The Acid–Base Function in Non-aqueous Solution. Part IV.† Evidence for Entropy Production by Solvent Exclusion in an Aprotic Solvent

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The entropies and enthalpies of some proton-transfer reactions in chlorobenzene solution have been measured spectrophotometrically. The results of these systems and some others previously measured are discussed. As the proton-transfer affinity is increased, either by increasing the strength of the acid or of the base, we find that the entropy of reaction, normally *ca.* −84 J K^{-1} mol^{-1}, becomes strongly positive (*ca.* +76 J K^{-1} mol^{-1}). We suggest that this is because solvent is excluded from the neighbourhood of the hydrogen bond if the latter is strong and therefore short.

PROTON transfer between amines (B) and nitrophenols (AH) in chlorobenzene follows equation (1). Previous

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

evidence [1] has led to the conclusion that in chlorobenzene the ΔH° and ΔS° values for this type of reaction do not contain contributions from solvation changes. Pearson and Vogelsong [2] have found evidence of specific solvation of non-bridging protons in ion pairs of the form B^+HA^- by considering the effects accompanying change of solvent and the addition of small amounts of a hydroxylic solvent and of salts having a cation in common with the reaction mixture.

We have now measured systems where the acid–base pair is stronger than previously and where there is steric hindrance around the reaction site. In these circumstances we find that there is a striking transition towards more positive entropies and less negative enthalpies of reaction owing, we suggest, to solvent exclusion when B^+HA^- is formed from B and AH.

EXPERIMENTAL

Materials.—Chlorobenzene was purified as previously described.[3] 2,4-Dinitrophenol, 2,6-dinitrophenol, and picric acid were recrystallised from aqueous ethanol, dried *in vacuo* over KOH for several days, and stored in a desiccator over P_2O_5. They had m.p. 112·5 °C (lit., 112·6 °C), 62·0 °C (lit., 62·2 °C), and 122 °C (lit., 122·0 °C) respectively.

All the amines were dried (KOH), then fractionated, and the middle fraction collected. They had b.p.s as follows: 2-methoxypyridine, 141·5 °C; 2-methylpyridine, 129 °C (lit., 129 °C); n-butylamine, 77·5 °C (lit., 77·7 °C), and tri-n-butylamine 213 °C (lit., 214 °C). The purity of these amines was checked by g.l.c. with 10—15% Lubrol M.O. or Carbowax on Celite as stationary phase.

Method.—A Zeiss PMQ II spectrophotometer provided with a water-jacketed cell holder and stirrer was used.

A photometric titration technique was employed with two 5 cm^3 Metrohm piston burettes to deliver solution into one of the two matched Vitreosil optical cells (path-length 2 cm). The piston burette and the titration cell were terminated by neoprene septa attached by brass fittings. Stainless steel needles were heat-sealed to the ends of the Polythene delivery tubes. The steel needles at the two ends of the Polythene tubing were pierced through the septa and displaced air escaped from the titration cell through a further fine-bore needle. In this way losses through evaporation at high optical cell temperatures were made insignificant.

Water was pumped from an insulated water-bath through the cell holder. The water-bath temperature was controlled within 0·1 °C of the set temperature between *ca.* 17 and 60 °C. A correction was applied for the difference between the cell and bath temperatures.

RESULTS

Absorption Spectra.—The spectra of acidic and basic solutions of 2,4-dinitrophenol in chlorobenzene have been discussed.[3] Ionised picric acid has a similar spectrum to that of ionised 2,4-dinitrophenol with an intense absorption peak near 360 nm and a shoulder having two-thirds of this intensity near 410 nm. This shoulder is absent from the spectra of ionised 2,6-dinitrophenol.

The molar absorbances of the un-ionised indicators and the AHB complexes at 410 nm are given in Table 1 together with the wavelengths of the maximum absorption of the AHB complexes and their corresponding molar absorbances which are reproducible to between ½ and 1%.

TABLE 1

Characteristics of the absorption spectra of various indicators alone and in the presence of an excess of various amines

Indicator	Amine	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/m^2 mol^{-1}	ε_{410}/m^2 mol^{-1}
Picric acid	Nil	410		10·3
	2-Methoxy pyridine	347	1490	740
	2-Methyl-pyridine	350	1517	740
	Mono-n-butylamine	360	1700	830
	Dibenzylamine	350	1590	840
	Tribenzylamine	350	1700	820 *
2,4-Dinitrophenol	Nil	410		2·8
	Mono-n-butylamine	355	1760	960
2,6-Dinitrophenol	Nil	443		0·0 †
	Mono-n-butylamine	445	970	910 †

The ε values given here in SI units are one-tenth of the numerical values in old units.

* $\lambda = 403$ nm. † $\lambda = 443$ nm.

Checks of the equilibrium type [3] required by reaction (1) were made for all the systems in Table 2. In all cases the plots of m_{AHB} against $m_{\mathrm{AH}}m_{\mathrm{B}}$ were found to be linear to the same precision as previously reported.

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† Part III, J. W. Bayles and B. Evans, *J. Chem. Soc.*, 1961, 6984.

[1] J. W. Bayles and A. F. Taylor, *J. Chem. Soc.*, 1961, 417.

[2] R. G. Pearson and D. C. Vogelsong, *J. Amer. Chem. Soc.*, 1958, **80**, 1038.

[3] J. W. Bayles and A. Chetwyn, *J. Chem. Soc.*, 1958, 2328.

TABLE 2

Experimental results for amine–acid systems in chlorobenzene

(i) 2-Methoxypyridine + picric acid in a 2-cm cuvette

$10^5 m_{AH}$	$10^2 m_B$	t/°C	D_{410}	$\log_{10} K_x$
6·78	0·990	26·3	0·286	2·490
		31·0	0·247	2·407
		35·9	0·210	2·318
		40·5	0·178	2·230
		45·1	0·153	2·151
6·47	1·89	26·3	0·430	2·510
		31·0	0·373	3·411
		35·9	0·324	2·321
		40·5	0·278	2·228
		45·1	0·243	2·151
6·19	2·71	26·3	0·518	2·541
		31·0	0·460	2·443
		35·8	0·402	2·343
		40·5	0·350	2·248
		45·1	0·300	2·149
8·19	0·605	26·3	0·230	2·472
		31·0	0·196	2·388
		35·8	0·168	2·310
		40·5	0·145	2·235
		45·1	0·123	2·153
7·81	1·54	26·3	0·440	2·481
		31·0	0·380	2·388
		35·9	0·330	2·304
		40·5	0·280	2·210
		45·1	0·248	2·144
7·47	2·39	26·3	0·575	2·523
		31·0	0·505	2·423
		35·9	0·440	2·327
		40·5	0·380	2·232
		45·1	0·330	2·146
4·78	3·26	26·3	0·396	2·451
		31·0	0·350	2·35
		35·8	0·305	2·249
		40·5	0·263	2·149
		45·1	0·225	2·050
4·59	3·92	26·3	0·420	2·467
		31·0	0·373	2·359
		35·9	0·326	2·251
		40·5	0·285	2·154
		45·1	0·250	2·066
6·56	2·96	26·2	0·540	2·488
		31·0	0·472	2·379
		35·8	0·410	2·276
		40·5	0·355	2·180
		45·1	0·308	2·091
6·28	3·78	45·1	0·354	2·103
		40·5	0·398	2·183
		35·9	0·458	2·286
		31·0	0·520	2·390
		26·3	0·580	2·490

(ii) 2-Methylpyridine + picric acid in a 2-cm cuvette

$10^5 m_{AH}$	$10^2 m_B$	t/°C	D_{410}	$\log_{10} K_x$
7·30	3·12	26·3	0·396	5·793
		31·0	0·365	5·643
		35·9	0·334	5·509
		40·5	0·298	5·362
		45·1	0·272	5·261
6·98	4·48	26·3	0·520	5·760
		31·0	0·480	5·631
		35·8	0·432	5·481
		40·5	0·385	5·341
		45·1	0·340	5·210
6·47	2·90	26·3	0·365	5·840
		31·0	0·335	5·685
		35·9	0·305	5·546
		40·5	0·275	5·415
		45·1	0·247	5·297
6·19	4·16	26·3	0·482	5·830
		31·0	0·445	5·696
		35·9	0·400	5·543
		40·5	0·358	5·407
		45·1	0·315	5·269
5·69	6·39	26·3	0·620	5·850
		31·0	0·568	5·699
		35·9	0·512	5·545
		40·5	0·460	5·408
		45·1	0·413	5·287
7·67	2·90	26·3	0·378	5·801
		31·0	0·348	5·640
		35·9	0·320	5·508
		40·5	0·287	5·364
		45·2	0·258	5·243
7·03	5·32	26·3	0·607	5·801
		31·0	0·557	5·654
		35·9	0·505	5·510
		40·5	0·455	5·378
		45·1	0·396	5·224
6·49	7·37	26·3	0·710	5·789
		31·0	0·650	5·636
		35·9	0·585	5·480
		40·5	0·529	5·352
		45·1	0·475	5·231
6·65	3·87	45·1	0·302	5·240
		40·5	0·340	5·366
		35·8	0·380	5·500
		31·0	0·417	5·630
		26·3	0·456	5·777
6·47	5·38	26·3	0·570	5·749
		31·0	0·530	5·635
		35·8	0·478	5·492
		40·5	0·429	5·361
		45·1	0·376	5·220
6·24	4·71	26·3	0·528	5·817
		31·0	0·483	5·670
		35·8	0·438	5·532
		40·5	0·390	5·390
		45·1	0·348	5·268

(iii) Tribenzylamine + picric acid in a 1-cm cuvette *

$10^4 m_{AH}$	$10^4 m_B$	t/°C	D_{403}	$\log_{10} K_x$
0·791	0·734	20·5	0·116	4·537
		21·5	0·112	4·534
		26·5	0·086	4·371
		35·3	0·064	4·204
		47·9	0·038	3·926
		59·8	0·026	3·730
2·02	2·26	17·5	0·573	4·549
		21·0	0·528	4·479
		27·0	0·415	4·290
		35·3	0·345	4·164
		47·9	0·228	3·908
		59·8	0·161	3·715
1·10	1·78	20·5	0·306	4·575
		25·0	0·255	4·436
		35·3	0·190	4·241
		48·0	0·125	3·994
		58·8	0·088	3·805

TABLE 2 (*Continued*)

(iv) Dibenzylamine + picric acid in a 1-cm cuvette *

10^4m_{AH}	10^4m_{B}	t/°C	D_{410}	$\log_{10} K_x$
1·10	2·25	18·0	0·748	5·451
		21·3	0·723	5·376
		35·0	0·676	5·265
		48·5	0·588	5·053
		59·0	0·530	4·926
0·437	0·424	22·0	0·173	5·563
		23·0	0·170	5·543
		26·0	0·163	5·497
		35·0	0·147	5·393
		49·4	0·111	5·143
		58·8	0·092	5·001
0·887	1·32	22·0	0·546	5·571
		26·0	0·532	5·528
		35·0	0·490	5·396
		49·4	0·431	5·225
		58·8	0·376	5·065
0·318	0·581	19·0	0·167	5·593
		22·0	0·159	5·531
		35·0	0·136	5·363
		49·4	0·106	5·137
		59·0	0·086	4·976
0·896	0·786	22·0	0·418	5·593
		23·0	0·400	5·520
		35·0	0·371	5·425
		48·6	0·320	5·248
		59·0	0·278	5·101

(v) Mono-n-butylamine + picric acid in a 1 cm cuvette

10^4m_{AH}	10^4m_{B}	t/°C	D_{410}	$\log_{10} K_x$
2·12	2·39	25·0	1·17	5·084
		26·5	1·17	5·086
		30·5	1·10	5·000
		36·0	1·13	5·046
		36·5	1·11	5·026
		49·0	1·09	5·009
		57·5	1·04	4·952
2·63	1·97	19·0	1·25	5·192
		19·5	1·22	5·151
		21·0	1·11	5·035
		33·5	1·08	4·983
		42·3	1·08	4·994
		63·3	1·09	5·037
		73·0	1·01	4·935
0·531	0·394	20·5	0·142	5·183
		26·0	0·107	4·958
		36·0	0·113	5·007
		49·0	0·103	4·947
		60·5	0·084	4·828

(vi) Mono-n-butylamine + 2,4-dinitrophenol in a 1-cm cuvette

10^5m_{AH}	10^2m_{B}	t/°C	D_{410}	$\log_{10} K_x$
6·32	1·30	19·0	0·52	3·375
		20·5	0·50	3·305
		30·0	0·43	3·102
		35·5	0·37	2·943
		47·0	0·25	2·630
		57·0	0·16	2·354
9·73	2·15	19·0	0·91	3·482
		20·5	0·90	3·452
		30·0	0·77	3·103
		35·5	0·70	2·962
		47·0	0·56	2·718
		57·0	0·41	2·464
11·1	1·39	18·0	0·95	3·434
		22·0	0·85	3·233
		24·5	0·79	3·130
		47·0	0·45	2·622
		57·0	0·28	2·324
9·66	1·02	21·1	0·678	3·239
		24·0	0·668	3·218
		29·5	0·587	3·077
		30·0	0·572	3·052
		47·1	0·305	2·583
		57·0	0·180	2·286

(vii) Mono n-butylamine + 2,6-dinitrophenol in a 1-cm cuvette

10^4m_{AH}	10^4m_{B}	t/°C	$D_{442-445}$	$\log_{10} K_x$
1·91	1·98	17·0	0·612	4·479
		25·0	0·391	4·157
		27·5	0·341	4·073
		36·0	0·181	3·719
		50·0	0·053	3·131
		57·5	0·015	2·568
1·91	2·97	19·0	0·670	4·315
		23·0	0·642	4·284
		26·0	0·571	4·199
		35·0	0·310	3·817
		36·5	0·283	3·766
		50·0	0·077	3·123
		57·5	0·028	2·668
2·86	1·98	18·5	0·696	4·341
		19·5	0·749	4·402
		20·5	0·733	4·385
		23·5	0·665	4·308
		35·0	0·320	3·834
		36·5	0·321	3·836
		50·0	0·138	3·400
		57·5	0·098	3·239
3·24	1·98	17·5	0·801	4·386
		22·0	0·647	4·216
		36·5	0·291	3·721
		50·0	0·092	3·150
		57·5	0·042	2·794
2·16	1·98	20·0	0·592	4·378
		21·5	0·542	4·312
		23·0	0·494	4·246
		24·5	0·458	4·195
		35·0	0·220	3·763
		48·0	0·071	3·210
		58·0	0·02	2·642

* See footnote to Table 3.

For each molality of amine and indicator the absorbancy was measured over the temperature range shown in Table 2. The molality of AHB was calculated by the method described by Bayles and Taylor.[1] The equilibrium constants were expressed as mole-fractional dimensionless quantities K_x by multiplying the molal constant by $1000/M$, M being the molar mass of the solvent. Over the experimental range of concentrations and temperature, log K_x is found to be linear function of T^{-1}. Therefore ΔH° is constant and $\Delta C_p{}^\circ = ca.\ 0$.

The thermodynamic quantities were calculated by computer from K_x and from the variation of log K_x with reciprocal temperature by use of the method of least squares. To calculate ΔG° and other thermodynamic quantities we have used $R = 8{\cdot}31$ J mol^{-1} K^{-1}.

The results are shown in Table 3 where the precisions are also shown as probable errors. The magnitude of the experimental scatter in terms of the quoted probable errors can also be seen by comparing the Figure with the tabulated results. In this respect the two systems plotted represent the extremes of errors.

TABLE 3

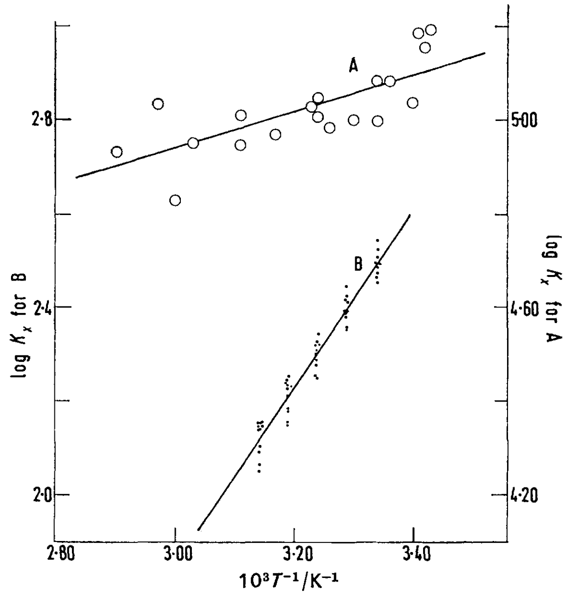
Thermodynamic functions for proton-transfer reactions between amines and indicators

AH	B	pK_a	ΔG°_{298}/kJ mol^{-1}	ΔH°_{298}/kJ mol^{-1}	ΔS°_{298}/J mol^{-1} K^{-1}
Group A					
Picric acid	2-Methoxypyridine	3·06	−14·40 ± 0·04	−38 ± 0·8	−71 ± 3
Picric acid	2-Methylpyridine	5·93	−33·41 ± 0·04	−53 ± 2	−67 ± 8
Picric acid	Tribenzylamine *		−25·31 ± 0·04	−37·7 ± 0·8	−42 ± 3
Picric acid	Dibenzylamine *		−31·44 ± 0·08	−25·8 ± 1	+20 ± 4
Picric acid	Mono-n-butylamine	10·59	−28·95 ± 0·12	−7·1 ± 2·6	+73 ± 8·8
Group B					
2,4-Dinitrophenol	Mono-n-butylamine	3·96	−18·38 ± 0·04	−49·5 ± 1	−105 ± 4
2,6-Dinitrophenol	Mono-n-butylamine	3·71	−23·68 ± 0·08	−75·6 ± 2·0	−174 ± 7·2
Picric acid	Mono-n-butylamine	0·38	−28·95 ± 0·12	−7·1 ± 2·6	+73 ± 8·8

* N. R. McFarlane, M.Sc. Thesis, University College of South Wales and Monmouthshire, Cardiff, 1961.

DISCUSSION

In unpublished work Chetwyn [4] found that the picric acid–n-butylamine and picric acid–dibenzylamine systems had high positive entropies and small negative enthalpies of reaction. We were unable to suggest a satisfactory explanation for this remarkable effect since it had been shown [5] that picric acid is not an associated solute in chlorobenzene. To explain the effect, it is necessary to account for a swing of *ca.* 147 J K^{-1} mol^{-1} positively for these reactions in comparison with the more usual values obtained. It is particularly difficult to explain how a reaction in which two molecules react to produce one can give rise to a positive entropy of reaction.



Graphs of log K_x against 10^3T^{-1} for the systems A, mono-n-butylamine–picric acid and B, 2-methoxypyridine–picric acid in chlorobenzene

We have therefore studied the effect on ΔS° and ΔH° of two kinds of alteration in the molecular situation. These are (*a*) change of proton affinity of the base (*b*) change of the acid strength of the acid, in the acid–base pair as predicted by electronic theory. In previous Parts it has been shown that the normal electronic theories of strength apply satisfactorily in chlorobenzene.

The effect occurs only when one of the stronger bases reacts with one of the stronger acids. The resultant value of ΔG° becomes, of course, an equivocal measure of the proton affinity between the reactants when compared with the values for systems not showing this effect. It is not possible for, *e.g.*, rotational freedom in the ion pair to account for the amount of entropy involved but, as the solutes are solvated before reaction, exclusion of solvent from the vicinity of the hydrogen bond could provide an explanation. Clearly any solvent molecule attached to N or to NH$^+$ will be excluded whatever reactant pair is involved. However, there will be other solvent molecules relatively loosely attached to the reactants, and these solvent molecules, though usually retained after reaction, could be excluded if the reaction bond were abnormally strong and hence presumably short.

Table 3 presents two groupings of the acid–base pairs which have been selected for study to present the gradations in properties required by (*a*) and (*b*) above. Groups A and B each contain a fixed acid and a sequence of bases of strengths which would increase according to electronic theories. Except for the benzylamines for which no pK_a value is available, the pK_a values in water for the amines of Group A do in fact increase. In this group, the positive entropies are found for the systems having the bases of highest strength. Moreover it was found that the monobenzylamine–picric acid system, which should on electronic grounds be expected to be the strongest acid–base pair involving picric acid and a benzylamine, yielded insoluble precipitates making it impossible to determine the equilibrium position. This observation supports the view that the positive entropies of reaction are connected with solvent exclusion following hydrogen-bond formation.

Group B demonstrates that with a fixed base and a sequence of acids of increasing strength, the positive ΔS° values again occur for the system with the highest proton affinity.

The effect, which may be termed ' entropy production

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[4] A. Chetwyn, Ph.D. Thesis, University College, Cardiff, 1958.

[5] J. W. Bayles and A. Chetwyn, *Chem. and Ind.*, 1958, 1204.

by solvent exclusion ' is therefore not a property peculiar to any one acid or base, but is generated in the formation of a hydrogen bond. Therefore when comparisons are made between the strengths of acid–base systems in non-aqueous solution where ion pairs are the result of proton transfer, one must be very careful to ensure that the systems react either all with or all without solvent exclusion. The implications of this and other effects on the definition of acid–base scales in non-aqueous solvents will be examined in a future paper.

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