

A THERMOGRAVIMETRIC STUDY OF ACIDIC AND BASIC SOLUTES IN TWO MOLTEN ALKALI METAL NITRATE EUTECTICS

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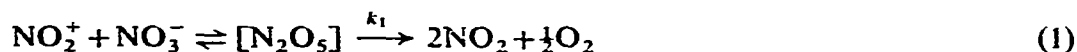
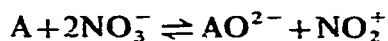
ABSTRACT

The reaction of ten oxyanions and oxides, acting as Lux-Flood acids have been studied in both lithium nitrate-potassium nitrate and sodium nitrate-potassium nitrate eutectics and the stoichiometries of the reactions established. A series of acids arranged in order of decreasing strength has been drawn up, which is very similar for both eutectic solvents.

Five Lux-Flood bases have also been studied in these two solvents. Sodium carbonate proved to be very stable to 500°C. Sodium peroxide revealed significant differences in stability and solubility in the two solvents, while lithium, sodium and potassium hydroxides showed differences in the two melts and also considerable differences between each other, suggesting that little cation exchange takes place in these solutions.

INTRODUCTION

The uses of thermogravimetric analysis are now extremely varied but perhaps one currently under-appreciated application is in establishing the stoichiometry of chemical reactions in molten salt solutions. In the particular case of molten nitrate solvents the reactions of both acidic and basic solutes can be studied by this technique. For example, among basic solutes, carbonates evolve carbon dioxide, peroxides evolve oxygen and hydroxides evolve water vapour, while all Lux-Flood acids react to evolve a gaseous mixture of nitrogen dioxide and oxygen. At the present time the actual reaction pathway of acidic solutes is still in dispute. Many following Duke and coworkers¹⁻³ postulate the existence of the nitryl ion, the formation of an ion pair with nitrate and eventual decomposition, i.e.



While others prefer the hypothesis of Topol et al.⁴ who, having been unable to establish the presence of the nitryl ion, postulated that nitrogen dioxide was the

acidic species, though without advancing an alternative reaction pathway. However, this difference does not effect the overall reactions as the ultimate products are identical.

The reactions of a number of Lux-Flood acids are here presented, the acids which are all either oxyanions or oxides being arranged in the order in which the central atom occurs in the Periodic Table. The five basic solutes are arranged in order of increasing reactivity. The reactions of both acidic and basic solutes were studied in two molten nitrate solvents, lithium nitrate-potassium nitrate eutectic (43 mole % lithium nitrate; m.p. 132°C) and sodium nitrate-potassium nitrate eutectic (50 mole % sodium nitrate, m.p. 220°C), in order to allow comparison between a melt containing the small acidic lithium cation and a more basic melt. Frequently, however, the former melt has been found to be more reactive, even in reactions with acids. Eutectic melts besides providing a conveniently low melting point, also allowed a larger temperature range for solution reaction to be explored since the eutectics did not commence to decompose until 500 and 550°C, respectively.

EXPERIMENTAL

Materials

Lithium nitrate-potassium nitrate eutectic was prepared as previously reported⁵, sodium nitrate-potassium nitrate eutectic was prepared similarly. Analar sodium carbonate, potassium dichromate and chromium trioxide, and reagent grade vanadium pentoxide, sodium metavanadate, molybdenum trioxide, tungsten trioxide, sodium metaphosphate and potassium pyrophosphate were all dried at 120°C for 6 h. Reagent grade lithium hydroxide monohydrate and Analar sodium and potassium hydroxides were used as received. Potassium pyrosulphate was prepared by heating Analar potassium persulphate for 24 h (purity 98.3% by titration with sodium hydroxide). Potassium trichromate was prepared by the method of Harbottle and Maddock⁶ (found: Cr, 40.1, calculated for $K_2Cr_3O_{10}$: Cr, 39.6%).

Physical measurements

Thermogravimetric analysis was carried out in air using a Stanton TR-1 thermobalance with a heating rate of 2°C min⁻¹. Two gram samples of the reactants were contained in 10 ml vitreosil crucibles covered with a small inverted funnel to prevent the emission of solid particles during rapid reactions. The weight losses were reported as a percentage by weight of the specified solute, a correction being made at high temperatures (> 500°C) by deducting the loss found for a pure melt under the same conditions. It was found necessary to grind and thoroughly mix the reactant and melt to obtain maximum separation and sharpness of the differential maxima, as otherwise on melting the viscous melt solutions took some time to achieve homogeneity. The derivative curves were plotted from the recorded weight loss at 5 min intervals versus the mean temperature.

RESULTS AND DISCUSSION

A. Acidic solutes

Pyro- and metaphosphates. Potassium pyrophosphate reacted with the liberation of a brown gas consisting of nitrogen dioxide and oxygen, when dissolved in both the lithium nitrate-potassium nitrate and the sodium nitrate-potassium nitrate eutectics though the temperature of reaction was considerably different in the two melts (Figs. 1 and 2). Sodium metaphosphate also reacted to give the same

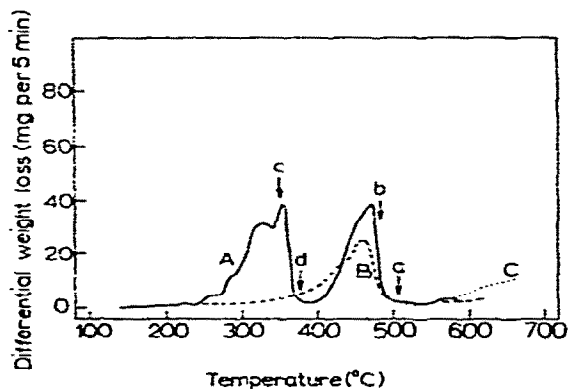


Fig. 1. Thermogravimetric analysis of phosphorus compounds in lithium nitrate-potassium nitrate eutectic. Curve A, 1.50 m NaPO_3 ; curve B, 0.75 m $\text{K}_2\text{P}_2\text{O}_7$; curve C, pure $\text{LiNO}_3/\text{KNO}_3$.

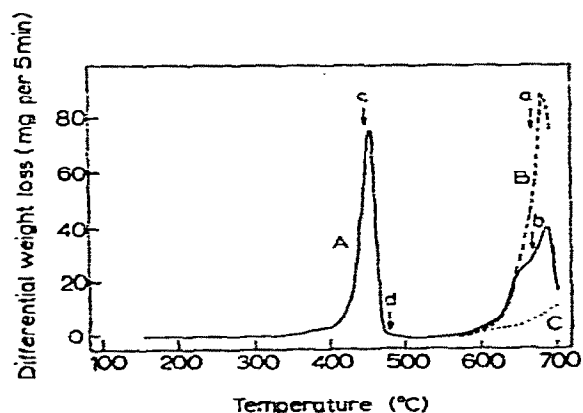
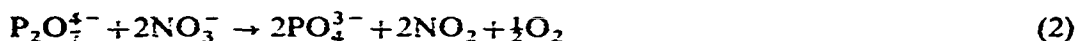


Fig. 2. Thermogravimetric analysis of phosphorus compounds in sodium nitrate-potassium nitrate eutectic. Curve A, 1.49 m NaPO_3 ; curve B, 0.77 m $\text{K}_2\text{P}_2\text{O}_7$; curve C, pure $\text{NaNO}_3/\text{KNO}_3$.

gaseous products but the reaction commenced at lower temperatures and was quite clearly separated into two parts at different temperatures, the second of these reactions showing great similarity to that of pyrophosphate. The weight loss of gaseous

products from the potassium pyrophosphate was close to that indicated by the reaction,

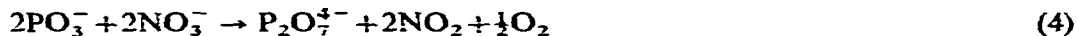


the calculated value of the loss of 2N + 5O per $\text{K}_4\text{P}_2\text{O}_7$ being 32.7%. The temperature at which this calculated loss had taken place is indicated on the curves of Figs. 1 and 2 by the arrow labelled a. The total weight loss due to the sodium metaphosphate reaction was likewise close to that for the reaction



the calculated value of the loss of 2N + 5O per mole NaPO_3 being 104.8% while the temperature at which it has occurred is indicated in Figs. 1 and 2 by arrow b. In the case of reactions in sodium nitrate–potassium nitrate the arrows a and b are at temperatures where the melt itself was commencing to decompose (to nitrite and oxygen). If allowance was made for melt decomposition the arrows came after the end of the period of rapid reaction (i.e., rapid weight loss) as was found for the lithium nitrate–potassium nitrate melt.

However, the minimum between the two parts of the metaphosphate reaction did not correspond to the simple formation of pyrophosphate, i.e.



A reaction which might have been supposed to be followed by reaction (2) which would have completed the overall reaction (3). The weight loss calculated for the loss of N + $\frac{5}{2}$ O per NaPO_3 , i.e. eqn (4), is 52.4% and is indicated in Figs. 1 and 2 by arrow c. In fact the weight loss at the minimum indicated the formation of ortho- as well as pyrophosphate, the ratio in both melts being 0.36 m ortho:0.57 m pyrophosphate, the weight loss corresponding to this ratio of products being indicated by arrow d. The ratio of products could in principle give information on the polymeric form of the metaphosphate, since a trimetaphosphate would be expected to give a 1:1 ratio, while a penta meta ring would give a 1:2 ratio on simple ring cleavage though it could also give a 3:1 ratio if the initial cleavage was followed by an "end-clipping" mechanism. In view of the variety of possible mechanisms and the number of different polymers which occur in the available sodium metaphosphate, detailed correlations of weight losses and products will be postponed until studies are carried out on polyphosphates of known structure.

The above explanation is preferred to the possible alternative which is that the first part of the reaction could indicate the formation of a compound of the stoichiometry $(3\text{P}_2\text{O}_7^{4-} \cdot 2\text{PO}_4^{3-})$ which would be analogous to a number of unusual phosphate polymers postulated by El Din et al.⁷, as products of potentiometric titrations in molten potassium nitrate. Evidence against this latter explanation is that the same ratio of ortho:pyrophosphate would be reached at 390°C in the reaction of pyrophosphate in lithium nitrate–potassium nitrate and at 640°C in sodium nitrate–

potassium nitrate and that there is no indication of any minimum at these points on the thermogravimetric curves of pyrophosphate in Figs. 1 and 2.

Potassium pyrosulphate. Reaction commenced at 160°C in lithium nitrate–potassium nitrate with slow evolution of brown nitrogen dioxide, but became more rapid with increasing temperature and was completed at 300°C (Fig. 3, curve A),

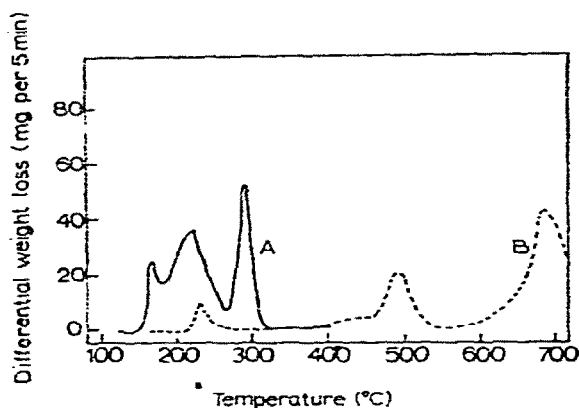
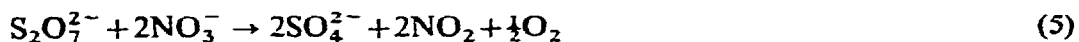


Fig. 3. Thermogravimetric analysis of potassium pyrosulphate in nitrate eutectics. Curve A, 1.49 m solution in $\text{LiNO}_3/\text{KNO}_3$; curve B, 1.51 m solution in $\text{NaNO}_3/\text{KNO}_3$.

when qualitative tests indicated that all the pyrosulphate had reacted with the formation of sulphate.



The total weight loss at this point (42.0%) was in excellent agreement with reaction (5) (calc. weight loss for $2\text{N} + 5\text{O}$ per mole $\text{K}_2\text{S}_2\text{O}_7$: 42.3%). The appearance of more than one maximum was very pronounced but the weight losses at the minimum varied with pyrosulphate concentration and did not appear to correspond to distinct compounds. It is suggested that if nitrogen dioxide is produced via a nitryl ion mechanism¹⁻³ then ion pairs might be formed between nitryl cations and sulphate or pyrosulphate anions and that these may have some modest thermal stability. The initial small peak could also be attributed to a nucleation effect (analogous to the “bumping” phenomenon in boiling) but it seems unlikely that all three maxima could be explained by purely physical effects. Similar but much less pronounced “multi-maxima” weight loss curves can be seen with certain other Lux–Flood acid reactions (e.g. Figs. 1, 3–5) and may be attributed to similar effects.

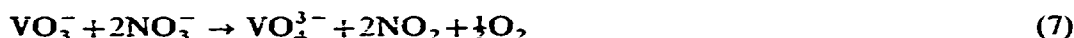
In the nominally more basic sodium nitrate–potassium nitrate melt the same three maxima were observed but completely separated, and extended over a remarkably wide temperature range (Fig. 3, curve B). Again the amount of reaction at each minima was concentration dependent and therefore not attributable to any stoichiometric stage in the reaction, but the position of the maxima was less variable, increasing by only 20°C for a doubling of pyrosulphate concentration.

The much slower loss of nitrogen dioxide and oxygen in the latter melt than in the lithium nitrate–potassium nitrate melt may be correlated, on a cation size basis, with the lower rate of evolution of gaseous products (i.e. k_1 of eqn 1) found by Luthy and Duke⁸ in sodium nitrate–potassium nitrate as the percentage of potassium ions was increased. The very considerable stability of the acidic species indicated here in the second and third maxima of curve B in Fig. 3 must also be reflected in the value of the equilibrium constant reported for



where K was found to increase with the percentage of potassium ions.

Vanadium(V) compounds. Sodium metavanadate commenced reacting in the lithium nitrate–potassium nitrate eutectic at 410°C and reached a maximum rate of evolution of brown nitrogen dioxide and oxygen at 480°C. The weight loss (of curve A of Fig. 4) after correcting for melt decomposition correlated well with the equation:



It should be noted that there is no indication of any pronounced stability of pyrovanadate (the weight loss corresponding to complete conversion to pyrovanadate being indicated by arrow a).

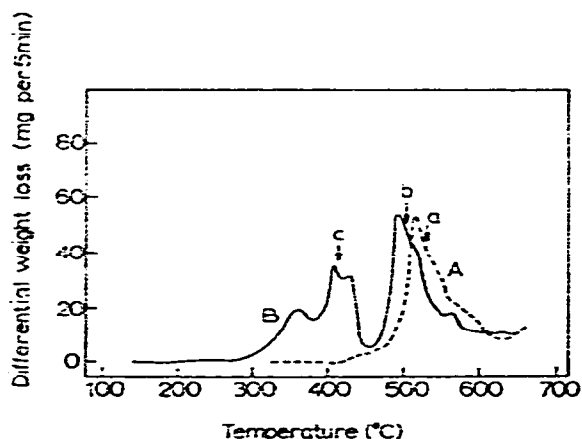


Fig. 4. Thermogravimetric analysis of vanadium compounds in lithium nitrate–potassium nitrate eutectic. Curve A, 1.52 m NaVO_3 ; curve B, 0.74 m V_2O_5 .

Vanadium pentoxide reacted in the same melt at 280°C (curve B of Fig. 4) and again the weight loss correlated with the formation of orthovanadate (calc. weight loss for $6\text{N} + 15\text{O}$ per mole V_2O_5 : 178%). From the similarity in reaction temperatures it appeared that the reacting species at the second maximum was also metavanadate, again there was no indication of any stable pyrovanadate (arrow b). As would be expected from the temperature overlaps of curves A and B, the metavanadate initially formed had already begun reacting before the minimum rate at

450°C was reached, the weight loss corresponding to complete formation of metavanadate being indicated by arrow c.

In the sodium nitrate–potassium nitrate eutectic rather similar effects were observed (Fig. 5) though as with other Lux–Flood acids the two phases of reaction

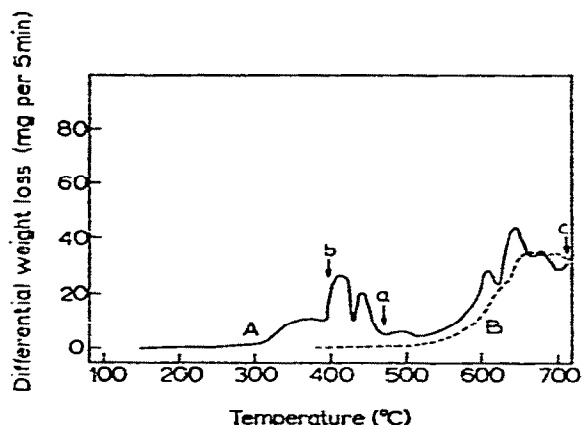


Fig. 5. Thermogravimetric analysis of vanadium compounds in sodium nitrate–potassium nitrate eutectic. Curve A, 0.74 m V_2O_5 ; curve B, 1.47 m $NaVO_3$.

were more clearly separated. As a consequence the weight loss after the first phase of reaction of vanadium pentoxide (curve A) corresponded closely to that expected, i.e.



(calc. for loss of 2N + 5O per mole V_2O_5 : 59.3%, indicated by arrow a on curve A of Fig. 5). Because of the large number of condensed forms known for vanadates, it is possible to correlate the subsidiary minima of the first phase with particular stoichiometries, for example the weight loss calculated for the formation of $V_4O_{11}^{2-}$ is indicated by arrow b. But the first maximum may also be attributed to nitril ion pairs or nucleation effects as discussed earlier.

The overall weight loss of curve A (Fig. 5) at 680°C corresponded to the formation of orthovanadate as did the reaction of sodium metavanadate (calc. for loss of 2N + 5O per mole $NaVO_3$: 83.5%, indicated by arrow c in curve B of Fig. 5). In neither case did pyrovanadate appear to be particularly stable, though this species has been reported to be stable in potassium nitrate at the much lower temperature of 350°C (ref. 9). A more obvious difference is in the reported reaction of vanadium pentoxide under those conditions to form variable amounts of pyrovanadate and a nitrate complex $[VO_3-O-NO_2^-]$, though this stoichiometry was derived from potentiometric titration data only¹⁰.

Chromium(VI) compounds. The temperatures of reaction of chromium(VI) oxide, potassium trichromate and potassium dichromate in sodium nitrate–potassium nitrate (Fig. 6) were closely similar to those previously reported for the same compounds in the lithium nitrate–potassium nitrate eutectic¹¹ and confirmed in this work.

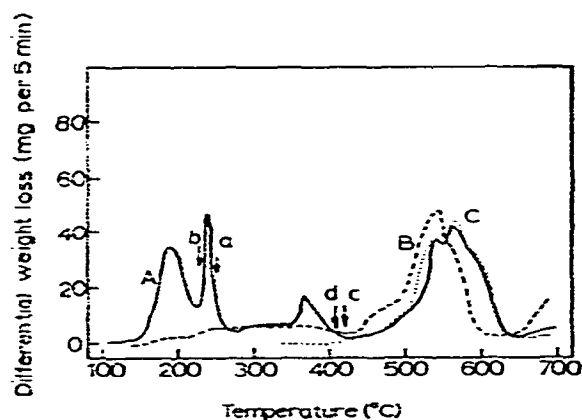
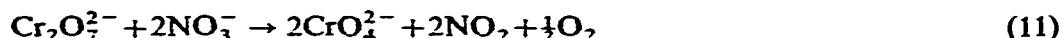
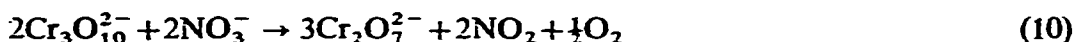
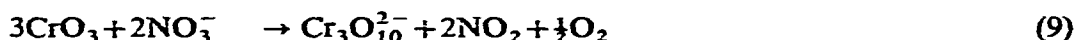


Fig. 6. Thermogravimetric analysis of chromium compounds in sodium nitrate–potassium nitrate eutectic. Curve A, 3.01 m CrO_3 ; curve B, 0.99 m $\text{K}_2\text{Cr}_3\text{O}_{10}$; curve C, 1.53 m $\text{K}_2\text{Cr}_2\text{O}_7$.

The weight losses in sodium nitrate–potassium nitrate indicated complete conversion to chromate at 620°C, and were for CrO_3 105% (calc. for $2\text{N} + 5\text{O}$ per mole CrO_3 : 108%) for $\text{K}_2\text{Cr}_3\text{O}_{10}$ 59% (calc. for $4\text{N} + 10\text{O}$ per mole $\text{K}_2\text{Cr}_3\text{O}_{10}$: 55%) and for $\text{K}_2\text{Cr}_2\text{O}_7$ 38% (calc. for $2\text{N} + 5\text{O}$ per mole $\text{K}_2\text{Cr}_2\text{O}_7$: 37%). The first two reactants had weight losses corresponding to the formation of dichromate at 420°C, i.e. for CrO_3 54% (calc. for $\text{N} + \frac{5}{2}\text{O}$ per mole CrO_3 : 54%) and for $\text{K}_2\text{Cr}_3\text{O}_{10}$ 15% (calc. for $\text{N} + \frac{5}{2}\text{O}$ per mole $\text{K}_2\text{Cr}_3\text{O}_{10}$: 14%). The above reactions can be expressed by the following equations, or by the combination of two or more.



Chromium(VI) oxide showed a weight loss corresponding to the formation of trichromate (calc. for $\frac{2}{3}\text{N} + \frac{5}{3}\text{O}$ per mole CrO_3 : 35%) indicated by arrow a, but it was evident that at this temperature, trichromate itself had begun to react and thus the reactions of the two species could not be clearly separated. Similarly the first minimum indicated by arrow b could be correlated with the formation of tetrachromate (calc. for $\frac{1}{2}\text{N} + \frac{5}{4}\text{O}$ per mole CrO_3 : 27%) but the initial maximum could equally be attributed to nucleation or ion pair formation as with other Lux–Flood acids. These results correlated reasonably with earlier potentiometric studies in pure potassium nitrate where a 0.3 m CrO_3 solution was reported to be completely converted to dichromate after 30 min at 350°C, no discontinuities corresponding to tetra- or trichromate being observed¹².

Molybdenum(VI) oxide. This compound reacted with three clearly defined maxima in both melts (Fig. 7) the weight loss at the first minimum correlating with the formation of trimolybdate (analogous to trichromate eqn 9), a weight loss of 25% being found in the lithium nitrate–potassium nitrate melt at 395°C and in the sodium

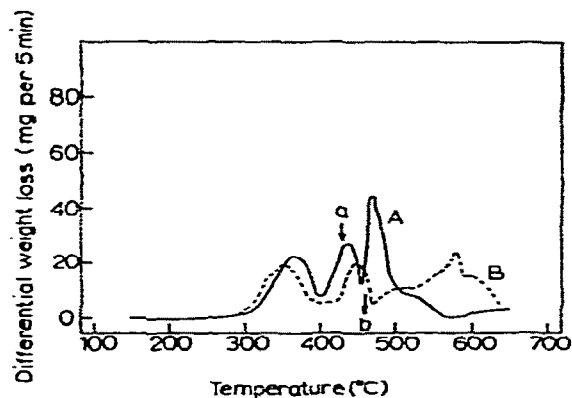


Fig. 7. Thermogravimetric analysis of molybdenum trioxide in nitrate eutectics. Curve A, 1.53 m solution in $\text{LiNO}_3/\text{KNO}_3$; curve B, 1.54 m solution in $\text{NaNO}_3/\text{KNO}_3$.

nitrate-potassium nitrate melt at 405°C (calc. for loss of $\frac{2}{3}\text{N} + \frac{5}{3}\text{O}$ per mole MoO_3 : 25%). The overall loss, 75% at 580°C and at 625°C , respectively, indicated the formation of orthomolybdate after the third maximum (calc. for loss of $2\text{N} + 5\text{O}$ per mole MoO_7 : 75%), analogous to eqn (11). At the second minimum, however, it was apparent that the observed weight loss was higher than that calculated for the formation of dimolybdate (analogous to the formation of dichromate, eqn (10). Calculated for loss of $\text{N} + \frac{1}{2}\text{O}$ per mole MoO_3 : 50%; indicated by arrows a and b on Fig. 7) which would suggest that the dimolybdate formed reacted further before all the trimolybdate had reacted.

These observations correlated with the potentiometric titration results of El Din and El Hosary¹² who reported that trimolybdate was formed by molybdenum(VI) oxide in potassium nitrate, rather better than with the report of Schlegel¹³ that dimolybdate was formed in sodium nitrate-potassium nitrate eutectic at 330°C .

The slightly lower temperature of reaction found with the lithium nitrate-potassium nitrate eutectic indicated the effectively higher Lux-Flood basicity of this melt as has been illustrated earlier in Figs. 1-5.

Tungsten(VI) oxide. The thermograms of this oxide (Fig. 8) were again basically similar for both nitrate eutectics. However, this oxide displayed a considerably lower Lux-Flood acidity and thus required a higher temperature for reactions analogous to eqns 9-11. Weight losses corresponding to the complete formation of orthotungstate occurred after the principal maximum, and were 54% in lithium nitrate-potassium nitrate at 600°C and 53% in sodium nitrate-potassium nitrate at 650°C (calc. for loss of $2\text{N} + 5\text{O}$ per mole WO_3 : 57%). The intermediate and rather small minimum could be connected with the formation of ditungstate (calc. for loss of $\text{N} + \frac{1}{2}\text{O}$ per mole WO_3 : 28%) indicated by arrows a and b in Fig. 8 at 510 and 545°C in the two eutectics. The alternative hypotheses of nucleation and ion pair formation are perhaps now less likely at these high temperatures of reaction.

The low reactivity of tungsten(VI) oxide shown here is parallel by its lack of reaction in potassium nitrate at 350°C (ref. 12), where it was titrated with sodium

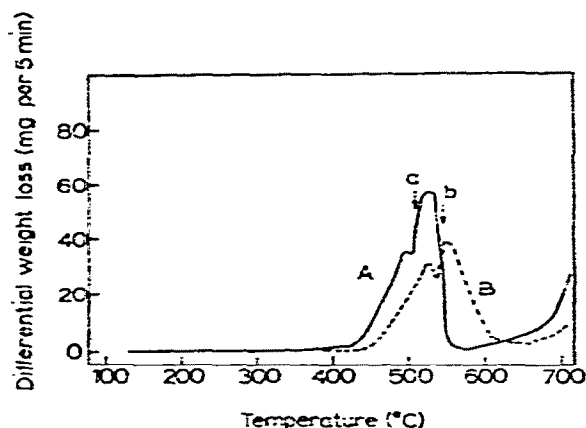


Fig. 8. Thermogravimetric analysis of tungsten trioxide in nitrate eutectics. Curve A, 1.48 m solution in $\text{LiNO}_3/\text{KNO}_3$; curve B, 1.49 m solution in $\text{NaNO}_3/\text{KNO}_3$.

peroxide with no discontinuity corresponding to ditungstate. However, the dimeric anion was found to be more stable in the presence of sodium cations, as it was indicated in phase diagrams of $\text{Na}_2\text{WO}_4\text{-WO}_3$ but not in those of $\text{K}_2\text{WO}_4\text{-WO}_3$ (ref. 14). Tungstate has also been found to have a greater tendency to dimerise in sodium nitrate-potassium nitrate than molybdate, though the equilibrium constant (1.8×10^{-2} at 370°C)¹⁵ was still very small.

A Lux-Flood acidity series in molten nitrates. Since the temperature of maximum rate of evolution of nitrogen dioxide/oxygen varied over a very wide temperature range with the various Lux-Flood acids considered above, the possibility arises of using this feature as a means of arranging the acids in a series of increasing strength. Such a sequence can be justified on the basis of either current hypothesis on the nature of the acid species in molten nitrates. On the nitril ion hypothesis of Duke and coworkers¹⁻³ increasing acid strength results in an increased concentration of nitril ion, and/or of its ion pair with nitrate anions, and thus ultimately an increased rate of evolution of nitrogen dioxide and oxygen, while the hypothesis of Topol et al.⁴ that nitrogen dioxide is the acidic species, indicates directly that as the acid strength of the solute increases so should the rate of evolution of the gaseous products.

The temperature at which the rate reaches a maximum is therefore taken to be an inverse function of the acid strength of the solute. The solute concentration will, of course, effect this temperature to some extent, but the concentrations recorded in Figs. 1-8 were chosen so as to be comparable and where the concentration has been varied by a factor of two the effect on the temperature of the maximum has not been large and generally very much smaller than the variation between one acid and another. Solubility of the product gases would of course delay the attainment of the maximum rate, but since such solubilities are small it is not envisaged that this effect will do other than slightly compress the temperature scale of reactivity.

The thermogravimetric maximum chosen for the correlation with acid strength is the one at the lowest temperature, since later maxima have been correlated with

reaction of new acidic species in the case of polybasic solutes and also possibly with ion pair formation. The nucleation effect mentioned earlier while possibly effecting the temperature of maximum loss, is not thought likely to vary the relative positions of maxima from different solutes. The acidity series derived from Figs. 1-8 are

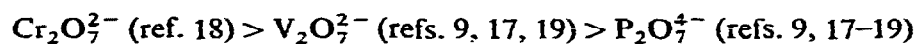


$\text{WO}_3 > \text{NaVO}_3 > \text{K}_2\text{Cr}_2\text{O}_7$ in the lithium nitrate-potassium nitrate eutectic and



$\text{K}_2\text{Cr}_2\text{O}_7 > \text{NaVO}_3 > \text{K}_4\text{P}_2\text{O}_7$ for the sodium nitrate-potassium nitrate eutectic.

These series correlated with what little quantitative information is presently available for these melts (i.e. that the acid dissociation constant of pyrosulphate is very considerably larger than that for dichromate in sodium nitrate-potassium nitrate¹⁻³) and correlates reasonably with the series derived from the measurements of El Din and co-workers. The results are scattered in a number of publications but all were conducted in potassium nitrate at 350°C, and indicate the sequence



which has been derived partly from the calculation of equilibrium constants^{12,17,19}, partly from the relative potentials of 10⁻² M solutions (though expressed in the form of "acidity numbers" by the use of some extremely dubious hypotheses^{17,18}) and partly from observations of immediate reaction^{10,12,16}.

As might be expected this "El Din series" is most closely similar to that for sodium nitrate-potassium nitrate found here. In fact the only difference from the latter series is the difference in the position of metavanadate, which El Din finds more reactive than it was in either eutectic used here. This difference most probably derives from the use of rather different polymeric forms of metavanadate or from the difficulties of the experimental techniques, rather than from a real difference between potassium nitrate and the two eutectic melts both of which contain a large proportion of potassium ions.

The difference in reaction temperatures in the lithium nitrate-potassium nitrate and sodium nitrate-potassium nitrate melts is in accord with the generally greater reactivity of melts containing lithium ions, though this increased reactivity has been more commonly observed in oxidation-reduction reactions. This point should thus be borne in mind when considering the more acidic nature usually attributed to melts containing lithium, the small cation being considered to be partially present as the basic LiO⁻ ion²⁰. Evidently the greater reactivity over-rides the less basic character

of the lithium nitrate–potassium nitrate eutectic, at least at temperatures appreciably above the melting point.

B. Basic solutes

The thermogravimetric curves for five solutes in lithium nitrate–potassium nitrate eutectic are shown in Fig. 9 and in sodium nitrate–potassium nitrate eutectic in Fig. 10.

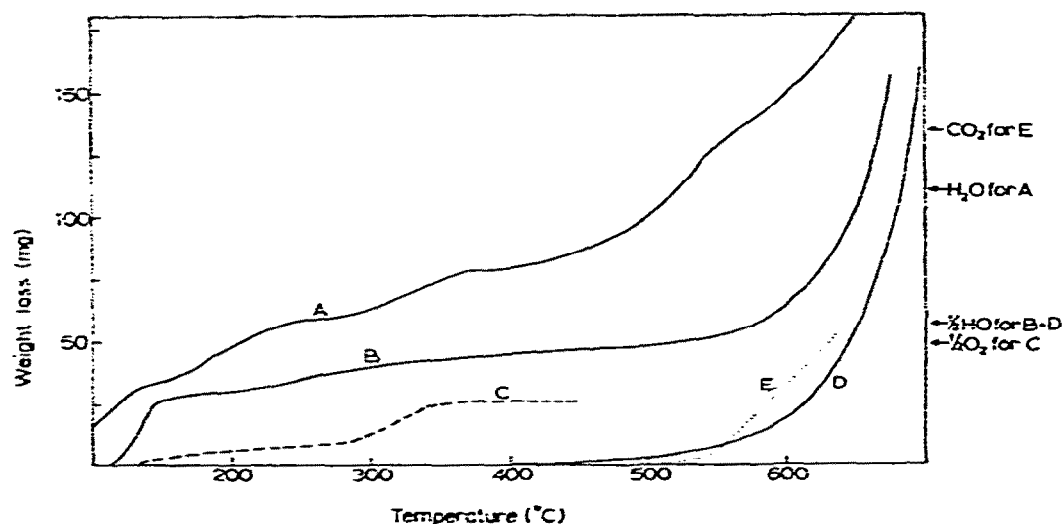


Fig. 9. Thermogravimetric analysis of bases in lithium nitrate–potassium nitrate eutectic. Curve A, 2.02 m $\text{LiOH} \cdot \text{H}_2\text{O}$; curve B, 2.04 m KOH ; curve C, 1.10 m Na_2O_2 ; curve D, 2.05 m NaOH ; curve E, 1.00 m Na_2CO_3 .

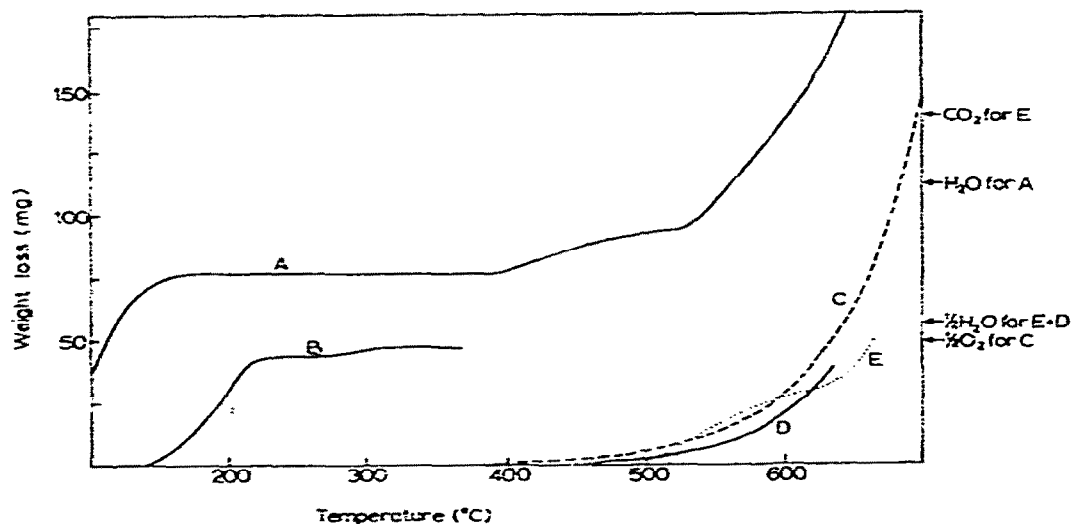


Fig. 10. Thermogravimetric analysis of bases in sodium nitrate–potassium nitrate eutectic. Curve A, 2.06 m $\text{LiOH} \cdot \text{H}_2\text{O}$; curve B, 2.05 m KOH ; curve C, 1.19 m Na_2O_2 ; curve D, 2.03 m NaOH ; curve E, 1.03 m Na_2CO_3 .

Sodium carbonate. This compound was little decomposed in either melt, most of the recorded weight loss being due to decomposition of the melt itself. (Compare curve E of Figs. 9 and 10 with curve C of Figs. 1 and 2.) This behaviour is in accord with the known stability of carbonates dissolved in nitrate melts when acids are not added. A rapid and complete reaction occurs when Lux–Flood acids are present^{21–24}. The carbonate dissociation constant in sodium nitrate–potassium nitrate determined by Kust²⁵ at 250 and 303°C, when extrapolated to 500°C indicates a value of 10^{-4} atm.

Sodium peroxide. By contrast this solute displayed a different behaviour in the two melts. In sodium nitrate–potassium nitrate it dissolved to a yellow solution (solubility ~ 0.1 m at 260°C) and only commenced to decompose slowly at 390°C. The weight loss at 500°C was 1.7% (calc. for loss of 1O per mole Na_2O_2 : 20.5%). However, in lithium nitrate–potassium nitrate, sodium peroxide was less soluble and the solid particles, initially yellow, rapidly changed to white at 260°C. The decomposition became more brisk above 300°C but the evolution of oxygen ceased at 350°C. Curve C of Fig. 9 indicated an overall loss of 10.7% (calc. for loss of 1O per mole Na_2O_2 : 20.5%). It was concluded that sodium monoxide was rapidly formed on the surface of the peroxide where it was in contact with the melt and that this surface layer eventually became thick enough to protect the peroxide at the centre of the particles from further decomposition.

The trend for peroxide to display greater stability in melts with larger cations may be an explanation of the discrepancy noted by El Din between his experimental “acidity number” of +4.65 for a 5×10^{-3} m sodium peroxide solution in potassium nitrate at 350°C and his theoretical value of +11.2 (refs. 17, 18). However, if a Lux–Flood acid was added to melts containing peroxide, oxygen was rapidly evolved. Sodium peroxide has been found to act as a very satisfactory base in numerous potentiometric titrations^{7,9,10,12,16,17,22,26}.

Lithium hydroxide. The monohydrate was only slightly soluble in either melt at 260°C but evolved water vigorously. Thermogravimetric analysis (curve A of Figs. 9 and 10) indicated that the weight losses became equivalent to the loss of hydrate water at 500°C. Thus water was retained quite strongly and the hydroxide ion itself appeared stable to at least 500°C. The low solubility in nitrate melts parallels that in water and of lithium monoxide in both nitrate melt and water²⁷.

Sodium hydroxide. As in aqueous solution, sodium hydroxide proved more soluble than lithium hydroxide in both nitrate melts, particularly in the sodium nitrate–potassium nitrate eutectic, and again showed considerable stability towards the dehydration reaction,



The total weight loss to 500°C was only 1.4% in lithium nitrate–potassium nitrate and 0.8% in sodium nitrate–potassium nitrate (calc. weight loss for $\frac{1}{2}\text{H}_2\text{O}$ per mole NaOH: 22.5%). In contrast complete dehydration of pure sodium hydroxide is reported to occur at 480° (ref. 28). This stabilisation observed in nitrate melts is no

doubt connected with the compound formation observed in sodium and potassium hydroxide/nitrate phase diagrams²⁹ but could be reversed, reaction (12) proceeding to completion if the melt solutions were evacuated for several hours.

Potassium hydroxide. The trends observed with the other two alkali metal hydroxides were continued in that potassium hydroxide was very soluble in both nitrate melts at 260°C, and also evolved water vigorously. Thermogravimetric analysis showed the weight loss to begin at 110°C in the lithium nitrate-potassium nitrate melt, reaching 13.6% at 500°C, while in the sodium nitrate-potassium nitrate eutectic decomposition began at 130°C, the evolution of water ceasing at 240°C when the total weight loss was 13.5%. These weight losses were close to the theoretical (calc. weight loss of $\frac{1}{2}$ H₂O per mole KOH: 16.0%), once allowance had been made for the lower purity of the solute (~85%). The slower loss from the former melt is again to be attributed to a strong water-lithium ion interaction.

The complete dehydration of potassium hydroxide is in accord with the observation of El Din et al.³⁰, that potassium hydroxide dissolved in potassium nitrate which had been heated for 6 h at 350°C gave a completely dry solid on quenching. It may be noted that at 231°C, the melting point reported for the 2:1 compound in the potassium hydroxide-potassium nitrate phase diagram²⁹, potassium hydroxide was found to be incompletely decomposed in either melt, but the loss of water from potassium hydroxide in sodium nitrate-potassium nitrate had ceased before 260°C, the melting point of the 2:1 and 1:1 compounds found in the sodium hydroxide-sodium nitrate phase diagram. However, the loss of water from sodium hydroxide solutions at this latter temperature was still very small.

These observations of the differences between the behaviour of the alkali metal hydroxides as solutes in nitrate melts point to the conclusion that there can be very little exchange of cations by the hydroxide ion and thus that the bonding involved is predominantly covalent. It is evident that, in future, more attention must be given to the cations of hydroxide solutes, a point which may explain apparently conflicting findings.

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