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Molten Sodium-Potassium Nitrite Eutectic: the Reactions of some Compounds of Silver

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The reactions of four silver compounds with sodium-potassium nitrite eutectic have been studied and the stoichiometries established. Metallic silver was produced in every case, the reaction with silver oxide being reduction with formation of nitrate, with silver nitrite thermal decomposition, and with silver nitrate and silver chloride an exchange of anions followed by thermal decomposition.

Introduction

Nitrite melts are among the least studied of those easily available alkali metal oxy-salts which have conveniently low melting points, despite the interest of a wide variety of potential reactions which could include reducing as well as oxidising behaviour, variation in the type of coordinating atom as well as in stereochemistry, basic properties *etc.* Indeed the previously reported studies have only comprised phase diagrams,[1] cryoscopy,[2] and an electrochemical investigation on the kinetics of discharged nitrite ions[3] whose conclusions have recently been seriously challenged.[4] The only published studies of chemical reactions have concerned the gases evolved from the reaction of dichromate in fused sodium nitrite[5] together with the reactions of a series of chromium(VI) and chromium(III) compounds in sodium-potassium nitrite eutectic,[6] which provided examples of a variety of chemical behaviour by the melt, which included oxidations, reductions and oxide ion donation (*i.e.* behaving as a Lux-Flood base). The results of a study of compounds of a noble metal, are now reported which provide other examples of the reducing action of the nitrite ion, anion exchange and the effect of the thermal instability of silver nitrite. The interpretation of these results again showed the importance of the further reaction of nitrogen dioxide, a product of many of the reactions, with the nitrite melt.

$$\textit{i.e.}\ NO_2+NO_2^- \longrightarrow NO_3+NO \qquad (1)$$

Experimental Section

The sodium-potassium nitrite eutectic was prepared and dehydrated as previously described.[6] Silver nitrate (A.R.) was powdered and dried at 110°. Silver chloride and silver oxide (B.D.H.) were dried at 120° and silver nitrite (B.D.H.) used without further treatment

The procedures for the reactions, thermogravimetric analysis, infrared spectroscopy and estimation of nitrate icns were also carried out as described earlier.[6] Silver was estimated gravimetrically after washing with water and drying at 120° as was the silver chloride from the solubility measurements after the samples of clear supernatent melt had been dissolved in water. The identity of the metal powders were confirmed by X-ray powder methods, using zirconium filtered CuKα radiation with a 12 cm camera and a Joyce microdensitometer.

Results

Silver Oxide, a black solid, was insoluble in the molten nitrite eutectic and showed little tendency to exchange anions since at no stage was silver nitrite detectable by infrared examination of mulls of the frozen melts, nor were silver ions detectable in aqueous solutions of the frozen melts. No gases were evolved during reaction under vacuum and no weight loss was found by thermogravimetry (Figure 1 curve C). Reaction did occur however with the formation of grey metallic particles, these, shown to be shiny under a microscope (x 50), by powder photography gave «d» spacings of 2.352(s), 2.045(s), 1.440(m), 1.233(s), 1.180(w), 1.020(w), 0.938(m), 0.914(w), 0.834(m). Values for B.D.H. silver powder were 2.348(s), 2.036(s), 1.442(m), 1.229(s), 1.171(w), 1.020(w), 0.936(m), 0.913(m), 0.834(m) and those given in the A.S.T.M. index for silver. 2.359(100), 2.044(40), 1.443(25), 1.231(26), 1.179(12), 1.021(4), 0.937(15), 0.913(12), 0.834(13). Nitrate ions were also found to be produced in the melt, the molar ratio NO_3^-: Ag: Ag_2O being $0.98\pm0.3:2.00\pm0.004:1$. This reaction was found to take place at all temperatures down to 230° when conversion to silver of melts containing 0.4 moles silver oxide in 1000 g melt, was found to be complete in 3-4 hr.

Silver nitrite was very soluble in the nitrite eutectic (>20% at 230°) and commenced to react immediately, with the production of grey particles of silver and

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(1) P. I. Protsenko and B. S. Medvedev, *Zhur. Neorg. Khim., 8,* 2737 (1963). P. I. Protsenko and R. P. Shisholina, *Zhur. Neorg. Khim., 8,* 2741, 2744 (1963). P. I. Protsenko and G. K. Shurdumov, *Zhur. Neorg. Khim., 9,* 1692 (1964). P. I. Protsenko and N. A. Brykova, *Zhur. Neorg. Khim., 10,* 1220 (1965). V. D. Polyakov and S. I. Berul, *Izvest. Sekt. Fiz. Khim. Anal., 26,* 164 (1955).

(2) T. R. Kozlowski and R. F. Bartholomew, *J. Electrochem. Soc., 114,* 937 (1967).

(3) A. J. Calandra and A. J. Arvia, *Electrochim. Acta, 11,* 1173 (1966); *12,* 95, 1441 (1967).

(4) A. Lundén, *Electrochim. Acta, 14,* 1068 (1969).

(5) R. N. Kust and R. W. Fletcher, *Inorg. Chem., 8,* 687 (1969).

(6) D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta, 3,* 667 (1969).

nitrate ions in the melt and the evolution of nitrogen dioxide. Thermogravimetric analysis (Figure 1, curve A) showed that though a small amount of decomposition occurred before melting of the eutectic, the main reaction was between 250 and 350°. Weight loss was rather variable, due to reaction (1) and the formation of nitrate, a typical result being 24% weight loss with a 0.56 m solution. Similar results were obtained for the thermal decomposition of pure silver nitrite (Figure 1, curve B), though the initial decomposition occurred at a rather lower temperature, but again with a variable weight loss (13-15% to the minimum at 350°). Infrared examination of the product of the product at 350° showed the presence of silver nitrate but the absence of silver nitrite. A second decomposition occurred between 425 and 500° with the evolution of nitrogen dioxide and oxygen and the formation of silver. The overall weight loss for both reactions was 30.5% (Clcd. for loss of 1N+2O per $AgNO_2$ 29.9%).

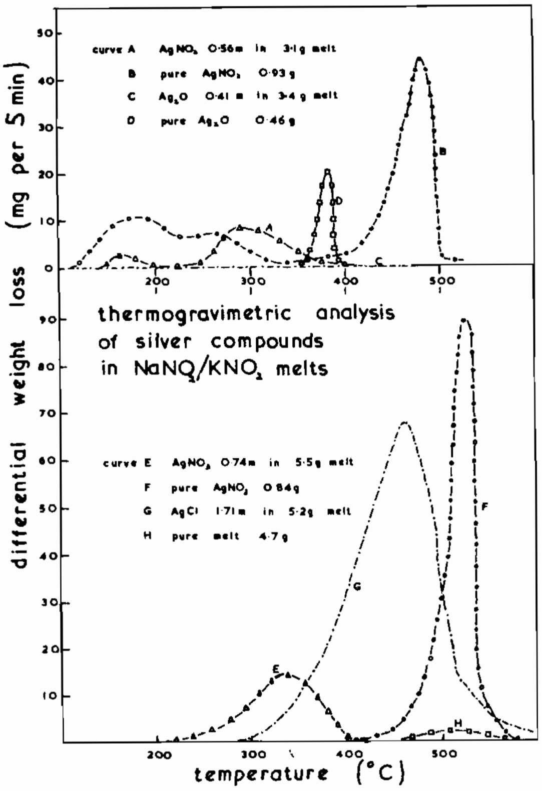

Figure 1.

Silver nitrate was readily soluble to give a stable colourless solution at 230°. Decomposition commenced at 250° and above with the formation of nitrogen dioxide and nitric oxide and the deposition of grey shiny particles of silver («d» values 2.337(s), 2.039(s), 1.440(m), 1.230(s), 1.181(w), 1.021(w), 0.938(m), 0.913(w), 0.834(m)) the molar ratio Ag: $AgNO_3$ being 1.00±.0001. No sign of any black precipitate of silver oxide was observed. Infrared examination of a sodium nitrite melt, 1.8 m in silver nitrate, quenched from 220° showed a band at 852 cm^{-1} characteristic of silver nitrite as well as the 808 cm^{-1} band of silver nitrate. Thermogravimetric analysis of silver nitrate in sodium-potassium nitrite (Figure 1, curve E) gave weight losses of 17.4-17.6% but when corrected for the additional nitrate formed via equation (1), the losses were 26.5±0.3%. ((Calcd. for 1N+2O per $AgNO_3$ 27.0%).

Silver chloride was only slightly soluble in melts at 230°, ($\sim 7.3 \times 10^{-3}$ m). The solution showed no visible sign of reaction but small amounts of silver (<1%) were formed after 24 hr. Infrared examination of the quenched melts showed no evidence of silver nitrite even when held at 230° for several days. Visible reaction commenced at 350° when nitrogen dioxide and nitric oxide were evolved, but no chlorine could be detected. Thermogravimetric analysis (Figure 1, curve G) showed a weight loss varying from 18.6 to 21.5% but after correcting for the variable amount of nitrate produced by reaction (1), the loss became 32.1±1.1 (Calcd. for 1N+2O per AgCl 33.0%). The residual melt contained nitrate and chloride ions together with grey shiny particles of silver («d» values 2.345(s), 2.020(s), 1.438(m), 1.228(s), 1.174(w), 1.019(w), 0.936(m), 0.912(w), 0.833(m). The molar ratio Ag: AgCl was found to be 0.99±0.01.

Discussion

The stoichiometry of the silver oxide reaction was clearly

$$Ag_2O + NO_2^- \longrightarrow 2Ag + NO_3^- \tag{2}$$

the nitrite ions acting as a reducing agent, apparently directly on the surface of the insoluble silver oxide at all temperatures upwards from the melting point of the eutectic. This mechanism is postulated since the alternative reactions, involving thermal decomposition of silver oxide

$$Ag_2O \longrightarrow 2Ag + \tfrac{1}{2}O_2 \tag{3}$$

followed by oxidation of nitrite by oxygen only occur at 360-380° (Figure 1, curve D) and at >550° respectively. Similarly the other alternative of anion exchange

$$Ag_2O + 2NO_2^- \longrightarrow 2AgNO_2 + O^{2-} \tag{4}$$

followed by silver nitrite decomposition

$$AgNO_2 \longrightarrow Ag + NO_2 \tag{5}$$

and finally by the reaction

$$2NO_2 + O^{2-} \longrightarrow NO_2^- + NO_3^- \tag{6}$$

is also unlikely since a temperature of 250-350° is required for reaction (5) and reaction (6) would not normally remove all nitrogen dioxide, thus some weight loss would have been expected, but this was not observed.

Reaction (5) (weight loss 29.9%) and reaction (7) (weight loss 9.7%)

$$2AgNO_2 \longrightarrow AgNO_3 + Ag + NO \tag{7}$$

were, however, both taking place during the decomposition of solid silver nitrite (where similar reactions have been observed by other workers[7]). In melt solutions the corresponding reactions are (5) and (8)

$$AgNO_2+NO_2^- \longrightarrow Ag+NO_3^-+NO \qquad (8)$$

(weight loss 19.4%). All the observed weight losses fell between these limits, though unexpectedly, reaction (1), and thus overall reactions (7) or (8), occurred to a lesser extent in melt solution than in the pure solid. However, the distinctly higher temperature of the melt reaction does indicate the stabilisation achieved by the coordination of nitrite ligands in the melt, probably because the silver ions are then in contact with more oxygen ligand atoms and no longer in closest contact with a nitrogen atom as they are in the solid.[8]

The reaction of silver nitrate solutions occurred at a temperature considerably lower than that of the thermal decomposition of the pure salt (Figure 1, curve F), and was considered to indicate substantial coordination of the silver by nitrite ions and consequent facilitation of reactions (5) and (7). Certainly the formation of silver nitrite in solidified sodium nitrite melts was not in doubt. However, the rather higher decomposition temperature of silver nitrate as compared to silver nitrite presumably indicated that some coordination of silver by nitrate still occurred in the molten state.

With silver chloride the overall reaction clearly was

$$AgCl+NO_2^- \longrightarrow Ag+Cl^-+NO_2 \qquad (9)$$

together with some formation of nitrate by reaction (1). This presumably occurred via the formation and subsequent thermal decomposition of silver nitrite, reaction (5). The high temperature at which this decomposition took place was attributed to the low solubility of the silver chloride rather than to any inherent difficulty in anion exchange. The solubility found at 230° in nitrite was, as might be expected, of the same order as that previously determined in sodium nitrate, 5.8×10^{-3} m at 300°.[9] The insolubility of silver oxide in nitrite melt was also in line with the very low solubility of the oxide determined in sodium-potassium nitrate, solubility product 1.5×10^{-14} mole^3 kg^{-3} at 250°.[10]

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(7) V. T. Oza, *J. Ind. Chem. Soc.*, *35*, 411 (1958).
(8) J. A. A. Ketelaar, *Z. Krist.*, *95A*, 383 (1936).
(9) R. P. Seward and P. E. Field, *J. Phys. Chem.*, *68*, 210 (1964).
(10) A. M. Shams El Din, T. Gouda, and A. A. El Hosary, *Electroanal. Chem.*, *17*, 137 (1968).