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Molten potassium pyrosulphate: Reactions of oxides of ten main-group elements

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Abstract

The reactions of MgO, CaO, SrO, BaO, ZnO, CdO, SnO, PbO, Pb_3O_4 and As_2O_3 with $K_2S_2O_7$ were investigated using TG and DTA methods of thermal analysis. The exothermic peaks diagnostic of acid–base reactions were observed in the reactions of MgO, CaO, SrO, BaO, ZnO, CdO, SnO, PbO and Pb_3O_4. However, As_2O_3 showed an endothermic redox reaction in which As_2O_3 was oxidised to As_2O_5 and the pyrosulphate reacted to evolve SO_2. In each metal oxide reaction the corresponding metal sulphate was produced. On the basis of acidimetric and TG results the stoichiometries are proposed for these reactions. © 1997 Elsevier Science B.V.

Keywords: Molten potassium pyrosulphate; Oxides of main group elements; Reactions stoichiometries; Thermal methods

1. Introduction

A systematic study of the inorganic reaction chemistry of molten potassium pyrosulphate ($K_2S_2O_7$) has shown that the pyrosulphate melt acts as a Lux–Flood acid as well as an oxidising medium [1–9]. Thus, for example, the pyrosulphate melt accepts oxide ions from bases such as alkali metal hydroxides, nitrites, nitrates, hydrogen carbonates, carbonates, basic carbonates and oxalates [1–3,6,9] and itself is converted into sulphate. It oxidises metals and lower metal cations to higher oxidation states and is converted into such lower valent species as sulphite, sulphur dioxide and elemental sulphur [4,5,7,8]. The systematic investigation has now been extended to include ten oxides of main group elements.

2. Experimental

2.1. Materials

Potassium pyrosulphate ($K_2S_2O_7$) was prepared and analysed as previously reported [7]. The sample of $K_2S_2O_7$ was found to melt at 413°C as compared with the literature value of 410°C [10]. Acidimetric analysis showed 98.7 ± 0.9% $K_2S_2O_7$.

B.D.H. (Laboratory Reagents): SnO (97%), As_2O_3 (99.8%), CaO (98%), Pb_3O_4 (98%), MgO (98%); May and Baker (Laboratory Chemicals): ZnO (99%); GFS Chemical: SrO (99.05%); Hopkin and Williams G.P.R: PbO (98%). Camelec LTD: BaO (98%); Ventron Alfa Products: CdO (99.9%) were used after

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drying at 120°C. The procedure, analysis and instrumentation have been described elsewhere [7].

3. Results and discussion

Table 1 shows DTA peak temperatures of $K_2S_2O_7$ alone and those of the reactions of MgO, CaO, SrO, BaO, ZnO, CdO, SnO, PbO, Pb_3O_4 and As_2O_3 with $K_2S_2O_7$ along with their acidimetric results. For $K_2S_2O_7$ alone, the endotherms at 328 and 413°C are due to phase change and melting of $K_2S_2O_7$, respectively [10]. The temperature values of these endotherms are affected by thermal activities in the reaction mixtures containing excess $K_2S_2O_7$. Thus in the reactions of MgO, CdO and SnO, values of both the endotherms change to a small extent. This indicates that a small amount of heat is involved in thermal activities of these reactions. In the BaO reaction the values of both the endotherms are substantially lowered by the exotherm reaction at 300°C. In the reactions of CaO and SrO the melting endotherms are absent whereas in the PbO reaction both the endotherms disappear from the DTA curve.

The absence of one or both the endotherms is due to strong exothermic processes taking place in these reactions. Thus, for example, the absence of the melting endotherms in the reactions of CaO and SrO may be due to the presence of exothermic peaks at 388 and 326°C, respectively. The absence of both the endotherms in the PbO reaction may be due to an exothermic reaction between PbO and $K_2S_2O_7$ at a low temperature of 231°C. This indicates that an exothermic activity takes place in the solid state producing enough heat to hide both the endotherms.

Table 1

DTA and acidimetric results of the reactions of the oxides of ten main group elements with $K_2S_2O_7$

Reactant	DTA peak temperature (°C)		Molar ratio $K_2S_2O_7$/oxide
	Endothermic	Exothermic	
$K_2S_2O_7$ alone	328, 413		
MgO	329, 402	378	1.20 ± 0.03
CaO	324,—	388	0.98 ± 0.01
SrO	322,—	326	1.02 ± 0.03
BaO	292, 344	300	1.05 ± 0.00
ZnO	336, 408	406	1.08 ± 0.01
CdO	330, 414	468	0.95 ± 0.01
SnO	328, 412	416	0.50 ± 0.02
PbO	—,—	231	0.96 ± 0.01
Pb_3O_4	338, 398	410	3.15 ± 0.08
As_2O_3	260, 308, 328	—	—

However, the most important thermal activity, in the present study, is the presence of exothermic peaks in the DTA curves of the acid–base reactions which take place between metal oxides and $K_2S_2O_7$. The values of the exothermic peak temperatures are shown in Table 1. In similar reactions involving donors of oxide ions such as oxalates and carbonates with $K_2S_2O_7$, the exothermic peaks have been assigned to acid–base reactions [3,11].

The absence of an exotherm in the DTA curve of the reaction of As_2O_3 and $K_2S_2O_7$ may be taken to indicate that it is not an acid–base reaction. However, Table 1 shows three values of endotherms at 260, 308 and 328°C. The TG curve of the reaction showed a mass loss of 65.3 ± 0.5% between 200 and 280°C with the evolution of SO_2. The endotherm at 260°C may therefore be due to an oxidation–reduction reaction between As_2O_3 and $K_2S_2O_7$. As the values of the other two endotherms are lower than those of the pure $K_2S_2O_7$, it may be concluded that the redox endotherm at 260°C is responsible for lowering these values. This reaction is discussed further in the acidimetric section.

The solid reaction products were stirred with water and an insoluble residue, obtained in most cases except those of MgO, ZnO and As_2O_3 was filtered and identified by the ν_4 vibration of the sulphate ion in its I.R. spectrum. The spectra of seven residues showed absorption in the range 601 to 620 cm^{-1} as it is sensitive to chemical environment [12]. This was taken to indicate that metal oxides were converted into corresponding metal sulphates.

The last column of Table 1 shows the $K_2S_2O_7$/oxide molar ratios. The results indicate that 1 mol of the metal oxides (MO = MgO, CaO, SrO, BaO, ZnO, CdO and PbO) reacts with 1 mol of $K_2S_2O_7$ suggesting that the reaction stoichiometries may be represented by a general Eq. (1).

$$MO + K_2S_2O_7 \Rightarrow MSO_4 + K_2SO_4 \qquad (1)$$

The acidimetric result of the reaction of SnO indicates that 2 mol of the oxide react with 1 mol of $K_2S_2O_7$.

The stoichiometry is shown by Eq. (2)

$$2SnO + K_2S_2O_7 \Rightarrow SnO \cdot SnSO_4 + K_2SO_4 \tag{2}$$

The presence of tin oxosulphate was confirmed by the I.R. spectrum of the product. The spectrum showed absorptions at 490 and 720 cm^{-1} due to tin–oxygen stretching [13] in addition to the ν_4 vibration of the sulphate ion at 618 cm^{-1}.

The TG curve for the reaction of Pb_3O_4 showed a mass loss of 2.9 ± 0.3% between 400 and 500°C as compared with 2.3% calculated for the decomposition of Pb_3O_4 to PbO as represented by

$$Pb_3O_4 \Rightarrow 3PbO + \tfrac{1}{2}O_2 \tag{3}$$

PbO thus produced reacts as shown by the general Eq. (1). Based on the above TG result and the acidimetric result of Table 1 indicating that 1 mol of Pb_3O_4 reacts with 3 mol of $K_2S_2O_7$ the overall stoichiometry of the reaction is expressed by

$$Pb_3O_4 + 3K_2S_2O_7 \Rightarrow 3PbSO_4 + 3K_2SO_4 + \tfrac{1}{2}O_2 \tag{4}$$

The TG curve of the reaction of As_2O_3 showed a mass loss of 65.3 ± 0.5% between 200 and 280°C as compared with 64.7% for the loss of 2 mol of SO_2 per mole of As_2O_3 with a corresponding endotherm at 260°C in the DTA curve as discussed earlier. The I.R. spectrum of the solid reaction products showed the presence of As_2O_5 as its characteristic absorptions were detected in the spectrum at 417, 583, 664 and 814 cm^{-1} [14].

The reaction stoichiometry may be deduced from the TG result which indicated the loss of 2 mol of SO_2 per mole of As_2O_3 as shown by

$$As_2O_3 + 2K_2S_2O_7 \Rightarrow As_2O_5 + 2K_2SO_4 + 2SO_2 \tag{5}$$

However, the determination of the reacted pyrosulphate by acidimetry indicated that the original amount of the pyrosulphate was present. It is contrary to the TG result which indicates the loss of 2 mol of SO_2 per mole of As_2O_3 as expressed in Eq. (5).

The acidimetric result indicating no consumption of the pyrosulphate may be reconciled by the dissolution of As_2O_5 to produce H_3AsO_4 which is a weak tribasic acid and is known to form such acid salts as Na_2HAsO_4 and $PbHAsO_4$ [15]. During acidimetric titration using phenol red as an indicator, H_3AsO_4 is neutralised to produce such a salt as indicated by the following reactions.

$$As_2O_5 + 3H_2O \Rightarrow 2H_3AsO_4 \tag{6}$$

$$H_3AsO_4 + 2NaOH \Rightarrow Na_2HAsO_4 + 2H_2O \tag{7}$$

In the acidimetric determination, this weak acid provides acidity equivalent to two protons per molecule or equivalent to the amount of consumed $K_2S_2O_7$ (cf. Eq. (5)).

It may be concluded that the characteristic endotherms of $K_2S_2O_7$ are affected differently by the thermal processes taking place in these reactions. Metal oxides react with $K_2S_2O_7$ to show acid–base reactions with exotherms in their DTA curves whereas As_2O_3 is oxidised to As_2O_5 with an endotherm. As usual the pyrosulfate acts as an acid as well as an oxidising agent.

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