MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC: THE REACTION OF BISMUTH COMPOUNDS

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ABSTRACT

Bismuth(III) chloride reacted in pure molten lithium nitrate–potassium nitrate eutectic, initially forming insoluble bismuth oxychloride from 210°C, and then substituting oxide for chloride from 425°C to give more complex oxychlorides. Melts containing potassium nitrite caused the same Lux–Flood acid–base reactions, though at lower temperatures, but melts containing potassium chloride stabilised bismuth(III) in solution until higher temperatures were reached.

Acidic melts containing potassium pyrosulphate reacted, but caused little difference in the bismuth(III) reactions. However, with the weaker Lux–Flood acid, potassium dichromate, chromate was substituted for chloride at higher temperatures, bismuthyl chromate being formed from bismuthyl chloride.

In basic melts containing sodium hydroxide, the initial bismuthyl oxychloride precipitate was converted to bismuth(III) oxide at higher temperatures, or higher hydroxide concentrations. However, when both the latter became even larger (e.g. at 500°C for 48 h, Bi:OH = 1:14.5) lithium orthobismuthate(V) was formed. Less extreme conditions for the formation of the bismuthate(V) were required when the melt was made basic with sodium peroxide, and when bismuth(III) nitrate was substituted for the chloride.

Sodium bismuthate(V) was not stable in pure nitrate eutectic, decomposing to bismuth(III) oxide and lithium bismuthate(III).

INTRODUCTION

The reactions of bismuth compounds in molten nitrates have been very little studied, the four existing reports being both short and incomplete. In chronological order, the first states that "bismuth(III) nitrate pentahydrate foamed and formed a cloudy solution which gave erratic polarographic results in lithium nitrate–sodium nitrate–potassium nitrate ternary eutectic at 160°C" [1]. This was followed by the possibly contradictory finding that "a bismuth(III) salt (not specified further) migrated towards the cathode under a 10 V/cm potential in lithium nitrate–potassium nitrate eutectic at 255°C" [2] and, therefore, that any Lux–Flood acid–base reaction was incomplete. The study reporting that bismuth(III) was sufficiently acidic to

liberate nitrogen dioxide from equimolar sodium nitrate–potassium nitrate at 240°C [3] may support the earlier statement. Finally, it was noted that iodide added to a bismuth(III) nitrate (hydrate) solution in lithium nitrate–potassium nitrate eutectic at 160°C caused precipitation of brick-red bismuth oxyiodide and evolution of iodine and nitrogen dioxide (suggesting the reaction $Bi^{3+} + 2I^- + NO_3^- \rightarrow BiOI + NO_2 + \frac{1}{2}I_2$ [4].

In view of the lack of information and these possible conflicts, a systematic investigation of the reactions of bismuth(III) chloride, bismuth(III) nitrate and of bismuthate(V) was initiated in pure (i.e. neutral) lithium nitrate–potassium nitrate eutectic and in eutectic containing dissolved Lux–Flood acids and bases.

EXPERIMENTAL

Materials

Potassium nitrate (AR, BDH) and lithium nitrate (RG, BDH) were dried at 150°C for 24 h, mixed to eutectic composition (43 mol% $LiNO_3$), evacuated to 0.01 Torr over 10 h and filtered at 180°C through a No. 4 grade glass-sinter in an oven. After solidification, the eutectic was broken up and stored in a dry box.

Bismuth(III) chloride (RG, Hopkins and Williams) was heated in a stream of chlorine at 140°C for 2 h. (Found: Bi, 65.6; Cl, 33.2. Calc. for $BiCl_3$: Bi, 66.3; Cl, 33.7%). Bismuth(III) nitrate pentahydrate (GR, Hopkins and Williams) was used as received (found: Bi, 42.8; NO_3, 38.0, Calc. for $Bi(NO_3)_3 \cdot 5H_2O$: Bi, 43.1; NO_3, 38.3%). Sodium bismuthate (AR, BDH) was also used as received. (Found: Bi, 59.9. Calc. for $NaBiO_3$: Bi, 74.6%). Sodium hydroxide, potassium nitrite and potassium chloride (all AR, BDH) were dried at 100°C (4 h), 200°C (6 h) and 150°C (2 h) respectively. Sodium peroxide (AR, BDH) was used as received and potassium pyrosulphate was prepared by heating potassium persulphate (AR, BDH) at 250°C for 10 h (67.8% $S_2O_7^{2-}$ by NaOH titration. Calc. for $K_2S_2O_7$, 69.2%).

Procedure

Qualitative reactions were carried out in Pyrex tubes closed with a silica gel drying tube and heated in an electric furnace fitted with an Ether Transitol (Type 1291 B) temperature controller.

Thermogravimetry was carried out using a Stanton TR-1 thermobalance at a heating rate of 2°C min^{-1}. The finely ground reactants and eutectic (3 g) were well mixed and contained in 10 ml silica crucibles. Weight losses are quoted as a percentage of reactant weight, and presented graphically as

differential weight loss/temperature plots (hatched lines indicate isothermal conditions; when 2°C equals 1 min).

Analyses on reaction products were by conventional qualitative and quantitative methods.

X-ray powder diffraction was carried out using a Phillips (Eindhoven) diffractometer using nickel-filtered copper $K\alpha$ radiation, the d spacings and intensities (listed in full in ref. 5) being matched with those of known compounds listed in the JCPDS Index.

RESULTS AND DISCUSSION

Bismuth(III) chloride reacted in lithium nitrate–potassium nitrate eutectic very slowly at 200°C producing a white suspension. Reaction became faster with increased temperature, brown nitrogen dioxide being evolved and a white precipitate formed. Above 400°C gas evolution largely ceased and above 480°C the precipitate became pale yellow and later orange. Thermogravimetric analysis (Fig. 1, curve A) indicated a similar reaction pattern. The first weight loss (210–400°C) of 30.7%, and quantitative analysis of the white precipitate after washing with water and drying (found: Bi, 79.9; Cl, 13.8, calc. for BiOCl: Bi, 80.2; Cl, 13.6%), together with the X-ray diffrac-
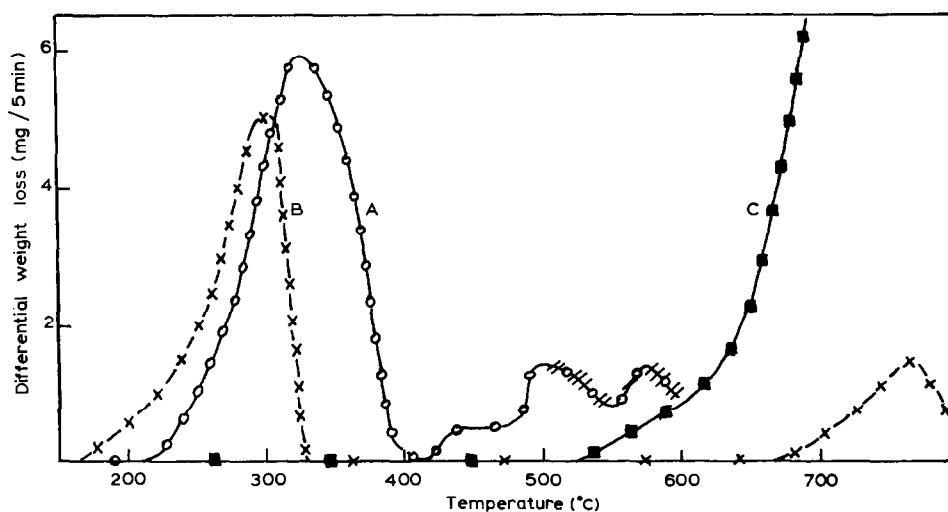

Fig. 1. Thermogravimetry of $BiCl_3$ in air and in pure nitrate eutectic: A, o———o, $BiCl_3$ (0.12 m) in $LiNO_3/KNO_3$ eutectic; B, ×———×, $BiCl_3$ (0.122 g) alone in air; and C, ■———■, $LiNO_3/KNO_3$ eutectic (3 g).

tion pattern giving the d spacings for BiOCl, all indicated that the reaction was

$$BiCl_3 + 2NO_3^- \rightarrow BiOCl + 2Cl^- + 2NO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

(Calc. weight loss for loss of 2N + 5O per $BiCl_3$, 34.2%)

This is analogous to the first reaction of bismuth(III) chloride heated in air (Fig. 1, curve B)

$$BiCl_3 + \tfrac{1}{2}O_2 \rightarrow BiOCl + Cl_2 \qquad (2)$$

(Calc. for loss of 2Cl and gain of O, 17.4%)

with analysis of the white product (found: Bi. 79.8; Cl, 13.0). The experimental weight loss of 26.9% indicated some loss of the trichloride by volatilisation.

At higher temperatures a second reaction occurred; in air this began at 650°C giving a yellow product (found: Bi, 89.5, calc. for Bi_2O_3: Bi, 89.7%) with an overall weight loss of 52.5% to 940°C, indicating the following reaction

$$2BiCl_3 + \tfrac{3}{2}O_2 \rightarrow Bi_2O_3 + 3Cl_2 \qquad (3)$$

$\left(\text{Calc. for loss of 3Cl and gain of } 1\tfrac{1}{2}O \text{ per } BiCl_3 \; 26.1\%\right)$

again with some loss of trichloride by volatilisation. In the melt, the second reaction began at 425°C giving, after 20 h isothermally at 500°C, a pale yellow product which after washing and drying had a much lower chloride analysis than before (found: Bi, 87.7; Cl, 3.0%); powder diffraction gave a number of lines characteristic of BiOCl, $Bi_{24}O_{31}Cl_{10}$ [6] and possibly other species. (The quantitative analysis is close to $Bi_{24}O_{33}Cl_6$: calc. Bi, 87.1; Cl, 3.7%). The overall weight loss (57.5%) indicates, besides the earlier volatilisation of trichloride, some melt decomposition, which begins at these temperatures (Fig. 1, curve C)

$$NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}O_2 \qquad (4)$$

This nitrite, being very considerably more basic than nitrate [7], may have been the source of the oxide which replaced the chloride anions in the crystal structure of the simple oxychloride formed at lower temperatures.

Certainly bismuth trichloride reacted with nitrate melt containing an excess of potassium nitrite at much lower temperatures (100°C, Fig. 2, curve A) but forming the same white low-temperature product (found: Bi, 79.8; Cl, 13.1, calc. for BiOCl: Bi, 80.2; Cl, 13.6%). The weight loss (26.2% calc. for $BiCl_3$) also confirms the reaction

$$BiCl_3 + 2NO_2^- \rightarrow BiOCl + 2Cl^- + NO_2 + NO \qquad (5)$$
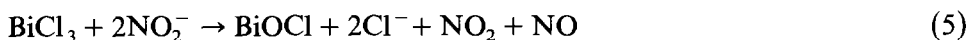
(Calc. for loss of 2N + 3O per BiOCl, 26.5%)

$\left(\text{Calc. for loss of N} + \tfrac{3}{2}O \text{ per } KNO_2, 49.2\%\right)$
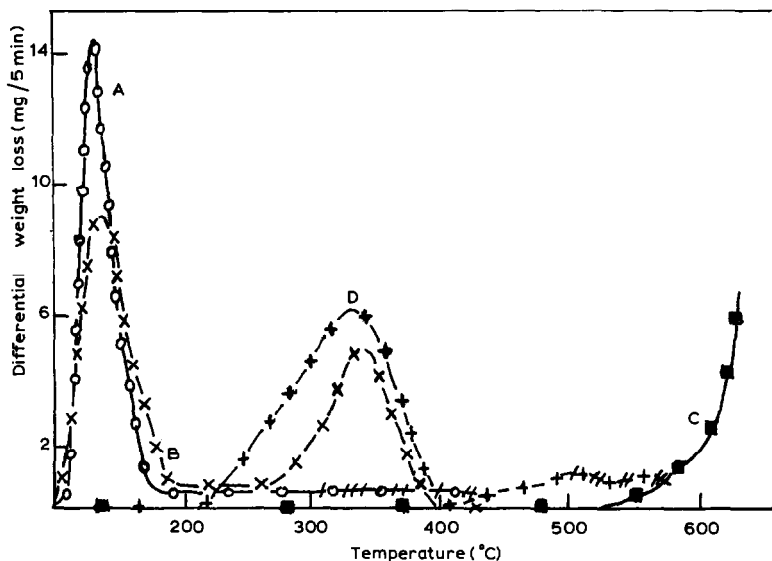
Fig. 2. Thermogravimetry of $BiCl_3$ in nitrate eutectic solutions: A, ○———○, $BiCl_3$ (0.13 m) + KNO_2 (0.54 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3:KNO_2 = 1:4$): B, ×———×, $BiCl_3$ (0.14 m) + KNO_2 (0.18 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3:KNO_2 = 1:1.2$); C, ■———■, KNO_2 (0.36 m) in $LiNO_3/KNO_3$ eutectic; and D, +———+, $BiCl_3$ (0.12 m) in $LiNO_3/KNO_3$ eutectic.

With a lower proportion of nitrite ($BiCl_3:KNO_3 = 1:1.2$), some bismuth trichloride reacted from 100 °C (Fig. 2, curve B) with a weight loss to 250 °C of 49.3%, calculated on the weight of potassium nitrite, again in agreement with eqn. (5), while the second weight loss from 260 °C represented the reaction of the remaining trichloride with nitrate (cf. Fig. 2, curve D). The weight loss to 400 °C of 33.7% (based on the calculated weight of trichloride remaining) was close to that calculated for eqn. (1). The product was analysed as bismuth oxychloride (found: Bi, 79.9; Cl, 13.2%).

The effect of added potassium chloride in the nitrate melt was to considerably increase the reaction temperatures (starting, maximum rate and completion temperatures) (Fig. 3). This is due to the stabilising effect of chloro-complex formation, as has already been shown to occur for iron(III) [8], cobalt(II) [9] and zinc(II) [10] cations in nitrate melts and probably also accounts for at least some of the increase in reaction temperatures of trichloride reacting in the melt when compared to the reaction in air (Fig. 1, curves A and B). Such stabilisation was not apparently complete even at the highest ratios used (Bi : Cl = 1 : 23, see inset of Fig. 3), suggesting that more than one complex was being formed, step-wise. The insoluble white product was also bismuth oxychloride (found: Bi, 79.9; Cl, 13.1%) and gave the expected powder diffraction lines. The weight losses for this (first) reaction varied very little with the chloride concentration (33.7 ± 0.5%) and again indicated that reaction still followed eqn. (1).
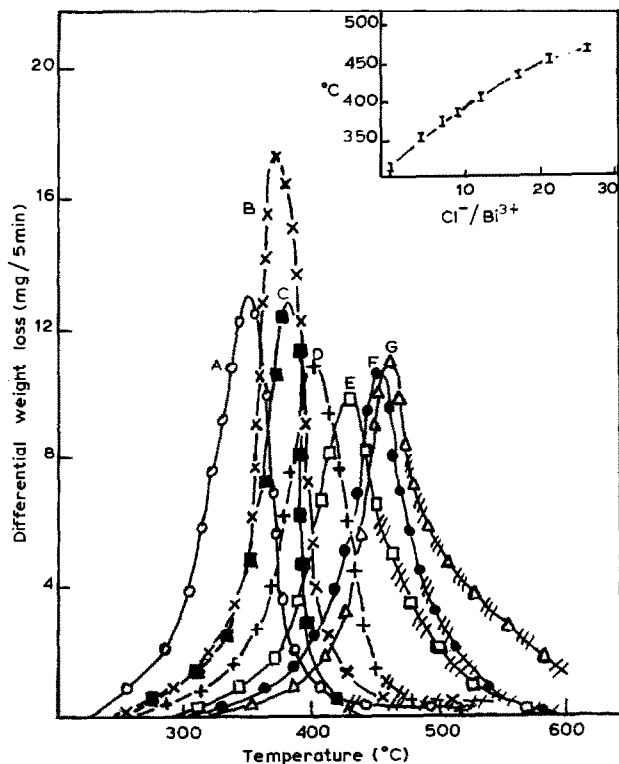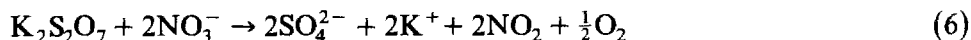
Fig. 3. Thermogravimetry of $BiCl_3$ in nitrate eutectic solutions of KCl: A, o———o, $BiCl_3$ (0.18 m) + KCl (0.18 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 1); B, ×———×, $BiCl_3$ (0.11 m) + KCl (0.45 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 4); C, ■———■, $BiCl_3$ (0.10 m) + KCl (0.57 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 5.7); D, +———+, $BiCl_3$ (0.18 m) + KCl (1.6 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 9); E, □———□, $BiCl_3$ (0.17 m) + KCl (2.2 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 13); F, ●———●, $BiCl_3$ (0.15 m) + KCl (2.65 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 17.7); and G, △———△, $BiCl_3$ (0.20 m) + KCl (4.6 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: KCl = 1 : 23). The inset shows the temperature of maximum rate of weight loss versus the chloride/bismuth ratio.

In nitrate melts containing additions of the strong Lux–Flood acid, potassium pyrosulphate, which would, at least initially, reduce the concentration of available oxide ions, the reaction of bismuth trichloride was little altered. The first observed reaction was the evolution of nitrogen dioxide (Fig. 4, curves A and B), similar to the reaction of pyrosulphate alone in the melt (curve C), the experimental weight loss ($33.3 \pm 0.2\%$ calculated on weight of $K_2S_2O_7$) being rather less than the equation for the latter

$$K_2S_2O_7 + 2NO_3^- \rightarrow 2SO_4^{2-} + 2K^+ + 2NO_2 + \tfrac{1}{2}O_2 \qquad (6)$$

(Calc. for loss of 2N + 5O per $K_2S_2O_7$, 42.0%)
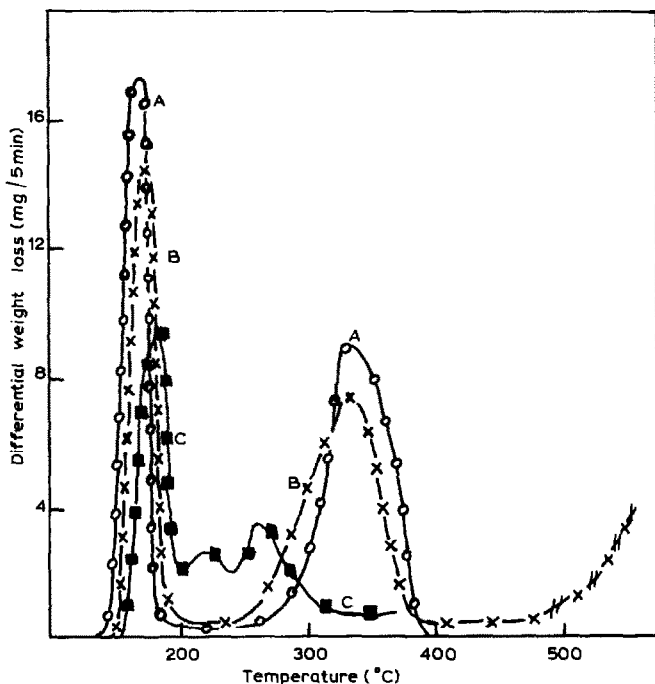
Fig. 4. Thermogravimetry of $BiCl_3$ in strongly acidic nitrate melts: A, o————o, $BiCl_3$ (0.084 m) + $K_2S_2O_7$ (0.067 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3 : K_2S_2O_7 = 1 : 0.8$); B, ×————×, $BiCl_3$ (0.095 m) + $K_2S_2O_7$ (0.130 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3 : K_2S_2O_7$ = 1 : 1.4); and C, ■————■, $K_2S_2O_7$ (0.12 m) in $LiNO_3/KNO_3$ eutectic.

probably because some reaction continues above 200°C (Fig. 4, curve C). The second reaction commenced at 250°C (curves A and B for different reacting ratios), a slightly higher temperature than in pure nitrate melt (Fig. 1, curve A) but the temperatures of maximum rate of loss and of termination of reaction were very similar, indicating very little stabilisation by sulphate anions (the product of reaction 6) and probably little influence from residual pyrosulphate. The weight loss for this second reaction (33.2 ± 0.2% based on weight of $BiCl_3$), the quantitative analysis (found: Bi, 79.8; Cl, 13.4%) and the diffraction lines (of BiOCl) all indicated reaction (1). As before, at higher temperatures the insoluble product became pale yellow as chloride was replaced (e.g. after 20 h at 470°, found: Bi, 83.4; Cl, 7.6%) and other diffraction lines appeared (of $Bi_{24}O_{31}Cl_{10}$ and probably other oxychlorides, as well as BiOCl).

Nitrate melts containing the weak Lux–Flood acid, potassium dichromate, as well as bismuth(III) chloride, became brown at 110°C with a dark brown precipitate from 180°C, probably of bismuth(III) dichromate. However, nitrogen dioxide was not visibly evolved until 260°C (Fig. 5, curves A and B) when the reaction was much like that of eqn. (1) (experimental
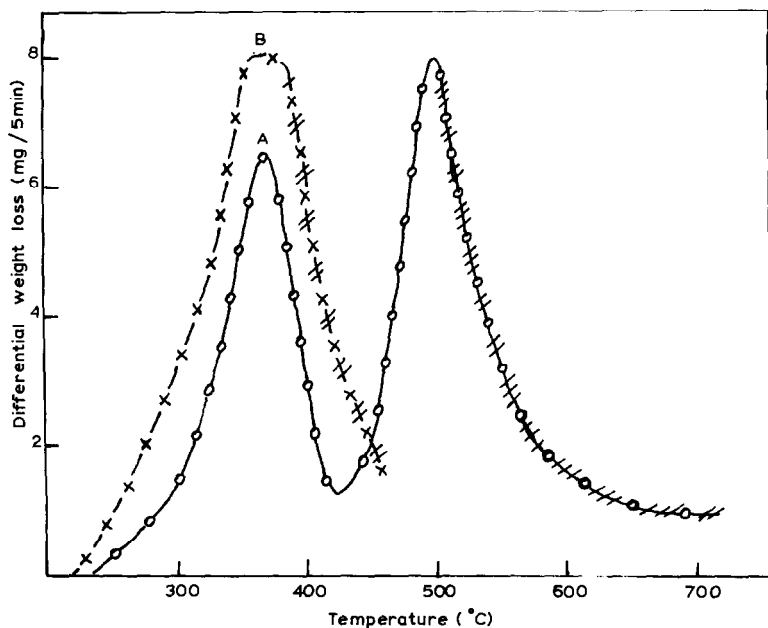
Fig. 5. Thermogravimetry of $BiCl_3$ in weakly acidic nitrate melts: A, $\circ$———$\circ$, $BiCl_3$ (0.13 m) + $K_2Cr_2O_7$ (0.26 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: $K_2Cr_2O_7$ = 1 : 2.0); and B, $\times$———$\times$, $BiCl_3$ (0.095 m) + $K_2Cr_2O_7$ (0.083 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: $K_2S_2O_7$ = 1 : 0.87).

weight loss, 33.5% to 370°C, found: Bi, 79.9; Cl, 13.2%). The X-ray diffraction pattern showed the lines of bismuth oxychloride.

At higher temperatures the precipitate steadily darkened to red and more nitrogen dioxide was evolved. After aqueous extraction and drying, the insoluble yellow product contained chromium (found: Bi, 82.9; Cr, 6.6%) and the diffraction lines of bismuth(III) oxide and bismuthyl chromate were obtained (calc. for Bi_2O_3: Bi, 89.7%. Calc. for $(BiO)_2CrO_4$: Bi, 73.8; Cr, 9.2%) indicating an easier substitution of oxide ions in this melt, possibly via bismuthyl chromate. Chromate was formed by the acid–base reaction

$$Cr_2O_7^{2-} + 2NO_3^- \rightarrow 2CrO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \tag{7}$$
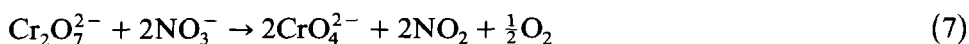
(Calc. for loss of 2N + 5O per $K_2Cr_2O_7$, 36.7%)

which begins at 400°C in a pure nitrate melt [11]. The experimental weight loss increased with time (from 41.4% after 1 h at 500°C, to 78.8% after 22 h) due to thermal decomposition of the melt (eqn. (4)).

In basic nitrate melts, rather different reactions occurred. For example with sodium hydroxide, although dilute solutions (e.g. $BiCl_3$: NaOH ratio = 1 : 0.4) gave reactions similar to eqn. (1) (Fig. 6, curve A), the white product gave the diffraction lines and analysis (found: Bi, 79.2; Cl, 13.4%) of
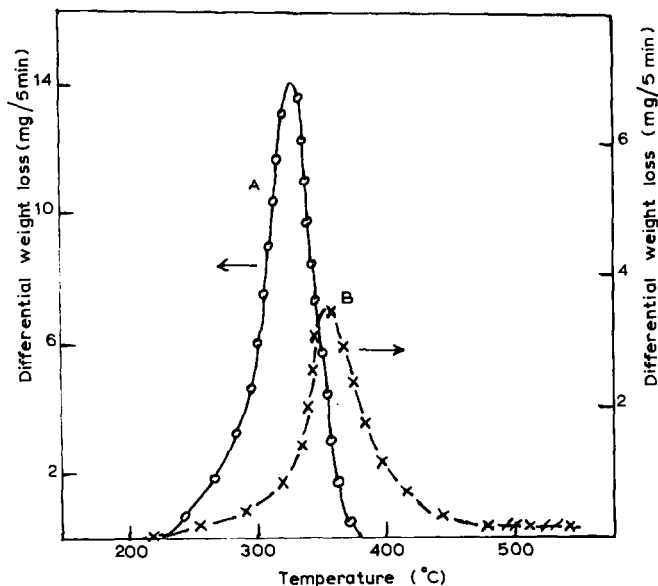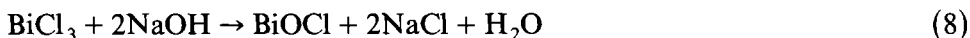
Fig. 6. Thermogravimetry of $BiCl_3$ in basic nitrate melts: A, $\circ$———$\circ$, $BiCl_3$ (0.15 m) + NaOH (0.06 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: NaOH = 1 : 0.4); and B, $\times$——— $\times$, $BiCl_3$ (0.10 m) + NaOH (1.30 m) in $LiNO_3/KNO_3$ eutectic ($BiCl_3$: NaOH = 1 : 13).

bismuth oxychloride with the experimental weight loss (24.8%) reduced from that of eqn. (1) because of reactions involving hydroxide
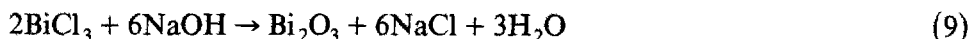
$$BiCl_3 + 2NaOH \rightarrow BiOCl + 2NaCl + H_2O \tag{8}$$

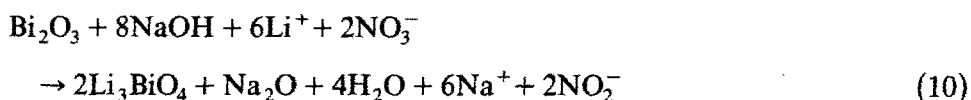(Calc. for loss of 2H + O per $BiCl_3$, 5.7%)

However, with higher ratios of hydroxide the initial reaction temperature decreased, the colour of the product became yellower and the chloride analysis decreased (at 1:1, 200°C, white product (found: Bi, 79.8; Cl, 13.1%) with lines of BiOCl; at 1:7, 190°C, pale yellow product (found: Bi, 86.6; Cl, 3.7%) with lines of BiOCl; at 1:18, pale yellow product (found: Bi, 89.3; Cl, 0.0%) with lines of Bi_2O_3). Evidently the more basic melts resulted in a more rapid exchange of oxide for chloride, or even in a more rapid initial precipitation of bismuth(III) oxide.

On heating such melt solutions for longer times, however, a different product was formed. For example, after 48 h at 500°C, a 1:14.5 ratio melt produced an orange precipitate which was filtered from the melt at 200°C when the colour changed to yellow. X-ray diffraction on the unwashed solid gave the lines of lithium orthobismuthate(V) (Li_3BiO_4) and of potassium nitrate. (Titration indicated the equivalent of 2.05 e per bismuth, i.e., $Bi^V \rightarrow Bi^{III}$.) With a 1:13 ratio after 6 h at 450°C, there was a yellow-orange precipitate and the melt contained nitrite. On washing with water the precipitate darkened to brown and still contained lithium as well as bismuth,

but no chloride (found: Bi, 79.8; Li, 1.9, calc. for LiBiO$_3$: Bi, 79.2; Li, 2.6%. Titration gave 1.8 e per Bi). Evidently dissolving away the excess hydroxide and melt caused some hydrolysis of the bismuthate (Bi$_2$O$_5$ is red-brown) as well as some reduction of bismuth(V). Thermogravimetry on a 1:13 ratio melt (Fig. 6, curve B) gave a weight loss of 23.4% after being maintained isothermally at 470°C for 20 h.

$$2BiCl_3 + 6NaOH \rightarrow Bi_2O_3 + 6NaCl + 3H_2O \tag{9}$$

$\left(\text{Calc. for loss of } 3H + 1\frac{1}{2}O \text{ per BiCl}_3, 8.5\%\right)$

$$Bi_2O_3 + 8NaOH + 6Li^+ + 2NO_3^-$$

$$\rightarrow 2Li_3BiO_4 + Na_2O + 4H_2O + 6Na^+ + 2NO_2^- \tag{10}$$

(Calc. for loss of $4H + 2O$ per BiCl$_3$, 11.3%)

On washing, the yellow quenched melt gave an insoluble brown powder, shown by qualitative tests to contain no chloride, sodium or potassium (found: Bi, 77.5; Li, 1.5%) while the filtrate gave positive tests for nitrite.

With basic nitrate melts containing sodium peroxide instead of hydroxide, the reactions were rather similar. First (with a BiCl$_3$:Na$_2$O$_2$ ratio of 1:1) a white precipitate formed at 200°C (found: Bi, 80.2; Cl, 13.2, calc. for BiOCl: Bi, 80.2; Cl, 13.6%) which also gave the d values for bismuth oxychloride. With a higher ratio (1:6), an orange precipitate formed after only 4 h at 450°C. After filtering from the melt at 200°C, the solidified product gave the diffraction lines of lithium orthobismuthate(V) and of potassium nitrate. The shorter reaction time and lower temperature suggested that the peroxide had probably acted as an oxidant as well as a base.

In view of the stabilising effect of chloride anions on bismuth(III), reactions with the same reagents were carried out using bismuth nitrate, only available as the hydrate (Bi(NO$_3$)$_3$·5H$_2$O). In the pure eutectic, nitric acid vapour was evolved from 120°C and a white precipitate formed, supporting the earlier remark by Steinberg and Nachtrieb [1]. Thermogravimetry showed that weight loss began in the solid phase (Fig. 7, curve A) and indeed slowed down at the eutectic melting point (132°C), probably due to the stabilising effect of coordinated nitrate anions. Nitrogen dioxide was evolved from 250 to 450°C and the colour of the precipitate changed from white to pale yellow. Analysis after washing gave negative tests for lithium and potassium (found: Bi, 89.5, calc. for Bi$_2$O$_3$: Bi, 89.7%). The overall weight loss to 480°C, was 52.9%

$$2Bi(NO_3)_3 \cdot 5H_2O \rightarrow Bi_2O_3 + 8H_2O + 4HNO_3 + 2NO_2 + \tfrac{1}{2}O_2 \tag{11}$$
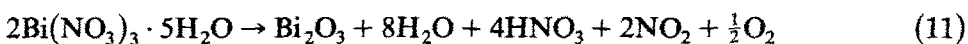
(Calc. for loss of $10H + 12.5O + 3N$ per Bi(NO$_3$)$_3$·5H$_2$O, 51.9%)

Without melt, the bismuth nitrate thermally decomposed to the same
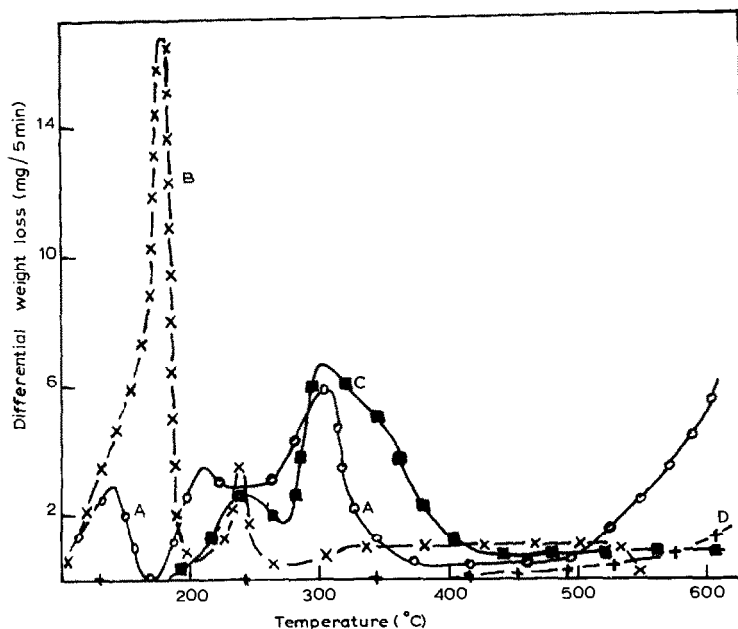
Fig. 7. Thermogravimetry of $Bi(NO_3)_3 \cdot 5H_2O$ in air and nitrate melts: A, o———o, $Bi(NO_3)_3 \cdot 5H_2O$ (0.11 m) in $LiNO_3/KNO_3$ eutectic; B, ×———×, $Bi(NO_3)_3 \cdot 5H_2O$ (0.144 g) in air; C, ■———■, $Bi(NO_3)_3 \cdot 5H_2O$ (0.07 m) + NaOH (1.9 m) in $LiNO_3/KNO_3$ eutectic; and D, +———+, NaOH (2.05 m) in $LiNO_3/KNO_3$ eutectic.

products, the first weight loss (Fig. 7, curve B) from 100 to 200 °C of 40.1%, indicating the reaction

$$Bi(NO_3)_3 \cdot 5H_2O \rightarrow BiONO_3 + 4H_2O + 2HNO_3 \tag{12}$$
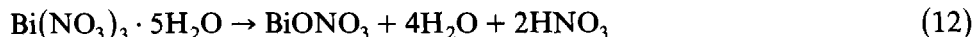
(Calc. for loss of $10H + 10O + N$ per $Bi(NO_3)_3 \cdot 5H_2O$, 40.8%)

The second weight loss from 200 to 550 °C of 11.7% occurred with formation of bismuth(III) oxide (found: Bi, 89.6%), the overall weight loss of 51.8% agreeing with eqn. (11).

In basic nitrate melts containing sodium hydroxide (ratio 1 : 27), a white precipitate formed from 200 °C (cf. Fig. 7, curve C). This was shown to be bismuth(III) oxide after 20 h at 250 °C (found: Bi, 89.5%) when the weight loss was 24.5% corresponding to

$$2Bi(NO_3)_3 \cdot 5H_2O + 6NaOH \rightarrow Bi_2O_3 + 6NaNO_3 + 13H_2O \tag{13}$$
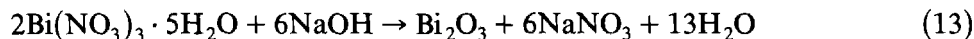
(Calc. for loss of $6\frac{1}{2}H_2O$ per $Bi(NO_3)_3 \cdot 5H_2O$, 24.1%)

Again at higher temperatures, further reaction occurred; for example after 4 h at 470° an orange precipitate gave the diffraction lines of lithium orthobismuthate(V) as well as bismuth(III) oxide (found: Bi, 79.4; Li, 3.1%). However, at longer times (24 h at 450 °C) only the lines of orthobismuthate (V) were found, and supported the analysis (found: Bi, 70.7; Li, 5.2;
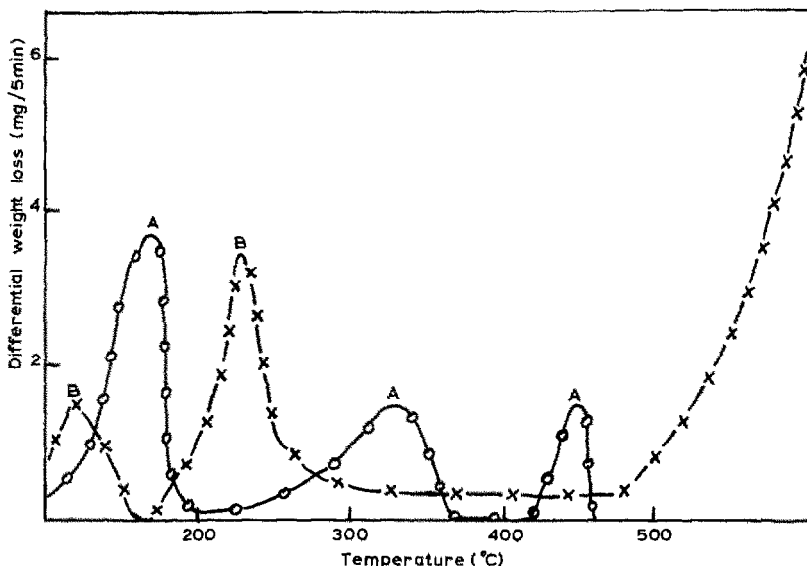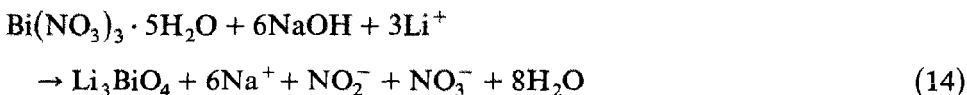
Fig. 8. Thermogravimetry of $NaBiO_3$ in air and in pure nitrate eutectic: A, $\circ$——$\circ$, $NaBiO_3$ (0.208 g) in air; and B, $\times$——$\times$, $NaBiO_3$ (0.19 m) in $LiNO_3/KNO_3$ eutectic.

oxidation 1.8 e, calc. for Li_3BiO_4: Bi, 71.1; Li, 7.1; oxidation 2.0 e). The experimental weight loss of 40.6% also suggested catalysed thermal decomposition of nitrate (eqn. (4)) as well as
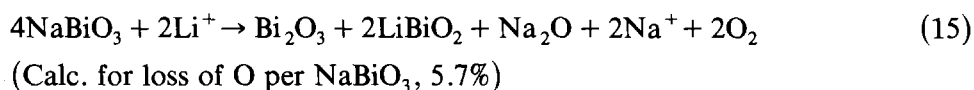
$$Bi(NO_3)_3 \cdot 5H_2O + 6NaOH + 3Li^+$$

$$\rightarrow Li_3BiO_4 + 6Na^+ + NO_2^- + NO_3^- + 8H_2O \tag{14}$$

$\left(\text{Calc. for loss of } 8H_2O \text{ per } Bi(NO_3)_3 \cdot 5H_2O, 29.7\%\right)$

With more sodium hydroxide (ratio of 1:35, also for 24 h at 450°), the same diffraction pattern was obtained but the analyses were a little closer to theoretical (found: Bi, 70.9; Li, 5.5; oxidation 1.9 e). Optimum conditions for the production of lithium orthobismuthate(V) are being further defined.

The only commercially available bismuthate(V) ($NaBiO_3 \cdot xH_2O$) when heated alone changed from yellow-brown to dark red at 500°C but again became yellow on cooling. Water was lost from 80 to 200°C, the first of three weight losses (Fig. 8, curve A), giving an experimental loss of 7.2%. Oxygen was lost above 200°C, the final product being bismuth(III) oxide after extraction with water (found: Bi, 89.4, calc. for Bi_2O_3: Bi, 89.7%). Before extraction the yellow solid appeared to be a mixture with sodium monoxide (found: Bi, 78.3, calc. for $Bi_2O_3 + Na_2O$: Bi, 79.1%), while the solid after heating to only 380°C suggested more sodium peroxide was present (found: Bi, 76.7, calc. for $Bi_2O_3 + Na_2O_2$: Bi, 76.8%), the experimental weight losses being 4.3% (200–300°C) and 1.5% (420–460°C) respectively.

In pure nitrate melt, the first weight loss (Fig. 8, curve B), from 50 to 180°C, of 6.7% was again attributed to evolution of water, but the second loss (9.4%) began at a lower temperature (170°C) and the colour changed to dark brown at 220°C. No further reaction was observed until catalysed thermal decomposition of the melt began at 480°C (eqn. (4)). After quenching from 500°C followed by washing and drying, the pale yellow powder gave the diffraction lines of bismuth(III) oxide together with some others (which were not assignable to lithium orthobismuthate (V)) attributed to the formation of some lithium bismuthate(III) (found: Bi, 86.8; Li, 0.65; oxidation 0.0 e, calc. for $Bi_2O_3 + 2LiBiO_2$: Bi, 86.9; Li, 0.86; oxidation 0.0 e), for example, by a reaction such as

$$4NaBiO_3 + 2Li^+ \rightarrow Bi_2O_3 + 2LiBiO_2 + Na_2O + 2Na^+ + 2O_2 \qquad (15)$$

(Calc. for loss of O per $NaBiO_3$, 5.7%)

These results indicate that bismuthate(V) is unstable in nitrate melt in the absence of dissolved sodium hydroxide.

The formation and stabilisation of bismuthate(V) may be paralleled by the formation of neptunium(VII) in sodium nitrate–potassium nitrate eutectic with bromate(V) as oxidant only when sodium hydroxide (7.5 M concentration) was present [12]; with no added hydroxide, neptunyl(V) only forms dineptunate(VI) with bromate(V) [13]. Similarly, manganate(VI) and manganate(V) are stabilised in nitrate melts containing sodium hydroxide [14].

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