## THE SILVER NITRATE-IODINE REACTION: IODINE NITRATE AS THE REACTION INTERMEDIATE\*

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Abstract—The reaction between  $AgNO_3$  and iodine has been studied in detail and the products of the reaction are found to be  $AgIO_3$ , AgI,  $NO_2$  and  $O_2$ . A reaction mechanism involving  $INO_3$  as the intermediate has been discussed. The dependence of the reaction on the phase, time, temperature and other factors has been investigated. Thermal decompositions of  $AgNO_3$ ,  $AgIO_3$  have also been examined.

## INTRODUCTION

WHILE reprocessing spent uranium elements from nuclear reactors, the elements are treated with nitric acid. One of the gases evolved in this treatment is iodine-131, which is radioactive and is a health hazard if released to the atmosphere. To remove this <sup>131</sup>I, a tower consisting of silver nitrate coated on ceramic packing is commonly used and the operating conditions are  $\sim 200^{\circ}$ C and 1 atm.<sup>(1)</sup> The overall equation in the unbalanced form was first given as,<sup>(2)</sup>

$$AgNO_3 + I_2 \rightarrow AgIO_3 + AgI + NO_2$$

BLASEWITZ and SCHMIDT<sup>(3)</sup> have recently reported the following reactions of gaseous iodine with solid AgNO<sub>3</sub> and have suggested that AgI is the thermodynamically stable product when the reaction is run at  $200^{\circ}$ C.

$$\begin{array}{c} \operatorname{AgNO_3} + \frac{1}{2}I_2 \rightarrow \operatorname{AgI} + \frac{1}{2}O_2 + \operatorname{NO_2} \\ \operatorname{AgNO_3} + \frac{1}{2}I_2 + O_2 \rightarrow \operatorname{AgIO_3} + \operatorname{NO_2} \\ \operatorname{AglO_3} \rightarrow \operatorname{AgI} + \frac{3}{2}O_2 \end{array}$$

The recent studies of LACKSONEN *et al.*<sup>(4)</sup> however, showed that  $AgIO_3$  is one of the stable products of the reaction and is stable up to  $300^{\circ}C$ .

In view of the lack of definite information on the reaction between iodine and silver nitrate, we have now examined this reaction in detail with particular reference

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- <sup>(1)</sup> Progress in Nuclear Chemistry, Series III, Process Chemistry, p. 420. Pergamon Press, London (1961).
- <sup>(2)</sup> C. WELTZIEN, Ann. chem. Pharm. 91-92, 33 (1854).
- <sup>(8)</sup> A. G. BLASEWITZ and W. C. SCHMIDT, Int. Conf. Peaceful Uses Atomic Energy, Geneva, p. 397 (1958).
- <sup>(4)</sup> J. W. LACKSONEN, W. H. KIRBY and C. E. DRYDEN, J. chem. Engng Data 8, 524 (1963).

to the thermodynamics, product identification, reaction conditions, reaction intermediates, reaction kinetics and mechanism. It was also necessary to study the thermal decomposition of silver nitrate and silver iodate in order to completely understand the nature of the reaction.

## EXPERIMENTAL

Analytical procedures. The quantity of I<sup>+</sup> in alcoholic or any other solution was determined by addition of potassium iodide to the solution and by titrating the liberated iodine with standard sodium thiosulphate solution. Ag<sup>+</sup> in solution was determined by gravimetric analysis as silver chloride. Determination of Ag<sup>0</sup> in presence of Ag<sup>+</sup> was accomplished by treating the mixture of Ag<sup>0</sup> and the silver salt with excess of aqueous HClO<sub>4</sub> and estimating the Ag<sup>+</sup> in solution by standard methods and weighing the Ag<sup>0</sup> as a precipitate. It is known that silver has no solubility in perchloric acid solution.<sup>(5)</sup>



Temperature .°C

FIG. 1.-Variation of mole ratio of AgI:AgIO<sub>3</sub> as a function of reaction temperature.

AgIO<sub>3</sub> could be identified and separated from AgI by reaction with ammonium hydroxide.<sup>(6)</sup> AgI does not form the silver-ammonia complex and remains as a residue while AgIO<sub>3</sub> goes into solution forming the complex and free  $IO_3^-$  in solution. AgIO<sub>3</sub> can then be reprecipitated by adding HNO<sub>3</sub>. Care was taken to see that there was no AgNO<sub>3</sub> in the solid.

Thermal decomposition of AgNO<sub>3</sub> and AgIO<sub>3</sub>. Weighed quantities of AgNO<sub>3</sub> (or AgIO<sub>3</sub>) were taken in quartz tubes and the tubes were inserted in a vertical tube furnace maintained at a fixed temperature. In the case of AgNO<sub>3</sub>, the sample tubes were connected to a force pump through a liquid nitrogen trap. Samples of the residues left in the reaction tubes were analysed at different intervals of time. In the case of the AgIO<sub>3</sub> decomposition, both AgI and AgIO<sub>3</sub> were determined, while in the AgNO<sub>3</sub> decomposition Ag<sup>0</sup> and NO<sub>3</sub><sup>-</sup> were determined. Quantitative i.r. spectroscopy (NO<sub>3</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup> absorption bands) was also employed to examine the solid residues.

Reaction between  $A_{g}NO_{3}$  and  $I_{2}$ . (a) The reaction between iodine vapour and  $A_{g}NO_{3}$  was carried out in an open reaction tube where iodine vapour generated in a flask was passed through silver nitrate maintained at a desired temperature for  $\sim 2$  hr (within this period most of the  $A_{g}NO_{3}$  reacts with iodine). In this arrangement the  $NO_{2}$  or  $O_{2}$  formed in the reaction could easily escape. The results of this study are indicated in Fig. 1.

(b) AgNO<sub>8</sub>-I<sub>2</sub> reaction was also performed in a closed system in an atmosphere of known partial pressure of NO<sub>2</sub>. The results of this study are indicated in Fig. 2.

(c) The reaction of AgNO<sub>3</sub> and  $I_2$  was carried out at different temperatures in a closed system with different proportions of AgNO<sub>3</sub> and  $I_2$ .

Trapping of INO<sub>3</sub>. Iodine vapour was allowed to react (at room temperature) with NO<sub>2</sub> obtained from the decomposition of AgNO<sub>3</sub> in presence of oxygen in a 50-ml flask and the flask was opened

<sup>(5)</sup> D. N. CRAIG, J. I. HOFFMAN, C. A. LAW and W. J. HAMER, J. Res. natn. Bur. Stand. 64A, 381 (1960).
<sup>(6)</sup> G. B. HEISIG, Semimicro Qualitative Analysis. Saunders, Philadelphia (1951).

to a trap cooled by liquid nitrogen after a few minutes of the reaction. The vapours were passed through a plug of glass wool placed at the centre of the inlet tube of the trap. A yellow solid was found to deposit in the trap. The solid was analysed for I<sup>+</sup> and NO<sub>3</sub><sup>-</sup>: I<sup>+</sup> found, 67.8% (calc., 67.2).



Temperature,°C

FIG. 2.—Dependence of the mole ratio of AgI:AgIO<sub>3</sub> on the partial pressure of NO<sub>2</sub>. When  $p_{NO_3}$  was 0.2 atm, the rest was air.

## **RESULTS AND DISCUSSION**

Silver nitrate melts at 211°C without decomposition and the decomposition becomes measurable only above 400°C. Just as in KNO<sub>3</sub> and other ionic nitrates,<sup>(7,8)</sup> AgNO<sub>3</sub> first decomposes giving the nitrite and oxygen. The AgNO<sub>2</sub> produced by the decomposition of the nitrate immediately gives out NO<sub>2</sub> and silver as metal. By quenching out partially decomposed AgNO<sub>3</sub> samples, it was possible to identify the co-existence of both the nitrate and nitrate employing spectroscopy.<sup>(9)</sup> Since the decomposition of AgNO<sub>3</sub> was found only at relatively high temperatures, it is obviously not an important step in the reaction between AgNO<sub>3</sub> and I<sub>2</sub>, which has been found to take place slowly even at ~30°C.

The reaction between AgNO<sub>3</sub> and I<sub>2</sub> was performed at several temperatures in the range 30-300°C in closed as well as open systems and the solid and gaseous products were identified. The only two solid products found were AgI and AgIO<sub>3</sub>. The gaseous products were NO<sub>2</sub> and O<sub>2</sub> and no traces of nitric oxide were found. Based on these products and the information from the earlier literature,<sup>(2,3)</sup> the following mechanism of the reaction between I<sub>2</sub> and AgNO<sub>3</sub> was considered:

$$AgNO_3 + I_2 \rightarrow AgI + INO_3 \tag{1}$$

$$2INO_3 + AgNO_3 \rightarrow AgIO_3 + 3NO_2 + \frac{1}{2}I_2$$
(2)

$$INO_3 \rightarrow NO_2 + \frac{1}{2}O_2 + \frac{1}{2}I_2 \tag{3}$$

The basis for suggesting the formation of  $INO_3$  in reaction (1) was by analogy with the reaction of  $I_2$  with AgNO<sub>3</sub> in alcoholic solution which is known to give rise

<sup>&</sup>lt;sup>(7)</sup> C. C. ADDISION and N. LOGAN, in *Advances in Inorganic and Radio Chemistry* (Edited H. J. EMELÉUS and A. G. SHARP), p. 71. Academic Press, New York (1964).

<sup>&</sup>lt;sup>(8)</sup> B. O. FIELD and C. J. HARDY, Q. Rev. chem. Soc, 18, 361 (1964).

<sup>&</sup>lt;sup>(9)</sup> C. N. R. RAO, *Chemical Applications of Infrared Spectroscopy*, Chap. VII. Academic Press, New York (1963).

to  $INO_3$  in solution.<sup>(10)</sup> The decomposition of  $INO_3$  in reaction (3) is analogous to that of other ionic nitrates.<sup>(8)</sup> According to the reaction sequence given above, in the limiting case where all the  $INO_3$  given by reaction (1) reacts with AgNO<sub>3</sub>, the net reaction will have the following stoicheiometry:

$$6AgNO_3 + 3I_2 \rightarrow 4AgI + 2AgIO_3 + 6NO_2 \tag{4}$$

Since the reaction between solid AgNO<sub>3</sub> and I<sub>2</sub> was observed to go at room temperature, thermodynamic calculations were made for reaction (4) making use of the standard data.<sup>(11)</sup> The heat of reaction was found to be  $+6\cdot1$  kcal/mole of AgNO<sub>3</sub> at 25°C. The results show that the reaction is slightly endothermic and spontaneous at 25°C.

According to reaction (4), the mole ratio AgI/AgIO<sub>3</sub> must be two in the limiting case. While this ratio is obtained under certain conditions, it is also found to vary with time and temperature and other reaction conditions. Deviation from the ratio of two can result if the AgIO<sub>3</sub> formed in reaction (2) decomposes as suggested earlier by BLASEWITZ and SCHMIDT<sup>(3)</sup> or if reaction (3) is of importance. In view of the conflicting reports on the melting and decomposition of AgIO<sub>3</sub> in the literature,<sup>(12-14)</sup> the thermal decomposition of AgIO<sub>3</sub> was examined. There was no decomposition when AgIO<sub>3</sub> was maintained at 215°C for 25 hr or at 250°C for 10 hr. AgIO<sub>3</sub> decomposes only above 300°C with measurable rates. The first order rate constant after the induction time\* is  $4.5 \times 10^{-3} \text{ min}^{-1}$  at 400°C and the energy of activation is 9 kcal/mole. Since this decomposition occurs only at temperatures considerably above the maximum reaction temperature for the AgIO<sub>3</sub> ratios in the present study.

The main problem faced with the proposed reaction mechanism for the  $AgNO_3-I_2$  reaction relates to the reaction intermediate  $INO_3$  which has not been clearly described in the literature. The reaction of  $AgNO_3$  and  $I_2$  in alcoholic solution gave  $INO_3$  and AgI as suggested earlier.<sup>(10)</sup> The stoicheiometry of the reaction was verified by the quantitative determination of I<sup>+</sup> in solution as well as of the AgI precipitate.  $INO_3$  could also be obtained in solution by passing an alcoholic solution of iodine through a cation exchange (Dowex 50) column<sup>(15)</sup> and by removing the I<sup>+</sup> in the column by the addition of dilute nitric acid. Attempts to obtain pure  $INO_3$  by stripping the alcohol solvent under vacuum at different temperatures were unsuccessful. Removal of the solvent always resulted in the decomposition of  $INO_3$ . Apparently,  $INO_3$  remains stable in solution due to solvation by the alcohol molecules.

Preparation of  $INO_3$  was accomplished by the reaction of  $NO_2$  and  $O_2$  liberated from the decomposition of  $AgNO_3$  in the 400-500°C range with excess of iodine

\* The induction times at  $325^{\circ}$ C and  $350^{\circ}$ C were  $\sim 3$  and  $\sim 1$  hr respectively. The magnitude of the induction time is much greater in AgIO<sub>3</sub> decomposition than in AgNO<sub>3</sub> decomposition.

(12) T. DUPIUS and C. DUVAL, C.r. hebd. Séanc. Acad. Sci., Paris 229, 51 (1949).

(15) H. BRUSSET and T. KIKINDAI, C.r. hebd. Séanc. Acad. Sci., Paris 232, 1840 (1950); H. KIKINDAI and M. CASSEL, C.r. hebd. Séanc. Acad. Sci., Paris 232, 1110 (1950).

<sup>(10)</sup> H. BRUSSET and T. KIKINDAI, C.r. hebd. Séanc. Acad. Sci., Paris 238, 1322 (1954).

<sup>&</sup>lt;sup>(11)</sup> J. H. PERRY, (Editor), Chemical Engineering Handbook. McGraw-Hill, New York (1950).

<sup>&</sup>lt;sup>(13)</sup> C. D. HODGMAN, (Editor), Handbook of Chemistry and Physics (35th Edn). Chem. Rubber Publishing, Cleveland (1953).

<sup>&</sup>lt;sup>(14)</sup> M. C. SNEED, J. L. MAYNARD and R. C. BRASTED, Comprehensive Inorganic Chemistry, Vol. II, p. 166. Van Nostrand, New York (1954).

vapour in a reaction tube (maintained at room temperature) and then trapping the products at liquid nitrogen temperature. A yellow solid\* found as a deposit on the surface of the trap melted at about  $-30^{\circ}$ C, decomposing to iodine and other products<sup>(16,17)</sup> as the temperature was increased to 0°C. The yellow solid gave the exact analysis for I<sup>+</sup> and NO<sub>3</sub><sup>-</sup> as required by INO<sub>3</sub>. These properties of the yellow solid, identified as INO<sub>3</sub>, are similar to those described by SCHEMISSER and co-workers<sup>(16,17)</sup> who have reported the formation of I(NO<sub>3</sub>)<sub>3</sub> by reacting IBr with Br(NO<sub>3</sub>)<sub>3</sub> and of INO<sub>3</sub> by reacting I(NO<sub>3</sub>)<sub>3</sub> with I<sub>2</sub> in CFCl<sub>3</sub>.

With the identification of  $INO_3$  from the vapour phase reaction of  $NO_2$ ,  $O_2$  and  $I_2$ , it becomes easier to understand the  $AgNO_3$ - $I_2$  reaction. The reaction mechanism was investigated in greater detail by determining the ratio of  $AgI:AgIO_3$  under different conditions. Before going into this aspect of the study, it is relevant to summarize the important results of the phase equilibria involving  $AgNO_3$ , AgI and  $AgIO_3$ .

The fusibility diagram of the AgI-AgNO<sub>3</sub> system has been studied by BOKHOVKIN.<sup>(18)</sup> The melting points of the compositions AgNO<sub>3</sub>·AgI and 2AgNO<sub>3</sub>·AgI are  $\sim 110^{\circ}$ C. The fusibility diagram of the AgNO<sub>3</sub>-AgIO<sub>3</sub> system<sup>(4)</sup> shows that the composition with 40 per cent (by weight) of AgIO<sub>3</sub> melts around 150°C. The fusibility diagram of the three component system shows that the lowest melting point eutectic at 76°C has the composition of 50% AgI, 23% AgIO<sub>3</sub> and 27% AgNO<sub>3</sub>.

When the reaction between  $I_2$  vapour and AgNO<sub>3</sub> was carried out by passing the  $I_2$  vapour over AgNO<sub>3</sub> maintained at a desired temperature in an open reaction tube, the AgI/AgIO<sub>3</sub> ratio showed an unusual variation with temperature (Fig. 1). The limiting ratio of two (in accordance with reaction 4) is found only in the temperature range 90–180°C. At higher as well as at lower temperatures, the ratio is greater than two. This may be because, below 90°C the reaction is primarily a solid-gas reaction and is diffusion-controlled. Above 90°C,  $I_2$  and INO<sub>3</sub> can react with the other reactants in liquid phase because the diffusion is much more rapid. Thus, any liberated INO<sub>3</sub> has a higher probability of reaction than decomposing. At temperatures higher than 180°C, however, decomposition of INO<sub>3</sub> (reaction 3) apparently becomes important and increases the AgI:AgIO<sub>3</sub> ratio.

When the reaction was performed under different partial pressures of  $NO_2$ , the ratio of AgI:AgIO<sub>3</sub> decreased with the increase of partial pressure of  $NO_2$  (Fig. 2). This seems to suggest that the decomposition of  $INO_3$  is suppressed at higher  $NO_2$  pressures and that more of AgIO<sub>3</sub> is formed from reaction (2). It appears that reaction (3) should probably be written as reversible.

Studies on the time-dependence of the  $AgNO_3-I_2$  reaction showed that the ratio of  $AgI:AgIO_3$  was  $\sim 2$  at the end of the first hour of the reaction when the reaction temperature was 100°C or greater. The ratio then increased with time, probably because the decomposition of  $INO_3$  becomes the controlling reaction rather than reaction (2). When the reaction was performed under identical conditions (150°C, 10 hr) in large excess of  $AgNO_3$ ,  $AgI:AgIO_3$  ratio was found to be ( $\sim 3$ ) much less than the ratio (5.0) obtained when the reaction was carried out with stoicheiometric

<sup>\*</sup>  $N_2O_4$  solid is colorless and melts at  $-11^{\circ}C$ .

<sup>&</sup>lt;sup>(16)</sup> M. SCHMEISSER and L. TAGLINGER, Angew. Chem. 71, 523 (1959).

<sup>&</sup>lt;sup>(17)</sup> M. SCHMEISSER and K. BRANDLE, Angew. Chem. 73, 388 (1961).

<sup>&</sup>lt;sup>(18)</sup> I. M. BOKHOVKIN, J. gen. Chem. U.S.S.R. 20, 419 (1950).

amounts of AgNO<sub>3</sub> and I<sub>2</sub>. In the presence of excess I<sub>2</sub>, AgI<sub>3</sub> was found in the reaction products, as identified by the characteristic tri-iodide bands at 297 and 363 m $\mu$ .<sup>(19)</sup> By taking  $k = A \exp -(E/RT)$ , it is possible to show that

$$R = \frac{\text{AgI}}{\text{AgIO}_3} = \frac{A_3}{A_2} \times \frac{1}{C_{\text{AgNO}_3} \times \exp(E_3 - E_2)/RT} + 1$$

where the subscripts refer to the reactions 3 and 2. In the above equation, it is likely that  $E_2 \ll E_3$ , since reaction (2) is diffusion-controlled. One can explain the data in Figs. 1 and 2 as follows. R increases with increase in temperature since  $E_3 - E_2$ is positive. At temperatures greater than 90°C, the diffusion will be into a liquid film instead of a solid film. The increased rate of the diffusion process will be accompanied by a larger  $A_2$  and a decrease in R in the region where the reaction mixture melts. Beyond 180°C, the exponential term, with  $E_3 > E_2$ , predominates and R again increases. The increase of R with time can be understood in terms of the increase in the  $A_3/A_2$  ratio and decrease of  $C_{AgNO_2}$  with time.

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