181. *Electrometric Studies of the Precipitation of Hydroxides. Part XIII. The Constitution of Aqueous Solutions of Silver Oxide in Ammonia, Mono-, Di-, and Tri-methylamine and -ethylamine, Pyridine and Ethylenediamine ; with a Note on the Dissociation Constants of the Amines.*

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COMPLEX silver–ammonia salts, $Ag(NH_3)_2X$, are formed in solution when silver salts, either soluble or insoluble, react with ammonia. They are not visibly decomposed on the addition of alkali, and the p_H values then set up indicate that little, if any, reaction can have taken place. It would appear, therefore, that the complex salts are those of strong bases, and Britton and Wilson (J., **1933**, **1050**) have already shown that the strong complex base, $Ag(NH_3)_2OH$, is actually formed when silver oxide is dissolved in ammonia. In the present work, we have studied the nature of the bases formed when silver oxide is dissolved in aqueous solutions of the bases specified in the title, in the hope that we might correlate the strengths of these bases with their tendencies to form co-ordinate linkages with silver. For this purpose, we employed both conductometric and potentiometric methods, and carried out a series of solubility determinations.

EXPERIMENTAL.

I. *Dissociation Constants of the Amines.*—As the dissociation constants recorded in the literature were, with one exception, obtained by methods other than potentiometric, it was considered advisable to redetermine them by means of the glass electrode—this electrode providing the only means of studying the variations in hydrogen-ion concentration during the neutralisation of the amine solutions of silver oxide. For this purpose, a series of dilute solutions of the bases were titrated with nitric acid at 18°, the glass-electrode system described by Morton (*J. Sci. Instr.*, 1930, **7**, 187) and the valve circuit introduced by Harrison (J., 1930, 1530) being used.

Table I records the p_H values obtained at different stages of typical titrations, and also the p_K values to which they correspond. The dissociation constants given in the last column are of the same order of magnitude as those obtained by other methods (see Landolt–Börnstein, "Physikalisch-Chemische Tabellen"). For instance, Bredig's values at 25° are: for methylamine, $5{\cdot}0 \times 10^{-4}$; dimethylamine, $7{\cdot}4 \times 10^{-4}$; trimethylamine, $7{\cdot}4 \times 10^{-5}$; diethylamine, $1{\cdot}26 \times 10^{-3}$; triethylamine, $6{\cdot}4 \times 10^{-4}$; from conductivity determinations. Harned and Owen (*J. Amer. Chem. Soc.*, 1930, **52**, 5090), however, obtained $4{\cdot}38 \times 10^{-4}$ at 25° for methylamine by an *E.M.F.* method, whereas our value at 18° is $3{\cdot}62 \times 10^{-4}$.

TABLE I.

Solutions titrated.	Titrant HNO_3, *N*.		p_H on addition of HNO_3, c.c. 10.	15.	20.	25.	Mean p_K.	*K*
0·04488*M*-NH_2Me (50 c.c.) ...	0·0660	p_H	11·11	10·87	10·62	10·32		
		p_K	3·47	3·43	3·43	3·44	3·44	$3{\cdot}62 \times 10^{-4}$
0·04118*M*-NH_2Et (100 c.c.) ...	0·1420	p_H	11·08	10·82	10·50	10·05		
		p_K	3·40	3·36	3·39	3·45	3·40	$3{\cdot}97 \times 10^{-4}$
0·04910*M*-NH_2Ph (50 c.c.) ...	0·05644	p_H	5·10	4·83	4·60	4·40		
		p_K	9·55	9·57	9·58	9·59	9·57	$2{\cdot}68 \times 10^{-10}$
0·05272*M*-C_5H_5N (50 c.c.) ...	0·05644	p_H	5·52	5·25	4·95	4·62		
		p_K	8·97	8·96	8·98	8·98	8·97	$1{\cdot}07 \times 10^{-9}$
0·04256*M*-$NHMe_2$ (50 c.c.) ...	0·0560	p_H	11·50	11·27	11·05	10·82		
		p_K	3·03	3·06	3·06	3·07	3·05	$8{\cdot}92 \times 10^{-4}$
0·03810*M*-$NHEt_2$ (50 c.c.) ...	0·0560	p_H	11·63	11·40	11·15	10·84		
		p_K	2·81	2·82	2·83	2·86	2·84	$1{\cdot}45 \times 10^{-3}$
0·04080*M*-NMe_3 (50 c.c.)	0·0560	p_H	10·45	10·19	9·97	9·71		
		p_K	4·23	4·23	4·20	4·21	4·21	$6{\cdot}15 \times 10^{-5}$
0·04610*M*-NEt_3 (50 c.c.)	0·0560	p_H	11·49	11·25	11·05	10·87		
		p_K	3·15	3·22	3·20	3·17	3·18	$6{\cdot}53 \times 10^{-4}$

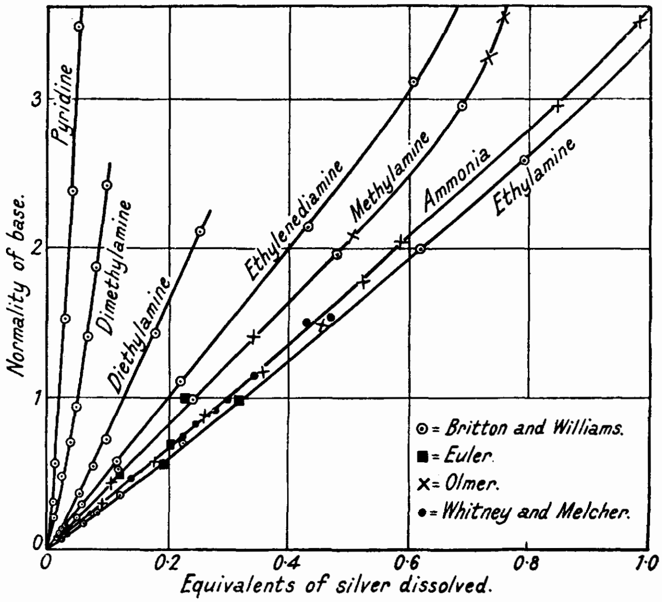
Bredig (*Z. physikal. Chem.*, 1894, **13**, 294) found the first dissociation constant of ethylenediamine at 25° to be $8{\cdot}5 \times 10^{-5}$, but the second dissociation constant has not hitherto been determined. The following data were obtained from a glass electro-titration of **50** c.c. of $0{\cdot}0451M$-ethylenediamine with $0{\cdot}1709N$-nitric acid at 18° :

HNO_3 added, c.c.	4·0	7·0	10·0	16·0	19·0	22·0
p_H	10·58	10·17	9·74	7·80	7·32	6·91
$p_{K_{b_1}}$	3·95	3·94	3·94	—	—	—
$p_{K_{b_2}}$	—	—	—	6·94	6·94	6·96

Hence $K_{b_1} = 1{\cdot}14 \times 10^{-4}$ and $K_{b_2} = 1{\cdot}13 \times 10^{-7}$.

II. *Solubility of Silver Oxide in Aqueous Solutions of Ammonia and Amines.*—As the solubility in ammonia has been thoroughly investigated by several workers (Whitney and Melcher, *J. Amer. Chem. Soc.*, 1903, **25**, 87; Euler, *Ber.*, 1903, **36**, 1854; Olmer, *Bull. Soc. chim.*, 1924, **35**, 333), no further determinations have been made. Their results, which are plotted in Fig. 1, show that the amount of silver oxide dissolved is almost directly proportional to the concentration of ammonia.

FIG. 1.



A few solubility determinations of silver oxide in aqueous methylamine have been made by Olmer (*loc. cit.*) and Euler (*Ber.*, 1903, **36**, 2878).

Table II gives the results of our solubility determinations at 15° in mono-, di-, and trimethylamine and -ethylamine, pyridine, and ethylenediamine solutions over a wide range of concentrations. The results, which are plotted in Fig. 1, yield straight lines except for the section of the methylamine curve above $2N$. Attempts to measure the solubility in aqueous aniline failed owing to the oxidation which occurred.

As the solubility of silver oxide is greatly enhanced by the presence of any free acid radical left in combination with it, every precaution was taken to ensure that the silver oxide used was quite pure. It was prepared by precipitation from dilute silver nitrate solution with the stoicheiometrical amount of sodium hydroxide, washed several times with hot water until free from electrolytes, and then filtered. In case drying should cause it to lose its aptitude to dissolve, it was kept in the moist condition in a light-proof bottle. As the solutions appear to be susceptible to light, saturation was carried out in blackened bottles which were mechanically shaken at 15° until equilibrium was reached.

The silver-ion concentrations of many of these solutions were determined by means of a silver electrode, which had been covered with a crystalline electro-deposit of silver. When immersed in $0{\cdot}1N$-silver nitrate solution and connected through a " salt-bridge " of saturated

TABLE II.

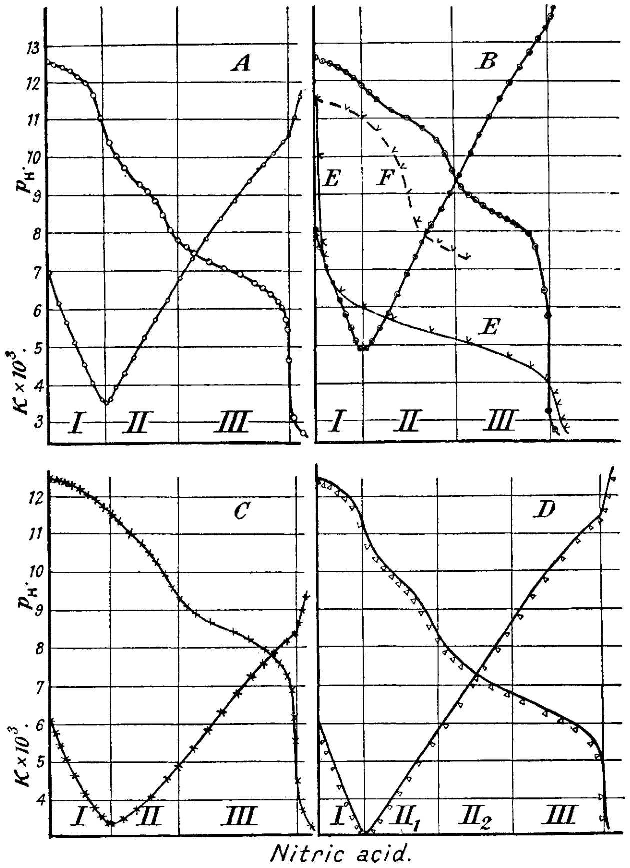
Solubility of Silver Oxide in Aqueous Solutions of Organic Bases at 15°.

Ammonia.									
NH_3, *N*	0·1	0·5	1·0	1·5	2·0	3·0			
Ag_2O, *N*	0·031	0·150	0·299	0·445	0·590	0·865			
K_{I} (sol.) $\times 10^8$	2·00	2·34	2·41	2·49	2·58	2·83	Mean 2·44		
Methylamine.									
NH_2Me, *N*	0·0403	0·0806	0·1007	0·2014	0·5035	0·9933	1·7613	2·9611	
Ag_2O, *N*	0·00919	0·01882	0·02338	0·04715	0·1150	0·2387	0·4107	0·6802	
E.M.F. (16°)	0·178	0·163	0·157	0·142	0·121	—	—	—	
$-\log [Ag^{\cdot}]$	5·92	6·18	6·28	6·54	6·91	—	—	—	
$K_{\mathrm{I}} \times 10^8$	6·03	6·52	6·65	6·97	8·02	Mean 6·84			
K_{I} (sol.) $\times 10^8$	6·52	6·92	7·08	6·87	7·56	6·35	6·67	7·55	Mean 6·94
Ethylamine.									
NH_2Et, *N*	0·07253	0·1793	0·2420	0·2500	0·3623	0·7106	2·000	2·5943	
Ag_2O, *N*	0·2331	0·05684	0·07337	0·0798	0·1169	0·2211	0·6200	0·7926	
E.M.F. (16°)	0·159	—	0·131	—	0·127	—	—	—	
$-\log [Ag^{\cdot}]$	6·24	—	6·75	—	6·81	—	—	—	
$K_{\mathrm{I}} \times 10^8$	1·78	—	2·20	—	2·40	Mean 2·13			
K_{I} (sol.) $\times 10^8$	1·65	1·77	2·31	1·72	1·61	1·96	2·00	2·15	Mean 1·90
Pyridine.									
C_5H_5N, *N*	0·3020	0·5612	1·5383	2·389	3·489				
Ag_2O, *N*	0·0060	0·0108	0·0275	0·03905	0·0546				
K_{I} (sol.) $\times 10^5$	3·11	3·24	3·87	4·67	5·11	Mean 4·0			
Ethylenediamine.									
$C_2H_8N_2$, *N*	0·0725	0·1162	0·145	0·2905	0·572	1·101	2·149	3·111	
Ag_2O, *N*	0·01544	0·02369	0·02947	0·05498	0·1160	0·2187	0·4480	0·6068	
E.M.F. (16°)	0·176	0·166	0·159	0·141	—	—	—	—	
$-\log [Ag^{\cdot}]$	5·96	6·12	6·25	6·56	—	—	—	—	
$K_{\mathrm{I}} \times 10^7$	1·23	1·50	1·41	1·62	Mean 1·44				
K_{I} (sol.) $\times 10^7$	1·00	1·12	1·14	1·44	1·14	1·23	1·03	1·27	Mean 1·17
Dimethylamine.									
$NHMe_2$, *N*	0·1858	0·4645	0·697	0·929	1·393	1·858	2·40		
Ag_2O, *N*	0·00891	0·0225	0·0370	0·0459	0·0633	0·0791	0·094		
E.M.F. (17°)	0·176	0·153	0·141	0·137	0·126	0·116	—		
$-\log [Ag^{\cdot}]$	5·93	6·33	6·54	6·61	6·80	6·97	—		
$K_{\mathrm{I}} \times 10^6$	3·72	3·67	3·02	3·75	3·43	3·91	Mean 3·58		
K_{I} (sol.) $\times 10^6$	4·67	4·62	3·78	3·10	5·33	6·15	7·34	Mean 5·0	
Diethylamine.									
$NHEt_2$, *N*	0·142	0·356	0·534	0·712	1·068	1·424	2·10		
Ag_2O, *N*	0·0212	0·0517	0·0756	0·0998	0·1281	0·1764	0·250		
E.M.F. (17°)	0·164	0·137	0·134	0·126	0·112	0·108	—		
$-\log [Ag^{\cdot}]$	6·14	6·61	6·66	6·80	7·04	7·11	—		
$K_{\mathrm{I}} \times 10^7$	5·01	4·67	4·17	4·24	2·99	3·42	Mean 4·08		
K_{I} (sol.) $\times 10^7$	2·73	3·17	2·58	3·55	5·35	4·75	5·43	Mean 4·0	
Trimethylamine.									
NMe_3, *N*	0·136	0·340	0·681	1·088	1·363	2·00			
Ag_2O, *N*	0·00039	0·00137	0·00293	0·0043	0·0057	0·0084			
E.M.F. (15°)	0·225	0·217	0·205	0·194	0·187	—			
$-\log [Ag^{\cdot}]$	5·13	5·25	5·48	5·67	5·80	—			
$K_{\mathrm{I}} \times 10^4$	3·39	4·68	5·13	5·89	5·37	Mean 4·89			
K_{I} (sol.) $\times 10^4$	[15·3]	8·24	6·81	8·37	7·48	7·41	Mean 7·7		
Triethylamine.									
NEt_3, *N*	0·12	0·34	0·48						
Ag_2O, *N*	0·00164	0·00547	0·00789						
E.M.F. (15°)	0·207	0·186	0·179						
$-\log [Ag^{\cdot}]$	5·44	5·81	5·93						
$K_{\mathrm{I}} \times 10^5$	3·09	3·09	3·24	Mean 3·14					
K_{I} (sol.) $\times 10^5$	6·76	4·90	4·57	Mean 5·4					

potassium nitrate solution to a normal calomel electrode, the cell gave an *E.M.F.* of 0·454 volt, corresponding to ${}_0\varepsilon_{Ag} = 0{\cdot}800$ volt (N-H = 0), the degree of ionisation being taken as 0·814. The *E.M.F.*'s recorded in Table II refer to cells: Ag | complex solution | satd. KNO_3 | *N*-calomel, at the temperatures indicated. The instability constants, $K_{\mathrm{I}} = [Ag^{\cdot}][B]^2/[AgB_2^{\cdot}]$, were calculated therefrom, it being assumed that (i) all the silver oxide had been converted into the complex base, AgB_2OH; (ii) the complex bases were completely ionised, thus $AgB_2OH \rightleftharpoons$

$AgB_2^{\cdot} + OH'$, whence concentration of silver oxide dissolved $= [AgB_2^{\cdot}]$ g.-equivs. per litre; (iii) as the result of the ionisation of the complex base, the excesses of the different organic bases were un-ionised, and their concentrations therefore equal to [B]. In order that the "instability constant" of the ethylenediaminosilver kation might be comparable with the other constants, the concentrations of ethylenediamine have been taken in g.-equivs. per litre, so that in calculating the constants the concentrations of free ethylenediamine have been squared.

FIG. 2.



III. *Electrometric Titrations of Aqueous Solutions of Silver Oxide in Ammonia and Amines.*—Typical glass-electrode titration curves at 18° and the corresponding conductometric curves at 25° are shown in Fig. 2. The solutions employed were:

A, 50 c.c. of $0{\cdot}0298M$-$Ag(NH_3)_2OH + 0{\cdot}0376N$-$NH_4OH$, titrated with $0{\cdot}2078N$-HNO_3;
B, 50 c.c. of $0{\cdot}03920M$-$Ag(NH_2Me)_2OH + 0{\cdot}0825M$-$NH_2Me$, titrated with $0{\cdot}3380N$-HNO_3;
C, 50 c.c. of $0{\cdot}03084M$-$Ag(NH_2Et)_2OH + 0{\cdot}03084M$-$NH_2Et$, titrated with $0{\cdot}1928N$-HNO_3;
D, 50 c.c. of $0{\cdot}02842M$-Ag en OH $+ 0{\cdot}04618M$-$C_2H_8N_2$, titrated with $0{\cdot}2368N$-HNO_3.

The same solutions were used to obtain the curves for κ, but 100 c.c. were used for each titration.

Both types of curve demonstrate the formation of a strong base of the general formula $Ag(B)_2OH$, becoming Ag en OH in the case of ethylenediamine. The curves may be divided into three sections, denoted by Roman numerals, corresponding to the addition of various amounts of nitric acid: I relates to the neutralisation of the strong complex base; II to that of the ammonia or amine in excess of that required to form the complex base; and III to the decomposition of the complex nitrate, $Ag(B)_2NO_3$ (B = unhydrated base), formed at the end of stage I, into silver nitrate and the nitrate of the simple base: $AgB_2NO_3 + 2HNO_3 \rightleftharpoons AgNO_3 + 2BHNO_3$, or $AgB_2^{\cdot} + 2H^{\cdot} \rightleftharpoons Ag^{\cdot} + 2BH^{\cdot}$. Hence

$$[Ag^{\cdot}][BH^{\cdot}]^2/[AgB_2^{\cdot}][H^{\cdot}]^2 = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and as $B + H_2O \rightleftharpoons BH{\cdot}OH \rightleftharpoons BH^{\cdot} + OH'$, therefore $[BH^{\cdot}][OH']/[BH{\cdot}OH] = K_b$.

If it is assumed that the undissociated base is also unhydrated, *e.g.*, that undissociated ammonium hydroxide molecules exist in solution as simply molecules of ammonia (see, *e.g.*, Calingaert and Huggins, *J. Amer. Chem. Soc.*, 1923, **45**, 915), and similarly that the undissociated substituted ammonia molecules exist as such when in the un-ionised state, then the concentration of the base, [B], is equal to that of the undissociated base, [BHOH], whence

$$[\mathrm{BH}^{\bullet}][\mathrm{OH}']/[\mathrm{B}] = K_b \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{2}$$

Combination of equations (1) and (2), and introduction of $K_w = [\mathrm{H}^{\bullet}] \times [\mathrm{OH}']$, give

$$[\mathrm{Ag}^{\bullet}][\mathrm{B}]^2/[\mathrm{AgB}_2^{\bullet}] = K \, . \, K_w^2/K_b^2 = K_{\mathrm{I}}$$

where K_{I} is the instability constant of the complex kation in question. It is seen therefore that the p_{H} during stage III depends on the instability constant of the complex kation and the dissociation constant of the base which it incorporates.

That 2 equivs. of the bases combine with one of silver is apparent from the fact that the amount of nitric acid used in stage III is exactly twice the amount required in stage I. Because methylamine and ethylamine are somewhat stronger bases than ammonia, stage II in *B* and *C* tends to merge into stage I without a well-defined inflexion. The termination of the neutralisation of the strong complex methylamino- and ethylamino-silver bases is, however, clearly indicated in the conductometric curves, sharp " breaks " being obtained. No further breaks were obtained until the complex ions had been entirely decomposed and free nitric acid began to be present in the solutions. This is to be ascribed to the fact that the mobilities of the kations involved do not differ greatly from one another.

As shown in the previous section, the solubility of silver oxide in pyridine is very small. Nevertheless, the high p_{H} values indicated during the initial portions of curves *E* and *F* in Fig. 2, which refer to the titrations of 50 c.c. of 0·0034*M*-$\mathrm{AgPy_2OH}$ + 0·2106*M*-pyridine with 0·3368*N*- and with 0·0129*N*-nitric acid respectively, show that the complex pyridine base is quite strong.

The equivalent conductivities of the complex bases and their apparent degrees of ionisation, α, given in Table III show that the complex bases, like the silver–ammonia base (Britton and Wilson, *loc. cit.*; Whitney and Melcher, *loc. cit.*) are very strong.

TABLE III.

Base.	G.-equivs. per litre. Base.	G.-equivs. per litre. $\mathrm{Ag_2O}$.	$\kappa \times 10^3$.	Λ.	p_{H}.	α.
Ammonia	0·0972	0·0298	—	—	12·57	0·90
Methylamine	0·1007	0·02338	4·64	189	12·48	0·78
Ethylamine	0·1210	0·03805	7·54	194	12·66	0·72
Ethylenediamine	0·1162	0·02369	4·85	202	12·47	0·78
Pyridine	0·2233	0·0034	0·620	201	11·58	0·76

The values of α were calculated from the p_{H} values, allowances being made for the concentrations of hydroxyl-ions originating from the excess of the organic bases; α thus represents

[Concentration of hydroxyl-ions from complex base]/[Concentration of complex base].

The specific conductivities of the small concentrations of ionised free base were calculated from the p_{H} values and the dissociation constants and then subtracted from the observed specific conductivities in order to find the specific conductivities caused by the complex bases and thence the equivalent conductivities.

Although the accuracy of these computations is necessarily minimised by the errors inherent in the use of the glass electrode in solutions of p_{H} above 12, they suffice to show (i) that the complex bases are all similar in strength to sodium hydroxide, and (ii) that the precise strength of the ammonia base bound up in the complex kation is without effect on the strength of the resulting complex base. For instance, pyridine and ethylamine are respectively the weakest and the strongest of the bases considered, yet the strengths of the complex bases are equal. Also, the widely different strengths of the two stages of dissociation of ethylenediamine appear to have no effect on their co-ordinating power.

If the previous assumptions used to interpret the p_{H} values set up during the third stages of the titrations *A*, *B*, and *C* (Fig. 2) are sound, then it is possible to calculate the " instability constants " of the complex ammonia, methylamine, and ethylamine kations from the dissociation constants and the ionic product of water.

The data in Table IV were obtained from the p_{H} values set up when 24 c.c. of titrant had been added in each of the three titrations, which corresponds very nearly to the mid-point of the third stages. The silver nitrate was taken as completely ionised, and if suitable allowance could have been made for its smaller ionisation in the presence of ammonium or substituted ammonium nitrates, the " instability constants " would have been slightly smaller. Attempts to measure the silver-ion concentrations of these solutions by the *E.M.F.* method did not lead to satisfactory results, apparently owing to the enhanced instability of the complex kations in such solutions, and the consequent sluggishness of the silver electrode to reach a state of equilibrium.

TABLE IV.

Titration.	Salt.	Silver salt decomposed, %.	p_H observed.	K.	K_I.
A	$Ag(NH_3)_2NO_3$	51·2	7·00	$2{\cdot}19 \times 10^{11}$	$3{\cdot}31 \times 10^{-8}$
B	$Ag(NH_2Me)_2NO_3$	51·8	8·45	$5{\cdot}62 \times 10^{14}$	$1{\cdot}86 \times 10^{-7}$
C	$Ag(NH_2Et)_2NO_3$	50·0	8·40	$1{\cdot}12 \times 10^{14}$	$3{\cdot}72 \times 10^{-8}$

DISCUSSION.

Silver oxide dissolves in solutions of ammonia and amines to form strong complex bases, AgB_2OH. It is possible to explain this solubility in terms of the instability constant of the complex kation formed and the solubility product of silver hydroxide, or conversely to calculate the instability constant of the complex kation. Thus, let the concentration of base be C g.-equivs. per litre, and the amount of silver hydroxide dissolved be S g.-equivs. per litre. This is equal to the concentration of the complex base, AgB_2OH. The concentration of base which co-ordinates with the silver hydroxide is $2S$, and consequently the concentration of free base is $C - 2S$. Hence, if the degree of ionisation of the complex base, AgB_2OH, is α, then $[Ag^{\cdot}][B]^2/[AgB_2^{\cdot}] = K_I = [Ag^{\cdot}](C - 2S)^2/\alpha S$, and as the solution is saturated with respect to silver oxide, $[Ag^{\cdot}][OH'] = L$; whence $K_I = L(C - 2S)^2/\alpha S[OH']$, and as $[OH']$ originates from the ionisation of the complex base, $[OH'] = \alpha S$, and therefore $K_I = L(C - 2S)^2/\alpha^2 S^2$.

Hence $C = S(2 + \alpha\sqrt{K_I/L})$, and consequently, if α is either unity or else constant, the solubility of silver oxide should be directly proportional to the concentration of the organic base as is shown by the curves in Fig. 1. In Table II, the instability constants, K_I (sol.), obtained by means of the above formula by putting $\alpha = 1$ and taking the solubility product of silver hydroxide as $1{\cdot}33 \times 10^{-8}$ (Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531), are compared with the values obtained from potential measurements with the silver electrode. In view of the approximate nature of the assumptions involved, the agreement is satisfactory.

There appears to be no relationship between the strength of the base, as shown by the dissociation constants in Table I, and the stability of the resulting complex kations. For instance, both dimethylamine and diethylamine are stronger than either ammonia or their respective primary bases, yet the instability constants of the dialkylaminosilver kations are appreciably greater, and although pyridine is so very much weaker as a base than either of the tertiary bases trimethylamine and triethylamine, yet the pyridinosilver kation is slightly more stable than the other two. Furthermore, as will be shown in a later paper a weak primary aromatic base such as aniline gives rise to an unstable complex kation.

As far as can be ascertained from the instability constants, except for the complex aniline kation, complex kations involving ammonia or primary amines are more stable than those involving secondary amines, which in turn are more stable than those involving tertiary bases. In other words, the order of the co-ordinating tendencies with regard to silver is primary > secondary > tertiary amines.

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