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Molten Lithium-Potassium Nitrate: the Reactions of Some Halogen Compounds

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The reactions of chloride, bromide and iodide with pure molten lithium-potassium nitrate eutectic, with nitrogen dioxide and with melts containing potassium dichromate and potassium pyrosulphate were investigated. The stoichiometry of the formation of iodine in pure melts and in dichromate melt solutions was determined, tri-iodide ions being shown to be the product in the presence of excess iodide. The reaction of chlorate, bromate and iodate with pure and acidic melts was also investigated. In the pure melt iodate was shown to react with the nitrite produced by thermal decomposition of the nitrate rather than with the nitrate itself. The stoichiometry of this reaction was determined.

Introduction

The chemistry of molten nitrates is still at an early stage of development, and consequently besides a general absence of reported observations on the reactions of compounds of elements occupying large areas of the periodic table, there are other areas where reports are more numerous but in some cases conflicting. Such an area is the reaction of halides and halates with both pure nitrate melts and with melts containing Lux-Flood acids.

For example, chlorides, bromides and iodides are reported to be stable in sodium-potassium nitrate eutectic on the basis of several electrochemical studies, at 250°,[1,2] and at 263° in equimolar sodium-potassium nitrate.[3] Other studies indicate greater stability, complex formation measurements showed chloride and bromide to be stable to 300° in sodium-potassium eutectic,[4] and to 306° in pure sodium nitrate by cryoscopy,[5] while a sparingly soluble bromide and chloride were studied to 387° in lithium, sodium and potassium nitrates and in sodium nitrate respectively.[6] In a direct investigation, iodide (expected to be the least stable of the trio) was reported to be stable in the equimolar melt at 300°.[7] In contrast it was claimed that iodide was oxidised in a sodium-potassium melt at 270-390° in accordance with the equation[8]

$$2KI+KNO_3 \longrightarrow I_2+KNO_2+K_2O \qquad (1)$$

while Delimarskii and Shilina[9] stated chloride, bromide and iodide ions were all oxidised to the halogen in ternary lithium-sodium-potassium nitrate at 150°-230°. Since the experiments here reported were completed the oxidation of iodide in lithium-potassium nitrate at 147° has been reported.[10]

Publications on the behaviour of halide ions in acidic melts are less extensive. The kinetics of oxidation of bromide by dichromate[11] and by metaphosphate[12] in sodium-potassium eutectic have been studied and the oxidation of iodide by metaphosphate or cobalt(II) in equimolar melt have been reported[7] Topol *et al.*[13] noted that iodide and bromide were oxidised by nitrogen dioxide as well as by dichromate, though it was stated that « four parts of dichromate to one of iodide » were required for complete oxidation and nitric oxide was the only gaseous product. The only report on the oxidation of chloride arises from a study of the reaction of chromium(III) chloride in potassium nitrate at 400°.[14]

The reactions of the halates have mostly been studied kinetically, largely by Duke and co-workers, who have reported the reaction of bromate in sodium-potassium eutectic with dichromate,[15] bromide,[16] bromide+lithium,[16] bromide+zinc ions,[17] and several transition metal ions,[18] when the gaseous products were bromine+oxygen,[15,18] oxygen,[16] and bromine.[16,17] The kinetics of chlorate decomposition in fused sodium-potassium nitrate containing dichromate were reported.[19,20] The reaction

$$Cr_2O_7^{2-}+ClO_3^{-}+Cl^{-} \longrightarrow 2CrO_4^{2-}+Cl_2+O_2 \qquad (2)$$

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being catalysed by both chloride and chlorine. Chlorate also oxidises iodide.[21] Iodate reacted with dichromate in sodium-potassium eutectic[22] when the relative acidity of the iodyl ion was intermediate between bromyl and chloryl. In pure nitrate melts chlorate is stated to be stable at 260°,[19] bromate below 300°[17] in sodium-potassium eutectic and iodate at 306° in sodium nitrate.[5]

The aim of the present investigation was to reexamine the reactivity of halides and halates under comparable conditions in the same nitrate melt (lithium-potassium eutectic) and thus determine the variation with temperature and with added acidic solutes. The scarcity of information on iodate and the conflicting reports on the reactivity of iodide directed attention to the iodine compounds and the stoichiometries of three reactions were determined.

Experimental Section

Materials. Lithium-potassium nitrate was prepared as previously reported.[23] Analar quality reagents were employed after drying at 110° for 24 h. Potassium pyrosulphate was prepared by heating Analar potassium persulphate at 250° for 24 h (98.3% $K_2S_2O_7$ by titration against alkali).

Procedure. Reactions were carried out in Pyrex tubes with B. 24 joints, closed with silica gel drying tubes, which fitted snugly into an electric furnace connected to an Ether Transitrol controller. Facilities for bubbling dry nitrogen through the melt were provided.

Analysis. Iodine was volatilised from the melts in a stream of nitrogen (150 ml/min) passed into aqueous potassium iodide and titrated against thiosulphate. The remaining constituents were estimated after freezing the melts and dissolving in water. In the case of the reaction of iodide with nitrate, the oxide produced was titrated against standard hydrochloric acid using bromothymol blue (since iodide and nitrite do not react at $pH < 6.0$[24]). Nitrite was estimated by the iodo-permanganate method and iodide after reaction with acidified nitrite solution and removing excess nitrite with urea. Melts from the reaction of iodide and dichromate were shown to contain no unreacted iodide. The dichromate and chromate contents were estimated spectroscopically in neutral solutions, total chromium being checked after addition of excess acid or alkali. The chromium content of the brown precipitate was also estimated spectroscopically as chromate after oxidation with sodium peroxide.

Melts containing iodide through which nitrogen dioxide was passed were analysed for iodide after reaction with acidified nitrite solution and removing excess nitrite with urea, and for nitrite by the iodopermanganate method. Melts in which the iodate-nitrite reaction had taken place were analysed for nitrite by the iodopermanganate method. Oxide was titrated against 0.01 *M* HCl using bromothymol blue (iodide reacts with iodate at $pH < 6.5$[24]) and iodide against 0.01 *M* $AgNO_3$ using fluorescein. In another sample iodide was oxidised to iodate with permanganate, excess of which was destroyed by nitrite. In turn, excess of nitrite was removed with urea and sodium carbonate. The total iodate (original iodate + iodide) was then titrated iodiometrically.

Nitrite was detected qualitatively with the sulphanilic acid -α-naphthylamine reagent (sensitivity 3 p.p.m. of nitrate melt).

Physical measurements. Visible and ultraviolet spectroscopy of aqueous solutions was carried out on a Unicam S.P. 800 and of melt solutions on a Unicam S.P. 700 modified for use up to 700°. Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance with a heating rate of 2° per minute. Mass and infrared spectroscopy of gases made use of A.E.I. MS. 3 and Perkin-Elmer 337 spectrometers respectively.

Results

Halides. Both potassium chloride and potassium bromide dissolved in the pure melt at 160° without visible reaction. The chloride solution did not commence decomposition until 470° when nitrite and oxygen were formed (Figure 1, curve C). However, the solution of bromide gave a positive test for nitrite at 300° while oxygen was evolved at temperatures above 350°, by thermogravimetric analysis (Figure 1, curve B) and visual observation. The solution became yellow but even after 3 hours no bromine or bromate were detected, all the solute remaining as bromide. Even when thermal decomposition became more rapid above 500° no bromine was formed.

Potassium iodide was less soluble[25] but the melt solution commenced to change from colourless to

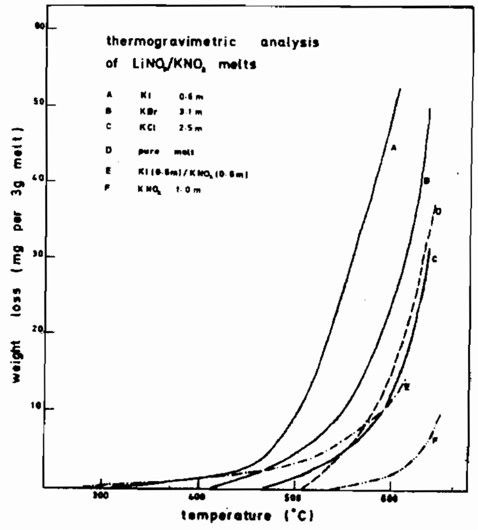

Figure 1.

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Table I.

Temp.	Time for reaction (h)	Melt (g)	Reactant Amount (m. mole)	Reactant Concentration (molal.)	Amount of Products (m.mole) I_2	O^{2-}	NO_2^-	Molar ratio $O^{2-}:I_2$	$NO^{2-}:I_2$
325°	12.5	16.8	0.952	0.056	0.055	0.058	0.067	1.05	1.22
	13	13.9	1.066	0.077	0.047	0.051	0.052	1.09	1.07
	11	10.7	1.016	0.095	0.049	0.055	0.064	1.12	1.30
340	8.5	20.1	1.011	0.050	0.055	0.056	0.056	1.01	1.01
	8.5	10.1	0.816	0.081	0.052	0.052	0.050	1.01	0.97
	13	17.9	1.104	0.062	0.069	0.071	0.072	1.03	1.04
355	6	20.2	0.662	0.033	0.055	0.055	0.062	1.00	1.13
380	5.5	20.0	0.474	0.024	0.063	0.069	0.064	1.09	1.02
	5	20.3	0.867	0.043	0.101	0.099	0.133	0.98	1.31
	6	10.2	0.882	0.088	0.121	0.108 [a]	0.344	0.89	2.84
	5	10.1	1.256	0.125	0.172	0.155 [b]	0.397	0.90	2.32

[a, b] 48.4 and 51.5% respectively of oxide present as precipitate in aqueous solution.

yellow above 220°. The solution darkened still further to orange, then brown with increasing temperature, until at 300° iodine distilled off as a purple vapour. After 2 days at 400° all the iodide had volatilised as iodine leaving a yellow melt containing a white precipitate of oxide. Aqueous solutions of the frozen melt contained much nitrite and alkali and if sufficiently concentrated a fine white precipitate of lithium hydroxide. Representative quantitive analyses of the reaction products in the melt and of the volatilised iodine are shown in Table I. The presence of nitrite in the melt retarded the reaction (Figure 1, curve E), suggesting an equilibrium. The yellow melts at 220°, from which iodine could be distilled on raising the temperature, were found to have a strong absorption band at 28,450 cm^{-1} (Figure 2, curve A). In separate experiments iodine crystals were found to be insoluble in pure nitrate eutectic but would dissolve in a melt containing potassium iodide. Pale yellow melts made in this way, being $1.1-1.4\times10^{-4}$ M in iodine, were found to have an extinction coefficient of $20,400\pm1100$ $l.mole^{-1}$ cm^{-1} ($40,500\pm2200$ Kg. $mole^{-1}$ cm^{-1}) at 28,450 cm^{-1} (160°) and to be stable under vacuum for 3 days. Isothermal spectroscopic measurements showed the reaction to be detectable ($>5\times10^{-7}$ M iodine) only at temperatures of 200° or above.

The three halides reacted at similar rates when potassium pyrosulphate was added to their melt solutions at 160°. Rapid evolution of nitrogen dioxide and the halogen was observed and confirmed by mass spectroscopy but no evidence was found for the presence of any nitryl or nitrosyl halide. Trace amounts of nitric oxide were detected and confirmed by infrared spectroscopy. With potassium iodide the iodine initially formed a brown solution, later a black precipitate and finally all sublimed to the cooler parts of the apparatus.

Similar, though slower, reactions occurred when potassium dichromate was added to chloride or bromide containing melts. With potassium chloride, reaction commenced slowly at 380° evolving chlorine, while potassium bromide commenced reacting at 300° liberating bromine from the yellow melt. Potassium iodide reacted readily at 160° however, forming iodine and a brown precipitate which settled out of the yellow chromate melt. Using an excess of dichromate the iodide was found to be completely oxidised and no soluble chromium(III) was found in the melt. No evidence of brown nitrogen dioxide was found, indicating that neither it nor nitric oxide were evolved. Representative analyses of products and unreacted dichromate are shown in Table II. The fine brown precipitate was filtered from the aqueous solution of the reacted melt on glass fibre filter paper (Whatman GF81) and dried at 110° for 12 h. Infrared spectroscopy showed the presence of water in the initially dried precipitate which was evolved at 160° (weight loss 13.7%) and the absence of water in the precipitate after heating to this temperature.

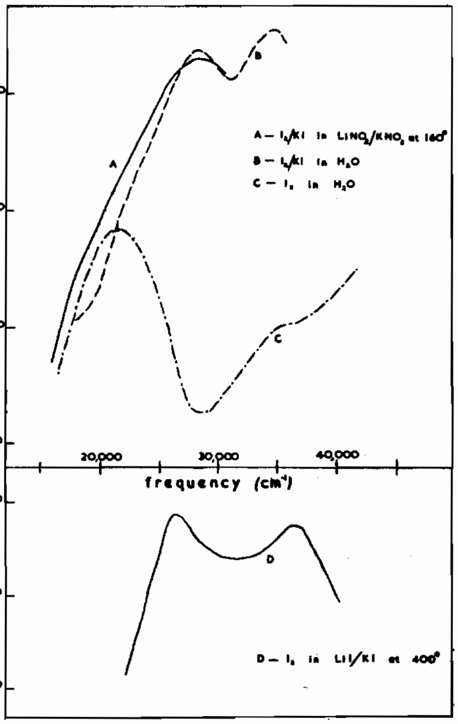

Figure 2.

In aqueous sodium hydroxide the initially dried precipitate dissolved giving a yellow solution of chromate and a green precipitate of chromium(III) oxide. Total chromium in the initially dried precipitate was analysed (Found: Cr, 48.2. Calcd. for $Cr_2(CrO_4)_3$.

Table II.

Temp.	Time for reaction (h)	Melt (g)	Amount of Reactant (m. mole) KI	$K_2Cr_2O_7$	Amount of Product (m. mole) CrO_4^{2-}	I_2	Unreacted $Cr_2O_7^{2-}$ (m. mole)	I_2formed: CrO_4^{2-} formed: $Cr_2O_7^{2-}$ reacted
160°	3	20.03	2.88	12.37	4.68	1.42	8.96	3 : 9.9 : 7.2
160°	3	20.05	2.02	8.28	3.67	0.99	5.45	3 : 11.1 : 8.5

Table III.

Temp.	Time (min.)	Melt (g)	Amounts of Reactant Gas	KI (m. mole)	I^- reacted (m. mole)	NO_2^- product (m.mole)
160°	30	10.4	NO_2	1.08	0.18	0.058
160°	30	10.3	NO_2/O_2	1.27	0.32	0.053

Table IV

Temp.	Time (h)	Melt (g)	Amounts of Reactant Gas	$NaNO_2$ (m. mole)	NO_2^- reacted (m. mole)	% reacted
160°	2	15.4	NO_2	7.85	7.02	89
160°	4	15.1	NO_2/O_2	7.75	7.53	97

$4H_2O$, Cr, 49.6; H_2O, 13.7%). The brown, initially dried, precipitate commenced reacting in lithium-potassium nitrate eutectic at 290° with an overall weight loss (to 500°) of 108.6%. (Calcd. for loss of $10N+22O+4H_2O$ per $Cr_2(CrO_4)_3 . 4H_2O$ 107.6%).

Nitrogen dioxide as the pure gas, when bubbled through the halide melts reacted slowly at 160° forming the free halogen, and less than the stoichiometric quantity of nitrite, but no oxide. Similar reactions occurred when the nitrogen dioxide/oxygen mixture, formed when a Lux-Flood acid reacts with nitrate melt, was used as the reactant gas (Table III). In separate experiments the reaction of these gases with nitrite was found to be considerably faster than the reaction with iodide (Table IV).

Halates. Potassium chlorate was stable in the melt until 390° when oxygen was evolved. Additions of chloride appeared not to affect this decomposition. Potassium bromate was stable to 230° when slow decomposition commenced forming oxygen and potassium bromide. At 400° the evolution of bromine commenced though only a small proportion of the bromine was evolved; *e.g.* a typical thermogram of a 1.5 m solution showed a weight loss corresponding to the loss (per $KBrO_3$) of 3/2 oxygen molecules but only 0.1 bromine molecule. Analysis showed the reacted melt to contain oxide, and bromide but no residual bromate. Addition of excess bromide to a bromate solution caused liberation of bromine at 370°.

Potassium iodate was stable to 500° when oxygen slowly evolved, the solution turning a pale yellow due to the formation of nitrite. Only when the temperature reached 600°, when oxygen evolution was rapid, was iodine observed to evolve. The possibility that the reaction at 600° was with nitrite ions produced during the thermal decomposition of the melt was then studied. Melts containing sodium nitrite and potassium iodate were found to commence reaction at 320° evolving iodine. The rate was found to increase significantly with temperature, being rapid at 370°. Some typical quantitative results for melts in which the reactants were dissolved at 200° and then raised rapidly to the reaction temperature (15 min.) at which they were held for 3½ hr are given in Table V.

In acidic melts reaction occurred more readily. Potassium chlorate in a melt containing dichromate liberated oxygen at 250° and chlorine above 280°, while potassium bromate liberated bromine readily above 210°. Potassium iodate reacted at 200° but very much more slowly, for example a 0.5 m $K_2Cr_2O_7$ melt containing 5 m mole of iodate through which nitrogen was passing only suffered a 6% decomposition after 1 h at 400°. Nitrogen dioxide also reacted with potassium iodate melts producing iodine but only above 280°.

Discussion

The stability range of chloride and bromide in lithium-potassium nitrate parallels the results of the

Table V.

		Amounts of Reactants (m. mole)				Amounts of Products (m. mole)			Ratios	
	Melt	Initially		Amount reacted						
Temp.	(g)	$NaNO_2$	KIO_3	$NaNO_2$	KIO_3	I_2	O^{2-}	I^-	$IO_3^-:I^-+2I_2:NO_2^-$	$I_2:O^{2-}$
380°	16.1	6.16	1.87	5.11	1.74	0.091	0.089	1.55	1:0.99:2.93	1:1.02
380°	16.3	12.87	3.82	11.16	3.81	0.178	0.171	3.44	1:1.00:2.93	1:1.04
400°	16.2	7.05	2.21	5.97	2.03	0.100	0.099	1.87	1:1.02:2.94	1:1.01
400°	16.4	7.32	2.19	6.06	2.06	0.081	0.082	1.92	1:1.01:2.95	1:0.99

majority of authors[1-6] who used the sodium-potassium melt. Moreover, it casts doubt on the claim[9] that these ions are completely oxidised in the ternary lithium-sodium-potassium melt. These ions do, however, appear to catalyse the normal thermal decomposition of the nitrate melt,

$$2NO_3^- \longrightarrow 2NO_2^- + O_2 \qquad (3)$$

as can be seen from Figure 1.

The oxidation of iodide follows the stoichiometry

$$2I^- + NO_3^- \longrightarrow I_2 + NO_2^- + O^{2-} \qquad (4)$$

though the reaction is probably an equilibrium. Difficulties in filtering and estimating the precipitate separately are considered to give rise to the low oxide/iodine ratios of Table I. Evidence for the catalytic activity of iodide ions on reaction (3), expected to be apparent well below 410° from the trend from chloride to bromide can be seen in the considerably increased nitrite/iodine and nitrite/oxide ratios at 380° when the iodide concentration was high.

Reaction (4) is in agreement with the recently published kinetic studies of Sacchetto *et al.*[10] in lithium-potassium nitrate, though they found the reaction to take place at $>147°$ rather than $>200°$, and to be « notably enhanced » rather than retarded by nitrite. However, reaction (4) is identical with the stoichiometry earlier reported for sodium-potassium nitrate[8] (eqn. 1) and gives some support to the claim for the formation of iodine in the ternary melts.

The absorption band at 28,450 cm^{-1} of iodine in an iodide containing melt was strikingly similar to that of tri-iodide in aqueous solution[26] (Figure 2, curve B) and close to that of tri-iodide in an iodide melt.[27] (Figure 2, curve D) and is therefore considered to be due to the same charge transfer transition.

The oxidation of halides in acidic lithium-potassium nitrate was broadly similar to that found in sodium-potassium[7,13] when the strongly acidic potassium pyrosulphate was the solute. However, in contrast to the assertion that nitryl chloride and nitrosyl chloride were evolved from potassium nitrate containing chloride and a Lux-Flood acid at 400°,[14] no evidence was found for these chlorides in the reaction at 160°, nor indeed for any other nitryl or nitrosyl halides, though where these are already known, decomposition could be expected at this temperature.

Nitrogen dioxide was found to act as an oxidant to all three halides apparently by the reaction

$$X^- + NO_2 \longrightarrow NO_2^- + \tfrac{1}{2}X_2 \qquad (5)$$

followed by further reaction of the nitrite, as suggested by Topol *et. al.*[13] and others.

$$NO_2^- + NO_2 \longrightarrow NO + NO_3^-$$

These observations extend those in sodium-potassium nitrate[13] where bromide and iodide were reported to react.

The reactions of all three halides with dichromate melt solutions producing free halogen are similar to those postulated in sodium-potassium nitrate for bromide[11] and iodide.[7] However, the stoichiometry for the reaction with iodide which the results of Table II indicate to be

$$6I^- + 8Cr_2O_7^{2-} \longrightarrow 3I_2 + Cr_2(CrO_4)_3 + 11CrO_4^{2-} \qquad (6)$$

is considerably different from that reported by Topol *et al.*[13] for sodium-potassium nitrate which required « about four parts of dichromate to one of iodide for complete iodide oxidation » and where nitric oxide was evolved in quantity (the reactants were deliberately placed in the melt in a 4:1 ratio in an effort to reproduce the results of Topol *et al*). The ratio now reported is also dissimilar from that suggested by Novik and Lyalikov[8] (1:3).

The reaction of potassium bromate in pure lithium-potassium melt, which was catalysed by bromide (bromine and oxygen being the products) was similar to that observed in sodium-potassium nitrate when lithium ions were present.[16] Potassium chlorate reacted some 160° higher than the bromate but again with oxygen as the gaseous product. Potassium iodate did not follow the trend in reaction temperatures for it was the most stable halate and evidently only reacted with the nitrite produced by thermal decomposition of the nitrate melt. (The oxygen evolved between 500 and 600° is unlikely to have formed by decomposition of iodate since any iodide produced would in turn have reacted with melt forming iodine). The reaction with nitrite occurred smoothly at 320° and above, in accordance with the stoichiometry,

$$IO_3^- + 3NO_2^- \longrightarrow I^- + 3NO_3^- \qquad (7)$$

while some 10% of the iodide formed reacted further in accordance with equation 4 as is shown by the ratios of Table V. Interestingly, unlike some earlier reactions in fused nitrate,[7,28] this and reactions

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4 and 6 do not parallel those between the same reactants in the aqueous system.

Comparison of the halate reaction temperatures with those for the onset of thermal decomposition in the pure salt ($KClO_3$ 495°, $KBrO_3$ 366°, $KIO_3 > 500°$)[29] show that nitrate ions are also involved in the melt reactions of chlorate and bromate, even though the decomposition products are similar. However, the iodate decomposition is more obviously different since the pure salt is stated to form iodide as well as oxygen and some iodine.[30]

The reactions of chlorate and bromate with dichromate containing melts appear to be closely similar to those in sodium-potassium nitrate.[15,19,20] However, the reaction of iodate with dichromate melts was markedly slower than could have been expected by extrapolation from the other halates. Similarly, less reaction than would have been expected was found with nitrogen dioxide. These findings compare with the aqueous system where the oxidation potentials in both acidic and basic solutions show iodate to be the most stable halate. They also add weight to the preliminary observation of Schlegel[19] of the lower reactivity of iodate in acidic sodium-potassium nitrate melts.

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