A STUDY OF THE REDUCING ACTION OF SODIUM UPON SALTS IN LIQUID AMMONIA SOLUTION

WAYLAND M. BURGESS AND EDWARD H. SMOKER

Department of Chemistry, University of Cincinnati, Ohio

Received January 31, 1931

INTRODUCTION

One of the outstanding properties of a solution of an alkali or alkaline earth metal in liquid ammonia is its powerful reducing action. This property is attributed to solvated electrons, the presence of which as anions has been demonstrated through a study of the electrical properties of metal solutions (1). In accord with this view, the reduction of many substances, when added to these solutions, takes place rapidly and effectively, so that this method offers unusual opportunities for the study of the reduction of all classes of compounds.

This paper describes specific examples of the reduction of inorganic salts by metals in liquid ammonia, with the formation of an insoluble product, usually very reactive towards air and water. Three types of reactions are illustrated: (I) The reduction product is the free metal; (II) The reduction product is an intermetallic compound; (III) The reduction product is the free metal, which takes part in additional reactions involving the solvent.

I. THE REDUCTION PRODUCT IS THE FREE METAL

The reduction of silver salts by sodium in liquid ammonia best illustrates the type of reaction in which the salt is reduced to the free metal. Sodium reacts very readily and smoothly with silver chloride, or with silver iodide, forming a black precipitate of metallic silver. No further reaction or evolution of gas takes place (2).

These reactions, and also those described later, were carried out at the temperature of boiling liquid ammonia in an apparatus designed to permit the following: an accurate determination of the amounts of reacting substances; collection and analysis of gases liberated in the course of the reaction; purification, by repeated washings with ammonia, of any precipitate formed; analysis of the precipitate, avoiding reaction with air (3).

The results with silver salts have been checked in two ways: by the ratio of the reacting substances and by analysis of the precipitate. The ratio of gram-atoms of sodium to moles of silver chloride, or of silver iodide, taking part in the reaction can be determined very accurately, the blue color of the dissolved sodium serving as a splendid endpoint. Values of 1.001 using silver chloride and 1.006 using silver iodide were obtained. Analyses of the precipitate gave 98.7 and 98.0 per cent silver for the two cases. The composition of the precipitate is low because of the inability to remove the adsorbed salts completely by washing.

These reactions are represented by the equations:

$$Na + AgCl \rightarrow NaCl + Ag \downarrow \tag{1}$$

$$Na + AgI \rightarrow NaI + Ag \downarrow \tag{2}$$

Other examples of this type of reduction reaction are reduction of cuprous iodide with sodium to free copper (4) and reduction of silver chloride and of silver iodide with potassium to free silver (5).

II. THE REDUCTION PRODUCT IS AN INTERMETALLIC COMPOUND

The reduction of inorganic salts with liquid ammonia solutions of a metal results, in the majority of cases, in the formation of an intermetallic compound of the reduced and reducing metal. The reaction between sodium and zinc cyanide has been studied in considerable detail (3), and the results are here presented as an illustration of this type.

Sodium reacts vigorously with zinc cyanide to form a black metallic precipitate. No gas is evolved. This reaction has been investigated by the determination of the ratio of the reacting materials and by analysis of the precipitate. The ratio of gram-atoms of sodium to moles of zinc cyanide was found to be 2.22. The average value for the zinc content of the precipitate was 91.8 per cent. Even when the reaction was carried out with an excess of sodium present, the composition of the precipitate did not change. Both the reaction ratio and the analysis indicate the formation of the compound, $NaZn_4$, whose theoretical zinc content is 91.9 per cent. Upon treatment with dilute acid, 9.05 equivalents of hydrogen per mole of sodium zinc were obtained, which agrees well with the theoretical yield of 9.0 equivalents for $NaZn_4$.

These results establish the following equation for the reaction:

$$9Na + 4Zn(CN)_2 \rightarrow 8NaCN + NaZn_4\downarrow \tag{3}$$

No evidence of the existence of a compound of this nature is found in the study of the freezing point diagram for zinc and tin (6).

As other examples of this type of reaction, the following insoluble compounds were obtained as products of reduction in liquid ammonia by Kraus and Kurtz (7): $NaHg$, $NaHg_2$, $NaCd$, Na_5Sb, Na_3Bi, Na_3Te_2, $CaAg$, Ca_7Zn, Ca_3Hg_2, Ca_2Pb_3, and Ca_5Sn. The ratio of reacting substances was used to determine the formula in each case. Identification of these compounds by analysis has not yet been made. In most cases, these compounds have not been found by the method of thermal analysis.

III. THE REDUCTION PRODUCT TAKES PART IN ADDITIONAL REACTIONS

As an illustration of the case where the reduced metal takes part in reactions involving the solvent, the reduction of manganous iodide with sodium will be described. Since this work has not been published elsewhere, and no similar reaction has been noted, it will be discussed more in detail than the other types.

The reaction between sodium and manganous iodide occurs very readily with the formation of a shiny black precipitate and considerable evolution of hydrogen. Contrary to previous reactions, no quantitative relations between the reacting substances can be established, all of the sodium being used up irrespective of the amount of manganous iodide employed. Neither is the reaction complete after the free sodium has disappeared, as indicated by the steady production of gas over a period of several days. Two series of reactions occur: the first of these takes place rapidly, with the reduction of the manganous iodide to free manganese, and the free metal thus formed catalyzes the reaction between sodium and ammonia, liberating hydrogen; in the second or slower reaction, the reduced manganese reacts with the sodium amide, formed in the previous steps, and the solvent ammonia.

The experimental data for this work will be summarized separately for each series of reactions. There are three facts of importance in establishing the first or rapid reaction: no definite ratio between the reacting substances was found to exist; considerable amounts of hydrogen were liberated; analysis of the precipitate showed that it contained manganese, sodium, and ammonia, as amide, in widely varying proportions.

The reaction ratio, or ratio of the gram-atoms of sodium to moles of the salt, is usually of prime importance in investigating the nature of these reactions. It can normally be determined very accurately. But with manganous iodide the values varied over a wide range; in fact, any amount of sodium could be used for a given amount of manganous iodide. The simple reduction of manganous iodide requires two gram-atoms of sodium to one mole of manganous iodide. But even with a reaction ratio of 30, all of the sodium reacted and the blue color disappeared within a period of half an hour. This establishes the fact that the sodium enters into reactions other than simple reduction of the manganese salt.

The liberation of hydrogen shows that these reactions involve the solvent ammonia. The amount of hydrogen liberated was found to vary directly as the amount of sodium not required for the simple reduction; that is, only a little hydrogen was liberated for a reaction ratio of 2. Here nearly all the sodium entered into the reduction of manganous iodide. But, as the amount of sodium in excess of that required for the reduction increased, the amount of hydrogen increased in the same proportion.

Upon analysis, the precipitate was found to contain varying amounts of manganese, sodium, and amide. These amounts, however, varied in a regular manner, the per cent of manganese reaching a maximum of 90 per cent for reaction ratios of approximately 2. Then, as the ratio increased over 2, the per cent of manganese decreased, and the amount of sodium and amide increased.

These results establish the following reactions as taking place concurrently:

$$2Na + MnI_2 \rightarrow 2NaI + Mn \downarrow \tag{4}$$

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2 \uparrow \tag{5}$$

Equation 4 represents the reduction of a metal halide to the free metal, as described under the reactions with silver salts. Equation 5 represents the reaction between sodium and the solvent, ammonia, and accounts for the liberation of hydrogen. For equivalent amounts of sodium and manganous iodide, the reaction proceeds largely according to equation 4. But even with equivalent amounts, the liberation of a small volume of hydrogen and the presence of sodium amide in the precipitate show that reaction 5 occurs concurrently. When the sodium is present in large amounts, all of the excess sodium reacts according to equation 5.

It is remarkable that the excess sodium should react so rapidly with the ammonia. Normally this reaction requires a catalyst and even then is slow. An especially favorable catalyst must be present in this case. It is, undoubtedly, the freshly reduced manganese formed in the initial step of the reaction.

That reactions other than those represented by equations 4 and 5 occur, is established by the slow but steady evolution of hydrogen for a considerable time after the blue color of the sodium has disappeared. Another product of these slow reactions is indicated by the fact that the solution becomes deep yellow. Bergstrom (8) found that potassium ammonomanganite, $Mn(NHK)_2$, dissolves somewhat in liquid ammonia to give a bright yellow solution. The similar color in this reaction, together with the liberation of hydrogen, indicates a reaction between manganese and sodium amide to form sodium ammonomanganite, as represented by the equation

$$Mn + 2NaNH_2 \rightarrow Mn(NHNa)_2 + H_2\uparrow \qquad (6)$$

However, it is not possible to explain the reactions that occur by this equation alone, because the amount of hydrogen liberated is greater than can be accounted for by equation 6. In the reactions that were followed to completion, the initial amounts of sodium and manganous iodide were such that the manganese formed by reduction was considerably in excess of the sodium amide that could be present. Yet the hydrogen collected was found to be closely equivalent to the manganese and in no way dependent upon the amount of sodium amide. This requires the slow reaction to involve not only manganese and sodium amide, but also the solvent ammonia.

It is not possible to establish definitely the steps of the slow reaction on the basis of the work already done. The following series of equations are proposed simply as one possible explanation:

$$Mn + 2NaNH_2 \rightarrow Mn(NH_2)_2 + 2Na \qquad (7)$$
$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2\uparrow \qquad (8)$$
$$2NaNH_2 + Mn(NH_2)_2 \rightleftarrows Mn(NHNa)_2 + NH_3 \qquad (9a)$$
$$2NaNH_2 + Mn \rightarrow Mn(NH_2)_2 + 2Na \qquad (9b)$$

Equations 7, 8, and 9a represent the process of the reaction in liquid ammonia between a metal and a strong base, as developed by Bergstrom (9). These same equations have been established by him using potassium amide instead of the sodium compound (8).

It is assumed that the sodium amide formed in equation 8 reacts in two ways. One reaction, equation 9a, is with manganous amide to form sodium ammonomanganite, the existence of which is shown by the yellow color of the solution. Concurrently, a reaction takes place with manganese, equation 9b, forming again manganous amide and sodium, which is, of course, a repetition of equation 7. This would be followed by a reaction of the sodium with ammonia, liberating hydrogen and regenerating sodium amide. In this way all of the hydrogen obtained is the result of the reaction of sodium and ammonia. Since the sodium amide is reformed, the amount of hydrogen would depend only on the manganese available, and this is found to be the case.

PROPERTIES OF THE REDUCTION PRODUCTS

In nearly all of the reactions studied, the reduction products have one characteristic property in common: they are particularly reactive towards air and water. Only in the case of silver salts has the product, silver, been non-reactive. Reduced copper prepared in this way becomes incandescent on exposure to air. Manganese sparks vigorously and becomes white hot. The product of the reduction of nickel salts behaves similarly (10). Sodium zinc reacts with explosive violence with either air or water. The compounds prepared by Kraus and Kurtz (7) were all found to be reactive.

Sodium zinc is the only one of these products for which any study has been made of the reaction that occurs with air or water (3). Here it was found that with dry oxygen at low concentrations, the oxidation reaction is divided into two distinct stages. At first, 0.5 gram-atom of oxygen per mole of sodium zinc is rapidly taken up with considerable evolution of heat. This corresponds to the formation of sodium monoxide. A secondary reaction, evidently the oxidation of the zinc, then proceeds at a very slow rate for a long period of time. Increased concentration of oxygen, or air, the presence of moisture, or heating all greatly accelerate the secondary oxidation. With water, a reaction liberating hydrogen continues with decreasing rate for a long time. In one month, approximately four equivalents of hydrogen were collected per mole of sodium zinc.

The excellent ability of the manganese to catalyze the reaction between sodium and ammonia further illustrates the active condition of these reduced metals. This reactivity is probably due to the finely divided state of the substance. On this basis, metals, or intermetallic compounds, formed by reduction in liquid ammonia, are obtained as very minute particles. This method of reduction may well be utilized in the preparation of metal catalysts, where an activated state or very large surface is essential.

REFERENCES

(1) Kraus: J. Am. Chem. Soc. **30,** 1323 (1908); **36,** 864 (1914).
(2) Burgess and Smoker: J. Am. Chem. Soc. **52,** 3573 (1930).
(3) Burgess and Rose: J. Am. Chem. Soc. **51,** 2127 (1929).
(4) Burgess: Unpublished observations.
(5) Holden and Burgess: Unpublished observations.
(6) Mathewson: Z. anorg. Chem. **48,** 196 (1906).
(7) Kraus and Kurtz: J. Am. Chem. Soc. **47,** 43 (1925).
(8) Bergstrom: J. Am. Chem. Soc. **46,** 1545 (1924).
(9) Bergstrom: J. Am. Chem. Soc. **45,** 2788 (1923); **47,** 1836 (1925).
(10) Hovey and Burgess: Unpublished observations.