bility studies is as follows. A dry organic solvent such as benzene could be used to extract the water from a solid sample by leaching or refluxing and the water present in the solvent could subsequently be determined.

The two chief objections to the calcium hydride method are the following. First, the method is limited to solvents which do not react with calcium hydride or otherwise react so slowly that necessary corrections can be applied; second, the method is not rapid, since the analyses are of one to three days' duration, although they do not require much actual time or care. The time required can be shortened for practical determinations since the reaction is about 95% complete in ten hours and the percentage of total moisture could then be estimated.

Summary

1. A new improved apparatus and method have been developed for the gasometric determination of water in certain organic solvents.

2. Calcium hydride has been shown to be a good reagent for the quantitative determination of water, giving an accuracy of 0.001% H_2O in determinations of about 0.1% H_2O.

3. The solubility of water in benzene, in carbon tetrachloride, and in toluene has been determined at various temperatures.

4. Benzene can be dried to a water content of 0.015% by distilling and discarding the first 10 to 20% of the liquid.

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A STUDY OF THE PRODUCTS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA SOLUTION. III. THE ACTION OF SODIUM UPON SILVER IODIDE AND SILVER CHLORIDE[1]

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RECEIVED JUNE 18, 1930 PUBLISHED SEPTEMBER 5, 1930

Introduction

In the first paper of this series,[2] there was described a reaction in liquid ammonia between sodium and a salt, which resulted in the formation of a compound of sodium and the reduced metal. In the present paper a simpler case is presented where the reduced metal is obtained without further reaction.

Kraus and Kurtz[3] found that sodium reacted readily with silver cyanide

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

[2] Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

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

or silver iodide in liquid ammonia, forming a metallic precipitate, inactive toward air and moisture. The reaction ratio of sodium to silver salt was given as 1.11 and 1.09. They concluded that no compound of sodium and silver was formed. A more accurate determination of this reaction ratio has been carried out, obtaining as an average value 1.00. The product of the reaction has been purified and shown by analysis to be metallic silver.

Experimental Method

Silver iodide (or silver chloride) was prepared by slowly mixing equal volumes of approximately 0.5 *N* solution of purified potassium iodide (or potassium chloride) and silver nitrate. The resulting precipitate was washed, filtered, dried at 110°, pulverized and kept in a brown bottle.

In carrying out the reaction, a small bent tube, containing a weighed amount of the silver salt, was placed in the side arm of a reaction tube, identical with the one used in the earlier work.[2] By gently tapping the tube, the powdered salt was slowly added to a liquid ammonia solution, containing a weighed amount of sodium, until the blue color just disappeared. The end-point of the reaction could be judged very accurately. From the weights of the silver salt and sodium used, the reaction ratio was calculated.

The precipitate formed by the reaction was washed according to the method previously described,[2] until the wash solution gave no test for soluble halides. The last trace of ammonia was allowed to evaporate against a slight pressure. Tests showed that the dried product did not gain weight in air, so it was removed from the reaction tube and weighed directly on a balance. The solid was then analyzed for silver by dissolving in concentrated nitric acid and precipitating as silver chloride. On a number of samples, determination of the loss in weight on heating to 100° and tests for iodides (or chlorides) and ammonia were made.

Experimental Data

In Tables I and II are summarized the experimental results for the reaction ratios and silver determinations.

TABLE I

REACTION RATIO AND SILVER ANALYSES USING SILVER IODIDE

No.	Na, g.	AgI, g.	Ratio Na/AgI	% Ag in product
178	0.1584	1.5981	1.012	96.4
179	.1581	1.5833	1.019	97.3
180	.1543	1.5728	1.000	97.1
194	.3181	3.2505	0.998	98.4
195	.2846	2.8812	1.008	98.3
198	.4652	4.7343	1.003	98.4

TABLE II

REACTION RATIO AND SILVER ANALYSES USING SILVER CHLORIDE

No.	Na, g.	AgCl, g.	Ratio Na/AgCl	% Ag in product
B3	0.4789	2.9957	0.997	..
B4	.4291	2.5840	1.007	98.8
B5	.4867	2.9451	1.030[a]	98.2
S1	.1756	1.0917	1.003	98.7
L1[b]	.2853	1.7751	1.002	..
L2	.2804	1.7458	1.001	..
L3	.2346	1.4644	0.999	..
L4	.2584	1.6118	.999	..

[a] Solution blue at end. [b] Those experiments marked L carried out by Mr. Hooper Linford in this Laboratory.

Several samples showed a slight loss in weight on heating to 100° in an evacuated tube for several hours. The loss was of the magnitude of 0.1–0.5%. In all cases, traces of iodides (or chlorides) were present in the product since the concentrated acid solution was always turbid. In a number of cases the dried precipitate was digested with water and the soluble iodides (or chlorides) determined. The values obtained varied from 0.1 to 0.8% of the total weight. Test made on the heated samples with Nessler's reagent showed that no ammonia was present. No gas was liberated during the reaction.

Discussion of Results

Both the reaction ratio and analysis of the product show that sodium reacts with silver iodide (or silver chloride) in liquid ammonia according to the following equation

$$Na + AgI \longrightarrow NaI + Ag$$

A product analyzing 100% silver could not be obtained because of the inability to wash the precipitate entirely free of adsorbed salts. That this was not due to inefficient washing was shown by digesting a dried sample with water before treatment with acid. Even then the acid solution was turbid, showing the presence of halogens.

The excellent agreement of the reaction ratio shows the high degree of accuracy with which the end-point of these reactions can be determined. It is suggested that free sodium in solution can be accurately determined by this method of adding a weighed quantity of silver chloride.

Summary

Sodium reacts with liquid ammonia solutions of silver iodide, or silver chloride, to form free silver and the corresponding sodium salt. No further reaction occurs.

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