

The reaction of potassium iodide in molten nitrate eutectics

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Abstract

Besides the known oxidation of iodide in molten nitrates to form iodine (e.g. at $\geq 220^\circ\text{C}$ in $\text{LiNO}_3\text{--KNO}_3$ eutectic), a further oxidation has been observed at higher temperatures ($\geq 400^\circ\text{C}$) to form I(VII) as paraperiodate. This anion has been found to precipitate in pure lithium nitrate–potassium nitrate eutectic, and in sodium, nitrate–potassium nitrate or lithium nitrate–potassium nitrate eutectics when containing calcium nitrate (as Li_3IO_6 , $\text{Ca}_5(\text{IO}_6)_2$ and LiCa_2IO_6 , respectively). Although it does not react significantly with iodate in pure nitrate melts, iodide is oxidised readily in the presence of protonic acids (NaHSO_4 , KHSO_4 or sulphamic acid), as are solutions of iodide alone.

INTRODUCTION

The chemistry of iodide anions in molten nitrates had appeared to be well understood and relatively unspectacular. In sodium nitrate–potassium nitrate eutectic, iodide was reported as stable up to at least 250°C [1,2] and 263°C [3] but, like chloride and bromide also, could be oxidised by nitrogen dioxide and by Lux–Flood acids (e.g. $\text{K}_2\text{Cr}_2\text{O}_7$) [4,5]. In lithium nitrate–potassium nitrate eutectic, iodide was found to be relatively insoluble (KI 0.01 m, KBr 0.36 m, KCl 1.0 m at 160°C [6] but also less stable, an appreciable reaction having been detected at 217°C electrochemically [7] and shown to have the stoichiometry



above 220°C [8]. Iodine is also formed on reaction with nitrogen dioxide or dichromate [8].

We report here a novel, higher temperature, reaction of iodide in nitrate melts, which results in the highest oxidation state (I(VII) in the form of the paraperiodate anion, IO_6^{5-}).

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EXPERIMENTAL

Lithium nitrate–potassium nitrate eutectic was prepared as previously reported [6] and sodium nitrate–potassium nitrate eutectic was prepared in an analogous fashion.

Potassium iodide and anhydrous calcium nitrate (both BDH reagent grade) were dried at 200°C for 10 h and 180°C for 16 h, respectively.

Calcium was determined quantitatively by EDTA titration using murexide indicator. The liberated iodine, formed by adding excess potassium iodide and concentrated hydrochloric acid to paraperiodate samples, was titrated against standard thiosulphate using starch as indicator. Lithium was determined by flame photometry.

Thermogravimetric analyses were carried out with a Stanton TR-1 thermobalance using 10 ml silica crucibles, at a heating rate of 2°C min⁻¹, sometimes continued isothermally at the maximum temperature. The results are reported as percentage weight loss, calculated on the weight of the specified reactant, and graphically as the differential weight loss (milligrammes per 5 min) against temperature. Isothermal losses are indicated by cross-hatching on the curve (when the scale is 10°C ≡ 5 min).

A Phillips X-ray diffractometer with Cu K α radiation was used to identify solid samples. The *d* spacing and intensities of the lines obtained (full lists are given in ref. 9) were matched with those given in the JCPDS Index.

Infra-red spectra were obtained from Nujol mulls using a Perkin-Elmer 580-B spectrophotometer with caesium chloride windows.

Solubility values were determined by the visual method.

RESULTS

Potassium iodide dissolved in molten lithium nitrate–potassium nitrate eutectic, forming a pale yellow solution at 250°C (solubility < 0.4 *m*) which darkened with increasing temperature. Moreover, above 290°C iodine vapour was slowly evolved, the rate of weight loss increasing slowly with temperature (Fig. 1, curve A). Though thermogravimetric analysis indicates small losses (e.g. 3.5% at 360°C and 7.0% at 490°C) and no stoichiometric reaction, the long-term loss can be large (e.g. 54% at 490°C for 19 h) and is to be attributed largely to melt decomposition, i.e.



possibly catalysed by iodide anions, as had been found for chloride and bromide anions [8].

A white precipitate was formed from 420°C which contained lithium and paraperiodate by qualitative analysis, and reacted quantitatively with aque-

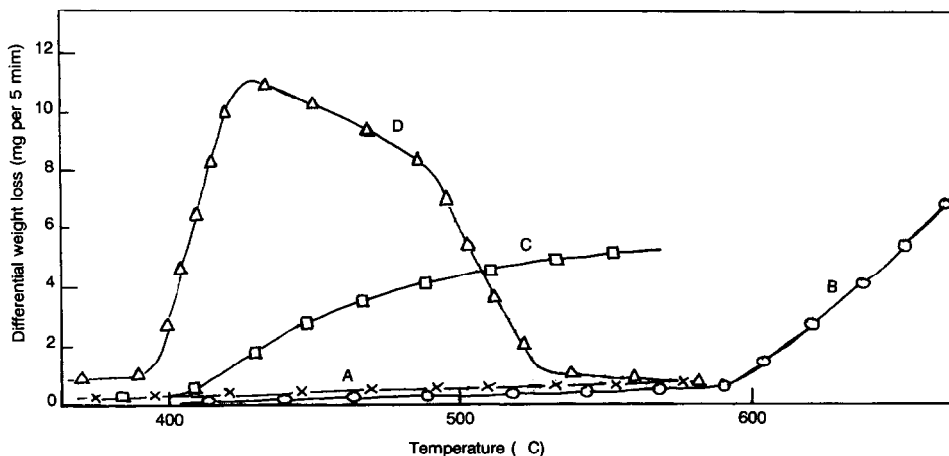
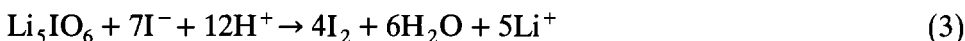


Fig. 1. Thermogravimetric analysis of potassium iodide in molten nitrate eutectics. (A): (\times), 0.12 *m* KI in LiNO₃-KNO₃ eutectic. (B): (\circ), 0.30 *m* KI in NaNO₃-KNO₃ eutectic. (C): (\square), 1.0 *m* KI + 0.36 *m* Ca(NO₃)₂ in NaNO₃-KNO₃ eutectic. (D): (Δ), 0.9 *m* KI + 0.30 *m* Ca(NO₃)₂ in LiNO₃-KNO₃ eutectic.

ous acidic iodide solution to give 342 ± 8 wt% of iodine by titration with thiosulphate. Equation (3) indicates 394 w% of iodine.



X-ray powder diffraction gave 26 lines [9], the principal one being 4.76 (100), 4.39 (92), 4.20 (96), 3.80 (93) (the *d* values are followed by the relative intensities in parentheses). However, even after long heating periods (e.g. 480°C for 17 h) the melt still contained iodide in solution, and was pale yellow in colour.

Potassium iodide did not react in sodium nitrate-potassium nitrate to give a precipitate, though it also dissolved (solubility > 0.35 *m* at 300°C) to a colourless solution which turned pale yellow at 350°C and then was again colourless with increasing temperature (the solution giving an absorption band at $26\,400\text{ cm}^{-1}$ which is characteristic of triiodide I₃⁻), finally becoming dark yellow at 480°C, but with little weight loss (Fig. 1, curve B). Even after heating for 19 h at 480°C the dark yellow solution gave positive qualitative tests for nitrite, paraperiodate and iodide, but not for iodate.

Incidentally, separate tests showed iodate (0.1 *m*) not to be markedly reduced by iodide (0.1 *m*) in neutral lithium nitrate-potassium nitrate melt (e.g. at 300°C only a little iodine was evolved from a pale yellow solution), but when protons were added (as NaHSO₄, KHSO₄, or sulphamic acid (0.2 *m*)) iodine was rapidly evolved. The reaction (eqn. (4)) would be analogous to that known for acidic aqueous solutions



and also analogous to the reaction of bromate and bromide in molten

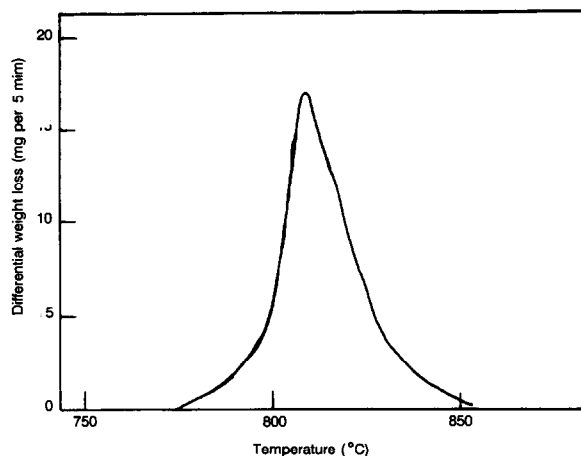
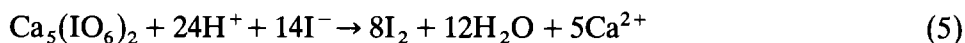


Fig. 2. Thermogravimetric analysis of white precipitate (0.03 g) from reaction of KI + $\text{Ca}(\text{NO}_3)_2$ in NaNO_3 - KNO_3 eutectic.

nitrate solution when Lux-Flood acids (e.g. $\text{Cr}_2\text{O}_7^{2-}$, Zn^{2+} and Ni^{2+}) [10,11] were present. Iodine was also evolved from a melt containing iodide (0.1 *m*) alone when sulphamic acid (0.2 *m*) was added, again analogous to the addition of a Lux-Flood acid (e.g. PO_3^-) [12].

When iodide (0.3 *m*) was heated in sodium nitrate-potassium nitrate eutectic containing calcium nitrate (0.1 *m*) under air or nitrogen, a colourless solution was formed which became pale yellow on heating up to 300°C and yellow at 340°C. At 400°C a white precipitate was deposited, iodine slowly evaporated (Fig. 1, curve C), and the colour became pale yellow. The reaction was slow, since a melt heated to 570°C for 23 h still contained soluble calcium and iodide ions, while the insoluble white precipitate contained only calcium and paraperiodate. Quantitative analysis showed 29.5% calcium and in aqueous acid 300 w% of iodine was produced. Pure calcium paraperiodate (eqn. (5)) would contain 30.9% and form 315%, respectively.

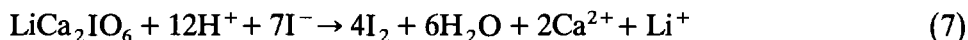


The washed white precipitate gave the X-ray powder diffraction pattern of calcium paraperiodate and similar infra-red absorptions [9,13]. On thermogravimetric analysis (Fig. 2), a weight loss of 56.0% was shown from 770 to 860°C, with a clear maximum at 810°C. The final white product analysed as 70.3% calcium (calcium in CaO , 71.5%) and gave the X-ray powder diffraction lines of calcium oxide, suggesting the reaction



(calculated for a weight loss of $2\text{I} + 7\text{O}$ per $\text{Ca}_5(\text{IO}_6)_2$ 56.6%)

When potassium iodide and calcium nitrate (again in a 3:1 ratio) were heated in lithium nitrate–potassium nitrate eutectic, similar colour changes occurred, though the weight loss was slightly greater (Fig. 1, curve D), indicating some melt decomposition, while the precipitate formed at 400°C was grey and contained calcium and lithium as well as paraperiodate. Quantitative analysis showed 25.8% calcium, 1.9% lithium and 300% iodine was formed in aqueous acid, which suggests the reaction



when 327% iodine is produced (calculated for LiCa_2IO_6 : 25.8% Ca, 2.25% Li). The X-ray powder diffraction pattern of the grey precipitate was determined [9], but that for lithium dicalcium paraperiodate has not been published.

The formation of paraperiodates by oxidation of iodide with molten nitrates has not been reported previously, but parallels, though under milder conditions, the oxidation of molten lithium iodide [14] and of iodide in chloride eutectic [15]. The milder conditions required are no doubt due to the fact that the nitrate melts are somewhat basic, because oxide is a product of the oxidation of iodide to iodine [8] (eqn. (1)).

Dratovsky et al. [16] have shown that in more strongly basic molten nitrates, oxygen or ozone will oxidise iodate at lower temperatures, e.g. 275°C in LiNO_3 to form Li_5IO_6 , 325° in NaNO_3 to form Na_5IO_6 , and 360° in KNO_3 to form K_5IO_6 .

Where, as here, there is a choice of cations, the paraperiodate precipitated is that which has the highest lattice enthalpy, as calculated from the Kapustinskii equation (the order being $\text{Li}_5\text{IO}_6 > \text{Ca}_5(\text{IO}_6)_2 \approx \text{LiCa}_2\text{IO}_6 > \text{NaCa}_2\text{IO}_6 > \text{KCa}_2\text{IO}_6 > \text{Na}_5\text{IO}_6 > \text{K}_5\text{IO}_6$), suggesting that the solvation enthalpies of the cations are quite similar.

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