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THE REACTION OF AMMONIUM SALTS IN MOLTEN ALKALI METAL NITRITES

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ABSTRACT

The thermal decomposition of ammonium chloride and sulphate in molten alkali metal nitrite eutectics cannot be represented by a simple stoichiometry. Nitrous oxide and nitric oxide are produced as well as nitrogen and water.

Thermogravimetry is complicated by loss of solid material when the extremely rapid reaction commences at temperatures just below the melting points of the nitrite eutectics and by volatilisation of unreacted ammonium compounds, largely chloride and nitrite/nitrate from reactant solutions of ammonium chloride and ammonium sulphate, respectively.

INTRODUCTION

The thermal decomposition of ammonium nitrite to water and nitrogen is generally known, as is the usefulness of preparing small quantities of nitrogen by heating an aqueous solution saturated with sodium nitrite and ammonium sulphate. Thus the reaction of ammonium salts dissolved in alkali metal nitrite melts was studied as a corollary to the report [1] that ammonium salts dissolved in alkali metal nitrate melts decomposed thermally to water and nitric oxide, as does ammonium nitrate itself.

EXPERIMENTAL

The nitrite eutectics were prepared as previously described [2]. Ammonium chloride and ammonium sulphate (B.D.H. Analar) were dried at 100° for 12 h.

Reactions were carried out in B24 tubes heated in an electric resistance furnace linked to a Transitrol controller. Infrared spectra of gaseous products were obtained using a 10 cm cell with KBr windows on a Unicam SP200. Mass spectroscopy was carried out on an AEI-MS12 spectrometer. Thermogravimetric analyses were performed on a Stanton TR-1 thermobalance with a heating rate of 2° min^{-1} in a 10 ml silica crucible covered

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with a perforated porcelain disc. Weight losses are given as a percentage of the weight of added solute.

RESULTS AND DISCUSSION

When mixtures of solid ammonium chloride and sodium nitrite—potassium nitrite eutectic were heated together in an air atmosphere, evolution of volatile material began well below the melting point of this eutectic (Fig. 1, curve A) and well below the temperature at which pure ammonium chloride sublimes (Fig. 1, curve B). The weight loss determined by thermogravimetry was, however, very variable (Table 1) and did not correlate with the concentration, or actual weight of ammonium chloride. It would have been attractive to interpret these variable weight losses as a combination of the expected decomposition (eqn. 1)

$$NH_4Cl + NO_2^- \rightarrow Cl^- + 2\,H_2O + N_2 \qquad (1)$$

(calc. weight loss 119.6%)

and the sublimation of ammonium chloride (i.e. a weight loss of 100%) since

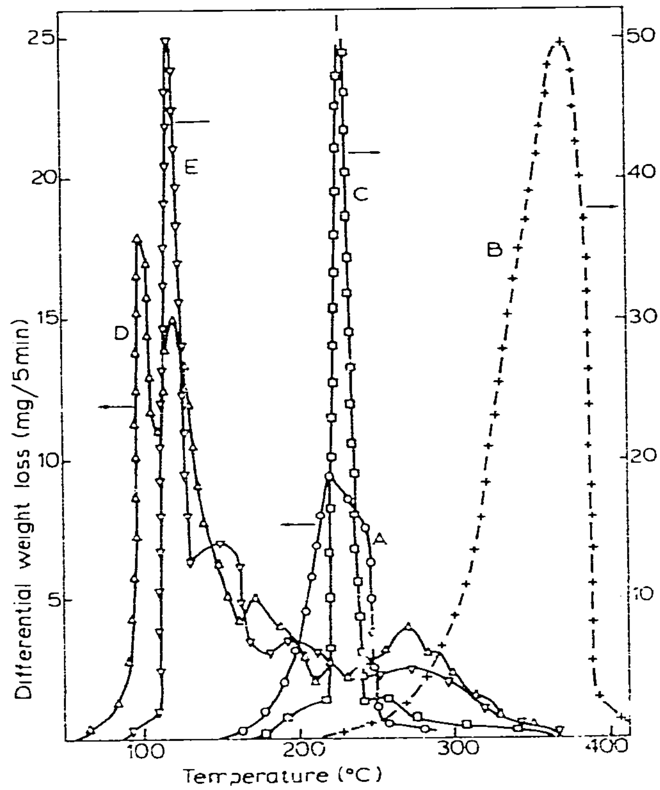

Fig. 1. Thermogravimetric analysis of ammonium chloride in nitrite eutectics. Curve A, ○, 0.16 m NH_4Cl in $NaNO_2/KNO_2$; curve B, +, 0.31 g NH_4Cl alone; curve C, □, 0.24 m NH_4Cl in $NaNO_2/KNO_2$; curve D, △, 0.70 m NH_4Cl in $LiNO_2/KNO_2$; curve E, △, 1.19 m NH_4Cl in $LiNO_2/KNO_2$.

TABLE 1

Thermogravimetric weight losses of ammonium chloride and sulphate in molten nitrite eutectics

Run no.	Nitrite melt		Solute			Weight loss (%)
	Eutectic	Weight (g)	Salt	Weight (g)	Molality (m)	
1	$NaNO_2/KNO_2$	2.93	NH_4Cl	0.023	0.15	100
2	$NaNO_2/KNO_2$	5.00	NH_4Cl	0.026	0.10	113
3	$NaNO_2/KNO_2$	4.95	NH_4Cl	0.042	0.16	109
4	$NaNO_2/KNO_2$	4.88	NH_4Cl	0.052	0.20	106
5	$NaNO_2/KNO_2$	5.08	NH_4Cl	0.065	0.24	119
6	$LiNO_2/KNO_2$	3.27	NH_4Cl	0.123	0.70	105
7	$LiNO_2/KNO_2$	2.66	NH_4Cl	0.169	1.19	120
8	$NaNO_2/KNO_2$	2.92	NH_4SO_4	0.125	0.32	93.8
9	$NaNO_2/KNO_2$	3.00	NH_4SO_4	0.137	0.35	94.6
10	$LiNO_2/KNO_2$	3.14	NH_4SO_4	0.144	0.34	100

qualitative analysis showed chloride and ammonium ions as well as water among the material condensed on the cooler upper part of the tube after heating to 200°.

The actual position was more complicated since, though quantitative analysis showed that 54.1% of the chloride originally added remained in the melt of Run No. 2, the experimental weight loss (Fig. 1, curve C) was equivalent to two thirds of the ammonium chloride reacting as in eqn. (1). The explanation lies in the correlation of high weight losses with curves including a period of extremely rapid weight loss. During the violent evolution of gaseous products some solid was probably also ejected despite the perforated disc.

Similar results were found when the lower melting lithium nitrite—potassium nitrite eutectic was used (m.p. 97° as compared with 220°C) except that the initial loss (Fig. 1, curve D) was at an even lower temperature. Though also still below the melting point of the nitrite eutectic, some liquid phase was probably formed at the contact points of the crystals as the ammonium chloride dissolved. The weight losses (Table 1) were again variable and again a high loss (Run No. 7) was accompanied by an extremely rapid weight loss (Fig. 1, curve E).

At higher temperatures (250°) infrared spectroscopy showed the presence of nitrous oxide and nitric oxide in the colourless gases evolved under vacuum. The identifications were confirmed by mass spectroscopy. When small amounts of air were admitted by the gas cell the colour of the sample changed to brown and the presence of nitrogen dioxide was shown by mass spectroscopy. These more varied products increase the difficulties of detailed interpretation of the weight loss curves.

When ammonium sulphate was used as the reactant, a sublimate was again obtained. This was shown to contain nitrite and nitrate in quantity as well as ammonia and water, when obtained under either air or nitrogen at 160—

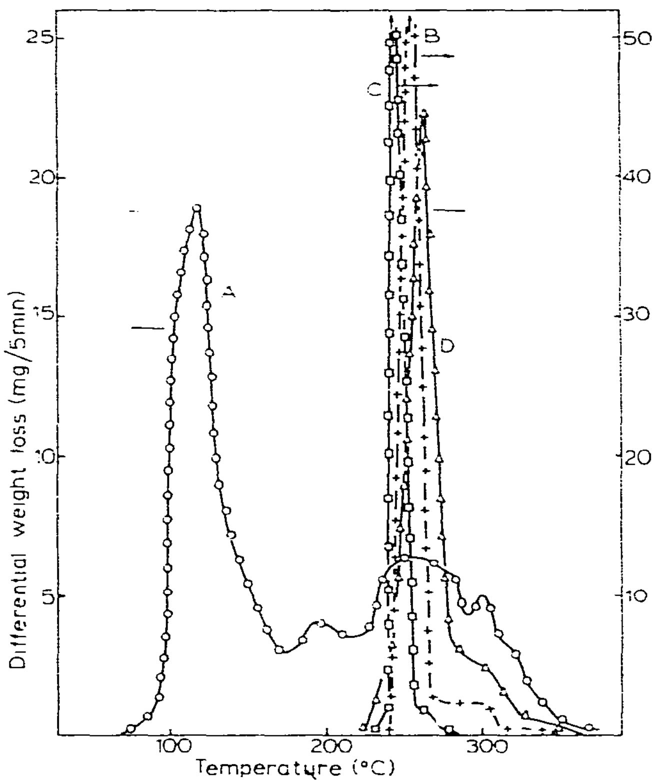

Fig. 2. Thermogravimetric analysis of ammonium sulphate in nitrite eutectics. Curve A, ○, 0.42 m $(NH_4)_2SO_4$ in $LiNO_2/KNO_2$; curve B, +, 0.34 m $(NH_4)_2SO_4$ in $NaNO_2/KNO_2$; curve C, □, 0.38 m $(NH_4)_2SO_4$ in $NaNO_2/KNO_2$; curve D, △, 0.16 m NH_4Cl in $NaNO_3/KNO_3$.

200°. The original anion was shown to be involatile and analysis of the thermogravimetric residues showed 101.3% of the original sulphate in Run 9 and 96.5% in Run 10 (Table 1). The weight loss maximum again occurred at a considerably lower temperature in the lower melting eutectic and again showed some extremely rapid rates of loss (Fig. 2, curves A, B and C) at temperatures close to those found with ammonium chloride. However, the overall weight losses (Table 1) were close to those for the decomposition

$$(NH_4)_2SO_4 + 2\,NO_2^- \rightarrow SO_4^{2-} + 4\,H_2O + 2\,N_2 \qquad (2)$$

or for the volatilisation

$$(NH_4)_2SO_4 + 2\,NO_2^- \rightarrow SO_4^{2-} + 2\,NH_4NO_2\uparrow \qquad (3)$$

since both equations give the same calculated weight loss of 96.9%. Lower losses would result if a side reaction similar to eqn. (4) occurred

$$2(NH_4)_2SO_4 + 4\,NO_2^- \rightarrow 2\,SO_4^{2-} + 2\,NH_4NO_3 + 2\,NH_3\uparrow + H_2O\uparrow + NO\uparrow + \tfrac{1}{2}\,N_2\uparrow \qquad (4)$$

(calc. weight loss 42.2%)

and in which at least some ammonium nitrate thus formed either decomposed [eqn. (5) has been found to hold when ammonium chloride reacted in molten sodium nitrate—potassium nitrate eutectic [1]. Fig. 2, curve D]

$$NH_4Cl + NO_3^- \rightarrow Cl^- + N_2O\uparrow + 2\,H_2O\uparrow \qquad (5)$$

or volatilised. Either process, if carried to completion, would, of course, result in the same weight loss as calculated for eqns. (2) and (3). In support, it was found that melts heated to 350° contained no nitrate.

In conclusion, it may be noted that reactions, even thermal decompositions, well known in aqueous solution do not necessarily occur in a molten solvent, nor is the reaction necessarily uncomplicated by side reactions or convenient to represent by a simple stoichiometry.

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