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Fused Zinc Chloride
Part IV: Reactions of some Transition Metal Ions and Oxyanions

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The reactions of four transition metal ions and oxyanions with fused zinc chloride have been elucidated. Potassium chromate dissolved in zinc chloride at 350° giving a solution with an absorption maximum at 26,000 cm^{-1} (ε_{max} = 1500 l mole^{-1}cm^{-1}) but at higher temperatures reacted to give zinc chromite, with slight oxidation of the melt. Potassium dichromate also gave zinc chromite, but with more extensive melt oxidation. Silver oxide reacted to give silver chloride, no decomposition to silver metal being found up to 680°. Sodium metavanadate reacted probably to give a zinc metavanadate species.

Introduction

The inorganic chemistry of fused zinc chloride has hitherto been little studied, but earlier papers in this series have recently reported the reactions of 23 anions,[1,2] which provided examples of varying chemical behaviour in the melt, including decompositions, oxidations, reductions and the formation of volatile oxyhalides.

In the present paper, a quantitative investigation into the stoichiometry of the reactions of four transition metal compounds in this melt are reported. Of chromium compounds, only the solubility, and hence stability, of chromium(III) chloride has previously been reported,[3] so that details of the reactions of chromium(VI) compounds are of interest for comparison with their behaviour in other melts. For silver, the silver chloride–zinc chloride phase diagram is known,[4] and it has been shown that silver nitrate decomposes in zinc chloride melts to oxide ion, nitrogen dioxide and oxygen.[1] As silver nitrate is known to decompose to metallic silver when heated in air, the behaviour of silver oxide in fused zinc chloride was studied, and is compared here with its decomposition in air. Earlier reports of the reactions of vanadium compounds in fused zinc chloride have not been found.

Experimental

Materials

B.D.H. zinc chloride (sticks) was purified, dehydrated[5] and analysed[1] as previously described. Analar K_2CrO_4 and $K_2Cr_2O_7$, and Reagent Grade Ag_2O and $NaVO_3$ were dried at 110° for ten hours.

Procedure

The procedure for reactions, thermogravimetric analysis and infrared spectra was similar to that reported earlier.[1] Visible and ultraviolet spectroscopy of aqueous solutions was carried out on a Unicam SP 800, and of melt solutions on a Unicam SP 700 adapted for use at temperatures up to 700°, using silica cells of 1 mm pathlength. The identity of certain reaction products was confirmed by X-ray powder methods, using nickel filtered CuKα radiation with a Phillips X-ray diffractometer. Chromium in insoluble residues was analysed quantitatively by peroxide fusion and estimation as Cr^{VI} (a) volumetrically with standard ferrous ammonium sulphate solution and (b) spectrophotometrically in 4.5*M* sulphuric acid.

Results

Potassium Chromate dissolved in fused zinc chloride at temperatures just above the melting point to give an orange-red solution. The spectrum of this solution over the frequency range 30,000–4,000 cm^{-1} at 350° showed one absorption maximum at 26,000 cm^{-1} (ε_{max} = 1,500 l mole^{-1} cm^{-1}). At higher temperatures the zinc chloride and potassium chromate reacted, so that the spectrum of the solution at 420° showed only an absorption edge descending from 40,000 cm^{-1} to 25,000 cm^{-1} with no absorption maximum.

Thermogravimetry indicated that reaction with the melt commenced at 370°, and was complete at 520°, the maximum rate being at 450°. During reaction the melt changed colour gradually from orange-red to an opaque dark brown–green, then to brown–black. Thermogravimetric analysis showed a weight loss of 13.5 ± 0.6%. Chlorine was present in the gaseous reaction products.

The solidified melt after reaction gave a negative result for chromate but contained a dark, brown–black solid, insoluble in water at 100° and hot concentrated hydrochloric acid, which contained 40.2% chromium (volumetrically) or 40.7% (colorimetrically); calculated for zinc chromite, $ZnCr_2O_4$, 44.4%. The brown–black solid by powder photography gave *d* spacings of 2.88 (m), 2.52(s), 2.41(w), 2.10(w), 1.70(w), 1.60(m). 1.47(m). Those given for $ZnCr_2O_4$ in the A.S.T.M. index were 2.92 (48), 2.50 (100), 2.40 (3), 2.07 (10), 1.69 (25), 1.60 (50), 1.47 (60).

Potassium Dichromate was found to react between 200° and 520°. However, thermogravimetry indicated a reaction in two stages with an inflection in the weight loss trace (representing a short temperature range of very low weight loss) at 400°. The weight losses were 16.4 ± 0.5% below and 12.5–13.5% above the inflection temperature, the second loss being approximate as the high temperature end of the trace merged with the loss due to zinc chloride evaporation. Chlorine was evolved in both stages, and in addition chromyl chloride below the inflection temperature, though spectroscopic determination of the chromyl chloride established that only 8×10^{-4} moles were produced per mole of dichromate reacting.

Samples of the melt quenched at 400° showed infrared absorption peaks at 727, 822 and 933 cm^{-1} (found for a K_2CrO_4–$ZnCl_2$ melt quenched from 430°, 728, 820 and 931 cm^{-1}). The water-soluble part of the quenched melt had an absorption maximum at 371 nm (for a K_2CrO_4–$ZnCl_2$ melt quenched from 430°, 371–372 nm) while the water-insoluble part, after treatment with dilute acid to remove insoluble chromate, gave a dark brown–black solid which contained 42.7% chromium (volumetrically) or 41.6% (colorimetrically); calculated for $ZnCr_2O_4$, 44.4%.

The melt quenched from 520°, at the end of the overall reaction, showed no chromate or dichromate infrared absorption bands, but contained the dark brown–black solid with zinc chromate *d* spacings: 2.87(m), 2.51(s), 2.40(w), 2.08(w), 1.70(w), 1.61(m), 1.47(m).

Silver Oxide reacted with zinc chloride at the melting point, a yellow insoluble material being formed around the oxide particles. The melt was an opaque yellow grey up to 580°, becoming more transparent above this temperature and etchig the Pyrex surface a permanent red–brown. The quenched melt was white and partly insoluble both in water and dilute nitric acid. The insoluble material dissolved in aqueous ammonia, and on acidification with dilute nitric acid was reprecipitated. No thermogravimetric weight loss (other than that due to zinc chloride evaporation) was observed up to 680°, the highest temperature reached.

Sodium Metavanadate reacted with zinc chloride as it melted, the melt being initially brown, and becoming yellow green at 400° and a dark yellow brown at 600°, with suspended solid of the same colour. On quenching and removal of adhering zinc chloride with acetone, a yellow–brown solid was obtained with a broad infrared absorption peak at 950 cm^{-1}. No thermogravimetric weight loss (other than zinc chloride evaporation) was observed to 680°, the highest temperature teached.

Discussion

Potassium Chromate

The spectrum of the chromate ion has been measured in various melts, including lithium–potassium nitrate at 160°,[6] potassium thiocyanate at 200°,[7] and lithium–potassium chloride at 370°;[8] the spectrum was very similar in each case, showing a charge transfer absorption maximum at about 26,000 cm^{-1}, $\varepsilon_{max} = 3{,}000$–$3{,}700$ l $mole^{-1}$ cm^{-1}. The maximum obtained in zinc chloride at 26,000 cm^{-1} was also considered due to this charge transfer transition; the low ε_{max} value as compared with those reported for other melts probably being due to partial reaction of the solute with fused zinc chloride, in spite of the low temperature used to prepare the spectroscopic solutions.

The insoluble product of the melt reaction, zinc chromite, has been reported as a product of decomposition of basic zinc chromate above 400°,[9]

$$2ZnCrO_4 \rightarrow ZnO + ZnCr_2O_4 + 1{}^1/_2O_2$$

and as the final product of reaction between zinc chloride and potassium dichromate,[10] but reports of formation of zinc chromite from chromate in melts have not hitherto been found.

The weight losses obtained were in fair agreement with the quantitative reduction of Cr^{VI} to Cr^{III}:

$$2CrO_4^{2-} + Zn^{2+} \rightarrow ZnCr_2O_4 + O^{2-} + 1{}^1/_2O_2$$

(loss calc. 12.4%, loss found 13.5 ± 0.6%), the slightly greater observed value being attributed to slight oxidation of zinc chloride to chlorine probably by the liberated oxygen. The weight losses and similarity of the reaction temperatures to that reported for the decomposition of basic zinc chromate suggested the reaction was probably not a direct oxidation of chloride ion by chromate.

Potassium Dichromate

The thermogravimetric results suggested that this reaction went in two stages, below and above the inflection temperature at 400°. The spectroscopic and quantitative analysis of melts quenched from this temperature established that zinc chromite and chromate ion were both produced in the first stage, so that the second stage was probably between the chromate produced and the melt; confirmatory evidence was provided by its temperature range of 400°–520°, similar to that reported for the zinc chloride–potassium chromate reaction (380°–500°, see above).

The gaseous reaction products of the first stage were shown to contain chromyl chloride, in small quantities only, and chlorine; an equation accounting for the reaction products and thermogravimetric weight loss (neglecting chromyl chloride) was

$$2K_2Cr_2O_7 + ZnCl_2 \rightarrow ZnCr_2O_4 + 2K_2CrO_4 + O_2 + Cl_2$$

(loss calc. 17.5%). Agreement with the observed (16.5 ± 0.5%) weight loss was not exact as the latter were measured to an inflection point rather than to a constant weight level.

An expression for the formation of the small quantity of chromyl chloride is, by analogy with the potassium pyrosulphate–zinc chloride reaction.[1]

$$2Cr_2O_7^{2-} + 2Cl^- \rightarrow 3CrO_4^{2-} + CrO_2Cl_2$$

although quantitative analysis indicated that this made a negligible contribution to the overall stoichiometry.

These results established that potassium dichromate had greater oxidising power than potassium chromate in fused zinc chloride; a similar observation has been made by Propp and Laitinen in fused magnesium–potassium–lithium chloride.[11]

The only existing report on the potassium dichromate–zinc chloride reaction showed an 83% yield of zinc chromite was produced when the reactants were heated in equimolar proportions.[10] The reaction, which was considered to be

$$2K_2Cr_2O_7 + 2ZnCl_2 \rightarrow 4KCl + 2ZnCr_2O_4 + 3O_2$$

started slowly at 372° and became more rapid at 580°. No mention was made of the intermediate formation of chromate ion. In contrast, in the present work, with zinc chloride in excess, conversion of dichromate to zinc chromite at 550° was essentially quantitative (except for the small amount of chromium that was evolved as chromyl chloride).

Details of the thermal stability of anhydrous zinc dichromate are not available; it seems, however, that it is unlikely to be very stable since the dihydrate is decomposed by boiling water.[12]

Silver Oxide

This reacted with zinc chloride, completely miscible with zinc chloride above 455°.[4] The equilibrium constant for the reaction

$$Ag_2O + ZnCl_2 \rightleftharpoons 2AgCl + ZnO$$

is approximately 10^{28} at 25° from standard free energy data, indicating an exceedingly small equilibrium concentration of silver oxide, so that decomposition to silver would be completely negligible within the time scale of the thermogravimetric experiment even at temperatures up to 680°, where silver oxide heated alone is totally decomposed.[13] The melt reaction is also in accord with the results of the silver nitrate–zinc chloride, when oxide ion (as zinc oxide) and not metallic silver was produced.[1] Silver chloride itself is thermally stable up to at least 946°,[13] and would not be expected to decompose at a lower temperature in zinc chloride.

Sodium Metavanadate

The solid reaction product was not unreacted starting material, nor was its infrared spectrum that of vanadium pentoxide. The absorption maximum at 950 cm^{-1} corresponded closely to the main band for sodium metavanadate, although without the multiple maxima found for that compound. On the basis of the available evidence, it is considered that the product was a zinc metavanadate species.

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