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MOLTEN POTASSIUM PYROSULPHATE: REACTIONS OF SOME METAL CARBONATES AND BASIC CARBONATES

A.N. FORD, G. HELOU and S.A. TARIQ

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083 (Australia)

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ABSTRACT

The reactions of $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, $MnCO_3$, $ZnCO_3ZnO$, $CoCO_3 \cdot Co(OH)_2$, $CuCO_3 \cdot Cu(OH)_2$, $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, and $NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O$ with $K_2S_2O_7$ were investigated by thermogravimetric and differential thermal analysis techniques. It was found that the initial reaction temperatures for weight losses were, in general, lower than the decomposition temperatures of the corresponding anhydrous compounds. Exothermic peaks diagnostic of acid–base reactions were observed in all reactions except the $CuCO_3 \cdot Cu(OH)_2$ reaction which showed an endotherm in the DTA curve. Pathways have been postulated on the basis of the analysis of the reaction products and the final stoichiometries of the reactions have been determined.

INTRODUCTION

From our previous studies [1–8], it has been concluded that $K_2S_2O_7$ acts as a Lux–Flood acid by accepting oxide ions from such bases as alkali metal oxides, hydroxides, nitrites, nitrates, hydrogen carbonates, carbonates and oxalates [1–3,6], and it is converted into sulphate after accepting oxide ions. It also shows oxidising properties and is converted into such lower valent species as sulphite, sulphur dioxide and elemental sulphur [4,5,7,8]. We now present the results of the reactions of some metal carbonates and basic carbonates to support our previous conclusion on the reactivity of $K_2S_2O_7$.

EXPERIMENTAL

Materials

$K_2S_2O_7$ was prepared and analysed as previously reported [3]. $MgCO_3$ and $SrCO_3$ (Hopkins and Williams, GPR 98%); $CaCO_3$ and $BaCO_3$ (BDH, Analar, 99%) were used as received. $MnCO_3$ (Ajax, Unilab Reagent: Mn found; 45.4%; calc., 47.8%); $CoCO_3 \cdot Co(OH)_2$ (May and Baker: Co found,

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52.2%; calc., 55.6%); $CuCO_3 \cdot Cu(OH)_2$(BDH, L.R.: Cu found, 54.5%; calc.; 57.4%); $ZnCO_3 \cdot Zn(OH)_2$ (Ajax, Unilab Reagent: Zn found, 62.3%; calc., 63.2%); basic magnesium carbonate (Hopkins and Williams, GPR, labelled as $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ was heated at 170 °C to a constant weight: H_2O found, 14.4%; calc. for $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, 14.8%; basic nickel carbonate (Hopkins and Williams, labelled as $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$) was heated at 110 °C to a constant weight: H_2O found, 9.7%; calc. for $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, 19.1% and for $NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O$, 10.5%; Ni, found, 49.7%; calc. for $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, 46.8% and for $NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O$, 51.0%. The procedure, analysis and instrumentation have been described elsewhere [3].

RESULTS AND DISCUSSION

The gaseous products of the reactions of metal carbonates and basic zinc carbonate were found, using mass spectrometry and IR spectroscopy, to contain CO_2, and those of the other basic carbonates involving hydroxo ions showed the presence of water as well as CO_2. Raman spectra of the solidified reaction products contained a band at 981 ± 5 cm^{-1} characteristic of sulphate in the presence of excess pyrosulphate [9].

The solidified reaction products were stirred with water and were found to be soluble except for the Ca, Sr and Ba reaction products which dissolved partially and deposited white insoluble substances. On washing and drying, the insoluble substance in each case was found by X-ray diffraction to be the corresponding alkaline earth metal sulphate. However, $CaSO_4$ precipitated as $K_2Ca_5(SO_4)_6 \cdot H_2O$ from the solution but was found as $K_2Ca_2(SO_4)_3$ in the solid products. The solutions of the completely soluble reaction products were found, by wet analysis and visible spectroscopy, to contain each metal cation in the same oxidation state as in the original reactant initially added to $K_2S_2O_7$.

Table 1 shows the DTA results of these reactions. Exothermic peaks were present in the DTA curves of all the reactions except the basic copper carbonate reaction which showed an endotherm. The presence of exotherms indicated the acid–base nature of the reactions in which $K_2S_2O_7$ acted as a Lux–Flood acid by accepting oxide ions from the carbonates and basic carbonates which acted as Lux–Flood bases. However, the decomposition of basic copper carbonate alone has been reported to be an endothermic process [11]. The presence of an endotherm in this reaction at 320 °C may therefore be taken to indicate that the amount of heat absorbed in the decomposition process was more than evolved as a result of the acid–base reaction and that the decomposition and the reaction took place simultaneously with an overall heat absorption.

TABLE 1

Differential thermal analysis results

Reactant	Peak temperature [a] (°C)	
	Endothermic	Exothermic
$MgCO_3$		393
$CaCO_3$		546
$SrCO_3$		405
$BaCO_3$		460
$MnCO_3$		418
$ZnCO_3 \cdot ZnO$	256, 438	416
$CoCO_3 \cdot Co(OH)_2$	150, 198, 298	492
$CuCO_3 \cdot Cu(OH)_2$	207, 320	–
$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	198	404
$NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O$	206	423

[a] Peak temperatures are those in addition to the phase change and melting point of $K_2S_2O_7$ at 328 and 410 °C respectively [10]

Table 2 lists the decomposition temperatures of reactants, and the thermogravimetric and acidimetric results of the reactions of metal carbonates and basic carbonates with $K_2S_2O_7$. A comparison of the exothermic peak temperature of each reaction shown in Table 1 with the corresponding decomposition temperature of each reactant alone, and the temperature range of the weight loss/reaction listed in Table 2 indicates the following conclusions.

(a) The carbonates of Mg, Ca, Sr, Ba and Mn would have reacted directly with $K_2S_2O_7$ below their decomposition temperatures because in each of these reactions, the exothermic peak was in the corresponding weight-loss

TABLE 2

Thermogravimetric and acidimetric results

Reactant	Temp. (°C)			Weight loss (%)		Molar ratio $K_2S_2O_7$/reactant
	Decomposition	Reaction		Found	Calculated	
		Initial	Final			
$MgCO_3$	400	240	557	53.6 ± 1.2	52.1	1.06 ± 0.05
$CaCO_3$	900	300	500	43.7 ± 0.7	44.0	1.07 ± 0.05
$SrCO_3$	1290	320	500	30.6 ± 1.3	29.8	1.05 ± 0.03
$BaCO_3$	1360	320	520	22.3 ± 1.0	22.3	0.97 ± 0.08
$MnCO_3$	355	277	457	39.2 ± 1.4	38.2	0.99 ± 0.09
$ZnCO_3 \cdot ZnO$	248	196	297	22.9 ± 1.4	21.3	2.17 ± 0.17
$CoCO_3 \cdot Co(OH)_2$	147	172	407	30.2 ± 1.9	29.2	1.87 ± 0.08
$CuCO_3 \cdot Cu(OH)_2$	311	186	340	28.5 ± 2.1	28.1	2.09 ± 0.12
$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	214	366	480	54.0 ± 0.9	55.8	3.90 ± 0.08
$NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O$	197	160	420	31.6 ± 2.1	32.4	3.21 ± 0.07

temperature range. The stoichiometries of these reactions can therefore be represented by the following general equation

$$MCO_3 + K_2S_2O_7 \rightarrow K_2SO_4 + MSO_4 + CO_2 \quad (1)$$

where M represents Mg, Ca, Sr, Ba and Mn metal cations.

For the basic carbonates, the exothermic peaks due to the acid–base reactions were, in most cases, above the corresponding weight-loss temperature ranges. This indicates that the basic carbonates were initially converted into the corresponding metal oxides which then reacted with $K_2S_2O_7$.

Each reaction is discussed as follows.

(b) The presence of an exothermic peak at a temperature much higher than the reaction temperature range indicated that basic zinc carbonate initially decomposed to form ZnO which reacted with $K_2S_2O_7$. The steps of the reaction may be represented by

$$ZnCO_3 \cdot ZnO \rightarrow 2ZnO + CO_2 \quad (2)$$

$$2ZnO + 2K_2S_2O_7 \rightarrow 2K_2SO_4 + 2ZnSO_4 \quad (3)$$

and the overall reaction stoichiometry by

$$ZnCO_3 \cdot ZnO + 2K_2S_2O_7 \rightarrow 2K_2SO_4 + 2ZnSO_4 + CO_2 \quad (4)$$

The endothermic peak at 256 °C corresponds with the weight loss indicated by reaction (2). The endothermic peak at 438 °C may be due to the melting of a compound or a double salt formed between K_2SO_4 and $ZnSO_4$ with the possible formulae $K_2Zn(SO_4)_2$ or $K_2SO_4 \cdot ZnSO_4$. During the study of the reaction of ZnO with $K_2S_2O_8$, the possibility of the existence of $K_2Zn(SO_4)_2$ was also suggested by Barbooti and Jasim as indicated by the presence of an endothermic peak at 462 °C [12]. The lower value of the melting point of the compound found in the present study seems to be due to the presence of excess $K_2S_2O_7$.

(c) The pathways of the reaction between $CoCO_3 \cdot Co(OH)_2$ and $K_2S_2O_7$ may be expressed by the following scheme

$$CoCO_3 \cdot Co(OH)_2 \rightarrow CoCO_3 \cdot CoO + H_2O \quad (5)$$

$$H_2O + K_2S_2O_7 \rightarrow 2KHSO_4 \quad (6)$$

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \quad (7)$$

$$CoCO_3 \cdot CoO \rightarrow 2CoO + CO_2 \quad (8)$$

$$2CoO + 2K_2S_2O_7 \rightarrow 2K_2SO_4 + 2CoSO_4 \quad (9)$$

giving an overall reaction stoichiometry

$$CoCO_3 \cdot Co(OH)_2 + 2K_2S_2O_7 \rightarrow 2K_2SO_4 + 2CoSO_4 + CO_2 + H_2O \quad (10)$$

The reaction steps (5)–(7) are supported by the presence of an endotherm at 150 °C, due to decomposition of the hydroxide part of the reactant without the corresponding loss of weight in the TG curve because of the consumption of the evolved water in the hydrolysis of $K_2S_2O_7$, and by the presence of an endotherm at 198° C characteristic of melting followed by decomposition of $KHSO_4$ [10]. Reaction (8) is justified by the presence of the third endothermic peak at 298° C with the corresponding weight loss in the TG curve. The exothermic peak at 492° C supports the acid–base reaction (9).

(d) The presence of the melting and decomposition endotherm of $KHSO_4$ at 207° C without any weight loss in the TG curve indicates that the initial step in the reaction of the basic copper carbonate is the decomposition of $CuCO_3 \cdot Cu(OH)_2$ to give H_2O which is consumed completely for the hydrolysis of $K_2S_2O_7$ to $KHSO_4$. The presence of the endothermic peak at 320° C within the reaction temperature range of 248–340° C indicates that a direct reaction takes place between the decomposition product of the basic carbonate and $K_2S_2O_7$. The pathways of the reaction including eqns. (6) and (7) may be represented by

$$CuCO_3 \cdot Cu(OH)_2 \rightarrow CuCO_3 \cdot CuO + H_2O \tag{11}$$

$$CuCO_3 \cdot CuO + 2K_2S_2O_7 \rightarrow 2K_2SO_4 + 2CuSO_4 + CO_2 \tag{12}$$

and the overall reaction stoichiometry by

$$CuCO_3 \cdot Cu(OH)_2 + 2K_2S_2O_7 \rightarrow 2K_2SO_4 + 2CuSO_4 + CO_2 + H_2O \tag{13}$$

(e) In the reaction of basic magnesium carbonate trihydrate with $K_2S_2O_7$, the DTA curve shows an endothermic peak at 198° C. Immediately following the endotherm, the TG curve shows weight loss up to 220° C. The endotherm may be taken to indicate the melting of the $KHSO_4$ formed as a result of the hydrolysis of $K_2S_2O_7$ by the water of crystallisation of the basic magnesium carbonate. The weight loss in the TG curve represents the decomposition of $KHSO_4$. The second weight loss accompanied by an exothermic peak at 404° C is due to a direct reaction between anhydrous basic magnesium carbonate and $K_2S_2O_7$ as shown by

$$3MgCO_3 \cdot Mg(OH)_2 \rightarrow 4MgO + 3CO_2 + H_2O \tag{14}$$

$$4MgO + 4K_2S_2O_7 \rightarrow 4K_2SO_4 + 4MgSO_4 \tag{15}$$

Analysis of the solid reaction products by X-ray diffraction indicates that K_2SO_4 and $MgSO_4$ were present as $K_2Mg_2(SO_4)_3$.

The results in Table 2 support the following overall reaction between basic magnesium carbonate trihydrate and $K_2S_2O_7$

$$\begin{aligned} 3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O + 4K_2S_2O_7 \rightarrow {} & 2K_2SO_4 + 2K_2Mg_2(SO_4)_3 \\ & + 4H_2O + 3CO_2 \end{aligned} \tag{16}$$

(f) In the reaction of the basic nickel carbonate, with $K_2S_2O_7$, the TG curve shows a weight loss which begins prior to the melting and decomposition endothermic peak of $KHSO_4$ at 206° C. This indicates that the water of crystallisation is partially lost and partially used for the hydrolysis of

$K_2S_2O_7$. The presence of the exotherm at 423°C, i.e. slightly above the weight-loss temperature range, indicates that the processes of dehydration and the decarboxylation of the basic carbonate to produce NiO overlap with the reaction of NiO with $K_2S_2O_7$. This reaction may be represented by the following pathways including eqns. (6) and (7) shown above

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O \rightarrow 3NiO + CO_2 + 4H_2O \qquad (17)$$

$$3NiO + 3K_2S_2O_7 \rightarrow 3K_2SO_4 + 3NiSO_4 \qquad (18)$$

The sum of these steps is represented by

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O + 3K_2S_2O_7 \rightarrow 3K_2SO_4 + 3NiSO_4 + CO_2 + 4H_2O \qquad (19)$$

It can therefore be concluded from this study that these carbonates and basic carbonates showed only Lux–Flood acid–base types of reactions with $K_2S_2O_7$ and that such transition metal cations as manganese(II), cobalt(II), nickel(II) and copper(II) could not be oxidised by $K_2S_2O_7$.

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