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Molten Sodium Nitrite-Potassium Nitrite Eutectic: the Reactions of Vanadium Compounds

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The reactions of five vanadium compounds of oxidation states (IV) and (V) in nitrite melts have been studied. Vanadyl(IV) sulphate and vanadium dioxide are initially oxidised to metavanadate, while vanadium pentoxide initially reacts to give both metavanadate and vanadium dioxide, the latter then reacting further to form metavanadate. Sodium metavanadate and the metavanadates formed in solution react further at about 300° to form orthovanadate which is moderately soluble and undergoes no further change. However, such solutions and those of sodium orthovanadate are found to catalyse the thermal decomposition of the nitrite melt. In each of the reactions nitrogen oxides (NO_2 and NO) are produced.

Introduction

The use of nitrite melts as non-aqueous reactive solvents is still relatively new, but despite the fact that much remains unknown sufficient information is now available to demonstrate the occurrance of oxidation-reduction reactions, behaviour as a Lux-Flood base, anion exchange and thermal decompositions of noble metal nitrites. The chemistry known up to the beginning of 1971 has been recently reviewed.[1]

At the present time reports have appeared of at least preliminary studies of most of the first row transition metals, and comprise investigations of the oxidation of titanium metal,[2] the gaseous products of dichromate/nitrite reactions[3] and the reactions of a series of chromium(VI) and chromium(III) compounds,[4] the stability of the higher oxidation states of manganese,[5] the acid-base and oxidation reactions of iron, cobalt and nickel[5] and of copper and iron pyrites.[7]

The notable exception in this list is vanadium and the reactions of five compounds of this element in oxidation states V and VI are now reported. These include a further example[4] of the unexpected formation of a lower oxidation state as a reaction intermediate, which is later reoxidised to the original oxidation state. This raises the question of how many other apparently simple overall Lux-Flood acid-base reactions actually involve a lower oxidation state intermediate, albeit of lower stability than the chromium(III) or vanadium(IV) formed in these two presently known examples.

Experimental Section

The nitrite eutectic was prepared as previously described.[4] Sodium orthovanadate, sodium metavanadate, vanadium pentoxide and vanadyl(IV) sulphate (B.D.H. reagent grades) were dried at 250° for 2 hr., 120° for 1 hr., 120° for 1 hr. and 300° for 6 hr. respectively. Results of analysis were respectively (Found: V, 34.8. Calc. for Na_3VO_4: V, 36.9%), (Found: V, 41.1. Calc. for $NaVO_3$: V, 41.8%), (Found: V, 55.4. Calc. for V_2O_5: V, 56.0%) and (Found: V, 30.2. Calc. for $VOSO_4$: V, 31.3%). Vanadium dioxide was prepared by the method of Tandy[8] (Found: V, 60.2. Calc. for VO_2: V, 61.4%).

The procedures for the reactions, thermogravimetric analysis, X-ray powder diffractometry, infrared spectroscopy of gaseous products and quantitative estimation of nitrate ion were carried out as previously described.[6] E.s.r. measurements were made using a Varian E-3 spectrometer operating at 9.20 GHz, and visible and ultraviolet spectroscopy of melt solutions on a Unicam SP 700 spectrophotometer modified for use up to 700°. Vanadium was estimated qualitatively by pH and precipitation methods[9] and quantitatively, after reduction with sodium sulphite, volumetrically with permanganate.

Results

Sodium orthovanadate is moderately soluble in sodium nitrite-potassium nitrite eutectic, approximately 1.3 m at 320°. Thin films of the solutions showed an absorptions at 35000 cm^{-1} as a shoulder on the intense nitrite band. Thermogravimetric analysis indicated that the solutions were stable up to 360° but that above this temperaure commenced to lose weight

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Table I. Decomposition rates of sodium nitrite-potassium solutions of vanadium compounds.

Expt.	Initial Solute	Solute Concn.	Weight of melt	Temperature	Rates of weight loss
1	Na_3VO_4	1.17 m	2.0g	380°	1.0 mg/5 min.
2	Na_3VO_4	1.71	1.9	430°	15
3	$NaVO_3$	1.36	2.0	490°	7
4	$NaVO_3$	1.14	3.3	530-650°	40
5	V_2O_5	0.48	2.2	390°	0.2
6	»	0.82	2.8	390°	0.7
7	»	0.76	1.9	450°	1.2
8	»	1.2	1.8	450°	2
9	$VOSO_4$	0.34	2.9	360°	0.7
10	»	1.15	1.8	470°	1.5

steadily (see curve A of Figure and the Table for typical results). The rate of loss increased with concentration of vanadate and with temperature and showed some dependance on the quantity of melt in the standard 10 ml silica crucibles. Analysis of the quenched melt indicated increased concentrations of oxide and of nitrate, for example with expt. 1 of the Table, after 19 hr. the oxide and nitrate concentrations reached 0.88 m and 1.25 m respectively.

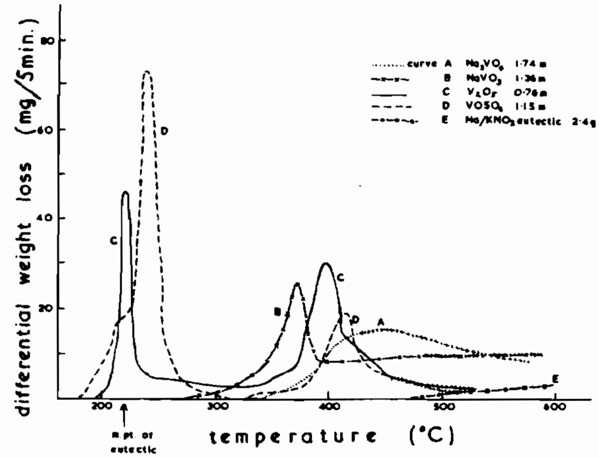

Figure 1. Thermogravimetric analysis of vanadium compounds in Na/KNO$_2$ eutectic.

Sodium metavanadate was almost insoluble in the nitrite eutectic (~ 10^{-4} m at 250°) but commenced reacting at 310° with the evolution of a mixture of nitrogen dioxide and nitric oxide. The other product, a white solid, dissolved as the temperature increased and was shown to be orthovanadate after quenching and solution in water. Thermogravimetric analysis showed weight loss to begin at 280° and to be continuous up to at least 480° and for times of at least 4 hr. The total weight loss varied from 87 to 123%. (Calc. for loss of 2 N + 3 O per $NaVO_3$ 62.3%). A typical experiment is represented as curve B of the Figure and other results are given in the Table. Vanadium pentoxide commenced reacting below the melting point of the eutectic (see curve C of Figure) with evolution of nitrogen dioxide and nitric oxide. On increasing the reaction temperature above the melting point of the eutectic, it was apparent that a white precipitate containing blue-black particles had formed. Rapid solution of the frozen melt in water allowed the extraction of the bulk of the white precipitate which was shown to be metavanadate. It did not prove possible to completely separate both precipitates as the blue-black particles tended to form a colloidal solution on continued washing. However, the particles remaining after thorough washing were dissolved in dilute sulphuric acid and formed a bright blue solution, shown to contain vanadium(IV) equivalent to 7% of the original vanadium. E.s.r. on the reacted melt also indicated the presence of vanadium(IV) with a g, factor of 1.939 which may be compared to the value of 1.94 found for pure vanadium dioxide.[10] X-ray diffraction gave lines with 'd' values of 3.25 (100%), 2.41 (60%) and 1.65 (60%), corresponding to those of vanadium dioxide in the A.S.T.M. Index 3.20 (100%), 2.42 (60%), 1.65 (60%).

On further increasing the temperature, or maintaining it at the melting point for some bours, the blue-black particles gradually reacted, at which stage all the vanadium was in the form of metavanadate. Isothermal thermogravimetric analysis showed that the weight loss after 4 hr. at 220° (m.p. of eutectic) was 31.6-32.6%. Assuming that all additional nitrate was formed by nitrogen dioxide, these could be

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

corrected to an average value of 41.4%. (Calc. for loss of 2 N + 3 O per V_2O_5 41.8%).

A further reaction commenced at about 310°, resulting in further evolution of nitrogen dioxide and nitric oxide, and eventually in the formation of orthovanadate. Thermogravimetry indicated a steadily increasing weight loss with time, of as much as 132%. (Calc. for loss of 6 N + 9 O per V_2O_5 125%). The variation of rate of weight loss with vanadium concentration and temperature (see Table) was found similar to those of other orthovanadate solutions.

Vanadyl(IV) sulphate also commenced to react in the solid state with evolution of a mixture of nitrogen dioxide and nitric oxide. On melting a cream coloured precipitate appeared, which after solidification and solution in water, was identified as metavanadate. Thermogravimetry (curve D of Figure) showed a weight loss of 55.5%. (Calc. for loss of 3 N + 3 O per $VOSO_4$ 55.2%. Correction of the values for the nitrate formed, via equation (1), gave a loss of 62.9% (Calc. for loss of 3N+4O per $VOSO_4$ 65.0%). On increasing the temperature of the melt, a second re-

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[10] S.M. Arija, S.C. Akopjan and W. Wintruff, *Z. Anorg. Chem.*, 352, 102 (1967).

action commenced at 320° with further evolution of nitrogen oxides and formation of orthovanadate. Weight losses ranged up to 160%. (Calc. for loss of 5N+7O per $VOSO_4$ 112%), the rates again varying with increasing vanadium concentration and temperature (see Table).

Vanadium dioxide commenced to react under nitrogen just below the temperature of the eutectic with evolution of nitric oxide, while formation of a white precipitate of metavanadate became evident on melting. Isothermal thermogravimetry gave a weight loss of 35.4%. (Calc. for loss of N + O per VO_2 36.2%). When the temperature rose to 300° a further reaction commenced with considerable evolution of nitrogen dioxide and nitric oxide and formation of orthovanadate.

Discussion

Orthovanadate was itself stable in nitrite melts, showing an absorption shoulder not far from that found for the charge transfer band in aqueous solution (36900 cm^{-1}),[11] but had an unexpected catalytic effect on the thermal decomposition of the nitrite, lowering the temperature of the onset of decomposition from 500° to 360°. The involatile products, oxide and nitrate, were also identified as the products of the uncatalysed decomposition,[12-14] while the dependance of decomposition rate on the silica/melt interface, as well as on the orthovanadate concentration and temperature suggests a heterogeneous mechanism as has also been postulated for the uncatalysed decomposition.[13,14] Catalysis by dissolved anions has not hitherto been observed in nitrite melts, though the catalytic decomposition of nitrate melts by chloride and by bromide anions has been reported.[15]

The reaction of sodium metavanadate followed that expected of a Lux-Flood acid and was in accord with equation (2) though the overall weight losses were

$$VO_3^- + 2NO_2^- \rightarrow VO_4^{3-} + NO_2 + NO \qquad (2)$$

much higher than could be expected from equation 2 and were attributed to catalytic decomposition of the melt by the orthovanadate formed.

Similarly the overall reaction of the vanadium pentoxide as a Lux-Flood acid followed the equation with

$$V_2O_5 + 6NO_2^- \rightarrow 2VO_4^{3-} + 3NO_2 + 3NO \qquad (3)$$

again the higher observed weight attributed to catalysis. The intermediate complete conversion to metavanadate likewise conformed to the expected equation

$$V_2O_5 + 2NO_2^- \rightarrow 2VO_3^- + NO_2 + NO \qquad (4)$$

The initial reaction which produced vanadium dioxide as well as metavanadate, illustrated the much less commonly found reducing character of nitrite melts and may be expressed,

$$V_2O_5 + NO_2^- \rightarrow VO_3^- + VO_2 + NO_2 \qquad (5)$$

though the proportions of the vanadium products could not be determined exactly.

The vanadium dioxide formed then reacted further, as did vanadium dioxide added as such,with a weight loss in agreement with the equation

$$VO_2 + NO_2^- \rightarrow VO_3^- + NO \qquad (6)$$

with the metavanadate product reacting further above 300° to form orthovanadate (eq. 2). The two equations 5 and 6 do, of course, sum to equation 4.

Confirmation that vanadium(IV) was not the stable oxidation state in nitrite melts was shown by the reaction of vanadyl(IV) sulphate solutions which were both oxidised and partially neutralised, conforming fairly closely with the equation

$$VOSO_4 + 4NO_2^- \rightarrow VO_3^- + SO_4^{2-} + NO_3^- + 3NO \qquad (7)$$

while after correcting for the nitrate formed by equation 1 the weight loss corresponded to

$$VOSO_4 + 3NO_2^- \rightarrow VO_3^- + SO_4^{2-} + NO_2 + 2NO \qquad (8)$$

The metavanadate formed reacted at higher temperature to give orthovanadate, which in turn catalysed the melt decomposition and led to larger weight losses than those calculated from the overall equation

$$VOSO_4 + 5NO_2^- \rightarrow VO_4^{3-} + SO_4^{2-} + 2NO_2 + 3NO \qquad (9)$$

The only previously known instance of the intermediate formation of a lower oxidation state of a transition metal solute in a nitrite melt before subsequent reoxidation to the original higher oxidation state, was found when both chromium(VI) oxide and trichromate ions were partially reduced to chromium (III).[4] The relative proportions of chromium(III) and the other product, chromate, depended on the initial concentrations of the reactants. The sole final product was chromium(VI) as chromate. With both chromium solutes and in the case of vanadium pentoxide described above,the reactant is a metal-oxygen polymer and it may be postulated that unsymmetrical rupture of the oxygen bonds surrounding any one metal could take place to form more fully neutralised anions (CrO_4^{2-} and VO_3^- polymers respectively) together with less highly coordinated ions, which would necessarily be oxocations (possibly CrO_2^{2+} and VO_2^+ respectively). Such oxocations would be expected to form ion pairs with nitrite and to behave as powerful oxidising agents, rapid reduction of the transition metal and evolution of nitrogen dioxide therefore ensuing. It may be noted that such unsymmetrical rupture of metal-oxygen bonds could not take place with dichromate anions, which have indeed been found not to form any chromium (III) as an intermediate.[4] The lower oxidation states not being stable in nitrite melt are then subsequently oxidised, e.g. as eqn. 6, thus making the overall reactions (eqns. 3 and 4 in the case of vanadium) appear to be of simple Lux-Flood acid-base type.

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(13) E.S. Freeman. *J. Phys. Chem.*, 60, 1487 (1956).
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Essentially the correlation is one of oxidation state with acidity, a lower oxidation state being one of the products of a more acidic environment (i.e. with a relative deficiency of oxide ions) while the higher oxidation state was reformed in the presence of nitrite where oxide ions are more readily available. Stabilisation of higher oxidation states in more basic melt solutions has already been observed fairly widely in melt chemistry. For example, in molten nitrates, neptunium(VII) is formed in hydroxide solutions[16] and the manganese(II)/manganese(IV) equilibrium is displaced as acidity decreases.[17] In borates, chromium(III) is formed in acidic glasses and chromium (VI) in more basic solutions[18] while the stabilisation of uranium(III) in the acidic lithium fluoride-berillium-fluoride-zirconium fluoride melt may be contrasted with its oxidation or disproportionation in the more basic lithium fluoride-sodium fluoride-potassium fluoride eutectic.[19]

Finally examples of the formation of low oxidation state compounds in chloride melts containing acidic aluminium trichloride are now becoming too numerous to enumerate. In this light the apparently anomalous behaviour of vanadium and chromium-oxygen polymers thus becomes explicable.

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