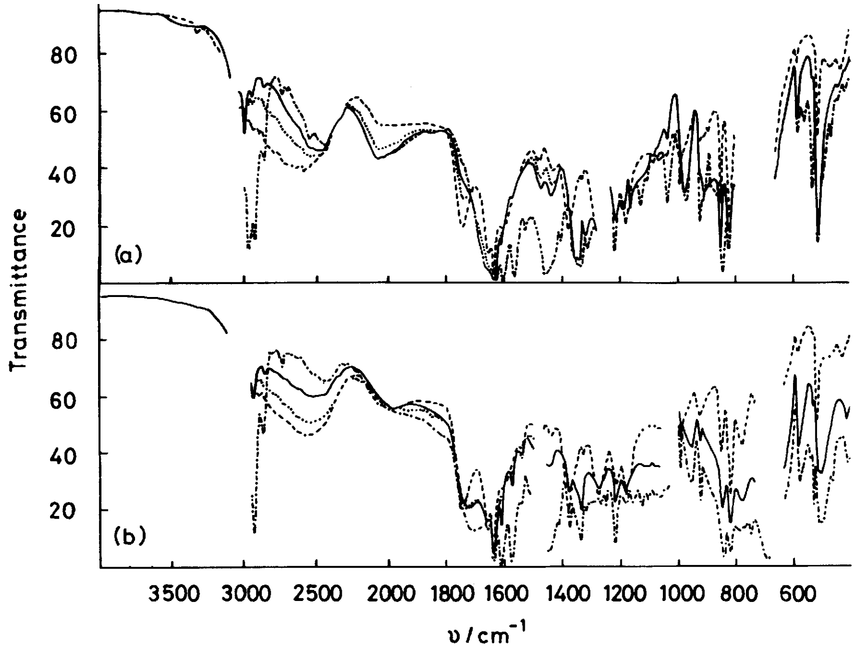


Figure 4. I.r. spectra of dichloroacetic acid (0.2M)–2,4,6-trimethylpyridine system (a) in CH_2Cl_2 and (b) in C_6H_6. The concentrations of 2,4,6-trimethylpyridine are: (- - - -) 0.1M; (· · · ·) 0.15M; (——) 0.2M; and (— · — · —) 0.8M

---

* V.p.o. is not affected by equilibrium (4). The average molecular weight (M) of the equimolar mixture of $B^+H(A^-\cdots HA)$ and B is equal to $B^+H\cdots A^-$ [$M = \frac{1}{2}(M_{2:1} + M_B) = M_{1:1}$].

Table 4. Frequencies for some carboxylic acids, their salts, and complexes

Compound	Solvent	$C^\circ_{AH}:C^\circ_B$	ν(C=O)*/cm^{-1}	ν_{as}(COO$^-$)/cm^{-1}	$\tilde{\nu}_H$/cm^{-1}
$CHCl_2COOH$	CH_2Cl_2		1 779m 1 760 (sh) 1 745d		3 460
	C_6H_6		1 780m 1 760 (sh) 1 745d		3 405
$CHCl_2COO^-N^+(Bu)_4$	CH_2Cl_2			1 658	
	C_6H_6			1 660	
$CHCl_2COOH{\cdot}TMP$	CH_2Cl_2	2:1	1 740	1 660 1 610	
		1:1	1 740 (sh)	1 660	1 700
		1:4		1 660	1 670
	C_6H_6	2:1	1 740	1 660 1 610	
		1:1	1 720	1 660	1 544
		1:4	1 710	1 665	1 414
$CH_3CCl_2COOH{\cdot}TMP$	C_6H_6	1:1	1 720	1 660	1 535
CF_3COOH	CH_2Cl_2		1 805m 1 782d		3 440
	C_6H_6		1 805m 1 782d		3 380
$CF_3COO^-N^+(Bu)_4$	CH_2Cl_2			1 688	
	C_6H_6			1 692	
$CF_3COOH{\cdot}TMP$	C_6H_6	2:1	1 780 1 750 (sh)	1 655	
		1:1		1 685	
		1:4		1 685	

* m = Monomer, d = dimer, sh = shoulder.

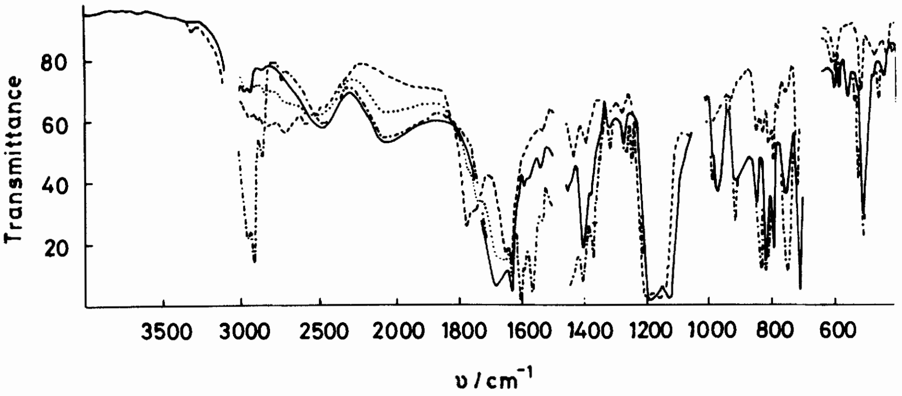


Figure 5. I.r. spectra of trifluoroacetic acid (0.2M)-2,4,6-trimethylpyridine system in C_6H_6. The concentrations of 2,4,6-trimethylpyridine are: (- - - -) 0.1M; (· · · ·) 0.15M; (——) 0.2M: and (— · — · —) 0.8M

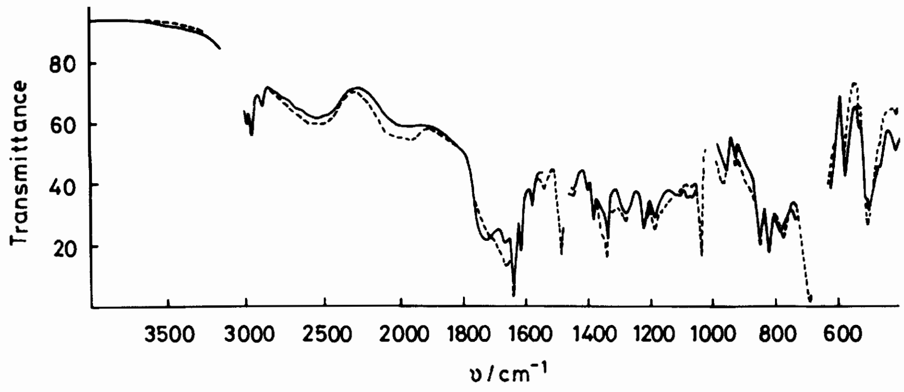
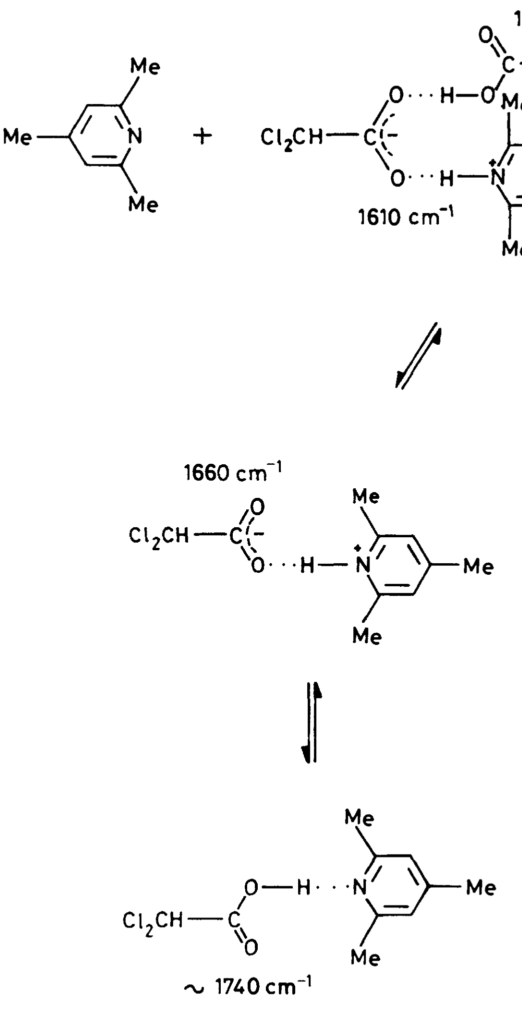


Figure 6. I.r. spectra of complexes of 2,4,6-trimethylpyridine with dichloroacetic acid in C_6H_6; (——) 0.08M; (- - - -) 0.514M

Thus, differences in the intensity between the spectra of 1:1 and 1:4 acid–base mixtures may be evidence that the $B^+H(A^- \cdots HA)$ species are present in the 1:1 acid–base mixtures. The relative content of 1:1 and 2:1 complexes under comparable conditions depends strongly on the proton-donating power of the acid and the nature of the solvent. In the case of TFA the 2:1 complex is formed when an excess of acid is present, since similar intensities of the continuous absorption are observed in the spectra of 1:1 and 1:4 acid–base mixtures (Figure 5). For the weaker dichloroacetic and dichloropropionic acids the equilibrium can be completely shifted to the 1:1 complex only for an excess of 2,4,6-trimethylpyridine (three-fold excess in benzene and two-fold in dichloromethane).

Supplementary arguments concerning equilibria in the investigated systems can be derived from the absorbance in the carbonyl–carboxy region (Table 4). In the spectra of the 2:1 mixture of DCA and 2,4,6-trimethylpyridine three bands at 1 740, 1 660, and 1 610 cm^{-1} are observed (Figure 4, Table 4). The intensity of the first band decreases when 2,4,6-trimethylpyridine is added, and disappears for a three-fold excess of 2,4,6-trimethylpyridine. The frequency of this band is close to the frequency of a dimer, and is also attributed to the ν(C=O) vibration of the second acid molecule in the $B^+H(A^- \cdots HA)$ complex.

In the spectrum of the equimolar acid–base mixture (Figure 4a) a shoulder at 1 740 cm^{-1} is present, which confirms the presence of $B^+H(A^- \cdots HA)$ complex in CH_2Cl_2 solution. The other two bands, at 1 660 and 1 610 cm^{-1}, belong to the $\nu_{as}(COO^-)$ vibrations. The second band is shifted *ca.* 45 cm^{-1} to a lower frequency relative to the tetra-alkylammonium salt (Table 4). Such lowering is caused by addition of the second acid molecule to the ionic pair.[22] Therefore, the band at 1 610 cm^{-1} should be ascribed to the $\nu_{as}(COO^-)$ vibration in the 2:1 complex, and the band at 1 660 cm^{-1} to the $\nu_{as}(COO^-)$ vibration in the 1:1 complex [equation(5)].



(5)

In benzene solution the spectra are more complex. Benzene (ε 2.3) is a less polar solvent than dichloromethane (ε 8.9), hence its solvation power is smaller. This caused a shift of the tautomeric equilibrium between the molecular complex and the ionic pair form to the molecular complex with lowering solvent polarity.[23] Larger amounts of the molecular complex in the benzene solution results in increasing the frequency (Table 4) relative to the dichloromethane solution.

In the spectra of 2,4,6-trimethylpyridine with TFA the absorption appears at a higher frequency (Figure 5). This is caused by the inductive effect of fluorine atoms. The carbonyl band at 1 780 cm^{-1} shows a shoulder at 1 750 cm^{-1} (Figure 5). On addition of base the intensity of the 1 780 cm^{-1} band decreases more strongly than that at 1 750 cm^{-1}. This may suggest that the band at 1 780 cm^{-1} is attributed to the ν(C=O) frequency of dimer, but that at 1 750 cm^{-1} to the second acid molecule in the $B^+H(A^- \cdots HA)$ complex.

I.r. spectra of the 1:1 complex of 2,4,6-trimethylpyridine with DCA and DCP in benzene are affected by concentrations proportional to the values of K_D. On increasing the concentration from 0.08 to 0.514M the intensity of the bands at *ca.* 2 500 and 1 900 cm^{-1} increases, but the bands at *ca.* 500 cm^{-1} decrease (Figure 6). Further changes are observed in the carbonyl–carboxy region. An increase in the concentration considerably increases the absorption of the carboxy band. Similar changes in absorption have been observed previously in the spectra of some pyridinium trifluoroacetates.[24] These alterations of the absorption are proportional to the dipolar association constant (K_D). The hydrogen-bonded ion pairs, being more polar than the molecular complexes, are capable of forming high molecular weight aggregates $(B^+H \cdots A^-)_n$. Thus the formation of aggregates shifts equilibrium between the molecular complexes and the ionic pair toward the latter.

Acknowledgements

We acknowledge financial support from the Polish Academy of Sciences (Project MR.I.9.4.4.4.).

References

1 M. M. Davis, 'Acid-Base Behaviour in Aprotic Solvents,' NBS Monograph 105, U.S. Government Printing Office, Washington, 1968; M. M. Davis in 'The Chemistry of Nonaqueous Solvents,' ed. J. J. Lagowski, Academic Press, 1970, vol. 3, ch. 1.
2 J. E. Gordon, 'The Organic Chemistry of Electrolyte Solutions,' Wiley, New York, 1975.
3 C. Reichardt, 'Solvent Effects in Organic Chemistry,' Verlag Chemie, Weinheim, New York, 1979.
4 J. Małecki in 'Molecular Interactions,' eds. H. Ratajczak and W. J. Orville-Thomas, Wiley, Chichester, 1982, vol. 3, ch. 4.
5 B. Y. Simkin and I. I. Sheikhet, *J. Mol. Liquid*, 1983, **27**, 79.
6 E. F. Caldin, *Q. Rev. Chem. Soc.*, 1953, **7**, 255.
7 Z. Dega-Szafran and M. Szafran, *J. Mol. Struct.*, 1978, **45**, 33.
8 Z. Dega-Szafran, M. Szafran, and M. Kręglewski, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1516.
9 Z. Dega-Szafran, *Adv. Mol. Relax. Interact. Processes*, 1980, **18**, 61.
10 Z. Dega-Szafran and M. Szafran, *J. Mol. Liquid*, 1983, **25**, 109.
11 C. A. Kraus, *J. Chem. Educ.*, 1958, **7**, 324.
12 S. K. Mehta and B. Chawla, *Electrochim. Acta*, 1982, **27**, 9.
13 G. M. Barrow, *J. Am. Chem. Soc.*, 1956, **78**, 5802.
14 D. Hadži, *J. Pure Appl. Chem.*, 1965, **11**, 435; *Chimie*, 1972, **26**, 7.

15 J. L. Wood in 'Infrared Spectroscopy of Molecular Complexes,' ed. J. Yarwood, Plenum Press, New York, 1973, ch. 4.
16 J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.
17 Z. Dega-Szafran and E. Dulewicz, *Org. Magn. Reson.*, 1981, **16**, 214.
18 D. L. Hughes and E. M. Arnett, *J. Am. Chem. Soc.*, 1983, **105**, 4157.
19 E. M. Arnett and B. Chawla, *J. Am. Chem. Soc.*, 1978, **100**, 217.
20 G. V. Gusakova, G. S. Denisov, A. L. Smolyansky, and V. M. Schreiber, *Dokl. Akad. Nauk SSSR*, 1970, **193**, 1065.
21 G. S. Denisov, Ya. Stavosta, and V. M. Schreiber, *Opt. Spektrosk.*, 1973, **35**, 447.
22 G. V. Gusakova, G. S. Denisov, and A. L. Smolyansky, *Opt. Specktrosk.*, 1972, **32**, 922.
23 Z. Dega-Szafran and E. Dulewicz, *J. Chem. Soc., Perkin Trans. 2*, 1983, 345.
24 Z. Dega-Szafran and M. Szafran, *J. Chem. Soc., Chem. Commun.*, 1984, 1470.

Received 31*st January* 1986; *Paper* 6/212