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Oxidative degradation of inorganic sulphides in the presence of a catalyst based on 3,3', 5,5'-tetra-tert-butyl-4,4'-stilbenequinone

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ABSTRACT

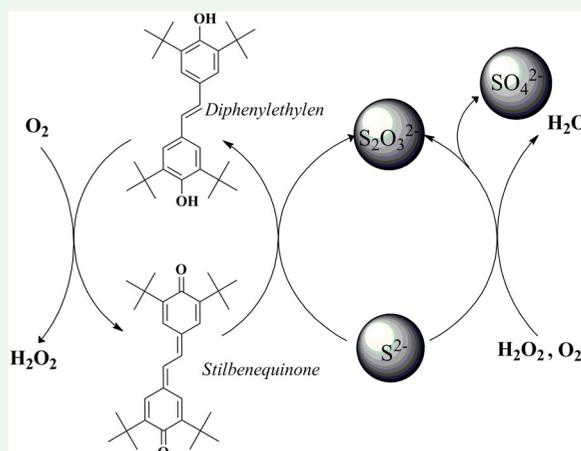
The aim of this study is to monitor the kinetics and mechanism of liquid-phase oxidation of inorganic sulphide by oxygen in the presence of a catalyst based on 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone. The research results point out that this reaction has a first order with respect to each reactant. The effects of temperature, initial sulphide concentration, intermediate and final oxidation products, the nature of inorganic sulphides as well as the catalyst concentration on aqueous sulphide oxidation efficiency were investigated. The catalytic cycle mechanism of sodium sulphide oxidation by 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone is presented.

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Catalytic sulphide oxidation; 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone; reaction kinetics; reaction mechanism; hydrogen peroxide



Introduction

For the past decades, finding suitable and effective methods to reduce air and water pollution has been considered as one of the most important and urgent tasks. In the industry, the petrochemical sector is one of the leading contributors to the world economy, but also one of the main sources of air and water pollution [1–2]. Recent reports about strategic development of heavy industries have placed the petrochemical sector at the second place in the volume of wastewater discharging into the environment as well as in the use of water resources from all industry sectors [1–2].

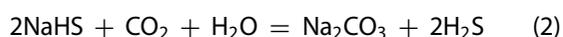
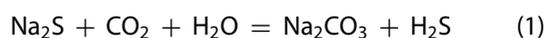
Industrial wastes from petrochemical activities defined by the presence of sulfur-containing compounds such as inorganic sulphides and mercaptides are called sulfur-alkaline waste (SAW). Due to the high toxicity, SAW is not allowed to be released into the environment, not even after being diluted or treated by other industrial effluents. Thus, a separate system for collecting and purifying SAW is required for petrochemical activities [3].

SAW can be treated by different methods, such as neutralization, oxidation methods, biological methods, etc. In reality, in most of the oil refineries, high pH SAW is directly transferred to biochemical treatment plants

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after discharged into the sulfur-alkaline sewage system (without local purification facilities). Because the optimal pH range for the biological system is between 7 and 7.8, the wastewater is usually neutralized with sulfuric or hydrochloric acid. This leads to forming and releasing free hydrogen sulphide, which is then combusted to SO₂ and discharged into the atmosphere, causing a serious environmental problem [4].

In order to reduce the amounts of sulfur compounds and spent-alkaline in SAW, the carbonization method is periodically used. The main objective of this method is to neutralize and acidify the wastewater using concentrated carbon dioxide with the simultaneous production of a soda as well as releasing acid compounds into the free state [5].



Similar to the neutralization method, the environmental pollution caused by the combustion of free hydrogen sulphide is serious disadvantage to be considered.

In the secondary petroleum refining processes, aqueous condensate from hydrogen sulphides and hydrosulphides the oil refineries are usually treated using a stripping method, in which the wastewater is heated to its boiling point at operating pressure in a column apparatus with the use of valve plates [6]. During this treatment, dissolved hydrogen sulphide will be collected by either a dry gas or a propane stream. Disadvantages of the stripping method are high-energy intensity and difficulty to recycle the formed gas containing hydrogen sulphide.

Chemical oxidation methods, in which inorganic sulphides are oxidized by strong oxidizing agents (for example, KMnO₄, K₂Cr₂O₇, O₃, Ca(ClO)₂, H₂O₂ and Cl₂) to form less toxic oxygen-containing products such as thiosulphate, sulphite and sulphate, have been widely used in petrochemical industry to purify SAW from the sulphides sulfur, [7,8]. However, using these oxidants leads to an increase in the treatment cost and the formation of additional pollutants as well as equipment corrosion. Both from an economic and ecological point of view, the oxygen (air) is the most reasonable oxidant for sulphide degradation. Nevertheless, oxygen has a low purification efficiency in treating SAW, which can be greatly enhanced by adding catalysts.

Applying catalyst to the oxidative degradation process of SAW remarkably reduces energy intensity of treatment process as well as increases its efficiency [9–11]. Transition metals and their compounds are widely considered as the potential catalysts for selective oxidation of sulphide in petrochemical industry [12–14]. Similarly, the transition-

metal phthalocyanines (primarily cobalt phthalocyanines and their derivatives) are one of the most common catalysts used in sulphide sulfur oxidation processes. Non-metals, transition-metal oxides (such as SiO₂, Al₂O₃, Fe₂O₃, MnO₂, TiO₂) and their derivatives such as mullit – CuMgCr₂O₄, ferrite – MFe₂O₄ (M = Fe, Cu and Co) are often used as heterogeneous catalysts in liquid-phase sulphide oxidation [12–16]. However, using these catalysts also has several serious disadvantages such as high cost of catalyst components and relatively low catalytic activity in treating concentrated sulphide wastewater, and most of all the possible pollution caused by heavy metals dissolved in treated wastewater.

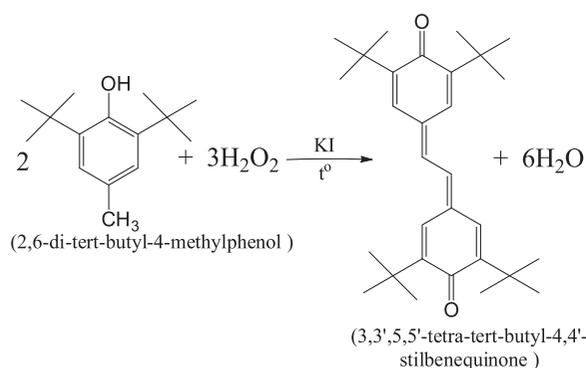
For the past few years, quinones and their derivatives, which has been widely applied to sulphide purification, particularly in Japan and the UK, have become an interesting target in the search for new catalysts for sulphide treatment [17–18]. Ueno H [18] have reported that hydroquinone, 1,2-naphthoquinone-4-sulfonic acid sodium salt, 1,4-naphthoquinone and their mixtures are capable of drastically enhancing the sulphide oxidation. The disadvantages of using these catalysts are high catalyst losses, labor-intensity of catalyst separation and hard to recover after effluent treatment [19]. Iwasawa [20] has shown that the polynaphthoquinone also has a high catalytic efficiency for sulphide oxidation. However, during the reaction, the disposition of formed sulfur on the surface of the polynaphthoquinone-catalyst was found, which possibly lead to a decrease in its activity.

In order to eliminate those mentioned above disadvantages, we propose a new quinone-catalyst based on 3,3',5,5'-tetra-tert-butyl-4,4' – stilbenequinone dissolved in kerosene fraction (hereafter, referred to as stilbenequinone) that has a high catalytic activity, high selectivity and stability in alkaline media. The choice of kerosene fraction as the catalyst carrier is due to its low aqueous solubility as well as low volatility. Moreover, the good solubility of stilbenequinone in kerosene fraction is also considered as an advantage. The aim of this study is to characterize kinetics, mechanism and regulation of the catalytic cycle of liquid-phase sulphide oxidation in the presence of a new catalyst based on stilbenequinone and to evaluate the factors affecting the reaction rate.

Experimental section

Catalyst preparation

The catalytic component – 3,3',5,5'-tetra-tert-butyl-4,4'-stilbenequinone was synthesized by oxidizing 2,6-di-tert-butyl-4-methylphenol with hydrogen peroxide in the presence of a catalyst based on potassium iodide (Scheme 1) as described in [21].



Scheme 1. Synthesis of stilbenequinone from 2, 6-di-tert-butyl-4-methylphenol.

Analysis results: melting point 315°C, IR spectrum, ν , cm^{-1} : 3003 (CH (Ar)), 1605 2952 2909 2865 (Me), 1640 1605 ((Ar) = C–C = (Ar)), 1605 (C = O), 1600 1454 (C = C (Ar)), 1360 1256 t-Bu; ^1H NMR (CD_3) 2SO, 600 MHz, δ ppm: 1.42 (s, 36H, C (CH₃)); 6.54 (s, 2H, =CH); 7.19 (s, 4H, C₆H₂). Found C, 82.80, 82.56; H, 9.73; O, 7.47, 7.71 C₃₀H₄₂O₂; Calculated: C, 82.55; H, 10.15; O, 7.3.

Reagents

During the experiments, the following reagents were used: technical gaseous oxygen in cylinders (Russia, GOST 5583-78), technical gaseous argon in cylinders (Russia, GOST 10157-79), kerosene fraction (Russia, GOST 10227-2013). Aqueous sulphide solutions were prepared by dissolving amounts of reagent grade Na₂S·9H₂O (Russia, GOST 2063-77) in deoxygenated distilled water. A solution of sodium hydrosulphide was prepared according to the method [22].

Catalytic oxidation of sulphide sulfur

Oxidation of inorganic sulphides was performed in a 150 mL three-necked cylindrical glass reactor. The reaction mixture involving 40 mL of inorganic sulphide solution with a concentration of 0.143–1.750 mol L⁻¹ and 20 mL of kerosene fraction was loaded into the reactor in the presence of certain amount of the catalyst component. Oxygen from the cylinder was injected into the reaction solution at 0–13 L h⁻¹. The reaction temperature was maintained in the range of 50–90°C and the reaction solution was stirred at speed of 0–1400 rpm by a thermally controlled magnetic stirrer.

Experimental-analytical methods

The quantitative content of inorganic sulphide was determined by potentiometric titration method UOP-209-00

(U.S.A.). The concentrations of thiosulphate and sulphite, as well as of hydrogen peroxide were identified by the iodometry method proposed in [23,24]. The concentration of sodium sulphate was determined using spectrophotometry (Eros PE5300B, regime A, wavelength $\lambda = 450$ nm path length $L = 50.0$ mm). Similarly, the stilbenequinone concentration was also determined by this method (Eros PE5300B, regime A, wavelength $\lambda = 500$ nm, path length $L = 10.0$ mm). Infra-red spectra (IR) of substances were recorded using Perkin Elmer Spectrum Two FTIR spectrometer, whereas ^1H Stilbenequinone NMR spectra were recorded using Bruker Avance 600 spectrometers at an operating frequency of 600 MHz. The melting point of the substances was determined by Buchi M-560. Elemental analysis of stilbenequinone was performed using workstation Auriga Cross Beam.

Results and discussion

Kinetics of liquid-phase oxidation of Na₂S in the presence of stilbenequinone-based catalyst

The reaction of liquid-phase sulphide oxidation in the presence of a stilbenequinone-based catalyst takes place in a three-phase system 'oxygen – hydrocarbon fraction – aqueous alkaline solution of inorganic sulphide'. Therefore, the catalytic oxidation rate of sulphide sulfur depends not only on the chemical reaction rate, but also on the reactant diffusion rate. The process of controlling catalytic sulphide oxidation in the presence of stilbenequinone was determined in a sequence of experiments, in which the initial volumetric concentration of oxygen diluted with argon and the rotational speed of the stirrer were changed whereas the initial sulphide and catalyst concentration remained constant.

Kinetic curves of Na₂S oxidation at different rotational speeds of the stirrer in the presence of a stilbenequinone-based catalyst are shown in Figure 1. The rate of Na₂S oxidation is technically influenced when the rotation frequencies of the stirrer vary from 500 to 1200 rpm, indicating that the catalytic reaction is diffusion-controlled. On the other hand, the reaction rate did not change when the stirrer reaches rotational speeds of 1200 rpm or over, indicating that the catalytic oxidation reaction occurs under kinetic control. As a result of which, all subsequent experiments were carried out at the stirring speed of 1400 rpm.

The effect of the supply rate of oxidant gas (which is a mixture of oxygen and argon) as well as of oxygen concentration on the catalytic oxidation rate of Na₂S is illustrated in Figure 2. It is evident that in a region bounded by the line $y = 0.0133$ and the curve $y = 0.0376x^{-1.66}$, the catalytic oxidation rate of sulphide becomes

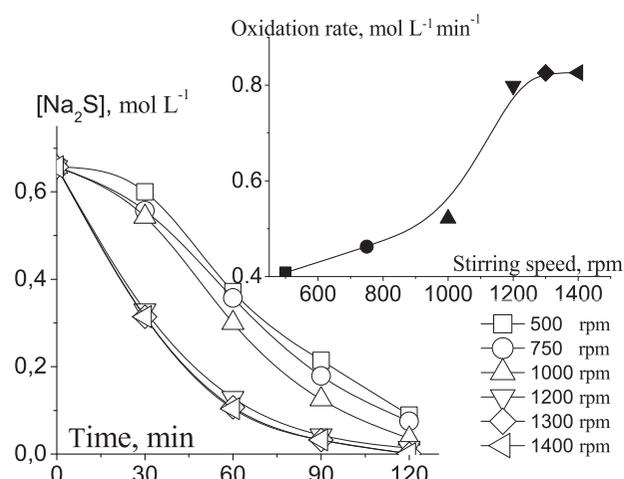


Figure 1. Kinetic curves of Na_2S oxidation at different rotational speeds of the stirrer in the presence of a stilbenequinone-based catalyst: $t = 80^\circ\text{C}$, $[\text{stilbenequinone}] = 0.029\text{ mol L}^{-1}$, the oxygen supply rate 13 L h^{-1} .

independent of the feed rate of oxidant gas. In other words, the process occurs under kinetical control.

The chosen ratio of kerosene fraction to Na_2S solution is 1:2, which is optimal for catalytic sulphide oxidation in the presence of stilbenequinone (Table 1). Apparently, this result may be explained by the fact that the maximum interphase area between the aqueous phase and hydrocarbon phase was formed.

In order to study the kinetic regularities as well as establish the kinetic equation for the reaction of liquid-

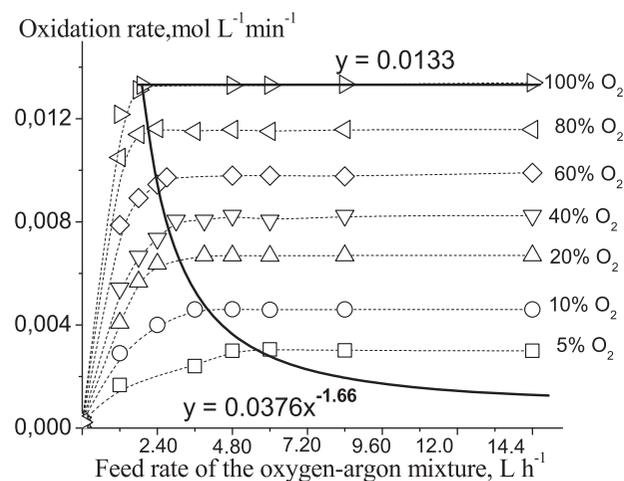


Figure 2. The rate of sulphide catalytic oxidation, influenced by the feed rate of gaseous oxidants and oxygen concentration: $t = 80^\circ\text{C}$, $[\text{stilbenequinone}] = 0.057\text{ mol L}^{-1}$, $[\text{Na}_2\text{S}] = 0.68\text{ mol L}^{-1}$.

Table 1. The ratio of kerosene fraction to Na_2S solution and corresponding reaction rate of sulfide oxidation: $t = 90^\circ\text{C}$, $[\text{Na}_2\text{S}] = 0.68\text{ mol L}^{-1}$, $[\text{stilbenequinone}] = 0.072\text{ mol L}^{-1}$.

Ratio of kerosene fraction to Na_2S solution	1:40	1:8	1:4	3:8	1:2	5:8	3:4	7:8	1:1
The reaction rate, $\text{mol L}^{-1}\text{ min}^{-1}$	0.0016	0.0030	0.0062	0.0104	0.0133	0.0132	0.0131	0.0125	0.0123

phase sulphide oxidation catalyzed by stilbenequinone, the order of this reaction was primarily determined by a differential method with varying initial concentration of the reaction reagents.

The kinetic curves of Na_2S oxidation at various initial concentrations of its reactants and the plots of the logarithmic initial oxidation rate of Na_2S ($\lg v_0$) against the logarithm of reactants concentrations are shown in Figure 3 (a,b,c). The initial rate of Na_2S oxidation was identified from the initial slope in the reaction curve (i.e. the volume of the consumed Na_2S versus reaction time).

The experiment results (Figure 3(a)) show that under kinetic control the catalytic oxidation of Na_2S is characterized by an induction period at initial sulphide concentration exceeding 0.7 mol L^{-1} . In the absence of the induction period, the plot of the logarithmic initial oxidation rate of Na_2S ($\lg v_0$) against the logarithm of its initial concentration is a straight line with a slope of 0.9509. In other words, the reaction is first order with respect to Na_2S . Similarly, the slopes of the plots of the $\lg v_0$ against the logarithm of initial stilbenequinone concentration ($\lg[\text{C}_{30}\text{H}_{42}\text{O}_2]$) as well as of initial oxygen concentration ($\lg[\text{O}_2]$) are 0.9411 and 0.910, respectively (Figure 3(b,c)). This allows the conclusion that the first order of catalytic sulphide oxidation with respect to oxygen, sulphide sulfur, and stilbenequinone was established. The kinetic equation of this reaction is of the following form:

$$v = k[\text{Na}_2\text{S}] \cdot [\text{O}_2] \cdot [\text{C}_{30}\text{H}_{42}\text{O}_2] \quad (3)$$

where v – the catalytic oxidation rate of Na_2S , k – the constant rate.

As under the kinetic control the oxidation reaction of Na_2S proceeds with an excess of both oxygen and catalyst, the order of the reaction can be attributed to the pseudo-first one with respect to sulphide. Therefore, the overall Equation (3) can be reduced to $v = k[\text{Na}_2\text{S}]$. Based on the kinetic regularities of the first-order reaction, a plot of $\ln[\text{Na}_2\text{S}]$ versus reaction time t is a straight line with a slope of constant rate – k and the activation energy of the reaction was obtained from the Arrhenius lots of the rate constants k at various temperatures ($50\text{--}90^\circ\text{C}$) as given in Figure 3(d). The value of activation energy was found to be 10.11 kJ mol^{-1} . The precoefficient in the Arrhenius equation at 90°C was also to be 1.29 min^{-1} .

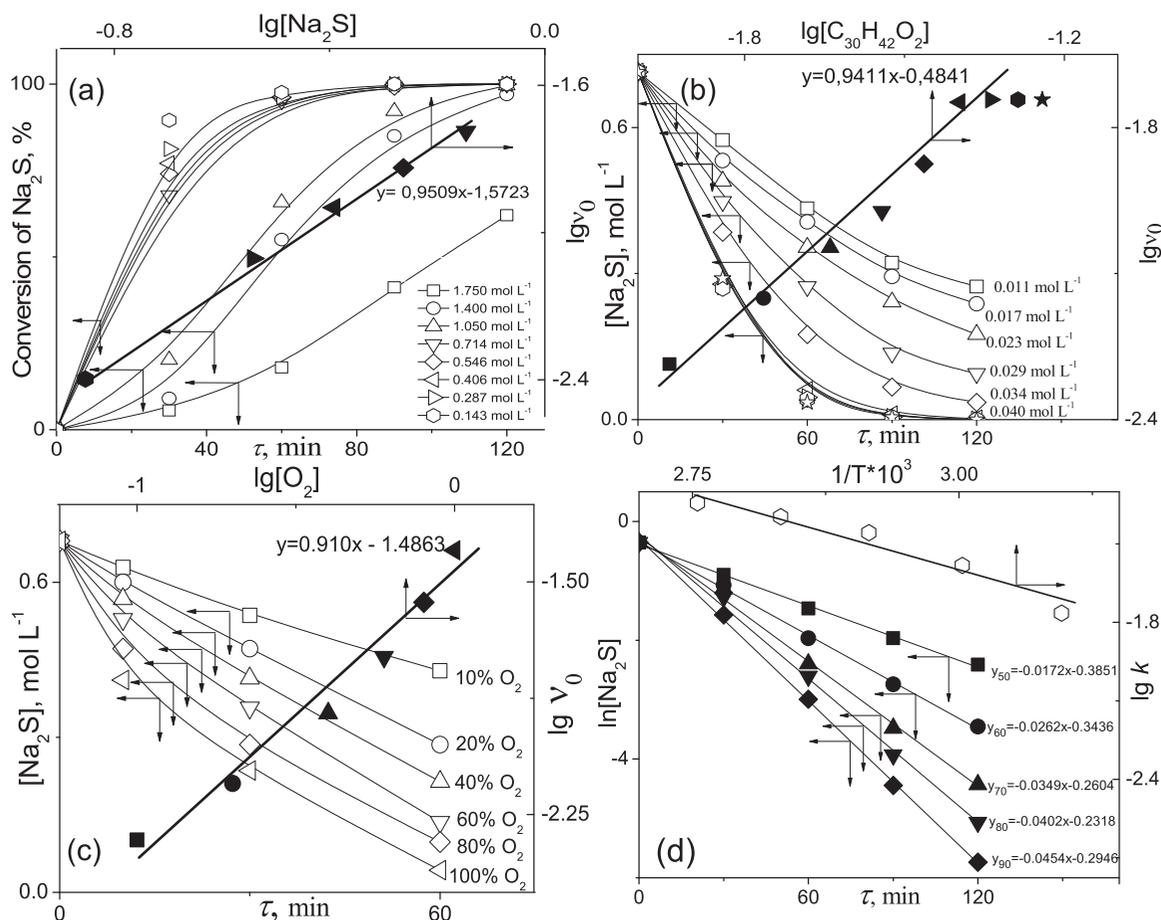


Figure 3. Kinetic curves for the Na₂S oxidation at various initial concentrations of the reacting reagents and the logarithmic dependence of the initial rate of Na₂S oxidation on initial concentrations of reagents (a, b, c). The Arrhenius plot of the oxidation of Na₂S in the presence of a stilbenequinone-based catalyst (d).

Mechanism of liquid-phase sulphide oxidation in the presence of a stilbenequinone-based catalyst

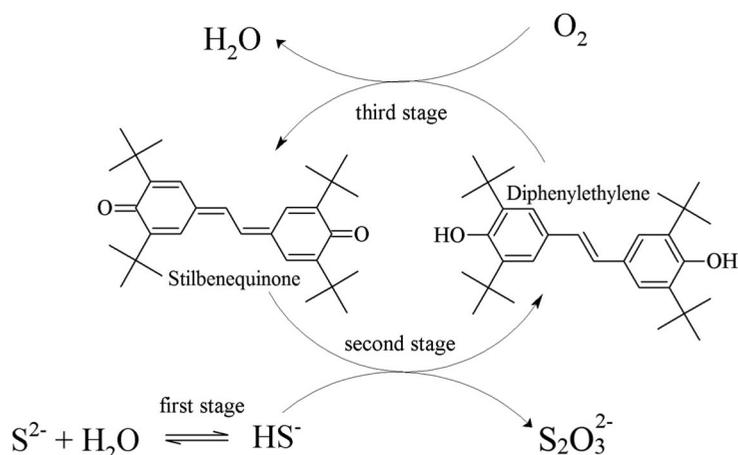
The sulphide oxidation in the presence of a catalyst based on stilbenequinone includes several stages. The research results in our previous paper [21] demonstrated that the stilbenequinone is an oxidation-reduction catalyst for the liquid-phase sulphide oxidation. The mechanism of which can proceed as follows (Scheme 2): the first stage – Na₂S is hydrolyzed to NaHS; the second stage – NaHS is oxidized by stilbenequinone to form Na₂S₂O₃, while stilbenequinone is reduced to 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxy-1,2-diphenylethylene (herein after referred to as diphenylethylene); the third stage – regeneration of catalyst by oxidizing diphenylethylene with oxygen to stilbenequinone in an alkaline medium.

The result of analysing intermediate and final reaction products indicated that thiosulphate and sulphate are the major products of the sulphide-oxidation reaction in the presence of stilbenequinone-based catalyst, whereas the formation of ion sulphite in this reaction

was not detected. Further studies on the mechanism of catalytic sulphide oxidation, its findings revealed that a significant amount of hydrogen peroxide is formed in an aqueous-alkaline medium during the regeneration of the catalyst (Figure 4).

The H₂O₂ accumulation in the aqueous-alkaline medium has been reported in several studies [25,26] which examined the mechanism of hindered hydroquinone oxidation in the presence of alkaline-based catalyst. The oxidative regeneration of stilbenequinone with the H₂O₂ formation involves several main stages, as described in Scheme 3. It is evident about that besides hydrogen peroxide, other active forms of oxygen such as O₂^{•-}, HO₂ are produced during the process of catalyst regeneration. These forms may promote oxidizing sulphide sulfur to the maximum oxidation degree (SO₄²⁻).

While studying the catalyst concentration change in the oxygen-saturated solution (Figure 5), the most interesting finding was that during the reaction course the concentration of stilbenequinone decreases to a certain minimum value, and then increases solely after sulphide has reached the point of complete exhaustion. This



Scheme 2. Oxidation of Na_2S in the presence of stilbenequinone-based catalyst.

implies that the rate of sulphide oxidation by stilbenequinone exceeds that of catalyst regeneration. In other words, the catalysts regeneration is the rate-limiting step in the oxidation reaction of sulphide sulfur in the presence of stilbenequinone.

In summary, the role of stilbenequinone in this case is to create a new and a more efficient way of transferring electrons from the reducing agent (i.e. sulphide sulfur) to the oxidizer (namely oxygen and its active forms) (Scheme 4).

Factors affecting liquid-phase sulphide oxidation in the presence of a stilbenequinone based-catalyst

In general, the catalytic reaction rate depends on a number of factors: temperature, pH medium, catalyst

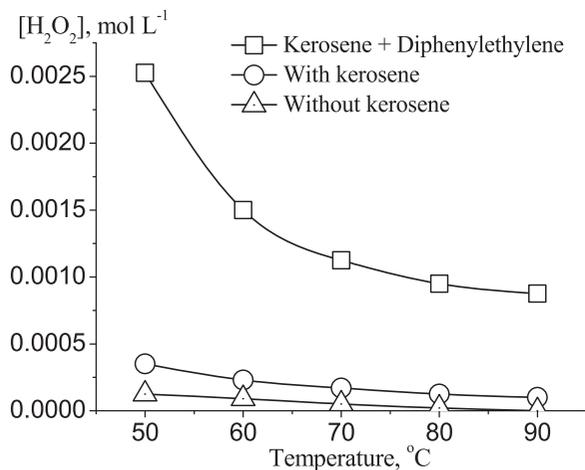
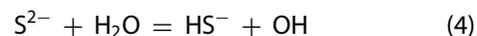


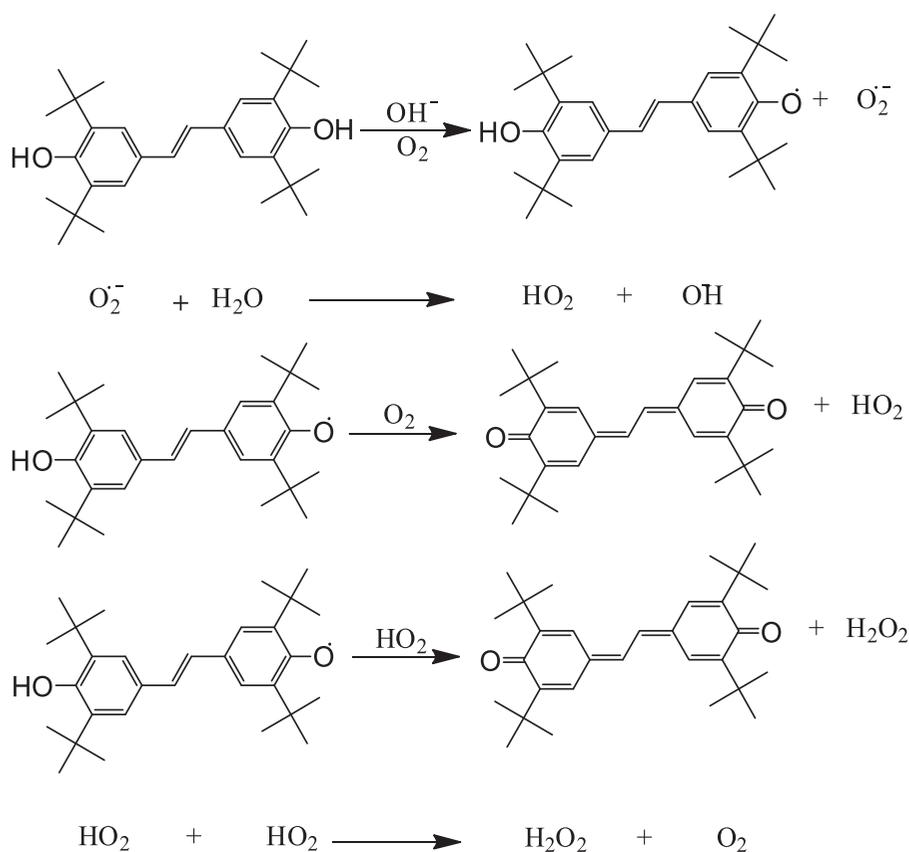
Figure 4. Kinetic curves of H_2O_2 accumulation in the process of regenerating the catalyst at different temperatures: [diphenylethylene] = 0.034 mol L^{-1} , $[\text{NaOH}] = 0.125 \text{ mol L}^{-1}$, the reaction time = 30 min.

nature and mechanism of catalyst action, etc. As shown in Figure 3(a), when the sodium sulphide concentration is above 0.7 mol L^{-1} , its oxidation in the presence of stilbenequinone occurs with a definite induction period. Furthermore, this period lengthens as the initial sulphide concentration increases. It is difficult to explain this phenomenon, but it might be related to the oxidation mechanism, that sulphide ion in water hydrolyses to form hydroxide and hydrosulphide anion (1st stage), as shown in Equation (4).



According to Le-Chatelier's principle, the degree of sulphide hydrolysis increases with dilution. Therefore, the dilution of Na_2S concentration in the reaction solution leads to an increase in the amount of HS^- ion entering into an elementary reaction with stilbenequinone (2nd stage) as well as in the amount of OH^- ions catalyzing the process of stilbenequinone regeneration with the formation of active oxygen forms [25,26] (3th stage). It is a cause for increasing the number of elementary acts in the limiting stage that leads to a reduction in the induction period.

Kinetic curves of Na_2S oxidation at various catalyst concentrations (Figure 3(b)) showed that the oxidation rate of Na_2S is directly proportional to the stilbenequinone concentration in the kerosene fraction. However, this does not apply when the catalyst concentration is above 0.040 mol L^{-1} . This result might be related to catalyst saturation in kerosene fraction. As mentioned above, the catalytic sulphide oxidation occurs at the interface between the aqueous and hydrocarbon phases (kerosene fraction). It can be seen from the data in Table 2 that the solubility of stilbenequinone in kerosene fraction only reaches 0.036 mol L^{-1} at 90°C . Therefore, further increasing the amount of



Scheme 3. Formation of H_2O_2 during the stilbenequinone regeneration.

stilbenequinone in hydrocarbon phases does not influence the oxidation rate of Na_2S .

As discussed above, the major products of the sulphide sulfur oxidation in the presence of a catalyst

based on stilbenequinone are thiosulphate and sulphate. Thiosulphate is the product of sulphide oxidation by stilbenequinone while the latter is the final product of sulphide sulfur and thiosulphate being oxidized by active

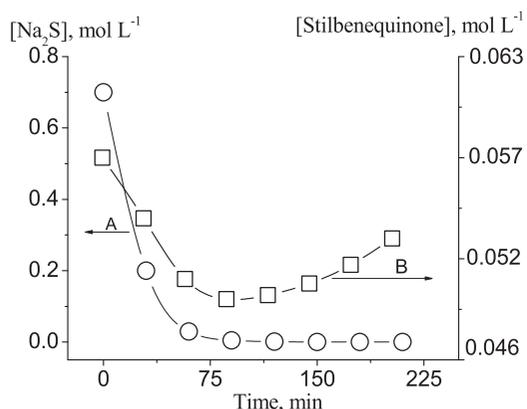
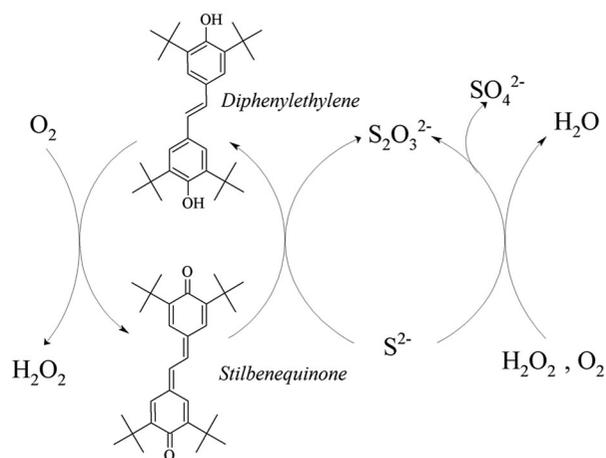


Figure 5. Kinetic curves of catalytic oxidation of Na_2S (A) and of the change in stilbenequinone concentration (B): $[\text{Na}_2\text{S}] = 0.7 \text{ mol L}^{-1}$, $t = 90^\circ\text{C}$, $[\text{stilbenequinone}] = 0.052 \text{ mol L}^{-1}$, the oxygen-supply rate = 13 L h^{-1} .



Scheme 4. Catalytic cycle of the sulphide sulfur oxidation in the presence of stilbenequinone.

Table 2. The solubility of stilbenequinone in the kerosene fraction at different temperatures.

Temperature, °C	40	50	60	70	80	90
Solubility of stilbenequinone in kerosene fraction, mol L ⁻¹	0.013	0.016	0.020	0.025	0.032	0.036

oxygen forms produced during catalyst regeneration. It should be noted that the stilbenequinone does not influence the thiosulphate oxidation [21]. Moreover, one cannot exclude the possibility of partial non-catalytic oxidation of sulphide sulfur with oxygen to form sulphate in a strongly alkaline medium [15]. Obviously, as shown in Figure 6, after complete exhaustion of the sulphide in the reaction solution the thiosulphate concentration decreases meanwhile the concentration of sulphate (the final product of non-catalytic oxidation) increases. Molar mass ratio of thiosulphate to sulphate after 600 min oxidation is 3:4.

A series of experiments was performed to investigate the effect of reaction products – thiosulphate and sulphate – on the rate of catalytic sulphide oxidation. Thiosulphate and sulphate did not show any impact on the rate of sulphide oxidation reaction (Figure 7).

Oxygen simultaneously participates in two processes of the sulphide catalytic oxidation namely the catalyst regeneration and the forming of active oxygen forms. In addition, oxygen is consumed in the non-catalytic oxidation reaction of sulfur-containing substances. The effect of oxygen concentration on catalytic sulphide oxidation under diffusion control was also examined. At low oxygen concentration (i.e. 5–20%) the Na_2S oxidation reaction catalyzed by stilbenequinone proceeded with an induction period.

Temperature was one of the most important factor affecting the rate constant of the sulphide sulfur oxidation. The internal energy of reactants increased as temperature increased and all of them then became active. In other words, the frequency of effective collisions per second between reacting molecules increases. This led to an increase in the chemical reaction rate. Figure 8 provides an overview of the effect of reaction

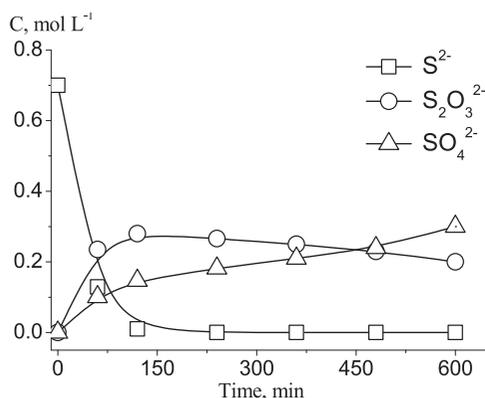


Figure 6. The change in concentration of Na_2S as well as in products of its oxidation catalyzed by stilbenequinone in the course of the reaction: $t = 90^\circ\text{C}$, $[\text{Na}_2\text{S}] = 0.7 \text{ mol L}^{-1}$, $[\text{stilbenequinone}] = 0.052 \text{ mol L}^{-1}$, the oxygen-supply rate = 13 L h^{-1} .

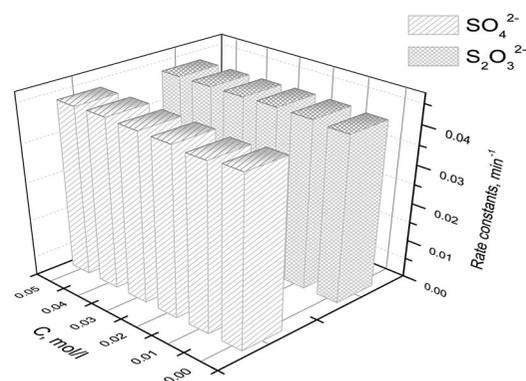


Figure 7. Effect of amount of added thiosulphate and sulphate on the rate of catalytic sulphide oxidation in the presence of stilbenequinone: $t = 90^\circ\text{C}$, $[\text{Na}_2\text{S}] = 0.7 \text{ mol L}^{-1}$, $[\text{stilbenequinone}] = 0.052 \text{ mol L}^{-1}$, the oxygen-supply rate = 13 L h^{-1} .

temperature on the Na_2S oxidation rate in the absence and presence of stilbenequinone-based catalyst. It is clear that in the absence of the catalyst, the sulphide oxidation rate increased as temperature grew up to 70°C and thereafter decreased when temperature grew up to 90°C . The possible cause of this phenomenon is the decrease of dissolved oxygen in the aqueous phase as the temperature increased.

However, in the presence of the catalyst, the sulphide-oxidation rate was directly proportional to reaction temperature. A possible explanation for this might be followed: as shown in Scheme 2, the efficiency of Na_2S oxidation depends on degree of its hydrolysis (1st stage) and on the rate of sulphide oxidation with stilbenequinone (2nd stage) as well as on the rate of diphenylethylene oxidation with oxygen (3th stage). As the hydrolysis reaction of Na_2S is endothermic, increasing the reaction

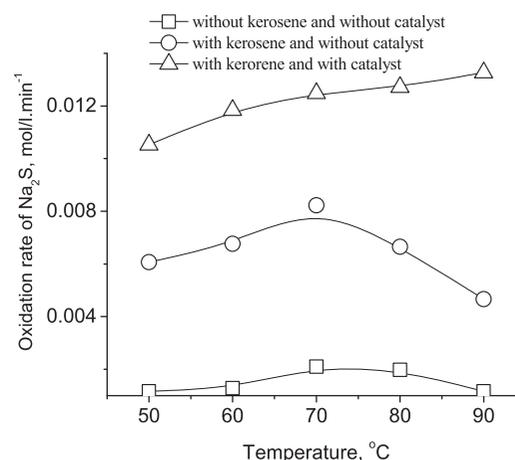


Figure 8. Effect of the temperature on the rate constants of the Na_2S oxidation with and without stilbenequinone-based catalyst: $[\text{Na}_2\text{S}] = 0.69 \text{ mol L}^{-1}$, $[\text{stilbenequinone}] = 0.052 \text{ mol L}^{-1}$, the oxygen supply rate 13 L h^{-1} .

Table 3. The change in concentration of stilbenequinone formed during the diphenylethylene oxidation catalyzed by NaOH at various temperatures: $[\text{NaOH}] = 0.25 \text{ mol L}^{-1}$, $[\text{diphenylethylene}] = 0.013 \text{ mol L}^{-1}$, the reaction time = 90 min, the oxygen supply rate 13 h L^{-1} .

Temperature, °C	60	70	80	90
Concentration of the formed stilbenequinone, mol L^{-1}	0.00550	0.00765	0.00917	0.01043

temperature led to an increase of the hydrolysis degree of Na_2S . Similarly, the sulphide oxidation rate with stilbenequinone [21] and the catalyst regeneration rate (presented in Table 3) also increased with increasing reaction temperature.

Nature of the reactants, solution pH were also important factors affecting the reaction rate. Oxidation rates of Na_2S , NaHS and of K_2S in the presence and absence of a catalyst based on stilbenequinone were compared in Figure 9. It is known [27,28] that a non-catalytic oxidation of sulphide sulfur with oxygen is a function of the solution pH. According to Chen and Morris [27,28] in acid solutions ($\text{pH} < 6$) the oxidation rate of sulphide is very slow. The specific rate increases greatly as pH increases to 8.0, and then decreases to near pH 9.0, whereupon increases again to near pH 11 and finally reduces again in more alkaline solution. From Figure 9 is evident that the rate of non-catalytic oxidation of NaHS ($\text{pH} \approx 9.1-9.5$) is higher than that of Na_2S and K_2S ($\text{pH} \approx 13.5-14$). On the other hand, in the presence of stilbenequinone the highest catalytic oxidation rate belonged to Na_2S , even though the oxidation rate of NaHS by stilbenequinone in an oxygen-free environment oxidation rate exceeded that of Na_2S and K_2S (Figure 10). This may be due to an increase in the amount of OH^- anion in Na_2S

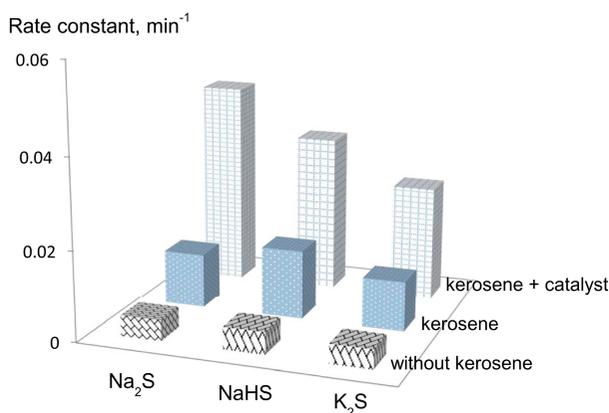


Figure 9. Effect of the sulphide sulfur nature on the rate constants of its oxidation in the presence and absence of stilbenequinone: $t = 90^\circ\text{C}$, $[\text{sulphide}] = 0.7 \text{ mol L}^{-1}$, $[\text{stilbenequinone}] = 0.052 \text{ mol L}^{-1}$ (for the experiment with catalyst), the oxygen supply rate 13 h L^{-1} .

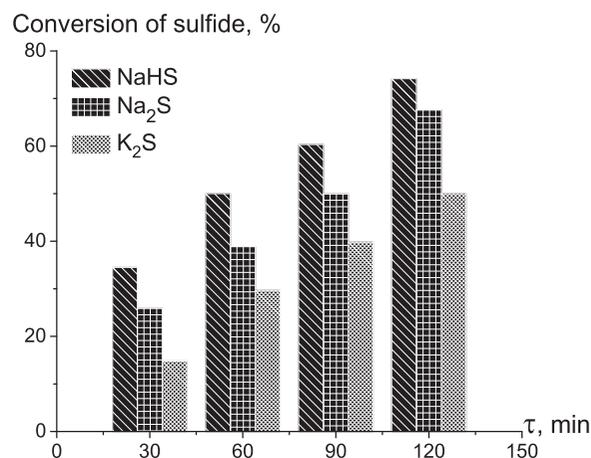


Figure 10. Efficiency of the sulphide sulfur oxidation with stilbenequinone in an oxygen-free environment: $t = 90^\circ\text{C}$, $[\text{sulphide}] = 0.09 \text{ mol L}^{-1}$, $[\text{stilbenequinone}] = 0.358 \text{ mol L}^{-1}$.

and K_2S solution compared to NaHS solution, which contributed to the process of catalytic regeneration with the formation of oxygen active forms.

In our opinion, the observed effect of sulphide sulfur oxidation by stilbenequinone may be related to a high concentration of cations H^+ in NaHS solution ($\text{HS}^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{S}^{2-}$). It is well known that quinones are conjugated α, β -unsaturated carbonyl compounds that perform a large dipole moment with the excess negative electron density on oxygen atoms. Therefore, quinones are very sensitive to electrophiles [29]. Compared to the cations Na^+ and K^+ , the proton H^+ has a significantly higher electrophilicity index ($H = 2.01 > \text{Na} = 0.88 > \text{K} = 0.76$) [30] as well as a small radius ($\text{H}^+ = 0.8751 \text{ fm} < \text{Na}^+ = 0.09 \text{ nm} < \text{K}^+ = 0.133 \text{ nm}$) [31]. As a result, the proton H^+ favourably attacks on the hindered carbonyl group of stilbenequinone, producing an intermediate cation that more easily forms an activated complex with the sulphide sulfur. This implies that, the rate of the sulphide sulfur oxidation with stilbenequinone in an oxygen-free environment decreases in the series: $\text{NaHS} > \text{Na}_2\text{S} > \text{K}_2\text{S}$.

Kerosene fraction in the sulphide catalytic oxidation was used as a catalyst carrier owing to its high boiling point [32] and its low solubility in water [33]. Moreover, the good solubility of stilbenequinone in this kerosene fraction was also an advantage. Consequently, the losses of this catalyst and its carrier during purification process can be minimized. Another important finding was that the presence of hydrocarbon phase led to accelerating the non-catalytic sulphide oxidation (see also Figures 8 and 9). It is possible that this result is due to the higher solubility of oxygen in kerosene compared to in the aqueous medium [34]. Thus, in the catalytic sulphide oxidation the kerosene fraction played both the

role of the catalyst carrier and the oxygen deposition enhancer.

Conclusion

In conclusion, the kinetics of liquid-phase oxidation of inorganic sulphides in the presence of stilbenequinone-based catalyst has been presented as a first-order reaction with respect to each reactant. The role of stilbenequinone is to create an efficient way of transferring electrons from the sulphide to active oxygen forms produced during the process of catalyst regeneration. The result of this study indicates that the products of sulphides oxidation catalyzed by stilbenequinone such as thiosulphate and sulphate did not affect this reaction rate. Interestingly, either at low oxygen concentration or at high sulphide concentration its catalytic oxidation in the presence of stilbenequinone proceeds with an induction period. Besides, efficiency of sulphide sulfur degradation decreases in the series $\text{Na}_2\text{S} > \text{NaHS} > \text{K}_2\text{S}$.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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