[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. IV. The Action of Potassium and Sodium upon Silver Salts

BY WAYLAND M. BURGESS AND FRANCIS R. HOLDEN[1]

Introduction

In investigating the reducing action of the alkali metals on liquid ammonia solutions of inorganic salts, but little attention has been given to potassium as the reducing agent. Weyl,[2] in the first recorded reaction ever carried out in liquid ammonia, condensed ammonia on both potassium and a salt, using salts of zinc, copper, mercury and silver. But in later work of this kind, sodium has been employed, and a detailed description of the reactions with salts of zinc, silver and manganese has been given in previous articles of this series.[3–5] From the concept of the alkali metal solutions, as developed by Kraus,[6] one would expect the reducing action of potassium to parallel that of sodium. However, with potassium the rate of reaction with ammonia, in which the amide and hydrogen are formed, is greater. Thus, an increased tendency for the concurrent reaction between the metal and the solvent, as was observed in the reduction of manganous iodide with sodium,[5] is to be expected.

In order to compare directly the reducing action of potassium and sodium, several silver salts have been reduced by each of these metals. The reactions are found to be similar in that the silver salt is reduced to free silver; but with potassium, there is always a concurrent reaction with ammonia, catalyzed by the freshly reduced silver. The effectiveness of the reduced silver as a catalyst is greater when potassium is the reducing agent, and also varies with different silver salts, silver cyanide in particular furnishing an active catalyst. The metallic precipitate from most reactions is inert in air, but in the reduction of silver cyanide with potassium a pyrophoric precipitate is obtained. Furthermore, the reduction may extend to the anion of the salt and, in the case of silver thiocyanate, the thiocyanate radical is reduced. The cyanate group, however, is stable in the presence of sodium and potassium in liquid ammonia solution.

The Reduction of Silver Iodide and Silver Chloride

In a previous paper[4] the reduction of silver iodide and silver chloride by sodium was shown to proceed smoothly with the formation of free silver and the corresponding sodium salt. The free silver so formed was non-reactive toward air and did not catalyze the reaction between sodium and ammonia. The ratio between the gram atoms of sodium and gram moles of silver salt reacting (called reaction ratio), was determined accurately and found to be close to 1.00.

Using the same experimental method, with Merck potassium (shown by analysis to be 99.85% potassium) as the reducing agent, higher values for the reaction ratio were obtained and a slight gas formation observed. The method was then modified to permit the collection of the gas. Upon analysis, this proved to be hydrogen. From the hydrogen volume so obtained, the amount of potassium reacting with ammonia was determined and the reaction ratio corrected for this loss of potassium. This was also checked by treating the product of the reaction, after evaporation of the ammonia, with distilled water, which reacted with the potassium amide, and titrating this basic solution, previously boiled, with tenth normal hydrochloric acid. From the acid used, the amount of potassium amide present was calculated, and the reaction ratio corrected for the loss of potassium as determined in this way.

The results of the reduction of silver chloride and silver iodide are given in Table I, in which reaction ratio of column 5 refers to the ratio between gram atoms of potassium and gram moles of silver salt employed; corrected ratios (1) and (2) are the values obtained when the potassium that reacted with ammonia, as determined by the collection of hydrogen and by the amide analysis, respectively, has been subtracted from the total potassium used.

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(1) This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Francis R. Holden in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

(2) Weyl, *Ann. Physik*, **123**, 350 (1864).

(3) Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

(4) Burgess and Smoker, *ibid.*, **52**, 3573 (1930).

(5) Burgess and Smoker, *Chem. Rev.*, **8**, 265 (1931).

(6) Kraus, THIS JOURNAL, **30**, 1323 (1908).

TABLE I

REDUCTION OF SILVER CHLORIDE WITH POTASSIUM

Expt.	K, g.	Ag salt, g.	H_2, cc. N. T. P.	Ratio K/AgCl (1)	Corr. ratio (1) K/AgCl (1)	Corr. ratio (2) K/AgCl (1)
22	0.9674	3.3412	[a]	1.06	..	..
112	.4021	1.4358	[a]	1.03	..	1.01
115	.3106	1.1235	2.6	1.01	0.99	1.00
116	.4535	1.5928	5.1	1.04	1.00	1.01
REDUCTION OF SILVER IODIDE						
36	0.4656	2.6785	3.6	1.04	1.02	1.01
41	.3895	2.2636	1.5	1.03	1.02	1.01
45	.3565	2.0614	0.8	1.04	1.03	1.00

[a] Hydrogen not collected.

The reaction ratio is slightly higher than 1.00 as obtained in the sodium reaction but this difference is, without doubt, due to the experimental error in determining the amount of potassium that reacted with the ammonia. Thus, potassium reduces silver chloride and iodide to free silver, with a small amount of concurrent reaction between potassium and ammonia.

The precipitated silver was found to be nonreactive toward air. An analysis of the precipitate from a reaction using silver iodide and potassium, where the precipitate had been washed carefully by a method described in an earlier paper,[3] gave a silver content of 98.5%. This purity is almost the same as found using sodium as the reducing metal and shows that all soluble impurities cannot be removed by washing with liquid ammonia.

Since the reaction with ammonia requires that there always be an excess of reducing metal used, a method was tried by which a large excess of potassium was added to a liquid ammonia solution of the silver salt. Then, after reduction was complete, the excess metal was destroyed by the addition of ammonium bromide. From the gas collected, the excess potassium was calculated. The results are given in Table II.

TABLE II

REDUCTION OF SILVER IODIDE WITH EXCESS POTASSIUM

Expt.	K, g.	AgI, g.	H_2, cc. N. T. P.	Ratio K/AgI	Corr. ratio K/AgI
209	0.3639	1.0428	53.8	2.10	1.01
210	.3344	1.0240	46.4	1.96	1.01

The corrected reaction ratio is 1.01, and shows that this procedure is a satisfactory method for study of these reduction reactions.

The Reduction of Silver Cyanide

The reduction of silver cyanide by sodium was investigated by Kraus and Kurtz,[7] who found that more sodium was necessary for the reaction than would be required for the simple reduction to metallic silver—a reaction ratio of the order of 1.1 being obtained. Preliminary work with sodium, in which the salt was added to the metal solution, gave a high ratio, averaging 1.03. This indicated that the silver might catalyze the reaction between sodium and ammonia. However, the formation of appreciable hydrogen was not detected. But when the silver cyanide was reduced with potassium, the precipitated silver was found to be a catalyst for the reaction between potassium and the solvent, much better than the reduced silver from the iodide or chloride. An accurate determination of the reaction ratio for both sodium and potassium was made by adding an excess of metal to a liquid ammonia solution of the salt and, in the case of sodium, destroying the excess metal with ammonium chloride. Ammonium chloride was not needed with the potassium reaction. The results are shown in Table III.

TABLE III

REDUCTION OF SILVER CYANIDE WITH SODIUM

Expt.	Na (or K), g.	AgCN, g.	H_2, cc. N. T. P.	Ratio Na(K)/AgCN	Corr. ratio Na(K)/AgCN
205	0.2502	0.9780	39.9	1.49	1.00
206	.2432	1.0118	33.1	1.40	1.01
REDUCTION OF SILVER CYANIDE WITH POTASSIUM					
199	0.4708	0.9967	50.4	1.62	1.01
200	.4420	.9837	41.8	1.54	1.03
203	.3905	1.0185	25.2	1.31	1.02

The corrected reaction ratio approaches 1.00 for sodium, but is slightly higher for potassium. In each case, the reaction parallels that with the other silver salts, except that the precipitated silver is very finely divided and distinctly more reactive. This was especially marked by the fact that the precipitate from experiments numbered 199 and 200 was pyrophoric, bursting into flame when exposed to air. That the activity of the precipitated metal may vary with the salt employed, has not been observed before. In run 203, ammonium chloride was added *after* the completion of the reaction and this reduced silver was not pyrophoric. Neither was the precipitate pyrophoric in those runs where an excess of silver cyanide was always present or where sodium was the reducing agent.

In some reduction reactions using nickel salts,[8] it has been shown definitely that a high reaction

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(7) Kraus and Kurtz, THIS JOURNAL, **47**, 43 (1925).

(8) Eastes, Ph.D. Thesis, University of Cincinnati, 1936.

ratio may be obtained due to hydrogen being adsorbed by the precipitated nickel. It is probable that the slightly higher ratio with potassium in all cases of silver salt reduction is due to a small loss of hydrogen through adsorption by the silver. It is also possible that the reduced silver owes its pyrophoric property to adsorbed hydrogen. In all cases in which the reduced metal was pyrophoric, the formation of hydrogen also occurred. In the work with nickel, it was shown that the addition of ammonium chloride released hydrogen adsorbed by the precipitated nickel. The effect of ammonium chloride in destroying the pyrophoric property of the reduced silver precipitate may be explained in a similar manner. A further study is being made of the nature and properties of pyrophoric precipitates formed by reduction in liquid ammonia.

The Reduction of Silver Thiocyanate and Cyanate

Because of solubility relations, there are relatively few salts that may be used for the reduction reaction in liquid ammonia. Some of the generally soluble salts, in particular the thiocyanates, cyanates and nitrates, have an anion that may not be stable in the presence of such a strong reducing reagent as the alkali metals. Having established a simple reduction in the case of several silver salts, a study was made of the reduction of silver thiocyanate and silver cyanate to determine the stability of these anions. With silver cyanate, excess metal was added to a solution of the salt, while with silver thiocyanate, the salt was added to a solution of the metal. The results are given in Table IV.

TABLE IV

REDUCTION OF SILVER THIOCYANATE WITH SODIUM

Expt.	Na (or K), g.	Ag salt, g.	H_2, cc. N. T. P.	Ratio Na(K)/ Ag salt	Corr. ratio Na(K)/ Ag salt
56	0.2645	1.7698	0.0	1.08	1.08
58	.2148	1.4451	.0	1.07	1.07
75	.4300	2.8657	.0	1.08	1.08
REDUCTION OF SILVER CYANATE WITH SODIUM					
207	0.2491	1.0109	46.3	1.61	0.99
208	.2433	1.0737	38.9	1.48	.99
REDUCTION OF SILVER THIOCYANATE WITH POTASSIUM					
46	0.4637	1.8015	1.4	1.09	1.08
48	.2454	0.9522	1.4	1.09	1.07
71	.3611	1.3745	0.7	1.12	1.11
72	.4605	1.8057	2.3	1.08	1.06
REDUCTION OF SILVER CYANATE WITH POTASSIUM					
201	0.4305	0.9951	48.2	1.66	1.01
202	.4288	1.0023	47.6	1.64	1.00

The average ratio for the reduction of silver thiocyanate is 1.08. This definitely points to another reaction, the most probable being the reduction of the thiocyanate anion. Evidently, the reduction is far from complete. The ratio for the reduction of the silver cyanate approaches 1.00 in each case, thereby proving that silver cyanate is reduced to silver and alkali cyanate, the cyanate radical not being attacked.

To confirm the reduction of the thiocyanate radical, qualitative tests, which were made on the product of the reduction after evaporation of the ammonia, showed the presence of cyanide. Furthermore, potassium was found to react slowly with potassium thiocyanate to form both sulfide and cyanide.

A preliminary study of the reduction of silver nitrate showed that the nitrate radical was readily reduced by both sodium and potassium in liquid ammonia solutions. Silver nitrate diammoniate, $AgNO_3 \cdot 2NH_3$, prepared by evaporating the ammonia from a liquid ammonia solution of silver nitrate, was found to be stable in air at room temperatures, but lost ammonia at 60°. The ratio for the reaction where this salt was added to a solution of the alkali metal, was 5.4 gram atoms of sodium per mole of salt, and 4.6 gram atoms of potassium per mole of salt. The reaction product when sodium was used was black and pyrophoric, and a good catalyst for the reaction between sodium and ammonia, this being the only case where the product of the sodium reduction showed these properties. Some work was done on the reduction of other nitrates with the following results. Using sodium nitrate and sodium, the reaction ratio was 3.5 gram atoms of sodium per mole of salt, and the reaction product was yellow and explosive in air. With potassium nitrate and potassium the ratio was 3.1 and the reaction product was yellow but not explosive. Using ammonium nitrate and potassium, practically no hydrogen was obtained, and the reaction ratio was 3.1 gram atoms of potassium per mole of ammonium nitrate. All of this work shows definitely that the nitrate anion is unstable in the presence of metal solution in liquid ammonia, but further study is necessary to determine the nature of the reduction products.

Summary

Silver salts are reduced by both sodium and potassium in liquid ammonia solution to free silver. This reduced silver may catalyze the reac-

tion between the alkali metal and ammonia. Its efficiency as a catalyst is greater when potassium is the reducing agent and it also varies with the silver salt. With silver thiocyanate, the thiocyanate radical is partially reduced, but with silver cyanate the cyanate group is stable in the presence of either sodium or potassium solutions.

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A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. V. The Action of Calcium upon Silver Salts

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Introduction

In a previous paper,[2] the reducing action of the two alkali metals, sodium and potassium, upon a number of silver salts was compared. The reactions were similar, forming free silver and the corresponding alkali metal salt, except that the precipitate from the potassium reactions was reactive in air and a better catalyst for the concurrent reaction between the metal and ammonia. A similar study, in which calcium has been used as the reducing metal, has led to the remarkable results that, with calcium, the reduction reactions are decidedly more vigorous, the precipitated silver is also reactive toward air, and is superior, as a catalyst, to that obtained with potassium. No reference to a previous investigation has been found that would indicate calcium solutions to be a better reducing medium than solutions of the alkali metals.

The Reduction of Silver Iodide and Silver Cyanide

To a solution of silver iodide in liquid ammonia, using an apparatus and procedure described in earlier papers,[2,3] was added an excess of Kahlbaum calcium, found by analysis to be 99.1% calcium. The reaction was rapid and the resulting black precipitate so fine that it settled very slowly. It was such an excellent catalyst for the reaction between calcium and ammonia that the excess metal was converted rapidly into calcium amide and hydrogen. The experimental results showing the amounts of the reacting substances and the volume of hydrogen collected are given in Table I.

TABLE I

REDUCTION OF SILVER IODIDE

Expt.	Ca, g.	Ag salt, g.	H_2, cc. N. T. P.	Ratio 1/2Ca/ AgI(CN)	Corr. ratio 1/2Ca/ AgI(CN)
182	0.2224	1.2903	62.7	2.02	1.00
183	.2709	1.3623	88.3	2.33	0.97
184	.2126	1.1741	62.5	2.12	1.01
REDUCTION OF SILVER CYANIDE					
178	0.2716	1.1993	48.4	1.51	1.03
179	.3254	1.0306	96.6	2.11	0.99
180	.2934	0.7564	100.4	2.59	1.01

Corrected reaction ratio, column 6, has been corrected by subtracting from the total calcium used, the amount of calcium that reacted with ammonia, as determined by the hydrogen collected. This is a true measure of the amount of calcium and silver salt that reacted. This value being 1.0, shows that the silver salt is reduced to free silver. Two concurrent reactions occur as presented by the equations

$$Ca + 2AgI \text{ (or } AgCN) \longrightarrow CaI_2 \text{ (or } Ca(CN)_2) + 2Ag$$
$$Ca + 2NH_3 \longrightarrow Ca(NH_2)_2 + H_2$$

In a study of the reaction between silver cyanide and calcium by Kraus and Kurtz,[4] it was postulated that a compound CaAg was formed. The average reaction ratio obtained by them was 2.12, but no attempt was made to determine the amount of hydrogen formed. The present work shows that their high ratio was due to the reaction of calcium and ammonia and that no compound of calcium and silver is prepared in this way.

The precipitated silver from the silver cyanide was pyrophoric and more reactive than that from the silver iodide reaction. In each case, the reduced silver from the calcium reaction was a better catalyst than that obtained by the reduction of the same salt with potassium or sodium. After the completion of one experiment, using calcium and silver cyanide, 0.06 g. of sodium was added to

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Francis R. Holden in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

[2] Burgess and Holden, THIS JOURNAL, **59**, 459 (1937).

[3] Burgess and Rose, *ibid.*, **51**, 2127 (1929).

[4] Kraus and Kurtz, *ibid.*, **47**, 43 (1925).