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Reactions in Liquid Ammonia. II. Reduction of Hexavalent Chromium Compounds[1a]

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An examination of the literature concerning the reactions of hexavalent chromium derivatives with liquid ammonia reveals little definite, uncontradicted information. Moreover, experimental procedures used in the previous studies of this problem are highly questionable.[1b,2,3,4,5,6,7] Some preliminary experiments by one of the authors[8] were of sufficient interest to lead the authors to undertake a more general study of the problem. This is a report of the results of the investigation of the reactions of chromic anhydride, potassium chlorochromate, ammonium dichromate, and ammonium chromate with liquid ammonia, with solutions of ammonium nitrate in liquid ammonia, and with solutions of water in liquid ammonia. These reactions were all carried out at the temperature of boiling ammonia.

Experimental

Materials.—Anhydrous synthetic ammonia with a purity of 99.95% was used. The use of ammonia which had been allowed to stand over sodium gave results which differed in no way from those in which the ammonia was not so treated.

Chromic anhydride of C. P. grade was used. It was dried for fifteen hours in an evacuated Abderhalden apparatus over phosphorus pentoxide at the temperature of boiling bromobenzene. The purity of the product was checked by *analysis:* Calculated for CrO_3: Cr^{VI}, 52.00. Found: Cr^{VI}, 51.55, 51.70; Cr (total) 51.90. This indicates that about 99.5% of the Cr is in the hexavalent state. Corrections for the 0.5% of reduced chromium were made in the analytical data for the experiments below.

Ammonium chromate, ammonium dichromate and ammonium nitrate of C. P. grade were used and were dried at appropriate temperatures in the oven.

The potassium chlorochromate used was prepared by the action of chromyl chloride on potassium chromate.[8]

Method.—The general method followed in these studies was to add a sample of the chromium compound to a definite volume of liquid ammonia or ammonia solution of water or ammonium nitrate, and to allow the reaction mixture to stand until the excess ammonia had evaporated and, along with the gases produced in the reaction, had passed into an absorption tower filled with water. The apparatus used in these experiments is illustrated in Fig. 1, in which A and B are tanks of ammonia, C the reaction chamber, E the cooling bath of liquid ammonia, G a mercury tube by means of which pressure was applied to the reaction chamber to bring about condensation of ammonia, and M the absorption tower filled with water which had been saturated with nitrogen under the conditions of the experiment. The general technique used was similar to that described by Johnson and Fernelius.[9] The most important innovation was that the sample was introduced from the tube D by forcing out the stopper with a stream of ammonia through the capillary I. This technique prevented contact between the chromium compound and ammonia vapor prior to the introduction of the solid into the liquid. The gas analyses were corrected for the volume of air in the capillary I and the unoccupied part of tube D (3.5 ml.). At the end of the experiment the solid residue in the reaction chamber was analyzed by methods described below, and the water-insoluble gas which had collected in the absorption tower was transferred to the gas analysis apparatus.

Analytical Methods.—Analyses for ammonia nitrogen were made by dissolving weighed portions of the product in concentrated sodium hydroxide solution, distilling the ammonia into standard acid and titrating with standard base.

Hexavalent chromium was determined by treating an aliquot portion of an acidified solution of a weighed portion of the product with excess standard ferrous sulfate solution, and titrating with standard chromate solution. Total chromium was similarly determined on a solution which had been subjected to prior treatment with ammonium persulfate. In most of the experiments where the interest was in the percentage of chromium reduced, the sample was dissolved directly in acid without weighing and analyzed for total and hexavalent chromium to determine the fraction of chromium reduced.

Gaseous products from these experiments were washed with dilute acid to remove traces of ammonia, and oxygen was determined by absorption in alkaline pyrogallol solution. The samples were then tested for oxides of nitrogen by washing with alkaline permanganate. The residue was assumed to be nitrogen.

Reaction of Chromic Anhydride with Liquid Ammonia at −33°.—When introduced into liquid ammonia, the dark red chromic anhydride was gradually converted to a yellow-tan solid which remained after the practically colorless supernatant liquid had evaporated. The substance had a marked vapor pressure of ammonia even after standing *in vacuo* for more than a month. In one series of experiments the residues were analyzed for ammonia nitrogen, total chromium, and hexavalent chromium. The following analytical results are typical: Cr^{VI}, 27.4, 26.55; Cr(total), 37.4, 37.1, 37.0; N, 24.6, 24.9, 25.1.

It should be pointed out that these reactions may be assumed to be complete, for in a few experiments several

TABLE I[a]

REACTIONS OF CrO_3 WITH LIQUID NH_3 AT −33°

Total Cr, g.	Hexavalent Cr, g.	Reduced Cr, g.	% Cr reduced	Analysis of gas, ml.[c] N_2	O_2	%[b] of theoretical nitrogen
0.463	0.342	0.121	26.1	15.4	0.8	..
.532	.387	.145	27.3	14.9	1.9	50
.808	.597	.211	26.1	21.6	1.6	49
.636	.469	.167	26.2	17.9	1.1	51
.617	.462	.155	25.1	16.2	1.6	50
.642	.475	.167	26.0	17.5	1.4	50
.650	.479	.171	26.3	17.4	1.2	48

[a] 50 ml. of liquid ammonia was used in all these experiments. [b] Based upon the total chromium reduced minus reduced chromium equivalent to the oxygen obtained. [c] Corrected to standard conditions.

[1a] For the first publication in this series see *Trans. Kans. Acad. Sci.*, **46**, 136 (1943).

[1b] Lowenthal, *Z. anorg. Chem.*, **6**, 355 (1894).

[2] Ohly, *Chem. News*, **80**, 134 (1899).

[3] Heintze, *J. prakt. Chem.*, [2] **4**, 214 (1871).

[4] Wyrouboff, *Bull. soc. chim.*, [3] **11**, 845 (1894).

[5] Meyer and Best, *Z. anorg. Chem.*, **22**, 197 (1900).

[6] Werner and Klein, *ibid.*, **9**, 291 (1895).

[7] Rosenheim and Jacobsohn, *ibid.*, **50**, 297 (1906).

[8] Sisler, *Trans. Kans. Acad. Sci.*, **46**, 136 (1943).

[9] Johnson and Fernelius, *J. Chem. Education*, **6**, 441–450 (1929).

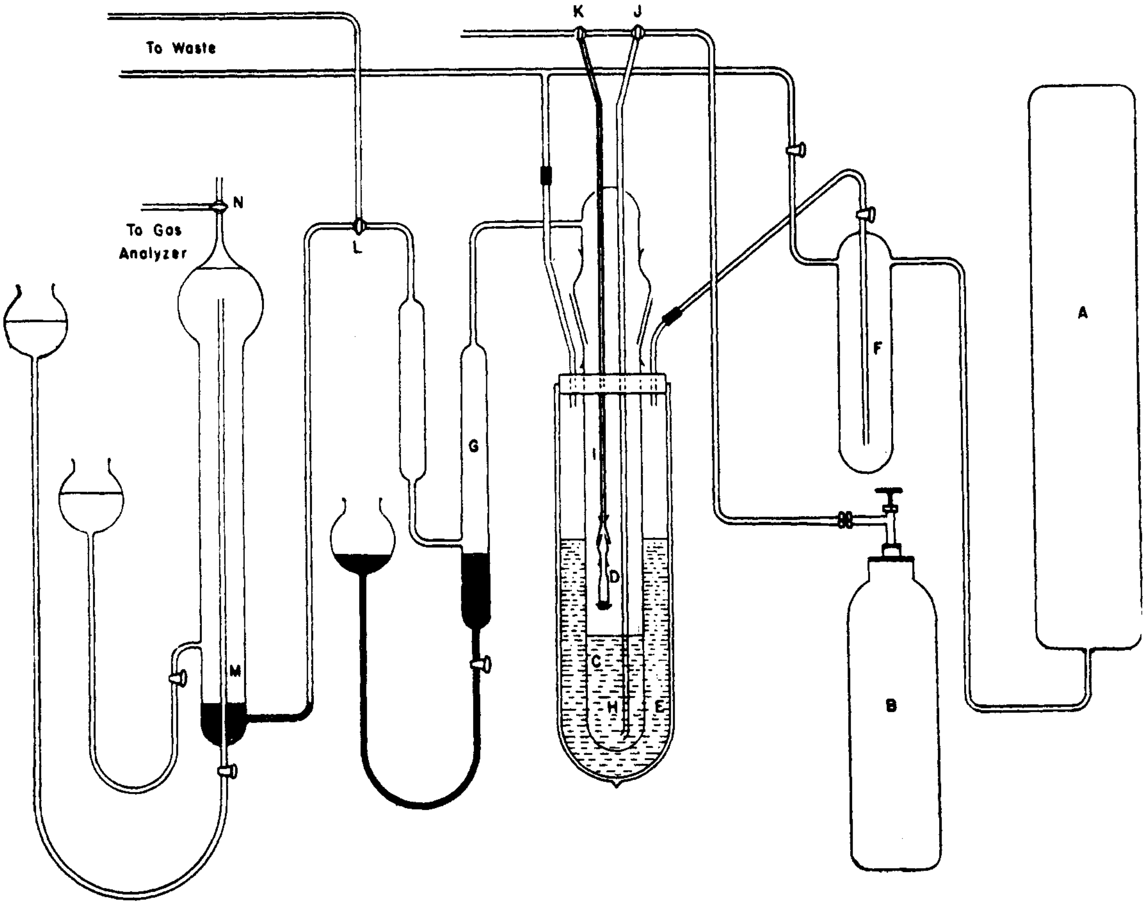

Fig. 1.

extra portions of liquid ammonia were condensed on the solid reaction product without further change.

In the second series of experiments only the percentage of chromium reduced was determined. The results of a series of these experiments are listed in Table I.

The above data indicate that some oxidation product other than gaseous nitrogen must have been formed in the above reaction. Tests for nitrate, nitrite, hydroxylamine and hydrazine, both on the solid residue and in the water in the absorption tower, and for oxides of nitrogen in the gaseous products, were all negative. A clue to the solution of this problem was found, when it was determined that when the solid residue from the above reaction was heated to temperatures above 100° the resulting thermal decomposition yielded, in addition to much ammonia, an amount of nitrogen in excess of that due to the additional reduction which took place during the thermal treatment. This "excess" nitrogen proved to be approximately equal to the missing 50% from the liquid ammonia reaction. Table II lists some typical results.

TABLE II

%[a] Cr reduced	% of theoretical N_2	Temp. of thermal treatment, °C.	Additional[b] % of theoretical N_2	Total % of[b] theoretical N_2
26.5	49	150	47	96
26.0	50	195	40	90
25.6	50	150	42	92
25.6	50	100	43	93

[a] In the reaction in liquid ammonia. [b] Based upon the Cr reduced in the reaction in liquid ammonia.

Experiments in which the reaction products from the chromic anhydride reaction were subjected to high pressures of nitrogen or were subjected to high vacua at a temperature of 50° and then subjected to the above thermal treatment did not differ appreciably from the above results. This indicates that the nitrogen in the solid is not held by physical adsorption.

Since hydronium ion is known to have marked effects on oxidation potentials in aqueous solutions, the authors were concerned with the determination of the effect of ammonium ion on the reaction of chromic anhydride with liquid ammonia. To this end, a series of experiments in

TABLE III[a]

REACTIONS OF CrO_3 WITH SOLUTIONS OF NH_4NO_3 IN LIQUID NH_3 AT −33°

Total Cr, g.	NH_4NO_3, g.	Hexavalent Cr, g.	Reduced Cr, g.	% Cr reduced	%[b] of theoretical N_2
0.895	6	0.625	0.270	30.1	48
.744	6	.532	.212	28.5	50
.875	9	.616	.259	29.6	53
.923	9	.634	.289	31.3	50
.880	12	.580	.300	34.1	51
.911	12	.578	.333	36.5	..
.665	30	.367	.298	44.8	52
.740	30	.438	.302	40.8	..

[a] In all these experiments the volume of the ammonia–ammonium nitrate solution was 50 ml. [b] See corresponding note under Table I.

which chromic anhydride was added to solutions of ammonium nitrate in liquid ammonia was carried out. The reactions proceeded much as in the above series except that the supernatant liquid left after the solid had settled out was of a definitely red color, indicating considerable solubility. The gas obtained was mainly nitrogen, with small amounts of oxygen. The results of a series of these experiments are listed in Table III.

A similar series of experiments involving the reaction of chromic anhydride with solutions of water in liquid ammonia was carried out. The gas obtained in these reactions was mainly nitrogen, with small amounts of oxygen. The results of these experiments are listed in Table IV.

TABLE IV[a]

REACTION OF CrO_3 WITH SOLUTIONS OF H_2O IN LIQUID NH_3 AT −33°

Total Cr, g.	H_2O, g.	Hexavalent Cr, g.	Reduced Cr, g.	% Cr reduced	% of[b] theoretical N_2
0.847	0.5	0.667	0.180	21.2	44
.840	.5	.665	.175	20.8	50
.737	1.0	.609	.128	17.4	53
.868	1.0	.710	.158	18.2	48
.770	1.0	.618	.152	19.7	44
.706	2.5	.608	.098	13.9	47
.780	2.5	.670	.110	14.1	46
.414	5.0	.356	.058	14.0	. .
.535	5.0	.465	.070	13.1	48
.749	5.0	.644	.105	14.0	. .
.633	10.0	.547	.086	13.6	. .
.868	18.2	.787	.081	9.3	. .

[a] In all these experiments the total volume of water–ammonia solution was 50 ml. [b] See corresponding note under Table I.

A further experiment was run in which chromic anhydride was added directly to liquid ammonia in which both ammonium nitrate and water were dissolved. When chromic anhydride (1.721 g.) was added to a solution of 2.5 g. of water and 12.0 g. of ammonium nitrate in enough liquid ammonia to give 50 ml. of solution, reduction to the extent of 19.0% of the chromium took place.

Reaction of Potassium Chlorochromate with Liquid Ammonia at −33°.—A series of experiments involving the reactions of liquid ammonia, solutions of ammonium nitrate in liquid ammonia and solutions of water in liquid ammonia with potassium chlorochromate was carried out. When potassium chlorochromate was added to liquid ammonia, there was formed immediately a dark reddish-brown precipitate. After the excess ammonia had evaporated, there remained a light yellow-tan product very similar in properties to that obtained from the chromic anhydride reaction. Representative data from this series of experiments are given in Table V.

TABLE V[a]

REACTION OF POTASSIUM CHLOROCHROMATE AT −33°

Total Cr, g.	H_2O, g.	NH_4NO_3, g.	Hexavalent Cr, g.	Reduced Cr, g.	% Cr reduced
0.1582	. . .	. .	0.1147	0.0435	27.4
.2279	. . .	. .	.1641	.0638	28.0
.0969	. . .	. .	.0709	.0260	26.8
.1915	2.5	. .	.1855	.0060	3.13
.1771	2.5	. .	.1720	.0051	2.88
.1696	. . .	12.0	.0850	.0846	49.3
.1712	. . .	12.0	.0978	.0734	43.8
.1819	. . .	25.0	.0374	.1445	79.5

[a] In all these experiments the total volume of solution was 50 ml.

Reactions of Ammonium Chromate and Ammonium Dichromate with Liquid Ammonia at −33°.—A further series of experiments was carried out on the reaction of ammonium dichromate with ammonia and solutions of water in ammonia. Ammonium dichromate did not dissolve appreciably in liquid ammonia, but on standing the orange-colored dichromate was gradually converted to a dull yellow-tan product. Representative data from this series of experiments are given in Table VI.

TABLE VI[a]

REACTION OF AMMONIUM DICHROMATE AT −33°

Total Cr, g.	H_2O, g.	Hexavalent Cr, g.	Reduced Cr, g.	% Cr reduced	% of[b] theoretical N_2
0.388	. .	0.340	0.048	12.4	. .
.544	. .	.476	.068	12.5	58
.677	. .	.588	.089	13.1	52
.504	1.5	.474	.030	5.9	. .
.744	2.5	.706	.038	5.1	. .
.601	2.5	.571	.030	6.0	. .
.452	5.0	.431	.021	4.6	. .
.607	5.0	.576	.031	5.1	. .
.625	10.0	.589	.036	5.8	. .

[a] In all these experiments the total volume of ammonia or water–ammonia solution was 50 ml. [b] See corresponding note under Table I.

In contrast to ammonium dichromate, ammonium chromate was not reduced by liquid ammonia even on standing in the ammonia for twenty-four hours. However, when ammonium chromate was allowed to react with ammonia solutions of ammonium nitrate containing 12 g. of the salt per 50 ml. of the solution, reductions up to 9% were obtained.

Discussion

The data in Tables I and V indicate that about one atom in four of the chromium in chromic anhydride or in potassium chlorochromate is reduced when these substances are added to liquid ammonia. The failure of the reaction to proceed beyond this point appears to be due to the formation of a precipitate of such low solubility as to prevent further reaction. The analytical data obtained do not clearly indicate any likely compound, but in general correspond to what might be expected of a highly ammonated chromic ammonium chromate or chromic amidochromate, such as, *e. g.*,

$$Cr(NH_4)_3(CrO_4)_3 \cdot xNH_3 \text{ or } Cr(CrO_3NH_2)_3 \cdot xNH_3.$$

As is indicated by the data in Table VI, only one atom of chromium in eight is reduced when ammonium dichromate reacts with liquid ammonia. Ammonium dichromate, however, may be considered to be an addition compound of ammonium chromate and chromic anhydride, $(NH_4)_2CrO_4 \cdot CrO_3$. Since ammonium chromate was shown to be unaffected by liquid ammonia, only one-half the chromium in ammonium dichromate may be considered as "available" for reduction. It is evident, therefore, that of the chromium thus "available," one atom in four is reduced.

The increase in the percentage reduction of the chromium in chromic anhydride, potassium chlorochromate, and ammonium chromate reactions brought about by considerable concentrations of ammonium nitrate is not surprising. It is a well-known fact that the solubility of slightly soluble chromates in water is increased by the presence of hydronium ion. The chromates are converted to the more soluble dichromates according to the equation

$$2MCrO_4 + 2H_3O^+ \rightleftarrows 2M^{++} + Cr_2O_7^{=} + 3H_2O \quad (1)$$

Since ammonium ion is an acid, it is to be expected that the solubility of the yellow-tan reduction product would be increased by the presence of ammonium salts. The red supernatant liquid obtained in the experiments involving ammonium nitrate supports this point of view. If the solubility is increased, more reduction will take place before the reaction is stopped by precipitation. The fact that ammonium chromate, although unaffected by liquid ammonia, nevertheless undergoes reduction in ammonia solutions of ammonium nitrate, is evidence for a chromate-dichromate shift in liquid ammonia. This change may be represented by the equation

$$2CrO_4^{=} + 2NH_4^+ \longrightarrow Cr_2O_7^{=} + 2NH_3 + H_2O \quad (2)$$

which is analogous to

$$2CrO_4^{=} + 2H_3O^+ \longrightarrow Cr_2O_7^{=} + 3H_2O \quad (3).$$

The extent and the rate of such conversion are less than in water, of course, since the solubilities of ammonia chromate and dichromate in liquid ammonia are small, and the proton-donor tendency of the ammonium ion is much less than that of the hydronium ion.

As is shown by the data in Tables IV, V and VI, the presence of even small quantities of water in the liquid ammonia causes marked reduction in the percentage of chromium reduced. This effect is undoubtedly due to the conversion of some of the chromic anhydride, dichromate, or chlorochromate into chromate, according to the equations

$$CrO_3 + H_2O + 2NH_3 \longrightarrow 2NH_4^+ + CrO_4^{=} \quad (4)$$

$$Cr_2O_7^{=} + H_2O + 2NH_3 \longrightarrow 2NH_4^+ + 2CrO_4^{=} \quad (5)$$

$$KCrO_3Cl + H_2O + 2NH_3 \longrightarrow K^+ + 2NH_4^+ + CrO_4^{=} + Cl^- \quad (6)$$

It should be noted that the equation (5) is just the reverse of the equation (2). That this reaction is reversible is shown by the fact that if *both* water and ammonium nitrate are added to the liquid ammonia the percentage of chromium reduced when chromic anhydride is added is higher than for the water–ammonia solution alone.

The reduction of hexavalent chromium by liquid ammonia cannot be as represented by the equation

$$2CrO_3 + 2NH_3 \longrightarrow 2Cr^{+++} + N_2 + 6OH^-$$

for only about one-half the nitrogen required according to this equation is obtained. Physical adsorption of nitrogen by the solid is not a likely explanation of this anomaly, since the solid failed to adsorb nitrogen on standing under pressure or to lose nitrogen on standing under vacuum. The fact that most of the "missing" nitrogen can be obtained by heating the reaction product (Table II) suggests rather that some of the oxidized nitrogen is held in the form of some chromic complex which breaks down on being heated.

Summary

A study of the reactions of compounds of hexavalent chromium with liquid ammonia and with liquid ammonia solutions of ammonium nitrate and of water at −33° has shown:

1. About one-fourth of the chromium in chromic anhydride or in potassium chlorochromate is reduced to the trivalent state on reaction with liquid ammonia. Ammonium dichromate is one-eighth reduced, while ammonium chromate is not affected.
2. The percentage of chromium reduced is increased by the presence of ammonium nitrate in the liquid ammonia; the presence of water produces the opposite effect.
3. The gaseous nitrogen obtained from these reduction reactions is only about one-half that which is equivalent to the amount of chromium reduced. The rest of the nitrogen may be obtained by heating the solid residue.

Certain theoretical aspects of these data have been discussed.

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