Thermochimica Acta, 136 (1988) 149–152
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC: THE REACTION OF TIN(II) CHLORIDE

D.H. KERRIDGE and W.M. SHAKIR

Department of Chemistry, University of Southampton, Southampton SO9 5NH (Gt. Britain)

(Received 21 January 1988)

ABSTRACT

Tin(II) chloride was oxidised in molten lithium nitrate–potassium nitrate eutectic from 200 °C (the maximum rate by TGA was at 270 °C; the reaction was complete at 310 °C). The oxidant was nitrate rather than air, in which oxidation does not begin until 275 °C, with a maximum rate at 480 °C. In both systems tin(IV) oxide was the product. Reaction in the melt occurred at a lower temperature if additions of more basic nitrite were present, but at a higher temperature with additions of chloride or bromide due to stabilisation as the tetrahalotin(II).

INTRODUCTION

Although a relatively common element the compounds of tin have been very little studied in molten nitrates, the published literature being limited to three very brief and somewhat conflicting references. A tin(II) salt (unspecified) was found to migrate cathodically in lithium nitrate–potassium nitrate eutectic on glass fibre paper at 255 °C under an electrical potential of 10 V cm^{-1}, which suggested that tin was in a stable cationic form under these conditions [1]. But in contrast Bondarevskii et al. [2] reported (in conference proceedings which were never published as a full paper) that a dilute solution of a tin salt was unstable in the ternary nitrate eutectic ($LiNO_3/NaNO_3/KNO_3$) at 120 °C where it precipitated as tin(IV) oxide. Studies of the reaction of metals in acidic nitrate melts showed metallic tin to be surface oxidised (in $LiNO_3/KNO_3 + 0.1$ M $K_2S_2O_7$) at 250 °C with no soluble tin species [3].

The evident discrepancies and extreme brevity of these accounts suggested that an examination of the reaction of tin(II) chloride in a well understood binary melt ($LiNO_3/KNO_3$) should be undertaken and reported.

0040-6031/88/$03.50

EXPERIMENTAL

Lithium nitrate–potassium nitrate eutectic was prepared as previously described [3]. Anhydrous tin(II) chloride (reagent grade), potassium chloride (AnalaR), potassium fluoride (reagent grade), potassium bromide (AnalaR) and potassium nitrite (reagent grade) were heated at 110 ° C, all for 2 h except for the last which was heated for 24 h.

The procedures for qualitative investigation of reactions and for thermogravimetry using a Stanton TR-1 thermobalance with a heating rate of 2 ° C min^{-1} were as previously described [3]. A Philips diffractometer was used with nickel filtered Cu $K\alpha$ radiation and the powder patterns compared with those of the JCDPS index.

RESULTS AND DISCUSSION

Tin(II) chloride was observed to form a white milky suspension in lithium nitrate–potassium nitrate eutectic at 160 ° C, which contained no soluble tin. Reaction began at 200 ° C with a slow evolution of brown nitrogen dioxide bubbles which became a rapid reaction at 270 ° C causing frothing, and ceased altogether after one hour at 310 ° C leaving a thick white suspension in the reaction tube. The latter after washing and drying gave the X-ray powder diffraction lines for tin(IV) oxide (*d* values 3.36(100), 2.63(80), 2.34(6), 1.75(62), JCDPS Index for SnO_2 3.35(100), 2.64(81), 2.36(24), 2.30(5), 1.76(63), 1.67(63), 1.49(13).

Thermogravimetry (Fig. 1, curve A) confirmed the course of this reaction and indicated a weight loss to 300 ° C of 48.5% in agreement with the postulated reaction

$$SnCl_2 + 2NO_3^- \rightarrow SnO_2 + 2Cl^- + 2NO_2 \qquad (1)$$

(Calculated wt loss of 2N and 4O per $SnCl_2$ 48.50%)

However, it is clear that a second reaction began at 450 ° C with a maximum rate at 510 ° C. This is considered to be due to melt decomposition, the lower starting temperature and faster rate than is found with pure eutectic (curve C) being due to catalysis, probably largely by chloride anions, which were earlier shown to cause significant catalytic decomposition from 470 ° C [4], and also probably partly by the tin(IV) oxide.

The oxidation expressed by eqn. (1) resulted from the presence of reactive nitrate rather than air, as was shown by comparison with the reaction of tin(II) chloride heated alone in air. Visually this initially white solid became yellow at 200 ° C and darkened to brown above 300 ° C, but thermogravimetry showed weight loss only to begin slowly above 275 ° C (Fig. 1, curve B) and not to become rapid until 400 ° C, with a maximum rate at 480 ° C. X-ray powder diffraction again showed the final product was tin(IV) oxide,

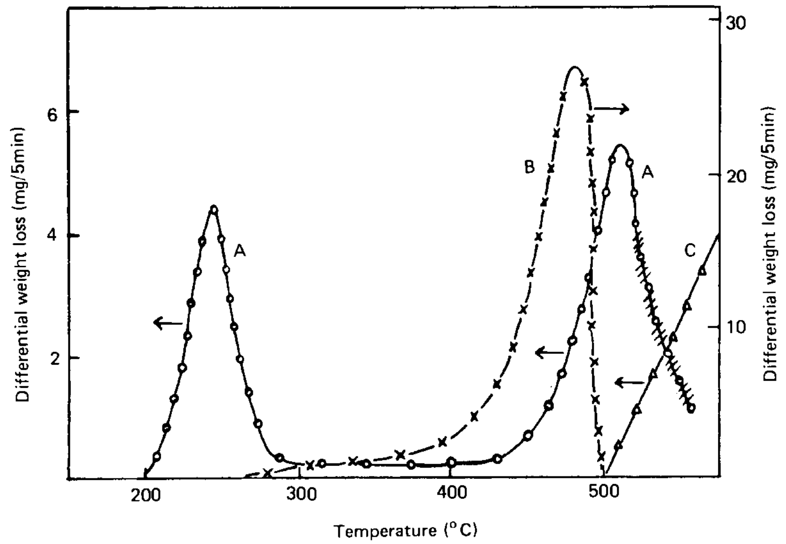

Fig. 1. Thermogravimetric analysis of tin(II) chloride. Curve A ○ 0.077 m $SnCl_2$ in $LiNO_3/KNO_3$ eutectic (left hand scale). Curve B × 0.265 g $SnCl_2$ alone in air (right hand scale). Curve C △ 2.850 g $LiNO_3/KNO_3$ eutectic alone (left hand scale).

but the overall weight loss of 43.0 ± 1.5% indicated a considerable amount of sublimation, perhaps as tin(IV) chloride, because the reaction written as eqn. 2 has a much lower weight loss.

$$SnCl_2 + O_2 \rightarrow SnO_2 + Cl_2 \qquad (2)$$

(Calculated for loss of 2Cl and gain of 2O per $SnCl_2$ 20.56%)

Additional chloride ($KCl : SnCl_2 = 1 : 1$) in the reacting melt produced a small stabilisation of tin(II), probably by formation of the tetrachloro complex, because the onset of rapid reaction was delayed until 300 °C. Similar stabilisation was achieved by the addition of fluoride or bromide ions ($KF : SnCl_2 = 1.8 : 1$; $KBr : SnCl_2 = 1.3 : 1$). However, additions of potassium nitrite ($KNO_2 : SnCl_2 = 1.65 : 1$) caused a lowering of the temperature of rapid reaction to 220 °C. This latter effect is in accord with the much higher basicity of nitrite since the dissociation constant of nitrite has been suggested to be some ten orders of magnitude greater than that of nitrate anions [5], and nitrite has already been noted as lowering the reaction temperatures of a number of Lux–Flood acids as well as those of oxidising agents when present in nitrate melts (e.g. with $Pb(NO_3)_2$ [6] and $KMnO_4$ [7] and similar differences of reaction temperatures are seen when comparing reactions of Lux–Flood acids in molten nitrites and in molten nitrates (e.g. $Cu(NO_3)_2$ [8,9], $LnCl_3$ [10,11], $K_2Cr_4O_{13}$ [12] $K_2Cr_2O_7$, $K_2Cr_3O_{10}$ and CrO_3 [13,14]).

These results confirm neither of the earlier studies [1,2] on tin salts completely, but show that the stability of tin(II) claimed by Bailey and

Steger [1] is possible in the presence of excess (stabilising) halide (alternatively perhaps their melt may have been somewhat wet, the glass fibre being "saturated with salt by evaporation of aqueous solution"). The results with the ternary eutectic [2] may have arisen from the presence of a considerable excess of basic impurity, since additions of nitrite (1.65 : 1) reduced the reaction temperature by 30 ° C.

ACKNOWLEDGEMENT

Grateful thanks are extended to the Ministry of Higher Education, Iraq, for a maintenance grant to W.M.S.

REFERENCES

1 R.A. Bailey and A. Steger, J. Chromatogr., 11 (1963) 122.
2 S.I. Bondarevskii, V.I. Izotov and V.V. Kopytov, Sovrem. Probl. Khim., (1973) 28.
3 B.J. Brough and D.H. Kerridge, Inorg. Chem., 4 (1965) 1353.
4 D.A. Habboush and D.H. Kerridge, Inorg. Chim. Acta, 4 (1970) 81.
5 R.N. Kust and J.D. Burke, Inorg. Nucl. Chem. Lett., 6 (1970) 333.
6 D.H. Kerridge and W.M. Shakir, Thermochim Acta, 101 (1986) 19.
7 B.J. Brough, D.A. Habboush and D.H. Kerridge, Inorg. Chim. Acta, 6 (1972) 259.
8 S.S. Al Omer and D.H. Kerridge, J. Chem. Soc. Dalton Trans., (1978) 1589.
9 H. Frouzanfar and D.H. Kerridge, J. Inorg. Nucl. Chem., 41 (1979) 181.
10 D.A. Habboush and D.H. Kerridge, Thermochim. Acta, 73 (1984) 25.
11 D.A. Habboush, D.H. Kerridge and S.A. Tariq, Thermochim. Acta, 65 (1983) 53.
12 D.H. Kerridge and S.A. Tariq, Thermochim. Acta, 106 (1986) 369.
13 D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 3 (1969) 667.
14 B.J. Brough, D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 1 (1967) 267.