

## PHYSICAL METHODS OF INVESTIGATION

# Liquid-Phase Oxidation of Inorganic Sulfides in Aqueous Media in the Presence of a Homogeneous Catalyst Based on 3,3',5,5'-Tetra-*tert*-Butyl-4,4'-Stilbenequinone

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**Abstract**—The rates and factors influencing the rates of liquid-phase oxidation of inorganic sulfides by oxygen in aqueous media in the presence of a homogeneous catalyst based on 3,3',5,5'-tetra-*tert*-butyl-4,4'-stilbenequinone dissolved in the kerosene fraction have been studied.

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Sulfur compounds are undesirable components in oils, as they sharply impair the quality of petroleum products and pollute the environment when used. Purification of petroleum products from sulfur compounds often produces sulfurous alkaline wastes (SAWs) that contain inorganic sulfides in high concentrations. Being toxic, SAWs cannot be discharged to water bodies or collected and purified together with the other industrial sewages even though considerably diluted.

There are various methods for decontaminating SAWs, the most promising being the liquid-phase oxidation of SAW by air oxygen in the presence of a catalyst [1–3]. In the present study, we propose a new homogeneous catalyst based on 3,3',5,5'-tetra-*tert*-butyl-4,4'-stilbenequinone (hereafter, referred to as stilbenequinone) dissolved in the kerosene fraction, for the liquid-phase oxidation of sulfide–hydrosulfide derivatives; this catalyst has high catalytic activity and selectivity and is stable in alkaline media. In choosing the kerosene fraction, we were guided by its low solubility in water, low volatility, and a satisfactory solubility of stilbenequinone in kerosene.

## EXPERIMENTAL

The catalytic component, 3,3',5,5'-tetra-*tert*-butyl-4,4'-stilbenequinone, was prepared by following method: a 500-cm<sup>3</sup> cylinder-shaped glass reactor was loaded with 30 g of 2,6-di-*tert*-butyl-4-methylphenol, 3 g of potassium iodide, and 120 mL of isopropanol,

and the contents were heated to 70°C under stirring. After the reaction mass was heated for 30 min, 42 mL of 35% aqueous hydrogen peroxide was dropped in, and the reaction was continued for 9 h at 70–75°C. The resulting mixture was cooled to room temperature; the precipitated crystals were filtered off and dried. The 3,3',5,5'-tetra-*tert*-butyl-4,4'-stilbenequinone yield was 98%.

An aqueous ammonium sulfide solution was prepared as described in [4]; sodium hydrosulfide solution was prepared as described in [5].

The sodium sulfide used corresponded to the GOST (State Standard) 2053-77. Sodium sulfide solutions were prepared by dissolving Na<sub>2</sub>S · 9H<sub>2</sub>O in distilled water.

Also used were: technical grade oxygen in cylinders (GOST 5583-78), aqueous ammonia (GOST 3760-79), technical grade argon in cylinders (GOST 10157-79), kerosene fraction (GOST 10227-2013), and technical grade toluene (GOST 14710-78).

The oxidation of inorganic sulfides was performed in a 150-cm<sup>3</sup> glass three-necked cylinder-shaped reactor. To the reactor, 40 mL of a solution of an inorganic sulfide and 20 mL of kerosene were poured in the presence of a calculated amount of the catalytic component. The oxygen was fed from a cylinder to the reaction solution at 0–625 h<sup>–1</sup>. The solution in the reactor was stirred at 1400 rpm. The temperature of the reaction solution was maintained at 90°C by a temperature-controlled stirrer. In certain periods during an experiment, oxygen feeding was stopped, the magnetic

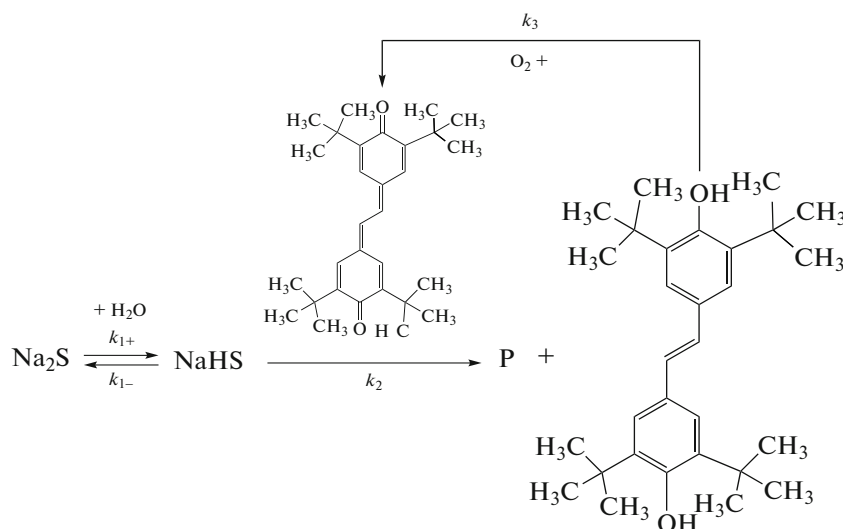
stirrer was switched off, and samples were taken to determine the sulfides by potentiometric titration according to GOST 22985-90. Sodium thiosulfate and sodium sulfite were determined by the method proposed in [6]; sodium sulfate was determined spectrophotometrically [7].

The 3,3',5,5'-tetra-*tert*-butyl-4,4'-stilbenequinone was determined by a photocolormetric method: From the three-necked cylinder-shaped reactor, a 0.5-mL sample of the kerosene phase was taken without pre-cooling, then the sample was diluted with toluene to 50 mL in a volumetric flask. The kerosene phase with the stilbene quinone dissolved therein colors toluene bright yellow, the color intensity increasing as the stilbene quinone concentration increases. Light absorption was determined on an Ecros PE5300V spectrophotometer at the wavelength  $\lambda = 500$  nm using a 10-cm cell, followed by the determination of catalyst concentration from a calibration plot.

## RESULTS AND DISCUSSION

### *Oxidation of Sodium Sulfide in the Presence of a Homogeneous Catalyst Based on a Stilbenequinone*

Sodium sulfide oxidation in the presence of a homogeneous catalyst based on a stilbenequinone has a complex scheme and comprises several stages. Menkovsky and Yavorsky [6] proposed a reaction scheme for the liquid-phase oxidation of sulfide sulfur in the presence of benzoquinone. According to these authors [6], mechanism of sulfide sulfur oxidation in the presence of stilbenequinone can occur as follows (Scheme 1): the first stage involves the hydrolysis of sodium sulfide; at the second stage, the sodium hydrosulfide produced at the first stage reacts with stilbenequinone to reduce it to 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl) (hereafter in the text, hydrostilbenequinone); and the third stage involves the regeneration of the catalyst by oxidizing the hydrostilbenequinone to stilbenequinone in an alkali medium.



**Scheme 1.** Oxidation of sodium sulfide in the presence of a homogeneous catalyst based on a stilbenequinone.  $k_1$ ,  $k_2$ , and  $k_3$  denote rate constants; P denote oxidation products.

The alkali-metal sulfides are well soluble in water and are strongly hydrolyzable, so the oxidation rate is controlled by the second or third stage.

In studying the rate of catalytic sodium sulfide oxidation as a function of oxygen concentration, we found that, initially, the reaction was independent of variations in oxygen concentration (Fig. 1a), but was determined only by the presence of stilbenequinone.

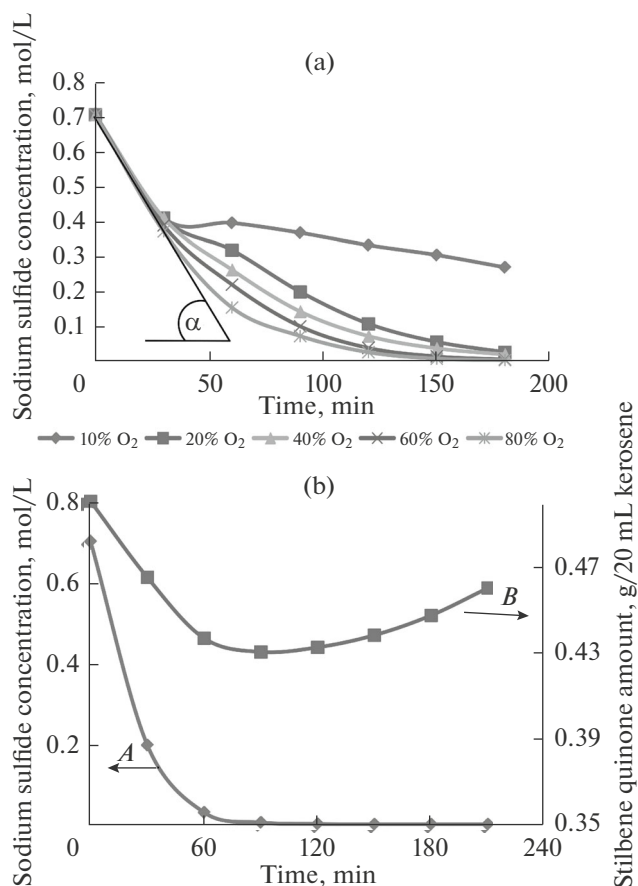
In studying the effect of oxygen amount on the catalytic oxidation of sodium sulfide, we also proved the absence of this effect on the initial reaction rate and on the complete exhaustion of sulfide sulfur at oxygen flow rates higher than  $45 \text{ h}^{-1}$  in an ideal mixing reactor (Table 1). From Fig. 1b one can infer that the stilbene quinone concentration in the oxygen-saturated reaction solution decreases in the course of reaction to a

certain minimal value and then increases again after the sodium sulfide is exhausted.

Our results provide evidence that the rates of sulfide sulfur oxidation by stilbenequinone are higher than the catalyst regeneration rates. Therefore, catalyst regeneration is the rate-controlling step in the reaction of sodium sulfide oxidation in the presence of stilbenequinone.

### *Influence of the Induction Period and the Catalyst Amount on the Sulfide Sulfur Oxidation Rate in the Presence of a Homogeneous Catalyst Based on Stilbenequinone*

The kinetic curve for the studied catalytic reaction is affected by two more factors, namely, the induction



**Fig. 1.** Panel (a): kinetics curves for catalytic sodium sulfide oxidation with various initial oxygen concentrations in the carrier gas. Panel (b): (A) rate curves for catalytic sodium sulfide oxidation and (B) variation in stilbenequinone concentration. The initial sodium sulfide concentration: 0.7 mol/L; reaction temperature: 90°C; stilbenequinone amount: 0.5 g; oxygen flow rate: 300 h<sup>-1</sup>; stirrer rotation velocity: 1400 rpm; kerosene volume: 20 mL; and aqueous sodium sulfide solution volume: 40 mL.

period and the amount of catalyst. Figure 2a shows rate curves for the oxidation of sulfide sulfur and hydrosulfide sulfur at various initial concentrations.

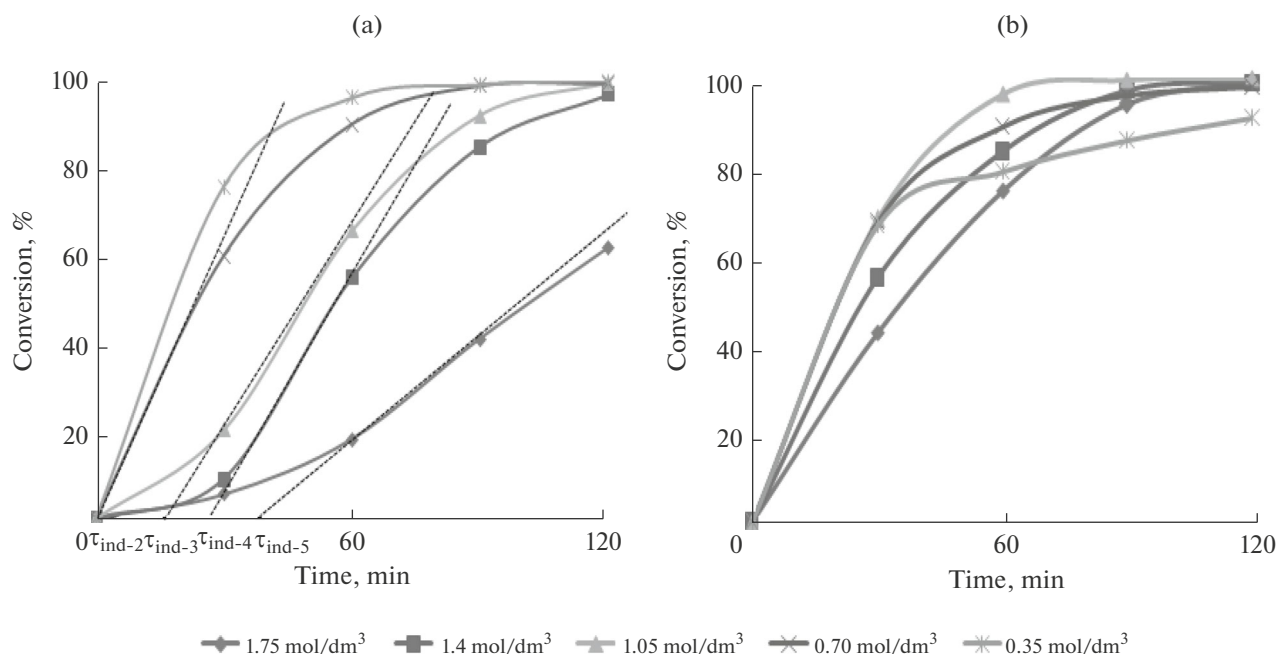
It is apparent from Fig. 2a that, in sodium sulfide oxidation, induction periods lengthen as the initial sodium sulfide concentration increases. The observed effect may be explained by a nearly complete hydrolysis of sodium sulfide upon its dissolution in water to form sodium hydrosulfide [8] (the 1st step). According to the Ostwald dilution law, the degree of dissociation of sodium hydrosulfide is reduced as its concentration rises [9]. Therefore, an increase in the initial sodium sulfide concentration in the reaction solution decreases the amount of Na<sup>+</sup> and HS<sup>-</sup> ions that enter the elementary reaction with stilbenequinone (the 2nd

step) and the amount of OH<sup>-</sup> ions that catalyze the reduction of stilbenequinone (the 3rd step) [10–12]. A consequence of this is a decrease in the number of elementary reaction acts and the associated lowering of the reaction rate.

Sodium hydrosulfide oxidation (Fig. 2b) has no induction period, but the effect of the catalyst amount is manifested at low initial hydrosulfide concentrations. This is likely to arise from high proton concentrations in sodium hydrosulfide solutions ( $\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{S}^{2-}$ ), the protons having a far higher electrophilicity index [13] and a small radius, which is responsible for an attack on the carbonyl group of sterically hindered quinone and the more facile formation of an activated complex with

**Table 1.** Average rates of catalytic sodium sulfide oxidation in the presence of stilbenequinone at various oxygen flow rates (the initial sodium sulfide concentration: 0.7 mol/L; reaction temperature: 90°C, stilbene quinone amount: 0.5 g; stirrer velocity: 1400 rpm; kerosene volume: 20 mL; aqueous sodium sulfide solution: 40 mL; reaction time: 120 min)

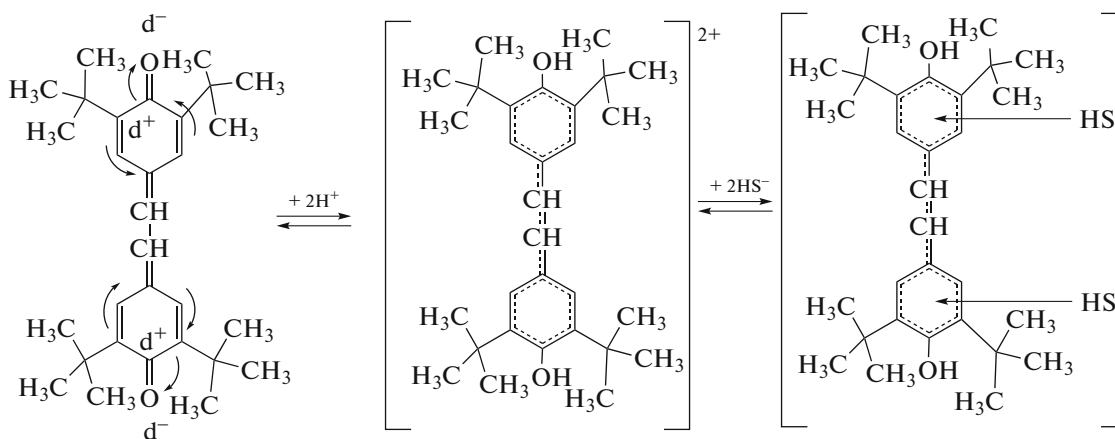
Oxygen flow rate, h <sup>-1</sup>	0	45	75	125	300	475	625
Average oxidation rate, mol/(L min)	0.0026	0.0099	0.0103	0.0105	0.0106	0.0106	0.0106



**Fig. 2.** (a) Sodium sulfide and (b) sodium hydrosulfide oxidation rates at various initial concentrations. Stilbenequinone amount: 0.42 g; the other experimental conditions are as in the legend to Fig. 1.

sulfide sulfur (Scheme 2). As a result, the rate of the second step is accelerated. The lower the pH, the more rapidly this reaction proceeds. On the rate curves with initial NaHS concentrations of 0.35 and 0.70 mol/L, one can see that, the higher the dilution of the initial concentration, the lower the pH. Due to this, stilbenequinone first rapidly converts to hydro-

stilbene quinone; the newly formed hydrostilbenequinone has not enough time to oxidize to stilbenequinone upon subsequent oxidation, thereby being responsible for the slowed down rates of sulfide sulfur oxidation. At higher initial sodium hydrosulfide concentrations, its oxidation rate and catalyst regeneration rate increase as pH rises.

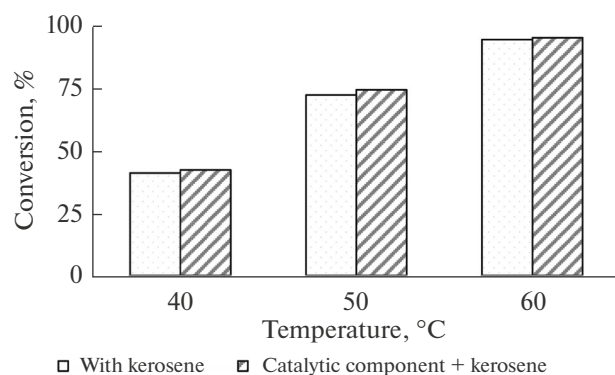


**Scheme 2.** Formation of an activated complex of stilbenequinone with proton.

#### *Influence of an Inhibitor on the Sulfide Sulfur Oxidation Rate in the Presence of a Homogeneous Catalyst Based on a Stilbenequinone*

Quinones are unsaturated cyclic diketones with fused structure, so they are very sensitive to electro-

philes. As mentioned above, the action of a stilbenequinone-based homogeneous catalyst consists primarily of the attack of an electrophile on the quinone carbonyl group, which is due to the formation of an activated complex with sulfide sulfur. In order to assess



**Fig. 3.** Ammonium sulfide conversion versus temperature in the presence and absence of stilbenequinone. Stilbene quinone amount: 0.45 g (for the catalytic experiment); aqueous ammonium sulfide solution: 40 mL; the other experimental conditions are as in the legend to Fig. 1.

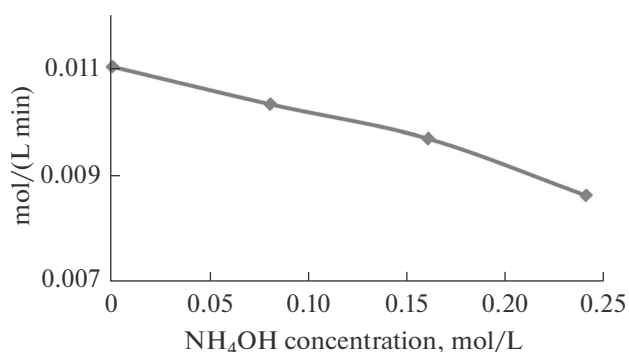
the effect of the electrophile on the catalytic oxidation process in the presence of stilbenequinone, we studied the oxidation rate of sulfide sulfur depending on its type. The results of these studies show that the rate of catalytic ammonium sulfide oxidation does not change compared to the noncatalytic process (Fig. 3). There is the following possible explanation: as known, in aqueous solutions of ammonium sulfide  $(\text{NH}_4)_2\text{S}$ , which is formed by a weak base cation and a weak acid anion, there exist ammonium and hydroxide ions, sulfide and hydrosulfide ions, neutral molecules of ammonia, hydrogen sulfide, etc. [14].

Ammonium ions are strong electrophiles and have a tetrahedral spatial configuration, hampering their addition at the carbonyl group of the sterically hindered stilbenequinone, and thereby inhibiting complexation with sulfide sulfur. In addition, neutral ammonia molecules with their lone pairs are nucleophiles that compete with sulfide ions for complexation (Scheme 2).

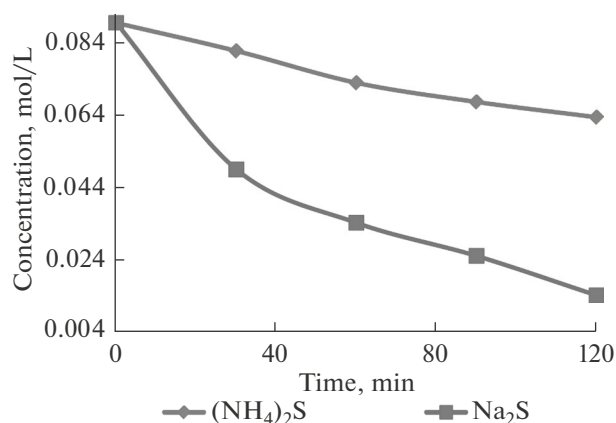
Figure 4 makes it clear that, when aqueous ammonia is added to a sodium sulfide solution, the catalytic oxidation rate is reduced. The higher the ammonia concentration, the lower the sodium sulfide oxidation rate.

Compared to sodium sulfide, ammonium sulfide is oxidized by stilbenequinone (second stage) slowly (Fig. 5). Our results convincingly prove that ammonium ion is an inhibitor of the oxidation of sulfide sulfur in the presence of stilbenequinone.

In summary, we have studied the effect of the initial concentrations of sodium sulfide and sodium hydrosulfide on their oxidation rates in the presence of a stilbenequinone-based homogeneous catalyst. We have shown that the regeneration of the catalyst is the rate-controlling step of sodium sulfide oxidation in



**Fig. 4.** Average rate of catalytic sodium sulfide oxidation in the presence of stilbenequinone versus aqueous  $\text{NH}_4\text{OH}$  concentration. The initial sodium sulfide concentration: 0.7 mol/L; reaction temperature: 70°C; stilbene quinone amount: 0.5 g; oxygen flow rate: 125  $\text{h}^{-1}$ ; stirrer rotation velocity: 1400 rpm; kerosene volume: 20 mL; total volume of the aqueous sodium sulfide solution and aqueous ammonia: 40 mL; and reaction time: 120 min.



**Fig. 5.** Kinetics curves for noncatalytic sulfide sulfur oxidation by stilbenequinone. The initial sulfide sulfur concentration: 0.09 mol/L; reaction temperature: 80°C; stilbene quinone amount: 1.25 g; stirrer rotation velocity: 1400 rpm; kerosene volume: 20 mL; aqueous sodium sulfide solution: 40 mL.

the presence of stilbenequinone and depends on pH. We have found that ammonium ion inhibits the oxidation of sulfide sulfur in the presence of stilbenequinone.

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