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THE REACTIONS OF SOME COMPOUNDS OF IRON, COBALT AND NICKEL WITH THE MOLTEN LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC

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ABSTRACT

The reactions of $FeCl_2$, $FeCl_3$, $CoCl_2$, $Na_3[Co(NO)_2)_6]$, $[Co(NH_3)_5H_2O]Cl_3$ and $NiCl_2$ with the molten alkali metal carbonate eutectic were investigated. It was found that $FeCl_2$ and $FeCl_3$ reacted with the melt to precipitate Fe_2O_3 which was converted into $LiFeO_2$ on further heating. Cobalt(II) added to the melt as $CoCl_2$ or produced by the decomposition of $Na_3[Co(NO_2)_6]$ was found to react with the melt to form Co_3O_4 which was also formed in the reaction of $[Co(NH_3)_5H_2O]Cl_3$ and was partially converted into $LiCoO_2$. Nickel(II) chloride reacted to precipitate stable NiO. The molten carbonate eutectic donated oxide ions in these reactions with the evolution of CO_2 which was partially reduced to CO in some reactions.

INTRODUCTION

The alkali metal carbonate melt has been employed in various fields as pointed out in a previous publication [1]. The lithium carbonate–sodium carbonate–potassium carbonate eutectic has been used, in recent years, for the investigations of Lux–Flood acid–base reactions. The eutectic acts not only as a reaction medium, but also as a donor of oxide ions with the evolution of CO_2 which can be determined quantitatively using a thermobalance. Thus, the reactions of acidic oxides and oxo anions of the main group elements [2], metal oxides and oxo anions of Group VB and VIB elements [3], some transition metal cations [4], iron(II) oxalate and basic nickel(II) carbonates [5], some compounds of manganese [6] and eleven compounds of copper, silver and chromium [7] with the molten carbonate eutectic have been reported. This paper reports the reactions of some compounds of iron, cobalt and nickel with the eutectic under argon as well as CO_2 atmosphere.

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EXPERIMENTAL

Materials

The carbonate eutectic was prepared as described previously [1]. Iron(III) chloride was prepared by passing chlorine gas over BDH electrolytic iron at 300 ° C. (Found: Fe, 34.6%; Cl, 65.3%. Calculated for $FeCl_3$: Fe, 34.4%; Cl, 65.6%). Iron(II) chloride was prepared by reduction of $FeCl_3$ in situ with a stream of hydrogen in a pyrex tube at 250 ° C. (Found: Fe, 44.2%; Cl, 55.6%. Calculated for $FeCl_2$: Fe, 44.0%; Cl, 56.0%). Cobalt(II) and nickel(II) chlorides were dehydrated with thionyl chloride by the method of Freeman and Smith [8]. (Found: Co, 45.3%; Cl, 54.4%. Calculated for $CoCl_2$: Co, 45.4%; Cl, 54.6%. Found: Ni, 45.2%; Cl, 54.3%. Calculated for $NiCl_2$: Ni, 45.3%; Cl, 54.7%). Aquapentammine cobalt(III) chloride was prepared by the method of Biltz and Biltz [9]. (Found: Co, 22.1%; Cl, 39.3%. Calculated for $[Co(NH_3)_5H_2O]Cl_3$: Co, 21.9%; Cl, 39.6%). Laboratory reagent grade (BDH) $Na_3[Co(NO_2)_6]$ was dried at 110 ° C in an oven.

The procedure, analysis and instrumentation have been described previously [1].

RESULTS AND DISCUSSION

Iron(II) chloride

The thermogram of the reaction of $FeCl_2$ with the carbonate eutectic showed two weight-loss steps. The gaseous product evolved in the first step was collected on the vacuum line and was found by IR and mass-spectral analysis to consist of a mixture of CO and CO_2. A red–brown precipitate deposited from the molten eutectic at the end of the first step. The reaction mixture was solidified, stirred with water and the precipitate was filtered off, washed, dried and analysed by X-ray and chemical methods. It was found to be Fe_2O_3. The filtrate showed the presence of chloride by chemical tests.

The experimental value of the weight loss obtained on the thermobalance under both carbon dioxide and argon atmospheres compared well with the calculated value as shown in Table 1. These results support the following stoichiometry of the first step of the reaction

$$2FeCl_2 + 2CO_3^{2-} \rightarrow Fe_2O_3 + 4Cl^- + CO_2 + CO \quad (1)$$

The gaseous product during the second weight-loss step was found to be CO_2. At the end of the step, the red insoluble product was separated, analysed as described above and was found to be $LiFeO_2$.

Therefore, the second step of the reaction may be represented by

$$Fe_2O_3 + Li_2CO_3 \rightarrow 2LiFeO_2 + CO_2 \quad (2)$$

TABLE 1

Thermogravimetric results

Reactant	No. of wt. loss steps	Temp. range (°C)	Atmosphere	Wt. loss (%)		Eqn. for the calc. wt. loss
				Found	Calc.	
$FeCl_2$	(i)	380–550	Ar, CO_2	27.06 ± 0.75	28.40	(1)
	(ii)	550–850	Ar, CO_2	45.17 ± 1.32	45.76	(3)
$FeCl_3$	(i)	200–500	Ar, CO_2	38.04 ± 0.47	40.69	(4)
	(ii)	650–840	Ar, CO_2	53.93 ± 0.40	54.25	(5)
$CoCl_2$	(i)	320–650	CO_2	29.65 ± 0.35	29.78	(6)
			Ar	31.23 ± 0.20		
$Na_3[Co(NO_2)_6]$	(i)	160–240	Ar, CO_2	19.22–22.92 (i)	30.20	(8)
				(ii)	18.32	(9)
	(ii)	590–710	Ar, CO_2	53.31–66.69 (i)	57.10	(14)
				(ii)	61.89	(15)
$[Co(NH_3)_5H_2O]Cl_3$	(i)	100–330	Ar, CO_2	63.53 ± 1.29	65.99	(17)
	(ii)	360–470	Ar, CO_2	70.87 ± 2.47	73.25	(19)
$NiCl_2$	(i)	400–570	Ar, CO_2	33.35 ± 0.49	33.95	(20)

When a reaction shows more than one weight loss step, the indicated value is the combined loss at the end of that step.

The overall reaction between $FeCl_2$ and the carbonate eutectic as based on the above results and those of Table 1 may be expressed by

$$2FeCl_2 + Li_2CO_3 + 2CO_3^{2-} \rightarrow 2LiFeO_2 + 4Cl^- + 2CO_2 + CO \qquad (3)$$

It has been reported that iron(II) chloride and other iron(II) compounds react with sodium–potassium nitrite [10] as well as lithium–potassium nitrate [11] melts forming only Fe_2O_3 as an insoluble product in a one-step reaction. In the present study, a further reaction of Fe_2O_3 with the eutectic may indicate that the carbonate melt is a stronger Lux–Flood base than the nitrite and nitrate eutectics.

Iron(III) chloride

Thermogravimetric results of the reaction of iron(III) chloride and the eutectic showed two distinct weight-loss steps. Carbon dioxide was the gaseous product in both steps. The red–brown precipitate in the first step was Fe_2O_3 which further reacted with the Li_2CO_3 constituent of the eutectic to produce $LiFeO_2$. The weight loss results of Table 1 are consistent with the stoichiometries of the reactions of the first and second steps as expressed by eqns. (4) and (2), respectively, and the overall reaction as shown by eqn. (5)

$$2FeCl_3 + 3CO_3^{2-} \rightarrow Fe_2O_3 + 6Cl^- + 3CO_2 \qquad (4)$$

$$2FeCl_3 + Li_2CO_3 + 3CO_3^{2-} \rightarrow 2LiFeO_2 + 6Cl^- + 4CO_2 \qquad (5)$$

Iron(III) oxide was found to be the only product of the reactions of iron(III) chloride with sodium–potassium nitrite eutectic [10] and with lithium–potassium nitrate eutectic [11]. This again supports that the carbonate melt is a stronger Lux–Flood base than those of nitrite and nitrate melts. As indicated in Table 1, iron(III) chloride reacted with the eutectic at a lower temperature of 200 °C than iron(II) chloride which was found to react at 380 °C. This may be taken to indicate that iron(III) is a stronger Lux–Flood acid than iron(II).

Cobalt(II) chloride

Cobalt(II) chloride was found to react with the eutectic showing one weight-loss step under carbon dioxide and argon atmospheres. However, the thermogravimetric results of Table 1 indicate that weight loss under carbon dioxide is about 2% less than that under argon. When the reaction was carried out under a vacuum, a mixture of CO and CO_2 was found to be present in the gaseous product.

The X-ray diffraction pattern of the insoluble product, separated under both the above gases, was similar. It gave *d* values of 4.66(w), 2.86(w), 2.44(s), 2.02(w) and 1.43(m) compared with the A.S.T.M. index values of 4.67(20), 2.86(40), 2.44(100), 2.02(25) and 1.42(45) for Co_3O_4 and 4.68(100), 2.40(16), 2.00(35) for $LiCoO_2$.

The insoluble product obtained under argon was found to contain 0.67 ± 0.05% lithium as compared with 7.09% lithium present in $LiCoO_2$. No lithium was found to be present in the product obtained under carbon dioxide. Thus, it was concluded that the insoluble product obtained under argon was a mixture of Co_3O_4 and $LiCoO_2$ with a small proportion of the latter. The X-ray results did not show conclusively the presence of $LiCoO_2$ in the mixture because the first three strongest lines for $LiCoO_2$ could also be for Co_3O_4, as shown above, and also because of its small proportion in the mixture as indicated by chemical analysis.

The results of Table 1 show that the experimental value of the reaction under CO_2 is comparable with the calculated value for the formation of Co_3O_4 as expressed by

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

The formation of $LiCoO_2$ in the reaction may be shown by eqn. (7) with a calculated weight loss of 44.65%

$$2CoCl_2 + 3Li_2CO_3 \rightarrow 2LiCoO_2 + 4LiCl + 2CO_2 + CO \qquad (7)$$

Therefore, the formation of a small amount of $LiCoO_2$ in the reaction would have resulted in an increased weight loss for the reactions carried out under argon as compared with the value calculated for eqn. (6). A calculation shows that a sum of 80% of reaction (6) and 20% of reaction (7) produces a calculated weight loss of about 31% as found under an argon atmosphere.

The influence of the atmosphere under which a reaction is carried out is highlighted by this reaction. It has been reported that the carbonate melt is less basic under carbon dioxide than under argon [6] and this would have resulted in the production of a small quantity of $LiCoO_2$ under the latter atmosphere.

The chemistry of $CoCl_2$ has been extensively studied in different molten salts. In general, $CoCl_2$ forms stable solutions in low melting salts and exists as a complex species in these solutions. However, during conductometric titrations of solutions of cobalt(II) in lithium–potassium nitrate melt containing alkali chloride, a complex species, $Li_4CoCl_2(NO_3)_4$ has been found to precipitate out of the solutions [12]. Cobalt(II) chloride has been found to react with sodium–potassium nitrite melt to produce Co_3O_4 [10] as found in the present study, but the existence of $LiCoO_2$ has not been claimed in the nitrite melt.

Sodium hexanitrito cobaltate(III)

The thermogram of the reaction of $Na_3[Co(NO_2)_6]$ with the eutectic showed two variable weight-loss steps as given in Table 1. The mass-spectral and IR analyses of the gaseous product, collected from the first step at about 200 °C, showed the presence of N_2O, NO and NO_2. The aqueous solution of the solidified melt produced an insoluble olive-green product found by the X-ray diffraction pattern to be cobalt(II) oxide, while the filtrate showed the presence of nitrite and nitrate by the usual chemical tests.

The absence of CO and CO_2 in the gaseous product was taken to indicate that the weight loss in the first step may be due to the decomposition of $Na_3[Co(NO_2)_6]$. Consequently, the presence of CoO, NO, NO_2 and nitrite in the products may be represented by the following decomposition reaction stoichiometry with a calculated weight loss of 30.20%

$$Na_3[Co(NO_2)_6] \rightarrow 3NaNO_2 + CoO + 2NO_2 + NO \qquad (8)$$

and that of nitrate, CoO, NO and N_2O may be shown by eqn. (9) with a calculated weight loss of 18.32%

$$Na_3[Co(NO_2)_6] \rightarrow 3NaNO_3 + CoO + NO + N_2O \qquad (9)$$

Based on the calculated and experimental weight-loss values, it would appear that the major decomposition reaction followed the stoichiometry of eqn. (9).

The reduction of cobalt(III) to cobalt(II) and its precipitation as CoO can be explained by the following reactions

$$Co^{3+} + NO_2^- \rightarrow Co^{2+} + NO_2 \qquad (10)$$

$$Co^{2+} + 2NO_2^- \rightarrow CoO + NO_2 + NO \qquad (11)$$

and the formation of nitrate and N_2O by the reactions (12) and (13)

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \quad (12)$$

$$NO_2^- + 2NO \rightarrow NO_3^- + N_2O \quad (13)$$

The formation of all the products shown in eqns. (8) and (9) may be explained by the proposed intermediate reactions (10)–(13). The heterogeneous nature of these intermediate reactions taking place between escaping gases and solid products may account for the variable weight losses observed in the decomposition of $Na_3[Co(NO_2)_6]$.

Gaseous products collected during the second weight-loss step at about 650 °C showed the presence of CO_2 and the oxides of nitrogen. The aqueous solution of the solidified melt, at the end of the second step, gave an insoluble product containing a mixture of $LiCoO_2$ and Co_3O_4. The filtrate was found to contain hydroxide, nitrite and nitrate.

In consideration of the oxidation states of carbon and nitrogen in the above gaseous products, it may be concluded that nitrite/nitrate would have acted as the oxidising species and lithium carbonate from the eutectic as a Lux–Flood base in the conversion of CoO into $LiCoO_2$ and Co_3O_4.

The presence of hydroxide in the filtrate may be due to the partial decomposition of nitrite/nitrate towards the end of the second weight-loss step producing oxide ions in the melt, since the decomposition temperatures of alkali metal nitrite/nitrate are much lower than those of carbonates [13]. The presence of a number of reacting species, i.e. CoO, NO_2^-, NO_3^- and CO_3^{2-} at the end of the first step, the possibility of further interactions between the gaseous, liquid and solid products during the second weight-loss step, and the thermal decomposition of nitrite/nitrate make the system quite complex. Therefore, the molar ratio of each nitrogen oxide and oxo anion could not be determined in order to express the reaction stoichiometry. The formation of Co_3O_4 and $LiCoO_2$ is shown by eqns. (14) and (15), respectively, in which the oxides of nitrogen are expressed as atomic species with complete decomposition of nitrite/nitrate for the sake of simplicity

$$6Na_3[Co(NO_2)_6] \rightarrow 2Co_3O_4 + 9Na_2O + 36|N|, 55|O| \quad (14)$$

$$2Na_3[Co(NO_2)_6] + Li_2CO_3 \rightarrow 2LiCoO_2 + CO_2 + 3Na_2O + 12|N|, 18|O| \quad (15)$$

As shown in Table 1, calculated weight losses for the reactions (14) and (15) are 57.10% and 61.89%, respectively, whereas the variation in the experimental values was found to be 53.31% to 66.96%.

In addition to the heterogeneous reactions (12) and (13), a reaction between NO_2 gas and the molten carbonate eutectic as shown in eqn. (16) can also change the weight-loss values from experiment to experiment

$$2NO_2 + CO_3^{2-} \rightarrow NO_2^- + NO_3^- + CO_2 \quad (16)$$

This reaction may also account for the existence of nitrite and nitrate at the end of the second step.

The complex has been reported to react with the lithium–potassium nitrate eutectic at 140 ° C, initially producing CoO, which on further heating is converted into Co_3O_4 [14]. However, in the nitrite eutectic, the complex is reported to produce Co_3O_4 at as low a temperature as 104° C [15]. The initial formation of CoO as found in the present study is supported by the reaction of the complex in the nitrate eutectic and there is no indication for the further reaction of Co_3O_4 to form $LiCoO_2$ in either nitrate or nitrite eutectic. This may be due to the fact that carbonate is a stronger Lux–Flood base than nitrate or nitrite [13].

Aquapentammine cobalt(III) chloride

On heating the complex with the eutectic, the thermogram showed two weight-loss steps as indicated in Table 1. At the end of the first step, the solution of the solidified melt in water gave an insoluble black product which was identified by the X-ray diffraction pattern to be Co_3O_4. The filtrate showed the presence of chloride. The gaseous product, collected at 290 ° C through a cold trap on the vacuum line and analysed by IR and mass-spectral methods, showed the presence of N_2, CO, CO_2 and NH_3. However, a white sublimate of NH_4Cl deposited on the cooler parts of the vacuum line, and droplets of water were present in the cold trap.

The above results and a comparison of the experimental and calculated values as shown in Table 1 support the following stoichiometry of the reaction in the first step

$$\begin{aligned}&6[Co(NH_3)_5H_2O]Cl_3 + 6CO_3^{2-}\\&\quad\rightarrow 2Co_3O_4 + 12Cl^- + 6NH_4Cl + 22NH_3 + 6H_2O + 4CO_2 + 2CO + N_2\end{aligned} \tag{17}$$

The gaseous product in the second step was a mixture of CO and CO_2, whereas the insoluble product consisted of a mixture of Co_3O_4 and $LiCoO_2$. This indicated that some of the Co_3O_4 reacted with Li_2CO_3 as represented by

$$2Co_3O_4 + 3Li_2CO_3 \rightarrow 6LiCoO_2 + 2CO_2 + CO \tag{18}$$

The partial conversion of Co_3O_4 into $LiCoO_2$ was also observed in the reactions of $CoCl_2$ and $Na_3[Co(NO_2)_6]$ as mentioned earlier.

The overall reaction of the complex with the eutectic for the complete conversion of Co_3O_4 into $LiCoO_2$ may be shown by eqn. (19) with a total calculated weight loss of 73.25% as compared with the experimental value of $70.87 \pm 2.47\%$

$$\begin{aligned}&6[Co(NH_3)_5H_2O]Cl_3 + 3Li_2CO_3 + 6CO_3^{2-}\\&\quad\rightarrow 6LiCoO_2 + 12Cl^- + 22NH_3 + N_2 + 6NH_4Cl + 6CO_2 + 3CO + 6H_2O\end{aligned} \tag{19}$$

A calculated weight loss for 80% conversion of Co_3O_4 into $LiCoO_2$ gives a value of 70.47% which compares very well with the above experimental value.

The reaction of a similar cobalt(III) cationic complex, $[Co(NH_3)_6]Cl_3$, has been reported in nitrate [14] and nitrite [15] melts indicating the formation of Co_3O_4 only as the insoluble product. As mentioned earlier, the conversion of Co_3O_4 into $LiCoO_2$ may be related to the stronger basic nature of the carbonate melt as compared with the nitrate and nitrite melts.

Nickel(II) chloride

The thermogram of the reaction of $NiCl_2$ and the eutectic showed a single weight-loss step between 400 and 570 °C. The gaseous product on the vacuum line was found to be CO_2 and the insoluble grey product gave the X-ray diffraction lines of NiO. The aqueous filtrate showed the presence of chloride.

The thermogravimetric weight loss of 33.35 ± 0.49% under both carbon dioxide and argon atmospheres compares well with the calculated value of 33.95% for the following reaction stoichiometry

$$NiCl_2 + CO_3^{2-} \rightarrow NiO + 2Cl^- + CO_2 \qquad (20)$$

In low-melting nitrite eutectic, $NiCl_2$ has been reported to form a green complex which ultimately deposits NiO on standing at 120 °C for 24 h or on heating above 200 °C [15]. However, there is no report to suggest the formation of an oxo anionic species similar to that of cobalt as discussed above.

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