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THERMOANALYTICAL INVESTIGATION OF SOME β-MANGANESE(IV) OXIDE-ALKALIMETALPERSULFATE SYSTEMS

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A TG and DTA investigation, under a static air atmosphere, of mixtures of β-MnO_2 and $Na_2S_2O_8$ or $K_2S_2O_8$ in different molar ratios is reported. β-MnO_2 lowers the initial decomposition temperatures of these persulfates by 25° through a catalytic effect. A mechanism is proposed for this effect. The X-ray diffractometry results in this investigation could be used to decide which type of semiconductor β-MnO_2 should be used for the best activity.

Stoichiometric molar ratios of 1 : 1 are established for the formation of $Na_2Mn(SO_4)_2$ and $K_2Mn_2(SO_4)_3$. These salts are thermally stable from ambient temperature to 940°. Reaction products are identified by X-ray diffraction.

The reactions between alkalimetalpersulfates and metallic oxides have been studied with a derivatograph [1–4] by several authors with many aims.

Barbooti and Jasim [1–3] used oxides of Cu(II), Ni(II), Zn(II) and Ti(IV), while Jaffer and Jasim [4] worked with oxides of Cr(III), Fe(III), Al(III) and Cd(II). The products of the thermal reactions are oxygen, sulfur trioxide, polymeric unstable intermediates and stable alkali metal compounds.

Lunenko and co-workers [5] suggested a mechanism for persulfate–pyrosulfate transformation *via* formation of a pair of radical ions ($\dot{S}O_4^-$).

The kinetic parameters [1] of conversion of sodium and potassium persulfates into the corresponding pyrosulfates have been determined too. Studies on the thermal characteristics of the effects of β-MnO_2 on the decomposition reactions of persulfates, using TG and DTA techniques, have not yet been reported.

In our present work, we describe some studies giving new information about the reactions in the solid phases between β-MnO_2 and sodium or potassium persulfate, and postulate the type of semiconductivity this oxide has under the described conditions.

Experimental

Analytical grade salts were used. The β-MnO_2 employed as the other reactants with a minimum β-MnO_2 content of 80%.

Chemical and physical changes were studied as a function of temperature by means of a Paulik-Paulik-Erdey, MOM, derivatograph in air atmospheric pressure from room temperature up to 1000°.

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MnO_2-$M_2S_2O_8$ mixtures of various molar ratios were prepared by careful grinding of the calculated amounts of oxide and persulfates for 20 min in an agate mortar to 200–300 mesh, then dried at 80° for 2 h.

Mixtures of oxide and sodium or potassium persulfate were systematically prepared with the following molar ratios: 1 : 6, 1 : 3, 2 : 3, 1 : 1 and 2 : 1. Samples of 200 mg were measured in a platinum crucible. The programmed heating rate was 10°/min.

Materials produced in the reaction, and components which had been in excess at the start, were identified by means of a Philips X-ray diffractometer, as instructed by the manufacturers.

Results and discussion

Semiconductive behaviour of the β-oxide

(1) *p-type mechanism*

Evaluation of the curves (Figs. 1 and 2) of the two binary systems results in the following data and conclusions.

The oxide acts as a catalyst for degradation of persulfates to pyrosulfates, and the initial decomposition temperature T_i was lowered by about 25° as compared

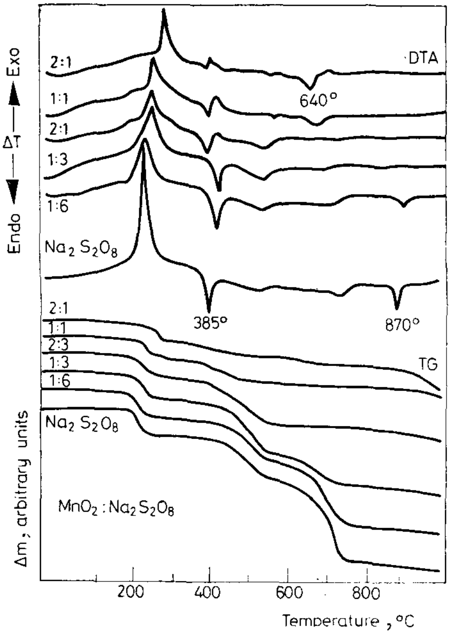


Fig. 1. TG and DTA curves of manganese(IV) oxide-sodium persulfate mixture

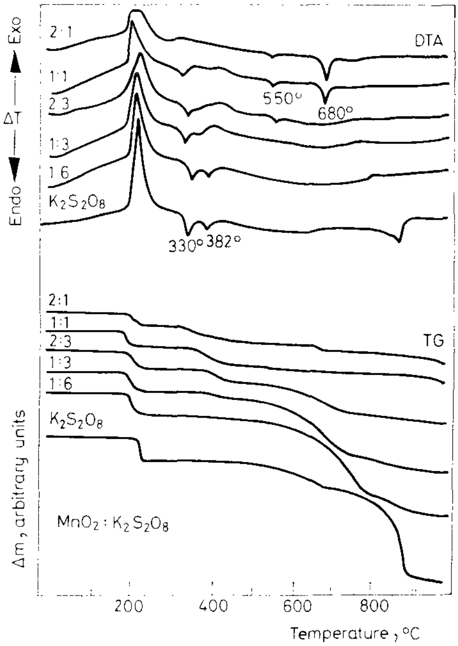


Fig. 2. TG and DTA curves of manganese(IV) oxide-potassium persulfate mixtures

with that of the pure persulfate (Tables 1 and 2). The interval between the initial and final decomposition temperatures for this stage increased as the amount of oxide increased, and reached its maximum value at MnO_2 : $Na_2S_2O_8$ molar ratios of 2 : 3, 1 : 1 and 2 : 1.

Table 1

Oxygen liberated during the decomposition of pure persulfate, and the temp. ranges, °C, for $Na_2S_2O_8$ decomposition and MnO_2—$Na_2S_2O_7$ reaction

MnO_2 : $Na_2S_2O_8$	mgs, O_2 lost		Decomp. of $Na_2S_2O_8$ to $Na_2S_2O_7$		Temp. range for MnO_2—$Na_2S_2O_7$ reaction	
	Theo.	Pract.	T_i	T_f	T_i	T_f
0 : 1	13.4	13.4	185	220	—	—
1 : 6	12.6	13.0	155	240	—	—
1 : 3	11.9	12.0	160	240	—	—
2 : 3	10.8	10.2	155	255	385	440
1 : 1	9.7	10.0	150	250	385	435
2 : 1	7.7	9.0	170	270	375	390

Table 2

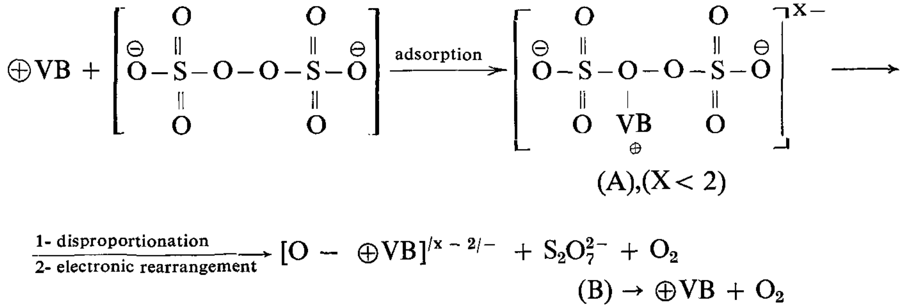
Oxygen loss of pure persulfate decomposition, and temperature ranges for persulfate decomposition and $MnO_2-K_2S_2O_7$ reaction

$MnO_2 : K_2S_2O_8$	mgs, O_2 lost		Decomp. of $K_2S_2O_8$ to $K_2S_2O_7$		Temp. range for $MnO_2-K_2S_2O_7$ reaction	
	Theo.	Pract.	T_i	T_f	T_i	T_f
0 : 1	11.8	11.0	182	200	—	—
1 : 6	11.2	11.0	160	210	490	—
1 : 3	10.6	10.0	160	210	360	445
2 : 3	9.7	10.0	160	210	350	450
1 : 1	8.9	9.0	160	210	350	450
2 : 1	7.2	7.0	160	200	280	410

Careful inspection of the TG, DTG and DTA curves for these mixtures indicates clearly that this decomposition goes *via* two separate steps, as seen from the knees in the TG curves at 200 and 240° for the above-mentioned molar ratios.

However, the two steps for persulfate–pyrosulfate decomposition become more evident at molar ratios of 1 : 1 and 2 : 1 in the MnO_2-$K_2S_2O_8$ system, as indicated by the two temperature stretches 160–180° and 180–210° in the TG curves.

An attempt was made to correlate the structural properties of the oxide with its catalytic activity, using the Freeman [6] and Lunenko [5] mechanisms for the effects of transition metal oxides on chlorate decomposition and for pure persulfate decomposition, respectively. The persulfate anion, $S_2O_8^{2-}$, is adsorbed on the surface of the proposed *p*-type oxide, with partial electron-transfer from oxygen atoms of the persulfate to the positive holes in the valence bond ⊕VB, of the oxide, and a surface complex is thereby formed. The mechanism can be expressed as in the following scheme:



$$\oplus VB + \left[\overset{\ominus}{O}-\underset{O}{\overset{O}{S}}-O-O-\underset{O}{\overset{O}{S}}-\overset{\ominus}{O}\right] \xrightarrow{\text{adsorption}} \left[\overset{\ominus}{O}-\underset{O}{\overset{O}{S}}-\underset{\overset{VB}{\oplus}}{O}-O-\underset{O}{\overset{O}{S}}-\overset{\ominus}{O}\right]^{x-} \longrightarrow$$

(A),(X< 2)

$$\xrightarrow[\text{2- electronic rearrangement}]{\text{1- disproportionation}} [O - \oplus VB]^{/x-2/-} + S_2O_7^{2-} + O_2$$

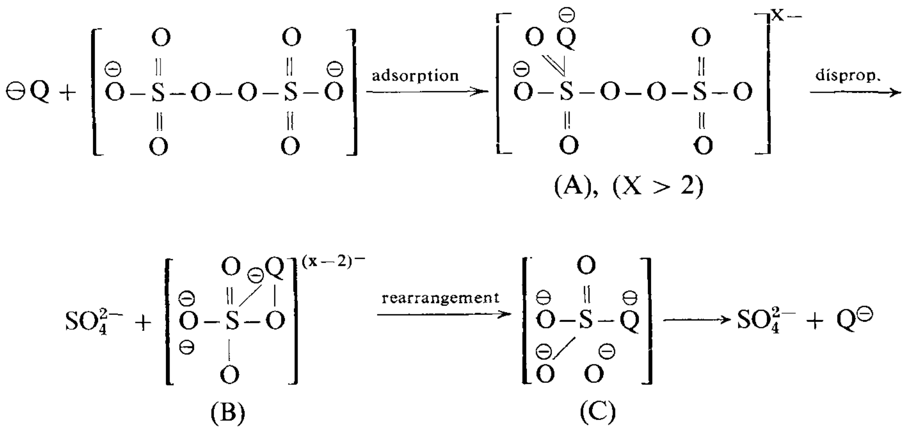
$$(B) \rightarrow \oplus VB + O_2$$

In this scheme, the oxygen atoms of the peroxide bond are the most preferable sites for adsorption as regards the valence bond of the oxide, because each has two lone-pairs of electrons ready to be shared with the positive holes, while other oxygen atoms are bound to sulfur atoms through partially double bonds. Thus, the number of electrons available for sharing with the valence bond will be less than in the case of the central oxygen atoms of the peroxy bond; hence, this partial charge transfer will make the peroxy bond weaker and the surface complex will decompose at lower temperatures. Firstly, the surface complex decomposes through radical ion disproportionation and electronic rearrangement to pyrosulfate, and consequently some of the atomic oxygen is liberated as gaseous molecules, whereas the rest is adsorbed in an unstable complex form, structure (B). Moreover, as the temperature increases, structure (B) decomposes and this remaining oxygen too will be liberated as gas molecules. Therefore, the overall oxygen liberated is seen as loss of weight in the TG curve.

The behaviour of the oxide as a *p*-type semiconductor was confirmed in practice by data obtained from the TG and DTA curves, as well by X-ray diffraction data, for samples of the 2 : 3 mixture of $MnO_2-Na_2S_2O_8$ at 200, 240 and 300°, while only sodium pyrosulfate and manganese dioxide were detected in the residue. Similarly, samples isolated from the 1 : 1 mixture of $MnO_2-K_2S_2O_8$ at 170 and 200° gave only MnO_2 and potassium pyrosulfate as by-products.

(2) *n-type mechanism*

In contrast, if we assume that MnO_2 is an *n*-type semiconductor, then the suggested mechanism for its catalytic effect on persulfate decomposition is based on the adsorption of a sulfur atom of the persulfate on the negative charge of the semiconductor, but this is because sulfur is less electronegative than any of the oxygen atoms in the persulfate ion, and a surface complex, structure (A), may be formed as follows:



This unstable structure finally forms more stable sulfate as end-product, *via* intermediate complex structures (B) and (C), which means that no pyrosulfate is formed.

This is, of course, inconsistent with what was confirmed by X-ray diffraction, which showed the formation of both pyrosulfate and oxide. By this reasoning, manganese(IV) oxide acts here as a *p*-type and not an *n*-type semiconductor.

Formation of stoichiometric compounds

MnO_2-$Na_2S_2O_7$ system. The reaction of the oxide with sodium pyrosulfate is shown as an endotherm in the DTA curves in the temperature ranges indicated in Table 1 for all mixtures except those with molar ratios of 1 : 6 and 1 : 3, where there is overlapping between the reaction exotherm and the pyrosulfate decomposition endotherm.

However, the TG and DTA curves (Fig. 1) indicate that the reaction between oxide and pyrosulfate at a molar ratio of 2 : 3 begins after the melting point of $Na_2S_2O_7$, which appears as a sharp endotherm at 385° in the DTA curve. An examination was made of the *d*-lines of the X-ray spectrum taken for a sample of this molar ratio, preheated at 500°. The sharp lines found at 3.82, 3.73 and 2.89 Å relate to beta-sodium manganese(II) disulfate, β-$Na_2Mn(SO_4)_2$, as indicated in the ASTM cards. Further calculations for the mixture with 1 : 1 molar ratio show that 89% pyrosulfate reacts with the oxide, which is the maximum as regards the molar ratios studied. This satisfies the stoichiometric reaction

$$\beta\text{-}MnO_2 + Na_2S_2O_7 \rightarrow \beta\text{-}Na_2Mn(SO_4)_2 + \tfrac{1}{2}\,O_2$$

The unreacted pyrosulfate present decomposes gradually up to 540°, as indicated by the TG and DTA curves (Fig. 1). Moreover, the DTA curves clearly reveal endotherms at 650 and 640° for the 1 : 1 and 2 : 1 mixtures, respectively. To establish the nature of these endotherms, two samples from the 1 : 1 mixture were preheated: that at 640° appeared in powder form, while that at 710° was seen as solidified melt. This fact leads us to consider the latter endotherm as occurring at the melting point of the disulfate salt, β-$Na_2Mn(SO_4)_2$.

For the 2 : 1 mixture, the DTA curve indicates decomposition of the excess oxide at 640°, superimposed on melting of the disulfate. β-$Na_2Mn(SO_4)_2$ is thermally stable up to 940°, but then decomposes gradually into the corresponding sulfate and oxide:

$$\beta\text{-}Na_2Mn(SO_4)_2 \xrightarrow{\Delta} Na_2SO_4 + \beta\text{-}MnO + SO_3$$

β-MnO_2 : $K_2S_2O_7$ system. The temperature ranges for the potassium pyrosulfate – manganese(IV) oxide reaction are indicated in Table 2. This reaction is exothermic, and as the amount of the oxide increases the initial reaction temperature decreases, due to the oxide activity [6], while the exotherm becomes smaller and its height is reduced. It is seen as a hump in the DTA curves of the 1 : 1 and 2 :1 mixtures, which is attributed to the thermoneutrality [2]: the endotherms at 330 and 370° for the phase change and the melting of potassium pyrosulfate overlap with the exotherm of the pyrosulfate – oxide reaction, with the subsequent for-

mation of the humps seen in the DTA curves. The 1 : 1 molar ratio represents the stoichiometric ratio where 70 % of the potassium pyrosulfate reacted with the oxide, with the formation of potassium manganese(II) trisulfate:

$$2\ MnO_2 + 2\ K_2S_2O_7 \rightarrow K_2Mn_2(SO_4)_3 + K_2SO_4 + O_2$$

This was identified by its sharp *d*-lines 3.18, 3.03, 2.69 Å. The unreacted pyrosulfate decomposes gradually to its sulfate in the intervals 445 – 750°, 450 – 750°, 450 – 550° and 410 – 550° for the 1 : 3, 2 : 3, 1 : 1 and 2 : 1 mixtures, respectively. Further, the DTA curves of 1 : 1 and 2 : 1 mixtures show a small endotherm at 550°. X-ray analysis of two samples preheated before and after this temperature gives no indication of any chemical change, und hence this endotherm may relate to a phase change of the trisulfate, $K_2Mn_2(SO_4)_3$.

A sharp endotherm was observed at 680° in the DTA curves for 1 : 1 and 2 : 1 mixtures, which was identified with the melting of potassium manganese(II) trisulfate; this was reasoned by preheating samples of 1 : 1 mixtures at 640 and 700°, where a powder and a solidified melt, respectively, were found. This trisulfate salt is thermally stable up to 940°, but then decomposes gradually as follows:

$$K_2Mn_2(SO_4)_3 \xrightarrow{\Delta} K_2SO_4 + 2\ MnO + 2\ SO_3$$

The lowering of the valence state from Mn(IV) to Mn(II) in the mixed sulfates formed could be accounted for [7] by the ability of transition metal ions of high oxidation states to accept electrons from electron-rich compounds such as pyrosulfates, thereby themselves being reduced to lower valence cations so as to form more a stable oxidation state and more stable compounds; this is why the mixed sulfates prepared are thermally stable up to 940°.

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Résumé — On décrit les études thermiques effectuées par TG et ATD en atmosphère statique d'air sur des mélanges (β-MnO_2—$Na_2S_2O_8$ ou $K_2S_2O_8$) de rapports molaires différents. β-MnO_2 abaisse d'un seul coup de 25° les températures de décomposition de ces persulfates, par un effet catalytique. On propose un mécanisme par lequel cet effet se produit. On a pu se servir également des résultats des études de diffraction des rayons X pour décider quel type de β-MnO_2 semi-conducteur devait être utilisé pour obtenir la meilleure corrélation avec son activité.

On a établi des rapports molaires stoechiométriques 1 : 1 pour la formation respective de $Na_2Mn\ (SO_4)_2$ et $K_2Mn_2\ (SO_4)_3$. Ces sels sont thermiquement stables, depuis la température ambiante jusqu'à 940°. On a identifié les produits de réaction par diffraction des rayons X.

Zusammenfassung — Es wird über die Untersuchung von Mischungen von (β-MnO_2—$Na_2S_2O_8$ oder $K_2S_2O_8$) verschiedener Molverhältnisse durch TG und DTA in statischer Luft-Atmosphäre berichtet. β-MnO_2 setzt die anfänglichen Zersetzungstemperaturen dieser Persulfate durch einen katalytischen Effekt um 25° herab. Ein Mechanismus wird für die Wirkungsweise dieses Effektes vorgeschlagen. Röntgendiffraktometrische Ergebnisse dieser Untersuchungen konnten zur Entscheidung des einzusetzenden Typs des Halbleiters β-MnO_2 herangezogen werden um die beste Korrelation zwischen diesem und seiner Aktivität zu erzielen.

Die stöchiometrischen Molverhältnisse 1 : 1 wurden für die Bildung von $Na_2Mn(SO_4)_2$ bzw. $K_2Mn_2(SO_4)_3$ beobachtet. Diese Salze sind von Raumtemperatur bis zu 940° stabil. Die Reaktionsprodukte werden durch Röntgendiffraktion identifiziert.

Резюме — Используя ТГ и ДТА, было проведено термическое исследование в атмосфере воздуха смесей β-MnO_2—$Na_2S_2O_8$ или $K_2S_2O_8$ с различным молярным соотношением. β-MnO_2 понижает на 25° начальные температуры разложения этих пересульфатов, вследствие своего каталитического действия. Предложен механизм для объяснения этого эффекта. Результаты рентгено-дифрактометрического анализа должны быть использованы при решении вопроса какой тип полупроводникового β-MnO_2 должен быть взят с целью наилучшей корреляции между вышеупомянутым эффектом и активностью этого соединения. Для образующихся соединений $Na_2Mn(SO_4)_2$ и $K_2Mn_2(SO_4)_3$ установлены стехиометрические молярные соотношения 1 : 1. Образующиеся соли термически стабильны до 940°. Продукты реакции идентифицированы рентгено-дифракционным анализом.