The Acid–Base Function in Non-aqueous Solution. Part V.[1] Entropy Changes due to Intramolecular and Solvation Effects in Aprotic Solvents

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The free energies, enthalpies, and entropies of proton transfer reactions for the following systems are discussed: (i) Bromothymol Blue + pyridine and substituted pyridines in chlorobenzene and (ii) picric acid + substituted pyridines and n-butylamine in chlorobenzene, benzene, and dioxan. The reactions occurring are of the type AH + B $\rightleftharpoons$ AHB. The results for the first indicate that negative contributions to entropy changes can be caused by restricted rotations in the hydrogen bonded ion-pair due to substituents in the base. In the second system there are no marked differences in solvation between the solvents benzene and chlorobenzene but in dioxan large positive entropy changes arise from solvent exclusion when the ion-pair is formed. For these systems therefore the thermodynamic functions do not simply reflect intramolecular effects alone despite the solvents being aprotic and of low dielectric constant.

In non-aqueous aprotic solvents, proton transfer reactions between amines (B) and nitrophenols (AH) lead to the formation of ion-pairs as represented by equation (1). In Part IV [1] a series of systems was measured in

$$B + AH \rightleftharpoons B^+HA^- \qquad (1)$$

chlorobenzene and there was evidence for entropy production due to solvent exclusion. As this effect should be solvent dependent we have now measured the equilibria between picric acid and four amines in three solvents of varying solvating properties, chlorobenzene, benzene, and dioxan. The amines have been chosen to have a range of proton affinities and minimum steric hindrance around the basic centre.

EXPERIMENTAL

Materials.—Chlorobenzene (B.D.H.) and benzene (B.D.H. AnalaR) were distilled and then dried over fresh phosphorus(v) oxide for 2—5 days. They were then refractionated and the middle fraction collected. Dioxan (May and Baker) was dried over sodium wire and distilled. The distillate was refluxed over sodium until no further reaction took place and fractionated. B.p.s were: chlorobenzene 131.5° (lit., 131.72°); benzene 80° (lit., 80.1°); dioxan 101° (lit., 101.3°). All the amines were dried over potassium hydroxide, then fractionated, and the middle fraction collected. B.p.s were: 3-chloropyridine 148° (lit., 148°); 3-methylpyridine 143° (lit., 143.8°); 2,6-dimethylpyridine 143° (lit., 143°); n-butylamine 77.0° (lit., 77.7°).

Bromothymol Blue (B.D.H.) was recrystallized from distilled benzene and dried *in vacuo* over potassium hydroxide pellets and stored over this material. The indicator decomposes before melting.

Picric acid was recrystallized from aqueous ethanol and washed with a quantity of iced aqueous ethanol. The crystals were dried *in vacuo* over phosphorus(v) oxide and stored over this material, m.p. 122—122.5° (lit., 122.0°).

Method.—A Varian Techtron u.v.–visible spectrophotometer model 635 provided with a water-jacketted cell holder and stirrer was used. Water was pumped from an insulated water-bath through the cell holder. The water-bath temperature was controlled within 0.1° of the set temperature, *ca.* 25—50°.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[1] Part IV, D. M. Parbhoo and J. W. Bayles, *J.C.S. Perkin II*, 1972, 1897.

To determine the difference between the cell and bath temperature a modified Wheatstone bridge circuit [2] with an arm consisting of a Stantel F23 thermistor was constructed. The thermistor was first aged and its resistance was calibrated as a function of temperature, enabling the cell temperature to be known at various bath temperatures.

RESULTS

Absorption Spectra.—The spectra of ionised picric acid in the three solvents are characterised by an intense absorption peak near 360 nm and a shoulder having two-thirds of this intensity near 410 nm. Bromothymol Blue has a single intense absorption near 360 nm in each solvent. The molar absorbances of the un-ionised indicators and the AHB complexes at 410 nm are given in Table 1.

Equilibria.—Checks of the equilibrium type [3] required by equation (1) were made for all systems and the results are given in Supplementary Publication No. SUP 21389 (11 pp.).† In all cases the plots of m_{AHB} against $m_{AH}m_B$ are found to be linear to the same precision as previously reported.

TABLE 1

Molar absorbances at 410 nm of picric acid alone and in the presence of excess of amines

	Solvent		
Added base	Chlorobenzene	Benzene	Dioxan
Nil	4	4	2.5
3-Chloropyridine	649	626	535
3-Methylpyridine	742	694	589
2,6-Dimethylpyridine		637	613
n-Butylamine	808	777	

The equilibrium constant K_x and the thermodynamic quantities ΔG^0, ΔH^0, and ΔS^0 were calculated as previously reported.

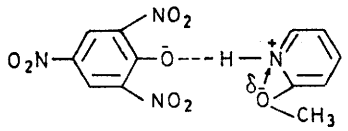
DISCUSSION

The factors governing the thermodynamic quantities associated with the reaction AH + B $\rightleftharpoons$ AHB have been discussed [4] and an increase in aqueous pK_a of the base would be expected to yield a negative contribution to the enthalpy change for proton transfer. It was also suggested that contributions to ΔS^0 should be proportional to ΔH^0 because the stronger the bond between the acid and base the less free to rotate will the participants be when combined. On the other hand if

[2] E. Pitts and P. Y. Priestly, *J. Sci. Instruments*, 1962, **39**, 75.
[3] J. W. Bayles and A. Chetwyn, *J. Chem. Soc.*, 1958, 2328.
[4] J. W. Bayles and A. F. Taylor, *J. Chem. Soc.*, 1961, 417.

there is any appreciable solvation of the solute molecules before the reaction, any desolvation after proton transfer will result in a positive contribution to the entropy change.

The reactions between the acids Bromothymol Blue, picric acid, and the substituted pyridines have been investigated [5] and the thermodynamic quantities obtained are given in Table 2. If $-\Delta G^0$ is taken as a measure of proton affinity, the order of basic strength observed in chlorobenzene is in the order predicted by the electronic theories and follows the pK_a values in water. The weak basicity of 2-methoxypyridine is due to the inductive effect resulting from the high electron affinity of the oxygen atom in the methoxy-group. Since 2-methylpyridine is a stronger base than 2-methoxypyridine we would expect that the values for the entropy changes for the former systems (*ca.* -66 J mol^{-1} K^{-1}) would be more negative than for the latter (*ca.* -73 J mol^{-1} K^{-1}). The observed anomaly can be explained by referring to structure (1) of the complex formed between picric acid and 2-methoxypyridine. The greater entropy loss could be due to an additional interaction between the high electron density on the oxygen of the methoxy-group and the positive amminium nitrogen resulting in a restriction in the rotation about the bond by which the methoxy-group is attached to the pyridine ring. As a result of this effect, the rotation of the molecule about the $\bar{O}\cdots\overset{+}{H}\overset{+}{N}$ bond may also be hindered. The identification of solvent exclusion effects depends on evidence of anomalous entropy production. When searching for this it is therefore important to avoid systems in which entropy effects of either sign can arise from intramolecular causes such as these.



(1)

We have therefore selected the amines 3-chloro- and 3-methylpyridine in preference to 2-methoxy- and 2-methyl-pyridine.

The thermodynamic functions for proton-transfer reactions between picric acid and some amines in three solvents are given in Table 3. In chlorobenzene it was found that the equilibrium between picric acid and 2,6-dimethylpyridine did not conform to that required by equation (1) when tested by the graphical method described in the Results section. We were also unable to obtain reliable values for the equilibrium constant

[5] D. M. Parbhoo, Ph.D. Thesis, University of Natal, 1967.

TABLE 2

Thermodynamic functions for the reactions of Bromothymol Blue and picric acid with various bases in chlorobenzene

	pK_a in water	ΔG^0 / kJ mol^{-1}	ΔH^0 / kJ mol^{-1}	ΔS^0 / J mol^{-1} K^{-1}
Bromothymol Blue +				
2-Methylpyridine	5.9	-31.21 ± 0.04	-51.0 ± 0.4	-67 ± 2
2-Ethylpyridine	5.9	-31.34 ± 0.04	-51.9 ± 1.3	-70 ± 4
2-Benzylpyridine	5.1	-27.24 ± 0.04	-47.8 ± 1.6	-69 ± 5
2-Methoxypyridine	3.1	-12.68 ± 0.04	-36.3 ± 0.8	-79 ± 3
Picric acid +				
2-Methoxypyridine	3.1	-14.40 ± 0.04	-38.0 ± 1.0	-71 ± 3
2-Methylpyridine	5.9	-33.41 ± 0.04	-53.0 ± 2.0	-67 ± 5

TABLE 3

Thermodynamic functions for proton-transfer reactions between picric acid and some amines in various solvents

Solvent	Amine	$\Delta G^0(298)$/kJ mol^{-1}	$\Delta H^0(298)$/kJ mol^{-1}	$\Delta S^0(298)$/J mol^{-1} K
Chloro-benzene	3-Chloropyridine (2.84) *	-15.26 ± 0.4	-39.25 ± 0.75	-80.4 ± 2.5
	3-Methylpyridine (5.52) *	-31.98 ± 0.04	-50.58 ± 1.59	-62.5 ± 5.0
	2,6-Dimethyl-pyridine (6.60) *			
	n-Butylamine (10.59) *	-28.95 ± 0.12	-7.1 ± 2.6	$+73$ $+9$
Benzene	3-Chloropyridine	-12.83 ± 0.04	-40.04 ± 0.92	-91.3 ± 3.3
	3-Methylpyridine	-28.63 ± 0.04	-46.52 ± 0.79	-59.9 ± 2.6
	2,6-Dimethyl-pyridine	-33.40 ± 0.05	-51.9 ± 1.4	-62.0 ± 4.6
	n-Butylamine	-33.44 ± 0.08	-3.8 ± 2.9	$+100$ $+10$
Dioxan	3-Chloropyridine	-9.87 ± 0.04	-24.58 ± 1.33	-49.5 ± 4.6
	3-Methylpyridine	-24.66 ± 0.25	-34.19 ± 0.92	-32.0 ± 3.1
	2,6-Dimethyl-pyridine	-28.65 ± 0.05	-38.2 ± 1.0	-31.9 ± 3.3
	n-Butylamine			

* pK_a of amine.

for the reaction between picric acid and n-butylamine in dioxan since the reaction was found to be virtually complete.

The enthalpies and entropies of reaction in chlorobenzene and benzene, allowing for experimental errors, are similar. Chlorobenzene is a weakly dipolar solvent (μ 1.55 D) in which the benzene ring is depleted of electrons inductively. Although benzene is non-polar, the benzene molecule is readily polarised and attachment through polarised π-electrons is possible. The results indicate that the solvation due to dipole–dipole interactions in chlorobenzene is thermodynamically equivalent to that due to dipole-induced dipole interactions in benzene. The swing towards more positive entropies of reactions from *ca.* −80 kJ mol^{-1} for the picric acid–chloropyridine system to *ca.* +100 kJ mol^{-1} for the picric acid–n-butylamine system can again [1] be explained as being due to the exclusion of solvent molecules around the hydrogen bond as the bond becomes stronger.

The entropy changes for the reactions between picric acid and substituted pyridines in dioxan are approximately half the corresponding values obtained in the solvents benzene and chlorobenzene. Picric acid is more strongly solvated in dioxan than in the other solvents because dioxan is a hydrogen bonding solvent and therefore competes with the internal hydrogen bonding in the picric acid molecules. The subsequent exclusion of these solvent molecules on complex formation would result in large positive contributions to entropy changes. This is why we find that even the relatively weaker acid–base pairs show more positive entropy changes in dioxan than in the other solvents. The stabilisation of the complex through relatively stronger solvation in dioxan also explains the virtually complete reaction between picric acid and n-butylamine. In dioxan the complex formed is more stabilised by solvation than in chlorobenzene and benzene. This would normally lead to the ΔG^0 values being more negative in dioxan than in benzene and chlorobenzene. The observed anomalies are due to the fact that the enthalpy changes are not linearly compensated by the corresponding changes in entropy which arise out of solvent changes.

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