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Molten Sodium-Potassium Nitrite Eutectic; the Reactions of Iron, Cobalt and Nickel Chlorides

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Received May 23, 1970

The reactions of iron(II), iron(III), cobalt(II) and nickel(II) chlorides in molten sodium-potassium nitrite eutectic have been studied and their stoichiometries established. In each case the most stable metal oxide was formed together with nitrogen dioxide and nitric oxide. The implications of the stoichiometry for the reaction pathways are discussed.

Introduction

Our understanding of the chemistry of molten nitrites is gradually increasing and has already revealed nitrite in the molten state as possessing an interesting variety of modes of chemical reaction. Published work at present consists of four studies on the gaseous reaction products of dichromate in molten sodium nitrite[1] and the reactions of sodium formate, acetate and propionate in the same melt;[2] together with the reactions of a series of chromium(VI) and chromium(III) compounds[3] and of four silver compounds[4] in sodium-potassium nitrite eutectic. These studies have provided evidence of the nitrite ion entering into both oxidising and reducing reactions, behaving as a Lux-Flood base and exchanging with other anions followed by thermal decomposition of noble metal nitrite. Thus nitrite melts have already displayed a considerably greater versatility of reaction than nitrate melts, though so far the latter have been studied more intensively. Where the same compound has been studied in both melts, nitrite has been shown to be considerably more reactive. In view of the current interest in hexanitrito/nitro complexes of the first row transition metals and the possibility of coordination in the melt, the behaviour of iron, cobalt and nickel chlorides in pure sodium-potassium nitrite melt were studied and the results are now reported. These provide further illustrations of the basic and oxidation reactions of this melt.

Experimental Section

The nitrite eutectic was prepared as described previously.[3] Cobalt(II) and nickel(II) chlorides were dehydrated with thionyl chloride by the method of Freeman and Smith.[5] (Found: Co, 45.9; Cl, 54.4. Calc. for $CoCl_2$: Co, 45.4; Cl, 54.6, and Found: Ni, 44.8; Cl, 55.2. Calcd. for $NiCl_2$: Ni, 45.3; Cl, 54.7). Iron(III) chloride was prepared by passing chlorine over B.D.H. electrolytic iron at 300°. (Found: Fe, 34.5; Cl, 65.6. Calcd. for $FeCl_3$: Fe, 34.4; Cl, 65.6) and iron(II) chloride by reducing the higher chloride *in situ* with hydrogen at 250° (Found: Fe, 43.8; Cl, 55.7. Calcd. for $FeCl_2$: Fe, 44.1; Cl, 55.9).

The procedures for the reactions, thermogravimetric analysis, infrared spectroscopy of gaseous products and quantitative estimation of nitrate ion were carried out as previously described.[3] The X-ray powder lines were obtained with a Philips (Eindhoven) Diffractometer using nickel filtered CuKα radiation. Nickel was estimated gravimetrically with dimethylglyoxime, cobalt by electrodeposition and iron volumetrically with dichromate.

Results

Iron(II) chloride, as white leaflets tinged with grey, when added to the nitrite eutectic under vacuum or dry nitrogen, did not appear to dissolve at 230° nor to react. However, as the temperature was increased, reaction commenced at 280° with the production of brown fumes, shown by infrared to consist of nitric oxide as well as nitrogen dioxide, and the formation of a red-brown precipitate (Found: Fe, 69.3. Calcd. for Fe_2O_3: Fe, 69.9). The powder pattern of the washed and dried precipitate («d» values 3.67(m), 2.70(s), 2.51(s), 2.21(m), 1.84(w), 1.69(w) Å) corresponding with that of α–Fe_2O_3 (A.S.T.M. index 3.66, 2.69(100), 2.51(80), 2.20, 1.84, 1.69(80). Thermogravimetric analysis also showed that there was no reaction below 260°, a very sharp weight loss maximum occurred at 275-300° but there was virtually no reaction above 320°. The overall weight loss varied from 49.3 to 51.8 but when corrected by the addition of one oxygen per nitrate formed, due to the reaction

$$NO_2 + NO_2^- \longrightarrow NO_3^- + NO \qquad (1)$$

the weight loss became 53.7 ± 1.2% (Calcd. for loss of $2N + 2\frac{1}{2}O$ per $FeCl_2$ 53.6%).

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[1] R. N. Kust and R. W Fletcher, *Inorg. Chem.*, *8*, 687 (1969).
[2] T. R. Kozlowski and R. F. Bartholomew, *Inorg. Chem.*, *7*, 2247 (1968).
[3] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, *3*, 667 (1969).
[4] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, forthcoming.
[5] J. H. Freeman and M. L. Smith, *J. Inorg. Nucl. Chem.*, *7*, 224 (1958).

Iron(III) chloride: the brown crystals reacted very rapidly with the eutectic at 230°, under vacuum or dry nitrogen, producing a red-brown precipitate (Found: Fe, 70.4. Calcd. for Fe_2O_3: Fe, 69.9) which gave the diffraction lines (3.67(m), 2.70(s), 2.51(s), 2.20(w), 1.84(w), 1.69(w)). Brown gases consisting of a mixture of nitrogen dioxide and nitric oxide were evolved. Thermogravimetry indicated that the reaction began at 130°, *i.e.* in the solid state, but that a maximum was reached at 250-280° with the reaction appearing complete at 310°. The overall loss of weight varied from 55.5 to 64.6% but when corrected for the nitrate formed, reaction (1), this became $70.7 \pm 0.1\%$ (Calcd. for loss of $3N + 4\frac{1}{2}O$ per $FeCl_3$ 70.3%).

Cobalt(II) chloride reacted immediately with the eutectic at 230° under both vacuum and dry nitrogen with the evolution of nitrogen dioxide and nitric oxide and the formation of a black precipitate (Found: Co, 72.2. Calcd. for Co_3O_4: Co, 73.5%) which after washing and drying gave the diffraction lines, 2.855(m), 2.42(s), 2.02(w), 1.43(w), [A.S.T.M. index for Co_3O_4 2.86(40), 2.44(100), 2.02(25), 1.43(45)].

Thermogravimetric analysis showed the reaction to begin at 130° in the solid state and to reach a fairly broad maximum at about 275°, the reaction being completed by 350°. The overall weight loss varied from 48.4 to 50.7, and became 53.8 ± 0.7 when corrected for the formation of nitrate, reaction (1). (Calcd. for loss of $2N + 2^2/_3O$ per $CoCl_2$ 54.4%).

Nickel(II) chloride also reacted immediately with the eutectic at 230° evolving brown fumes of nitrogen dioxide and nitric oxide and forming a grey precipitate. The powder pattern of the washed and dried precipitate [2.41(s), 2.08(s), 1.48(m)] corresponding well with that of NiO [A.S.T.M. index 2.41(91), 2.09(100), 1.48(57)]. Thermogravimetry showed that the reaction began at 130°, reached a maximum at 250-270° and was concluded at 360°. The weight loss was 55.8-57.9% but after correction for nitrate formation (reaction (1)) became $58.9 \pm 0.4\%$. (Calcd. for loss of $2N + 3O$ per $NiCl_2$ 58.6%).

Discussion

All four reactions fitted the stoichiometries

$$2FeCl_2 + 4NO_2^- = Fe_2O_3 + 3NO + NO_2 + 4Cl^- \qquad (2)$$

$$2FeCl_3 + 6NO_2^- = Fe_2O_3 + 3NO + 3NO_2 + 6Cl^- \qquad (3)$$

$$3CoCl_2 + 6NO_2^- = Co_3O_4 + 4NO + 2NO_2 + 6Cl^- \qquad (4)$$

$$NiCl_2 + 2NO_2^- = NiO + NO + NO_2 + 2Cl^- \qquad (5)$$

after correction for the further reaction of nitrogen dioxide with nitrite melt, equation (1). In reactions (2)-(5) the metal ions were evidently acting as Lux-Flood acids, abstracting oxide ions from nitrite, in a manner analogous to their behaviour in molten nitrates. The nitrite melt has appreciably more basic character however, since the reactions occured more vigorously and at considerably lower temperatures. Indeed, with three of the salts the reaction commenced well below the melting point. The metal oxides formed as the final products were the same as those produced in nitrate melt and in each case were the most stable oxides. In those cases where oxidation of the original metal ion occurred it was evident that this was almost immediate in the case of cobalt but considerably delayed in the case of iron(II). The inertness of this latter chloride below 270° was attributed to its almost complete insolubility in molten nitrite.

When comparing the stoichiometries of the reactions of the iron(II) and iron(III) chlorides it became evident that the reaction of iron(II) chloride to form ferric oxide was more likely to have occurred via the initial formation of ferrous oxide followed by its oxidation rather than via the formation of ferric ions and their subsequent combination with oxide from nitrite. However, in both cases either the formation of dinitrogen trioxide must be postulated (though this is almost certainly completely dissociated at 200°) together with its complete reaction with oxide ions to give nitrite; or possibly more plausibly the reaction of nitrogen dioxide with oxide ions to give nitrate and nitrite, and the subsequent complete reaction of this nitrate with nitric oxide to produce nitrite. Completion of the latter reactions is made unlikely however by the necessarily low concentrations of oxide and nitrate ions, the low partial pressure of nitric oxide, and the inherent likelihood of some of the excess nitric oxide reacting with the nitrate produced via reaction (1). Evidently the latter did not occur since the corrected thermogravimetric weight losses were very close to those expected from equations (2) to (5).

An alternative hypothesis, that an ionisation occurred in nitrite melt analogous to that postulated by Duke[6] in nitrate melts enables a much simpler reaction pathway to be envisaged

i.e. $NO_2^- \longrightarrow NO^+ + O_2^-$

$$Fe^{2+} + O^{2-} \longrightarrow FeO$$

$$2FeO + 2NO_2^- \longrightarrow Fe_2O_3 + 2NO + O^{2-}$$

$$NO^+ + NO_2^- \longrightarrow NO + NO_2$$

The same point can frequently be made for other reactions but in itself of course provides no conclusive proof that any such ionisation has occurred.

Acknowledgments. Thanks are expressed to the Science Research Council for a fellowship (to S.A.T.) and to Professor F. Hodson for use of the diffractometer.

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(6) R. N. Kust and F. R. Duke, *J. Amer. Chem. Soc.*, *85*, 3338 (1963).