Thermochimica Acta, 97 (1986) 61–66
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MOLTEN Li_2CO_3–Na_2CO_3–K_2CO_3 EUTECTIC: THE EFFECT OF ADDED Cl^-, Br^-, AND I^- ON THE REACTIVITY OF SOLUTIONS OF Mn(II), Co(II), Ni(II), AND Cu(II)

S.S. AL OMER †

Department of Chemistry, College of Science, University of Baghdad, Baghdad (Iraq)

D.A. HABBOUSH

Department of Chemistry, Sacred Heart University, Bridgeport, CT 06606 (U.S.A.)

D.M. HUSSAIN

Department of Chemistry, College of Science, University of Basrah, Basrah (Iraq)

(Received 17 June 1985)

ABSTRACT

Thermogravimetry gave evidence of a significant stabilization of Ni(II) solution in the molten Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic when Cl^-, Br^- or I^- was added to this solution. The stabilization effect of these halides followed the trend $Cl^- > Br^- > I^-$. No evidence was found, however, to indicate a similar effect on Mn(II) and Cu(II) melt solutions. Reflectance spectra of Ni(II) and Co(II) solutions illustrated their much greater stability than that of the other two cations.

INTRODUCTION

The chemistry of transition metal compounds in molten carbonates is still largely unknown, despite the varied interest in these liquids 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], and as the scrubbing medium for the removal of sulfur from stack gases and from coal undergoing gasification [3]. Electrochemical studies have been made of the reduction process in pure carbonate melts [4] which led to measurements of the corrosion of various metals [4,5]. The reactions of some transition metal oxides and oxyanions in molten carbonate have been studied [6] and compared with those of main-group acidic oxides and oxyanions [7]. The most recent report studied the reaction of four lanthanide(III) chlorides in molten carbonate [8].

† Deceased.

0040-6031/86/$03.50

A thermogravimetric [9] study of the reaction of six first-row transition metal chlorides with the Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic showed that all the metal chlorides studied commenced reacting at temperatures well below the melting point of the eutectic. $NiCl_2$, the least reactive of the six, reacted between 350 and 500°C according to the equation

$$MCl_2 + CO_3^{2-} = MO + 2Cl^- + CO_2 \qquad (1)$$

where M = Ni. $MnCl_2$ and $CoCl_2$ reacted between 300 and 600°C according to the stoichiometry

$$3M'Cl_2 + 3CO_3^{2-} = M'_3O_4 + 6Cl^- + 2CO_2 + CO \qquad (2)$$

where M′ = Mn or Co. $CuCl_2$ reacted between 260 and 550°C according to eqn. (1), where M = Cu. The remaining two chlorides of Fe(II) and Fe(III) reacted at much lower temperatures around 160 and 100°C, respectively.

In the present work, the effect of added Cl^-, Br^-, and I^- on solutions of the four less reactive cations Mn(II), Co(II), Ni(II), and Cu(II) in molten carbonate, was examined by thermogravimetry and reflectance spectroscopy.

EXPERIMENTAL

Materials

The Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic was prepared as previously described [7]. Anhydrous $MnCl_2$, $NiCl_2$, and $CuCl_2$ were prepared by heating their hydrates (BDH AnalaR) at 300, 166, and 100°C, respectively [10]. The weight losses and quantitative analyses for these three compounds were as follows. $MnCl_2$: weight loss, 36.8%; calculated for loss of $4H_2O$ from $MnCl_2 \cdot 4H_2O$, 36.4%; found: Cl, 56.1%; calculated for $MnCl_2$: Cl, 56.3%. $NiCl_2$: weight loss, 45.4%; calculated for loss of $6H_2O$ from $NiCl_2 \cdot 6H_2O$, 45.5%; found: Cl 54.1%; calculated for $NiCl_2$: Cl, 54.7%. $CuCl_2$: weight loss, 21.1%; calculated for loss of $2H_2O$ from $CuCl_2 \cdot 2H_2O$, 21.1%; found: Cl, 52.5%; calculated for $CuCl_2$: Cl, 52.7%. Anhydrous $CoCl_2$ (BDH) was heated to a constant weight at 220°C (found: Cl, 53.8%; calculated for $CoCl_2$: Cl, 54.6%). KCl, KBr, and KI (BDH AnalaR) were dried for 24 h at 120°C.

Method

Reactions were carried out in a 10-ml gold crucible on a Stanton-Redcroft MF-H5 massflow thermobalance under a CO_2 atmosphere, using a heating rate of 5°C min^{-1}. All reactants were ground to a fine powder and very well mixed in a dry box. Reflectance spectra of the powdered solidified melt solutions were taken on a Pye Unicam SP8-100 spectrophotometer using the attachment SP790824.

RESULTS AND DISCUSSION

$NiCl_2$ commenced reacting with the solid Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic at 300°C (Fig. 1, curve A). The reaction exhibited its maximum rate in the solid state, subsided to a minimum around 400°C (m.p. of the carbonate eutectic is 397°C), and continued steadily to 600°C. The reaction stoichiometry (Table 1) was in agreement with eqn. (1) [9].

Analogous reactions, but with increasing quantities of KCl, KBr, and KI added to the carbonate eutectic, showed thermogravimetric curves (Fig. 1, curves B–E) that have similar features to that of the pure eutectic (Fig. 1, curve A). Although by no means reproducible and dependent on the extent of mixing and particle size of the powdered mixture, a slight reduction in the overall weight loss at the minimum (~ 400°C, Table 1) was expected and observed. This effect was attributed simply to a lower mole fraction of the carbonate.

A more interesting effect, however, is the significant reduction in the overall weight loss beyond the melting point of the eutectic. Thus, the concentration of unreacted Ni(II) at 600°C was compared to that remaining at 400°C and is expressed as the percentage stabilization in Table 1. These comparisons and the continued upward trend with increasing halide con-

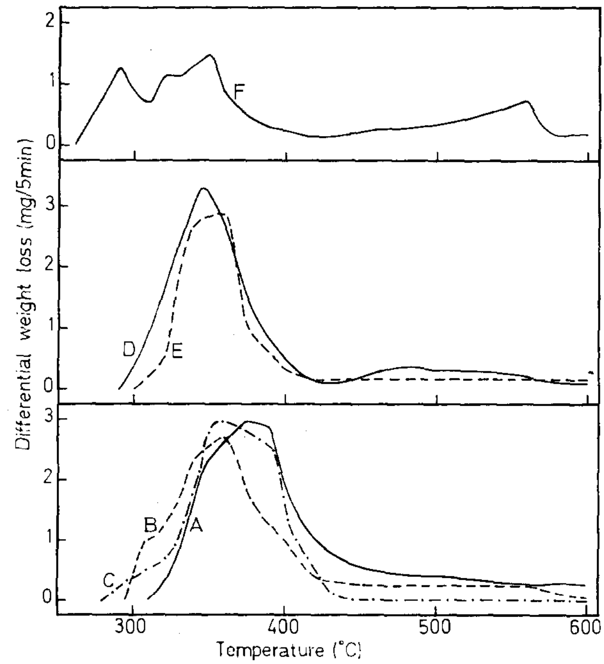

Fig. 1. Thermogravimetry in 1 g of Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic. (A) 0.24 *m* $NiCl_2$; (B) 0.23 *m* $NiCl_2$ +0.46 *m* KCl; (C) 0.25 *m* $NiCl_2$ +1.25 *m* KCl; (D) 0.25 *m* $NiCl_2$ +2.00 *m* KBr; (E) 0.25 *m* $NiCl_2$ +1.00 *m* KI; (F) 0.25 *m* $MnCl_2$.

TABLE 1

Thermogravimetry of $NiCl_2$ in the Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic and its mixtures with KCl, KBr, and KI

Initial concentration				At 400°C						At 600°C		Percentage stabilization [d]
$NiCl_2$ (*m*)	KCl (*m*)	KBr (*m*)	KI (*m*)	Weight loss (%)	Ni(II) [a] (*m*)	Cl^-/Ni(II)	Br^-/Ni(II)	I^-/Ni(II)	X^-/Ni(II) [b]	Weight loss [c] (%)	Ni(II) [a] (*m*)	
0.24	–	–	–	24.8	0.065	7.4	–	–	7.4	34.0	0	0
0.23	0.25	–	–	24.4	0.065	11.0	–	–	11.0	30.7	0.022	33.8
0.23	0.46	–	–	24.2	0.067	13.8	–	–	13.8	29.2	0.033	48.7
0.23	0.86	–	–	23.6	0.071	18.7	–	–	18.7	27.2	0.047	65.6
0.24	1.27	–	–	23.3	0.076	23.1	–	–	23.1	24.2	0.070	91.5
0.25	–	0.25	–	27.4	0.049	10.4	5.1	–	15.5	32.3	0.012	24.8
0.25	–	2.00	–	25.3	0.064	7.9	31.5	–	39.4	29.2	0.035	55.4
0.30	–	–	0.27	24.3	0.084	7.1	–	3.1	10.2	31.9	0.018	21.9
0.25	–	–	0.50	25.5	0.062	8.1	–	7.9	16.0	30.9	0.023	36.4
0.25	–	–	1.00	24.7	0.069	7.4	–	14.7	22.1	29.9	0.030	43.2

[a] Concentration of Ni(II) remaining; calculated from the weight loss.
[b] Total halide/Ni(II) ratio.
[c] Calculated for loss of 1C+2O per $NiCl_2$ is 34.0%.
[d] Percentage of Ni(II) at 600 compared to that at 400°C.

centration provided some evidence of stabilization by the formation of halo complexes, and are analogous to the effect of added KCl on some cations, e.g., Co(II) in nitrate [11]. The results also show that the stabilization effect of the added halides followed the trend $Cl^- > Br^- > I^-$ as one would expect from their effectiveness when acting as ligands.

Spectroscopic measurements, however, showed no change when more Cl^- was added nor for that effect when either Br^- or I^- was added to the Ni(II) melt solution. Thus it did not provide support for the halo complex formation. The reflectance spectrum of the powdered solid of the pale green melt solution (0.25 *m* $NiCl_2$ + 1.00 *m* KCl at 450°C) showed two absorptions at 13 870 and 21 740 cm^{-1} which are attributed to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}(P)$ of Ni(II) octahedrally coordinated to oxygen of the carbonate ligand [9], and two more intense transitions (presumably charge-transfer) at 37 300 and 43 850 cm^{-1}.

Reflectance measurements (Fig. 2, curve A) of the solidified deep-blue solution of Co(II) in the carbonate eutectic containing KCl gave a band at 17 125 cm^{-1}. The striking similarity between this band with its fine structure and the visible spectrum of the tetrahedral CoF_4^{2-} (Fig. 2, curve B) [12] supported the assignment of this band to the transition $^4A_2(F) \rightarrow {}^4T_2(P)$ in a tetrahedral Co(II) species formed in the carbonate melt solution. The energy of this transition, however, was much higher than that expected for a tetrahedral chloro-coordinated Co(II) species [13]. Also, the spectrum did not show changes when more Cl^- was added, as one would expect from the progressive formation of chloro complexes (as, for example, has been found in molten nitrate [14]), nor when Br^- or I^- was added instead of Cl^-. Thus, it seems most likely that Co(II) is coordinated to the oxygen atoms of the carbonate ligands.

$MnCl_2$ commenced reaction with the carbonate eutectic at 270°C (Fig. 1, curve F). The average overall weight loss at 600°C was 31.9%, in accord with

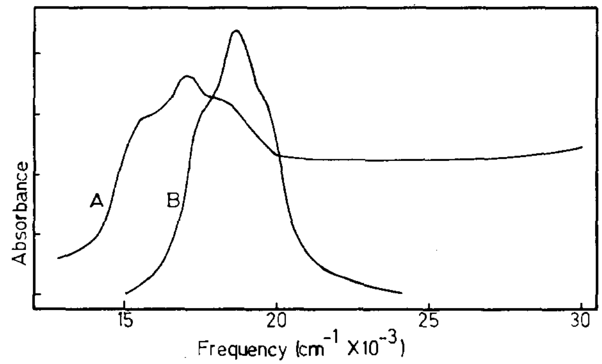

Fig. 2. Absorption spectra of: (A) powdered solid from 0.25 *m* $CoCl_2$ + 0.50 *m* KCl in molten Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic at 450°C; (B) Co(II) in CdF_2 crystal at 25°C.

the stoichiometry of eqn. (2) [9]. (Calculated weight loss for 1C + 5/3O per $MnCl_2$, 30.7%.) Thermogravimetry of a mixture of $MnCl_2$ and carbonate containing potassium halides, however, gave no evidence of the stabilization effect of the added halides observed in the case of the Ni(II) solution.

Mn(II) and Cu(II) reacted with the carbonate/halide mixtures at 450°C forming black residues of Mn_3O_4 and CuO, respectively. Thus, both were not stable enough for the measurement of their reflectance spectra.

Although spectroscopy did not provide supporting evidence for the concept of stabilization by halo complex formation, it did illustrate the much greater stability of Ni(II) and Co(II) solutions in molten carbonate containing KCl, KBr, or KI, compared to that of their solutions in pure molten carbonate and to that of the other two cations studied.

ACKNOWLEDGEMENTS

Grateful thanks are extended to the Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq, for supporting this work which was carried out in its laboratories and for a scholarship to D.M.H.

DEDICATION

This article is dedicated to one of us, Dr. Sabah S. Al Omer, who passed away after this work was completed.

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 P.K. Lorenz and G.J. Janz, Electrochim. Acta, 15 (1970) 1025, 201.
5 O.P. Penyagina, I.N. Ozeryanaya, M.V. Smirnov, B.S. Shibonov and N.D. Shomanova, Zashch. Met., 8 (1972) 312.
6 D.A. Habboush, D.H. Kerridge and S.A. Tariq, Thermochim. Acta, 28 (1979) 143.
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, 84 (1985) 13.
9 D.A. Habboush and D.H. Kerridge, Thermochim. Acta, 44 (1981) 151.
10 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.
11 H. Frouzanfar and D.H. Kerridge, Thermochim. Acta, 25 (1978) 11.
12 C. Simo, E. Banks and S. Holt, Inorg. Chem., 8 (1969) 1446.
13 F.A. Cotton, D.M.L. Goodgame and M. Goodgame, J. Am. Chem. Soc., 83 (1961) 4690.
14 D.H. Kerridge, P.S.G. Bull., (1967) 508.