

Physicochemical properties of phenol photolysis products

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This paper presents the results of phenol photolysis in aqueous media irradiated with a high-pressure mercury lamp. The spectral-luminescent manifestations of phenol photolysis are compared with the results of analysis of the photoproducts obtained using liquid chromatography. It seems that such experiments can make a contribution to understanding the mechanisms of phenol decomposition.

Introduction

In recent decades the environmental problems have become more and more urgent due to the increasing chemical pollution of the biosphere with toxic wastes that can even lead to dangerous ecological situations.

The territory of Tomsk Region and Western Siberia, on the whole, is subject to contamination by xenobiotics due to various industrial factors (plants on processing and transportation of coal and oil products). One of the most dangerous xenobiotics is phenol and its derivatives.¹ Under the action of temperature, solar radiation, and other factors, the initial phenols yield a wide spectrum of new, sometimes even more dangerous products.² For this reason the study of phenol transformations in the environment is one of the most urgent problems in ecological chemistry. There are many papers devoted to this problem but they describe only the final products of phenol transformation, while saying almost nothing about

mechanisms of the transformation reactions. The reactions of phenol compounds photooxidation in water solutions have not yet been studied sufficiently well although this is one of the main ways of phenols' transformation in the environment. In this paper, we present an attempt made to gain a more thorough theoretical knowledge of this subject.

Figure 1 presents the products of phenol photooxidation proposed based on literature data. The products of primary oxidation are, first of all, isomeric dihydroxybenzenes (2–4); second, isomeric dimeric forms of phenol (5–9). The products of secondary oxidation are, first, isomeric quinones (10, 11); second, 2-hydroxy-4-quinone (12), and products of condensation and polymerization, including crossed polymerization, of primary and secondary oxidation products (typical are (13, 14)). The mechanism of some of these reactions was discussed in Ref. 3.

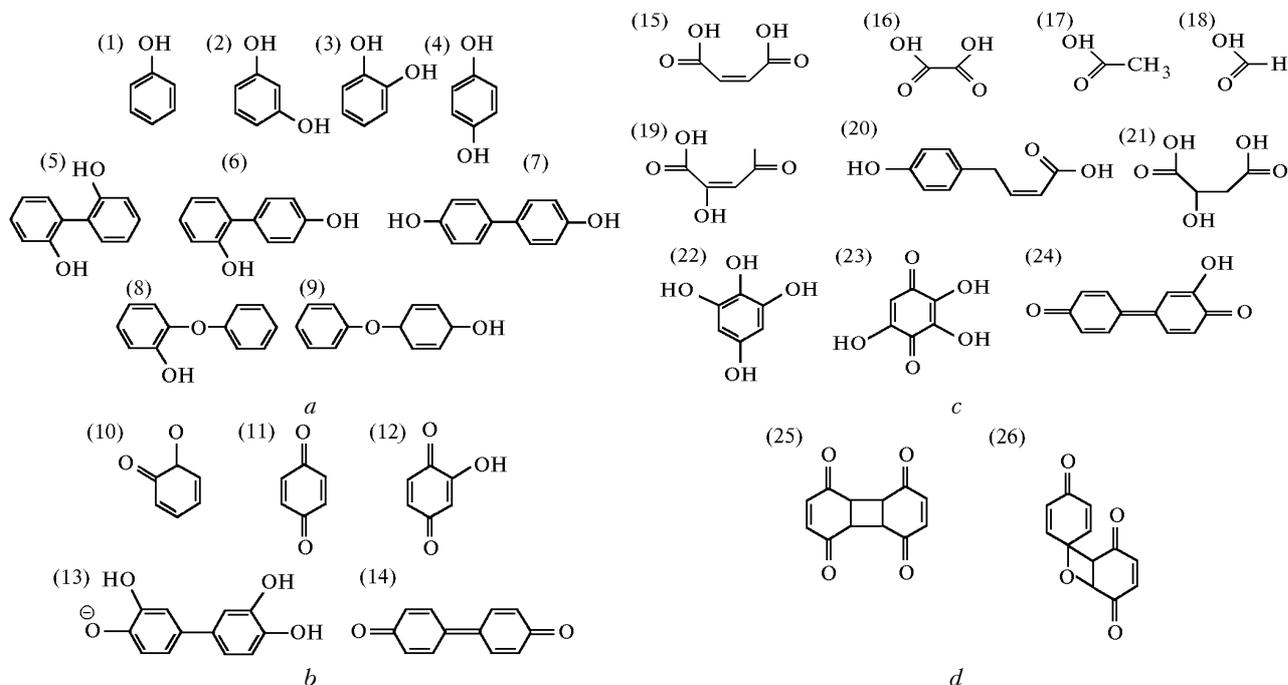


Fig. 1. Proposed products of phenol photooxidation: primary oxidation (a), secondary oxidation (b), deep oxidation (c) and photocyclization (d).

Among the products of deep oxidation there are the organic acids like fumaric acid (15), oxalic acid (16), acetic acid (17), formic acid (18), various hydroxyl acids formed both from phenol and from primary and secondary products of its oxidation (typical are (19–21)), and various polyoxy-benzenes and quinones (typical are (22–24)). Besides, the products of complete oxidation, CO, CO₂, and water, must be also formed.

It must be noted that the probability of photocyclization is different for products of phenol oxidation. These reactions are most typical for compounds of quinoid type (typical are (25, 26)). The mechanism of these reactions is well described in Ref. 4.

Experimental technique

The work was performed by methods of capillary gas chromatography, spectrophotometry, and potentiometry with selective electrodes. We also studied the spectral-luminescent properties of the objects. The gas chromatographic analysis was performed using a "Chom-5" chromatograph with a glass capillary column (WLOT) (length is 27 m, internal diameter is 0.52 mm) with grafted immobile phase XE-60 ($\sigma = 1 \mu\text{m}$). Input pressure of the carrier gas (helium) was $P = 3.5 \text{ atm}$. Retaining time was determined with an LX-1097 integrator. Model phenol solutions were irradiated with a DRLF-400-1 lamp (the spectrum is presented in Ref. 5). The newly prepared phenol solutions of concentration $5 \cdot 10^{-3}$ and 10^{-3} M were poured into an open quartz cell of 12 ml volume up to the mark and placed in the working camera of the lamp. Exposition time was 0 s to 60 min. After the irradiation, solutions were placed to a container isolated from the sun light.

To determine concentration of the dissolved oxygen in the irradiated solutions, a calibrated detector was immersed into the solutions of 10 ml volume placed in a chemical glass so that the thermisar leads on the lateral surface of the sensor were under the surface of the solution. The oxygen content was read out after stabilization of the sensor readouts, but no later than 15 minutes after the beginning of measurements. The measurement results were recalculated in accordance with the manual of the oxygen detector type No. 5972.

To study the influence of different spectra of exciting light upon phenol photolysis, a set of color optical glasses was used. Electron spectra of absorption and fluorescence were observed by the standard technique with a "Specord M40" spectrophotometer and a "Hitachi M850" spectrofluorometer, respectively.

Experiment

In the course of this study, we have developed a technique for gas-chromatographic identification of the products of phenol photolysis. To determine kinetic parameters of the reaction in relation to the main

component (phenol), analysis of samples taken in different ways was performed in the isothermal regime at $T_{\text{column}} = 130^\circ\text{C}$. Duration of the determination under these conditions was 2.5 min. It must be noted that efficiency and selectivity of the column remained high at such a high analysis rate.

Identification of the composition of the irradiated phenol solutions is complicated by the great difference in physicochemical properties of its photolysis products. In this connection, optimum conditions for chromatographic determination were sought by programming of the thermostat temperature. The following conditions appeared to be most appropriate: the initial temperature of the column 130°C , rapid heating at a rate of 10°C per minute up to 180°C followed by the isothermal regime during 10 minutes. Thus, total duration of the determination was 15 minutes. It is important that high degree of the peak separation was observed in this case ($R_{\text{min}} = 1.5$). One of the typical chromatograms obtained by use of this technique is presented in Fig. 2a. Optimum temperatures of the detector and vaporizer are 200°C and 260°C , respectively. The time of holding the compounds under study is presented in Table 1.

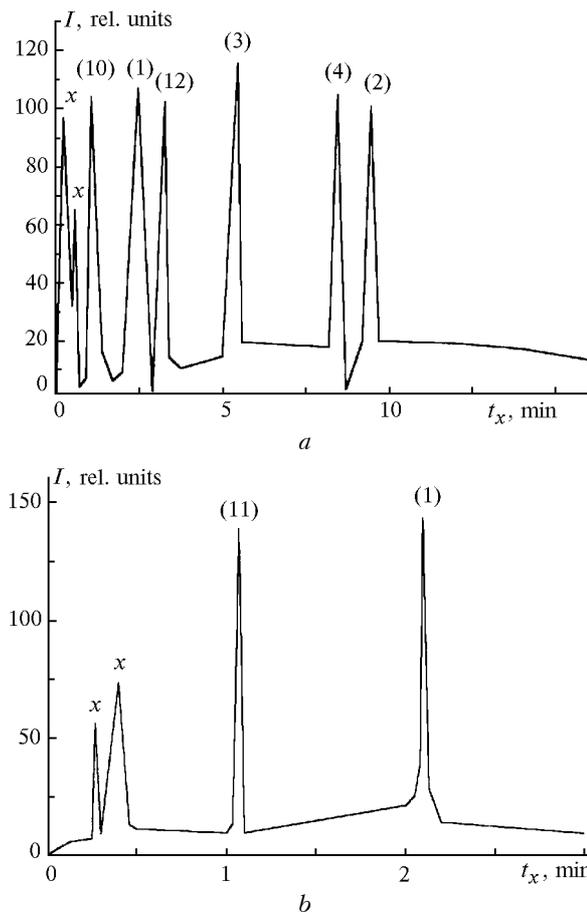


Fig. 2. Chromatogram of a model water solution of phenol with addition of the proposed products (a). Chromatogram of a phenol water solution after 60 min of irradiation with a Hg lamp (b).

Table 1. Holding time for some products of phenol photolysis

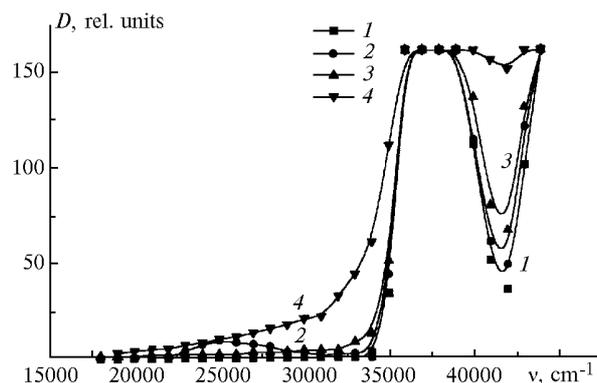
Compound	Isothermal regime, min	Programmed regime, min
Phenol (1)	2.32	2
<i>n</i> -Quinone (10)	1.18	0.46
Pyrocatechol (3)	—	5.04
Hydroquinone (4)	—	8.43
Resorcinol (2)	—	9.12

To increase the sensitivity of analysis to the products of phenol photolysis, we applied a technique of liquid-extraction concentrating. The extraction degree (for resorcinol) was no less than 95%, the extraction factor was 250 times. The detection limit of the proposed technique was 10^{-5} M (for phenol); with the allowance for concentrating, $5 \cdot 10^{-8}$ M (for hydroquinone). The results of chromatographic analysis on phenol in the irradiated solutions without admixtures at different exposure times are given in Table 2. As seen from the table, phenol is rather badly decomposed under UV radiation, especially if one takes into account high intensity of the irradiation. Figure 2b presents the chromatogram for the extract of water solution of phenol that was being irradiated during 60 minutes.

Table 2. Phenol content in the irradiated solutions

Exposure time, min	Phenol concentration $5 \cdot 10^{-3}$, l	Phenol content, % of the initial one
0	5.0	100
1	4.7	97
3	4.5	94
5	4.2	86
10	3.8	76
20	3.6	72
35	3.2	69
60	3.0	63
120	2.4	49

The study of this and other irradiated solutions of the type described above demonstrates that the main products of phenol photolysis under these conditions are *n*-quinone (10) and oligomerization products of phenol and isomeric quinones. Their presence was confirmed by the methods of electron spectroscopy. Analysis of spectral-luminescent properties of the irradiated phenol solutions demonstrates that *n*-quinone is really a product of phenol photolysis. This is observed in the absorption spectrum within the 42000 cm^{-1} and $28000\text{--}24000 \text{ cm}^{-1}$ bands (Fig. 3, curve 2) of the water solution of phenol after 35 min of UV irradiation. The spectral study of the *n*-quinone⁶ demonstrated that it does not fluoresce. However, after irradiation of water solution of phenol we observe the successively appearing fluorescence bands in the regions near 350 nm, 370 nm, 415 nm, and 460 nm. They belong to fluorescence of the products of phenol oligomerization.^{7,8}

**Fig. 3.** Phenol absorption spectra (concentration $5 \cdot 10^{-3}$ M) in water after irradiation by a Hg lamp. Irradiation time: 0 (1); 35 (2); 90 (3); 60 min, the solution with added $5 \cdot 10^{-4}$ M of hydrogen peroxide (4).

To prove that the character of phenol decomposition is the photochemical one, we have isolated some portions from the spectrum of the lamp used. The results of analysis of the parts irradiated in such a way are presented in Table 3. In all the cases, exposition time was similar (30 minutes).

Table 3. Phenol decomposition rate as a function of the exciting light wavelength

Band of wavelengths, nm	Phenol concentration $5 \cdot 10^{-3}$, M	Phenol content, % of the initial one
The initial solution	1.00	100
Full spectrum	0.73	72
248–365	0.84	84
313–365	0.95	95
365–446	0.98	98

As seen from the table, the decrease in the decomposition rate is directly connected with the removal of the UV portion of the lamp spectrum (248–365 nm). This can be considered as a proof for the above statement. The variation of phenol concentration in the latter two cases is within the error of determination, i.e., decomposition maybe does not take place at all.

Analysis of phenol solutions with an admixture of hydrogen peroxide demonstrated sharp increase in the decomposition rate (approximately by 10 times). The results are given in Table 4.

Table 4. Phenol content in the irradiated phenol solutions with an admixture of hydrogen peroxide

Exposure time, min	Phenol concentration $5 \cdot 10^{-3}$, M	Phenol content, % of the initial one
0	1.00	100
1	0.95	95
3	0.89	89
5	0.83	83
10	0.69	69
20	0.57	57
35	0.41	41
60	0.25	25
120	0.16	16

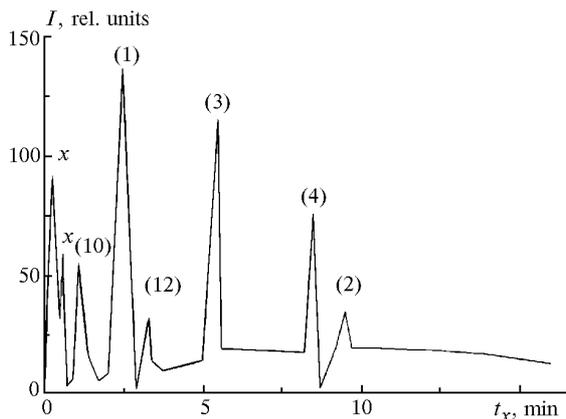


Fig. 4. Chromatogram of a phenol water solution with an admixture of $5 \cdot 10^{-4}$ M of hydrogen peroxide after 60 min of irradiation with a Hg lamp.

It is important that qualitative and quantitative content of photolysis products sharply changed. A typical chromatogram of the extract of the irradiated phenol solution is presented in Fig. 4. As seen from the chromatogram, the main products are pyrocatechol ((3) 10%), hydroquinone ((4) 2%) and *n*-quinone.

Thus, it is demonstrated that phenol photolysis in water goes through *n*-quinone, without hydroquinone. During phenol photolysis in water with hydrogen peroxide, isomeric dihydrobenzenes are formed.

Acknowledgments

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