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SOME SUPPLEMENTARY DATA ON PARTICULAR FEATURES OF THE THERMAL BEHAVIOUR OF POTASSIUM PERSULFATE

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The effects of preliminary mechanical activation and thermal treatment of potassium persulfate on the thermal and electrical characteristics of its thermal decomposition were studied by DTA, TG, evolved gas volumetry and high-frequency thermal analysis.

The thermal decomposition of metal persulfates, studied by thermoanalytical methods, IR and EPR spectroscopy [1–7], still requires further investigations; the mechanism of the process and the dynamics of the structural transformations are particularly intricate.

According to [1–3], the decomposition is described by the following equation:

$$M_2S_2O_8 \rightarrow M_2S_2O_7 + \frac{1}{2}O_2 \tag{1}$$

In the general case, the reaction is accompanied by heat evolution; and exception is $(NH_4)_2S_2O_8$, which decompose endothermically. The thermal effect of reaction (1) for $K_2S_2O_8$ is 57.2±6.3 kcal/mol. The solid residue has been determined via the mass loss and the heat balance; the mass loss amounts to 5.19% and 6%, respectively for oxygen, close to the theoretical value of 5.9%. The energy of splitting of the O–O and S–O bonds is 34 and 65 kcal/mol, respectively, and hence it appears obvious that the first stage of decomposition consists in the splitting of the weaker O–O bond and the formation of the free readicals $[SO_4]$; these then participate in a complex chain of transformations accompanied by oxygen evolution.

Another mechanism of decomposition is also known for $K_2S_2O_8$ [4–6], characteristic for thin-layer specimens (100–300 μm) and proceeding at around 210° to the accompaniment of the evolution of much heat:

$$K_2S_2O_8 \rightarrow K_2SO_4 + SO_3 + \frac{1}{2}O_2 \tag{2}$$

Indirect proof for the existence of this mechanism is the appearance of the five IR absorption bands of the ion $[SO_4]^{2-}$, replacing the absorption bands of the initial material. It has also been found that in the solid-phase process $[S_2O_8]^{2-} \rightarrow [SO_4]^{2-}$ the symmetry of the ions $[SO_4]^{2-}$ formed changes in the following manner: $C_v \rightarrow C_{3v} \rightarrow T_d$. The symmetry C_{3v} indicates that one of the oxygen atoms in the ion

$[SO_4]^{2-}$ has a non-equivalent position as compared to the other three oxygen atoms, and the structure of a molecule of this type is intermediate between the pyramidal (C_v) and tetrahedral (T_d) structures, i.e. in the solid-phase decomposition of the $K_2S_2O_8$ crystal with trigonal syngonism, K_2SO_4 with higher, rhombic symmetry is formed. An absorption band also appears at 875 cm^{-1} in the decomposition of thin $K_2S_2O_8$ layers; the characteristics of its change differ essentially from those of the absorption bands of $[SO_4]^{2-}$, indicating the formation of peroxomonosulfate groups $[SO_5]^{2-}$ via the possible participation of unstable free radicals and atomic oxygen in the decomposition process.

Potassium persulfate decomposition effected by shock waves proceeds in a different manner than on thermal initiation [4]. Here the reaction product is a mixture of $K_2S_2O_7$ and K_2SO_4, as evidence that two parallel reactions proceed, corresponding to reactions (1) and (2):

$$2\,K_2S_2O_8 \begin{array}{l} \nearrow K_2S_2O_7 + \frac{1}{2}O_2 \\ \searrow K_2SO_4 + SO_3 + \frac{1}{2}O_2 \end{array} \tag{3}$$

With increasing closeness of the crystal packing (porousness of the specimen) the amount of K_2SO_4 in the product increases. Consequently, the decomposition of $K_2S_2O_8$ in dense layers proceeds according to the second mechanism and directly in the shock wave, not as a result of secondary heating-up.

Obviously, particular kinetics correspond to each mechanism. According to [3], the activation energy for reaction (1) is $E = 86.4 \pm 6.2$ kcal/mol. The value of E calculated from DTA data [2] is in the range of 67.7 to 68.1 kcal/mol, and the somewhat surprising order of this one-stage reaction (1.8–2.3) clearly indicates that the decomposition process does not proceed by the topochemical mechanism of a shift of the interface between the phase [8]. The authors of [2] do not report a value for the frequency factor in the Arrhenius equation, but it can be calculated by means of the equation in [9]:

$$A = \frac{(1-\alpha_m)^{1-n}}{n}\,\frac{E\beta}{RT_m^2}\exp\left(\frac{E}{RT_m}\right) \tag{4}$$

where the ratio $(1-\alpha_m)^{1-n}/n \cong 1$, T_m is the temperature at the point where the transformation rate is maximum (according to [2] $T_m = 216°$), β is the linear heating rate, α_m is the fraction reacted at the temperature T_m, and n is the order of reaction. All kinetic values are listed in Table 1; the calculated values of A are extremely high and have no physical meaning. This circumstance also demonstrates that the transformation mechanism accepted in this case, namely the shift of the interface between the phases [10], is inadequate. Considering the data in [7], it appears that the transformation process presumably has a free radical chain character.

The authors of [5, 6], investigating the kinetics of reaction (2), concluded from the increasing intensity of the IR absorption bands with time at various temperatures, that the formation of $[SO_4]^{2-}$ and $[SO_5]^{2-}$ is well described by a first-order equa-

Table 1 Kinetic parameters of $K_2S_2O_8$ decomposition: $[S_2O_8]^{2-} \rightarrow [S_2O_7]^{2-}$

Parameters	Order of reaction *n*				Heating rate β, degree/min
	1.8	2.0	2.15	2.3	
E, kcal/mol	76.6	69.1	70.3	80.3	5
kJ/mol	320.5	294.1	294.1	337.2	
log *A*	32.12	28.74	29.28	33.91	
E, kcal/mol	67.0	67.7	65.6	63.1	10
kJ/mol	280.3	283.2	274.5	264.0	
log *A*	28.10	28.41	27.46	26.33	

tion. Values of E and A are assigned to each frequency; these are correlated by the equation of a compensational relationship: $\log A = 4.6 \cdot 10^{-4}, E - 3.5$ (the dimension of E is cal/mol). An isokinetic temperature $T_x = 200°$ corresponds to this equation; this value lies in the temperature range of the start of $K_2S_2O_8$ decomposition. It is important to note that the activation energy of the decomposition $[S_2O_8]^{2-} \rightarrow$ $\rightarrow [SO_4]^{2-}$ is lower by a factor of two to three as compared to the value of E obtained by the authors of [2, 3] for the reaction $K_2S_2O_8 \rightarrow K_2S_2O_7$.

What has been said demonstrates that the process of decomposition of potassium persulfate depends on the experimental conditions. It therefore appeared desirable to study the effect of preliminary mechanical milling in a vibration mill at ambient temperature on the mechanism of thermal decomposition. The transformation process was followed by classical thermoanalytical methods and by a new method: high-frequency thermal analysis, which allows recording of the particular features of structural transformations in solids in a relatively simple manner.

Experimental

The material used was analytical-grade potassium persulfate. The effect of mechanical milling was followed in an apparatus described earlier [11]. This apparatus allows continuous measurement of the gaseous products formed during mechanical treatment. The gas evolved in the reactor of the vibration mill passes through a flexible polyethylene tube into a buffer vessel connected to a mercury manometer. The quantity of evolved gas is measured via the height of the mercury level. For this purpose, a platinum wire is mounted in the bend of the manometer tube, and is connected in a balanced resistance bridge. The imbalance of the bridge is recorded on a record chart.

The conditions of mechanochemical activation: frequency 23 Hz, amplitude of vibrations 12 mm, mass of specimen 5 g, mass of the 5 mm diam. balls 100 g, temperature 20 and 70°.

The method of high-frequency thermal analysis combines thermal analysis with continuous recording of the electrical properties at radiofrequencies; its physical sense is dielectric spectroscopy of disordered structures [12]. The particular features of the method are the application of contactless cells, the absence of inertia, and the possibility of investigating powders (no tablet pressing is needed). Owing to these characteristics, experimental work is substantially simpler, and qualitatively new information is obtained regarding the processes studied, and simultaneously regarding the electrical properties of stable and intermediate phases.

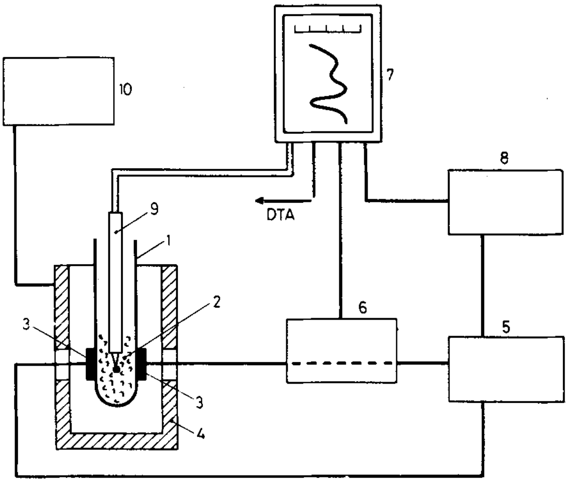


Fig. 1 Diagrammatical representation of the apparatus for high-frequency thermal analysis

The principle of the method is represented diagrammatically in Fig. 1. A quartz test tube *1* containing the material to be studied *2* is placed between the plates of a capacitor *3* mounted in an electric furnace *4*, forming the measuring cell. High-frequency current (1 MHz) from the generator *5* flows through the walls of the quartz test tube and the material being investigated. The conductance of the cell is expressed by the general formula

$$y = g + i\omega C$$

where $i = \sqrt{-1}$, ω is the angular frequency at which the measurement is performed, C is the capacitance of the cell, and g is the ohmic component of conductance. The values of g and y depend in a complex manner on the permittivity and conductivity of the object being investigated, g characterizing the dielectric losses, since by definition

$$\tan\delta = \frac{g}{\omega C}$$

To record the cell parameters g and C, the block *6* is inserted into the cell circuit; its output signal g is recorded directly by the recorder *7*. The capacitance C is measured by the beat method; the frequency difference is fed into the frequency meter *8*, and the signal from the frequency meter is recorded by the same recorder *7*. The temperature of the specimen is measured by the thermocouple *9*. The temperature control *10* ensures heating of the oven in conformity with the present program.

In the phase trasnformation process, the initial phase becomes structurally disordered, and new solid phases are formed. In such cases the interaction of the high-frequency electromagnetic field and the material being investigated changes essentially: dielectric losses increase and the polarization becomes stronger. The dynamics of the structural transformations are reflected by the character of the thermal curves of the electrical properties. Hence, disordering and ordering processes are of outstanding importance in the interpretation of the results of high-frequency thermal analysis.

Results and discussion

DTA and evolved gas analysis were performed simultaneously, using a self-designed apparatus (Fig. 2a). A few differences compared with the temperatures reported in the literature [1–3] were discovered. The decomposition of potassium persulfate accompanied by oxygen evolution starts at 265° and proceeds with maximum intensity at 282°. The thermal effects at 320° and 410° are reversible: the first corresponds to the polymorphous transformation of $K_2S_2O_7$, and the second to the melting of this compound. The quantity of oxygen evolved corresponds to $5.8 \pm 0.3\%$; this was confirmed by weighing the residue in the crucible and by identifying it by X-ray phase analysis as $K_2S_2O_7$.

It is known [13, 14] that under the action of mechanical forces deep physicochemical changes take place in solids, resulting from complex transformations of mechanical energy into other energy forms. In particular, mechanical processing leads to the increased reactivity of the solid phase, owing to the accumulation of intrinsic energy; by means of adequately vigorous mechanical processing, reactions may be stimulated in the solid phase which could not proceed under normal conditions.

We found that, under the mechanochemical conditions of activation chosen for our experiments, $K_2S_2O_8$ does not decompose, i.e. no oxygen evolution is observed, indicating that no local overheating ($>250°$) takes place in the reactor of the vibration mill which would lead to the irreversible decomposition of the initial material. However, mechanical activation in the vibration mill lowers the energy barrier that must be overcome to start thermal decomposition, and hence the thermal decomposition of $K_2S_2O_8$ due to mechanically processed in the vibration mill will begin at a lower temperature, around 180° (Fig. 2b). A stepwise decomposition is observed: three overlapping exothermic peaks appear in the DTA curve, at 183°, 210° and 251° The energy accumulated on mechanical activation is liberated in the form of heat in the reaction and is added to the exothermic effect, increasing the overall area of the peak by a factor of about 1.3.

The data obtained with the high-frequency apparatus indicate that the deviation of the DTA curve from the baseline always begins at a temperature between 205 and

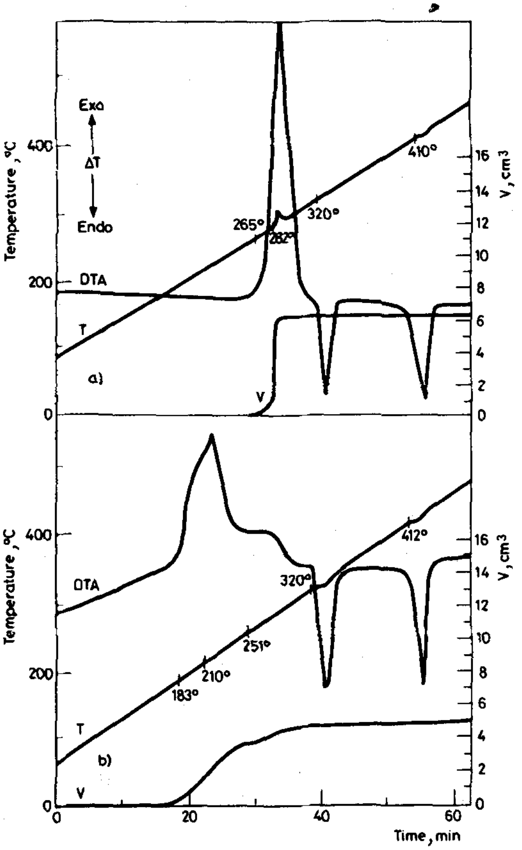
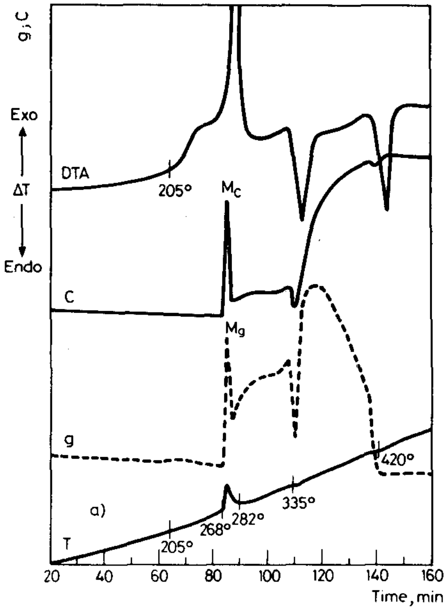


Fig. 2 a) DTA and gas-volumetric curves for initial potassium persulfate, b) DTA and gas-volumetric curves for potassium persulfate after milling in a vibration mill

208°. The thermal decomposition of the initial $K_2S_2O_8$ not subjected to mechanical processing is characterized by one or two exothermic peaks (Fig. 3a, b), the sum of the areas of the two peaks begin equal — within experimental limits — to the area of the single peak. Two endothermic peaks, the phase transition at 332—338° and the melting at 421°, relate to potassium pyrosulfate, $K_2S_2O_7$, the decomposition product of the persulfate. It is a particular feature of $K_2S_2O_8$ decomposition that the starting temperature of transformation is dependent on the conditions of the preliminary thermal history of the specimen: it was kept for 45 minutes at 130° before the experimental and subsequently subjected to further heating for recording of the high-frequency thermoanalytical curves. The results shown in Fig. 3c indicate that preliminary heating of the specimen reduces the decomposition temperature by almost 40°, i.e. it has a similar effect to that of mechanical activation, but in contrast to the latter, the reaction does not proceed stepwise, but in one stage.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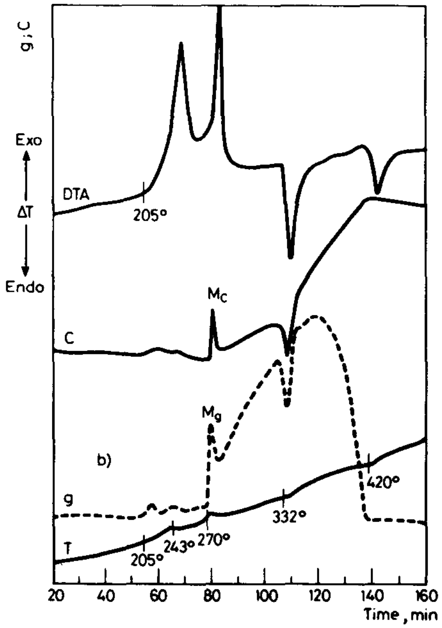
Time, min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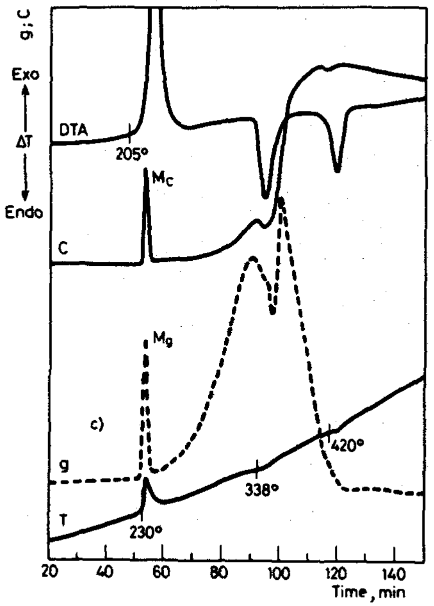

Fig. 3 a, b) DTA and high-frequency thermoanalytical curves for initial potassium persulfate, c) DTA and high-frequency thermoanalytical curves for potassium persulfate after preliminary heating for 45 min at 130°

Let us consider how the course of the electrical property curves reflects the dynamics of the structural transformations during heating. As shown by Figs 3a, b, a very weak change in electrical properties corresponds to the first transformation (at 243°), indicating that no deep change in the order of the initial structure of $K_2S_2O_8$ has occurred as yet. Only at the temperature of 268° (peaks M_c and M_g), when the lattice dramatically loses stability, does the peak M_g appear in the curve of the ohmic component g; its height and width reflect the degree and period of time of the breakdown of the structure. Thus, oxygen evolution, slow in the beginning and sudden subsequently, coincides with the abrupt change in electrical properties. These phenomena indicate that the initial structure of potassium persulfate loses its stability after around 20% of the total evolved oxygen has been released.

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Zusammenfassung — Die Wirkungen von einer vorausgehenden mechanischen Aktivierung und der thermischen Behandlung von Kaliumpersulfat auf die thermischen und elektrischen Charakteristika der Zersetzung dieser Verbindung wurde mittels DTA, TG, volumetrische Messung des freigesetzten Gases und thermische Hochfrequenz-Analyse untersucht.

Резюме — Методами ДТА, ТГ, Термогазоволюметрии и Высокочастотного термического анализа изучено влияние предварительной механической активации и термической обработки исходного персульфата калия на температурные и электрические характеристики процесса его термического разложения.