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SIMULTANEOUS THERMOANALYTICAL EXAMINATIONS OF Si–$X_2S_2O_8$ (X = Na, K) BINARY SYSTEMS

FADHIL JASIM * and HADI H. JASIM

Department of Chemistry, College of Sciences, University of Baghdad, Jadiriya, Baghdad (Iraq)

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ABSTRACT

The non-isothermal thermoanalytical curves (T, TG, DTG and DTA) of various molar ratios of binary mixtures of Si–$X_2S_2O_8$ have been examined using a MOM derivatograph. Silicon can catalytically lower the T_i values of both persulfates by about 15–20°C, and that of the corresponding pyrosulfates by 10°C. No solid-state reaction has been observed between Si and the two peroxosalts or their pyrosulfates but their by-products, X_2SO_4 (X = Na, K), reacted and yielded the respective mixed oxides, $Na_2Si_3O_7$ and $K_2Si_2O_5$, and gaseous SO_3 and SO_2. Intermediate and final products are identified by X-ray diffraction. Silicon powder is not oxidised in static air even at temperatures as high as 1050°C.

INTRODUCTION

For the last three decades Si has been used in the presence of some dopants as a p- or n-type semiconductor. It is the most commonly used semiconductor and today constitutes about 90% of the electronic industry for manufacturing transistors and integrated circuits. Another important use is in the building of Si-based solar energy cells for terrestrial applications such as direct conversion of solar energy into electricity. As insulators and semiconductors for axial and other cables, Si rubbers are in huge industrial demand. Silicone greases and oils are used for vacuum lines, baths and as lubricating oils since they have good antioxidation stability [1]. The TG, DTG and DTA analyses were performed on semiconductor chalcogenides [2]. The chemical literature lacks data on the derivatographic thermoanalytical behaviour of pure Si, alone or in mixtures with peroxosalts, and their solid thermal decomposition products. In the present paper we aim to determine the thermal stability, catalytic activity and types of compounds formed during non-isothermal solid-state reactions between Si and other reactants.

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* To whom correspondence should be addressed.

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EXPERIMENTAL

All of the molar ratio binary mixtures were prepared from analytical grade reagents. Si (0.05 μm mesh) was puriss grade from Fluka AG, Buchs; α-alumina, excited at 1300°C, was inert reference material, $Na_2S_2O_8$ and $K_2S_2O_8$ were from BDH.

Apparatus, measurement techniques, procedure and X-ray diffraction analyses were as described previously [3].

RESULTS AND DISCUSSION

Thermoanalysis of Si

No signs of physical or chemical changes are observed for Si samples subjected to heating from ambient to the ceiling temperature of the programme (the derivatograms are not shown for the sake of brevity). This is contrary to its group IV congeners (Ge, Sn and Pb) which show some transformations on heating in a static air atmosphere.

Thermoanalysis of the $Si–Na_2S_2O_8$ system

The derivatograms of various $Si–Na_2S_2O_8$ molar ratios are depicted in Fig. 1, from which no detectable reaction could be seen between Si and $Na_2S_2O_8$. Nevertheless, the former could catalytically lower the T_i of the latter from 180 to 165°C (for the ratios 1 : 4 and 1 : 1), and to 160°C (for the ratios 1 : 2 and 2 : 1). Table 1 indicates that the practical and calculated values of the liberated oxygen are almost the same. The melting temperature of $Na_2S_2O_7$ is also lowered (from 385 to 375°C), i.e. by 10°C for the ratios 1 : 4 and 1 : 2, and from 385 to 365°C, i.e. by 20°C for the 1 : 1 and 2 : 1. Careful examination of the TG curve of the 1 : 4 mixture reveals a small plateau between 215 and 260°C which may be due to an unstable intermediate adduct of Si pyrosulfate, which is so far unknown. Other ratios do not show this plateau. After melting, the pyrosulfate follows the usual route of a two-step decomposition.

The exotherms appearing around 885°C for all ratios proved to pertain to redox solid-state reaction between Si and the by-product Na_2SO_4; the areas under these exotherms increase as the proportion of Si increases. The disappearance of the melting endotherms of Na_2SO_4 for the ratios 1 : 1 and 2 : 1 is due to thermal neutrality, brought about by exo and endotransformations occurring in the same region. XRD patterns for samples heated to 890°C confirm the presence of the mixed oxides $Na_2Si_3O_7$ (Table 2) in addition to those of unreacted Na_2SO_4 and Si [4]. Identical bright *d*-lines were obtained for the final products at 1050°C which ratify that $Na_2S_2O_7$ is

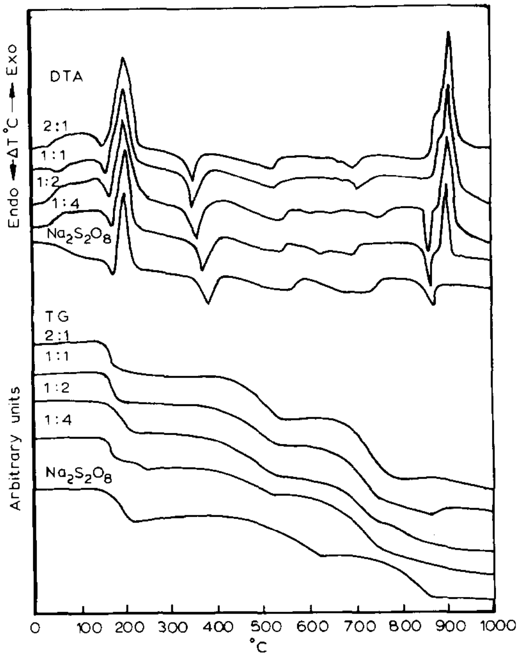

Fig. 1. TG and DTA curves for various molar ratios of the Si–$Na_2S_2O_8$ binary system.

TABLE 1

Preparation of standard molar ratios and TG results of Si–$Na_2S_2O_8$ binary mixtures

Si–$Na_2S_2O_8$ molar ratio	Si (mg)	$Na_2S_2O_8$ (mg)	O_2 lost from $Na_2S_2O_8$ decomp.				SO_3 lost from $Na_2S_2O_7$ decomp.				Na_2SO_4 reacted (wt.%)
			Theor. (mg)	Exp. (mg)	T_i (°C)	T_f (°C)	Theor. (mg)	Exp. (mg)	T_i (°C)	T_f (°C)	
1:4	5.70	194.30	12.4	12.2	165	230	62.0	60	380	750	8.3
1:2	11.11	188.89	12.1	12.0	165	230	60.5	57	380	750	16.6
1:1	21.05	178.95	11.4	11.0	160	230	57.2	56	380	740	33.1
2:1	38.09	161.91	10.32	10.3	160	230	51.6	51	380	730	65.2

TABLE 2

d-Spacings [a] versus intensities of bright lines of the 1:1 mixture of Si:$Na_2S_2O_8$ heated to 1000°C

d (Å)	4.72	3.46	3.41	2.76	2.54	2.2
I/I_o	70	100	100	35	38	25

[a] Typical for $Na_2Si_3O_7$ [5].

thermally stable to beyond the ceiling temperature of the programme. It could be concluded from the above that Si actually reacts with molten Na_2SO_4, therefore several runs for various Si : Na_2SO_4 ratios were similarly conducted. The 3 : 1 mixture of Si : Na_2SO_4 was found to be the stoichiometric ratio for which the stoichiometric reaction is given as:

$$Na_2SO_4 + 3\ Si + 3\ O_2 \xrightarrow{\Delta} Na_2Si_3O_7 + SO_3$$

A mechanism for this reaction may be proposed. In the presence of excess Si powder, molten Na_2SO_4 is catalytically disproportionated to form Na_2O_2 and SO_2 (SO_2 gas has been detected experimentally) and in the presence of air or oxygen, a compositional oxidation of Si occurs with Na_2O_2 to yield $Na_2Si_3O_7$ ($Na_2SiO_3 \cdot 2SiO_2$); meanwhile SO_2 is instantaneously oxidised by a secondary process to SO_3 with the liberation of excess heat which is indicated by the sharp overlapping exotherms around 870°C (in the case of the 1 : 1 ratio) on the DTA derivatogram of Fig. 1. The small weight increase between 840 and 870°C is presumably due to the oxidation of SO_2 to SO_3.

Thermoanalysis of the Si–$K_2S_2O_8$ system

From the derivatograms of the various molar ratios prepared (Table 3) and subjected to the heating programme (Fig. 2) it seems that, although no reaction occurs between $K_2S_2O_8$, or its by-product $K_2S_2O_7$, and Si, Si can catalytically lower their T_i values by 10 and 20°C, respectively. For instance the α to β phase transition (see DTA curve for the 1 : 4 ratio) of $K_2S_2O_7$ is catalytically shifted from 330 to 310°C; this causes the melting and decomposition endotherms of $K_2S_2O_7$ to overlap forming a wide, combined endotherm that extends between 330 and 480°C. Beyond 870°C the usual two-step endotherm of the K_2SO_4 [6] phase change disappears and instead a wide exothermic hump (1 : 4 ratio) appears. As the ratio becomes 1 : 2 it splits into two exo-peaks representing two consecutive reactions, the first due to the formation of $K_2Si_2O_5$ and SO_2 and the oxidation of the latter,

TABLE 3

Preparation of standard molar ratios and TG results of the Si–$K_2S_2O_8$ binary mixture

Si–$K_2S_2O_8$ molar ratio	Si (mg)	$NaK_2S_2O_8$ (mg)	O_2 lost from $K_2S_2O_8$ decomp.				SO_3 lost from $K_2S_2O_7$ decomp.				K_2SO_4 reacted (wt.%)
			Theor. (mg)	Exp. (mg)	T_i (°C)	T_f (°C)	Theor. (mg)	Exp. (mg)	T_i (°C)	T_f (°C)	
1:4	5.07	194.93	11.4	11.2	170	200	57	56	385	870	12.8
1:2	9.85	190.15	11.2	11.1	170	200	56	52	380	870	24.8
1:1	18.90	181.10	11.0	10.9	170	200	55	52	385	880	50.4
2:1	36.10	163.90	9.6	9.5	170	200	48	45	380	880	91.2

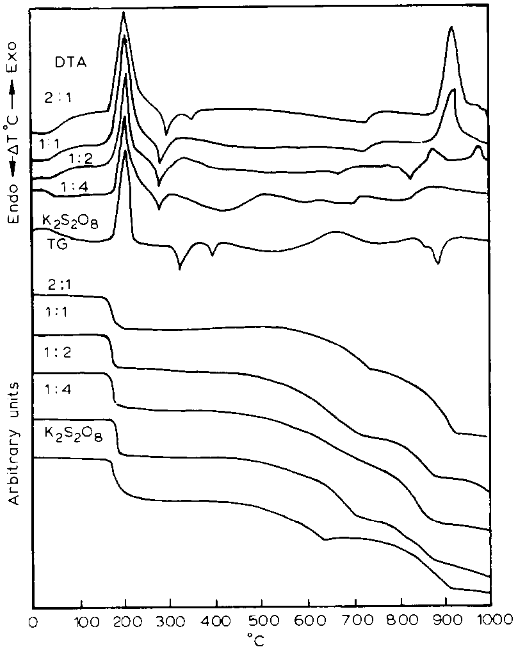

Fig. 2. TG and DTA curves for various molar ratios of the Si–$K_2S_2O_8$ binary system.

and the second, at 940°C, due to the phase crystallisation of the former which is accompanied by its oxidation. With more Si (ratio 2 : 1) the reaction with K_2SO_4 becomes more vigorous and the exo-peak, representing the oxidation of SO_2, sharpens and becomes steeper near 875°C. Between 870 and 985°C a small weight-gain, probably due to oxidation or polymerisation of $K_2Si_2O_5$, is observed; this is indicated by the small exotherm appearing at 940°C. The next smaller exotherm at 985°C may belong to a crystallisation process. Very intense and bright *d*-lines (Table 4) as well as calculations from TG curves (Fig. 2) reveal that 91.2 wt.% of $K_2S_2O_8$ indirectly reacts with Si (Table 3), this convinces us that 2 : 1 is the stoichiometric molar ratio and therefore the stoichiometric reaction is:

$$K_2S_2O_8 \xrightarrow{\Delta} K_2SO_4 + SO_3 + \tfrac{1}{2}\,O_2$$

$$K_2SO_4 + 2\,Si + \tfrac{3}{2}\,O_2 \xrightarrow{\Delta} K_2Si_2O_5 + SO_2$$

TABLE 4

d-Spacings [a] versus intensities of bright lines for the 2:1 mixture of Si–$K_2S_2O_8$ heated to 1000°C

d (Å)	3.80	3.13	3.10	2.96	2.87	2.78	2.43
I/I_0	90	50	30	100	60	40	60

[a] Typical for $K_2Si_2O_5$ [7].

CONCLUSION

Under a static air atmosphere Si powder was found to be thermally stable up to the end of the heating programme (1050°C). It acts as a semiconductive catalyst to lower the T_i values for the thermal decomposition of persulfates or phase transformations of pyrosulfates. At higher temperatures it reacts with solid Na_2SO_4 or K_2SO_4 to form the mixed oxides $Na_2Si_3O_7$ and $K_2Si_2O_5$, respectively, whose identities were checked by X-ray diffraction. The stoichiometric equations for these solid-state reactions have been established.

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