Thermochimica Acta, 45 (1981) 49—54
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMOANALYTICAL BEHAVIOR OF CADMIUM(II) OXIDE—ALKALI PERSULFATE BINARY SYSTEMS

HAMID J. JAFFER and FADHIL JASIM *

Department of Chemistry, College of Science, Baghdad University, Baghdad (Iraq)

(Received 2 October 1980)

ABSTRACT

The non-isothermal behavior of two binary CdO—persulfate systems has been investigated. The molar ratios and T_i—T_f are established. The temperatures for the α- to β-Na_2SO_4 phase transition, as well as for α- to β- to γ-$CdSO_4$ of the CdO—$Na_2S_2O_8$ system have been fixed. No evidence for the occurrence of the β- to γ-$CdSO_4$ polymorphic transformation has been obtained from the reaction of the CdO—$K_2S_2O_8$ system. This is because of the formation of a $CdSO_4/K_2SO_4$ eutectic mixture which melts at 653°C, i.e., before the β- to γ-phase change transition, which usually occurs later. No basic cadmium sulfate has been identified. The excess cadmium oxide acts as a p-type semiconductor which accelerates the thermal decomposition of pyrosulfates.

INTRODUCTION

Cadmium(II) oxide forms cubic crystals [1] which act as n-type semiconductors when prepared in air at 650°C. The crystals contain an excess, y (= 5.5×10^{-4}), of Cd^{2+} in comparison with its stoichiometric structure, $Cd_{1+y}O$. However, once it deviates from stoichiometry, its electric conductance increases. It sublimes at high temperatures, and its sublimation pressure reaches 1 atm at 1559°C [2].

The thermal decomposition of cadmium sulfate has been studied by many authors, and the formation of a liquid phase during its thermal decomposition has been noted on several occasions [3—11]. It was found by Shargorodskii [3] that at 1015—1050°C simultaneous fusion and decomposition occur. Margulis and Remizov [4] observed that the material fused at temperatures higher than 990°C and the fusion products due to the formation of a mixture of $CdSO_4$ and its decomposition products are melted at those temperatures. Ketov et al. [5] found that decomposition and fusion occurred at 1006°C when $CdSO_4$ was heated in air. Also, on mixing with carbon in the specified stoichiometric ratio, the cadmium sulfate starts decomposition at 681°C

$$2\,CdSO_4 + C \rightarrow 2\,CdO + 2\,SO_2 + CO_2$$

---

* To whom correspondence should be addressed.

Panetier et al. [6] found from TG curves that a partial decomposition of $CdSO_4$ into $CdSO_4 \cdot 2\,CdO$ occurs at 955—1000° C, depending on the heating rate and the atmosphere. All these transformations were studied using isothermal heating.

It therefore seems worthwhile investigating the effects of this oxide on the non-isothermal decomposition of sodium and potassium persulfates for the sake of disclosing some parameters of their intermediate and final products.

RESULTS AND DISCUSSION

Figures 1 and 2 exhibit the TG and DTA curves of the thermal decomposition of sodium and potassium persulfates in intimate mixtures of each salt with CdO. These curves reveal a slight shift toward higher temperatures for the decomposition of the persulfates into pyrosulfates as the amount of oxide increases. The shift is attributed to the dilution effect of the oxide [12,13].

CdO—$Na_2S_2O_8$ system

The DTA curves of Fig. 1 and Table 1 show that lowering of the melting point of $Na_2S_2O_7$ occurs when the oxide content increases and is 345° C for

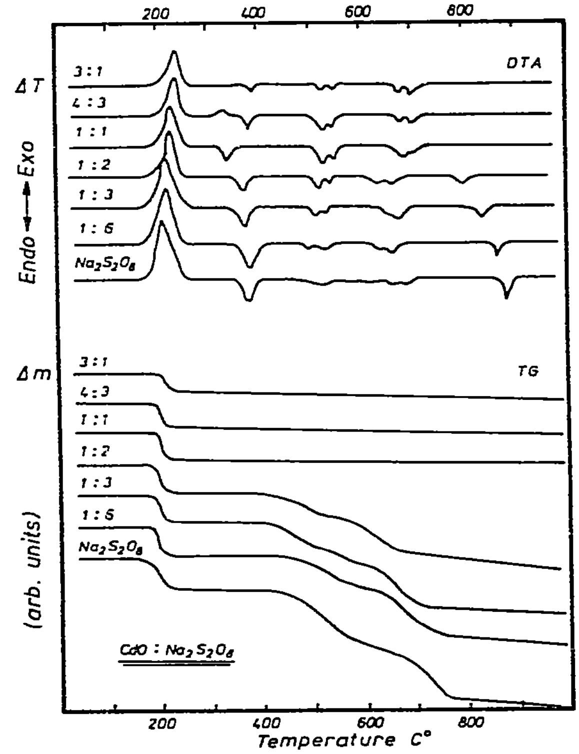

Fig. 1. TG and DTA curves of cadmium(II) oxide—sodium persulfate mixtures.

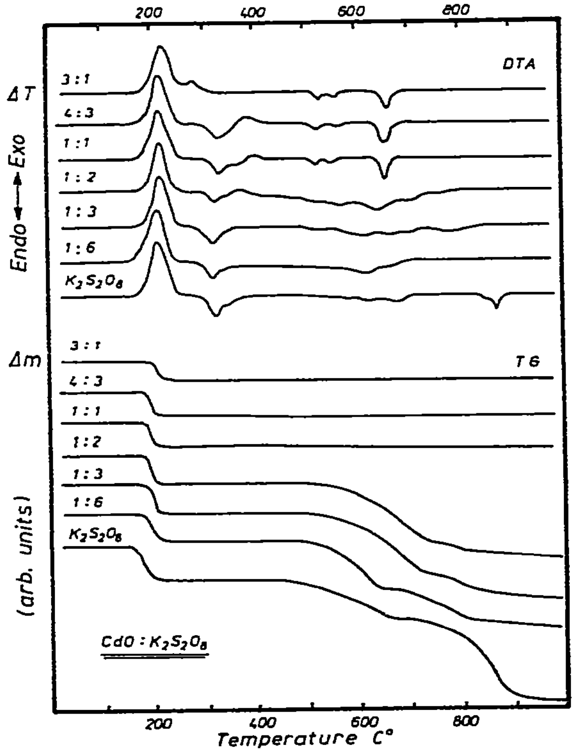

Fig. 2. TG and DTA curves of cadmium(II) oxide—potassium persulfate mixtures.

TABLE 1

Thermoanalytical data obtained with the CdO—$Na_2S_2O_8$ system

CdO : $Na_2S_2O_8$	M.p. $Na_2S_2O_7$ (°C)	SO_3lost(mg)		$Na_2S_2O_7$ decomp. (%)	M.p. Na_2SO_4 (°C)
		Theor.	Pract.		
1 : 6	382	61.64	50.00	81.10	862
1 : 3	375	56.95	37.00	64.96	833
1 : 2	370	52.92	25.00	47.23	800
1 : 1	345	43.65			700
4 : 3		39.08			700
3 : 1		25.66			700

a 1 : 1 molar ratio. As for the ratios 4 : 3 and 3 : 1, the melting endotherm of pyrosulfate disappeared, but a small exopeak appeared at 330°C for the former ratio. This indicates that the reaction between the oxide and pyrosulfate occurs in the solid state, i.e., below the melting point of $Na_2S_2O_7$. On the other hand, the disappearance of the reaction exotherm in the 3 : 1 molar ratio is caused by the degradation of the small portion of persulfate in the ratio mixture, which naturally leads to the liberation of a small amount of heat and a little pyrosulfate. Consequently the exothermic oxide pyrosulfate reaction is so weak that its DTA measurement occurs outside the detection limit of the recording assembly of the derivatograph.

The endotherms at 390 and 395°C for the 4 : 3 and 3 : 1 ratios, respectively, are due to the α—β-polymorphic transition of Na_2SO_4, a fact which has been confirmed by X-ray powder analysis. Other ratios produce β-Na_2SO_4 directly.

From calculation of the TG curve (Fig. 1) for molar ratios 1 : 6, 1 : 3, and 1 : 2, it is clear that CdO reacts with its equivalent of pyrosulfate, and at the same time accelerates, through catalysis, the thermal decomposition of excess pyrosulfate into sulfate. For this reason, Na_2SO_4 is formed at a temperature lower than expected from degradation of the pyrosulfate alone [14]. Calculation from TG curves for the 1 : 1, 4 : 3 and 3 : 1 ratios, complemented by X-ray diffraction analysis, indicates that all the pyrosulfate present is consumed on reacting with CdO. As for the 4 : 3 and 3 : 1 ratios in particular, an excess of pyrosulfates remains unreacted.

XRD patterns (Table 2) for products heated at 460°C and 1000°C for the stoichiometric 1 : 1 ratio indicate the formation of $CdSO_4$ and Na_2SO_4. The reaction is

$$Na_2S_2O_7 + CdO \rightarrow CdSO_4 + Na_2SO_4$$

However, the *d*-lines for products obtained by heating samples at 600°C for the molar ratio 4 : 3 point to the presence of CdO in addition to sulfates of cadmium and sodium.

It has been shown (Fig. 1) that $CdSO_4$ does not decompose until the ceiling temperature of the heating program has been attained [3,5,6,8]. It is to be emphasized that ratios beyond 1 : 1 contain an excess of oxide. To

TABLE 2

X-Ray diffraction patterns for compounds involved in the thermoanalytical study of $CdO—Na_2S_2O_8$ and $CdO—K_2S_2O_8$ systems

Compound	XRD patterns, d(Å)
CdO	2.72, 2.35, 1.66
$CdSO_4$	3.32, 3.26, 2.95
Na_2SO_4	2.81, 2.63, 3.92
K_2SO_4	2.90, 3.00, 2.87

explain the high temperature reaction between $CdSO_4$ and CdO, Margulis and Remizov [4] proposed that the solid sulfate dissociates into basic oxide sulfate, $CdSO_4 \cdot 2\ CdO$, with the liberation of sulfur trioxide. The latter in turn reacts with excess metal oxide, thereby producing more oxide sulfate, and the overall reaction is the formation of basic sulfate. In the present work $CdSO_4$ does not dissociate within the temperature range of the heating program (ambient—1050°C), and as such, no reaction between the $CdSO_4$ and excess CdO has been found.

Further scrutiny of the DTA curves shows two polymorphic transformations of cadmium(II) sulfate, i.e., from α-$CdSO_4$ to β-$CdSO_4$ and from β-$CdSO_4$ by γ-$CdSO_4$. The α—β phase transition takes place at the temperature intervals 495—515°C, 512—532°C, 520—540°C, 530—550°C for the ratios 1 : 6, 1 : 3, 1 : 1, 4 : 3, and 3 : 1, respectively. However, it has been noted that the transformation temperatures are highly influenced by the type of substances present in the mixture [7] and also by the history of the $CdSO_4$ used [8,9].

Regarding the β- to γ-transition, the DTA curves of the 1 : 6 ratio expose two phase changes of cadmium sulfate at 633 and 655°C, which are combined in a single broad endotherm at 660°C for the 1 : 3 ratio, and are once more resolved at 627°C and 650°C for the 1 : 2 ratio. Concerning the 1 : 1, 4 : 3, and 3 : 1 ratios, one endothermic effect is observed which is attributable to this transition at 678, 668, and 668°C, respectively. The second endotherm may be embedded in that belonging to the melting of Na_2SO_4 [11]. Also the latter is changed by the amount of cadmium sulfate formed

TABLE 3

Thermoanalytical data obtained with the $CdO—K_2S_2O_8$ system

$CdO : K_2S_2O_8$	SO_3 lost(mg)		Decomp. $K_2S_2O_7$ (%)	$K_2S_2O_7$, T_f (°C)
	Theor.	Pract.		
1 : 6	54.84	44.50	81.14	825
1 : 3	51.09	33.00	64.58	810
1 : 2	47.82	23.50	49.13	800
1 : 1	40.12			
4 : 3	36.41			
3 : 1	24.40			

during the reaction and it becomes 700° C for the ratios 1 : 1, 4 : 3, and 3 : 1 (Table 3).

CdO—$K_2S_2O_8$ system

The DTA curves (Fig. 2) exhibit no shift in the melting point of potassium pyrosulfate, for all ratios, in comparison with that of pure persulfate [14,15], excluding the 3 : 1 ratio, where a small exotherm, appearing at 280° C (i.e. before melting of $K_2S_2O_7$) indicates a solid state reaction of hitherto unknown nature.

From calculations of the TG curves for the ratios 1 : 6, 1 : 3, and 1 : 2, it is to be concluded that CdO reacts with an equivalent amount of molten pyrosulfate. Excess of the latter then dissociates, in the thermal mode, into K_2SO_4 and SO_3 gas. The TG curves of the 1 : 1, 4 : 3, and 3 : 1 ratios expose plateaux that remain horizontal to the end of the heating program. This means that the reaction products are thermally stable up to 1050° C. Evidently, the reaction for the 1 : 1 stoichiometric ratio is

$$K_2S_2O_7 + CdO \rightarrow K_2SO_4 + CdSO_4$$

For ratios 4 : 3 and 3 : 1, their XRD patterns disclose that an excess of CdO remains unreacted. X-ray analysis of samples of the 1 : 1 ratio heated at 600 and 1000° C substantiates the presence of sulfates of sodium and cadmium (Table 2), while those obtained for samples of the 4 : 3 ratio at 550° C verify the presence of CdO, $CdSO_4$ and K_2SO_4.

The DTA curves (Fig. 2) disclose that the heat effects of the α—β-transitions of $CdSO_4$ [9] related to the 1 : 6, 1 : 3 and 1 : 2 ratios are overlapped by those belonging to the decomposition of excess $K_2S_2O_7$. A similar transition has been observed in the temperature range 523—550° C, 525—550° C, 530—560° C for the 1 : 1, 4 : 3, and 3 : 1 ratios, respectively. The temperature ranges depend upon such factors as the presence of K_2SO_4 and CdO in the heated samples, as well as the mode of preparation of $CdSO_4$ [7,8].

No evidence has been shown by DTA curves (Fig. 2) for the occurrence of the β—γ transition of $CdSO_4$. This is because of the formation of a $CdSO_4$/K_2SO_4 eutectic mixture which melts at 653° C. This, of course, obscures the β—γ phase change which usually occurs later.

Similar to the previous system, the TG curves of the 1 : 6, 1 : 3, and 1 : 2 ratios indicate that as the oxide content increases, a greater depression in the final decomposition temperatures of $K_2S_2O_7$ occurs (Table 3). This is caused by the catalytic effect of excess oxide present, which in turn accelerates the thermal decomposition of the pyrosulfate.

REFERENCES

1 D. Nicholls, in A.F. Trotman-Dickinson (Ed.), Comprehensive Inorganic Chemistry, Vol. 3, Pergamon, Oxford, 1973, p. 266.
2 Per Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience, New York, 1972, p. 203.
3 S.D. Shargorodskii, Ukr. Kh. Zh., 16 (1949) 310.

4 E.V. Margulis and Yu.S. Remizov, Gornoe Delo, Obogashchenie, Metallurgiya Tsvetnzk Metallov, Sbornik Trukov VIITs VETMETAa, No. 6, Metallurgizdat, Moscow, 1960, p. 171.
5 A.N. Ketov, V.V. Peschkovkii, N.P. Starkov and B.N. Varskoi, Russ. J. Inorg. Chem., 9 (1961) 1028.
6 G. Panetier, J.M. Bregeanlt and J. Guenot, Bull. Soc. Chim., Fr. (1962) 2158; Chem. Abstr., 58 (1963) 7600g.
7 E.V. Margulis, N.I. Kopylov and N.S. Grishankina, Russ. J. Inorg. Chem., 10 (1965) 542.
8 E.V. Margulis, Yu.S. Remizov and N.I. Kopylov, Russ. J. Inorg. Chem., 8 (1963) 969.
9 G.V. Maximova, Zh. Neorg. Khim., 4 (1959) 506.
10 G. Hoschek, Monatsh. Chem., 93 (1962) 826.
11 E.L. Bakumskaga and A.G. Bergman, Zh. Neorg. Khim., 1 (1956) 1035.
12 W.W. Wendlandt, Thermal Methods of Analysis, Wiley-Interscience, New York, 1974, 2nd edn., p. 175.
13 E.M. Barrall and L.B. Rogers, Anal. Chem., 34 (1962) 1106.
14 M.M. Barbooti and F. Jasim, Thermochim. Acta, 16 (1976) 402.
15 E.L. Bakumskaga and A.G. Bergman, Zh. Neorg. Khim., 1 (1956) 1629.