CCXXXII.—*Reduction of Silver Compounds in Alkaline Solution.*

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THE object of the present investigation was to ascertain the conditions of experiment leading to the production of a maximum yield of metallic silver when ammoniacal solutions of certain silver compounds are reduced in the presence of aluminium and aqueous caustic alkali.

The reduction of silver oxide, prepared from silver nitrate, may be simply represented by the equations

$$\text{(i)}\ 6AgNO_3 + 6KOH = 3Ag_2O + 6KNO_3 + 3H_2O,$$
$$\text{(ii)}\ 2Al + 6KOH = 2Al(OK)_3 + 3H_2,$$
$$\text{(iii)}\ 3Ag_2O + 3H_2 = 6Ag + 3H_2O,$$

one g.-atom of aluminium being equivalent to 3 g.-atoms of silver.

Preliminary experiments indicated that, in the absence of aluminium, heating of ammoniacal silver solutions in the presence of potassium hydroxide was followed by detonation. Addition of potassium hydroxide to concentrated solutions of silver compounds in aqueous ammonia caused the formation of black precipitates. Hydrolysis in the presence of traces of aluminium led to the detonation of such reaction mixtures. Hydrolysis of the dried black precipitates by potassium hydroxide gave silver oxide as the final product. In the presence of ammonia, spongy silver was formed. Analysis of the dried black precipitates by the Kjeldahl method showed that they were mixtures of silver nitride with relatively small quantities of silver oxide.

EXPERIMENTAL.

Series I.—An ammoniacal solution of silver nitrate containing 2 g. of the salt, 25 c.c. of ammonia (*d* 0·880), and 25 c.c. of water was treated with 25 c.c. of 3*N*-potassium hydroxide, and heated at 100° in a water-bath. At once a black film began to form on the walls of the reaction vessel, and its appearance was followed by an explosion which shattered the reaction vessel. This phenomenon occurred in three consecutive experiments, detonation taking place after a lapse of 12, 14, and 15 minutes from the commencement of the reaction.

Series II.—Aqueous silver nitrate solutions of various concentrations were treated with just sufficient ammonia (*d* 0·880) to redissolve the precipitated silver oxide, and to each solution were added 10 g. of potassium hydroxide dissolved in 15 c.c. of water. A brown precipitate formed; this was followed by a black precipitate as more caustic alkali was added. The final heavy precipitate was uniformly black in colour. The reaction vessel was then placed in a water-bath and heated to 100°. The black precipitate was thereby progressively reduced to a grey, metallic powder. The reduced metal was filtered, washed, dried, and analysed. In all cases, the filtrates were free from silver. Under the conditions of these experiments, it was observed that quantities of silver nitrate not exceeding 5 g. could be quantitatively reduced to metal. Attempts to reduce the silver salt in larger quantities invariably led to the explosion of the product. Typical results are given in Table I.

TABLE I.

Wt. of $AgNO_3$ (g.)......	0·5	1·0	2·0	3·0	4·0	5·0
% Ag ppd.	99·82	99·85	99·91	99·83	99·87	99·89
% Ag in ppt.	99·61	99·70	99·82	99·80	99·84	99·85

The conversion of the black precipitate into metallic silver was associated with the evolution of a gas, which was found to be nitrogen. The results of a quantitative examination of this reaction are summarised in the first two lines of Table II, and the last two lines show that the nitrogen evolved is chemically equivalent to the silver nitrate used. A similar result was obtained with silver chloride.

TABLE II.

Wt. of $AgNO_3$ (g.)	0·1619	0·2269	0·3176	0·4035	0·5892
Nitrogen (c.c. at *N.T.P.*)...	3·41	4·86	6·72	8·62	12·41
$AgNO_3$ (mg.-equiv.)	0·95	1·33	1·87	2·37	3·47
$\frac{1}{3}$N (mg.-equiv.)	0·91	1·30	1·80	2·31	3·33

Series III.—Several samples of the black product were prepared as in Series II, 0·5 g. of silver nitrate being used in each case. Ordinary test-tubes were used as reaction vessels. One fragment of aluminium filings was quickly dropped into each reaction mixture, and the tubes were immediately immersed in vessels containing water at known temperatures. The observations were as follows :

(*a*) At 50°, crackling sound; (*b*) 60°, report; tube intact; (*c*) 70°, report, but louder; tube intact; (*d*) 90°, explosion; tube shattered; (*e*) 100°, violent explosion; tube shattered.

Analysis of the Black Precipitate.—A quantity of the black precipitate was prepared as in Series II. After 15 minutes, the supernatant liquor was decanted off, and the precipitate was washed by decantation with water and transferred to a filter. After thorough washing with water, the black precipitate was washed into a small tared evaporating dish, the excess of water evaporated on the water-bath, and the final drying completed by preserving over concentrated sulphuric acid. The product, which did not smell of ammonia, was then analysed. Owing to the great instability of the product, which exploded on percussion and even on touching with a spatula, it was deemed advisable to analyse it in bulk according to the following scheme :

(*a*) The black product was hydrolysed by means of strong caustic alkali, and the evolved ammonia estimated by absorption in standard sulphuric acid.

(*b*) The residual silver oxide was washed, dried, weighed, converted into nitrate, precipitated as chloride, and weighed in this form.

(*c*) The alkaline filtrate, from which the black product had been isolated, was examined for dissolved silver, which was precipitated and weighed as chloride. A typical result is given in Table III.

TABLE III.

Wt. of black ppt. = 1·133 g.
Nitrogen in ppt. = 3·59%
Ag in ppt. = 95·48%
$AgNO_3$ precipitated = 85·13%
$AgNO_3$ remaining in solution = 15·03%

From the above result, it would appear that the product was not homogeneous. In order to test this view the final, dry, black precipitate, prepared as above, was extracted several times with 50 c.c. of 10% ammonia solution. Analysis of the product after extraction and of the ammoniacal extract gave the following result.

TABLE IV.

Wt. of ppt. before extraction = 1·132 g.
Wt. of ppt. after extraction = 0·989 g.
Nitrogen in ppt. = 4·11%
Silver in ppt. = 95·50%
% of total $AgNO_3$ ppd. = 84·68
% of $AgNO_3$ in extract = 10·33
% of $AgNO_3$ in solution = 15·19

From a series of experiments, it was ascertained that a similar black precipitate containing nitrogen could be obtained when silver chloride was used instead of silver nitrate.

Series IV.—Reduction at 100°, *in ammoniacal solution, using varying quantities of aluminium and definite amounts of dissolved silver in the presence of potassium hydroxide.* The required quantity of the silver compound, containing silver equivalent to that present in 2 g. of the nitrate, was treated in an ammoniacal solution, containing 25 c.c. of ammonia (*d* 0·880) and 25 c.c. of water, with 25 c.c. of 3*N*-potassium hydroxide. A definite quantity of aluminium filings was then added and the reduction carried out at 100°; a black product was deposited, the colour of which changed rapidly to grey; from this stage onwards the quantity of the reduced metal increased continuously throughout the experiment. The final product formed grey, coherent masses of reduced silver possessing a vesicular structure. The reduction was complete in 1½ hours, and the reaction liquid was then treated with 10 c.c. of ammonia (*d* 0·880), allowed to stand for 15 minutes with frequent shaking, diluted with half its bulk of distilled water, and filtered through a tared Gooch crucible. The reduced silver was thoroughly washed, dried at 100°, weighed, and analysed. The results for silver nitrate are given in Table V, and those for silver oxide and silver chloride were very similar.

TABLE V.

Al used (g.)	0·05	0·10	0·20
Ag ppd., %	99·88	99·82	99·79
Ag in ppt., %	99·83	99·89	99·87

Series V.—A solution was prepared exactly as in Series IV, a strip of sheet aluminium was placed in it, and, immediately, a black deposit formed on the surface of the metal. After 30 seconds, the strip was removed, the deposit transferred to a beaker by means of a jet of water, and the strip reimmersed in the silver solution. This was repeated (10 times) until the deposit had been obtained in a quantity sufficient for analysis, which showed it to be elementary silver.

Series VI.—Ammoniacal solutions of silver nitrate were prepared, the ammonia content being just sufficient to retain the silver in solution. 2 C.c. of ammonia (*d* 0·880) were added, *i.e.*, excess sufficient to prevent the formation of black precipitates (total maximum bulk, 10 c.c.). Each solution was treated with 2 g. of potassium hydroxide dissolved in 5 c.c. of water, the required quantity of aluminium added, and the dissolved silver submitted to reduction at 100°. The volume of gas evolved was determined, and the gas proved to be nitrogen. Typical results are given in Table VI.

TABLE VI.

Wt. of Al (g.)	0·01	0·01	0·01	0·02	0·03
Wt. of AgNO$_3$ (g.)	0·2884	0·5378	0·7500	0·7500	0·7500
Nitrogen (c.c. at *N.T.P.*)	1·92	7·33	11·97	7·89	3·78
% Ag ppd.	99·52	99·81	99·82	99·88	99·84

It was observed that the evolution of nitrogen was retarded.

The results obtained indicate that the amount of silver reduced is stoicheiometrically equal to the aluminium dissolved *plus* the nitrogen evolved, *i.e.*, that Ag$^+$ reduced = Al oxidised + NH$_3$ oxidised, thus (in mg.-equivs.):

$\frac{1}{3}$Al	1·1	1·1	1·1	2·2	3·3
$\frac{1}{3}$N	0·5	2·0	3·2	2·1	1·0
Sum	1·6	3·1	4·3	4·3	4·3
AgNO$_3$	1·7	3·2	4·4	4·4	4·4

Series VII.—Reduction at 100°, *in ammoniacal solution, using a fixed quantity of aluminium, and varying amounts of dissolved silver in the presence of potassium hydroxide.* The object of this series was to ascertain the maximum effect of a definite quantity of aluminium under given conditions of experiment. 0·05 G. of aluminium was used in each case. The bulk of the mixed solutions and the concentration of ammonia were similar to those of Series IV. The quantities of silver compound used were equivalent to 2—8 g. of nitrate. In all experiments up to a silver content equivalent to 6 g. of nitrate, a quantitative yield of silver was obtained. The use of more concentrated solutions of silver frequently resulted in explosions. In this series it was observed that the first-formed, coherent masses of silver gradually changed to a granular powder. The results are given in Table VII.

TABLE VII.

Wt. of Ag compd. (g.)	2	3	4	5	6
Wt. of Ag ppd. (g.)	1·27	1·90	2·54	3·17	3·80
% Ag ppd.	99·73	99·82	99·79	99·83	99·89
% Ag in ppt.	99·79	99·88	99·85	99·80	99·84

Series VIII.—Reduction at 100°, *in ammoniacal solution, using definite quantities of aluminium in the presence of potassium hydroxide, the solutions of silver used during the process of reduction being added from time to time in measured volumes of known ammonia and silver content.* From the preceding series it seemed probable that the concentration of the silver salt relative to the ammonia content of the alkaline solution employed is a factor governing the stability of the ammoniacal solutions submitted to reduction. The present series was carried out to test this view.

A solution containing 2 g. of silver salt, prepared as in Series IV, was treated with 0·05 g. of aluminium filings. An additional series of solutions was prepared containing 2 g. of the same silver salt in 25 c.c. of ammonia (*d* 0·880) and 25 c.c. of water. At the end of consecutive intervals of 20 minutes, these solutions were, in turn, added to the reaction liquid undergoing reduction. The total quantity of silver salt thus added was equivalent to 8 g. of the silver salt employed. The resulting reduced silver formed grey, coherent masses. The results are given in Table VIII.

TABLE VIII.

	From $AgNO_3$.	From AgCl.
Wt. of ppt. (g.)	4·26	3·64
% Ag in ppt.	99·89	99·85
% Ag ppd.	66·94	48·27

Series IX.—As in Series VIII, activated silver being used instead of aluminium filings. Quantities of reduced silver, prepared as in Series IV, were activated by heating in a vacuum in a quartz tube for 3 hours at 900°, the samples of the metal obtained from the different salts being submitted to heat treatment separately. The method of experiment was as in Series VIII. The total quantity of silver salt added was equivalent to 8 g. of the silver salt used. Two series of experiments were carried out on activated silver from (i) silver nitrate, and (ii) cf. silver chloride. Table IX contains the results for the first series.

TABLE IX.

Activated Ag used (g.).	$AgNO_3$. Wt. of ppt. (g.).	% Ag in ppt.	% Ag ppd.	AgCl. Wt. of ppt. (g.).	% Ag in ppt.	% Ag ppd.
0·4	2·54	99·89	39·91	1·96	99·87	26·05
0·6	3·11	99·92	48·89	2·73	99·90	36·29
0·8	3·61	99·87	56·80	2·81	99·88	37·42
1·0	3·95	99·84	62·15	3·08	99·85	40·82

Discussion and Conclusions.

Under the conditions of experiment for hydrolysis at 100°, the black precipitates are transformed to metallic silver, while the reaction liquids are found to be free from dissolved silver. In so far as the black precipitates are unstable in the presence of traces of aluminium, it would seem that deposition of silver nitride, prior to the final separation of metallic silver, is entirely inhibited with respect to the different processes of reduction which proceed without detonation of the reaction mixture.

In the absence of aluminium, the different amounts of dissolved silver quantitatively separated as reduced metal are equivalent to the volumes of nitrogen evolved. In the presence of aluminium, the evolution of nitrogen is inhibited : the formation of this gas does not commence until every trace of metallic aluminium has been dissolved as aluminate.

The quantitative yields of reduced silver obtained under conditions for the production of nitrogen in presence of aluminium would appear, therefore, to be the cumulative effect of two distinct reactions. In the first reaction, metallic silver is separated from the solution in a quantity equivalent to the amount of aluminium employed. The newly deposited silver, being in a finely divided condition, serves to stabilise the ammoniacal solution containing the remainder of the silver present in the dissolved state, and, as in the experiments involving the employment of activated silver (compare Series IX), it imparts to the silver solution the increment of energy necessary for the commencement of the second reaction. The second reaction then proceeds to completion, the deposition of silver being accompanied by the evolution of nitrogen in the proportion of 3 atoms of silver to 1 atom of nitrogen.

It would seem, therefore, that, in the presence of ammonia, caustic alkali effects precipitation of silver nitride, with small amounts of silver oxide, through the formation of an intermediate complex, $(NH_3)_2AgOH$, according to the following equations :

$$\begin{aligned}
&\text{(Ai)}\ (NH_3)_2AgNO_3 + KOH = (NH_3)_2AgOH + KNO_3,\\
&\text{(Aii)}\ (NH_3)_2AgCl + KOH = (NH_3)_2AgOH + KCl,\\
&\text{(B)}\ 3(NH_3)_2AgOH + 2H_2O = 5NH_4OH + NAg_3,\\
&\text{(C)}\ 2(NH_3)_2AgOH + 3H_2O = 4NH_4OH + Ag_2O
\end{aligned}$$

(compare Bodländer and Fittig, *Z. physikal. Chem.*, 1902, **39**, 597; Straub, *ibid.*, 1911, **77**, 331).

At 100° the reactions represented by (B) and (C) are suppressed, decomposition of the diamminoargentic complex, evolution of nitrogen, and separation of silver taking place according to the equation

$$\text{(D)}\ 6(NH_3)_2AgOH + 4H_2O = 6Ag + N_2 + 10NH_4OH.$$

It is concluded that the first reaction takes place, in the presence of aluminium, accompanied by changes conveniently represented by the equations given on p. 1772. The second reaction involves transformations represented by the equations (Ai or Aii), (B), (C), and (D).

The results of Series IV and VII show that the extent of reduction is determined by the conditions of experiment. Thus, in Series VII, 6 g. of silver nitrate in 75 c.c. of reaction solution are completely reduced by the introduction of 0·05 g. of aluminium. By the modifications introduced in Series VIII larger quantities can be reduced without explosion, and 0·05 g. of aluminium reduces 6·694 g. of silver nitrate or 4·827 g. of silver chloride.

Series IX shows that, in absence of aluminium, ammoniacal solutions of silver nitrate or silver chloride may be reduced by means of freshly reduced silver from Series IV, activated by heating in a vacuum for 3 hours at 900°, 1 g. of activated silver being capable of reducing 6·215 g. or 4·082 g. of silver nitrate or chloride, respectively.

The continuous separation of finely divided silver in the form of grey, coherent masses possessing a vesicular structure is constantly exposing an ever-increasing surface of metal to the ammoniacal solution undergoing reduction. Uninterrupted contact between the surface of the newly deposited metal and the solution induces energy changes involving decay in the activity of the reduced metal followed by the separation of further quantities of silver from the solution. Prolonged contact between the reduced metal and the solution ultimately brings about a marked decay in the activity of the reduced metal, and this change is accompanied by the following characteristic effects. The coherent masses of reduced metal gradually break down to a powder, whilst the continued isolation of silver from the solution is ultimately brought to a limit beyond which no further appreciable deposition of reduced metal takes place.

In the presence of relatively large amounts of ammonia, separation of silver from ammoniacal silver solutions can be effected only when a suitable source of energy is introduced into the reacting system. Under given conditions of experiment, aluminium, in the presence of aqueous caustic alkali, may be employed to induce and control the production of reduced silver. When the ammoniacal concentration of the solution undergoing reduction has fallen to a certain limiting value, the concentration of the dissolved silver rises to a value such that it is unnecessary to supply energy to the reacting system : the residual ammonia is then unable to control the reaction, whilst the external heat applied in order to maintain the temperature of the reaction becomes more than sufficient to supply the energy necessary to allow the reaction to continue, with the result that the reaction is accelerated, and ultimately proceeds with explosive velocity. In these circumstances, therefore, the employment of aluminium, in the presence of caustic alkali, is quite unnecessary, and can lead only to an increase in the intensity of the explosive effects observed (compare Baly, *Ann. Report*, 1921, **18**, 40).

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