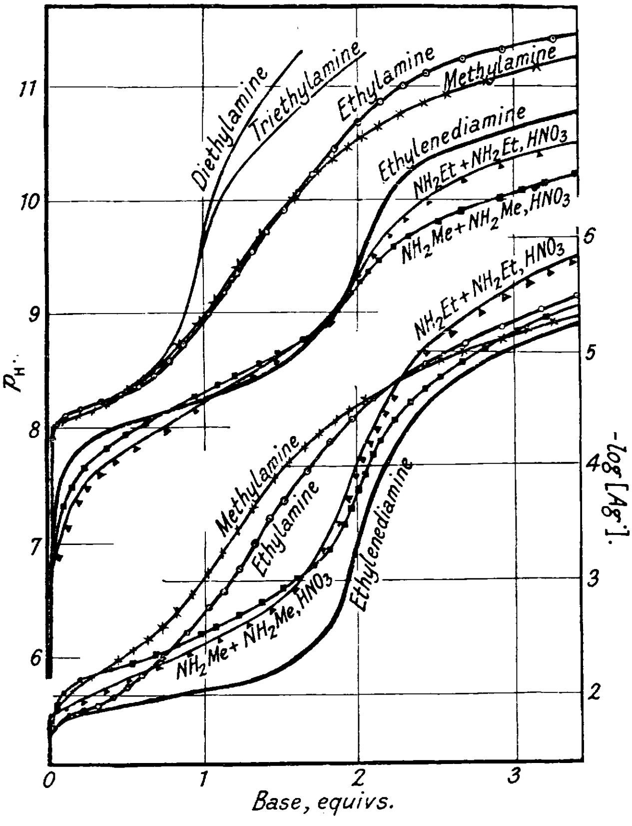
22. *Electrometric Studies of the Precipitation of Hydroxides. Part XIII. The Reactions between Silver Nitrate and Methylamine, Mono-, Di-, and Tri-ethylamine, Ethylenediamine, Aniline, and Pyridine in Solution.*

By H. T. S. Britton and William G. Williams.

This communication reports a study of the formation of complex silver kations when various organic bases are added to a solution of silver nitrate. As might be expected, the extent to which bases precipitate silver oxide and the amounts which must be added to effect its redissolution depend on the instability constant of the complex kation, the solubility product of silver oxide, and the dissociation constant of the organic base.

Fig. 1.



The curves in the upper section of Fig. 1 represent glass-electrode titrations at 18° of 100 c.c. of $0{\cdot}02N$-silver nitrate with $0{\cdot}0896N$-diethylamine, $0{\cdot}102N$-triethylamine, $0{\cdot}09775N$-

ethylamine, 0·0953*N*-methylamine, and 0·225*N*-ethylenediamine. A faint opalescence was soon formed in the last titration, but disappeared immediately 2 equivs. had been added. In the two titrations illustrated by the two lowest p_H curves sufficient nitrate of the base was inserted in the silver nitrate solutions so that on treatment with the respective base no precipitate appeared. In these cases, therefore, and also in that of ethylenediamine, the silver must have been held in solution in the form of complex kations : this is reflected in the titration curves by the inflexions with 2 equivs. of the bases.

The addition of di- and tri-ethylamine caused extensive precipitation of silver oxide, as indicated by the appearance of well-defined inflexions with 1 equiv. of each base. With both ethylamine and methylamine the precipitation was less : the curves have inflexions extending from 1 to 2 equivs.

The silver electro-titration curves (lower part of Fig. 1), which refer to the solutions and titrants of the same concentrations as above, have similar characteristics. The ethylenediamine curves bring out clearly the fact that the complex salt involves one molecule of the base, $AgNO_3 + C_2H_4(NH_2)_2 \longrightarrow Ag[C_2H_4(NH_2)_2]NO_3$. [The complex kation is usually represented by $AgEn^{\bullet}$ (see, however, Traube, *Ber.*, **1911**, **44**, **3320**).] The proportion of silver oxide precipitated at various stages of the titrations was determined by precipitation of the silver in solution as chloride. To 100 c.c. of 0·02*N*-silver nitrate various amounts of base were added, mechanically shaken for some time at room temperature, and the silver in the liquid phase estimated. The results obtained are given in Table I.

TABLE I.

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·0956N-*methylamine.*

x, c.c.	10	15	20	25	30	40	45	50	60
$NH_2Me/AgNO_3$	0·48	0·72	0·96	1·19	1·43	1·91	2·15	2·49	2:87
Ag pptd., % (obs.)	46·1	66·6	78·3	75·9	65·3	42·4	34·8	26·5	14·5
,, (calc.)	47·5	57·1	78·4	—	64·7	38·3	—	21·5	14·8

100 *C.c. of* 0·1N-*silver nitrate* + x *c.c. of* 0·5087N-*methylamine.*

x, c.c.	5	10	15	20	25	30	35	40	45	48
$NH_2Me/AgNO_3$	0·25	0·51	0·76	1·02	1·27	1·53	1·78	2·03	2·29	2·54
Ag pptd., % (obs.)	25·4	46·5	69·8	77·7	67·3	46·9	29·9	17·3	9·2	5·0
,, (calc.)	25·5	48·7	70·2	79·7	73·6	50·2	30·2	14·8	—	—

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·0973N-*ethylamine.*

x, c.c.	10	15	20	25	30	35	40	45	50
$NH_2Et/AgNO_3$	0·48	0·73	0·97	1·21	1·46	1·70	1·94	2·19	2·43
Ag pptd., % (obs.)	41·0	56·7	66·2	60·4	49·0	33·2	21·3	12·5	4·4
,, (calc.)	44·6	60·7	67·3	—	56·9	36·9	—	12·2	—

100 *C.c. of* 0·1N-*silver nitrate* + x *c.c. of* 0·4676N-*ethylamine.*

x, c.c.	5	10	15	20	25	30	35	40	45	48
$NH_2Et/AgNO_3$	0·23	0·47	0·70	0·94	1·17	1·40	1·64	1·87	2·10	2·22
Ag pptd., % (obs.)	20·3	38·8	55·3	65·7	63·2	51·1	34·3	15·7	5·9	2·7
,, (calc.)	22·6	43·0	59·2	67·3	—	60·2	37·6	16·9	—	—

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·0896N-*diethylamine.*

x, c.c.	5	10	15	20	25	30	40	60	80
$NHEt_2/AgNO_3$	0·22	0·45	0·67	0·90	1·12	1·34	1·79	2·69	3·59
Ag pptd., %	22·4	45·0	66·4	85·1	94·2	96·0	76·6	60·8	41·9

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·112N-*triethylamine.*

x, c.c.	5	10	15	20	25	30	40	60	80
$NEt_3/AgNO_3$	0·26	0·51	0·77	1·02	1·27	1·53	2·04	3·06	4·08
Ag pptd., %	22·9	51·0	75·0	91·6	97·5	97·5	95·0	93·0	91·6

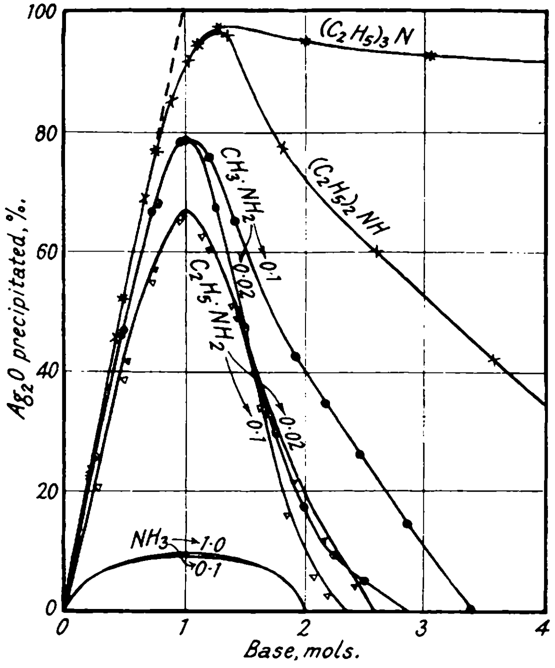
The results are plotted in Fig. 2, in which are also curves showing the percentage of silver oxide precipitated when 0·1*N*- and 1·0*N*-silver nitrate solutions are treated with ammonia (see Britton and Wilson, J., **1933**, **1050**). The broken line represents the normal precipitation of silver oxide with sodium hydroxide, Unlike ammonia, none of the organic bases causes the silver oxide to redissolve when 2 mols. of base per mol. of silver nitrate have been added. Reychler (*Ber.*, **1883**, **16**, **990**) and Herz (*Z. anorg. Chem.*, **1910**, **67**, **248**) considered the ratio 2 : 1 to indicate formation of the complex kation, $Ag(NH_3)_2^{\bullet}$, but, as the following considerations show, such a ratio is fortuitous in that the precise ratio depends on the three factors mentioned on p. **96**.

When a base, B, is added to silver nitrate, two reactions occur simultaneously: (i) the partial precipitation of silver oxide, (ii) conversion of some silver nitrate into the complex nitrate, AgB_2NO_3. These two reactions bring into play the equilibria $AgB_2^{\cdot} \rightleftharpoons Ag^{\cdot} + 2B$, $B + H_2O\ (= BH{\cdot}OH) \rightleftharpoons BH^{\cdot} + OH'$, and $AgOH$ (solid) $\rightleftharpoons AgOH$ (dissolved) $\rightleftharpoons Ag^{\cdot} + OH'$, which are governed by the expressions $K_I = \frac{[Ag^{\cdot}][B]^2}{[AgB_2^{\cdot}]}$; $K_b = \frac{[BH^{\cdot}][OH']}{[B]}$; $L = [Ag^{\cdot}][OH']$,

whence $$K_I \,.\, K_b^2/L^2 = [BH^{\cdot}]^2/[Ag^{\cdot}][AgB_2^{\cdot}] \qquad (1)$$

and $$K_I \,.\, K_b/L = [BH^{\cdot}][B]/[AgB_2^{\cdot}] \qquad (2)$$

FIG. 2.



Equation (1) is applicable particularly to the first stage of the reaction of the base with silver nitrate, *i.e.*, when there is an appreciable silver-ion concentration originating from any unattacked silver nitrate (Case I), and equation (2) refers to the second stage where some of the added base has failed to react, either in precipitating silver oxide or in forming the complex salt, AgB_2NO_3 (Case II). From a knowledge of the three constants involved, it is possible to calculate the extents to which the base has reacted in (*a*) precipitating silver oxide and (*b*) complex formation. Thus, let the original concentration of silver nitrate be c, and the total concentration of added base $2a$; of the silver nitrate reacted upon, suppose a fraction, x, yielded an equivalent quantity of silver oxide.

Case I.

$$2axBH{\cdot}OH + 2axAgNO_3 = 2axB,HNO_3 + 2axAgOH$$
$$2a(1 - x)B + a(1 - x)AgNO_3 = a(1 - x)AgB_2NO_3.$$

The complete ionisation of B,HNO_3, AgB_2NO_3, and any unattacked $AgNO_3$ being assumed, it follows that $[BH^{\cdot}] = 2ax$, $[AgB_2^{\cdot}] = a(1 - x)$, and $[Ag^{\cdot}] = \{c - a(1 - x) - 2ax\}$, whence $K_I \,.\, K_b^2/L^2 = 4ax^2/(c - a - ax)(1 - x)$ from which the fraction of silver oxide precipitated, *viz.*, $2ax/c$, can be calculated.

Case II.

$$2c(1 - x)B + c(1 - x)AgNO_3 = c(1 - x)AgB_2NO_3$$
$$xcBH{\cdot}OH + xcAgNO_3 = xcB,HNO_3 + xcAgOH$$
$$[BH^{\cdot}] = xc,\ [B] = \{2a - xc - 2c(1 - x)\},\ [AgB_2^{\cdot}] = c(1 - x)$$

Hence $K_I \,.\, K_b/L = x(2a + xc - 2c)/(1 - x)$ and the fraction of oxide precipitated is xc/c. With $L_{AgOH} = 1{\cdot}33 \times 10^{-8}$ (Britton and Robinson, *Trans. Faraday Soc.*, **1932**, **28**, **539**) and with the dissociation constants of the bases and instability constants of the complex kations found by us in Part XII (J., **1935**, **796**), the percentages of silver precipitated as oxide were calculated and are recorded in Table I. In view of the approximations involved, the agreement between the calculated and the observed results is satisfactory. This is also the case in regard to the extent of precipitation from silver nitrate solutions with ammonia as found by Britton and Wilson (J., **1933**, **1050**). With $p_{K_{NH_4OH}} = 4{\cdot}72$ and $p_{K_{Ag(NH_3)_2^{\cdot}}} = 7{\cdot}70$, calculation shows that 7·83, 9·18, and 7·83% of the total silver nitrate should be precipitated with 0·5, 1·0, and 1·5 equivs. of ammonia respectively, whereas the proportions found were 7·68, 8·83, 7·81% and 7·81, 9·68, 7·95% from 0·1*M*- and 1·0*M*-silver nitrate respectively. For the methylamine calculations, $p_{K_{NH_2Me}} = 3{\cdot}43$ and $p_{K_{Ag(NH_2Me)_2^{\cdot}}} = 7{\cdot}10$ were adopted, and for those with ethylamine, $p_{K_{NH_2Et}} = 3{\cdot}40$ and $p_{K_{Ag(NH_2Et)_2^{\cdot}}} = 7{\cdot}70$.

The p_H values (Fig. 1) of the solutions after the silver oxide had dissolved in both the methylamine and the ethylamine titrations indicate buffer action which must have been caused by the presence of the nitrates of these bases. The existence of these salts shows that the silver nitrate could not have been quantitatively converted into the complex salts, AgB_2NO_3.

As it is probable that, in those titrations which involved the redissolution of silver oxide, a state of equilibrium was not immediately reached, several series of solutions containing various excesses of the organic bases were prepared, mechanically shaken in light-proof bottles for 24 hours at room temperature, and their silver- and hydrogen-ion concentrations determined by means of the silver and the glass electrode respectively. The silver electrodes were prepared by electrodepositing coarsely crystalline silver on silver rods. The glass cell *E.M.F.*'s were measured by means of an electrometer–triode valve and a sensitive galvanometer. The normal electrode potential of the silver electrode was 0·801 volt (*N*-H = 0). Table II gives the results obtained; each solution was 0·02*N* with respect to silver nitrate; the concentration of methyl- and ethyl-ammonium nitrate (sections *b* and *d* respectively) entirely prevented the precipitation of silver oxide.

From the p_H values and the *E.M.F.* data, the instability constants, K_I, of the complex kations were calculated. As methylamine and ethylamine are both appreciably ionised, it is necessary, in order to calculate [B], to deduct the concentration $[BH^{\cdot}]$ from the concentration of the base in excess of the 2 mols. going to form the complex kation. On the assumption that $[BH{\cdot}OH] = [B]$, we have $[BH^{\cdot}] = [OH'] = K_w/[H^{\cdot}]$.

TABLE II.

Cell: Ag | 0·02*N*-$AgNO_3$ + *xN*-NH_2Me (or NH_2Et) | satd. KNO_3 | *N*-Calomel.

(*a*) Solutions: 0·02*N*-$AgNO_3$ + *xN*-NH_2Me.

NH_2Me, *x*.	$\frac{[NH_2Me]}{[AgNO_3]}$.	p_H at 17·5°.	$10^3[OH']$.	*E.M.F.*	$-\log [Ag^{\cdot}]$.	$K_I \times 10^8$.
0·2276	11·38	11·70	3·5	0·111 (16°)	7·10	12·9
0·9108	45·54	12·26	12·9	0·029	8·53	11·9
1·1280	56·90	12·30	14·0	0·016	8·76	11·1

Mean $K_I = 12{\cdot}0 \times 10^{-8}$

(*b*) Solutions: 0·02*N*-$AgNO_3$ + 0·063*N*-NH_2Me,HNO_3 + *xN*-NH_2Me.

NH_2Me, *x*.	$\frac{[NH_2Me]}{[AgNO_3]}$.	p_H at 17·5°.	$10^3[OH']$.	*E.M.F.*	$-\log [Ag^{\cdot}]$.	$K_I \times 10^8$.
0·0814	4·07	10·76	—	0·168 (19°)	6·03	7·92
0·1017	5·08	10·92	—	0·148 (19°)	6·46	7·58
0·1220	6·10	11·01	—	0·137 (19°)	6·58	8·71

Mean $K_I = 8{\cdot}1 \times 10^{-8}$

(*c*) Solutions: 0·02*N*-$AgNO_3$ + *xN*-NH_2Et.

NH_2Et, *xN*.	$\frac{[NH_2Et]}{[AgNO_3]}$.	p_H at 17·5°.	$10^3[OH']$.	*E.M.F.*	$-\log [Ag^{\cdot}]$.	$K_I \times 10^8$.
0·2123	10·62	12·11	9·19	0·072 (18°)	7·72	2·63
0·4246	21·23	12·315	14·6	0·034	8·38	2·95
0·8494	42·46	12·415	18·4	0·000	8·97	3·24
1·698	84·92	12·57	26·0	−0·035	9·58	3·44

Mean $K_I = 3{\cdot}1 \times 10^{-8}$

(*d*) Solutions: 0·02*N*-$AgNO_3$ + 0·1013*N*-NH_2Et,HNO_3 + *xN*-NH_2Et.

NH_2Et, *xN*.	$\frac{[NH_2Et]}{[AgNO_3]}$.	p_H at 17·5°.	$10^3[OH']$.	*E.M.F.*	$-\log [Ag^{\cdot}]$.	$K_I \times 10^8$.
0·09020	4·51	10·75 *	—	0·130	6·69	2·56
0·1082	5·41	10·88 *	—	0·113	6·98	2·40
0·1173	5·86	10·98 *	—	0·106	7·12	2·23

Mean $K_I = 2{\cdot}4 \times 10^{-8}$

* At 18°.

The values of the instability constant for $Ag(NH_2Me)_2^{\cdot}$ [Table II (*a*)] tend to decrease as the concentration of free base increases, whilst those given in Table II (*b*) are still smaller. The lower values, indicating increased stability of the complex kation, are believed to be the result of the repression of ionisation of the excess of base, in the first case by the greater concentrations of methylammonium ions owing to the added nitrate, and in the second by the relatively high concentration of hydroxyl-ions originating from the complex base. Euler (*Ber.*, **1903**, **36**, 1854, 2878) obtained values ranging from $1{\cdot}19 \times 10^{-7}$ to $2{\cdot}5 \times 10^{-7}$ for the methylamine complex kation.

The ethyl base shows a similar behaviour [Table II, (*c*) and (*d*)]. The lower value, $2{\cdot}4 \times 10^{-8}$, compares satisfactorily with the values, $1{\cdot}88 \times 10^{-8}$ and $2{\cdot}13 \times 10^{-8}$, obtained from the aqueous ethylamine solutions of silver oxide. The difference in the stability of the complex methylamine and ethylamine kations is apparent from the relative proportions of the two bases required to bring silver oxide into solution as shown in Fig. 2.

The data in Table III are derived from electrometric titrations of solutions containing ethylenediamino-, dianilino-, and dipyridino-silver ions in the presence of various amounts of the respective bases. The well-defined inflexion in the ethylenediamine curve (Fig. 1) shows the complex kation to be quite stable. The mean "instability constant," $2{\cdot}0 \times 10^{-7}$, agrees with that of the kation which ionises from the complex base, [Ag en]OH, *viz.*, $1{\cdot}15$—$1{\cdot}44 \times 10^{-7}$.

If aniline and pyridine did not enter into complex formation with silver ions, then, despite their weakness as bases, they should, when added in sufficient excess to silver nitrate solution, be able to set up p_H values which would cause the precipitation of some silver oxide. Complex kations, however, are formed, and consequently no silver oxide is precipitated. This will be seen from the diminished silver-ion concentrations recorded in Table III, (*b*) and (*c*). As the relatively large values of K_I (last columns) show, the complex kations are much less stable than any of the other kations investigated in this paper.

TABLE III.

Electrometric titrations (glass and silver electrodes) of 100 *c.c. of* 0·02N-$AgNO_3$ *with various organic bases.*

(*a*) Ethylenediamine (0·2250*N*); 18°.

Base, c.c.	$\frac{\frac{1}{2}[C_2H_4(NH_2)_2]}{[AgNO_3]}$	p_H.	$10^4[OH']$.	*E.M.F.**	$-\log[Ag^{\cdot}]$.	$K_I \times 10^7$.
40	4·50	10·87	6·92	0·192	5·63	1·52
60	6·75	11·08	8·91	0·165	6·10	2·18
80	9·00	11·20	11·75	0·147	6·41	2·06
90	10·10	11·25	13·20	0·141	6·51	2·07

Mean $K_I = 2{\cdot}0 \times 10^{-7}$

(*b*) Aniline (0·3534*N*); 17°.

Base, c.c.	$\frac{[C_6H_5{\cdot}NH_2]}{[AgNO_3]}$.	p_H.	*E.M.F.**	$-\log[Ag^{\cdot}]$.	$K_I \times 10^4$.
50	8·84	7·63	0·322	3·39	2·51
70	12·35	7·72	0·312	3·57	2·85
80	14·13	7·75	0·308	3·64	3·75
100	17·62	7·79	0·301	3·77	4·58

Mean $K_I = 3{\cdot}4 \times 10^{-4}$

(*c*) Pyridine (0·5834*N*); 18°.

Base, c.c.	$\frac{[C_5H_5N]}{[AgNO_3]}$.	p_H.	*E.M.F.**	$-\log[Ag^{\cdot}]$.	$K_I \times 10^5$.
30	13·47	8·50	0·275	4·18	3·80
50	19·45	8·72	0·246	4·70	3·55
70	24·03	8·83	0·230	4·97	3·63
90	27·64	8·92	0·218	5·19	3·47

Mean $K_I = 3{\cdot}6 \times 10^{-5}$.

* Cell of same type as in Table II.

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