

Synthesis of Methyl - 2,5 - Dihydroxyphenylsulfide and Study of its Antioxidant Action

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ARTICLE INFO

Article history:

Received: 30 March 2017;

Received in revised form:

2 May 2017;

Accepted: 11 May 2017;

Keywords

Antioxidant action,
Methyl-2-
dihydroxyphenylsulfide,
Synthesis,
Cumene peroxide,
Inhibitor.

ABSTRACT

Methyl-2-dihydroxyphenylsulfide was synthesized with the aim of characterizing antioxidant action. Its ability to break off oxidation chain in the reaction with peroxide radicals, as well as parameter of $f \cdot k$ which characterizes inhibiting activity of inhibitor, were studied.

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1. Introduction

Sulfur-containing phenyls have antioxidant properties of complex action. Phenols effectively break off oxidation chains by interacting with peroxide radicals and inhibiting their growth. Sulfides and other sulfur-containing agents actively destroy hydroperoxides [1, 2]. Research of mechanisms of antioxidant action of phenol sulfides showed that simultaneous existence of phenol OH and sulfide fragments in molecules imparts them properties of bifunctional inhibitors of oxidation. Mechanism of their antioxidant action consists in effective break of oxidation chain of phenol group by suppressing peroxide radicals and in catalytic destruction of hydroperoxides by ion mechanism [4, 8]. Sulfur-containing derivatives – hydroquinones are also of great interest as potential antioxidants. Presence of two OH groups in their molecules can contribute to increasing induction period of oxidation by the interaction with two peroxide radicals ROO^{\bullet} and break of two oxidation chains.

2. Experimental Part

As a model hydrocarbon for oxidation we used cumene, and its purification was conducted by standard technique [3, 5]. Kinetics of oxidation of cumene was studied on standard manometric device [6]. Auto-oxidation was performed at 110°C. but initiated oxidation was conducted at 60°C. As an initiator we selected azoisobutyronitrile (AIBN), concentration of which in all tests was equal to $2 \cdot 10^{-2}$ mol/l.

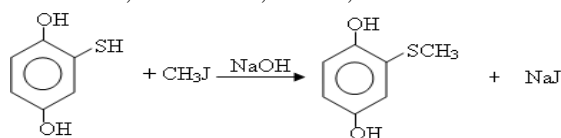
3. Results and Discussion

To obtain methyl-2,5-dihydroxyphenylsulfide we dissolved 3.6 g (0.025 mol) of 2,5-dihydroxybenzenethiol in 15 ml isopropanol, added 1 g (0.025 mol) of sodium hydrate into 5 ml water at 5–10°C and sparged with nitrogen. 3.6 g

(0.025 mol) of methyl iodide was supplied through drop funnel. The mixture was mixed 2 hours. After distillation of solvent, the residue was dissolved in ether, washed out with 2 n chlorohydric acid and then with water till Reaction scheme, neutral reaction. After distillation of water the residue was dissolved in benzene, dried on non-aqueous sodium sulfate. Benzene was distilled and 2.9 g of methyl-2,5-dihydroxyphenylsulfide (74% from theoretical) was separated. The product was distilled under vacuum in inert medium (123–125°C, 0.4 mm of mercury). $R_f = 0.82$.

Founded, %: C 54.27; H 5.01; S 20.92.

Calculated, %: C 53.85; H 5.13; S 20.51.



For quantitative characteristics of inhibiting action of methyl-2,5-dihydroxyphenylsulfide during oxidation of cumene we calculated stoichiometric inhibition coefficient f , equal to number of oxidation chains, which break off in one molecule of inhibitor and rate constant of interaction of inhibitor with cumene peroxide radicals K_7 , and they characterize its reactivity [6, 7].

$$f = \frac{\tau \cdot W_i}{[J_n H]_0}$$

τ – induction period, sec; W_i – initiation rate, equal to $2.02 \cdot 10^{-7}$ mol/l · sec; $[J_n H]$ – starting concentration of inhibitor.

$l \cdot \text{sec}$

Rate constant of reaction K_7



$$K_7 = \frac{tg \alpha \cdot K_2 \cdot [RH] \cdot W_i}{f \cdot [J_n H]_o}$$

Comparison of inhibiting properties of methyl-2,5-dihydroxyphenylsulfide with known industrial antioxidant-2,6-ditert-butyl-4-methylphenol (ionol) during auto-oxidation of cumene showed essential superiority of the test substance (fig.). Amount of oxygen absorbed in the presence of methyl-2,5-dihydroxyphenylsulfide was three times less than with ionol – 0.06 ml opposite to 0.18 ml.

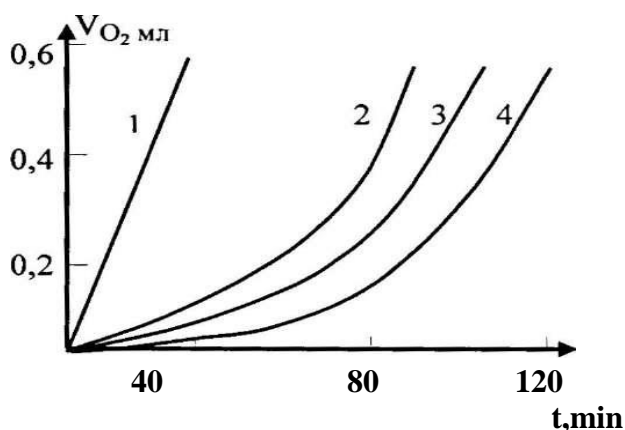
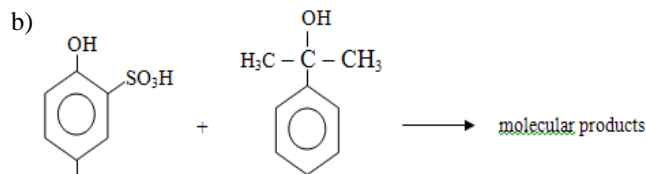
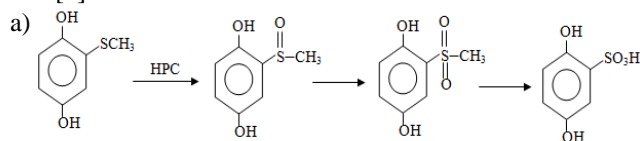


Figure. Kinetics of initiated oxidation curves of cumene during different concentrations of methyl-2,5-dihydroxyphenylsulfide [I_nH].

1 - [I_nH] = 0; 2 - [I_nH] = 1·10⁻⁴ mol/l; 3 - [I_nH] = 3·10⁻⁴ mol/l; 4 - [I_nH] = 5·10⁻⁴ mol/l.

Superiority of antioxidant action of methyl-2,5-dihydroxyphenylsulfide on ionol during auto-oxidation is explained by additional inhibiting effect of transformation products of sulfides capable of catalyzing the decay of hydroperoxidecumene (HPC) by molecular mechanism and contributing the increase of antioxidant of antioxidant action. Oxidative transformation of methyl-2,5-dihydroxyphenylsulfide during interaction with hydroperoxidecumene – initial oxidation product of cumene can be represented in the form of the following reaction [a] and [b]:



Intensification of inhibiting effect of methyl-2,5-dihydroxyphenylsulfide can be explained only by ion-molecular decay of HPC.

4. Conclusions

Optimal conditions were determined and methyl-2,5-dihydroxyphenylsulfide was synthesized as a potential antioxidant of alkylaromatic hydrocarbons. Obtained inhibitor exceeds industrial antioxidant ionol due to sulfide group and ability of its oxidative transformation products to catalyze the decay of hydroperoxidecumene by ionol mechanism.

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