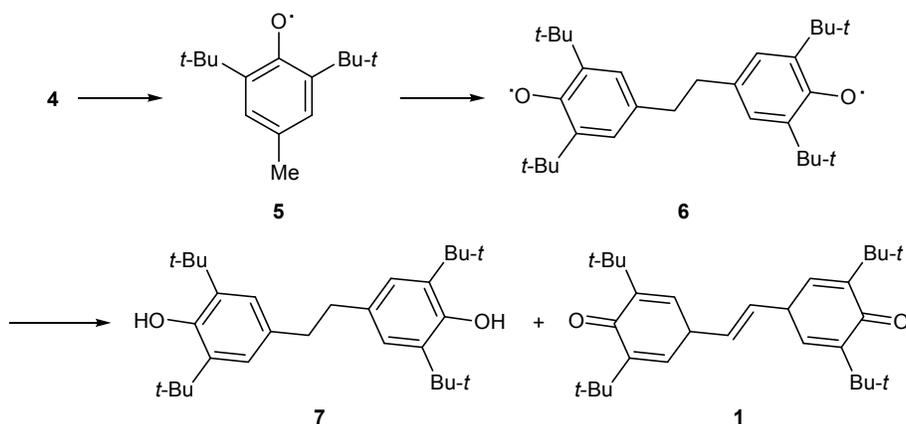
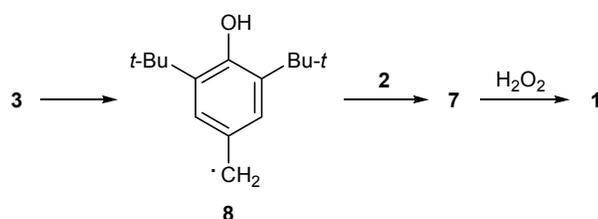


Scheme 2.



Scheme 3.



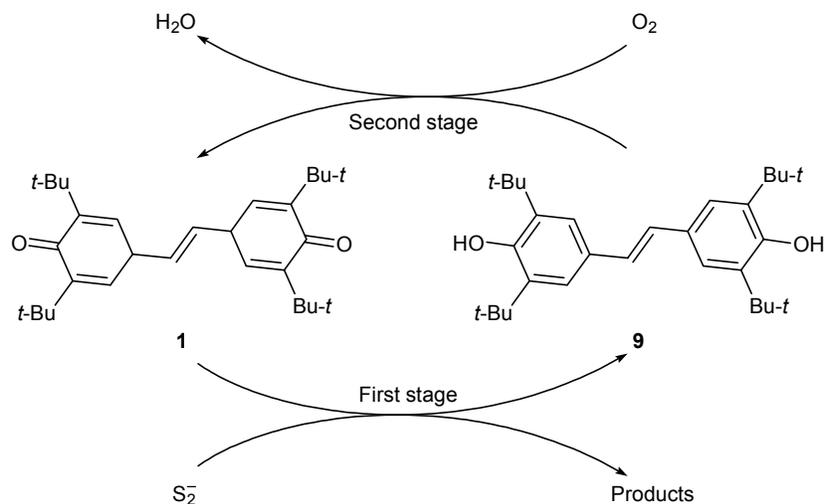
stable. It undergoes disproportionation to initial phenol **2** and methylenequinone **4** [12, 13]. The reaction mixture acquires lemon yellow tint due to formation of **4**. Spontaneous dimerization of unstable methylenequinone **4** gives bisphenoxy radical **6** which is converted to a mixture of stilbenequinone **1** and dihydroxydiphenylethane **7** (Scheme 2) [12–15].

Apart from disproportionation, initially formed radical **3** is capable of isomerizing to hydroxybenzyl radical **8** via hydrogen transfer from the methyl group to oxygen [16–21]. Dimerization of **8** leads to the

formation of compound **7** which is oxidized with hydrogen peroxide to final stilbenequinone **1** (Scheme 3).

In the preceding study [22] we presumed that stilbenequinone acts as redox catalyst in the oxidation of sulfide sulfur. This process is likely to include two stages: (1) oxidation of S^{2-} with stilbenequinone **1** and reduction of the latter to dihydroxydiphenylethane **9** and (2) regeneration of the catalyst by oxidation of **9** in alkaline medium (Scheme 4). In order to confirm the proposed mechanism, in this work we studied the oxidation of sodium sulfide with stilbenequinone **1** at

Scheme 4.



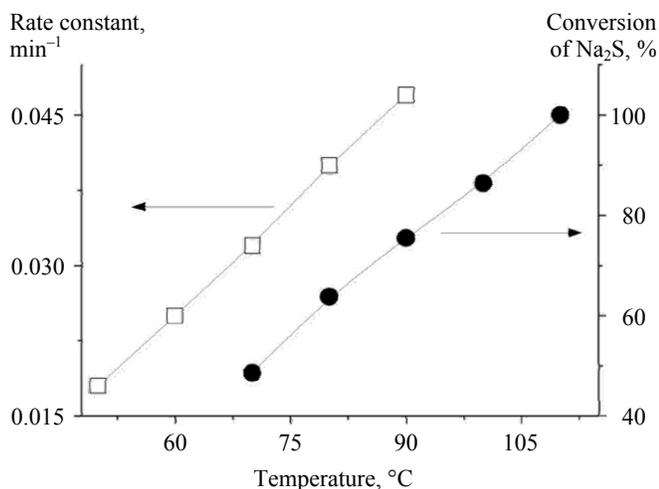


Fig. 1. Temperature dependences of the (1) rate constant of catalytic oxidation of Na₂S in the presence of stilbenequinone **1** and (2) conversion of Na₂S.

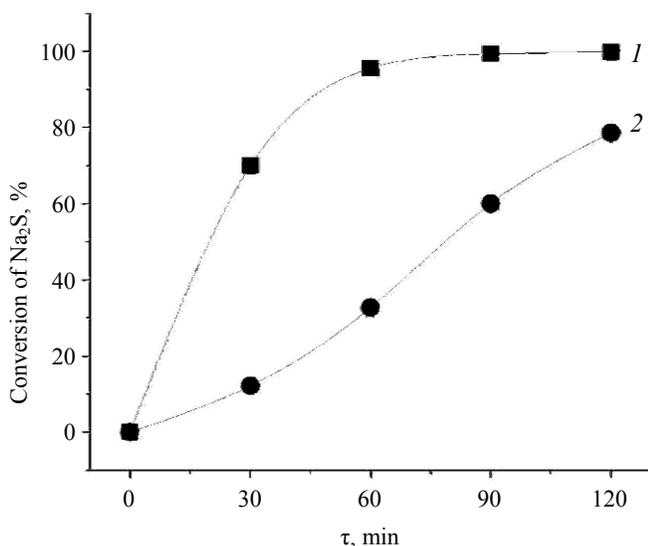


Fig. 2. Kinetic curves for the oxidation of Na₂S in the presence of (1) stilbenequinone **1** and (2) diphenoquinone **10**; [Na₂S]₀ = 0.7 M, [quinone]₀ = 0.05 M, oxygen flow rate 300 L/h, temperature 90°C.

70–110°C in an inert medium (Figs. 1, 2); after completion of the reaction, the light yellow powder separated from the reaction mixture was analyzed to identify compound **9**.

The rate of oxidation of sodium sulfide with stilbenequinone **1** in an inert medium increased with rise in temperature. The IR spectrum of **9** lacked absorption bands due to conjugated diene fragment (C=C, 1640–1605 cm⁻¹) and carbonyl group (C=O, 1605 cm⁻¹) typical of stilbenequinone **1**. Instead, absorption bands belonging to OH groups (3627–3607, 1420, 1231–1133 cm⁻¹), and C=C double bond

appeared (960 cm⁻¹). The melting point of the product coincided with that reported in the literature for compound **9** (240°C [21]).

The catalytic activity of stilbenequinone **1** is determined by a number of factors, including temperature, pH, sulfide nature, etc. The rate of oxidation of sulfide sulfur (Fig. 1) and regeneration of stilbenequinone **1** (Fig. 3) increased as the temperature rose; correspondingly, the efficiency of catalytic oxidation increased.

The catalytic activity of stilbenequinone is also sensitive to pH of the medium. The data in Table 1 illustrate variation of the conversion of sodium sulfide (pH 13.5) and sodium hydrogen sulfide (pH 9) in the presence of stilbenequinone **1**. It is seen that the rate of oxidation of Na₂S is higher than the rate of oxidation of NaHS. According to published data [24, 25], hydroxide ions catalyze oxidation of hydroquinone to benzoquinone; therefore, higher concentration of OH⁻ ions favors regeneration of the catalyst in the oxidation of sulfide sulfur.

Addition of an inhibitor could reduce the catalytic activity or completely deactivate the catalyst. This was observed in the oxidation of ammonium sulfide in the presence of stilbenequinone **1**. The rate of catalytic oxidation of (NH₄)₂S was the same as the rate of non-catalytic process. Furthermore, addition of aqueous ammonia to a solution of Na₂S appreciably reduced the rate of catalytic oxidation of the latter: $y = -0.0098x + 0.0111$, where y is the rate of catalytic oxidation of Na₂S, and x is the concentration of ammonia.

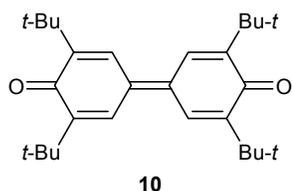
The observed pattern can be rationalized as follows. Quinones are conjugated α,β-unsaturated dicarbonyl compounds characterized by large dipole moments, and excess electron density therein is localized on the oxygen atom. Therefore, quinones are very sensitive to electrophiles [26]. Ammonium ions generated by dissociation of ammonium sulfide are strong electrophilic species capable of blocking active sites of the catalyst with subsequent complete deactivation.

Table 1. Oxidation efficiency (%) of inorganic sulfides in the presence of stilbenequinone **1**^a

Sulfide	Oxidation time, min				
	0	30	60	90	120
Na ₂ S	0.00	70.89	96.56	99.99	100.00
NaHS	0.00	65.00	88.00	96.02	98.36

^a Temperature 90°C, initial sulfide concentration 0.7 M, amount of stilbenequinone 0.45 g, oxygen flow rate 300 L/h.

The structure of quinones largely determines their ability to participate in chemical reactions. With the goal of elucidating the relation between the structure of quinones and their catalytic activity in the oxidation of sodium sulfide, we compared the activities of stilbenequinone **1** and 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenylquinone [1,1'-bi(cyclohexa-2,5-dien-1-ylidene)-4,4'-di-one] **10**. It is seen (Fig. 2) that the catalytic activity of **1** is higher than the activity of **10**. Presumably, this is related to the mechanism of oxidation of sulfide sulfur in the presence of quinones, which is determined by both stages (Scheme 4).



This assumption was confirmed by the results of oxidation of Na₂S with quinones in an inert medium (first stage in Scheme 4). Stilbenequinone **1** is superior to diphenylquinone **10** in the oxidizing ability (Fig. 4). Unlike compound **10**, the two cyclohexadiene fragment in molecule **1** are separated by two CH units. The higher reactivity of stilbenequinone **1** is determined by higher accessibility of the CH groups to attack of nucleophile [6, 27].

The second stage in the catalytic oxidation of sulfide sulfur in the presence of quinones (Scheme 4) is the oxidation of **9** or 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-4,4'-diol (**11**, reduced form of **10**). Here, the polarity of the hydroxy group is important. Change of the O–H bond polarity in going from one hydroquinone to another determines the difference in the energies of dissociation of that bond and hence their different oxidizabilities [28].

Unlike compound **11**, the conjugated bond system in molecule **9** includes the CH=CH double bond in addition to the aromatic rings. Therefore, the electronegativity of the oxygen atom in **9** is higher, and the Coulomb integral of the oxygen δ -orbitals is more negative. Such change of the δ -electron structure of the OH bond increases its polarity and reduces the energy of dissociation, so that compound **9** should be oxidized more readily than **11**. This was confirmed experimentally (Fig. 4).

Thus, we have shown that the rate of regeneration of stilbenequinone **1** is higher than the rate of regeneration of diphenylquinone **10**.

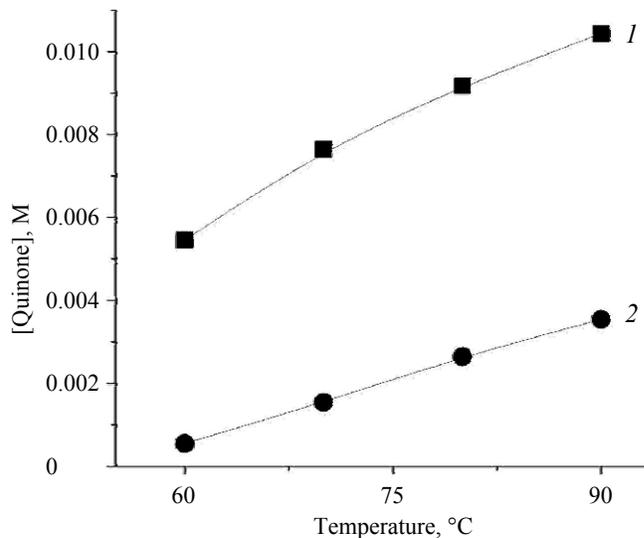


Fig. 3. Temperature dependences of the accumulation of (1) stilbenequinone **1** and (2) diphenylquinone **10** in the oxidation of their reduced forms at different temperatures in the presence of 10% NaOH; initial concentration of the reduced form 0.013 M, oxygen flow rate 300 L/h, kerosene volume 50 mL, regeneration time 90 min.

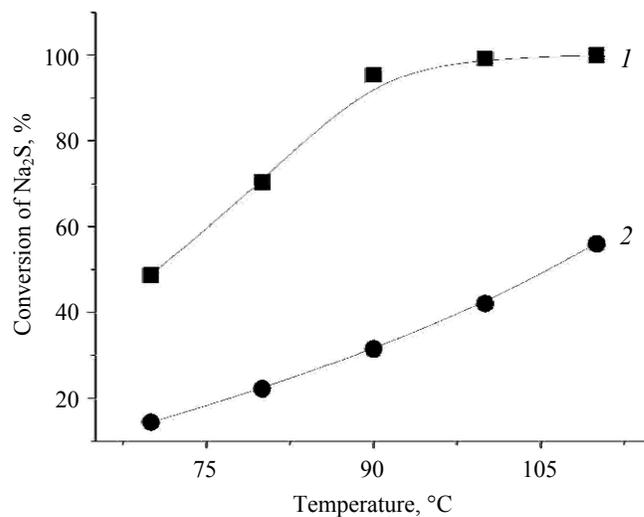


Fig. 4. Temperature dependences of the conversion of Na₂S in the oxidation with (1) stilbenequinone **1** and (2) diphenylquinone **10**; [Na₂S]₀ = 0.09 M, [quinone]₀ = 0.14 M, 90 min.

EXPERIMENTAL

The IR spectra were recorded on a Perkin Elmer Spectrum Two spectrometer equipped with an ATR accessory. The ¹H NMR spectra were recorded on a Bruker Avance-600 spectrometer using DMSO-*d*₆ as solvent and reference (δ 2.50 ppm). The elemental analysis of stilbenequinone was obtained with an AURIGA Cross Beam workstation equipped with an IncaX-MAX energy dispersive spectrometer (reso-

lution 127 eV). The melting points were measured on a Buchi M-560 melting point apparatus.

The concentration of quinone was determined by photocalorimetry. A 0.5-cm³ sample of kerosene fraction was withdrawn from a three-necked cylindrical reactor without preliminary cooling. The sample was diluted with toluene to a volume of 50 cm³ (by a factor of 100) in a volumetric flask. The kerosene fraction containing dissolved quinone endows toluene solution with a bright yellow color which becomes more intense as the concentration of quinone increases. The absorbance at λ 500 nm was measured with an Ekros PE5300V spectrophotometer using a 10-cm path-length cell, and the concentration of quinone was calculated using a calibration curve.

The concentration of sulfides was determined by potentiometric titration according to GOST (state standard) no. 22985.

4,4'-(Ethan-1,2-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one) (1). A mixture of 30 g of compound **2** and 3 g of potassium iodide in 120 mL of propan-2-ol was stirred at 70°C in a 500-mL cylindrical glass reactor. After 30 min, 42 mL of a 35% aqueous solution of hydrogen peroxide was added, and the mixture was stirred for 9 h at 70–75°C. The mixture was cooled, and the red–orange crystalline solid was filtered off, recrystallized from toluene, and dried for 1 h at 120°C. Yield 98%, mp 315°C. IR spectrum, ν , cm⁻¹: 3003 (C–H_{arom}), 2952, 2909, 2865 (Me), 1640, 1605 (=C–C=), 1605 (C=O), 1600, 1454 (C=C_{arom}), 1360, 1256 (*t*-Bu). ¹H NMR spectrum (600 MHz), δ , ppm: 1.42 s (36H, *t*-Bu), 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; N 10.15; O 7.30.

Catalytic oxidation of inorganic sulfides was carried out in a 150-ml cylindrical glass reactor which was charged with a mixture of 40 mL of an inorganic sulfide solution, 20 mL of kerosene, and a required amount of the catalyst. Oxygen was passed through the mixture under stirring at 1400 rpm using a magnetic stirrer on heating at a required temperature.

The oxidation of inorganic sulfides with quinones in an inert medium was carried out in a 150-mL stainless steel high-pressure reactor. A mixture of 40 mL of an inorganic sulfide solution, 20 mL of kerosene, and a required amount of the catalyst was stirred at 1400 rpm.

Hydrogen peroxide of chemically pure grade, 2,6-di-*tert*-butyl-4-methylphenol, propan-2-ol, potas-

sium iodide, sodium sulfide, toluene, and aqueous ammonia of analytical grade, 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone, 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-4,4'-diol, and straight kerosene fraction of pure grade, and oxygen and argon of ultrapure grade (from gas cylinders) were used. Solutions of sodium hydrogen sulfide and ammonium sulfide were prepared according to the procedures described in [28, 29].

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