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Fused Zinc Chloride

Part III: Reactions of some Halates, Perhalates and Pseudohalides

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The stoichiometries of the reactions of eight halogen and pseudohalide anions with fused zinc chloride have been established. Perchlorate decomposed to oxide, oxygen and chlorine and chlorate to oxygen, chlorine and oxide with partial intermediate formation of perchlorate. Both bromate and iodate gave oxide, oxygen and free halogen, together with extensive oxidation of the melt, while periodate gave oxygen and iodate and at a higher temperature oxide, with oxidation of the melt at each stage. Of the pseudohalides, cyanide did not react; cyanate gave cyanide as the main product, while thiocyanate formed sulphide, cyanide and sulphur. The influence of added metaphosphate, on the perchlorate–zinc chloride reaction was elucidated.

Introduction

In an earlier paper,[1] the reactions of fifteen anions with fused zinc chloride were reported as a first contribution to the study of its inorganic chemistry. The study is here extended to include the reactions of halates, perhalates and three common pseudohalides.

Though the behaviour of halates and perhalates in nitrate melts have been extensively investigated, their reactions in fused halides, in which melt oxidation becomes possible in addition to the expected solute decomposition, have not hitherto been studied. The properties of pseudohalides at high temperatures in melt solution are less familiar, although of course fused potassium thiocyanate and to a lesser extent potassium cyanide are attracting increasing attention as reducing melts.

Few studies have hitherto been made of the effect of Lux–Flood acids[2] on inorganic reactions in fused halides. It would be anticipated that if an oxyanion were reacting in fused zinc chloride to give oxide ion, e.g.

$$2ClO_4^- \rightarrow O^{2-} + Cl_2 + 7/2\ O_2 \qquad (1)$$

addition of a Lux–Flood acid might, by reaction with oxide ion, i.e.

$$PO_3^- + O^{2-} \rightarrow PO_4^{3-} \qquad (2)$$

reduce the temperature at which the oxyanion reacted, though possibly without altering its reaction stoichiometry. The potassium perchlorate–zinc chloride reaction was suitable for study, as it took place very largely above the melting point of zinc chloride and was independent of solute concentration. It was, of course, essential to use a Lux–Flood acid which did not itself decompose in contact with the melt. Sodium metaphosphate was a suitable acid, whereas pyrosulphates, bisulphates, chromates and dichromates, which have all been shown to react with the melt, were not.[1,3]

Experimental Section

Materials

B.D.H. zinc chloride (sticks) was purified, dehydrated,[4] and analysed[1] as previously described. Analar $KClO_3$, $KBrO_3$, KIO_3 and KIO_4, and Reagent Grade $KClO_4$ and $NaPO_3$ were dried at 110°, Reagent Grade KCN and KCNO at 200° for ten hours, and Analar KSCN at 200° in vacuo.

Procedure

The procedure used in following the reactions, in analysis and in physical measurement has been described earlier.[1] All reagents were finely ground and intimately mixed with the anhydrous zinc chloride before heating. The thermogravimetric curves for all the solutes described are recorded elsewhere,[5] Figure 1 being included as an example. Percentage weight losses were independent of solute concentration unless otherwise stated.

Results

Potassium Chlorate reacted between 200° and 300°, with a maximum rate at 240°; followed by a further reaction with a slight weight loss between 390° and 500°. Thermogravimetric analysis showed weight losses of 48.3–53.4% in the first reaction and 8.7–12.7% in the second. The overall loss was 61.0 ± 1.7% (calculated for loss of $Cl_2 + 2^1/_2O_2$ per $2KClO_3$, 61.6%).

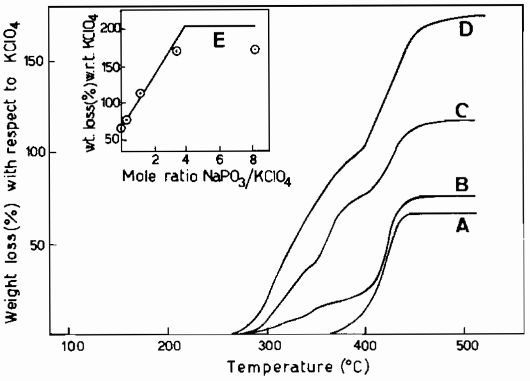

Figure 1. Thermogravimetric analysis of the sodium metaphosphate–potassium perchlorate–zinc chloride system.
Curve A 0.41*M* $KClO_4$, nil $NaPO_3$
Curve B 0.70*M* $KClO_4$, 0.25*M* $NaPO_3$
Curve C 0.62*M* $KClO_4$, 0.74*M* $NaPO_3$
Curve D 0.71*M* $KClO_4$, 2.37*M* $NaPO_3$
Inset, circles are experimental values, line is value calculated according to equations 16–18.

To establish the species produced in the first reaction, a potassium chlorate–zinc chloride system was heated to 325° and quenched. The infrared spectrum of the residue showed absorption peaks at 1088, 940 and 632 cm^{-1} (found for potassium perchlorate 1090, 935 and 630 cm^{-1}). The residue after the second reaction showed no infrared peaks. Chlorine was evolved but no gas absorbing in the infrared. The solidified residue after either reaction was yellow and opaque when hot, becoming white on cooling.

Potassium Perchlorate reacted steadily between 350° and 460°, the maximum rate being at 420°. Thermogravimetric analysis showed a weight loss of 65.4 ± 0.1% (calc. for loss of $Cl_2 + 3^1/_2O_2$ per $2KClO_4$, 66.0%). Chlorine was evolved; the melt after reaction being yellow and opaque when hot, becoming white on cooling.

Potassium Bromate reacted between 100° and 250°, the maximum rate being at 190°. Thermogravimetric analysis showed dependence of the percentage weight loss on the bromate molality, as follows:

$KBrO_3$ molality	0.05	0.20	1.26	3.56	14.2
% loss	119.2	110.3	103.3	91.9	69*

* Approximate

Chlorine was evolved in addition to bromine and oxygen. The residue, yellow at 300°, became less deeply coloured on cooling, and gave a negative reaction for bromide ion.

Potassium Iodate reacted between 260° and 500°, the maximum rate being at ca. 460°. Thermogravimetric analysis showed that the percentage weight loss depended on the iodate molality, as follows:

KIO_3 molality	0.26	0.66	2.77
% loss	91.2	93.5	96.4

The melt was slightly brown at 330°, the colour deepening very rapidly with increasing temperature. Chlorine was evolved in addition to iodine and oxygen, and the solidified residue gave a negative reaction for iodide ion.

Potassium Periodate reacted in two stages between 210° and 280°, and between 300° and 490°, the maximum rates being at 250° and 460° respectively. Thermogravimetric analysis showed a dependence of the percentage weight loss in each stage on the reactant concentration as follows:

KIO_4 molality	0.47*	0.70	2.42
% loss 1st stage	11.5	18.7	19.2
% loss 2nd stage	88.0	91.1	94.9
% loss overall	99.5	109.8	114.1

* Not mixed

A potassium periodate–zinc chloride melt heated just to the end of the first stage and quenched, showed an infrared spectrum with the same absorption maxima as a potassium iodate–zinc chloride melt heated until reaction was about to begin.

Potassium Cyanide did not react with zinc chloride up to 590°, the maximum temperature investigated. A system 2.2 *M* in potassium cyanide gave a colourless melt at 590°, although containing small black particles probably resulting from slight carbonisation of the solute.

In a separate experiment, reagent grade zinc cyanide, heated alone in air, was found to react between 250° and 730°, the weight loss of 30.4% corresponding to that calculated for the conversion of zinc cyanide to zinc oxide:

i.e. $Zn(CN)_2 \rightarrow ZnO$ + gaseous products (3)

calc. for loss of 2C + 2N + gain of 1 O per $Zn(CN)_2$, 30.7%.

Potassium Cyanate reacted between 150° and 300°, with a maximum rate at 240°; there was a further slight weight loss between 330° and 420°. Thermogravimetric analysis showed weight losses of 23.5 ± 0.3% in the first reaction and ca. 3% in the second (calc. for loss of $^1/_2O_2$ per KCNO, 19.7%). Infrared analysis showed the presence of carbon dioxide and water vapour in the gases evolved, and the presence of cyanide ion in the solidified residue, the latter being confirmed by the picric acid test. The melt at 500° was clear, becoming opaque on solidification.

Potassium Thiocyanate reacted slowly above 250°, the colour of the melt darkening from pale yellow at 250° to dark brown at 350°. Thermogravimetric analysis showed that appreciable loss of weight commenced at 280°, but quantitative data was not obtainable, as the rate of weight loss increased with temperature, eventually merging with the normal zinc chloride evaporation trace. Sulphur sublimed from the melt, but no gas was detected by infrared analysis. Chlorine was not found. The residue gave positive reactions for sulphide and cyanide ions.

Sodium Metaphosphate–Potassium Perchlorate–Zinc Chloride

This ternary system reacted between 220° and 480°. The thermogravimetric results are summarised in Table I and shown in Figure 1.

TABLE 1.

$NaPO_3$ molality	$KClO_4$ molality	Molality Ratio $NaPO_3$:$KClO_4$	% loss (w.r.t.) $KClO_4$
–	0.41	0	65.4
0.25	0.70	0.36	75.4
0.74	0.62	1.19	117.0
2.37	0.71	3.34	173.1
1.80	0.22	8.12	176.5

Chlorine was detected in the volatile reaction products, but volatile chlorides or oxychlorides of phosphorus were not present. The solidified residues showed no infrared absorption peaks.

Discussion

Potassium Chlorate

The reaction of this compound with zinc chloride can be expressed by the overall equation

$$2KClO_3 + ZnCl_2 \rightarrow 2KCl + ZnO + Cl_2 + 2^1/_2O_2 \quad (4)$$

(loss found 61.0, loss calc. 61.6%). The thermogravimetric and infrared data established that in the first stage most of the chlorate reacted according to this equation, and that 10–20% reacted to produce perchlorate, i.e.

$$4ClO_3^- \rightarrow 3ClO_4^- + Cl^- \quad (5)$$

The subsequent reaction of this perchlorate with zinc chloride, occurring over a temperature range similar to that for potassium perchlorate heated in zinc chloride *ab initio* (see next section), caused the second, high-temperature stage.

Potassium chlorate heated alone decomposes ultimately to chloride and oxygen, mostly around 580°; via the intermediate formation of perchlorate, though manganese dioxide catalyses this decomposition at 370°. A similar reaction scheme occurs here in a zinc chloride melt, though at much lower temperatures. The intermediate formation of perchlorate has also been reported in the decomposition of several other Group IA and IIA chlorates.[6] Data for the thermal behaviour of anhydrous zinc chlorate is not available, although von Heinrich and Mathies have shown that zinc chlorate dihydrate began to decompose at its melting point (114° C), and that heating it in vacuo at 60°–70° to form the anhydrous salt resulted in partial decomposition and a residue of the basic chlorate.[7]

The present report is therefore the first to establish the reaction between zinc and chlorate ions under anhydrous conditions. The reaction was independent of chlorate molality, indicating its stoichiometry was not dependent on the excess of zinc chloride present.

Thus the chlorine evolved in the reaction was produced by the quantitative decomposition of chlorate, and not by melt oxidation, indicating chlorate was a weaker oxidising agent in zinc chloride than bromate, iodate or periodate (see below). Details of the reaction of chlorate ion with other chloride melts are not available, so no comparison of oxidising powers in the absence of heavy metal ions can be made.

Potassium Perchlorate

The reaction of this compound with zinc chloride can be expressed by the overall equation

$$2KClO_4 + ZnCl_2 \rightarrow 2KCl + ZnO + Cl_2 + 3^1/_2O_2 \quad (6)$$

Weight loss found 65.4%, loss calc. 66.0%.

Potassium perchlorate heated alone decomposes to chloride and oxygen at 580 to 630°; and contrasts with the stoichiometry and much lower temperatures of its reaction with zinc chloride. As reaction (6) is between zinc and perchlorate ions under anhydrous conditions, comparison can be made with the reported thermal behaviour of anhydrous zinc perchlorate. This compound, prepared by Chudinova[8] by heating the zinc perchlorate with six dioxan molecules of crystallisation in vacuo at 60°–130°, was of 99.62–99.87% purity, and decomposed rapidly between 190°–230° when heated at 10° per minute. On more rapid heating, it'decomposed explosively. As the potassium perchlorate–zinc chloride reaction reported here took place at 350°–460°, i.e. in the melt and not between solids, inhibition of the reaction by the physical state of the reactants would not be anticipated. Confirmation of this reaction temperature came from the earlier section on the potassium chlorate–zinc chloride reaction when it was noted that the perchlorate produced decomposed in the melt above about 350°. In subsequent sections, it will be shown that the bromate–zinc chloride and iodate–

zinc chloride reactions took place at the same or lower temperatures than reported for the corresponding anhydrous zinc salt heated alone. It therefore seems anomalous that the anhydrous zinc perchlorate prepared by Chudinova should decompose at 190°–230° (although her use for a higher heating rate in a vacuum would be expected to cause some reduction in temperature), particularly as Gordon and Campbell found that the zinc perchlorate hexahydrate decomposed between 260–420° with the evolution of "chlorous fumes".[9] It is therefore suggested that the anhydrous zinc perchlorate may have contained significant residual traces of dioxan, which could have been responsible for the low decomposition temperature, and for behaviour similar to the well known explosive mixtures of heavy metal perchlorates and organic compounds.

Potassium Bromate

When heated alone, this compound is known to decompose to bromide and oxygen, mostly around 520° C (calc. for loss of 3 O per $KBrO_3$, 28.7%). The weight losses found in the reaction with zinc chloride were, however, much too great for this decomposition route and, except when the zinc chloride was not in excess, too great also for the alternative reaction

$$2KBrO_3 + ZnCl_2 \rightarrow ZnO + 2KCl + Br_2 + 2^1/_2O_2 \quad (7)$$

(loss calc. 71.8%) for which losses found were 91.9–119.2% though falling to 69% when $ZnCl_2$ was not in excess. The weight loss figures, and the presence of chlorine in the reaction products, indicated that there was very considerable oxidation of the zinc chloride in the reaction, possibly by bromate itself or by a bromine oxyanion intermediate, or possibly also *via* the reaction

$$ZnCl_2 + {}^1/_2O_2 \rightarrow ZnO + Cl_2 \quad (8)$$

No details are available of the reaction of bromate with other chloride melts, so no comparisons with related systems not containing heavy metal ions can be made. The reaction is, however, closely related to thermal decomposition of anhydrous zinc bromate, reported to decompose 99% to zinc oxide, bromine and oxygen (and only 1% to zinc bromide) between 125°–195°, with a maximum rate at 175°.[10] The melt reaction occurred at similar temperatures (range 100°–250°, maximum rate 190°) and, when the zinc:bromate ratio in the melt was 1:2 (i.e. ~ 14.2 *M* in $KBrO_3$), with a similar weight loss. A possible reason for the extent of melt oxidation increasing with decreasing bromate molality is that the oxygen evolved was able to contact and oxidise progressively more zinc chloride before leaving the reaction region, as the reaction was taking place at temperatures well below the melting point of either reactant.

Potassium Iodate

Heated alone, this compound decomposes at about 600° mainly to iodide and oxygen,

$$2KIO_3 \rightarrow 2KI + 3O_2 \quad (9)$$

and to a small extent by the alternative route

$$2KIO_3 \rightarrow K_2O + I_2 + 2^1/_2O_2 \quad (10)$$

In the present work, the thermogravimetric weight losses indicated about 4% was decomposing by the second route (loss found 24.7%, loss calc. for (9) 22.4%, for (10) 78.0%).

In contrast the weight losses found in the reaction with zinc chloride were too great for the melt reaction equivalent to (10), i.e.

$$2KIO_3 + ZnCl_2 \rightarrow ZnO + 2KCl + I_2 + 2^1/_2O_2 \quad (11)$$

(loss calc. 78., losses found 91.2–96.4%). This, together with the presence of chlorine in the reaction products, indicated extensive oxidation of the melt. The melt reaction occurred at 260°–500°, temperatures considerably lower than the 520°–670° reported by Varhelyi and Kekedy for the thermal decomposition of anhydrous zinc iodate,[11] and thus suggested it was largely a direct oxidation of zinc chloride by iodate, rather than displacement of chlorine from chloride by oxygen generated thermally (a reaction shown to occur when zinc chloride is heated in an oxygen atmosphere). The slight rise in extent of melt oxidation with increasing iodate molality, an effect opposite to that observed with bromate, may have been caused by an increasing breakdown of the melt structure with added solute allowing progressively more oxidation.

Potassium Periodate

When heated alone, this compound is known to decompose in two stages, to iodate and then iodide, with evolution of oxygen at each stage.[12] When heated with zinc chloride, there was again a two stage reaction, with iodate ion as the product of the first stage, but the weight loss in each stage was much larger than those for the decomposition of pure periodate:

$$2KIO_4 \rightarrow 2KIO_3 + O_2 \quad (12)$$

(loss calc. 7.0, found 7.1% for KIO_4 alone and 11.5–19.2% for first stage of KIO_4–$ZnCl_2$ reaction).

$$2KIO_3 \rightarrow 2KI + 3O_2 \quad (13)$$

(loss calc. 20.9%, found 21.4 for KIO_4 alone, and 88.0–94.9 for second stage of KIO_4–$ZnCl_2$ reaction).

The extra weight loss in the first stage might result from (a) the oxidation of some zinc chloride to chlorine, and corresponding reduction of periodate to iodate, or (b) the partial reduction of periodate directly to iodide, with or without some oxidation of the melt. If suggestion (a) occurred all periodate would necessarily be converted to iodate in the first stage, so that the weight loss of 88.0–94.9% for the second stage, with respect to KIO_4, could be expressed as 94.6–102% with respect to intermediate KIO_3. As this was close to the 91.2–96.4%

observed for the potassium iodate–zinc chloride reaction (above), it was concluded that suggestion (a) was followed, rather than suggestion (b), which would have resulted in less iodate being available for the second stage.

A possible stoichiometry for the oxidation via scheme (a) is

$$KIO_4 + ZnCl_2 \rightarrow ZnO + KIO_3 + Cl_2$$

which would give a calculated weight loss of 30.8%. The actual values of 11.5–19.2% would then indicate only partial oxidation, possibly because of the solid state of the reactants at the reaction temperature. This would also explain the particularly low value with unmixed reactants, when there was least contact.

No comparative data on the behaviour of periodates in other chloride melts or on the thermal decomposition of pure zinc periodate is available for comparison.

Potassium Cyanide

The results have shown that the potassium cyanide–zinc chloride system was stable up to at least 590°. Details of the thermal stability of zinc cyanide are not available in the literature, though it was shown (above) to be oxidised when heated to more than 250° in air.

Potassium Cyanate

The weight loss in the main reaction was significantly greater than calculated for decomposition to cyanide (i.e. 23.5% loss. Calc. 19.7%). However, the absence of chlorine in the reaction products showed the extra loss did not result from melt oxidation. It is therefore likely that part of the reaction was by an alternative route, possibly

$$5CNO^- \rightarrow 3CN^- + O^{2-} + 2CO_2 + N_2 \qquad (14)$$

(loss calc. 28.9%) to the extent of about 40%. The small high temperature loss, though too great to be caused by the 0.5% carbonate impurity in the cyanate, may have resulted from additional carbonate produced by a reaction similar to (14). Again no details of the thermal decomposition of pure zinc cyanate are available.

Potassium Thiocyanate

The wide temperature range of the thermogravimetric weight loss suggested a rather complex reaction or reactions. Potassium thiocyanate heated alone is reported to decompose slowly above 400° [12] by the dissociation,

$$KSCN \rightleftharpoons KCN + S \qquad (15)$$

followed by sublimation of sulphur. In the reaction with zinc chloride, sulphide ion was produced in addition to cyanide and sulphur, suggesting that an additional redox reaction was taking place. However, chlorine and cyanogen, the likely oxidation products, were not detected, and the nature of the redox reaction is therefore still obscure. It has been observed that zinc chloride was almost insoluble in fused potassium thiocyanate,[13] but no report of the thermal stability of zinc thiocyanate has been found.

Sodium Metaphosphate–Potassium Perchlorate–Zinc Chloride

The results showed that the simple hypothesis outlined earlier predicting the effect of a Lux–Flood acid on an oxyanion decomposition in zinc chloride was incorrect; the decomposition temperature was lowered, as predicted, but, in addition, the weight loss relative to the oxyanion was very much increased, including values greater than 100%. The absence of volatile chloride or oxychlorides of phosphorus showed that the increased loss was not caused by a perchlorate-promoted oxidation of zinc chloride by metaphosphate ion (in the presence of atmospheric oxygen, sodium metaphosphate is known to oxidise sodium chloride at 540°–960° [14]).

An alternative approach is to consider the general decomposition of a halate or perhalate to oxide, oxygen and halogen, e.g. for perhalate

$$2XO_4^- \rightarrow O^{2-} + X_2 + 3\tfrac{1}{2}O_2 \qquad (16)$$

which in the presence of excess zinc chloride has been shown above to be accompanied by the further reaction (8). It was seen that this equilibrium of reaction (8) lay effectively to the left with chlorate or perchlorate, and considerably to the right with bromate. With perchlorate, the added metaphosphate, by taking up oxide ion:

$$PO_3^- + O^{2-} \rightarrow PO_4^{3-} \qquad (17)$$

might displace (8) to the right, causing an increased weight loss proportional to the amount of metaphosphate added relative to perchlorate. To react with all the oxide resulting if (8) occurred quantitatively would require 4 moles of metaphosphate per mole of perchlorate. At this ratio, chlorine should be the only gas evolved (loss calc. 205%

$$\text{i.e. } 4PO_3^- + ClO_4^- + 7Cl^- \rightarrow 4PO_4^{3-} + 4Cl_2 \qquad (18)$$

relative to $KClO_4$), and a further increase in the metaphosphate–perchlorate ratio should have no corresponding effect on the weight loss.

These weight-loss predictions plotted against the sodium metaphosphate–potassium perchlorate molar ratio are compared with the experimental values in Figure 1. It is seen that agreement was very good at values of the ratio less than 4. Although at high values of the ratio, agreement was less good, the experimental values did tend towards the theoretical maximum, and since the reaction occurred in part between solid reactants, agreement is considered satisfactory.

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