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Fused Zinc Chloride. I. The Reactions of some Anions Containing Carbon, Nitrogen, Phosphorus, Oxygen and Sulphur

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The stoichiometries of the reactions of fifteen oxyanions with fused zinc chloride have been established. With hydroxide, carbonate, nitrate, peroxide and sulphite, oxide ion was the product; bicarbonate also decomposed to oxide, with the formation of an intermediate, possibly a basic carbonate chloride. Nitrite gave oxide as the final product, with partial intermediate formation of nitrate. Sulphate did not react, but its solutions and those of metaphosphate and pyrophosphate could be quenched to glasses. Thiosulphate gave sulphide and sulphate as nonvolatile products while pyrosulphate, persulphate and bisulphate gave sulphate; metabisulphite produced sulphate, sulphide and oxide, the proportions varying with concentration.

Introduction

The current revival of interest in the chemistry of fused zinc chloride has not hitherto extended to reactions of inorganic compounds dissolved in it. Although binary (and ternary) M^ICl-zinc chloride systems have been extensively studied as reaction media and catalysts for organic, and a few cases for inorganic, reactions,[1] no extensive account has been published of the inorganic chemistry of pure fused zinc chloride. As a first contribution to the field, the stoichiometries of the reactions of fifteen oxyanions, generally introduced as the corresponding alkali metal salt, with fused zinc chloride are reported. The reactions are compared with the behaviour of the corresponding zinc oxysalt, and with the reaction of the anion in lithium/potassium chloride eutectic, where these are known.

Experimental Section

Materials. B.D.H. zinc chloride (sticks) was purified and dehydrated as previously described[2] (Found: Zn, 48.0; Cl, 51.9. Calc. for $ZnCl_2$, Zn, 48.0; Cl, 52.0%). Analar Na_2CO_3, $NaHCO_3$, KNO_3, $AgNO_3$, $NaNO_2$ and $K_2S_2O_5$, and Reagent Grade $LiNO_3$, KNO_2, $NaPO_3$, $K_4P_2O_7$, Na_2SO_3 and $Na_2S_2O_3$ were dried at 110° for 10 hours. Analar NaOH, Na_2O_2, $KHSO_4$ and $K_2S_2O_8$ from fresh bottles were used without drying, the absence of water being confirmed by thermogravimetric analysis. Basic zinc carbonate, $Zn(NO_3)_2 \cdot 6H_2O$ and $ZnSO_3 \cdot 2H_2O$ (approx.) were used without drying. Anhydrous zinc sulphate was prepared by heating Analar $ZnSO_4 \cdot 7H_2O$ at 300° for one hour (Found: Zn, 40.5; SO_4, 59.2. Calc. for $ZnSO_4$, Zn, 40.5; SO_4, 59.5%). Potassium pyrosulphate was prepared by heating Analar $K_2S_2O_8$.[3]

Procedure. Reactions were carried out in Pyrex tubes with B 24 joints, which fitted snugly into an electric furnace connected to an Ether Transitrol Controller, a steady supply of dry, oxygen-free nitrogen being passed over the melt during reactions at about 80 ml per minute.

Analysis. Gaseous reaction products were carried by the nitrogen flow into an appropriate aqueous solution or through a u-tube immersed in a suitable freezing mixture for subsequent analysis and identification. Provision was also made for performing experiments with the reaction tube connected to a high vacuum system, to enable the collection of gaseous products in a 10 cm. gas cell for identification by infrared spectroscopy. The melt remaining after a reaction was quenched and dissolved for subsequent analysis and identification.

Physical Measurements. Infrared spectra of gases were obtained on a Unicam S.P. 200G with sodium chloride optics using a 10 cm cell, and of solids as Nujol or Hexachlorobutadiene mulls on the same instrument. Raman spectra were examined using the Spex 1401 D with 514.5 mμ incident radiation (Argon ion laser).

Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance, normally in a current of dry, oxygen-free nitrogen and at a heating rate of 2° per minute. With the exception of sodium hydroxide, used as pellets, reagents were finely ground and intimately mixed with the zinc chloride before heating. A small funnel was inverted on top of the crucible before the reaction started, to prevent splashing and therefore possible erroneous weight losses during a vigorous reaction. The weight losses, as an average of three or more determinations, are repor-

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(1) W. Sundermeyer, *Angew. Chem. Internat. Edit.*, *4*, 222 (1965).
(2) D.H. Kerridge, *J. Chem. Soc.*, 1178 (1963).
(3) *Inorganic Thermogravimetric Analysis*, C. Duval, Elsevier, Amsterdam (1963).

Table I.

Reactant	Temp. range of reaction	Temp. of max. reaction rate	Experimental % weight loss	Weight loss calculated for loss of N+2½O per M^INO_3 (%)
$LiNO_3$	325-540°	420°	78.9	78.3
KNO_3	290-490°	420°	52.7	53.4
$AgNO_3$	160-460°	380°	31.3	31.8
$LiNO_3/KNO_3$	140-550°	420°	58.8	60.8

ted as a percentage by weight of the solute, due allowance being made for losses due to zinc chloride evaporation which was only significant above 500°C. The thermogravimetric curves for the solutes described are recorded elsewhere.[4]

Results

Sodium Carbonate reacted between 160° and 385°, the maximum rate being at 290°. Thermogravimetric analysis showed a weight loss of 41.0±0.1% (Calc. for CO_2 per Na_2CO_3 41.5%). The solidified residue was an opaque yellow when hot, the colour fading on cooling. and showed no carbonate infrared absorption bands.

Thermogravimetric analysis of basic zinc carbonate under comparable conditions showed continuous weight loss from room temperature to 550°; with the maximum rate of loss between 220° and 240°.

Sodium Bicarbonate reacted between 60° and 460° in two stages, the maximum rates being at 180° and 270°; the stages of the reaction were separated by a point of inflection in the weight loss curve at 210°. Thermogravimetric analysis showed an overall weight loss of 62.6±0.1% (Calc. for H_2O+2CO_2 per $2NaHCO_3$ 63.1%) with a loss of 44.45% to the point of inflection. Samples of the melt quenched at the inflection point showed infrared absorption at 3450, 2940, 1450-1380 and 882 cm^{-1}. The solidified residue after the second stage was an opaque yellow when hot, the colour fading on cooling.

Nitrates. The results obtained when various nitrates and the low melting binary eutectic, lithium nitrate-potassium nitrate (39 mole% $LiNO_3$, m.pt. 132°) reacted with zinc chloride, are summarised in Table I. The solidified residues were an opaque yellow when hot, the colour fading on cooling, and showed no nitrate infrared absorption bands.

Thermogravimetric analysis of zinc nitrate hexahydrate in zinc chloride, like that of zinc nitrate hexahydrate alone, showed that decomposition of the oxyanion began before all the water of crystallisation was lost. However, when zinc nitrate hexahydrate (1.2 *m* solution) was heated with potassium nitrate, thermogravimetric analysis showed decomposition to be in two distinct stages, the first, from 60°-350°, corresponding to the loss of $6H_2O$ per $Zn(CO_3)_2 . 6H_2O$ (found: 36.5; Calc. 30.3%) and the second, from 390° to 550°, to the loss of 2N+5O per $Zn(CO_3)_2 .6 H_2O$ (found 35.6; calc. 36.3%).

Sodium Nitrite reacted in two distinct stages, between 120° and 250°, and between 300° and 500°, the maximum rates being at 220° and 410°. When the lower-melting sodium nitrite-potassium nitrite eutectic (65 mole % $NaNO_2$, m.pt. 220°) was substituted for sodium nitrite, the temperature range of the first stage was between 80° and 250°, the maximum rate being lowered to 170°, while the second stage temperatures were unaltered.

Thermogravimetric analysis showed an almost constant overall weight loss of 55.2±0.4% (expressed with respect to $NaNO_2$, calculated for N+1½O per $NaNO_2$ 55.1%), but the losses in the individual stages were more variable, being between 30.8 and 36.7 per cent in the first stage and between 18.5 and 24.2 per cent in the second stage, the lowest figure in the first and highest figure in the second stage being achieved using the eutectic.

The infrared spectrum of a sodium nitrite-zinc chloride system which had been heated to the end of the first stage and then quenched showed absorption peaks at 1786, 967 and 840 cm^{-1} (Found for sodium nitrate-zinc chloride heated just to the start of reaction, 1785, 961 and 836 cm^{-1}). Infrared analysis of the gases evolved in the two stages of the reaction showed a mixture of nitrogen dioxide with small amounts of nitric oxide in the first stage and nitrogen dioxide with traces of nitric oxide in the second. The solidified residues after cooling at the end of the first or second stage were yellow and opaque when hot, becoming white on cooling.

Sodium Metaphosphate and Potassium Pyrophosphate. Thermogravimetric analysis showed no weight loss when either salt was heated with zinc chloride, other than that due to zinc chloride evaporation. On cooling, the melts gave slightly cloudy glasses which had no appreciable infrared absorption.

Sodium Hydroxide reacted with zinc chloride between 100° and 500°, the maximum rate being at 220°. Thermogravimetric analysis showed an overall weight loss of 22.6±0.4%. (Calc. for $½H_2O$ per NaOH 22.5%). The solidified residue was an opaque yellow when hot, the colour fading on cooling, and showed no hydroxide infrared absorption bands. The pH of the aqueous suspension from the solidified melt was between 5.5 and 7.0.

Sodium Peroxide reacted between 140° and 265°, with an exceedingly rapid weight loss at 265°. Ther-

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(4) I.A. Sturton, Ph.D. Thesis, University of Southampton (1972).

mogravimetric analysis showed a total weight loss of 24.5%. (Calc. for $\tfrac{1}{2}O_2$ per Na_2O_2, 20.5). The residue was an opaque yellow on solidification, the colour fading on cooling. No chlorine was found in the gaseous reaction products.

Zinc Sulphate. The behaviour of zinc sulphate heptahydrate heated alone is well established.[5] Results obtained in the present work were consistent with this, the temperature ranges being 50° to 330° for loss of water, and 660° to 980° for loss of sulphur trioxide. Similarly when the heptahydrate was heated with zinc chloride, all water was lost by 320°; the volatility of zinc chloride prevented meaningful weight loss figures being obtained when zinc chloride-zinc sulphate systems were heated to the expected decomposition range of zinc sulphate. The systems quenched to give glasses.

Sodium Sulphite reacted between 300° and 460°, the maximum rate being at 330°. Thermogravimetric analysis showed a weight loss of 47.5±0.3%. (Calc. for SO_2 per Na_2SO_3 50.8%). The gas evolved reduced potassium dichromate and had infrared absorption frequencies at 1150 and 1365 cm^{-1} (quoted for sulphur dioxide 1151 and 1362 cm^{-1}). Infrared examination of the solidified residue showed no sulphite or sulphate absorption; qualitative tests on the aqueous extract of the residue were positive for sulphide ion and slightly positive for sulphate ion (the sodium sulphite itself gave a negative sulphide test and a slightly positive sulphate test).

Reagent grade zinc sulphite, hydrated and shown qualitatively to contain sulphate ion, lost weight on the thermobalance from 60° to 340° with a point of inflection at 200°C. There was no further weight loss until sulphate decomposition began at about 680°.

Potasisum Metabisulphite reacted between 100° and 420°, the maximum rate being at about 200°. Thermogravimetric analysis showed weight losses between 43.6 and 49.0%. (Calc. for 2S+2O per $2K_2S_2O_5$ 21.6%), the actual figure depending appreciably on reactant concentration (greater at higher conc.) and heating rate (greater at 8°/min. than at 2°/min.). The gas evolved in the reaction reduced potassium dichromate and had infrared absorption characteristic of sulphur dioxide; sulphur was not produced. Qualitative examination of the solidified residue showed the presence of oxide, sulphate (slight) and sulphide (slight) ion, the sulphate being confirmed by infrared analysis.

Sodium Thiosulphate was found to react between 240° and 360°, the maximum rate being at 280°. Thermogravimetric analysis showed a weight loss of 31.3±0.6%. The presence of sulphide and sulphate ion in the quenched residue was shown by qualitative tests on its aqueous solution; the presence of sulphate ion being confirmed by infrared spectroscopy. The molar ratio of initial thiosulphate: final sulphate: final sulphide was found to be 1:0.45:0.45. The gas evolved in the reaction reduced potassium dichromate and had infrared absorption frequencies characteristic of sulphur dioxide, while a distinct fall in the gas cell transmission at higher infrared frequencies was attributed to the deposit of a thin layer of sulphur, also evolved in the reaction, on the inside of the windows.

Potassium Pyrosulphate reacted between 210° and 420°, the maximum rate being at 330°. Thermogravimetric analysis showed a weight loss of 26.3±0.3%. (Found for potassium pyrosulphate heated alone 31.2 % calculated for SO_3 per $K_2S_2O_7$ 31.5%). The volatile reaction products, when dissolved in distilled water, gave an acidic solution with weakly positive tests for chloride and sulphate ion, and white fumes above the water. The zinc chloride reaction was also performed in a test-tube under vacuum, the volatile product being condensed by liquid nitrogen in a fine capillary and sealed off under vacuum. The Raman spectrum of the product showed the presence of sulphur trioxide and chlorosulphonic acid (the first hydrolysis products of sulphuryl chloride) and certain frequencies of sulphuryl chloride. The molar ratio of initial pyrosulphate: final sulphate was determined as 1: 1.32. The melt after reaction was clear, cooling to a slightly opaque glass.

Potassium Persulphate reacted between 180° and 430°, the maximum rate being at 260°. Thermogravimetric analysis showed a weight loss of 29.8±0.7%. (Found for potassium persulphate heated alone 5.9 and 29.3% in two stages; calculated for $\tfrac{1}{2}O_2$ and for SO_3 per $K_2S_2O_8$, 5.9 and 29.6% respectively). Infrared examination of the solidified residue indicated the presence of sulphate but no persulphate. Qualitative tests also indicated that no persulphate ion remained in the solid residue. Chlorine was found to be evolved in the reaction and when the volatile reaction products were passed into distilled water, positive identifications were obtained for chloride, hypochlorite and sulphate ion, and a negative result for zinc ions. The molar ratio of initial persulphate: final sulphate was determined as 1: 1.6. The melt after reaction was clear and very slightly yellow.

Potassium Bisulphate reacted between 135° and 400°, the maximum rate being at 215°. Thermogravimetric analysis showed a weight loss of 25.0±0.7%. (Found for potassium bisulphate heated alone 35.8; calc. for $\tfrac{1}{2}H_2SO_4$ per $KHSO_4$ 36.0%). When the acidic volatile reaction products were dissolved in sodium hydroxide solution, it subsequently gave a positive identification for chloride ion, and negative results for zinc, sulphate and hypochorite ion. The molar ratio of initial bisulphate: final sulphate was determined as 1: 1.0. The melt after reaction was a clear pale yellow.

Discussion

Sodium Carbonate. The reaction of this compound with zinc chloride can be satisfactorily expressed by the equation

$$Na_2CO_3 + ZnCl_2 \longrightarrow 2NaCl + ZnO + CO_2$$

The result of thermoanalysing basic zinc carbonate indicated that most carbonate decomposition took place between 220° and 240°. It is therefore suggested that the onset of reaction between sodium carbonate and zinc chloride was inhibited by the physical state of the reactants. Duval, in discussing basic zinc carbonate[3] has mentioned that one preparation method resulted in a compound $5ZnO . CO_2$, stable to 880°, whereas other basic carbonates were completely decomposed at 250°. The loss of carbon dioxide in the present work was quantitative within the limits of experimental error, and no carbonate residue was detected in this solidified residue; it is therefore concluded that no thermally stable basic carbonate was being produced.

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

$$2NaHCO_3+ZnCl_2 \longrightarrow 2NaCl+ZnO+2CO_2+H_2O$$

The percentage weight loss was greater than when sodium bicarbonate was heated alone (39.1%), as in the latter case decomposition is only to the carbonate ion; the instability of the latter ion in zinc chloride is established above. The existence of the point of inflection at a characteristic weight loss and temperature on the thermogravimetric trace suggest the formation of a moderately stable intermediate. By comparison with the infrared frequencies reported for related compounds, the peaks observed in the melt quenched at the inflection point were assigned as follows:[5,6] 3450 cm^{-1}: O-H stretching mode similar to that in $Zn(OH)Cl$ or $Zn_5(OH)_8Cl_2$ species. 2940 cm^{-1}: very weak peak reported for $Zn_5(OH)_8Cl_2$ but not assigned. 1450-1380 cm^{-1}: carbonate ν_3 frequency. 882 cm^{-1}: carbonate ν_2 frequency or deformation vibration of –OH of $Zn_5(OH)_8Cl_2$. The evidence may therefore indicate the presence of a basic chloride carbonate intermediate, but is not conclusive. In principle, the heating of sodium bicarbonate and zinc chloride in various molar proportions might be expected to give more definite evidence of the formation of intermediate species, but an increase in sodium bicarbonate concentration resulted in increased overlapping of the two stages of weight loss, so that the inflection point became less distinct.

Nitrates. The reaction of the alkali metal nitrates with zinc chloride can be expressed by the equation

$$2MNO_3+ZnCl_2 \longrightarrow 2MCl+ZnO+2NO_2+\tfrac{1}{2}O_2$$

Detailed thermogravimetric studies of anhydrous zinc nitrate have not been reported in the literature, although it is recorded as decomposing slowly when heated alone in vacuo in the range 100°-240°, and rapidly above 240°.[7] Further information has now been obtained by experiments on zinc nitrate hexahydrate. Its decomposition with hydrolysis when heated alone on the thermobalance was typical of hydrated transition metal nitrates[8] but in contrast the effect of heating it in a potassium nitrate melt was to promote the loss of water and retard the decomposition of nitrate ion, to the extent that the region of negligible weight loss between 350° and 390° corresponded to the formation of anhydrous zinc nitrate in potassium nitrate, behaviour similar to that reported for solutions of hydrated cobalt nitrate in lithium nitrate-potassium nitrate.[9] When decomposition began again at 390°, the weight loss curve was very similar to those for the alkali metal nitrate-zinc chloride reactions, suggesting that the latter reactions involved the formation and subsequent decomposition of anhydrous zinc nitrate in the fused chloride environment.

The silver nitrate-zinc chloride reaction took place at a significantly lower temperature than the other reactions, implying that the presence of silver ions had catalysed the reaction slightly. The observed weight loss of 31.3% (Table I) was in agreement with decomposition of nitrate to oxide (calc. 31.8%) and not to silver metal (calc. 36.5%) while the absence of metallic silver in the residue was confirmed by its total solubility in ammonium hydroxide solution. The colour of the residue indicated that the oxide ions produced were combined with zinc and not silver, as is required by thermodynamic considerations; in addition, silver oxide heated alone is unstable above 450°.[3]

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

$$2NaNO_2+ZnCl_2 \longrightarrow 2NaCl+ZnO+NO+NO_2 \qquad (1)$$

It is apparent from the infrared data that in the first stage nitrite ion reacted to form (at least in part) nitrate ion, and that the second stage resulted from the reaction of this nitrate with zinc chloride. While the total weight loss figures agreed well with equation (1), (calc. 55.1, found 54.6-55.7%) the weight losses in the two stages showed considerable variation, and were also too large and too small respectively for the simple two-stage decomposition pathway A and B below.

	% loss w.r.t. $NaNO_2$		
	Calc.	Found	
$3NO_2^- \rightarrow NO_3^- + O^{2-} + 2NO$	28.9	30.8-36.9	(A)
$NO_3^- \rightarrow \tfrac{1}{2}O^{2-} + NO_2 + \tfrac{1}{2}O_2$	26.2	24.2-18.5	(B)

The closest aproach to the calculated figures resulted from heating the sodium-nitrite-potassium nitrite eutectic with zinc chloride and it is therefore suggested that the initial reaction step is (2)

$$2NO_2^- \longrightarrow O^{2-}+NO+NO_2 \qquad (2)$$

followed by he well-established[10] reaction between nitrogen dioxide and unreacted nitrite ion,

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(5) O.K. Srivastava and E.A. Sacco, *Can. J. Chem.*, *45*, 585 (1967).

(6) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York and London (1963).

(7) C.C. Addison, J. Lewis, and R. Thompson, *J. Chem. Soc.*, 2829 (1951).

(8) C.C. Addison and N. Logan, *Adv. Inorg. Chem.* and *Radioche.*, 6, 73 (1964).

(9) B.J. Brough and D.H. Kerridge, *J. Chem. Eng. Data*, *11*, 260 (1966).

(10) F.R. Duke, in Fused Salts (page 409) ed. B.R. Sundheim, McGraw-Hill, New York (1964).

$$NO_2 + NO_2^- \longrightarrow NO_3^- + NO \qquad (3)$$

varying proportions of nitrogen dioxide escaping to the atmsphere before reaction (3) occurred. The nitrate then reacted further, so that the overall stoichiometry was that of equation (1).

The very rapid onset and high rate of the first stage, at temperatures well below the nitrite or nitrite eutectic melting point, and the reduction in reaction temperature caused by using the eutectic, suggested that initiation of the reaction was inhibited by the physical state of the reactants, and that use of a very low melting nitrite eutectic might result in still lower reaction temperatures. No comparison with the reaction temperatures for the corresponding zinc compound can be made, since detailed reports on the thermal stability of anhydrous zinc nitrite have not appeared, although it has been sublimed without decomposition at 300° and 10^{-2} mm pressure;[11] zinc nitrite trihydrate may be crystallised from aqueous solution, but any attempts at dehydration caused the evolution of nitric oxide and the formation of a basic nitrate.[12] It seems certain that zinc nitrite is thermally very unstable; this is consistent with the observation that the nitrite-zinc chloride reaction proceeded very rapidly after initiation.

Sodium Metaphosphate and Potassium Pyrophosphate. The results for these compounds indicate considerable solubility in the melt, but do not indicate conclusively whether or not a definite reaction is taking place. It is certain that any reaction taking place is not accompanied by a weight loss, and a reaction involving extensive polymerisation of the phosphate ions which would not cause a weight loss, would also be expected to give a very weak infrared spectrum as found.

Sodium Hydroxide. The reaction of this compound with zinc chloride can be expressed by the equation

$$2NaOH + ZnCl_2 \longrightarrow 2NaCl + ZnO + H_2O$$

as indicated by the colour of the residue and the pH of the aqueous solution. The decomposition range contrasted with the temperatures reported for ε-Zn(OH)$_2$, the most stable form of zinc hydroxide, which decomposed in a single step between 130° and 197°, although a slight further weight loss up to 343° was due to the removal of water from the interior of the crystals.[13] The higher reaction temperatures observed for the reaction of sodium hydroxide with zinc chloride were probably caused by the difficulty of interaction between a reagent present in pellet form and a very viscous melt.

Sodium Peroxide. The reaction of this compound with zinc chloride can be expressed by the equation

$$Na_2O_2 + ZnCl_2 \longrightarrow 2NaCl + ZnO + O_2$$

The observed weight loss (24.5%) was significantly greater than the calculated value (20.5%). One possible explanation for this discrepancy, that the melt was being partly oxidised to chlorine,

$$\tfrac{1}{2}O_2 + 2Cl^- \longrightarrow O^{2-} + Cl_2$$

was eliminated as chlorine was not evolved. It is believed that the high weight loss resulted from the very rapid reaction at 265°, causing loss of some solid material in spite of the inverted funnel on the crucible. Since the poorly defined peroxides of zinc have been reported to decompose explosively at temperatures between 178° and 212°,[14] it is probable that the zinc chloride reaction was inhibited by the physical state of the reactants.

Zinc Sulphate. The hexahydrate, whether heated in zinc chloride or alone, evolved water without hydrolysis of the sulphate ion. This ion in zinc chloride is proved to be the only stable oxyanion of sulphur, not reacting at least up to 600°.

Sodium Sulphite. The reaction of this compound with zinc chloride can be expressed by the equation

$$Na_2SO_3 + ZnCl_2 \longrightarrow 2NaCl + ZnO + SO_2$$

However, the actual weight losses were appreciably less than the calculated value (47.5 as compared to 50.8%). The probable explanation is that about 6% of the reaction took place by an alternative route to give sulphide (shown to have been produced during the reaction) and sulphate ion, without weight loss:

$$4SO_3^{2-} \longrightarrow 3SO_4^{2-} + S^{2-}$$

This explanation is supported by reports of the thermal behaviour of zinc sulphite, partly basic and containing about 2% water, which when heated to 600° in nitrogen, decomposed to zinc oxide and sulphur dioxide, with minor amounts of sulphide and sulphate.[15] The present thermogravimetric analysis of hydrated zinc sulphite suggested that the weight loss up to 200° was mainly water, and that the loss above the point of inflection corresponded to sulphite decomposition. It is suggested that the onset of reaction between sodium sulphite and zinc chloride was inhibited by the physical state of the reactants, so that reaction between sodium sulphite and a low-melting binary zinc chloride eutectic should occur at lower temperatures than the 300° observed using pure zinc chloride.

Potassium Metabisulphite. The thermal decomposition of potassium metabisulphite is reported[16] to proceed according to

$$2K_2S_2O_5 \longrightarrow 2K_2SO_4 + S + SO_2 \text{ (calc. 21.3\%)}$$

the weight loss found in the present work being 21.6 per cent and the decomposition range 190°-280°. The reaction with zinc chloride occurred over a wider

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(11) B.O., Field, Private Communication, 1971.
(12) J. Lang. *J. Prakt. Chem.*, *86*, 295 (1862).
(13) O.K. Srivastava and E.A. Secco, *Can. J. Chem.*, *45*, 579 (1967).
(14) J.W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London, 1946, Vol. 4, 530.
(15) M. Cola and S. Tarantino, *Gazz. Chim. Ital.*, *92*, 174 (1962).
(16) F. Førster and G. Hamprecht, *Z. anorg. Chem.*, *158*, 277 (1926).

temperature range and with a much higher weight loss, producing oxide and sulphide ions in addition to sulphate, and evolving sulphur dioxide but not sulphur vapour. It is suggested that reaction may have proceeded according to the equations

$$S_2O_5^{2-} \longrightarrow O^{2-} + 2SO_2 \text{ (Calc. for } 2SO_2 \text{ per } K_2S_2O_5 \text{ 57.5\%} \quad (4)$$

$$4S_2O_5^{2-} \rightarrow S^{2-} + 3SO_4^{2-} + 4SO_2 \text{ (Calc. for } SO_2 \text{ per } K_2S_2O_5 \text{ 28.8\%)} \quad (5)$$

Reaction (4), accounting for a much greater loss than the observed 43.6 to 49.0%, was considered to predominate at higher temperatures and greater solute concentrations, as in these cases the percentage loss increased, whereas reaction (5) seemed to be favored by lower temperatures and concentrations. The variability of the reaction may have been because it took place place largely between solids, rather than in a melt.

Sodium Thiosulphate. The thermal decomposition of sodium thiosulphate heated alone cannot be represented by a single equation, though the decomposition, beginning at 410°, was mainly to sulphate with varying proportions of sulphite and sulphide.[3] In contrast, sodium thiosulphate reacted with zinc chloride in a single well characterised stage, over a definite temperature and with a reproducible weight loss. The reaction could be expressed by the equation

$$2S_2O_3^{2-} \longrightarrow S^{2-} + SO_4^{2-} + S + SO_2$$

which acocunted for the reaction products detected qualitatively and agreed with the actual weight losses (found 31.3, calc. 30.35%) and the quantitative analysis of the residue.

No report of the preparation of anhydrous zinc thiosulphate has been found, so details of its thermal stability are not available; it is, however, probably very unstable as its aqueous solutions are reported to decompose above 100°.[17] Thiosulphate ion has been reported to decompose in lithium chloride-potassium chloride with formation of sulphur, but no equation was given.[18] One explanation of the single stoichiometric reaction with fused zinc chloride may be the instability in the melt of the sulphite ion, one of the decomposition products of thiosulphate ion usually met with.

Potassium Pyrosulphate. The reaction between potassium pyrosulphate and zinc chloride occurred at a much lower temperature and with a significantly lower weight loss than found for potassium pyrosulphate heated alone, which was

$$K_2S_2O_7 \longrightarrow K_2SO_4 + SO_3 \quad (6)$$

The qualitative tests and Raman evidence suggested that sulphuryl chloride rather than sulphur trioxide was the predominant volatile reaction produced by the equation:

$$2S_2O_7^{2-} + 2Cl^- \longrightarrow 3SO_4^{2-} + SO_2Cl_2 \quad (7)$$

(weight loss found 26.3; calc. for $\frac{1}{2}SO_2Cl_2$ per $K_2S_2O_7$, 26.5%; calc. for SO_3 per $K_2S_2O_7$, 31.5%). Further evidence for this equation is provided by the initial pyrosulphate: final sulphate ratio (found 1:1.32; from equation (6) 1:1, and from equation (7) 1:1.5). The intermediate value of the ratio suggested that while the majority of the potassium pyrosulphate reacted with zinc chloride forming sulphuryl chloride, some also decomposed to sulphate ion and sulphur trioxide directly. Delarue has reported that potassium pyrosulphate decomposed in the lithium chloride-potassium chloride eutectic to give sulphur trioxide, but the evidence for this identification is not reported.[18] It is suggested that the reaction in the chloride eutectic needs further investigation, as a subsidiary experiment in the present work gave a weight loss of 27% for potassium pyrosulphate in potassium chloride, consistent with the formation of sulphuryl chloride but not sulphur trioxide.

Potassium Persulphate. The reaction between potassium persulphate and zinc chloride occurred at a much lower temperature and with a significantly lower weight loss than found for the (two-stage) decomposition of potassium persulphate heated alone. The qualitative tests established the production of chlorine and a volatile sulphur-containing species; by analogy with the pyrosulphate-zinc chloride reaction, the possible reactions can be expressed by the equations

$$S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_3 + \tfrac{1}{2}O_2 \text{ (8, calc. loss 35.5\%)}$$

$$2S_2O_8^{2-} + 2Cl^- \rightarrow 3SO_4^{2-} + SO_2Cl_2 + O_2 \text{ (9, calc. loss 30.9\%)}$$

$$S_2O_8^{2-} + 2Cl^- \rightarrow 2SO_4^{2-} + Cl_2 \text{ (10, calc. loss 26.2\%)}$$

Reaction according to (8), (9) or (10) would result respectively in 1.0, 1.5 or 2.0 moles of sulphate being formed per initial mole of persulphate. The actual figure was 1.6 moles, and the actual weight loss 30.2 per cent, suggesting reaction proceeded mainly according to equation (9), with slight oxidation of the melt to chlorine (equation (10)). This is in contrast to the reported reaction of potassium persulphate with lithium chloride-potassium chloride eutectic, which was oxidised to chlorine without other volatile products, *i.e.* equation (10) alone.[18]

Potassium Bisulphate. The reaction of potassium bisulphate with zinc chloride can be expressed by the equation

$$HSO_4^- + Cl^- \longrightarrow SO_4^{2-} + HCl$$

which agreed with the evidence from the qualitative tests (HCl but no Cl_2 or volatile sulphur compound), the quantitative analysis (one mole sulphate produced per initial mole of bisulphate) and the thermogravimetric analysis (found 25.0; calc. 26.8%). This is in accord with the behaviour reported by Delarue for the reaction of bisulphate ion with the lithium chloride-potassium chloride eutectic.[18]

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