Thermochimica Acta, 44 (1981) 151—156
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

MOLTEN LITHIUM CARBONATE—SODIUM CARBONATE—POTASSIUM CARBONATE EUTECTIC: THE REACTION OF SIX FIRST ROW TRANSITION METAL CATIONS

D.A. HABBOUSH * and D.H. KERRIDGE

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

(Received 19 August 1980)

ABSTRACT

The reactions of manganese(II), iron(II), iron(III), cobalt(II), nickel(II) and copper(II) chlorides with the molten alkali metal carbonate eutectic have been studied by thermogravimetry. The insoluble products (binary or ternary metal oxides) have been identified by X-ray diffraction and reaction stoichiometries are suggested. Nickel(II) solutions were sufficiently stable for electronic spectroscopy and indicated, as did thermogravimetry, that addition of potassium chloride did not cause significant formation of chloro complexes

INTRODUCTION

Virtually no systematic studies have been published on the reactions of transition metal compounds in molten carbonates despite the many sided interest of these liquids, for example as highly basic solvents for the preparation of oxy compounds of the less acidic oxidation states [1], as the electrolyte of high temperature fuel cells [2], as the scrubbing medium for the removal of sulphur from stack gases and from coal undergoing gasification [3] and when containing dissolved cyanide as carburizing (case hardening) baths for mild steel [4].

Electrochemical studies have been made of the reduction processes in pure carbonate melts [5] and have led on to measurements of the corrosion of various metals. For example, it has been reported that Armco iron formed two layers (of $LiFeO_2$ and Fe_3O_4) at 600°C while nickel gave a film of nickel(II) oxide with some alkali metal oxide incorporated [6].

In the absence of any other reports of the reactions of compounds of the later first row transition metals, it was decided to commence a systematic study of these weaker Lux-Flood acidic cations to compare with parallel studies of the more strongly acidic oxides and oxyanions formed by main group and early transition elements [7,8].

---

* Present address: Department of Chemistry, Faculty of Science, University of Basrah, Iraq

EXPERIMENTAL

Materials

The carbonate eutectic was prepared as previously described [7]. Manganese(II) chloride was prepared by heating the Analar tetrahydrate (BDH) at 300°C to constant weight [9]. (Weight loss 36.8%, calc. for loss of 4 H_2O from $MnCl_2 \cdot 4\ H_2O$ 36.4%; found Cl 56.1%, calc. for $MnCl_2$ Cl, 56.3%.) Iron(II) chloride, nickel(II) chloride and copper(II) chloride were prepared similarly be heating the BDH Analar hydrates to constant weight at 212, 166 and 100°C. respectively [9]. The weight losses and quantitative analyses for these three compounds were as follows. Iron(II) chloride weight loss 36.2%, calc. for loss of 4 H_2O from $FeCl_2 \cdot 4\ H_2O$ 36.2%; found Cl 55.1, calc. for $FeCl_2$ Cl 55.9%: nickel(II) chloride weight loss 45.4%, calc. for loss of 6 H_2O from $NiCl_2 \cdot 6\ H_2O$ 45.5%; found Cl 54.1, calc. for $NiCl_2$ Cl 54.7%: copper(II) chloride weight loss 21.2%, calc. for loss of 2 H_2O from $CuCl_2 \cdot 2\ H_2O$ 21.1%; found Cl 52.5, calc. for $CuCl_2$ Cl, 52.7%. Iron(III) chloride was dehydrated with thionyl chloride [10] (found Cl 64.3, calc. for $FeCl_3$ Cl, 65.6%). Anhydrous cobalt(II) chloride (BDH) was heated to constant weight at 220°C (found Cl 53.8, calc. for $CoCl_2$ Cl, 54.6%). Analar potassium chloride (BDH) was dried for 6 h at 120°C.

Procedure

The thermogravimetric analyses were carried out as described previously [7], as was the reflectance spectroscopy [8]. X-Ray diffraction was carried out with a Unicam 19 cm camera of Debye—Scherrer type using zirconium filtered molybdenum or nickel filtered CuK_α radiation from a General Electric XRD6 generator. The experimental *d*-spacings and intensities were compared with those for that compound listed in the ASTM Index or other quoted reference. The transmission spectra were obtained from a Unicam SP-700 spectrometer with reversed optics, the melt solutions being contained in square silica tubing of 10 mm nominal pathlength placed in stainless steel susceptors heated by a Redifon Type 1H24B RF generator.

RESULTS AND DISCUSSION

Manganese(II) chloride commenced to react well below the melting point of the carbonate eutectic (397°C) but with a marked increase in rate around this temperature, reaching a maximum rate near 420°C (Fig. 1, curve A). A second maximum in the rate loss curve occurred above 500°C and a distinct minimum (marked a) near 600°C. At this stage the melt on solution in water gave an insoluble brown powder with the X-ray diffraction lines of trimanganese tetraoxide. The average weight loss to this minimum was 33.6%, in accord with the stoichiometry of eqn. (1).

$$3\ MnCl_2 + 3\ CO_3^{2-} \rightarrow Mn_3O_4 + 6\ Cl^- + 2\ CO_2 + CO \qquad (1)$$

(calculated weight loss for C + $1\frac{2}{3}$O per $MnCl_2$ 30.7%)

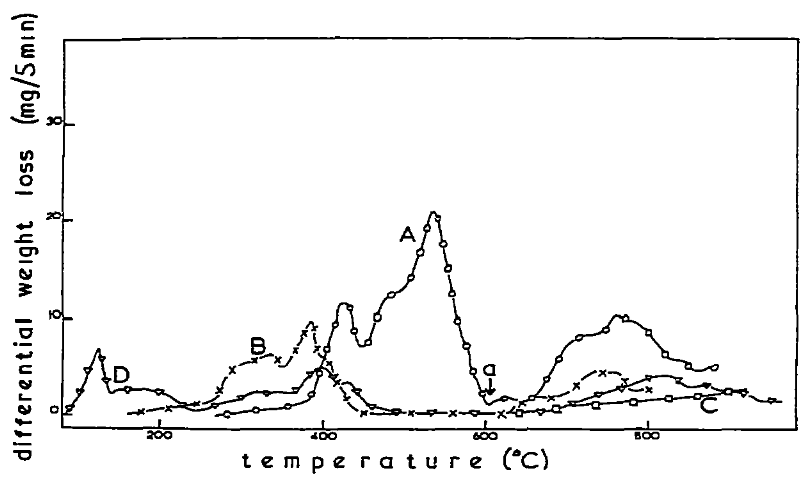

Fig. 1. Thermogravimetry in lithium carbonate—sodium carbonate—potassium carbonate eutectic with transition metal chlorides A (○———○) 2 14 m $MnCl_2$; B (X———X) 1.29 m $FeCl_2$; C (□———□) 1.90 g carbonate eutectic alone, D (▽———▽) 0.68 m $FeCl_3$

The washed brown solid after drying at 260°C was 61.2% of the weight of the original manganese(II) chloride (calculated 60.6%).

Some further reaction even below 600°C was indicated by these figures and by curve A of Fig. 1. This high temperature weight loss increased slightly in rate to a small maximum at 730°C and persisted to 870°C. X-Ray diffraction of the insoluble black product showed the lines of two lithium manganates ($LiMnO_2$ and Li_2MnO_3). The average total weight loss was 49.1%, supporting the formation of a mixture of manganates, but with more manganate(III) than manganate(IV)

$$2\,MnCl_2 + 3\,CO_3^{2-} + 2\,Li^+ \rightarrow 2\,LiMnO_2 + 4\,Cl^- + 2\,CO_2 + CO \qquad (2)$$

(calculated weight loss for 1.5 C + 2.5 O per $MnCl_2$ 46.1%)

$$MnCl_2 + 2\,CO_3^{2-} + 2\,Li^+ \rightarrow Li_2MnO_3 + 2\,Cl^- + CO_2 + CO \qquad (3)$$

(calculated weight loss for 2 C + 3 O per $MnCl_2$ 57.1%)

as did the lithium analysis (found Li 8.2%, calc. for $LiMnO_2$ Li 7.4%, calc. for Li_2MnO_3 Li 11.9%) and as did the yield of black product (75.5% of original $MnCl_2$; calc. for $LiMnO_2$ 74.6% and for Li_2MnO_3 92.9%).

Iron(II) chloride started to react with the solid eutectic around 160°C, the rate increasing to a maximum close to the melting point (Fig. 1, curve B) and ceasing at 460°C, the average loss to this point being 29.2%. The reddish-brown solid produced after washing and drying gave the X-ray lines of α-iron(III) oxide, suggesting the stoichiometry

$$2\,FeCl_2 + 2\,CO_3^{2-} \rightarrow Fe_2O_3 + 4\,Cl^- + CO_2 + CO \qquad (4)$$

(calculated weight loss for C + 1.5 O per $FeCl_2$ 28.4%)

A second very distinct weight loss began at 630°C after a considerable interval without reaction. This reached a maximum near 790°C and was still continuing at 870°C. The brown-black solid after washing and heating to 900°C gave the diffraction lines of α-lithium ferrate(III) ($LiFeO_2$) [11]. This evidence was corroborated by analysis (found Li 6.5%, calc. for $LiFeO_2$ Li 7.3%) and the yield (73.2% of original $FeCl_2$; calc. for $LiFeO_2$ 74.8%) which all supported the overall reaction

$$2\ FeCl_2 + 3\ CO_3^{2-} + 2\ Li^+ \rightarrow 2\ LiFeO_2 + 4\ Cl^- + 2\ CO_2 + CO \qquad (5)$$

(calculated weight loss for 1.5 C + 2.5 O per $FeCl_2$ 45.8%)

However, the actual weight losses (62.6—78.8% to 870°C) were considerably greater than this calculated value. Since they continued without an obvious break and were also much larger than the loss from a pure melt (Fig. 1, curve C) it is suggested that the carbonate decomposition is catalysed by the presence of lithium ferrate(III).

Iron(III) chloride reacted in the solid phase at an even lower temperature (Fig. 1, curve D), in accordance with its more acidic character, the first weight loss being completed by 500°C. The average loss of 43.4% was in accordance with the reaction

$$2\ FeCl_3 + 3\ CO_3^{2-} \rightarrow Fe_2O_3 + 6\ Cl^- + 3\ CO_2 \qquad (6)$$

(calculated weight loss for 1.5 C + 3 O per $FeCl_3$ 40.7%)

as were the diffraction lines of the red-brown product which again indicated the α form of the oxide, and the yield (49.4% of original $FeCl_3$; calc. for Fe_2O_3 49.1%).

Once again the weight loss recommenced at a higher temperature (660°C) with formation of the same product as formed by iron(II) chloride. The actual loss (74.9%) again indicated the catalytic decomposition of carbonate

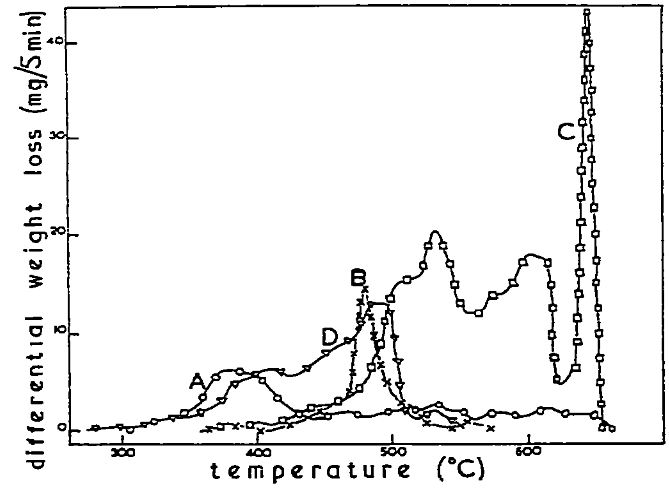

Fig 2. Thermogravimetry in lithium carbonate—sodium carbonate—potassium carbonate eutectic with transition metal chlorides. A (○——○) 1.20 m $CoCl_2$; B (X——X) 0.30 m $NiCl_2$; C (□——□) 1.81 m $NiCl_2$ with 5.37 m KCl; D (▽——▽) 1.56 m $CuCl_2$.

in addition to the reason

$$FeCl_3 + 2\ CO_3^{2-} + Li^+ \rightarrow LiFeO_2 + 3\ Cl^- + 2\ CO_2 \qquad (7)$$

(calculated weight loss for 2 C + 4 O per $FeCl_3$ 54.3%)

Cobalt(II) chloride commenced reaction at 300°C, the weight loss continuing until 650°C with a maximum near 400°C (Fig. 2, curve A). X-Ray diffraction showed that the black product was tricobalt tetraoxide, in accordance with the yield (61.6% of original $CoCl_2$; calc. for Co_3O_4 61.8%) and overall weight loss of 30.7% (calculated weight loss of C + $1\frac{2}{3}$ O per $CoCl_2$ to form Co_3O_4 29.8%. Calculated for loss of C + 2 O per $CoCl_2$ to form CoO 33.9%), thus indicating the stoichiometry

$$3\ CoCl_2 + 3\ CO_3^{2-} \rightarrow Co_3O_4 + 6\ Cl^- + 2\ CO_2 + CO \qquad (8)$$

Nickel(II) chloride was less reactive, beginning to react only very slowly at 350°C, with an increase in rate at 450°C and finishing at 550°C after rising to a maximum at around 480°C (Fig. 2, curve B). The dark grey insoluble product gave the X-ray diffraction lines of nickel(II) oxide, which together with the overall weight loss (33.6%) and the yield (56.7% of original $NiCl_2$; calc. for NiO 57.6%) gave support for the reaction

$$NiCl_2 + CO_3^{2-} \rightarrow NiO + 2\ Cl^- + CO_2 \qquad (9)$$

(calculated weight loss for C + 2 O per $NiCl_2$ 34.0%)

Analogous reactions but with increasing quantities of potassium chloride added to the carbonate eutectic showed very similar overall weight losses (Table 1) but with some increase in the decomposition temperatures providing some evidence of stabilisation by the formation of chloro complexes, though not the continuing increase found for some cations, for example cobalt(II) in nitrate melts [12], when potassium chloride was added. The considerable increase in temperature of the maximum for the chloride/nickel ratio of 4.32 : 1 was probably largely due to the four-times higher concentration of nickel and a relatively slow reaction since the rate was found to increase markedly from 500°C (Fig. 2, curve C).

TABLE 1

The reaction of nickel(II) chloride with molten lithium carbonate—sodium carbonate—potassium carbonate eutectic in the presence of potassium chloride

$NiCl_2$ concentration (molal)	Cl/Ni ratio	Overall wt loss (%)	Temp. of max. rate (°C)	Temp. range of wt. loss (°C)
0.30	2.00 : 1	33.6	490	350—550
1.65	2.00 : 1	33.1	510	350—550
1.18	4.32 : 1	33.8	650	370—660
0.30	5.94 : 1	33.4	530	360—570
0.30	6.00 : 1	33.3	560	350—620
0.30	11.97 : 1	34.8	500	360—560

Spectroscopic measurements also showed little change with increasing added chloride. The pale green melt (0.8 m $NiCl_2$ with no additional chloride) at 420°C showed a slight shoulder at 23 000 cm^{-1} ($\epsilon \sim 30$ l $mole^{-1}$ cm^{-1} on an absorption edge at 28 000 cm^{-1}, while the reflectance spectrum on the same solution after solidification showed a small maximum at 22 200 cm^{-1} and more intense transitions (presumably charge transfer) at 37 000 and 45 500 cm^{-1}. With a nickel concentration of 0.50 m and a chloride/nickel ratio of 6.0 : 1 the more intense reflectance absorptions were at 38 000 and 46 500 cm^{-1} and the weaker at 22 700 cm^{-1}, and thus did not show the changes which would be expected from the progressive formation of chloro complexes (as for example has been found in molten nitrates [13]) but did illustrate the much greater stability of nickel(II) as compared to that of any other of the cations studied. The absorption at 22 200—23 000 cm^{-1} seems most likely to be the $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) band of nickel(II) octahedrally coordinated by oxygen, which would imply that the ligand field of carbonate anions was only a little lower than that of molten nitrate (23 000 cm^{-1}) but definitely less than that of water (25 000 cm^{-1}).

Copper(II) chloride commenced reaction with solid carbonate eutectic at 260°C, with a considerable increase in rate near the melting point, reached a maximum rate at 480°C and ended at 550°C (Fig. 2, curve D). The black insoluble solid gave the diffraction lines of copper(II) oxide. The overall weight loss (32.7%) and yield (59.2% of original $CuCl_2$; calc. for CuO 54.2%) also supported the stoichiometry of the simple acid—base reaction

$$CuCl_2 + CO_3^{2-} \rightarrow CuO + 2\,Cl^- + CO_2 \tag{10}$$

ACKNOWLEDGEMENT

Grateful thanks are extended to the University of Basrah, Iraq, for the grant of sabbatical leave to D.A.H.

REFERENCES

1 M.G. Barker, Inorganic Chemistry Series One, Vol 2, M T.P. Int Rev. Sci., Butterworths/University Park Press, New York, 1972, Chap. 1.
2 D.A.J Swinkels, Adv Molten Salt Chem., 1 (1971) 163
3 S J Yosim, L F. Grantham, D.E McKenzie and G.C. Stegmann, Adv Chem. Ser., 127 (1973) 174.
4 E.C Rollason, Metallurgy for Engineers, Arnold, London, 4th edn , 1973
5 P K. Lorenz and G J Janz, Electrochim. Acta, 15 (1970) 1025, 2001.
6 O.P. Penyagina, I N. Ozeryanaya, M.V Smirnov, B S Shibonov and N.D. Shomanova, Zashch. Met., 8 (1972) 312.
7 D.A Habboush, D.H. Kerridge and S.A. Tariq, Thermochim. Acta, 25 (1978) 357.
8 D.A. Habboush, D.H. Kerridge and S A. Tariq, Thermochim Acta, 28 (1979) 143
9 C Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963
10 J.H. Freeman and M.L. Smith, J Inorg. Nucl. Chem., 7 (1958) 224.
11 J C. Anderson and M. Schieber, J. Phys. Chem Solids, 25 (1964) 961
12 H Frouzanfar and D.H. Kerridge, Thermochim Acta, 25 (1978) 11.
13 T.R. Griffiths and P.J. Potts, Inorg. Chem., 14 (1975) 1039