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### Investigation of 3,3',5,5'-tetra-tert-butyl-4,4'stilbenequinone-based catalyst in the reaction of liquid-phase oxidation of inorganic sulfides

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#### ABSTRACT

In this paper, the intermediate and final reaction products of catalytic oxidation of inorganic sulfides in the presence of oxygen dissolved in the kerosene fraction and 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone were investigated. The thiosulfate and sulfate are major products of the oxidation of sodium sulfide under these conditions. The intermediate and final products in the catalytic oxidation of sulfide sulfur do not affect the rate of its oxidation. The yield of catalytic oxidation products depends on the nature of the sulfide and on the pH of the solution. The catalytic cycle for sulfide oxidation in the presence of 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone is shown. The role of 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone is to create a new and a more effective way of electron transfer from the reducing agent (sulfide) to the oxidant (oxygen).



#### **KEYWORDS**

Inorganic sulfides; 3,3',5,5'-tetra-tert-butyl-4,4'stilbenequinone; sodium thiosulfate; sodium sulfate; catalytic mechanism



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### 1. Introduction

One of the main environmental problems in oil refining and the petrochemical industry is the treatment and utilization of highly toxic sulfurous alkaline wastes (SAW) with high concentrations of inorganic sulfides. The current effluent guidelines do not allow the discharges of these pollutants into water or their treatment together with other industrial wastewater even after their considerable dilution. It is advisable to create separate systems for the collection and the purification of SAW [1].

A number of processes have been developed for treating SAW. Some of the inorganic sulfide can be removed by simple stripping, especially at high pH values ( $\geq$  9); however, oxidation of the sulfide is very necessary for complete removal.

The chemical oxidation of the sulfide can be achieved by strong agents such as potassium permanganate, potassium dichromate, chlorine, bleaching powder, ozone and hydrogen peroxide. However, the cost of the chemicals and possible pollution by the oxidation agents are serious disadvantages [1].

Nowadays, a common method of SAW treatment is their liquid-phase catalytic oxidation in an atmosphere of air in the presence of various catalysts [2]. Many authors have investigated the oxidation of sulfide in water by oxygen in the presence of activated carbon [3,4]. The reaction rate strongly depends on the pH of the solution and the mass transfer of oxygen to the aqueous suspension of activated carbon.

The liquid-phase oxidation of sulfide was found to be much faster in the presence of transition-metal complexes [5–7]. Currently, transition-metal oxides based on a polymer matrix are the main heterogeneous catalysts used in the oxidation of sulfide and hydrosulfide anions. Transition-metal oxides were distributed evenly on the catalyst surface and were strongly adhered. During the catalyst process, the complexes between transition-metal oxides and sulfide ions on the catalyst surface were formed [8].

The main disadvantages of the proposed methods in the previous studies are the low activity of catalysts and the contamination of the treated effluents. In order to eliminate the above disadvantages, we propose a new heterophase process in the presence of a catalyst based on 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone (here in after stilbenequinone) that is dissolved in the kerosene fraction. The hydrocarbon phase (kerosene fraction) simultaneously performs both the role of the catalyst carrier and the role of the oxygen deposition. The purpose of this study is to investigate the role of the stilbenequinone-based catalyst in the liquid-phase oxidation of inorganic sulfides, and to evaluate the factors that affect the reaction.

### 2. Results and discussion

# **2.1.** The reaction products of the liquid-phase oxidation of sodium sulfide in the presence of catalyst based on stilbenequinone

The process of liquid-phase oxidation of sulfide sulfur with oxygen depends on a number of factors: temperature, pH, the oxygen concentration, the nature of inorganic sulfides, the nature of catalyst, etc., where upon various products are formed (Scheme 1). In the course of this reaction, the oxidation number of sulfur varies from -2 to +6.

In the presence of catalysts, the main products of the sulfide sulfur oxidation are thiosulfate, sulfite and sulfate [9]. Figure 2 shows the change in sodium sulfide concentrations and



Scheme 1. Products of the oxidation of sulfide by oxygen.



Figure 1. The lab. unit of sulfide oxidation.

products of its catalytic oxidation in the presence of stilbenequinone. As can be seen from Figure 2, sodium thiosulfate and sodium sulfate are the main products of the oxidation of sulfide sulfur in the presence of stilbenequinone. The mass ratio of sulfate to thiosulfate is 4:3 after oxidizing for 600 min.

Oxidation of sulfide sulfur in the presence of stilbenequinone proceeds through two stages: the first stage is the oxidation of sulfide sulfur with stilbenequinone to 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxy-1,2-diphenylethylene (here in after diphenylethylene); the second stage is the regeneration of the catalyst by oxidation of diphenylethylene to stilbenequinone in alkaline medium (Scheme 2).

To confirm the mechanism, the possibility of the reaction of sodium sulfide oxidation with stilbenequinone in the range 70–110°C in an oxygen-free environment was studied with subsequent analysis of the light yellow powder precipitated after the reaction at room temperature that presumably was diphenylethylene (Table 1). It is shown that the reaction rate of the oxidation of sodium sulfide with stilbenequinone increases with increasing temperature.

In the stilbenequinone spectrum, there are peaks for the stretching vibrations of the conjugated diene (Ar=C-C=Ar) 1605 cm<sup>-1</sup> and the carbonyl group (C=O) 1605 cm<sup>-1</sup>,



**Figure 2.** The change in sodium sulfide concentrations and products of its catalytic oxidation in the presence of stilbenequinone.



**Scheme 2.** The catalytic oxidation of sulfide sulfur in the presence of 3,3',5,5'-tetra-tert-butyl-4,4'- stilbenequinone.

which are absent in the spectrum of the proposed diphenylethylene (see the upplementary Material). It is characterized by absorption bands due to stretching vibrations of the hydroxyl group (OH<sup>-</sup>) 3627–3607, 1420 and 1231–1133 cm<sup>-1</sup> and the double bond (-C=C-) 960 cm<sup>-1</sup> [10].

**Table 1.** The degree of conversion of sodium sulfide under the action of stilbenequinone at different temperatures.

| <i>Temperature</i> , °C            | 70   | 80   | 90   | 100  | 110   |
|------------------------------------|------|------|------|------|-------|
| Conversion of Na <sub>2</sub> S, % | 48,6 | 63,8 | 75,5 | 86,4 | 100,0 |

**Table 2.** The change in sodium sulfide concentrations and products of its oxidation in the presence of stilbenequinone in an inert medium.

|   | Temperature, °C |       |       |       |       |
|---|-----------------|-------|-------|-------|-------|
|   | 70              | 80    | 90    | 100   | 110   |
| Products oxidation of sodium sulfide          |                 |       |       |       |       |
| Na <sub>2</sub> S                             | 0.046           | 0.033 | 0.022 | 0.013 | 0.002 |
| Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 0.022           | 0.029 | 0.034 | 0.039 | 0.044 |
| Na <sub>2</sub> SO <sub>4</sub>               | 0.000           | 0.000 | 0.000 | 0.000 | 0.000 |

Additional confirmation for the formation of diphenylethylene was obtained by comparing its melting point (240°C) to an authentic sample [10]. Thus, all the obtained results confirmed the proposed mechanism of the catalytic oxidation of sulfide sulfur in the presence of stilbenequinone (Scheme 2).

According to Agayev and Nasteka [11], the catalytic oxidation of sulfide sulfur in the presence of quinones may lead to non-catalytic oxidation. For this purpose, the change in the concentration of products of the sodium sulfide oxidation with stilbenequinone (first stage, which determines the products of catalytic oxidation of sulfide sulfur) was studied at a series of different temperatures in an autoclave in an inert medium (Table 2).

The results showed selective formation of sodium thiosulfate in the oxidation of sodium sulfide with stilbenequinone in an oxygen-free environment. It is assumed that the sulfate ion formed in the catalytic oxidation of sodium sulfide in the presence of stilbenequinone is a product of non-catalytic oxidation of thiosulfate ions by oxygen. The yield of sodium sulfate during the oxidation of sodium thiosulfate in the presence and the absence of stilbenequinone was compared to confirm this thesis. The obtained data (Figure 3) showed that stilbenequinone does not affect the oxidation of sodium thiosulfate.

Obviously, concentration of thiosulfate decreases after complete exhaustion of the sulfide in the solution (Figure 2). It should be noted that sulfide ions can be oxidized to sulfate ions in strongly alkaline media [12] by the following reactions:

$$2HS^{-} + 2O_2 \to S_2 O_3^{2^-} + H_2 O, \tag{1}$$

$$HS^{-} + 2O_2 + OH^{-} \rightarrow SO_4^{2^-} + H_2O,$$
 (2)

$$2S^{2-} + 2O_2 + OH^- \to S_2O_3^{2-} + OH^-,$$
(3)

$$S^{2-} + 2O_2 \to SO_4^{2-}, \tag{4}$$

$$2HS^{-} + 3O_2 + 2OH^{-} \rightarrow SO_3^{2-} + H_2O,$$
 (5)

$$2S^{2-} + O_2 \to SO_3^{2-}, \tag{6}$$



**Figure 3.** The accumulation of sodium sulfate in the sodium thiosulfate oxidation by oxygen in the presence of stilbenequinone and without it.

$$SO_3^{2-} + O_2 \to SO_4^{2-},$$
 (7)

$$S_2O_3^{2-} + OH^- \to SO_4^{2-} + H_2O.$$
 (8)

It is known that reaction (7) proceeds much faster than reactions (5) and (6), thus it can be assumed that thiosulfate and sulfate are main products of the oxidation of sulfide sulfur [13].

# **2.2.** Influence of the nature of sulfides on the formation of final products in the presence of stilbenequinone

One of the most important factors affecting the formation of reaction products is the nature of the reactants. Figure 4 shows the kinetics of the change in the concentrations of  $Na_2S$ , NaHS, and their products during oxidation in the presence of a stilbenequinone-based catalyst.

At the initial time, the amount of thiosulfate formed during the catalytic oxidation of Na<sub>2</sub>S is higher than its formation during oxidation of NaHS. The opposite result is observed upon further oxidation, which is caused by the change in the pH of the solution.

It is known that hydroxide ion (OH<sup>-</sup>) is a catalyst for the oxidation of hydroquinone to quinone [14–16], which means that the increase of the amount of OH<sup>-</sup> anions contributes to the catalyst regeneration process in the oxidation of sulfide sulfur, so the rate of the catalytic oxidation of Na<sub>2</sub>S (pH = 13.5) is higher than NaHS (pH = 9). Therefore, the amount of thiosulfate formed during the catalytic oxidation of Na<sub>2</sub>S is greater than its formation during oxidation of NaHS at the initial time.

On the other hand, the rate of oxidation of the obtained thiosulfate to sulfate during catalytic oxidation of Na<sub>2</sub>S is faster than the oxidation rate of obtained thiosulfate during oxidation of NaHS in a strongly alkaline medium (pH > 12) [17,18]), which is confirmed by the results of the oxidation of sodium thiosulfate by oxygen in a strongly alkaline



**Figure 4.** The change in Na<sub>2</sub>S and NaHS concentrations and products of their catalytic oxidation in the presence of stilbenequinone.

**Table 3.** The influence of alkaline medium on quantitative formation of sodium sulfate in the reaction of non-catalytic oxidation of sodium thiosulfate.

| Quantity of NaOH, g                                      | 0.00   | 0.25   | 0.50   | 0.75   | 1.00   |
|--|--------|--------|--------|--------|--------|
| pH of solution   | 6.9    | 13.10  | 13.49  | 13.66  | 13.75  |
| Concentration of Na <sub>2</sub> SO <sub>4</sub> , mol/l | 0.0005 | 0.0060 | 0.0090 | 0.0110 | 0.0125 |

medium (Table 3). Consequently, the amount of thiosulfate ions yield by the catalytic oxidation of  $Na_2S$  is less in comparison with NaHS with further oxidation.

In addition, the possibility of the partial non-catalytic oxidation of sulfide sulfur in a strongly alkaline medium cannot be excluded [17,18] with the formation of sulfate.

# **2.3.** Effect of reaction products on the liquid-phase oxidation of sulfide sulfur in the presence of catalyst based on stilbenequinone

The intermediate and final products of the oxidation of sulfide sulfur can affect the process of the catalytic oxidation. Figure 5 shows the results of the effect of sodium thiosulfate and sodium sulfate on the rate of the catalytic oxidation of sodium sulfide. It can be seen that sodium thiosulfate and sodium sulfate do not affect the rate of oxidation of sodium sulfide in the presence of stilbenequinone.

### 3. Conclusions

The kinetics of the formation of products of the oxidation of sulfide sulfur in the presence of a catalyst based on stilbenequinone were studied. It has been established that



**Figure 5.** The dependence of the rate constants of sodium sulfide oxidation on the concentration of its intermediate and final oxidation products.

stilbenequinone is reduced to the corresponding diphenylethylene during the oxidation of sulfide sulfur. It has been proved that intermediate and final products of the catalytic oxidation of sulfide sulfur do not affect the rate of its oxidation, and sodium thiosulfate and sodium sulfate are the final products of the oxidation of sulfides. Selective formation of sodium thiosulfate was established during the oxidation of sodium sulfide with stilbenequinone. It is shown that the kinetics of the formation of products of the catalytic oxidation of sulfide sulfur depends on the pH of the medium.

### 4. Experimental section

The catalytic component of 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone was synthesized by the following method: 30 g of 2,6-di-tert-butyl-4-methylphenol, 3 g of potassium iodide, and 120 ml of isopropanol were charged into a glass cylindrical reactor with a volume of 500 ml and heated with stirring to 70°C. A solution of 42 ml of 35% hydrogen peroxide was added after heating for 30 min, and the reaction was continued for 9 h at 70–75°C. The obtained mixture was cooled to room temperature, and the precipitated crystals were filtered and dried. The yield of 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone was 98%. <sup>1</sup>H NMR spectra of stilbenequinone were recorded on a Bruker Avance 600 spectrometer at an operating frequency of 600 MHz:  $\delta$  ppm: 1.42 (s, 36H, C(CH<sub>3</sub>)); 6.54 (s, 2H, = CH); 7.19 (s, 4H, C<sub>6</sub>H<sub>2</sub>). An additional confirmation is the melting point of stilbenequinone (315°C), which was determined on a Buchi M-560 device [10].

A solution of sodium hydrosulfide was prepared according to the procedure of US 4439411 [19]. During the experiments, the following reagents were used: Na<sub>2</sub>S (Russia, GOST 2053–77), O<sub>2</sub> (Russia, GOST 5583-78), and kerosene fraction (Russia, GOST 10227-2013).

Catalytic oxidation of inorganic sulfides was conducted in a glass reaction vessel (Figure 1). Forty milliliter of an aqueous solution of inorganic sulfide and 20 ml of a kerosene fraction were added into the reactor in the presence of certain amount of the catalyst. Oxygen from the cylinder was injected into the reaction solution at  $130 \text{ lh}^{-1}$ .

The solution inside the reactor was stirred at a speed of 1400 rpm. The temperature of the reaction solution was maintained at 90°C with a thermally controlled magnetic stirrer.

The quantitative content of sulfides was determined by potentiometric titration in accordance with GOST 22985-90. The concentration of thiosulfate and sodium sulfite was determined by the method proposed by Papp [20], and the concentration of sodium sulfate was determined by a spectrophotometric method [21]. Infrared spectra (IR) of substances were recorded on a Perkin-Elmer Spectrum Two FTIR spectrometer.

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### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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