

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 thiocya-

nate 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.

(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 fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

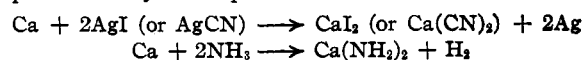
(2) Burgess and Holden, *THIS JOURNAL*, **59**, 459 (1937).

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

TABLE I

Expt.	Ca, g.	Ag salt, g.	H ₂ , cc. N. T. P.	REDUCTION OF SILVER IODIDE	
				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



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

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

the solution and it was converted to sodium amide in less than fifteen minutes. Silver cyanide reduced by sodium gives silver whose catalytic power is negligible.

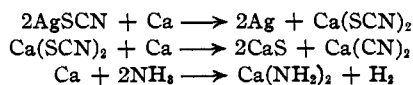
The Reduction of Silver Thiocyanate and Silver Cyanate

It has been shown previously² that in the reduction of silver thiocyanate to free silver using potassium and sodium, a small amount of the alkali metal was used in the concurrent reduction of the thiocyanate group to sulfide and cyanide. With silver cyanate, the cyanate radical appeared to be stable in the presence of the alkali metal solutions. In view of the more vigorous reduction of the silver iodide and cyanide with calcium, the reaction between silver thiocyanate and calcium offers another opportunity to compare the reducing powers of calcium and the alkali metals. The results obtained by adding an excess of calcium to solutions of sodium thiocyanate are shown in Table II.

TABLE II
REDUCTION OF SILVER THIOCYANATE

Expt.	Ca, g.	AgCNS, g.	H ₂ , cc. N. T. P.	Ratio 1/2Ca/AgCNS	Corr. ratio 1/2Ca/AgCNS
175	0.3949	0.9960	15.2	3.28	3.06
176	.5054	.9979	79.6	4.20	3.01
177	.4705	1.0061	58.4	3.88	3.01

The corrected ratio should be 1.0, if the silver thiocyanate were reduced to silver and no other reaction occurred. The value is close to 3.0, indicating that the reduction of the thiocyanate group to cyanide and sulfide, which requires two additional equivalents of calcium per mole of silver thiocyanate, does occur and goes to completion. The reduction of silver thiocyanate then may be represented by three equations



In the reduction of silver cyanate with calcium,

it was found that when approximately equivalent amounts of the calcium and silver cyanate were employed, the only reaction to occur was the reduction of the salt to free silver; but with an excess of calcium, a partial reduction of the cyanate radical did occur. These results are shown in Table III, where the first three experiments are with nearly equivalent amounts, and the last three with an appreciable excess of calcium.

TABLE III
REDUCTION OF SILVER CYANATE

Expt.	Ca, g.	AgCNO, g.	H ₂ , cc. N. T. P.	Ratio 1/2Ca/AgCNO	Corr. ratio 1/2Ca/AgCNO
169	0.0213	0.1514	0.5	1.05	1.01
170	.0320	.2275	.5	1.05	1.02
171	.0319	.2148	.8	1.11	1.06
174	.2752	1.0000	62.9	2.06	1.22
166	.3498	1.0020	102.4	2.61	1.24
167	.4367	1.1983	131.7	2.73	1.26

In those experiments where but a very small excess of calcium was used, the corrected ratio shows that little, if any, reduction of the cyanate radical occurred. However, with an excess of calcium, an appreciable reduction of the cyanate group took place. This was also confirmed by the analysis of the products of experiment 174 after evaporation of the ammonia. Strong positive tests for the presence of cyanides were obtained. Thus, we have further evidence that a solution of calcium in liquid ammonia is a stronger reducing agent than solutions of the alkali metals.

Summary

Silver salts are reduced by calcium in liquid ammonia solution to free silver. The reduced silver is pyrophoric and a good catalyst for the reaction between calcium and ammonia. The thiocyanate group of silver thiocyanate is reduced completely to sulfide and cyanide, and the cyanate group of silver cyanate is partially reduced to cyanide when an excess calcium is present.

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