SHORT COMMUNICATIONS PHOTOCHEMISTRY

On the Photolysis of Barium Thiosulfate

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The photolysis of thiosulfates of alkali and nonferrous metals is well-documented [1-5]. This cannot be said on the photolysis of alkaline earth metal thiosulfates; therefore, in this work, we studied the photolysis of barium thiosulfate (BaS₂O₃) in order to reveal the conditions of photolysis and to determine the final products.

We found experimentally that solid $BaS_2O_3 \cdot H_2O$ and its deaerated aqueous solutions are insensitive to UV radiation. The irradiation of air-saturated aqueous solutions of BaS_2O_3 leads to a decrease in the concentration of barium ions in solution (Fig. 1) and to the formation of a colloidal solution, which decomposes with time to form a white precipitate.

The synthesis of $BaS_2O_3 \cdot H_2O$ was carried out in accordance with a published procedure [6]. A solution of BaS_2O_3 with a concentration of 7.5 × 10⁻³ mol/L and a volume of 40 mL was irradiated with the full light of a DRT-240 high-pressure mercury-vapor lamp for 40 min at room temperature. The resulting precipitate was separated from the solution by centrifuga-



Fig. 1. Changes in the concentration of barium ions in an aqueous solution of BaS_2O_3 (7.5 \times 10⁻³ mol/L) depending on the time of UV irradiation.

tion, triply washed with water and then with ethanol, and dried in a vacuum desiccator. The precipitate preparation procedure was multiply repeated to accumulate an amount sufficient for analysis. The concentrations of barium ions before and after photolysis were determined on an ICAP 6300 Duo atomic emission spectrometer.

The diffractograms were recorded on a Rigaku Miniflex 600 diffractometer. The IR spectra were measured on a Nicolet 6700 Fourier transform IR spectrometer in a range from 400 to 4000 cm⁻¹. The samples were prepared as pellets with KBr. The values of pH were measured on an inoLab pH/Ion 740 WTW ion meter with the use of a Sentix 81 combined electrode.

The diffractogram of the precipitate obtained by photolyzing aqueous BaS_2O_3 solutions contained only lines due to the $BaSO_4$ phase (PDF 01-072-1390). An IRspectroscopic study of the precipitate showed that the IR spectrum contained absorption bands at 1170, 1117, 1074, 997, and 611 cm⁻¹, which are characteristic of $BaSO_4$. Furthermore, the sediment exhibited absorption bands at 925, 635, and 497 cm⁻¹ characteristic of $BaSO_3$ and absorption bands at 686, 556, and 540 cm⁻¹ characteristic of BaS_2O_3 . The intensity of the absorption bands of $BaSO_4$ was considerably higher than that of absorption bands due to $BaSO_3$ and BaS_2O_3 .

The treatment of the photolysis product of BaS_2O_3 solutions, which was separated by centrifugation, with *n*-hexane showed that the electron spectrum of the extract did not contain absorption bands characteristic of dissolved elemental sulfur. Its absence from the solid-phase products of photolysis is a distinctive feature, as opposed to the products of photolysis of the aqueous solutions of lead thiosulfate [7].

It was organoleptically revealed that the UV irradiation of the air-saturated solutions of BaS_2O_3 was accompanied by the release of sulfur-containing gas. The gas released during the photolysis of a BaS_2O_3 solution was transferred into a receiver by passing air through the solution and analyzed with the aid of a TRACE DSQ gas chromatography–mass spectrometry instrument. The analysis showed that in addition to the peaks of ions due to the components of air (N₂, O₂, Ar, CO₂, and H₂O), the gas phase exhibited the peaks of ions with mass numbers (m/z) of 48 and 64, which belong to the fragment radical ion SO⁺ and the molec-

ular ion SO_2^+ . This fact is indicative of the formation of sulfur dioxide (SO₂) in the course of the photolysis of the BaS₂O₃ solution.

The initial solutions of BaS_2O_3 had nearly neutral values of pH. The irradiation of 20 mL of a solution for 10 min was accompanied by a change in the pH from 6.11 to 5.05. Thus, the photolysis of the aqueous solutions of BaS_2O_3 led to the accumulation of hydrogen ions.

The experiments showed that $BaSO_4$, $BaSO_3$, SO_2 , and H^+ are the final products of the photolysis of airsaturated aqueous solutions of BaS_2O_3 .

Taking into account the fact that the S–S bond is the weakest bond in the thiosulfate ion [8] and the thiosulfate group in $BaS_2O_3 \cdot H_2O$ is mainly coordinated to the barium atom through oxygen [9], we believe that the most obvious pathway of the formation of the photolysis products is the direct decomposition of dissolved BaS_2O_3 by UV radiation in the presence of oxygen:

$$BaS_2O_3 + hv \rightarrow BaSO_3 + S.$$
 (1)

Then, the primary products $BaSO_3$ and S react with the components of the solution to form $BaSO_4$ and SO_2 , which can dissolve in aqueous solution with the formation of H_2SO_3 :

$$BaSO_3 + 1/2O_2 \rightarrow BaSO_4, \tag{2}$$

$$S + H_2O + O_2 \rightarrow H_2SO_3. \tag{3}$$

Thus, the photolysis of air-saturated aqueous solutions of BaS_2O_3 can be represented by the overall reaction scheme

$$BaS_2O_3 + H_2O + 1.5O_2 + hv \rightarrow BaSO_4 + H_2SO_3$$
. (4)

The dissolved BaS_2O_3 and H_2SO_3 can interact to give $BaSO_3$:

$$BaS_2O_3 + H_2SO_3 \rightarrow BaSO_3 + H_2S_2O_3.$$
 (5)

This reaction is feasible because of a difference between the solubility products of BaS₂O₃ and BaSO₃, which are 1.6×10^{-5} and 8.0×10^{-7} , respectively [10].

The presence of solid BaS_2O_3 in the products of photolysis can be due to the occlusion of the initial solution, which is possible at a high rate of formation of the crystal lattice of the resulting particles.

In summary, we experimentally found that only air-saturated aqueous solutions of BaS_2O_3 lead to its photolysis by UV light, identified the final products, and proposed a reaction scheme for the UV photolysis of aqueous solutions of BaS_2O_3 with the participation of water and oxygen.

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