

CHEMICAL KINETICS  
AND CATALYSIS

## Aqueous Solutions of Sulfur Produced via Low-Temperature Hydrogen Sulfide Catalytic Decomposition

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Received January 23, 2014

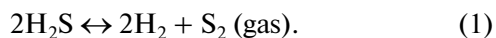
**Abstract**—White globules of solid sulfur modification are obtained from saturated aqueous solutions. The chemical composition, morphology, and structure of the white sediment are investigated by means of X-ray fluorescence analysis, scanning electron microscopy, and high resolution transmission electron microscopy. It is shown that the white sediment contains an unknown modification of globular hexagonal sulfur with globule sizes of 5–10  $\mu\text{m}$  and interplanar distances of 0.45, 0.29, and 0.15 nm. A single absorption band at  $880\text{ cm}^{-1}$  is found in the Raman scattering spectra of the saturated solutions above the sediment. It is suggested that the white sediment consists of condensed  $\text{S}_2$  phase.

**Keywords:** hydrogen sulfide decomposition, diatomic gaseous sulfur, aqueous solutions, globular hexagonal sulfur, X-ray fluorescence analysis, scanning electron microscope, energy dispersive analysis, high resolution transmission electron microscope, electron diffraction.

DOI: 10.1134/S0036024415010252

### INTRODUCTION

It is well known that solid sulfur is practically insoluble in water under normal conditions; data on its interaction with boiling water are sparse [1]. Nevertheless, there are colloid hydrophobic sols of  $\text{S}_8$  sulfur, 0.1–1.0  $\mu\text{m}$  in size, that are thermodynamically unstable with respect to their transformation into orthorhombic sulfur  $\text{S}_8$  [2]. At the same time, the diatomic gaseous sulfur formed during the decomposition of hydrogen sulfide on metallic catalysts at room temperature is readily soluble in water until its concentration exceeds 0.5 wt % [3–5]:



Aqueous solutions of sulfur are colorless and have neutral pH, while their refractive index corresponds to the refractive index of water. All these properties are characteristic of dissolved gas compounds that do not react with water. Some of the properties of aqueous solutions of gaseous sulfur and the white sediment obtained from their saturated solutions are considered in this work.

### EXPERIMENTAL

Experimental techniques for decomposing hydrogen sulfide in the flow gas phase, autoclave, and triple phase regimes were described in [3–5]. Our Raman scattering spectra were recorded on a RFS 100/S Bruker FT-Raman spectrometer (Germany) in the

range of 100–3600  $\text{cm}^{-1}$ . The 1064-nm line of a 450 mW Nd-YAG laser served as our source of excitation.

Quantitative sulfur determination was conducted on an ARL Advant’X 3600 sequential X-ray fluorescence spectrometer. The measurements were made in a helium atmosphere using plastic cuvettes sealed with Spectrolene Six film. Quantitative determination was performed using the QuantAS software suite for standardless analysis.

Our qualitative analysis of each sample and the investigation of their surface morphology was conducted on a scanning electron microscope (JSM-6460LV) JEOL with an attached INCA Energy-350 energy dispersive spectrometer (Oxford Instruments).

Transmission electron microscopy and electron diffraction images were acquired on a JEM-2010 (JEOL) instrument with a lattice resolution of 0.14 nm at an accelerating voltage of 200 kV. The white precipitate from the sparger walls was resuspended in a minimal aliquot of ethanol, and the suspension was transferred onto perforated carbon films fixed on a standard copper grid. Images were obtained and electron diffraction measured from the thin sample layers covering the carbon film holes. It was noticed that the electron beam could result in structural changes and evaporation of the sulfur sample. Hence, ultralow intensities of radia-

Hydrogen sulfide decomposition at room temperature on stainless steel chips placed in a layer of solvent (catalyst mass, 2.0 g)

Solvent	$V$ , mL	$\tau$ , min	$v_{\text{H}_2\text{S}}$ , mL/min	$x_{\text{H}_2\text{S}}$ , mmol	$x'_{\text{H}_2\text{S}}$ , mmol	$\sigma_{\text{H}_2\text{S}}$ , %	$c_{\text{S}}$ , wt %	$m_{\text{S}}$ , g	$m'_{\text{S}_2}$ , g
							after argon purging		
Gas phase	—	80	3.9	9.23	8.81	4.6			
Water	100	45	4.07	7.26	3.95	45.6	0.042	0.0042	0.101
Ethanol	100	70	4.07	12.7	6.09	52.2	0.10	0.10	0.13
5% HH in water	77	120	3.64	19.5	0.29	98.5	0.60	0.46	0.19

HH, hydrazine hydrate;  $V$ , solvent volume;  $\tau$ , reaction time;  $v_{\text{H}_2\text{S}}$ , rate of  $\text{H}_2\text{S}$  supply;  $x_{\text{H}_2\text{S}}$ , amount of  $\text{H}_2\text{S}$  supplied;  $x'_{\text{H}_2\text{S}}$ , amount of  $\text{H}_2\text{S}$  captured in absorber;  $\sigma_{\text{H}_2\text{S}}$ ,  $\text{H}_2\text{S}$  conversion;  $c_{\text{S}}$ , concentration of sulfur in solution (according to X-ray fluorescence analysis data);  $m_{\text{S}}$ , amount of sulfur in solution;  $m'_{\text{S}_2}$ , amount of volatilized sulfur.

tion were used in imaging in order to avoid adverse effects on the sample.

## RESULTS AND DISCUSSION

The synchronous release of two gaseous reaction products was observed when the hydrogen sulfide was passed through metallic catalysts at room temperature; equilibrium hydrogen sulfide conversion on platinum catalysts is approximately 15% during the process [3–5]. Hydrogen sulfide conversion on bulk stainless steel chips with low specific surface area was 4.6%, but when the chips were placed under a layer of water, hydrogen sulfide conversion rose considerably to 45.6% (see table) due to the solubility of gaseous sulfur in water, shifting of the equilibrium of reaction (1) to the right. Hydrogen sulfide conversion on the same catalyst under a layer of solvents that readily dissolve solid sulfur is presented in the table for comparison. Note that the release of gaseous sulfur is observed in all experiments together with hydrogen release in the gaseous phase. The residual sulfur content in water was shown to be negligible following the reaction and after purging the reactor with argon to remove all unreacted hydrogen sulfide.

The autoclave technique for hydrogen sulfide decomposition was used to obtain more concentrated sulfur solutions [3–5]. A 5-g aliquot of stainless steel chips was placed in a 300-mL volume autoclave along with 50 mL of distilled water; 2 g of hydrogen sulfide was added upon autoclave cooling after the removal of dissolved air under vacuum. The autoclave was opened the next day and purged with argon to eliminate the sharp nauseous smell of the gaseous phase. According to X-ray fluorescence analysis, the concentration of sulfur in the solution was 0.51 wt %; this included 0.26 g of sulfur, and no other elements from F to U were found in the solution spectrum. The colorless solution of sulfur had the same pH and refractive index as the initial water,

and no other bands were found in the Raman spectrum. Such properties are characteristic of solutions containing dissolved diatomic gases (e.g., nitrogen, oxygen, and hydrogen) that do not interact with water, so the presence of hydrogen sulfide in the solution is ruled out.

The solution was placed into an absorber at the outlet of the catalytic unit [3–5]. According to the accepted procedure for hydrogen sulfide decomposition, the unreacted hydrogen sulfide in the catalytic reactor is trapped by the zinc acetate solution, so only the products of the hydrogen sulfide decomposition reaction (hydrogen and gaseous sulfur) are present in the gas phase at the outlet of the catalytic unit. The gaseous products released during the experiments were passed through the end (terminal) absorber, and after each experiment it was isolated in an enclosed volume (the inlet and outlet were shut) to prevent sulfur volatilization. This process of solution saturation facilitates coagulation of the

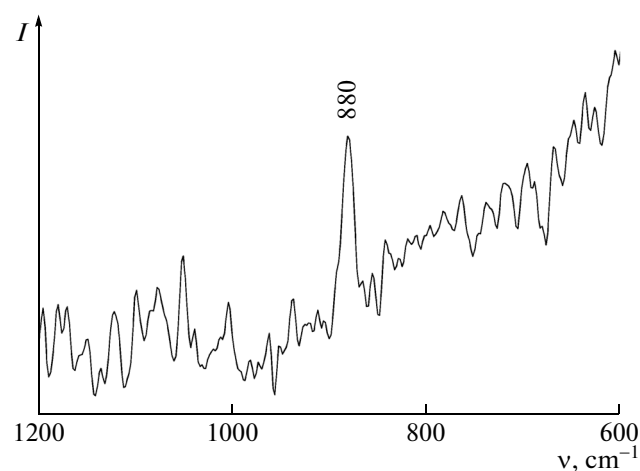


Fig. 1. Raman scattering spectrum of our saturated aqueous solution of sulfur.

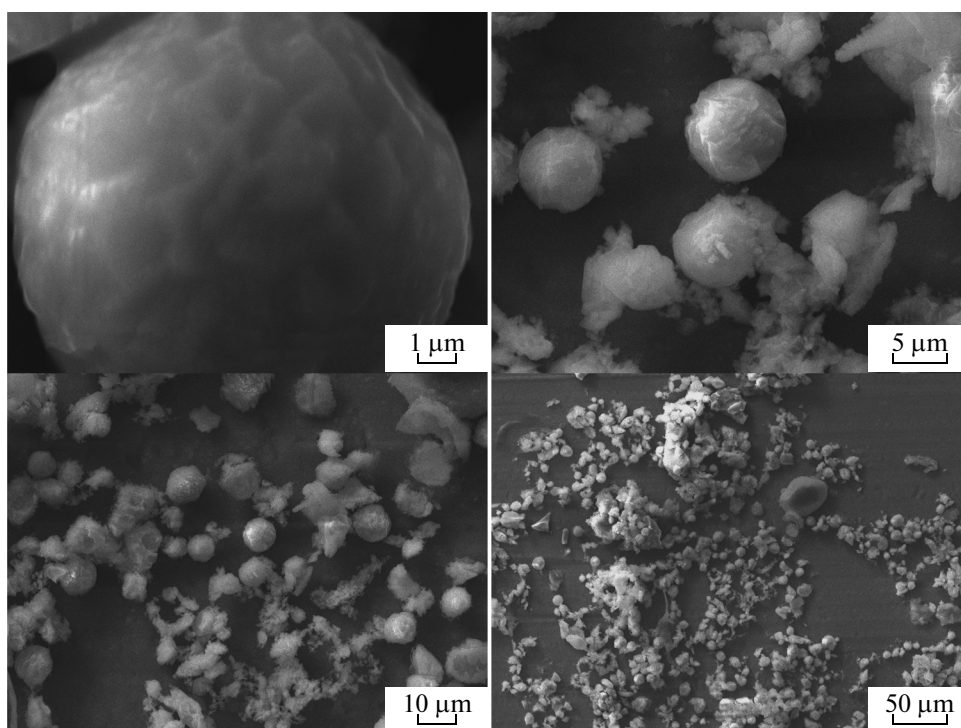


Fig. 2. Electron microscopic images of white sulfur, acquired with our scanning electron microscope.

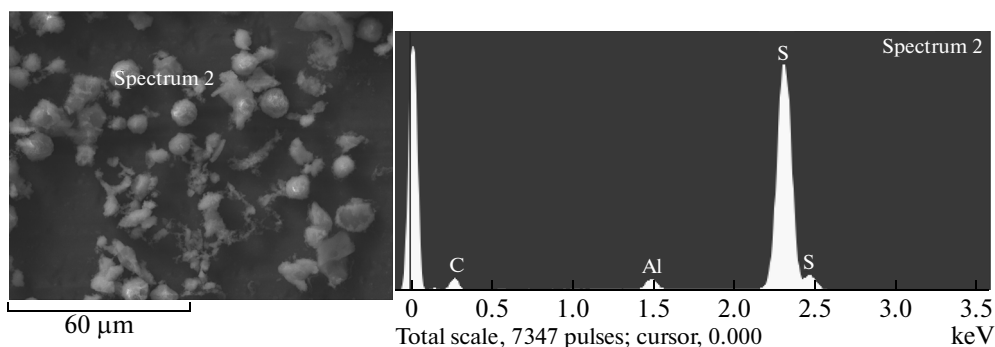


Fig. 3. Energy-dispersive spectrum of an individual sulfur globule produced by precipitation from aqueous solutions.

dissolved diatomic molecules and the formation of sulfur nuclei, resulting in the formation of a white sediment. A single  $880\text{ cm}^{-1}$  band was observed in the Raman scattering spectrum of the saturated aqueous solution, and was attributed to the valence vibrations of the  $\nu_{\text{S-S}}$  sulfur–sulfur bond in colloid particles (the nuclei of the white deposits). The lack of other absorption bands clearly indicates a lack of  $\text{S}_8$  colloid particles or other fragments of polyatomic sulfur particles (Fig. 1).

The excess pressure after all of the autoclave experiments in was released through water, and similar white sediments were obtained as a result.

Scanning electron microscope investigation of the white sediment's morphology showed that the particles were globular with sizes of  $5\text{--}10\ \mu\text{m}$  (Fig. 2). The energy dispersive spectrum obtained from the  $\sim 10\text{-}\mu\text{m}$  size globule marked on the microphotograph in Fig. 3a is presented in Fig. 3b as spectrum 2. Intense peaks at  $E_p \sim 2.3$  and  $2.5\text{ keV}$  are visible in the spectrum. These peaks correspond to the sulfur  $Ka_{1,2}$  and  $Kb_1$  peaks with  $E_p = 2.31$  and  $2.46\text{ keV}$ , respectively. Weak peaks from Al and C with  $E_p = 0.28$  and  $1.49\text{ keV}$ , obtained from the substrate material, were also observed. It is apparent that these peaks emerged as a result of the electrons of the primary electron beam with  $E_p = 20\text{ keV}$  penetrating to depths greater than the sizes of sulfur globules.

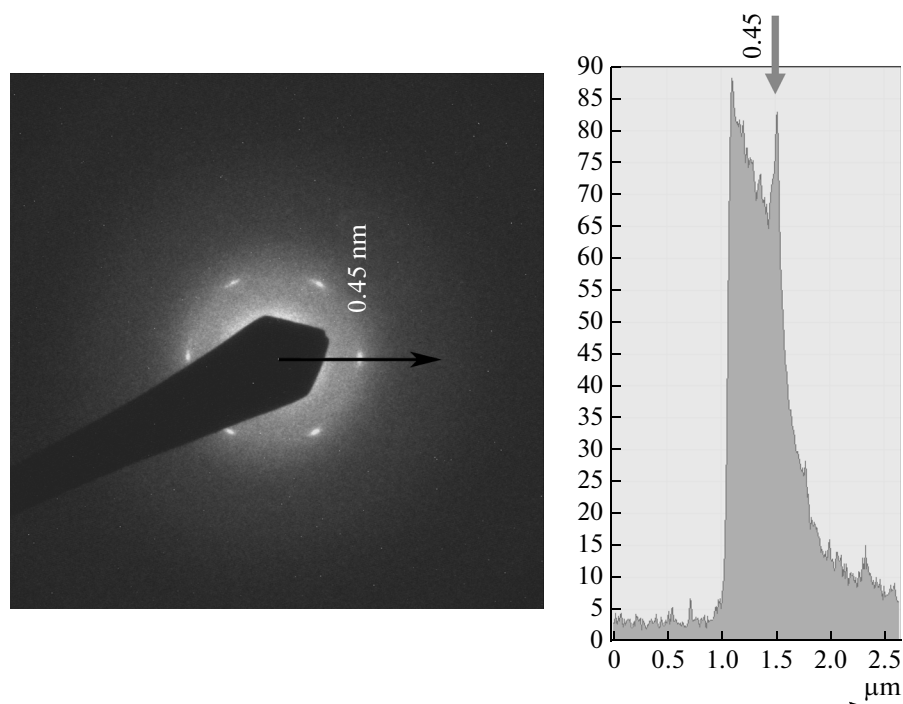


Fig. 4. Hexagonal symmetry of reflexes in the electronogram of the white sulfur single crystallite.

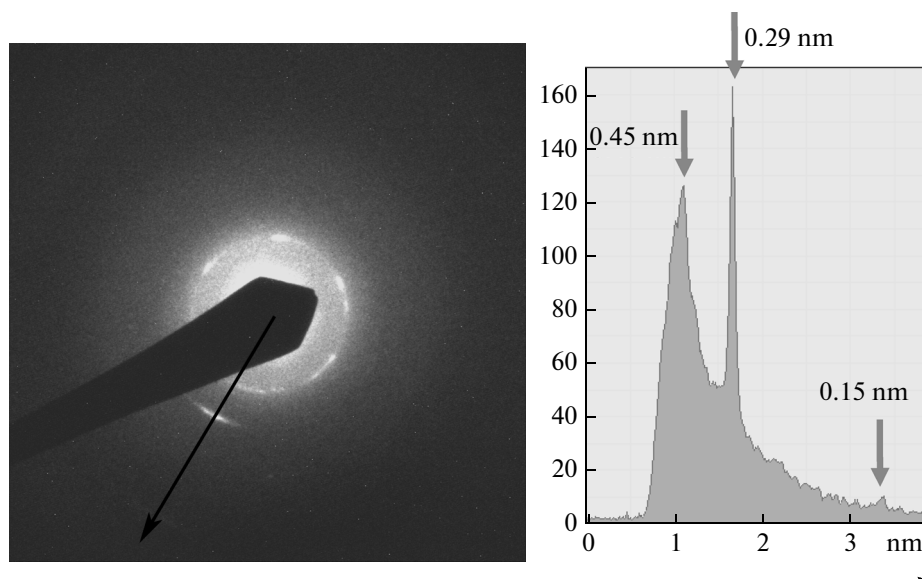


Fig. 5. Electron diffraction on the white sulfur crystallite with the intensity profile along the indicated direction. Interplanar distances are given.

Electron diffraction on the sulfur globules indicated a hexagonal structure for the sulfur crystallites (Fig. 4) with interplanar parameters indicated in Fig. 5. More than 30 allotropic modifications of solid sulfur are currently known [6] with changes in color from red to black, but no white hexagonal sulfur with interplanar distances of 0.45, 0.29, and 0.15 nm was found in the database [7]. Since the resulting sulfur

evaporated under the electron beam and only a single absorption band at  $880\text{ cm}^{-1}$  was observed in the Raman scattering spectra, we would suggest that the white sediment was obviously composed of  $\text{S}_2$  condensed phase.

Surprisingly, in terms of particle morphology and properties our white sulfur closely resembled the globular sulfur produced in nature by sulfur bacteria [8–

10]. Colorless sulfur bacteria are chemoautotrophic microorganisms that use the energy generated via hydrogen sulfide oxidation with the formation of elemental sulfur to synthesize organic compounds, and colloidal globules with sizes of up to 1  $\mu\text{m}$  are found both inside and outside each bacterial cell during the process. It has been proven that the properties of the sulfur in live sulfur bacteria are fundamentally different from normal inorganic sulfur. The density of sulfur globules produced by bacteria (1.22 g/cm<sup>3</sup>) is lower in particular than that of orthorhombic sulfur (2.07 g/cm<sup>3</sup>), and they exhibit hydrophilic properties, in contrast to the well-known hydrophobicity of inorganic solid sulfur.

### CONCLUSIONS

There are conflicting opinions on the nature of elemental sulfur in globules of chemotrophic bacteria; while there is no direct experimental evidence of globule structure in the literature, such views include the existence of unknown sulfur modifications [9, 10]. The problem is that the sulfur in the globules changes to an orthorhombic modification when the bacteria dries or is exposed to radiation. It is generally accepted that hydrogen sulfide is a source of hydrogen in sulfur bacteria, but the proposed scheme of the sulfur formation ( $2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S}^0 + 2\text{H}_2\text{O}$ ) contradicts this idea, since hydrogen is consumed in forming water. These contradictory data give grounds for suggesting that sulfur globules in sulfur bacteria could form as a result of the nucleation of diatomic sulfur formed according to

reaction (1) as the condensed hydrophilic phase  $\text{S}_2$ , and the resulting hydrogen participates in reactions of chemosynthesis.

### ACKNOWLEDGMENTS

We are grateful to E.A. Kravtsov for conducting our X-ray fluorescence analysis.

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*Translated by L. Brovko*