Complex-ion Formation. Part III. The Entropies of Reaction of the Silver and Hydrogen Ions with Some Aliphatic Amines.*

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The entropies of reaction of the methylamines and ethylamines with the silver ion and of the ethylamines with the hydrogen ion have been measured at 25° in aqueous solution. The different orders of base strength observed with the two acceptor ions find some explanation in the entropies of reaction.

When the base strengths of amines are considered with reference to the silver and the hydrogen ion, although, in general, there is a close correlation between the orders, yet there are several exceptions. For instance, with reference to the hydrogen ion we have the orders of decreasing strength: $NHMe_2 > NH_2Me > NMe_3 > NH_3$; $NHEt_2 > NH_2Et > NEt_3 > NH_3$; while with the silver ion the order is $NH_3 > NH_2Me > NMe_3$; $NH_2Et > NH_3 > NHEt_2 > NEt_3$. It appears that steric effects may play an important part, indicated from the work of Brown and his co-workers (*J. Amer. Chem. Soc.*, 1945, **67**, 374, 378, 1452, 1767; 1948, **70**, 2802), and these effects should be demonstrated in the entropies of reaction.

Measurement of the entropy of reaction of ammonia with the silver ion has been described earlier (*J.*, 1952, 2023), and Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, **35**, 1380) reported entropies of reaction of the hydrogen ion with ammonia and the methylamines.

In the present investigation the entropies of reaction of the ethylamines with the hydrogen ion have been obtained from measurements of the dissociation constants from 20° to 45°. The heats of reaction of the silver ion with methyl-, dimethyl-, ethyl-, and diethyl-amine were obtained by direct calorimetric measurement, and the free energies of formation of these complexes were obtained from simple concentration cells. In these cell measurements, the silver concentration was between 0·01 and 0·001M. In calculating the formation constants it was assumed that the activity coefficients were identical with those of silver nitrate at the same concentrations. Values of activity coefficients were taken from McInnes (*Chem. Reviews*, 1936, **18**, 341).

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EXPERIMENTAL

The heats of reaction of the methylamines and ethylamines with silver nitrate were measured in the calorimeters already described (*J.*, 1952, **2023**). In all cases, 10 c.c. of M-silver nitrate were added to 100 c.c. of M-amine, and corrections for heats of dilution were made. The values of the heats of reaction are given in Table 5.

The free energies of formation of the silver complexes were obtained from silver-concentration cells with ammonium nitrate bridges. The constants obtained were, in comparable cases, in excellent agreement with those of Bjerrum (*Chem. Reviews*, 1950, **46**, 381). The entropies of reaction of the ethylamines with the hydroxonium ion were calculated from the temperature coefficients of the dissociation constants of the alkylammonium ions. Normally, in precise electrometric measurement of dissociation constants of acids and bases, a silver–silver chloride electrode is used with the hydrogen electrode to avoid junction potentials. However, the use of the silver chloride electrode is not desirable in cells containing a highly complexing amine, and the hydrogen electrode was used with a calomel electrode and a salt bridge. To attempt to minimise junction potentials Hitchcock and Taylor's method (*J. Amer. Chem. Soc.*, 1937, **59**, 1812) was used (see also Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1950). In this method the potential of the calomel electrode is redetermined so that it will give true dissociation constants at infinite dilution. In the present case the electrode was standardised by using the dissociation constant of ammonia determined by Everett and Wynne-Jones (*Proc. Roy. Soc.*, 1938, **169**, 190). A value of 0·2445 v was used for this potential with the normal temperature coefficients of the electrode (see Table 1).

All cells were of the type:

$$H_2(Pt) \mid \text{Amine, Amine } H^+ \mid \text{KCl satd.} \mid \text{KCl satd., } Hg_2Cl_2 \mid Hg$$

The hydrogen electrode was a platinum foil heavily coated with platinum black, and cylinder hydrogen was carefully purified by passing it over palladised copper in a tube furnace and saturated with water and amine at the same concentration as in the cell. All potentials were corrected to normal atmospheric pressure. Amines were purified by recrystallisation of the hydrochlorides, and solutions of the free amines were prepared by steam-distillation from alkali.

The following Tables summarise the results. The values for triethylamine are less accurate than those for other amines. With this amine, potentials tended to drift, and errors of 1—2 mv are possible. In the Tables, $E - E_0$ refers to the measured potential minus the standard calomel electrode potential; pK is the negative logarithm of the dissociation constant, and pK_0

TABLE 1. *Dissociation constant of the ammonium ion at* 25°: $E_0 = 0·2445$ v.

$[NH_4^+] = 0·0173$; $[NH_4OH] = 0·0173$.

$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK
0·5518	0·14	9·54	0·5468	0·06	9·39	0·5425	0·00	9·25
0·5485	0·10	9·45	0·5440	0·02	9·30		Mean pK_0	9·22

TABLE 2. *Dissociation constant of the ethylammonium ion.*

At 20°.					At 25°.				
$E - E_0$	$[NH_3Et^+]$	$[NH_2Et]$	[KCl]	pK	$E - E_0$	$[NH_3Et^+]$	$[NH_2Et]$	[KCl]	pK
0·6317	0·0349	0·0349	0·14	11·06	0·6349	0·0349	0·0349	0·14	10·95
0·6317	—	—	0·10	11·00	0·6343	—	—	0·10	10·89
0·6307	0·0241	0·0241	0·08	10·97	0·6319	0·0241	0·0241	0·08	10·85
0·6280	—	—	0·04	10·90	0·6300	—	—	0·04	10·79
0·6265	—	—	0·00	10·83	0·6291	—	—	0·00	10·71
			Mean pK_0	10·79				Mean pK_0	10·67
At 35°.					At 45°.				
0·6399	0·0349	0·0349	0·14	10·69	0·6347	0·0349	0·0349	0·14	10·42
0·6384	—	—	0·10	10·64	0·6414	—	—	0·10	10·36
0·6366	0·0241	0·0241	0·08	10·59	0·6409	0·0241	0·0241	0·08	10·33
0·6353	—	—	0·04	10·50	0·6399	—	—	0·04	10·27
0·6333	—	—	0·00	10·44	0·6377	—	—	0·00	10·18
			Mean pK_0	10·40				Mean pK_0	10·14

TABLE 3. *Dissociation constant of the diethylammonium ion:* $[NH_2Et_2^+] = 0{\cdot}0192$; $[NHEt_2] = 0{\cdot}0192$.

At 20°.			At 25°.			At 35°.			At 45°.		
$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK
0·6306	0·14	11·30	0·6491	0·14	11·18	0·6574	0·14	10·97	0·6494	0·14	10·70
0·6378	0·10	11·27	0·6488	0·10	11·15	0·6568	0·10	10·92	0·6486	0·10	10·66
0·6338	0·04	11·17	0·6475	0·04	11·08	0·6546	0·04	10·84	0·6469	0·04	10·58
0·6332	0·02	11·17	0·6458	0·02	11·03	0·6544	0·02	10·81	0·6468	0·02	10·55
0·6329	0·00	11·14	0·6466	0·00	11·02	0·6545	0·00	10·97	0·6470	0·00	10·53
	Mean pK_0	11·11		Mean pK_0	10·98		Mean pK_0	10·76		Mean pK_0	10·50

is this value graphically extrapolated to zero ionic strength. Potassium chloride was added to most cells to vary the ionic strength.

DISCUSSION

Table 5 summarises the thermodynamic data calculated from the present results along with those of Everett and Wynne-Jones (*loc. cit.*). Free energies and heats are listed only to an accuracy consistent with experimental errors and are certainly no more accurate than this, as pK values are accurate to only $\pm 0{\cdot}01$. The entropies are probably only accurate to the nearest unit. In calculating the heats of reaction from the temperature coefficients it was assumed that log K is a linear function of $1/T$ and the data were fitted by least squares.

In Table 6 are summarised the formation constants of the various species determined in the present investigation along with those recently determined by other workers. It will be noticed that different workers seldom agree better than to approximately 0·1 in

TABLE 4. *Dissociation constant of the triethylammonium ion:* $[NHEt_3^+] = 0{\cdot}0211$; $[NEt_3] = 00211$.

At 20°.			At 25°.			At 35°.			At 45°.		
$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK	$E - E_0$	[KCl]	pK
0·619	0·14	11·03	0·634	0·14	10·93	0·641	0·14	10·70	0·634	0·14	10·46
0·619	0·10	10·99	0·634	0·10	10·89	0·640	0·10	10·65	0·634	0·10	10·42
0·615	0·06	10·90	0·629	0·06	10·78	0·637	0·06	10·58	0·630	0·06	10·33
0·614	0·02	10·84	0·630	0·02	10·76	0·637	0·02	10·53	0·630	0·02	10·29
0·615	0·01	10·83	0·629	0·01	10·72	0·635	0·01	10·49	0·628	0·01	10·24
	Mean pK_0	10·78		Mean pK_0	10·67		Mean pK_0	10·45		Mean pK_0	10·21

TABLE 5. *Thermodynamic functions:* 25°.

A. Reaction: Amine + H^+ = Amine H^+.

Amine	$-\Delta G$ (kcal.)	$-\Delta H$ (kcal.)	ΔS (cal./mole)
NH_3 [a]	12·562	12·400	0·54
NH_2Me [a]	14·484	13·092	4·7
$NHMe_2$ [a]	14·721	11·880	9·5
NMe_3 [a]	13·384	8·828	15·3
NH_2Et	14·55	11·15	11·4
$NHEt_2$	14·97	10·3	15·7
NEt_3	14·55	9·7	16·3

B. Reaction: 2 Amine + Ag^+ = Ag $Amine_2^+$.

Amine	$-\Delta G$ (kcal.)	$-\Delta H$ (kcal.)	ΔS (cal./mole)
NH_3	9·85	13·5	−12·2
NH_2Me	9·26	11·5	− 7·5
$NHMe_2$	7·32	9·7	− 8·0
NH_2Et	9·98	13·0	−10·1
$NHEt_2$	8·70	10·65	− 6·5

[a] Everett and Wynne-Jones (*loc. cit.*).

TABLE 6.

	Temp.	Present result log K_H	Other workers log K_H
NH_2Et ...	18°	10·83	10·60 [a]
	25	10·67	11·11,[b] 10·81 [c]
$NHEt_2$ ...	18	11·18	11·16 [a]
	25	10·98	11·11 [b]
	30	10·87	10·96 [f]
NEt_3 ...	18	10·83	10·81 [a]
	25	10·67	10·80,[b] 10·77 [d]

	Temp.	Present result log K_{Ag}	Other workers log K_{Ag}
NH_3 ...	25°	7·22	7·23 [e]
NH_2Me	25	6·79	6·68 [d]
$NHMe_2$	25	5·37	5·30 (18°) [e]
NH_2Et...	25	7·32	7·30 (30°) [c]
$NHEt_2$...	25	6·38	6·20 (30°) [f]

[a] Britton and Williams, *J.*, 1935, 796; 1936, 96. [b] Akerlof, *J. Amer. Chem. Soc.*, 1928, **50**, 733. [c] Bruehlman and Verhoek, *ibid.*, 1948, **70**, 1401 (0·5M-KNO_3). [d] Bjerrum, *Chem. Reviews*, 1950, *loc. cit.* (0·4M-amine nitrate). [e] Bjerrum, "Metal Ammine Formation" (corrected for salt). [f] Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334 (0·5M-KNO_3).

pK. In the case of the amine ions the present method should be capable of better results than others as these are the only results calculated for zero ionic strength. In the case of the silver results the agreement between present results for ammonia corrected for activities and measured at low ionic strength and those of Bjerrum corrected for salt effects is very good. Other values are not immediately comparable owing to salt concentrations and the different temperatures used.

In all cases of proton amination the entropy of reaction is positive. Presumably, this effect is due to the smaller amount of hydration around the larger cations which will also be less polar. With increasing complexity of the amine the entropy of protonation becomes more positive, and this, in turn, should increase the stability of the ammonium ion. There are no obvious structural factors operating in these processes which account for the change in sign of the entropies of reaction in the two series. In general, we must suppose that the entropy of hydration of the hydroxonium ion is greater than that of the ammonium ion, while the same effect is not so pronounced when the silver aquo-cation is compared with the ammino-cation. This is not surprising, as the entropy of hydration is a function of size, and in the case of the small hydroxonium and ammonium ions, small differences will lead to large differences in entropy of hydration. With the larger complex ions of silver, small changes will have less effect, as these cations will have smaller entropies of hydration in the first place.

When the base strengths are considered, it is apparent from the data of Table 5 that in a series such as the methylamines, the heat-content term has the major effect in decreasing the strength of a base such as trimethylamine.

If the inductive effect was the most important influence trimethylamine should be the strongest base. The small value of ΔH for this base must arise very largely from repulsions introduced when rehybridisation necessary to form the more or less tetrahedral ammonium-type ion occurs. Rehybridisation must tend to crowd the methyl groups together. Such effects appear less pronounced when the chain lengthens in the ethylamines, for in such a group the polarity will be more widely spread. To some extent the same factors appear to influence combination with the silver ion but, as would be expected, the different size of the final grouping causes a different gradation in the position of appearance of such effects. It appears from the present results that perfect correlations between orders of base strength are not to be expected, as Brown *et al.* have already demonstrated so clearly.

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