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Study of Photolysis of $K_4[Cd(S_2O_3)_3]$ Solutions in Aqueous Isopropanol

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Abstract—Photolysis of $K_4[Cd(S_2O_3)_3]$ solutions in aqueous isopropanol under irradiation with high-pressure mercury-quartz lamp has been studied by spectroscopy methods. The photolysis products have been identified by X-ray diffraction analysis; their formation mechanism has been suggested. The primary photolysis product is nanosized CdS, its irradiation initiating further redox transformations of the solution components to give the final products.

Keywords: photolysis, potassium trithiosulfatocadmate, spectroscopy

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Cadmium thiosulfates are interesting objects due to variable stereochemistry [1–5], catalytic properties [6–8], and ability to yield cadmium sulfide upon decomposition [9–11]. Due to the latter property, cadmium thiosulfates are promising precursors of CdS nanoparticles [12–15].

Photolysis of aqueous solution of cadmium thiosulfates may lead to formation of nanoparticles of CdS cubic modification; simultaneously, SO_4^{2-}, $S_4O_6^{2-}$, and H^+ ions are accumulated in the solution [16–20]. Even after thorough washing, the formed CdS nanoparticles contain surface-adsorbed $S_2O_3^{2-}$ ions that provide for electrostatic repulsion preventing the particles enlargement [21]. Hence, $S_2O_3^{2-}$ ions act both as sulfur source and CdS nanoparticles stabilizer.

The solvent nature is known to significantly affect the features of photolysis of chalcogenide compounds, including structure and size of the formed semiconductor nanoparticles [22]. In this work, we studied photolysis of potassium trithiosulfatocadmate in water–isopropanol media.

Figure 1 presented electronic absorption spectra of $K_4[Cd(S_2O_3)_3]$ solutions in aqueous isopropanol after photolysis. As seen from Fig. 1, introduction of isopropanol led to significant increase of the photolysis product absorption. In other words, $K_4[Cd(S_2O_3)_3]$ became more light-sensitive in the presence of isopropanol, the effect being enhanced with increase of the alcohol concentration in the mixture. Evidently, substitution of water molecules solvating $K_4[Cd(S_2O_3)_3]$ with the alcohol molecules reduced the complex compound stability. That was confirmed by IR spectroscopy as well: the frequency of ν_s(S–O) vibration of thiosulfate group, being of 996 cm^{-1} in the aqueous solution, shifted to 1005 cm^{-1} in the case of solutions in aqueous isopropanol. The absorption band

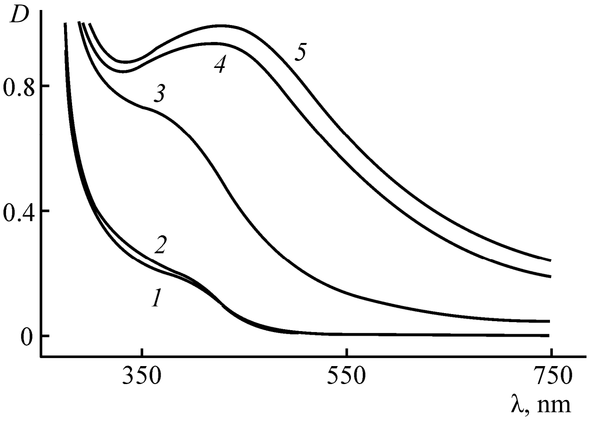

Fig. 1. Electronic absorption spectra of $K_4[Cd(S_2O_3)_3]$ solutions (0.01 mol/L) in water (*1*) and in aqueous isopropanol (*2–5*) after photolysis during 2 min. The binary solvent composition (water : isopropanol): 7.3 : 1 (*2*), 4 : 1 (*3*), 2 : 1 (*4*); 1 : 1 (*5*).

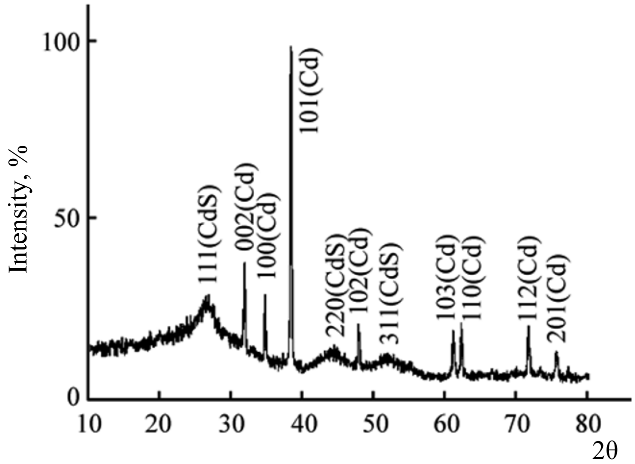

Fig. 2. X-ray diffraction pattern of products of photolysis of $K_4[Cd(S_2O_3)_3]$ solution in aqueous isopropanol.

shift reflected the higher strength of S–O bond in the thiosulfate group and weakening of the cadmium–thiosulfate bond.

X-ray diffraction study of the photolysis product (Fig. 2) confirmed formation of Cd^0 and cubic modification of CdS in the course of $K_4[Cd(S_2O_3)_3]$ photolysis in aqueous isopropanol medium.

Noteworthily, the particles formed in solutions in aqueous isopropanol were larger than those formed in aqueous solution. In particular, the only type of particles (~100 nm) was formed at the initial stage of photolysis of $K_4[Cd(S_2O_3)_3]$ aqueous solution (0.02 mol/L), whereas in the case of solutions in aqueous isopropanol two types of particles were formed (~1000 nm and ~20000 nm). The particles grew larger in the course of photolysis.

Figure 3 shows the representative curves of size distribution of particles formed after 2 min of photolysis of $K_4[Cd(S_2O_3)_3]$ in aqueous as well as in the aqueous-alcoholic solutions. In the case of aqueous solution, the 175 ± 90 nm particles were observed, whereas in the case of water–isopropanol mixed solvent two types of particles were revealed, with sizes of 860 ± 110 and 24000 ± 4600 nm. The effect of the solvent nature on rates of formation and growth of the particles can be explained by decreased stability of $K_4[Cd(S_2O_3)_3]$ in the case of the mixed solvent. Hence, the X-ray diffraction and particles size analysis revealed that the changes of electronic absorption spectra (Fig. 1) were due to formation of CdS and Cd^0 particles as well as due to their enlargement.

According to the results reported in [21], UV irradiation of aqueous solutions of cadmium thiosulfates did not yield elemental sulfur. In the case of $K_4[Cd(S_2O_3)_3]$ photolysis in the presence of isopropanol, S^0 was extracted with *n*-hexane from the photolysis product (Fig. 4).

After addition of $CaCl_2$ solution to the photolyzed solution of $K_4[Cd(S_2O_3)_3]$ in aqueous isopropanol, precipitate was formed with IR spectrum being identical to that of $CaSO_4$ (Fig. 5, curves *1*, *2*); thus pointing at formation of SO_4^{2-} ions in the course of photolysis.

The presence of SO_4^{2-} ions was further confirmed by IR spectra of water-washed and dried product of photolysis of $K_4[Cd(S_2O_3)_3]$ solution in aqueous isopropanol (Fig. 5, curve *3*), whereas IR spectrum of the product of the aqueous solution photolysis contained the absorption bands typical of $S_2O_3^{2-}$ [21].

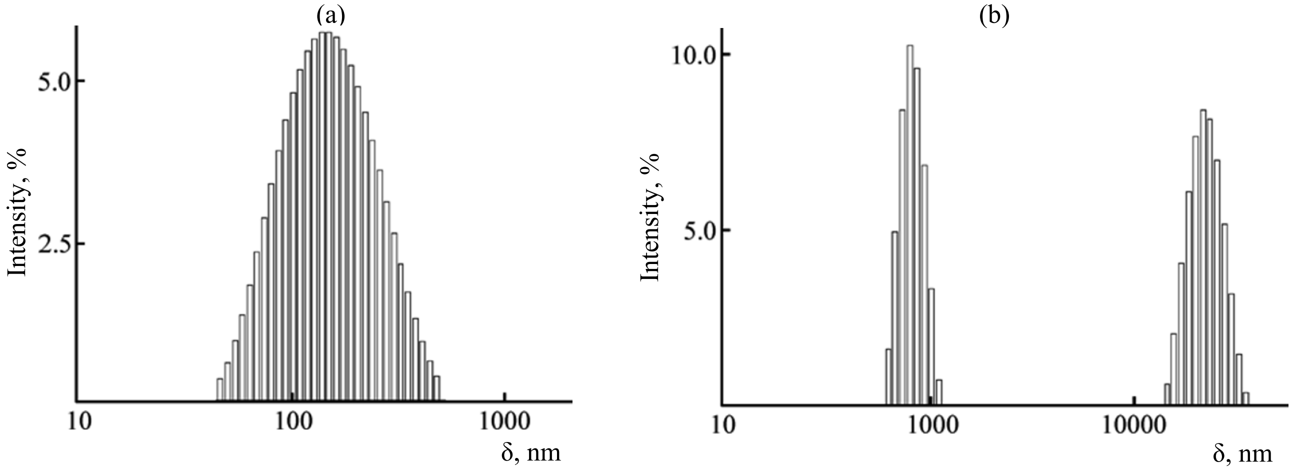

Fig. 3. Size distribution of the particles obtained via photolysis of $K_4[Cd(S_2O_3)_3]$ solutions (0.02 mol/L) during 2 min: (a) aqueous solution and (b) solution in the water–isopropanol 2 : 1 mixture.

For reference, IR spectrum of $CdSO_4$ is shown in the same plot (Fig. 5, curve *4*). As $CdSO_4$ is readily water-soluble (76.4 g $CdSO_4$/100 g H_2O [23]), and the photolysis product had been thoroughly water-washed, we suspect that $CdSO_4$ was formed at the surface of CdS particles in the course of oxidative-photolytic corrosion [Eq. (1)] discussed in [24, 25].

$$CdS + 2O_2 + h\nu \rightarrow CdSO_4. \qquad (1)$$

The starting solution of $K_4[Cd(S_2O_3)_3]$ in aqueous isopropanol was weakly acidic. In the course of photolysis, H^+ ions were accumulated in the solution.

Study of the photolysis products by means of IR spectroscopy (ATR) revealed that, similarly to the case of the aqueous solutions, photolysis of $K_4[Cd(S_2O_3)_3]$ in water-isopropanol media yielded $S_4O_6^{2-}$ ions. IR spectra of the starting and the photolyzed solutions of $K_4[Cd(S_2O_3)_3]$ are collected in Fig. 6. As seen from the figure, in the course of photolysis the absorption bands with maxima at 1038 and 1015 cm^{-1} appeared and grew stronger. For reference, IR spectra of $K_2S_4O_6$ solution and of isopropanol are shown in the same plot (Fig. 6, curves *5*, *6*). The maxima at 1038 and 1015 cm^{-1} were assigned to stretching of $S_4O_6^{2-}$ [26]. Moreover, the IR data confirmed that isopropanol was not chemically changed in the course of photolysis.

To summarize, the following species were identified in the products of photolysis of $K_4[Cd(S_2O_3)_3]$ solutions in aqueous isopropanol: CdS, Cd^0, S^0, H^+, SO_4^{2-}, and $S_4O_6^{2-}$.

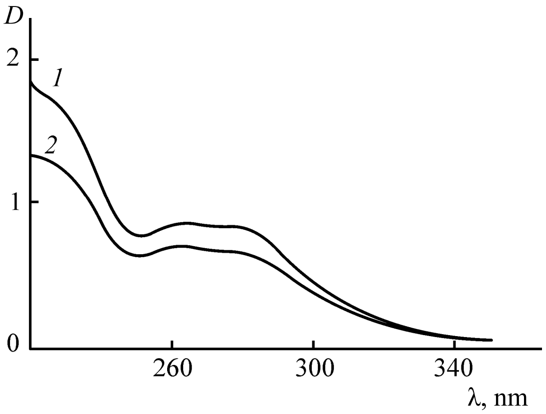

Fig. 4. Electronic absorption spectra of elemental sulfur in *n*-hexane (*1*) and of the substance extracted with *n*-hexane from solid product of photolysis of $K_4[Cd(S_2O_3)_3]$ solution in aqueous isopropanol (*2*).

In aqueous solutions, CdS is formed in the course of photochemical decomposition of $K_4[Cd(S_2O_3)_3]$ following Eq. 2 [21].

$$K_4[Cd(S_2O_3)_3] + H_2O + h\nu \rightarrow CdS + H_2SO_4 + 2K_2S_2O_3. \qquad (2)$$

Photolysis of $K_4[Cd(S_2O_3)_3]$ solutions in water as well as in aqueous isopropanol yielded cubic modification of CdS, pointing at similar reaction mechanism. In the case of solutions in aqueous isopropanol, CdS was the primary product of $K_4[Cd(S_2O_3)_3]$ photolysis, whereas Cd^0 and S^0 were formed via secondary reactions. Other products of $K_4[Cd(S_2O_3)_3]$ photolysis

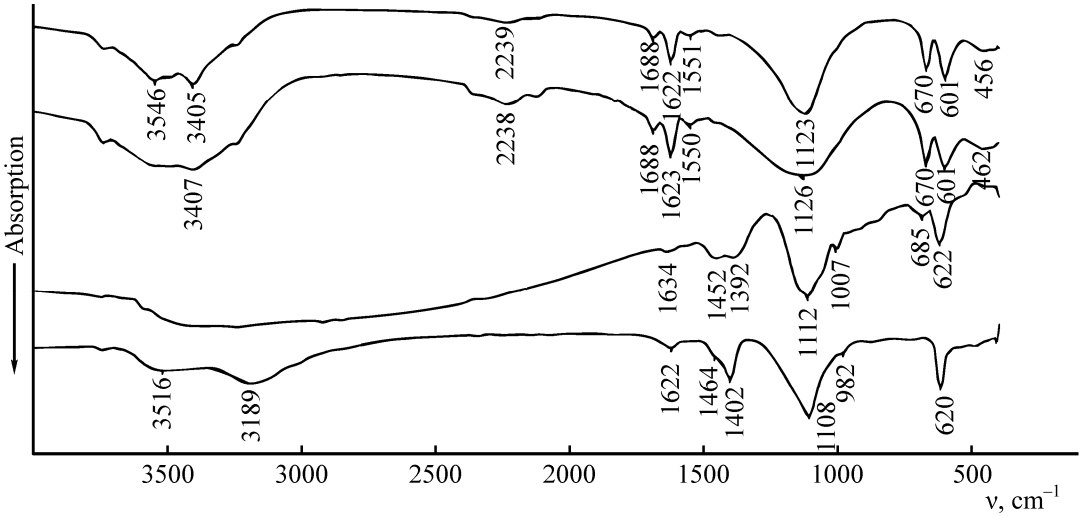

Fig. 5. IR spectra of the precipitate obtained upon addition of $CaCl_2$ to the photolyzed solution of $K_4[Cd(S_2O_3)_3]$ (*1*), $CaSO_4$ (*2*), and the solid product of photolysis of $K_4[Cd(S_2O_3)_3]$ solution in the water–isopropanol 3 : 1 mixture (*3*) (3 : 1); and reference spectrum of $CdSO_4$ (*4*).

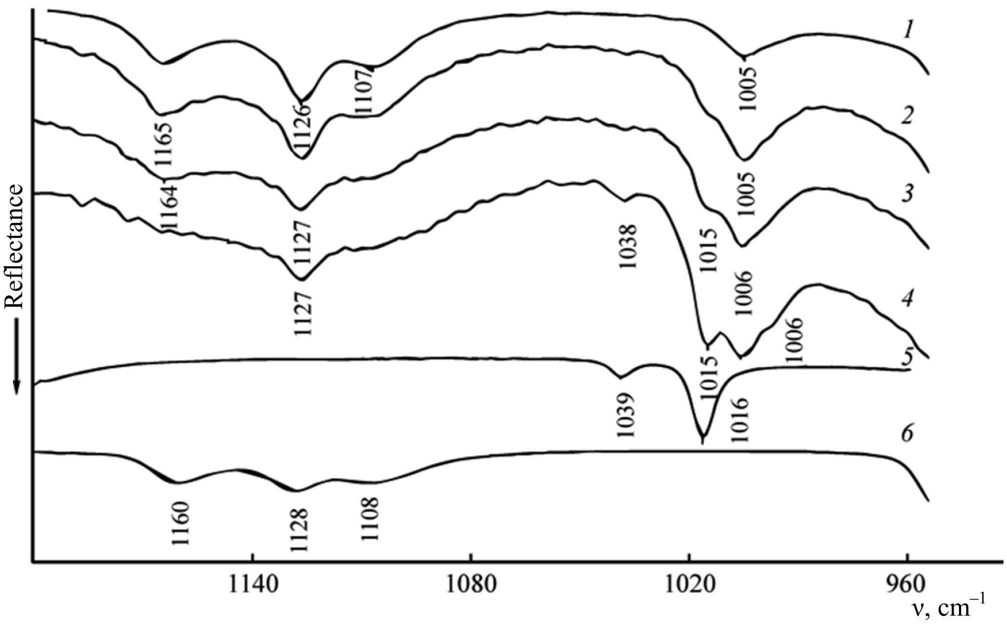

Fig. 6. ATR IR spectra of $K_4[Cd(S_2O_3)_3]$ solutions in aqueous isopropanol before (*1*) and after (*2–4*) photolysis during 60 (*2*), 80 (*3*), and 120 min (*4*); and reference spectra of $K_2S_4O_6$ aqueous solution (*5*) and isopropanol (*6*).

could not lead to formation of Cd and S, they should have resulted from photochemical reduction of CdS.

The obtained experimental data suggested the following scheme of the secondary photochemical processes involving CdS particles. Absorption of the radiation quantum with CdS nanoparticles resulted in formation of electrons (e^-_{CB}) in the carrier band and of the holes (h^+_{VB}) in the valence band [Eq. (3)].

$$CdS + h\nu \rightarrow CdS\ (e^-_{CB} + h^+_{VB}). \tag{3}$$

Due to the low diffusion time, the photochemically generated electrons and holes were predominantlyocalized at the surface of CdS nanoparticles in the form of $S^{\cdot-}$ anion-radicals and Cd^+ cations [Eqs. (4) and (5)].

$$S^{2-} + h^+_{VB} \rightarrow S^{\cdot-}_{surf}, \tag{4}$$

$$Cd^{2+} + e^-_{CB} \rightarrow Cd^+_{surf}. \tag{5}$$

The charged particles could be consumed in the reactions with electron-donating species adsorbed at CdS. In aqueous solutions, the charged particles could interact with $S_2O_3^{2-}$ ions and with water molecules [Eqs. (6)–(11)].

$$S^{\cdot-}_{surf} + S_2O^{2-}_{3surf} \rightarrow S^{2-}_{surf} + S_2O_3^{\cdot-}, \tag{6}$$

$$Cd^+_{surf} + nH_2O_{surf} \rightarrow Cd^{2+}_{surf} + e^-_{aq}, \tag{7}$$

$$Cd^{2+}_{surf} + S^{2-}_{surf} \rightarrow CdS_{surf}, \tag{8}$$

$$e^-_{aq} + S_2O_3^{2-} \rightarrow SO_3^{2-} + S^{\cdot-} + nH_2O, \tag{9}$$

$$S_2O_3^{2-} + S^{\cdot-} \rightarrow S^{2-} + S_2O_3^{\cdot-}, \tag{10}$$

$$2S_2O_3^{\cdot-} \rightarrow S_4O_6^{2-}. \tag{11}$$

In the aqueous-isopropanol media, additional interaction with the alcohol molecule was possible [Eq. (12)].

$$Cd^+_{surf} + S^{\cdot-}_{surf} \xrightarrow{i\text{-PrOH}} Cd^0 + S^0. \tag{12}$$

To conclude, formation of elemental Cd^0 and S^0 upon photolysis of solutions of $K_4[Cd(S_2O_3)_3]$ in aqueous isopropanol could be due to participation of isopropanol in the charge transfer.

The absence of S^{2-} and SO_3^{2-} ions in the photolysis products could be either due to their oxidation with air oxygen into SO_4^{2-} or due o their interaction with photochemically generated holes followed by recombination of the formed anion-radicals into $S_2O_3^{2-}$ [Eqs. (13)–(15)], see discussion in [25]).

$$S^{2-} + h^+_{VB} \rightarrow S^{\cdot-}, \tag{13}$$

$$SO_3^{2-} + h^+_{VB} \rightarrow SO_3^{\cdot-}, \tag{14}$$

$$S^{\cdot-} + SO_3^{\cdot-} \rightarrow S_2O_3^{2-}. \tag{15}$$

In order to discriminate the possible pathways of S^{2-} and SO_3^{2-} consumption, additional experiments under inert atmosphere are required.

EXPERIMENTAL

$K_4[Cd(S_2O_3)_3]$ was prepared from $K_2S_2O_3$ (Aldrich) and $CdCl_2$ (*analytical pure* grade) as described in [27].

The prepared salt photolysis was studied using solutions of $K_4[Cd(S_2O_3)_3]$ (0.01 mol/L) in water–isopropanol mixtures (24 : 1 v/v to 1 : 1 v/v). Further increase of isopropanol fraction led to salting out of $K_4[Cd(S_2O_3)_3]$.

A high-pressure mercury-quartz lamp was used as UV radiation source. In order to eliminate the possible direct photochemical decomposition of water, filtrating layer of NaOH solution (0.02 mol/L) was applied, cutting off the short-wavelength part of the radiation ($\lambda < 200$ nm).

Photolysis, registration of electronic absorption spectra, and determination of the particles size were carried out in the quartz cell (optical path 1 cm). Electronic absorption spectra were recorded using the EVOLUTION UV600 spectrophotometer at 190–900 nm. Particles size and size distribution were determined with the Shimadzu SALD-7101 analyzer.

X-ray diffraction patterns of the photolysis products were recorded with the D8 DISCOVER diffractometer (CuK_α, λ 1.54056 Å). In the experiment, $K_4[Cd(S_2O_3)_3]$ solution (0.1 mol/L) in water–isopropanol mixture (1 : 1 v/v) was used. Photolysis was repeated until amount of the product was sufficient for the analysis; each portion of the solution was irradiated during 30 min. The solid photolysis products were isolated by centrifugation. The precipitate was sequentially washed with water (3 times) and with ethanol, and then dried in vacuum dessicator.

IR spectra were recorded using the Nicolet 6700 IR Fourier spectrometer. Solid samples were examined in the form of pellets with KBr (400–4000 cm^{-1}); solutions of $K_4[Cd(S_2O_3)_3]$ (0.1 mol/L) were examined using the ATR attachment (600–4000 cm^{-1}).

pH was measured using the inoLab pH 740 ionometer equipped with the Sentix 81 combined electrode.

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