Antimony Halides as Solvents. Part X.[1] The Lewis Basicity of Amines in Liquid Antimony Trichloride

By **Philip V. Johnson** * and **Edward C. Baughan**, Department of Chemistry and Metallurgy, Royal Military College of Science, Shrivenham, Swindon SN6 8LA

The Lewis basicity of 12 amines has been measured by electrical conductance for the reaction $\mathrm{Am{:}} + 2\mathrm{SbCl_3} \rightleftharpoons \mathrm{Am{:}SbCl_2^+} + \mathrm{SbCl_4^-}$ (A) in liquid antimony trichloride medium at 75 °C. Compared with their pK_a's (proton basicity) in water tertiary amines are stronger bases than primary amines towards the $\mathrm{SbCl_2^+}$ ion. For primary amines the pK_a's are linearly related to the equilibrium constants in equation (A). Octadecylamine appears to form micelles.

PARTS V [2] and VIII [3] showed by conductance and spectral studies respectively that polycyclic aromatic hydrocarbons $\mathrm{R{:}}$ ionise in pure liquid antimony trichloride by the co-ordination reaction (2), the aromatic hydrocarbon $\mathrm{R{:}}$ donating a pair of electrons to the solvent cation $\mathrm{SbCl_2^+}$ from the self-ionisation (1) of the solvent.

$$2\mathrm{SbCl_3} \rightleftharpoons \mathrm{SbCl_2^+} + \mathrm{SbCl_4^-} \quad \text{Self ionisation} \qquad (1)$$

$$\mathrm{R{:}} + \mathrm{SbCl_2^+} \rightleftharpoons \mathrm{R{:}SbCl_2^+} \quad \text{Lewis acid–base reaction} \qquad (2)$$

Similar equilibria also occur for hydrocarbons in strong proton acids like HF,[4] these two processes are linearly related by the equation $\mathrm{p}K = -0{\cdot}27\mathrm{p}K_a + 3{\cdot}1$. It has only recently been realised (i) that for restricted classes of compound this is a general phenomenon,[5] straight-line relationships of the form (3) being found

$$\mathrm{p}K = a\mathrm{p}K_a + b \qquad (3)$$

for many Lewis acids with several classes of base,† and (ii) that moreover, the variation of simple proton-transfer reactions from one solvent to another shows variation of the same formal type, in which cases *a*, the slope, is about unity but *b*, the intercept, varies for different classes of base. Such variation in *b* must occur if the solvents have different dielectric constants [6] and the reactions are also of different charge type,[7] *e.g.* (4) and (5). The intercept also varies

$$\mathrm{NH_3} + \mathrm{H_3O^+} \longrightarrow \mathrm{NH_4^+} + \mathrm{H_2O} \qquad (4)$$

$$\mathrm{AcO^-} + \mathrm{H_3O^+} \longrightarrow \mathrm{AcOH} + \mathrm{H_2O} \qquad (5)$$

in proton-transfers to primary amines compared with tertiary amines where the reactions are of the same charge type.[8] To demonstrate relations like equation (3) it is therefore necessary to study a significant number of bases (or acids) within one class reacting with a single acid (or base) under identical experimental conditions. We have therefore started a programme of study of Lewis basicity of different classes of compound in liquid antimony trichloride. The present paper presents results for 12 amine bases, 8 primary, 2 secondary, and 2 tertiary, and gives equilibrium constants for 6 of them. For such measurements liquid antimony trichloride is peculiarly suitable because (*a*) its high dielectric constant (36·2 at 75 °C),[9] the large size of the ions, and the abnormal mobility of the $\mathrm{SbCl_4^-}$ anion make conductance data easy to interpret;[10] (*b*) many bases are easily soluble; and (*c*) a wide range of basicity can be directly studied. In some cases however the results are 'levelled' in Hantzch's sense since the bases are strong electrolytes.

EXPERIMENTAL

The conductance technique, the handling technique, and the purification of the solvent have been described.[10] All measurements were made at 75 °C. The liquids were added from an Agla micrometer syringe calibrated for each liquid in a nitrogen-filled desiccated dry-box. All solutes were the purest commercially available. The solids were further purified by recrystallisation twice from AnalaR ethanol, and the liquids distilled twice under reduced pressure of dry nitrogen.

RESULTS AND DISCUSSION

The conductance results are in Table 1. The tertiary amines acridine and tribenzylamine and the primary amines pentylamine and cyclohexylamine are all highly ionised and are 1 : 1 strong electrolytes. Successive extrapolation of the data for these electrolytes to zero concentration by use of the theoretical Debye–Hückel–Onsager slope gives equation (6), where $\Lambda_0 = 87$, and 79 is the correct slope for this Λ_0. Aniline, *p*-toluidine, *p*-nitroaniline, *m*-nitroaniline, diphenylamine, and indole are 1 : 1 weak electrolytes and the equilibrium constants can be found. The method was essentially similar to

---

† In our case since we have to work at 75 °C and not 25 °C it might be considered better to express the equation in the form $\Delta G_L^\circ = a\Delta G_{H^+}^\circ + b$ where ΔG_L° and $\Delta G_{H^+}^\circ$ are the free energy changes for the Lewis acid and Brønsted acid reaction respectively (see Appendix).

[1] Part IX, M. Hiscock and G. B. Porter, *J.C.S. Perkin II*, 1972, 79.

[2] Part V, P. V. Johnson and E. C. Baughan, *J. Chem. Soc.* (*A*), 1969, 2686.

[3] Part VIII, P. V. Johnson, *J. Chem. Soc.* (*A*), 1971, 2856.

[4] E. L. Mackor, A. Hofstra, and J. H. Van der Waals, *Trans. Faraday Soc.*, 1965, **54**, 66.

[5] D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, 1969, **69**, 251.

[6] J. N. Brönsted, A. Delbanco, and A. Tovborg-Jensen, *Z. phys. Chem.*, 1934, **169**, *A*, 361.

[7] J. N. Brönsted, *Z. phys. Chem.*, 1934, **169**, *A*, 52.

[8] A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1949, 1293.

[9] L. Patzitka and R. Bertrum, *J. Electroanalyt. Chem.*, 1970, **28**, 119.

[10] J. R. Atkinson, T. P. Jones, and E. C. Baughan, *J. Chem. Soc.*, 1964, 5808.

that outlined in ref. 2 but equation (6) was used to correct for interionic forces, and differs slightly from the equation used previously since we now accept the recent value for the dielectric constant at 75 °C.[9]

$$\Lambda = 87 - 79\sqrt{C} \qquad (6)$$

The thermodynamic equilibrium constants were calculated by assuming the same activity coefficients as found for triphenylmethyl chloride.[11] The self-conductivity of the solvent was subtracted from the observed conductance at each concentration: this correction which is very small for these electrolytes has been discussed previously.[10,12]

TABLE 1

K = Specific conductance/ohm^{-1} cm^{-1}, C = molar concentration

Aniline							
10^6K	9·70	1070	1490	1910	2450	2860	3230
10^3C	0	18·4	33·7	46·0	63·0	77·5	90·1
Λ		58·4	44·2	41·8	38·9	36·8	35·8
p-Toluidine							
10^6K	7·32	975	1370	1900	2500	3430	
10^3C	0	17·5	29·5	49·4	77·9	126	
Λ		55·7	46·5	38·5	32·1	27·2	
n-Pentylamine							
10^6K	9·28	598	1070	1510	1940	2810	
10^3C	0	7·10	14·3	20·8	27·8	40·4	
Λ		84·2	75·1	72·1	70·0	69·4	
Cyclohexylamine							
10^6K	4·64	829	1420	2010	2610	3170	3740
10^3C	0	10·6	20·7	31·0	42·2	51·6	61·3
Λ	78·4	68·4	64·9	62·0	61·5	61·0	
m-Nitroaniline							
10^6K	7·00	424	472	517	602	669	
10^3C	0	4·98	7·69	12·7	18·3	27·2	
Λ		85·1	61·4	40·8	33·0	24·6	
p-Nitroaniline							
10^6K	7·34	725	1180	1470	1800	2100	
10^3C	0	9·11	27·4	58·6	90·8	119	
Λ		79·6	43·1	25·1	19·8	17·6	
Acridine							
10^6K	10·8	149	173	581	863	1370	2020
10^3C	0	1·53	1·82	6·40	9·96	18·2	30·0
Λ		97·4	95·0	90·8	86·6	75·1	67·3
Indole							
10^6K	10·9	745	907	1150	1410	1650	
10^3C	0	9·67	21·7	36·0	57·3	87·2	
Λ		77·0	41·8	31·9	24·7	18·9	
Tribenzylamine							
10^6K	5·60	139	252	470	715	991	1320
10^3C	0	1·54	2·91	5·73	8·72	12·2	16·6
Λ		89·9	86·6	82·1	82·0	81·3	79·5
Octylamine							
10^6K	9·43	495	804	1030	1240	1680	
10^3C	0	5·10	10·1	15·4	20·2	30·0	
Λ		97·1	79·9	67·3	61·7	55·9	
Octadecylamine							
10^6K	6·91	43·3	207	280	356	572	807
10^3C	0	0·43	3·50	4·88	6·00	9·62	13·8
Λ		101	59·0	57·5	59·2	59·5	58·3
10^6K	1020	1270					
10^3C	17·8	22·5					
Λ	57·1	56·5					

The thermodynamic equilibrium constant K_{th} for reaction (7) is given by equation (8), where f = mean

$$\mathrm{Am}{:} + 2\mathrm{SbCl_3} \rightleftharpoons \mathrm{Am{:}SbCl_2^+} + \mathrm{SbCl_4^-} \qquad (7)$$

$$K_{th} = \frac{f^2[\mathrm{Am{:}SbCl_2^+}][\mathrm{SbCl_4^-}]}{\{C - [\mathrm{Am{:}SbCl_2^+}]\}} \qquad (8)$$

ionic activity coefficient and C = stoicheiometric concentration of added amine. In Table 2 we present the thermodynamic equilibrium constants as pK's (*i.e.*, $-\log K_{th}$) together with the pK_a [13,14] (the acid dissociation exponent of the conjugate acid cation AmH$^+$).

TABLE 2

Amine	Class [a]	$-\log K_{th}$ [=pK]	pK_a
Amylamine	P	S.e.	10·44 [b]
Cyclohexylamine	P	S.e.	10·6
p-Toluidine	P	1·80	5·1
Aniline	P	1·67	4·6
p-Nitroaniline	P	2·29	1·0
m-Nitroaniline	P	2·47	2·50
Diphenylamine	S	2·64	0·78
Indole	S	2·23	−2·4 [c]
Acridine	T	S.e.	5·6
Tribenzylamine	T	S.e.	9·2
Octylamine	P	*d*	
Octadecylamine	P	*d*	

[a] P = Primary, S = secondary, T = tertiary. [b] C. L. Ligry, *Rec. Trav. chim.*, 1960, **79**, 731. [c] G. Berti, *Gazzetta*, 1961, **91**, 571. [d] Micelle formation.

Primary and Tertiary Amines.—Comparison of the tertiary amines with the primaries shows that the tertiary amines are stronger Lewis bases towards SbCl$_2^+$ than are primary amines of the same pK_a by at least one pK unit. Unfortunately a quantitative measure of this effect cannot be made as the tertiary amines are 'levelled' as strong electrolytes. This difference between primary and tertiary amines is also shown in their reactions as Lewis bases towards the silver cation Ag$^+$ [15] and in other reactions mentioned in the Introduction.[8,16] The Lewis base strengths of primary amines reacting with covalent metal halide neutral molecules usually show linear relations [equation (3)] with a slope between 0·7 and 1·0. The base strengths here presented involved a cation (SbCl$_2^+$) derived from a covalent metal halide (SbCl$_3$). These also show a linear dependence on pK_a with equation pK = $-0{\cdot}20$pK_a + 2·7. But two other remarkable features appear.

---

[11] G. B. Porter and E. C. Baughan, *J. Chem. Soc.*, 1958, 744.

[12] A. G. Davies and E. C. Baughan, *J. Chem. Soc.*, 1961, 1711.

[13] J. F. King, in 'Elucidation of Structures by Physical Chemistry Methods,' ed. K. W. Bentley, Wiley, New York, 1963, ch. 6.

[14] 'Stability Constants,' Chemical Society Special Publication No. 17, 1964.

[15] R. J. Bruehlman and F. H. Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

[16] R. P. Bell, 'The Proton in Chemistry,' Methuen, London, 1959, ch. 4.

First the slope a is much less (0·20 instead of 0·7—1·0 for the neutral Lewis acids); a similarly low slope (0·25) is shown by primary amines with the silver cation Ag^+. The low slope was thought to be due to the larger size of the silver cation than the hydrogen ion and this is supported here, the larger $SbCl_2^+$ ion giving an even smaller slope. Copper complexes with amines also show this effect.[15] Secondly, this straight line has similar slope and intercept to that for the polycyclic aromatic hydrocarbons though there is some uncertainty in this (see Appendix). Now silver cations also coordinate with aromatic hydrocarbons [17] but it is unreasonable to compare the argentation equilibria for aromatic hydrocarbons and amines in this way since the two sets of results were determined under different experimental conditions. Indeed in Part V, from measurements for anthracene, phenanthrene, and benz[*a*]anthracene, we stated that argentation equilibria of hydrocarbons showed no correlation with protonation equilibria. However, if the argentation equilibrium constants are plotted directly against the $SbCl_2^+$ equilibrium constants for these three hydrocarbons and benz[*a*]pyrene ($-\log K_{th} = 3{\cdot}02$) [18] which has now been determined, there is a straight-line relationship within the stated experimental error of the argentation equilibrium constants. The equation is (9), the very small slope being consistent with the fact that $SbCl_2^+$ forms a σ-bond and Ag^+ a π-bond; the silver cation being further away in the π-bond is very insensitive to changes in basicity even compared with $SbCl_2^+$. It is perhaps surprising to find a linear relationship at all.

$$\log K_{Ag^+} = 0{\cdot}07 \log K_{SbCl_2^+} + 0{\cdot}43 \qquad (9)$$

Diphenylamine and Indole.—Diphenylamine proved to be extremely sensitive to oxygen in this solvent. On its admission a reaction occurred corresponding to the formation of a 1 : 1 strong electrolyte, the solution becoming intensely dark blue,[19] presumably owing to quantitative formation of a free-radical cation by oxidation. However in our normal method of working the blue colour was hardly visible and equilibrium constants based on two separate determinations gave $K_{th} = 1{\cdot}9 \times 10^{-3}$ and $2{\cdot}9 \times 10^{-3}$ respectively. There is thus a little uncertainty in this K_{th}. Indole was a weak base, but it is more basic in antimony trichloride than expected from its pK_a by *ca.* one pK unit compared with primary amines. This may be a special case, for protonation occurs at the position of highest electron density which is the reactive 3-position and not the nitrogen atom.

Octylamine and Octadecylamine.—Conductance runs for these amines are also in Table 1. Octadecylamine shows complete ionisation at low concentration, as might be expected from the results of pentylamine and cyclohexylamine. At higher concentrations however the Λ's are much less (*ca.* 58) and are independent of concentration. This behaviour has been explained in the case of some alkyl chloride solutes [11] by the ionisation scheme (10) with the equilibrium completely over to

$$2RCl + SbCl_3 \rightleftharpoons R_2Cl^+ + SbCl_4^- \qquad (10)$$

the right. But the maximum value of Λ in this mode can only be $\frac{1}{2} \times \Lambda_0$ (where $\Lambda_0 = ca.\ 90$) and not as high as 58, so this mode of ionisation cannot operate here. However this behaviour is very similar to the behaviour of these amine hydrochlorides in aqueous solution [20] where the phenomenon is known to be due to micelle formation. Octylamine shows this phenomenon as well, though it is much less pronounced. These observations were not pursued further.

APPENDIX

As antimony trichloride solidifies at 73·17 °C we cannot work at 25 °C and in comparing our equilibrium constants at 75 °C with their pK_a's in aqueous solution at 25 °C we must assess the likely change in pK between these two temperatures. For anilinium and *o*-chloroanilinium the entropy changes of ionisation are small and the heat-capacity changes zero and the differences in their equilibrium constants are almost entirely due to different heats of ionisation.[21] Therefore $T \ln K$ is constant rather than $\ln K$ itself. It is perhaps more appropriate to compare free-energy changes ($\propto T \ln K$) rather than compare the equilibrium constants themselves. If this is done the correlation still holds but the slope is $-0{\cdot}17$ instead of $-0{\cdot}20$. For the aromatic hydrocarbons the pK_a's are inferred from their basicity in HF at 0 °C; nothing is known about their variation with temperature. But for the aromatic hydrocarbons the effect of temperature on pK_a should be similar to that for primary amines since (*a*) the attachment of the proton and carbon is a typical covalent bond (spectroscopic evidence [22]), and (*b*) the centres of attachment, carbon and nitrogen respectively, have about the same radii and hence the Born-charging effects should be about the same. Hence in this case we should also compare free energies ($\propto T \ln K$) rather than equilibrium constants and the slope becomes $-0{\cdot}29$ instead of $-0{\cdot}27$.

[3/733 *Received, 6th April, 1973*]

---

[17] R. E. Kofahl and H. J. Lucas, *J. Amer. Chem. Soc.*, 1954, **76**, 3931.

[18] P. V. Johnson, Ph.D. Thesis, Council for National Academic Awards, London, 1970.

[19] D. Bauer and J. P. Beck, *Coll. Czech. Chem. Comm.*, 1971, **36**, 940.

[20] A. M. Schwartz and J. W. Perry, 'Surface Active Agents,' Interscience, New York, 1949, p. 295.

[21] R. P. Bell, 'The Proton in Chemistry,' Methuen, London, 1959, p. 65.

[22] C. MacLean, J. H. van der Waals, and E. L. Mackor, *Mol. Phys.*, 1958, **1**, 247.