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MOLTEN POTASSIUM PYROSULFATE: REACTIONS OF SEVEN METAL SULFIDES

P.J. MINEELY

Department of Physical Chemistry, Monash University, Clayton, 3168 Victoria (Australia)

S.A. TARIQ

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

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ABSTRACT

The reactions of $Na_2S \cdot 9H_2O$, K_2S_3, ZnS, CdS, Sb_2S_3, PbS and FeS with molten potassium pyrosulfate were studied. The presence of sulfate, sulfur dioxide and sulfur was confirmed in all the reactions of the anhydrous sulfides. However, when a hydrated sulfide was used H_2S was found to be an additional product. The temperatures and stoichiometry of reaction for each sulfide were determined by thermal methods of analysis.

INTRODUCTION

The highly reactive nature of $K_2S_2O_7$ has been known for a long time in such processes as the decomposition of ores [1,2] and the dissolution of carbide alloys [3] and noble metals [4], and its industrial importance in combination with V_2O_5 for the oxidation of SO_2 to SO_3 during the manufacture of sulfuric acid has also been known for a long time [5]. Despite these important applications the reaction chemistry of pyrosulfate has only recently begun to be systematically investigated. Studies to date include acid–base reactions of molten $K_2S_2O_7$ with hydroxides, hydrogen carbonates, carbonates, oxalates, nitrites and nitrates [6–8] and its oxidation–reduction reactions with metals, halides and lower-valent sulfur-oxy anions [9–12].

Sulfide ores are amongst the major minerals mined today for the recovery of base metals. Metallurgical extraction for the recovery of sulfide minerals involves either roasting, solvent extraction or electrolysis. Recently, molten salt media have been advocated for the decomposition of sulfide ores to overcome the problems of scum formation prevalent in electrolytic methods [13]. It is therefore of fundamental interest to study the reactions of metal sulfides in molten salt media. Past studies include the decomposition of pyrite and chalcopyrite in KNO_3 and $NaNO_2$ melts [14] and reactions of

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transition metal sulfides in KNO_3 melt [15]. In all these cases sulfide was quantitatively oxidized to sulfate and the metal was deposited as oxide. In this communication we report the findings of the reactions of seven metal sulfides with molten potassium pyrosulfate, using mainly differential thermal analysis (DTA) and thermogravimetric techniques.

EXPERIMENTAL

Material

Potassium pyrosulfate was prepared and analyzed as described previously [10]. Acidimetric analysis showed 98.9 ± 0.8% $K_2S_2O_7$.

The following sulfides were used: $Na_2S \cdot 9H_2O$ (AJAX 95%); FeS (May and Baker 95%); ZnS (Hopkins and Williams 98%); CdS (BDH 98%); Sb_2S_3 (Alfa 98%); PbS (BDH 98%). Potassium sulfide from Ventron was reported to contain 44% K_2S, the balance being K_2S_{1+n}. Analysis of the material showed a total sulfide content of 54.5 ± 1.5%, calculated as 55.17% for the average composition K_2S_3.

Procedure, analysis, physical measurements and instrumentation have been described previously [10].

RESULTS AND DISCUSSION

Raman spectra of the solidified products of all the reactions showed a band at 980 ± 2 cm^{-1}, diagnostic of sulfate in the presence of excess $K_2S_2O_7$ [16]. Mass spectra of gaseous products in all the reactions indicated

TABLE 1

Thermogravimetric and acidimetric results for sulfide–pyrosulfate reactions

Compound	$S_2O_7^{2-}/S^{2-}$ molar ratio		Weight loss %	
	Found	Theoretical	Found	Theoretical
$Na_2S \cdot 9H_2O$	1.59 ± 0.05	1.50	89.17 ± 2.87	90.76
K_2S_3 [a]	1.96 ± 0.05	2.00	79.83 ± 5.77	90.01
ZnS	2.10 ± 0.10	2.00	98.80 ± 4.71	98.59
CdS	2.00 ± 0.15	2.00	64.99 ± 0.06	66.44
Sb_2S_3	1.92 ± 0.10	2.00	88.42 ± 2.53	84.78
PbS	1.92 ± 0.08	2.00	40.51 ± 0.24	40.12
FeS [b]	–	–	–	–

[a] Sulfur retained in melt; the theoretical value is for complete retention.

[b] Incomplete reaction, less than 4% (10 mg) reacted which was insufficient for quantitative analysis (see text).

TABLE 2

Differential thermal analysis of sulfide–pyrosulfate reaction

Compound	Peak [a] (°C)	
	Endothermic	Exothermic
$Na_2S \cdot 9H_2O$	44, 116, 144, 200	360
K_2S_3	–	–
CdS	–	–
Sb_2S_3	570	438
PbS	–	440
Zns	419	440
FeS	480, 570	420

[a] Peaks are those in addition to the α–β phase transition and melting point of $K_2S_2O_7$ at 328 and 410 °C respectively [17].

the presence of SO_2 and in addition H_2S was found in the gaseous product of the $Na_2S \cdot 9H_2O$ reaction. However, sulfur was identified in all the reaction products by the presence of a yellow sublimate (m.p. 118 ± 2 °C) deposited on the cooler parts of each test tube.

Table 1 shows the thermogravimetric and acidimetric titration results for all the reactants with $K_2S_2O_7$ except FeS, which was found to react at > 440 °C with the evolution of only small amounts of SO_2 and S. Table 2 lists the temperatures of peaks present in DTA curves, in addition to those endotherms for the α–β transition (325 °C) and the melting point of $K_2S_2O_7$ (410 °C) [16].

Sodium sulfide nonahydrate

The sodium sulfide reacted quickly with molten $K_2S_2O_7$ at 440 °C. Endotherms present in the DTA at 44, 116 and 144 °C (Table 2) were assigned to the dehydration process. The endotherm at 200 °C can be compared with the reported melting point of $KHSO_4$, 207 °C [17]. The formation of $KHSO_4$ can arise from hydrolysis of $K_2S_2O_7$ by water produced as a result of dehydration of $Na_2S \cdot 9H_2O$ as indicated by reactions (1) and (2)

$$Na_2S \cdot 9H_2O \rightarrow Na_2S + 9H_2O \quad (1)$$

$$9H_2O + 9K_2S_2O_7 \rightarrow 18KHSO_4 \quad (2)$$

The presence of H_2S in the vapor above the melt can therefore be explained by eqn. (3)

$$Na_2S \cdot 9H_2O + 2KHSO_4 \rightarrow K_2SO_4 + Na_2SO_4 + H_2S + 9H_2O \quad (3)$$

The presence of SO_2 and S can be explained by the reactions shown in eqns.

(4) and (5). The exotherm at 360 °C (Table 2) is thought to indicate a redox process and a Lux–Flood acid–base reaction occurring simultaneously.

$$S^{2-} + S_2O_7^{2-} \rightarrow O^{2-} + SO_4^{2-} + SO_2 + S \qquad (4)$$

$$O^{2-} + S_2O_7^{2-} \rightarrow 2SO_4^{2-} \qquad (5)$$

The reactions of sulfide and oxide ions with pyrosulfate as indicated above have been reported previously [10,11]. On the basis of weight loss, titrimetric analysis and the identification of reaction products the overall reaction can be expressed as

$$2Na_2S \cdot 9H_2O + 3K_2S_2O_7 \rightarrow 2Na_2SO_4 + 3K_2SO_4 + SO_2 + S + H_2S + 17H_2O \qquad (6)$$

Potassium sulfide

The DTA profile for the reaction of K_2S_3 with molten $K_2S_2O_7$ drifted endothermically to 500 °C. However, a region of thermoneutrality existed between 420 and 440 °C. This region may represent an exothermic process which could have balanced the energy of the endothermic drift. Reactions of the form given in eqns. (4) and (5) are possibilities. The solidified melt showed the presence of sulfate and partial retention of sulfur. Gas analysis of the vapor above the melt indicated SO_2. A calculated loss of 80.92% was close to that found experimentally ($79.83 \pm 5.77\%$) with the evolution of about 80% of the sulfur produced in the reaction. The reaction can be expressed as follows

$$K_2S_3 + 2K_2S_2O_7 \rightarrow 3K_2SO_4 + SO_2 + 3S \qquad (7)$$

Zinc sulfide

The endotherm at 419 °C may be due to dissolution of ZnS in $K_2S_2O_7$, whilst the exotherm at 440 °C represents reactions similar to those expressed in eqns. (4) and (5). The rhombic–cubic transformation of K_2SO_4 was identified by the endotherm at 570 °C [16]. This endotherm appears if the amount of K_2SO_4 present is $> 4\%$ by weight [16], and is therefore not always present in $K_2S_2O_7$ reactions. The total weight loss compared favourably with the calculated value of 98.51%, whilst qualitative analysis confirmed the reaction products shown in eqn. (8)

$$ZnS + K_2S_2O_7 \rightarrow ZnSO_4 + 2K_2SO_4 + SO_2 + S \qquad (8)$$

Zinc sulfate has been reported to be present in the complex form $K_2[Zn(SO_4)_2]$ [7]. It is probable that such a phase may be formed in the present reaction, but which could not be conclusively identified.

Cadmium, lead and antimony sulfides

Solidifed products of the reactions of CdS, PbS and Sb_2S_3 showed the presence of sulfate and the absence of yellow particles of sulfur which would have evolved completely in these reactions. Aqueous solutions of the products from CdS and Sb_2S_3 showed the presence of metal cations in their original oxidation states. The white precipitate of $PbSO_4$ was identified from X-ray diffraction patterns. Reactions of CdS and PbS with $K_2S_2O_7$ can be represented by general eqn. (9) where M represents Cd and Pb and the reaction of Sb_2S_3 by eqn. (10).

$$MS + 2K_2S_2O_7 \rightarrow MSO_4 + 2K_2SO_4 + SO_2 + S \tag{9}$$

$$Sb_2S_3 + 2K_2S_2O_7 \rightarrow Sb_2(SO_4)_3 + 2K_2SO_4 + S \tag{10}$$

Iron(II) sulfide

The reaction of FeS with $K_2S_2O_7$ was slow at temperatures up to 500 °C, above which pyrosulfate decomposes rapidly [17]. The unreacted sulfide was removed by filtration of the molten solution under vacuum and the filtrate solidified. Analysis of the aqueous solution of the solidified melt confirmed the presence of Fe^{3+}.

Endotherms at 480 and 570 °C were assigned to partial decomposition of $Fe_2(SO_4)_3$ [18] and the rhombic–cubic phase transition of K_2SO_4 [16]. The endotherm at 420 °C corresponds to the redox and acid–base reactions shown by eqns. (4) and (5).

On the basis of the qualitative identification of Fe^{3+}, SO_2, S and SO_4^{2-} as the main products, this slow and incomplete reaction between FeS and $K_2S_2O_7$ can be expressed as

$$FeS + 6K_2S_2O_7 \rightarrow Fe_2(SO_4)_3 + 6K_2SO_4 + 3SO_2 + S \tag{11}$$

The slow and incomplete nature of the reaction could be due to the formation of a protective sulfate layer arising from the Lux–Flood reaction between Fe_2O_3 and $K_2S_2O_7$, as shown by eqn. (5).

CONCLUSIONS

This study has shown that, in general, 1 mol of sulfide ions reacts with 2 mol of pyrosulfate, the exception being iron(II) sulfide for which the stoichiometry is suggested to be 3 mol of pyrosulfate. Thus the general stoichiometry of reaction given below

$$S^{2-} + S_2O_7^{2-} \rightarrow O^{2-} + SO_4^{2-} + SO_2 + S$$

$$O^{2-} + S_2O_7^{2-} \rightarrow 2SO_4^{2-}$$

may apply only to those reactions in which the oxidation state of the cation remains unchanged. Furthermore the stoichiometry of reaction deduced for metal sulfides supports the previously postulated pathway [10] for the reactions of NaCl and CsCl, involving the formation of the sulfide ion. The oxidation state of FeS after reaction in the melt was found to be Fe^{3+}.

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