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MECHANISM OF THERMAL DECOMPOSITION OF LEAD THIOSULPHATE

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The thermal decomposition of lead thiosulfate (LTS) was studied by various methods: X-ray phase analysis, IR and ESR spectroscopy, etc. A mechanism of thermal decomposition is suggested, including rupture of the S—S bond and the formation of radicals. According to the mechanism, the reaction rate can be enhanced in the presence of the PbS phase. The formation of PbS is the cause of the topochemical character of the reaction. The composition of the thermolysis products of LTS containing a radioactive isotope of sulfur is predicted.

The thermal decomposition of lead thiosulfate (LTS) was studied earlier, and shown to proceed in two steps [1].

Our aim is to determine the general features of the reaction mechanism of thermal decomposition of LTS on the basis of experimental and literature data.

Experimental

The synthesis of LTS is described in [1]. IR spectra were recorded with a UR-10 spectrophotometer with a thermocell. The samples were prepared by pressing LTS powder with potassium bromide at 10 t cm^{-2}. Thermogravimetric analysis was performed with a vacuum thermobalance at 176–225°. ESR spectra recorded with A Bruker ER-200D spectrometer at a frequency of 9.62 GHz. The sample was heated for 4 min at 250°, then cooled down to 77 K, and the spectrum was recorded.

Results and discussion

The solid product of the thermal decomposition of LTS is an equimolar mixture of lead sulfide and lead sulfate. The thermal decomposition proceeds as follows:

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$$PbS_2O_3 \rightarrow PbS + SO_3 \tag{1}$$

$$\underline{SO_3 + PbS_2O_3 \rightarrow PbSO_4 + SO_2 + S} \tag{2}$$

$$2\,PbS_2O_3 \rightarrow PbS + PbSO_4 + SO_2 + S \tag{3}$$

Kharitonov et al. [2] have shown that the decomposition of thiosulfate ions is initiated by excitation and rupture of the sulfur-sulfur bond. Comparison of this bond energy (64 kcal mol^{-1}) [3] with the activation energy of stage (1) (22 kcal mol^{-1}) points to a more complicated character of the primary process: simultaneous rupture of the sulfur-sulfur bond with the formation of a sulfur-lead bond.

The decomposition is characterized by the appearance and then the disappearance of an additional absorption at 1070 cm^{-1}, observed as a "shoulder" of the sulfur-oxygen bonding vibration band at 1180–1200 cm^{-1}. The dependence of the thermogravimetrically determined decomposition rate at 190° and the dependence of the absorption at 1070 cm^{-1} on the decomposition time are symbatic. The absorption at 1070 cm^{-1} perhaps results from the appearance of an intermediate. The absorption band shifts to longer waves relative to 1180 cm^{-1}, the latter value being characteristic of oxygen-sulfur bond vibrations in thiosulfate and sulfate ions. This is evidence of a weaker oxygen-sulfur bond in the intermediate, e.g. as a result of an elongation of this bond.

The authors recorded an ESR signal during the thermal decomposition of LTS. The signal relates to radicals with a *g*-factor equal to 2.010. As in Hubin–Gabelica's work [4] this signal is identified with the intermediate appearance of SO_2-species.

S-shaped kinetic curves in the coordinate system degree of decomposition *vs.* time, drawn from thermogravimetric experiments in the isothermal mode of decomposition, provide evidence of the topochemical character of the process. In such a case, the acceleration of a topochemical conversion reaction at the reagent-product interface can become much easier if charge transfer is achieved in an indirect way, through the product phase. Hence, the formation of lead sulfide (the electronic conductivity of which is very high) as a reaction product allows an explanation of the autocatalytic character of the topochemical decomposition of LTS.

On the basis of the experimental and literature data, the mechanism of thermal decomposition of LTS can be written as:

$$PbS_2O_3 \rightarrow PbS^+ + SO_3^- \tag{4}$$

Heteropolar sulfur-sulfur bond breaking, leading to the appearance of SO_3^- radicals and simultaneous transformation of the lead-sulfur bond.

$$SO_3^- + PbS_2O_3 \rightarrow PbSO_4 + S_2O_2^- \tag{5}$$

Interaction of SO_3^- with lead tiosulfate, leading to reformation of oxygen-sulfur bonds and formation of solid product, i.e. lead sulfate (X-ray phase analysis); the intermediate state recorded by IR spectroscopy is presumably formed in this stage.

$$S_2O_2^- \rightarrow SO_2^- + S \tag{6}$$

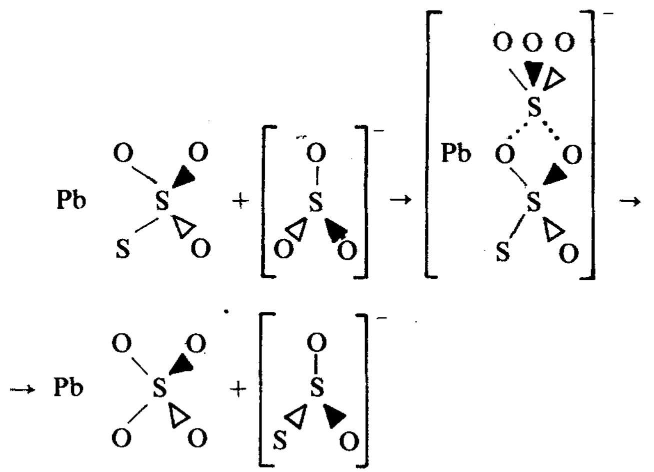
Decay of intermediate species, leading to experimentally recorded SO_2^- radicals (ESR) and formation of atomic sulfur (mass-spectrometry).

$$SO_2^- + PbS^+ \rightarrow PbS + SO_2 \tag{7}$$

Formation of neutral products i.e. sulfur dioxide and lead sulfide (mass-spectrometry and X-ray phase analysis).

It should be noted that reactions analogous to (5) are known in thiosulfate solution chemistry [5], where the destruction was shown to start with the formation of a three-centre bimolecular complex consisting of two thiosulfate ions.

In our case, the IR-spectrometric data indicating the formation of a new oxygen-sulfur bond during the thermal decomposition show that step (5) is also connected with the formation of a three-centre activated complex, where the reformation mentioned above takes place



In an analysis of the proposed mechanism, it may be observed that the incorporation of a radioactive sulfur isotope into LTS in the synthesis should result in a set of final poducts which differ in isotopic composition, Let S*, e.g. S(35) be in the thiosulfur state. Then

$$2\,PbS^{*}SO_3 \rightarrow PbS^{*} + PbSO_4 + SO_2 + S^{*}$$

Similarly, for S* in the sulphosulfur state:

$$2\,PbSS^*O_3 \rightarrow PbS + PbS^*O_4 + S$$

Thus one can test the proposed mechanism experimentally, by performing the thermal decomposition of LTS with different sulfur isotope compositions.

References

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Zusammenfassung — Die thermische Zersetzung von Bleithiosulfat PbS_2O_3 wurde durch Röntgenphasenanalyse, IR- und ESR-Spektroskopie und Thermogravimetrie untersucht. Ein Mechanismus der thermischen Zersetzung wird angegeben, der über die Trennung von S—S-Bindungen und die Bildung von Radikalen verläuft. Nach diesem Mechanismus wird die Reaktionsgeschwindigkeit in Gegenwart der PbS—Phase beschleunigt, was den topochemischen Charakter der Reaktion bedingt.

Für die Verteilung radioaktiven Schwefels auf die Zersetzungsprodukte unterschiedlich markierten (PbS^*SO_3 bzw. $PbSS^*O_3$) Bleithiosulfats wird eine Vorhersage gemacht.

Резюме — Методами рентгенофазового анализа, ИК- и ЭПР спектроскопии изучено термическое разложение тиосульфата свинца. Предложен механизм термического разложения, включая расщепление связи S—S и образование радикалов. Согласно предложенному механизму, скорость реакции может увеличиваться в присутствии сульфида свинца. Образование сульфида свинца вызывает топохимический характер реакции. Установлен состав продуктов термолиза тиосульфата свинца, содержащих радиоактивный изотоп серы.