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MOLTEN SODIUM NITRITE–POTASSIUM NITRITE EUTECTIC: THE REACTION OF SOME COMPOUNDS OF MOLYBDENUM

S. S. AL OMER AND D. H. KERRIDGE
Department of Chemistry, The University, Southampton S09 5NH (England)
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ABSTRACT

Molybdenum(VI) oxide, ammonium molybdate and molybdic acid reacted in molten sodium nitrite–potassium nitrite eutectic to form orthomolybdate, nitrogen dioxide and nitric oxide (with nitrate as a secondary product), a more polymerised polymolybdate being formed as an intermediate product. Tungsten(VI) oxide reacted similarly but less rapidly. Molybdenum and tungsten metals reacted to form the orthoxyanion and nitrogen, the latter metal reacting considerably faster and forming smaller amounts of nitric oxide and nitrous oxide. Reaction temperatures and stoichiometries are given and reaction pathways suggested.

INTRODUCTION

Molten nitrite chemistry is at present little known and might be imagined as analogous to that in molten nitrates but already shows a number of differences from the chemistry of the more studied and better understood molten nitrates. Among these differences are reducing as well as oxidising behaviour, the lower oxidation states such as chromium(III) and vanadium(IV) appearing as intermediates before final oxidation to the stable states of chromium(VI)[1] and vanadium(V)[2]; a suggestion that the self-ionization constant for the equilibrium

$$NO_2^- \rightleftharpoons NO^+ + O^{2-} \quad (1)$$

is very much larger than the analogous dissociation of the nitrate anion (measured as 10^{-9} and 10^{-19} in $NaNO_3/KNO_3$ at 300°C respectively[3, 4]): and the possibility of ambidentate behaviour (nitrite anions having been shown to coordinate to transition metal cations through nitrogen as well as through oxygen, in the melt as well as via aqueous solutions[5]).

In the case of molybdenum and tungsten compounds, nothing was previously known of their behaviour in molten nitrite except from the report of the molar volumes of potassium molybdate(VI) and tungstate(VI) in potassium nitrite, thus presupposing stability up to at least 440°C[6]. A study was therefore undertaken of the reactivity of molybdenum(VI) compounds and of molybdenum metal in sodium nitrite–potassium nitrite eutectic in order to compare the acid–base and oxidation–reduction behaviour with the corresponding molten nitrates. Such reactions can be conveniently followed by use of a thermogravimetric balance and the stoichiometry of the gas evolving reactions established.

EXPERIMENTAL

Materials

Sodium nitrite–potassium nitrite eutectic was prepared as previously described[2]. Molybdenum and tungsten metals, molybdenum(VI) and tungsten(VI) oxide (all of reagent grade) were dried at 120°C for 12 h, as was Analar sodium orthomolybdate(VI) (B.D.H.). Reagent grade sodium orthotungstate(VI) was dried at 150°C for 2 h. Analar molybdic acid was dried at 120°C for 12 h (Found: Mo, 59.5; calc. for H_2MoO_4: Mo, 59.3%) and Analar ammonium molybdate (B.D.H.) at 100° for 12 h. (Found: Mo, 58.8; calc. for $(NH_4)_6Mo_7O_{24}$: Mo, 58.6%).

Procedure

Reactions were carried out in pyrex tubes with B.24 joints, closed with silica gel drying tubes, which fitted snugly into an electric resistance furnace connected to an Ether Transitrol controller. The melts were quenched, dissolved in water and analysed qualitatively and quantitatively, nitrate being estimated by the method of Leithe[7]. Thermogravimetric analyses were carried out with a Stanton TR-1 thermobalance with a heating rate of 2°C min^{-1}. The silica crucible was covered with an inverted funnel to minimise the emission of solid particles. The curves shown are typical of those obtained from 3–6 determinations. Weight losses were calculated as a percentage of the reactant indicated.

The gases evolved were collected via a vacuum system and identified by infrared in a 85 mm gas cell with silicon windows using a Unicam SP200 spectrophotometer and by mass spectroscopy after trapping in liquid nitrogen using an AEI-MS12 spectrometer.

RESULTS AND DISCUSSION

Sodium molybdate(VI) dissolved in the molten nitrite eutectic to give a yellow solution (concentration ~ 0.95 m at 230°C) with no visual evidence of reaction to 400°C. Similarly thermogravimetry showed no weight loss to this temperature (Fig. 1, curve A). Such stability would be in accord with that inferred from the density measurements on potassium nitrite–potassium molybdate melts[6].

As expected the acidic molybdenum(VI) oxide showed considerably greater reactivity, when added to nitrite melt at 230°C a brown gas, consisting of a mixture of nitrogen dioxide and nitric oxide, was evolved and an insoluble suspension appeared initially in the melt which dissolved after five minutes to form a yellow solution. Thermogravimetric analysis also showed reaction commencing at 175°C, below the

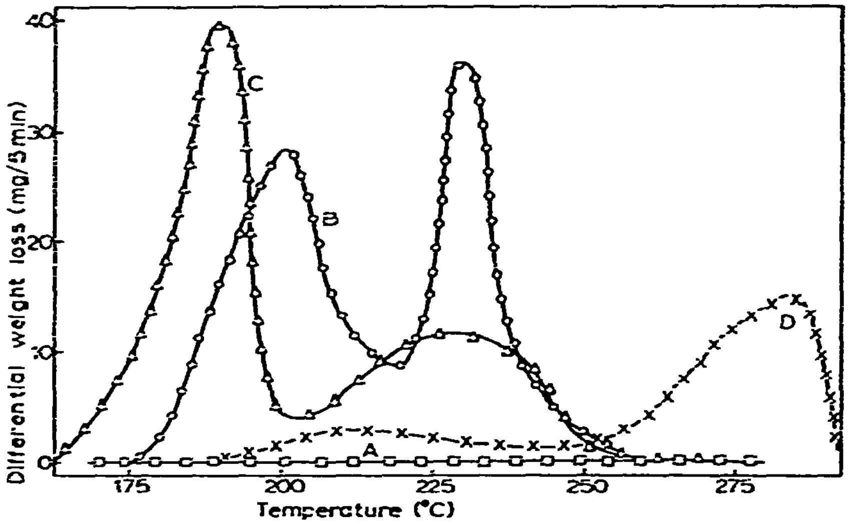

Fig. 1. Thermogravimetric analysis of molybdenum compounds in sodium nitrite–potassium nitrite eutectic. Curve A, □—□, 0.35 m Na_2MoO_4; curve B, ○—○, 0.094 m MoO_3; curve C, △—△, 1.1 m H_2MoO_4; curve D, X—X, H_2MoO_4 alone (0.57 g).

melting point of the eutectic but clearly consisting of two distinct stages of weight loss (Fig. 1, curve B). The total weight loss to 260°C varied from 38.1 to 44.2%, a similar variation has previously been found when nitrogen dioxide was a reaction product[1]. In fact, part of the gas had reacted with the melt in accordance with the equation

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \qquad (2)$$

and when the weight losses were corrected for the amount of nitrate which analysis showed to be formed [i.e., as if no nitrogen dioxide had reacted via eqn (2)], they gave a value of 51.2% in accordance with the equation

$$MoO_3 + 2NO_2^- \rightarrow MoO_4^{2-} + NO_2 + NO \qquad (3)$$

(Calc. for loss of 2N + 3 O per MoO_3, 52.7%)

Analysis showed the presence of orthomolybdate in the solution at the completion of both reactions.

Unfortunately, it did not prove possible to conclusively identify the product of the first reaction by allowing molybdenum trioxide to react isothermally at 220°C (the temperature of minimum rate of weight loss) since some molybdate(VI) (i.e., the product of the second reaction) was also formed. However, the corrected weight loss for the isothermal reaction was 23.9% much closer to that calculated for the formation of dimolybdate (Calc. for loss of N + 3/2 per MoO_3, 26.3%) than for the formation of trimolybdate (Calc. for the loss of 2/3 N + O per MoO_3, 17.6%). In agreement with the fact that, when reactions of this type overlap, the point of minimum rate of weight loss is pushed to lower temperatures and thus smaller apparent percentage weight losses. Some further evidence for a stepwise reaction may be indicated by the insoluble material observed for the first minutes of a reaction. This

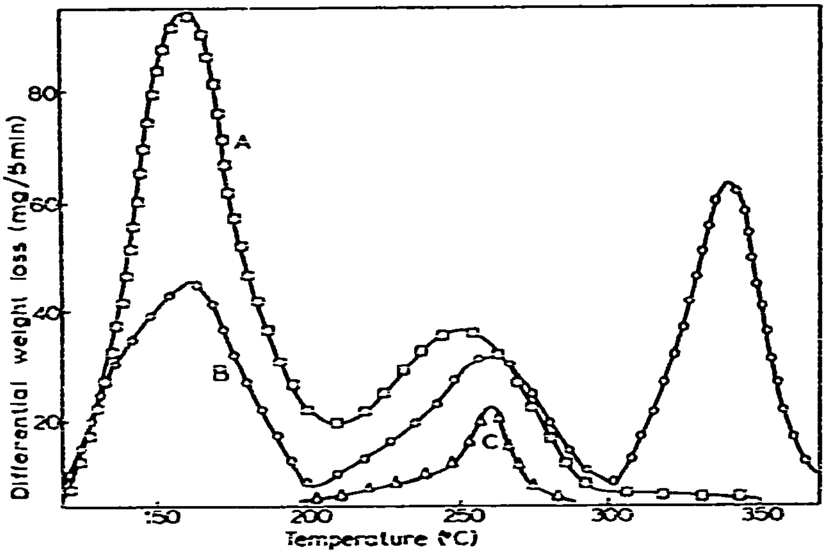

Fig. 2. Thermogravimetric analysis of molybdenum compounds in sodium nitrite–potassium nitrite eutectic. Curve A, □—□, 0.26 m $(NH_4)_6Mo_7O_{24}$; curve B, ○—○, $(NH_4)_6Mo_7O_{24}$ alone (1.92 g); curve C, △—△, Mo metal (0.114 g in 1.54 g melt).

could have been a more polymeric molybdate which then reacted further to the more soluble dimolybdate.

Molybdic acid and ammonium molybdate reacted in a somewhat similar fashion (Fig. 1, curve C and Fig. 2, curve A) although the temperature of the first reaction was lower. The actual weight losses for the overall reaction, when orthomolybdate was identified as the final product together with nitrogen dioxide and nitric oxide were again variable (around 53.0 and 54.3%, respectively) but became constant after correction for formation of nitrate (eqn (2)) at 57.1 and 58.0% which corresponded to the stoichiometries.

$$H_2MoO_4 + 2NO_2^- \rightarrow MoO_4^{2-} + H_2O + NO_2 + NO \tag{4}$$

(Calc. for loss of 2H + 2N + 4 O per H_2MoO_4, 58.0%)

$$(NH_4)_6Mo_7O_{24} + 14NO_2^- \rightarrow 7MoO_4^{2-} + 6NH_3 + 3H_2O + 7NO_2 + 7NO \tag{5}$$

(Calc. for loss of 21H + 20N + 24 O per $(NH_4)_6Mo_7O_{24}$, 59.1%)

The gases formed in the latter reaction were shown to be ammonia and water, as well as nitrogen dioxide and nitric oxide. Thermogravimetry clearly showed both this and reaction (4) to occur in two stages, but because of overlap in neither case was it possible to separate the weight losses. However, the coincidence of the first maximum with that of the first phase of thermal decomposition of ammonium molybdate (Fig. 2 curves A and B) where the product analyses as an equimolar mixture of ammonium di- and trimolybdates[8], shows the greater reactivity of part of this newly formed product (presumably of extremely small particle size) as compared to the much larger particles of the solid molybdenum(VI) oxide (Fig. 1, curve B). A similar coincidence of the second maxima of curves A and B of Fig. 2, where ammonium tetramolybdate is considered to be the thermal decomposition product, again shows the reactivity of the newly formed molybdate. By contrast, molybdic acid decomposed thermally at a higher temperature and the first maximum of Fig. 1, curve C is therefore the reaction of the acid itself with the melt.

Powdered molybdenum metal reacted only slowly when added to the molten eutectic at 230°C, forming a solution containing a white suspension and a colourless gas which was shown by mass spectrometry to be nitrogen only. After some hours, the suspension dissolved to a clear yellow melt which contained orthomolybdate. Thermogravimetry (Fig. 2, curve C) showed reaction to have commenced below the melting point of the eutectic and the rate to increase slowly to give only one maximum. The total weight loss was found to be 32%, in reasonable accord with the stoichiometry

$$Mo + 2NO_2^- \rightarrow MoO_4^{2-} + N_2 \qquad (6)$$

(Calc. for loss of 2N per Mo, 30%)

Again, it seems likely that the oxidation and addition of oxide ions is a stepwise process, e.g.,

$$Mo \rightarrow MoO_3 \rightarrow Mo_2O_7{}^{2-} \rightarrow MoO_4{}^{2-}$$

but investigation of the polymerisation of the initial insoluble solid did not prove possible. Such polymerised species are certainly less stable than in the corresponding nitrate melts where trimolybdate has been reported stable in potassium nitrate at 350°C[9], although Schlegel and Bauer[10] claimed that this anion reacted in sodium nitrate–potassium nitrate and that dimolybdate was the stable species. The greater basicity of nitrite melts accords with the much larger self-dissociation constant for nitrite reported by Kust and Burke[11].

The reaction of molybdenum metal though visually less rapid than that of tungsten at 230°C, had a rate of gas evolution some 15 times greater at 260°C. This

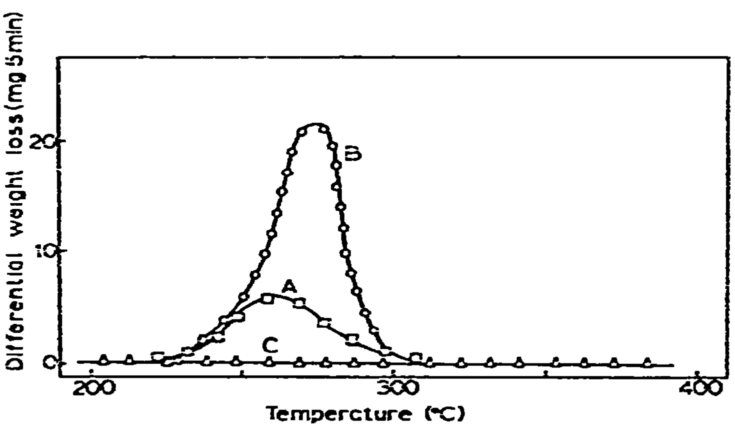

Fig. 3. Thermogravimetric analysis of tungsten compounds in sodium nitrite–potassium nitrite eutectic. Curve A, □—□, W metal (1.49 g in 2.37 g melt); curve B, ○—○, 0.36 m WO_3; curve C, △—△, 0.24 m Na_2WO_4.

variation in reactivity was in contrast to that reported for a mixture of sodium nitrate–potassium nitrate–sodium nitrite (7, 53, 40%) at 350°C[12] where the rate of reaction of tungsten was approximately twice that of molybdenum, though it should be noted that the rate of reaction of molybdenum at 350°C was found to be slightly greater in pure sodium nitrate than in pure sodium nitrite melt.

Thermogravimetric analysis of the powdered tungsten–molten nitrite eutectic gave a variable weight loss of 15.5 to 16.3% (Fig. 3 curve A). A white precipitate of orthotungstate formed and a mixture of colourless gases was evolved which consisted of nitrogen with smaller amounts of nitrous oxide and nitric oxide. The proportions varied, rather more of the nitrogen oxides being formed if the mixture of reactants were heated slowly from room temperature than if the metal was added to the melts at 230°C when a violent reaction occurred. This reaction can be reasonably represented by the stoichiometry

$$W + 2NO_2^- \rightarrow WO_4^{2-} + N_2 \qquad (7)$$

(Calc. for loss of 2N per W, 15.2%)

though the route may well be via lower oxidation state nitrogen oxyanions decomposing thermally to form nitrogen oxides as well as nitrogen. Similar mechanisms have been postulated for the reaction of reactive metals with molten nitrates[13].

By contrast, tungsten(VI) oxide reacted with the melt at a higher temperature (Fig. 3, curve B) indicating a lower Lux-Flood acidity than that of molybdenum(VI) oxide. A white precipitate of orthotungstate was formed together with nitrogen dioxide and nitric oxide. The weight loss varied from 23.5 to 29.3% which, when corrected for the formation of nitrate (eqn (2)), gave an average loss of 31.2% in accordance with the equation

$$WO_3 + 2NO_2^- \rightarrow WO_4^{2-} + NO_2 + NO \qquad (8)$$

(Calc. for loss of 2N + 3 O per WO_3, 32.7%)

As was found for the orthomolybdate(VI), sodium orthotungstate(VI) did not react, no weight loss being detected up to 400°C (Fig. 3, curve C).

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