Reactions of Cadmium Sulphate and Oxide in the Molten Lithium Nitrate–Potassium Nitrate Eutectic

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Cadmium sulphate reacts at 440 °C in pure lithium nitrate–potassium nitrate eutectic, but at much lower temperatures when Lux–Flood bases (Na_2O_2, Na_2O, and Na[OH]) are present, in accord with the relative availability of oxide ions. The product is cadmium oxide, except in the presence of moisture or hydroxide when cadmium hydroxide is formed preferentially. Cadmium oxide does not catalyse decomposition of the melt, and there is no evidence for the formation of anionic cadmate species.

THE known chemistry of cadmium in molten nitrates can be readily summarised. Cadmium(II) complexes in molten nitrate solutions have been the subject of many studies; fluoride, chloride, bromide, iodide, cyanide, sulphate, and ethylenediaminetetra-acetate (edta) ligands have been investigated by e.m.f., solubility, chromatographic, solvent-extraction, cryoscopic, and Raman methods, although most frequently by polarography. Cadmium, as the metal or amalgam, has been reported to be oxidised at 143 °C in lithium nitrate–potassium nitrate,[1] and the metal at 250 °C in sodium nitrate–potassium nitrate,[2] but no reaction of 0.0011 mol dm^{-3} amalgam was mentioned in $Li[NO_3]$–$Na[NO_3]$–$K[NO_3]$ at 160 °C.[3]

Little is known of the reactions of cadmium(II) cations except that a 1 : 1 compound was formed with electrolytically generated oxide in $Na[NO_3]$–$K[NO_3]$ at 240 °C,[4] although it may be inferred from compleximetric studies that the cation is stable to at least 290 °C in $Li[NO_3]$–$K[NO_3]$ [5] and to 320 °C in $Na[NO_3]$–$K[NO_3]$.[6] Thus the conditions required for the reaction of Cd^{II} as a Lux–Flood acid have been determined and the stoicheiometry of the reactions has been established both in pure nitrate and in melts containing added Lux–Flood bases. The latter reactions are of particular interest because of the possible formation of anionic cadmium species.

EXPERIMENTAL

Materials.—The melt was prepared as previously described.[7] AnalaR hydrated cadmium sulphate (B.D.H.) was dehydrated at 270 °C for 4 h (Found: Cd, 53.4; SO_4, 46.2. Calc. for $Cd[SO_4]$: Cd, 53.9; SO_4, 46.1%) and then handled in a dry-box. Cadmium oxide (B.D.H., >99.5%) was dehydrated at 400 °C for 1 h. AnalaR sodium peroxide (Fisons Scientific) and sodium hydroxide (B.D.H.) were used as received. Sodium mono-oxide was prepared by heating the peroxide at 620 °C *in vacuo*;[8] titration against hydrochloric acid indicated a purity of 96.2% and the residual peroxide ($K[MnO_4]$ titration) was 1.1%.

Procedure.—Reactions were carried out as previously described.[7] Cadmium was estimated gravimetrically as the ammonium phosphate monohydrate and sulphate as barium sulphate. Nitrogen dioxide was identified by i.r. and mass spectroscopy. The presence of oxygen was confirmed by use of pyrogallol.

Physical Measurements.—Thermogravimetric analyses were made using a Stanton TR-1 thermobalance with a heating rate of 2° min^{-1}. The silica crucible was covered with an inverted funnel to prevent emission of solid particles. The curves shown in the Figure are typical of those obtained from 3—6 determinations. To assist in the separation of consecutive reactions, weight losses were sometimes followed at constant temperature, isothermal results being indicated by broken lines (10 °C on abscissa ≡ 5 min). Weight losses were calculated as a percentage of the amounts of reactants. Infrared spectra were recorded with an 85-mm gas cell with silicon windows on a Perkin-Elmer 157G spectrometer. The gaseous products were also identified using a mass spectrometer (A.E.I. MS 12) and the presence of oxygen was confirmed by using alkaline pyrogallol. *X*-Ray powder diffractometry was carried out either on the solidified melt or on water-extracted samples using a Philips (Eindhoven) instrument with nickel-filtered Cu-K_α radiation.

RESULTS AND DISCUSSION

Anhydrous cadmium sulphate was moderately soluble in the lithium nitrate–potassium nitrate eutectic at 300 °C (*ca.* 1.2M), similar to zinc sulphate.[9] Reaction commenced at 440 °C when the melt became brown and nitrogen dioxide and oxygen were evolved. A black compound was precipitated over the course of a few hours. This, after quenching the reacted melt, was shown by *X*-ray diffraction to be cadmium oxide, *d* 1.66(40), 2.34(80), and 2.70(100) Å [A.S.T.M. Index: 1.661(43), 2.349(88), and 2.712 (100) Å]. Extraction of the reacted melt with water and analysis of the insoluble portion confirmed that the compound was cadmium oxide (Found: Cd, 87.2. Calc. for CdO: Cd, 87.5%), but *X*-ray diffraction indicated that cadmium hydroxide had also been formed [*d* 2.54(100), 3.02(70), and 4.69(80); A.S.T.M. Index: 2.55(100), 3.03(65), and 4.70(70) Å]. This hydrolysis reaction was not found with zinc oxide, probably because of the greater thermodynamic stability of cadmium hydroxide relative to the oxide. The initial brown colouration may be an indication of the formation of a basic cadmium species before the precipitation of cadmium oxide. Thermogravimetry [Figure, curve (○)] indicated a weight loss of 50.2% in accordance with reaction (1) (Calc. for loss of 2N + 5O per $Cd[SO_4]$:

$$Cd[SO_4] + 2[NO_3]^- \longrightarrow CdO + [SO_4]^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \quad (1)$$

51.8%). This reaction took place at a temperature well above those used for compleximetric studies, which are thus not invalidated, and also of the analogous reaction of zinc [9] thus demonstrating the lower Lux–Flood acidity of the larger cadmium cation.

In nitrate melts containing sodium peroxide, $Cd[SO_4]$ reacted at a very much lower temperature, oxygen being evolved and the melt becoming brown at >150 °C. *X*-Ray diffraction showed CdO to be present in the solidified melt. Thermogravimetric analysis [Figure, curves (×) and (△)] showed that the maximum rate of evolution occurred at 170—180 °C. With an excess of peroxide the weight loss was 8.3% (Calc. for loss of 1 O

$$Cd[SO_4] + Na_2O_2 \longrightarrow CdO + Na_2[SO_4] + \tfrac{1}{2}O_2 \quad (2)$$

per $Cd[SO_4]$: 7.7%) and a second reaction occurred at 240—340 °C [Figure, curve (×)], maximum rate at 300 °C, weight loss 14.6—17.4%. This second reaction is considered to be the decomposition of the excess of peroxide {*cf.* the decomposition curve of pure Na_2O_2 in

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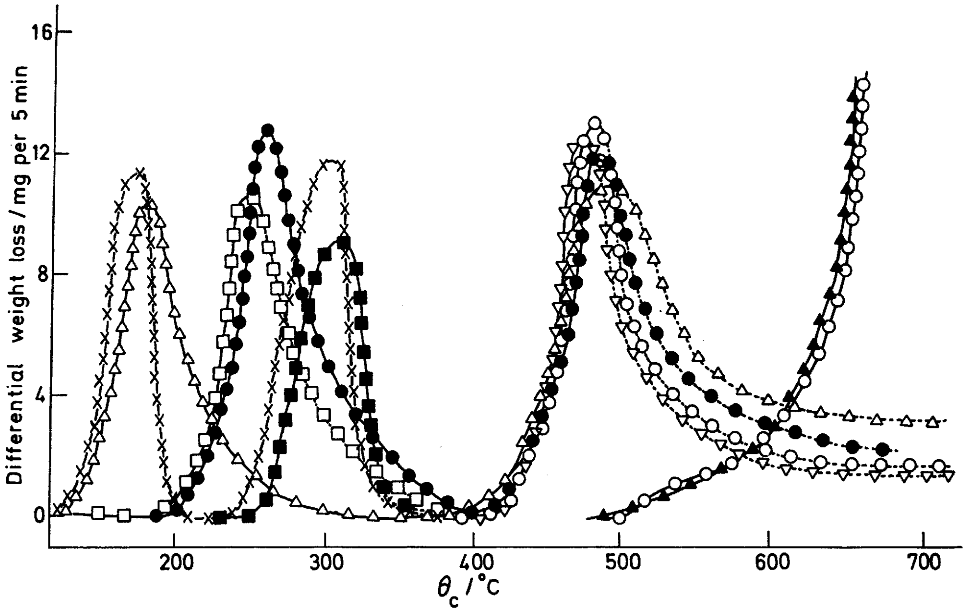
[8] G. W. Horsley, U.K. Atomic Energy Research Establishment, Rep. M/R 1441, 1956.

[9] D. H. Kerridge and J. Cancela Rey, *J. Inorg. Nuclear Chem.*, 1975, **37**, 975.

the nitrate melt [Figure, curve (■)]. (Calc. for loss of 1 O per Na_2O_2 : 20.5%)}, but with the insoluble layer of Na_2O produced around a particle protecting an unchanged core of peroxide from the nitrate melt.[10] In contrast, with an excess of $Cd[SO_4]$ over Na_2O_2 the second reaction did not commence until 450 °C [Figure, curve (△)] when NO_2 and oxygen were evolved, *i.e.* as in equation (1). The first reaction producing cadmium oxide (confirmed by *X*-ray diffraction) was still that of equation (2), weight loss 21.0% (Calc. for loss of 1 O per Na_2O_2 : 20.5%).

$$Na_2O_2 \longrightarrow Na_2O + \tfrac{1}{2}O_2 \qquad (3)$$

With melts containing Na_2O, cadmium sulphate reacted at <250 °C, producing a brown colouration although no gas was evolved. With an excess of Na_2O, *X*-ray diffraction lines due to cadmium hydroxide as well as cadmium oxide were found. With an excess of $Cd[SO_4]$, however, a second reaction occurred at 400 °C with volatile products, *i.e.* as in equation (1) [Figure, curve (▽)].



Thermogravimetric analysis of cadmium compounds in the molten lithium nitrate–potassium nitrate eutectic: (○), 0.30M $Cd[SO_4]$; (×), 0.37M $Cd[SO_4]$ + 2.06MNa_2O_2; (△), 1.01M $Cd[SO_4]$ + 0.72M Na_2O_2; (▽), 0.57M $Cd[SO_4]$ + 0.33M Na_2O; (□), 1.18M $Cd[SO_4]$ + 2.86M $Na[OH]$; (●), 1.39M $Cd[SO_4]$ + 2.31M $Na[OH]$; (○), 1.51M CdO; (▲), 2.9 g of pure $Li[NO_3]$–$K[NO_3]$; (■), 3.72M Na_2O_2. Broken lines indicate isothermal conditions (100 °C on abscissa ≡ 50 min)

When sodium hydroxide was dissolved in the nitrate melt $Cd[SO_4]$ began to react at 200 °C, water being evolved. The temperature of reaction reflected the relative availability of oxide ions; equilibrium constants for the equilibria $[O_2]^{2-} \rightleftharpoons O^{2-} + \tfrac{1}{2}O_2$, $2[OH]^- \rightleftharpoons O^{2-} + H_2O$, and $[NO_3]^- \rightleftharpoons [NO_2]^+ + O^{2-}$ under approximately comparable conditions in $Na[NO_3]$–$K[NO_3]$ melts are 10^{-5}, 10^{-16}, and 10^{-19} respectively. Thermogravimetry showed that the maximum rate for this reaction occurred at 250 °C [Figure, curves (□) and (●)]. In the presence of an excess of $Na[OH]$ the weight loss of 8.6% [*e.g.* Figure, curve (□)] was attributed to reaction (4) analogous to equation (2) (Calc. for loss of 2H + 1 O per $Cd[SO_4]$: 8.6%). However, *X*-ray diffraction of the solidified melt showed the presence of CdO but with larger amounts of $Cd[OH]_2$, no doubt formed by reaction with excess of hydroxide so that equation (4) could be written as (5). When an excess of the other bases was present, no diffraction lines were observed attributable to an anionic cadmate(II) species of the type $[CdO_x]^{(2x-2)-}$. In support of the stoicheiometry of equation (4), when an excess of $Cd[SO_4]$ was present [Figure, curve (●)], although reaction again began at 200 °C, with a weight loss of 22.8%, *i.e.* as in equation (4) (Calc. for loss of 1H + $\tfrac{1}{2}$O per $Na[OH]$: 22.5%), this was followed by a second reaction at 400 °C analogous to that found with a pure melt [equation (1)]. In support, *X*-ray diffraction on the quenched melt showed the lines of cadmium oxide but not hydroxide, although the latter did appear when soluble products and the melt were removed with water.

$$Cd[SO_4] + 2Na[OH] \longrightarrow CdO + Na_2[SO_4] + H_2O \qquad (4)$$

$$Cd[SO_4] + 4Na[OH] \longrightarrow Cd[OH]_2 + Na_2[SO_4] + Na_2O + H_2O \qquad (5)$$

Thermogravimetric analysis showed that cadmium(II) oxide did not react with the nitrate melt nor catalysed the melt decomposition [Figure, curve (○) as compared to (▲)]. When heated in melts containing Na_2O_2, there was no weight loss at a lower temperature other than that due to the decomposition of sodium peroxide [Figure,

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[10] D. A. Habboush and D. H. Kerridge, *Thermochim. Acta*, 1974, **10**, 187.

curve (■)], but again Cd[OH]$_2$ as well as CdO was found in the water-insoluble portion of the solidified melt. In melts containing Na[OH], cadmium oxide reacted to give cadmium hydroxide.

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