

Investigation of Lead Thiosulfate Photolysis in Aqueous Solutions

N. B. Egorov

Tomsk Polytechnic University, pr. Lenina 30, Tomsk, 634050 Russia

e-mail: egorov@tpu.ru

Received August 7, 2013

Abstract—A model of photolysis of PbS_2O_3 aqueous solutions has been proposed on the basis of identified photolysis products and semiempirical quantum-chemical calculations. The degradation of PbS_2O_3 starts with the dissociation of the sulfur–sulfur bond in the thiosulfate group via photochemical excitation and transition of the system a whole to the activated state, which is decomposed by the solvent. The interaction of the primary photolysis products with PbS_2O_3 results in the formation of final products.

DOI: 10.1134/S0018143914010056

The photolysis of crystalline lead thiosulfate (PbS_2O_3) results in the formation of lead sulfite (PbSO_3) and elemental sulfur (S) [1], whereas the photolysis of aqueous solution of the lead thiosulfate complexes ($\text{Na}_{2(x-1)}[\text{Pb}(\text{S}_2\text{O}_3)_x]$, where the number of the ligands x varies from two to four depending on the solution concentration and on the thiosulfate to lead ion molar ratio taken for synthesizing the compound) yields lead sulfide (PbS) and S [2–4]. These findings suggest that water is an immediate participant, not an inert medium, in the photochemical degradation of lead thiosulfate.

The objective of this work was to study the photolysis products of PbS_2O_3 aqueous solutions and to reveal the role of water in the photochemical transformation of lead thiosulfate.

EXPERIMENTAL

Lead thiosulfate PbS_2O_3 was prepared as described in [5]. PbS_2O_3 is sparingly soluble in water and alcohol and insoluble in ether. The solubility in water is 6.32×10^{-4} mol/L ($K_{\text{sp}} = 4 \times 10^{-7}$) [6]. Saturated aqueous solutions of PbS_2O_3 were used in the photolysis experiments.

The source of UV radiation was a high-pressure mercury lamp.

Photolysis, and recording of electronic absorption spectra, and determination of a particle size were conducted in a fused-silica cell with an optical path length of 1 cm using an Evolution 600 spectrophotometer. The particle size and particle size distribution were determined with a Delsa Nano C analyzer.

An inoLab pH/Ion 740 WTW ionmeter with a SenTix 81 combination electrode was used for pH measurements.

A solution (20 mL) was placed under the mercury lamp and irradiated for 10 min at room temperature.

The procedure of the precipitate formation was repeated many times to accumulate an amount sufficient for analysis. The precipitate formed was separated by centrifugation, washed three times with water and ethanol, and dried in a vacuum desiccator.

X-ray diffractograms were recorded on a D8 DISCOVER diffractometer with CuK_α radiation ($\lambda = 0.154056$ nm).

IR spectra were recorded on a Nicolet 6700 Fourier-transform IR spectrometer in the $400\text{--}4000$ cm^{-1} range. Samples were prepared by pelletizing with KBr. The IR spectra of PbS_2O_3 solutions were recorded in the range of $600\text{--}4000$ cm^{-1} using an ATR attachment.

Geometry optimization and molecular dynamics calculations were performed with the use of the HyperChem software. The molecular mechanics method and the PM3 semiempirical quantum chemistry method were used. By molecular mechanics calculation, an optimized model of PbS_2O_3 was obtained by, which was next surrounded with 27 water molecules (“periodic box” option) and calculated by the PM3 method.

RESULTS AND DISCUSSION

Electronic absorption spectra of the initial and photolyzed solutions of PbS_2O_3 are presented in Fig. 1. The spectrum of the initial PbS_2O_3 solution is characterized by the presence of two absorption bands in the ultraviolet region: the 215-nm band due to charge transfer from thiosulfate ions to solvent molecules and the thiosulfate to lead ion charge-transfer band of the at 256 nm [7]. The irradiation of a PbS_2O_3 solution results in a decrease in the intensity of these bands, which is accompanied by the emergence of absorption in the region of 300–900 nm without a distinct maximum, with the solution taking a brown color.

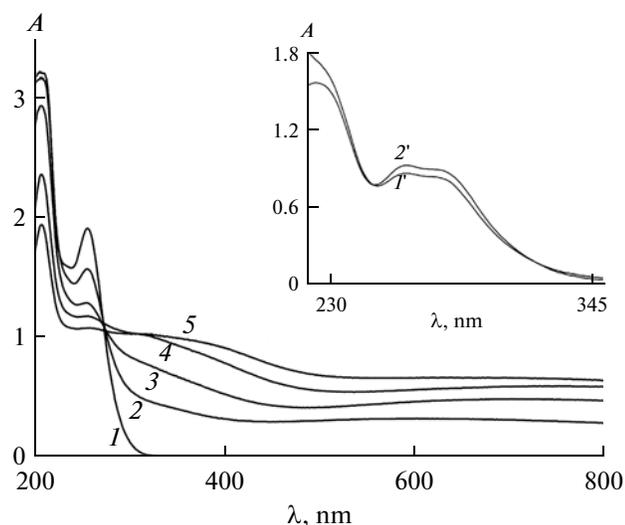


Fig. 1. Electronic absorption spectra of the PbS_2O_3 solutions: (1) initial; and irradiated for (2) 1, (3) 2, (4) 4, and (5) 6 min. Inset: electronic spectra of (1') elemental sulfur in *n*-hexane, and (2') compounds extracted with *n*-hexane from the solid product of PbS_2O_3 photolysis.

The formation of colored solutions with a broad absorption band in the visible spectral region indicates that photolysis results in a PbS colloid solution [2]. According to the particle-size distribution curves, a fraction of particles of a ~ 240 nm size forms a peak during the initial time (10 s) of the photolysis. As the photolysis time increases (5 min), the average particle size increases to ~ 550 nm. At a longer irradiation time (10 min), the photolysis is characterized by a broad size distribution of particles from 500 nm to 10 μm , which have no aggregation stability and precipitate from the bulk of the solution.

The initial PbS_2O_3 solutions are slightly acidic. Photolysis results in buildup of hydrogen ions in the solution (Fig. 2).

The treatment with *n*-hexane of the PbS_2O_3 photolysis product isolated from the solution by centrifugation showed that the electronic absorption spectrum of the extract contain bands characteristic of dissolved S^0 [8] (Fig. 1, inset).

Figure 3 presents the X-ray diffraction pattern of the solid product obtained after 10-min irradiation of PbS_2O_3 aqueous solutions. There are reflections attributed to PbS, PbSO_4 , and PbSO_3 .

The IR study of the precipitate (Fig. 4, curve 1) showed the presence of absorption bands at 1169, 1056, and 597 cm^{-1} characteristic of PbSO_4 (Fig. 4, curve 2) and bands at 959, 882, 629, and 480 cm^{-1} characteristic of PbSO_3 (Fig. 4, curve 3). These results of the IR study are consistent with the X-ray diffraction data.

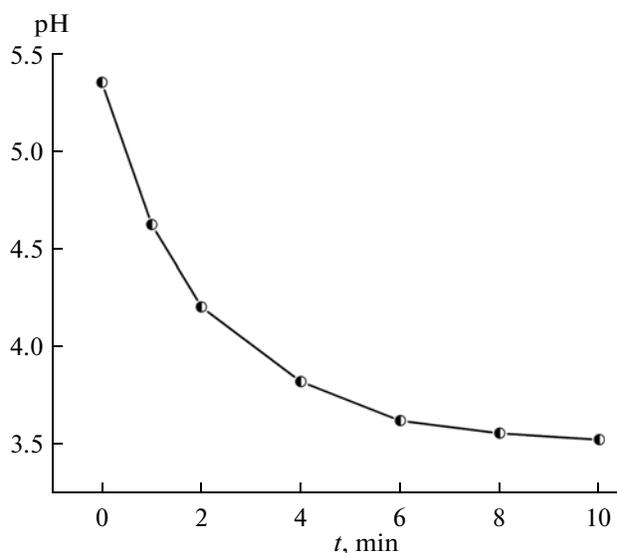


Fig. 2. Changes in pH of the PbS_2O_3 solution during its photolysis.

Thus, the identified products of the photolysis of PbS_2O_3 aqueous solutions are PbS, PbSO_4 , PbSO_3 , S^0 , and H^+ .

To elucidate the structure of PbS_2O_3 in aqueous solutions, we measured its IR spectrum and compared with the IR spectrum of crystalline PbS_2O_3 (Fig. 4, curve 4, 5). As shown in [7] the $\nu_a(\text{SO})$ vibration mode is the most useful for determining the structure of thiosulfate compounds: >1175 cm^{-1} (S-bridging), 1175–1130 cm^{-1} (S-coordinated), ~ 1130 cm^{-1} (ionic $\text{S}_2\text{O}_3^{2-}$); and <1130 cm^{-1} (O-coordinated). A displacement of the $\nu_s(\text{SO})$ vibration frequency above 1000 cm^{-1} indicates coordination through the sulfur atom, and a shift below 1000 cm^{-1} suggests coordination through the oxygen atom.

The frequency values in the PbS_2O_3 IR spectra indicate that the thiosulfate group is coordinated to the lead atom through the sulfur and oxygen and manifests itself as a bidentate ligand. The results are confirmed by the data on the PbS_2O_3 crystal structure as reported in [9]. It was found that the lead atom in PbS_2O_3 coordinates six oxygen atoms and three sulfur atoms.

The thiosulfate group does not undergo significant changes upon dissolution of PbS_2O_3 in water as shown by the positions of its stretching vibration bands $\nu_a(\text{SO})$ and $\nu_s(\text{SO})$, which change only slightly. This indicates that PbS_2O_3 in water exists in the form of neutral molecule, in agreement with published data [10]. It is also noteworthy that the splitting of the anti-symmetric stretching vibrations in the IR spectrum of the PbS_2O_3 aqueous solution becomes more pro-

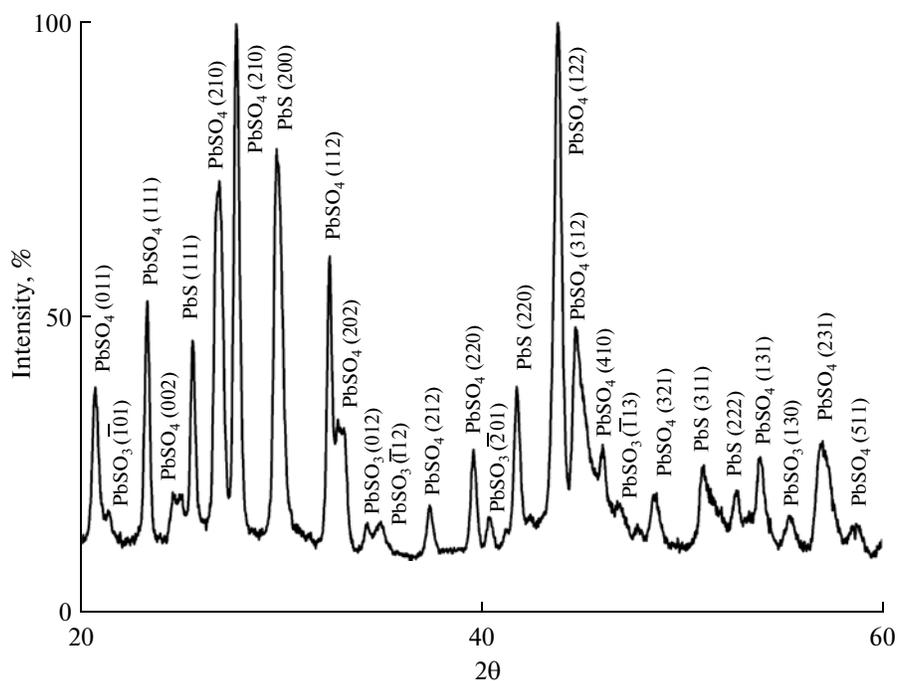


Fig. 3. Diffractogram of the solid product of 10-min photolysis of an aqueous PbS_2O_3 solution.

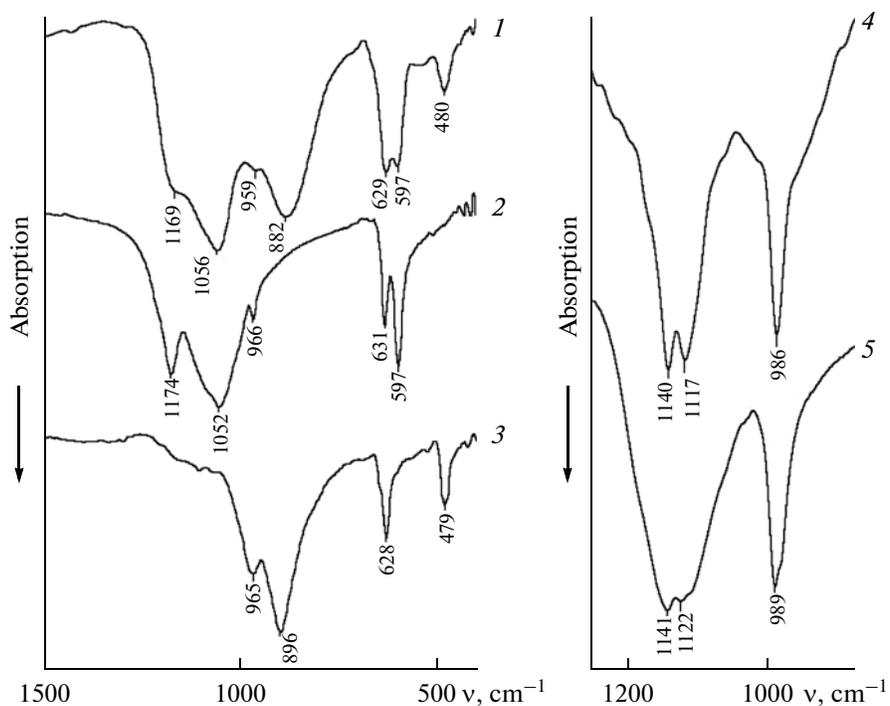


Fig. 4. IR spectra of (1) the product of 10-min photolysis of an aqueous PbS_2O_3 solution, (2) $PbSO_4$, (3) $PbSO_3$, (4) PbS_2O_3 aqueous solution, and (5) crystalline PbS_2O_3 .

Table 1. S–S bond lengths (d) in some thiosulfate compounds

Compound	d_{S-S} , Å
PbS ₂ O ₃	2.110 [9]
Na ₂ S ₂ O ₃ · 5H ₂ O	2.024 [12]
NiS ₂ O ₃ · 6H ₂ O	2.015 [13]
CdS ₂ O ₃ · 2H ₂ O	2.056 [14]
BaS ₂ O ₃ · H ₂ O	1.964 [15]
NaAgS ₂ O ₃ · H ₂ O	2.050 [16]
Na ₃ Au(S ₂ O ₃) ₂ · 2H ₂ O	2.060 [17]
Tl ₂ S ₂ O ₃	1.750 [18]
Pb ₃ (S ₂ O ₃) ₂ (CH ₃ COO) ₂	2.045 [19]

nounced, which may be related to the enhancement of nonequivalence of the three thiosulfate oxygen atoms.

Calculation of the force constants [11] showed that the S–S bond is the weakest in the thiosulfate ion. Analysis of the data on the crystal structure of thiosulfate compounds showed that the S–S bond in PbS₂O₃ has a large length (Table 1) and is evidently easy to break upon excitation.

The stretching vibrations in the IR spectrum of the PbS₂O₃ aqueous solution are slightly shifted toward lower frequencies in comparison with the IR spectrum of crystalline PbS₂O₃ (Fig. 4, curves 4, 5). Such a shift of vibration frequency indicates an increase in the length of bonds between the atoms in the thiosulfate group (S–O and S–S) upon transition from the crystalline to the dissolved state and, hence, their further weakening.

Computational methods were used to explain the effect of water on the photolysis of PbS₂O₃ and to

reveal possible routes of its photodegradation in aqueous solutions and in the solid state. In the quantum-chemical experiment, the results of calculation of the bond lengths in the suggested structures were compared. The results of the IR study—coordination of the lead atom by the sulfur and oxygen atoms of the thiosulfate group—were used for building the spatial model of PbS₂O₃.

Consideration of the sequence of transformations was based on the assumption that the S–S bond is the weakest bond in the thiosulfate group and it is from its dissociation that the degradation of PbS₂O₃ begins upon photochemical excitation. This assumption is indirectly confirmed by the fact that aqueous PbS₂O₃ solutions undergo partial decomposition yielding PbS during their long-term storage in the light or in the dark. The formation of PbS by hydrolysis would be unlikely if the S–S bond were strong. In addition, it was taken into account that the PbS₂O₃ decomposition to the final products is determined by the reactivity of the solvent, since water molecules can add to the S–S bond dissociation sites, both S⁶⁺ and S²⁻.

Figure 5 presents the scheme of transformation of hydrated PbS₂O₃. The calculated bond lengths are given in Table 2.

The calculations showed that the elongation of the Pb–O bond with simultaneous shortening of the other bonds take place after the rupture of the S–S bond in the thiosulfate group (Fig. 5, structure II). Thus, the distance between the sulfur (+6) and sulfur (–2) atoms and water molecules decreases from 3.454 to 1.703 Å, indicating the possible addition of water molecules to the S–S bond dissociation sites.

The addition on waters molecule binding to the central sulfur (+6) and the sulfide sulfur (–2) (Fig. 5, structure III) results in further elongation of the Pb–O bond (from 2.862 to 5.897 Å) and shortening of the Pb–S bond (from 2.304 to 2.243 Å), which actually

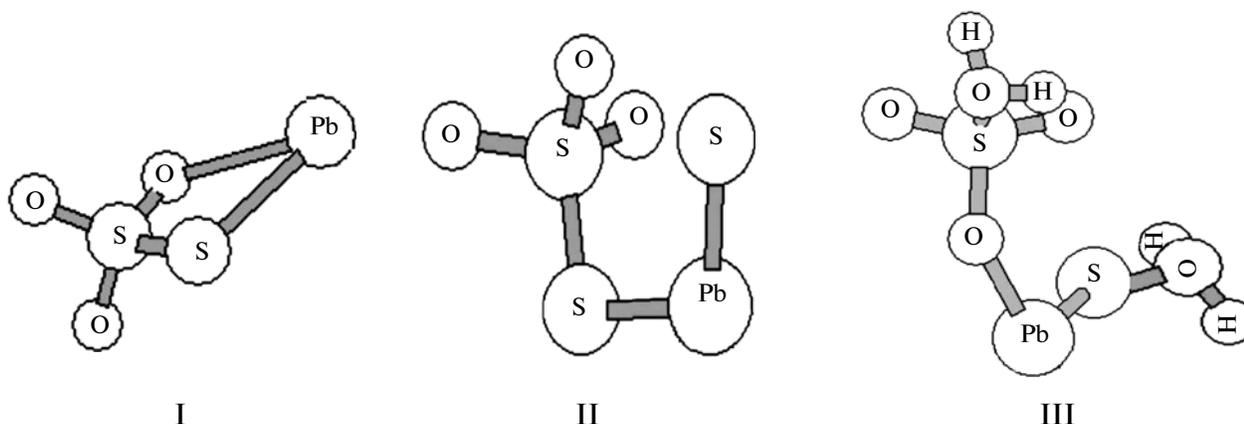


Fig. 5. Scheme of the transformations of hydrated PbS₂O₃ during photolysis: (I) PbS₂O₃ structure before S–S bond dissociation, (II) PbS₂O₃ structure after S–S bond dissociation, and (III) PbS₂O₃ structure after the S–S bond dissociation and addition of water molecules to S⁶⁺ and S²⁻.

Table 2. Bond lengths (d) of the suggested PbS_2O_3 structures, which change during photolysis, as calculated by the semiempirical PM3 method

Bond	d , Å in structure I	d , Å in structure II	d , Å in structure III
Pb–S	2.839	2.304	2.243
Pb–O	2.098	2.862	5.897
S–O (1)	1.619	1.495	1.415
S–O (2)	1.484	1.464	1.431
S–O (3)	1.465	1.482	1.432
S–S	2.146	–	–

imply the detachment of the hydrated SO_3 group from the lead atom to give PbS and H_2SO_4 .

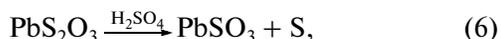
Thus, proceeding from the general concepts of the photolysis mechanism, we can assume that the primary stage of the photolysis of PbS_2O_3 aqueous solutions is the excitation and dissociation of the S–S bond in the thiosulfate group resulting in the formation of an activated complex, which is hydrolyzed to give PbS and H_2SO_4 :



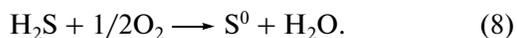
The results obtained by the computational methods explain only the formation of the primary photolysis products PbS and H_2SO_4 . It is obvious that the presence of PbSO_4 , PbSO_3 , and S^0 in the photolysis products is due to secondary reactions.

It is known that acidification of $\text{Na}_2\text{S}_2\text{O}_3$ solutions results in their decomposition with the formation of thiosulfuric acid $\text{H}_2\text{S}_2\text{O}_3$, which is very unstable and can decompose to give S^0 and H_2SO_3 [20].

With allowance for the buildup of H^+ during the photolysis in our case (Fig. 2), the following reactions are possible:



Since the photolysis was run in the presence of air oxygen, H_2S could be oxidized according to the following reaction:



It is likely that the difference in the photolysis products between crystalline PbS_2O_3 and PbS_2O_3 aqueous solutions is due to the impossibility of form-

ing a strong bond between the lead and sulfur atoms after the dissociation of the S–S bond in the thiosulfate group, since the conditions for the formation of the strong Pb–S bond are less favorable in the solid state because of the rigidity of the crystal lattice. The presence of negatively charged oxygen and sulfur ions in crystalline PbS_2O_3 creates a field that prevents the lead and sulfur atoms from approaching one another, thereby ultimately resulting in enhancement of the Pb–O bond and the rupture of the Pb–S bond to give PbSO_3 and S^0 , the experimentally proved products [1].

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Translated by L. Brovko