

KINETICS AND MECHANISM OF THE REACTION OF OZONE WITH
PHENOL IN ALKALINE MEDIA

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The kinetics of the reaction of O_3 with PhOH in alkaline medium has been studied. The rate of oxidation of phenol by ozone is directly proportional to the concentrations of reactants and increases in a complex manner with increase in alkali content in aqueous solution. The composition of the reaction products was investigated and it was found that dimers and oligomers of phenoxyl radicals predominate in alkaline medium. A mechanism is proposed for the process.

The kinetics and mechanism of the reaction of ozone with phenols has been frequently discussed in connection with the need to break them down in natural and waste waters [1-2]. It has been found that the reaction is appreciably faster in an alkaline medium than in neutral or acid media [3-5]. The composition of the reaction products also depends on the pH of the medium although this has not been studied in detail. According to the data of Singer and Gurol [4], the main product of the reaction in alkaline medium is pyrocatechol. In the majority of cases it was assumed that in alkaline medium the ozone initially reacts with hydroxyl ion, forming a hydroxyl radical [4] which inserts itself into the aromatic nucleus with formation of dioxybenzenes. It has been suggested [5] that the reason for the speeding up of the reaction in alkaline medium is the faster reaction of ozone with the phenolate ion in comparison with the original phenol, but no arguments in favor of this have been produced.

This study deals with the kinetics and composition of products for the reaction of ozone with phenol in alkaline medium together with a study of the mechanism of the process.

EXPERIMENTAL

Ozone was synthesized in a discharge apparatus by passing an O_2 jet between the electrodes. The O_3 concentration was measured spectrophotometrically at $\lambda = 254$ nm, $[O_3] = 5 \cdot 10^{-5} - 5 \cdot 10^{-3}$ M. The reaction of O_3 with PhOH was carried out in a bubbler reactor over the temperature range 0-20°C. The PhOH used in the experiments was chemically pure grade.

To determine the composition of the reaction products, 100 mg PhOH was dissolved in an aqueous solution of alkali, ozonized to 30% PhOH, then the solution was neutralized with acetic acid and evaporated. The conversion of PhOH was determined from the difference between the amount of PhOH added and that unreacted using GLC in a Tsvet-100 chromatograph (1 m column, chromosorb W phase E-30, 3%, helium, 132°C), and also from the amount of O_3 absorbed for a stoichiometric reaction coefficient $n = \Delta[O_3]/\Delta[PhOH]$ determined according to the published procedure [6].

The residual dark oil was separated on a chromatographic column (silica gel μ 40/100, solvent 2:1 $CH_3OH:H_2O$, 1% CH_3COOH). The yield of products from the column was monitored using TLC. The nature of individual substance was established from IR and PMR spectra, melting point, and mean molecular weight determined ebullioscopically [7], and the amount of products formed using TLC. After separation on a plate, the substances to be analyzed together with adsorbent were transferred to a container, washed free from adsorbent, then transferred to a measurement cuvette [8].

The following reaction products were isolated: pyrocatechol (VI), mp 105-106°C (decomp.), recrystallized from C_6H_6 ; hydroquinone, mp 170-171°C (decomp.), recrystallized from H_2O ; muconic acid, mp 305°C (decomp.), recrystallized from C_2H_5OH ; 2,2-dihydroxydiphenyl (IV), mp

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TABLE 1. Composition of Products of the O₃ Reaction with PhOH for Different NaOH Concentrations (degree of PhOH conversion 30 mole %)

Compound	Product	Yield (mole %) for NaOH concentration (moles/liter)				
		1·10 ⁻⁷	1·10 ⁻⁵	1·10 ⁻⁴	1·10 ⁻³	1·10 ⁻²
(VI)	Pyrocatechol	37,3	40	32	26	17
	Hydroquinone	26	20	11,2	7	—
(IV)	Muconic acid	36,7	40	—	—	—
	2,2-Dihydroxydiphenyl	—	13,2	28	23	18,2
(V)	2,4-Dihydroxydiphenyl	—	10	13,2	11	16
(III)	2-Hydroxydiphenyl ether	—	6,8	6,8	10	8
	Condensation products of phenoxy radicals	—	—	8,8	23	41
	n	3	3,7	5	5,6	6,2

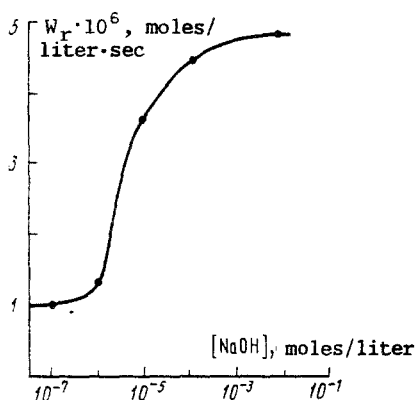


Fig. 1. Reaction rate of O₃ with PhOH as a function of NaOH concentration.

110°C (decomp.), recrystallized from C₂H₅OH; 2,4-dihydroxydiphenyl (V) mp 162°C (decomp.), recrystallized from CH₃OH; 2-hydroxydiphenyl ether (III), mp 106°C (decomp.), recrystallized from H₂O, PMR spectrum (CDCl₃, δ, ppm): 5.57 s (1H, OH), 6.8-7.4 m (9H, ArH). All the substances enumerated are chromatographically identical to known samples and their mixtures give no melting-point depression. In addition to these individual compounds, the oxidate contains condensation products of phenoxy radicals. Molecular weight 390-394. Infrared spectra (KBr pellet, ν, cm⁻¹): 3620 (OH), 1610-1520 (C=C), 1260 (C-O-C).

RESULTS AND DISCUSSION

When ozone-oxygen mixtures come into contact with PhOH solutions O₃ is vigorously absorbed from the gas mixture. When a gas flow rate of 100 ml/min 70-80% of the O₃ in the gas stream is able to react during the contact time of ~0.2 sec. Diffusion restraints are absent in our experimental conditions and the rate of O₃ absorption characterizes the chemical reaction rate [9]:

$$W_r = \frac{W_g}{V_s} ([O_3]_0 - [O_3]_g),$$

where W_g is the flow rate of the gas mixture into the reactor (liters/sec), V_s is the volume of solution (liters), $[O_3]_0$ and $[O_3]_g$ are the O₃ concentrations in the gas mixture at the entry and exit of the reactor respectively (moles/liter).

The reaction rate increases appreciably with increase in NaOH concentration (Fig. 1).

In a neutral medium O₃ reacts directly with the phenol molecule [2]:

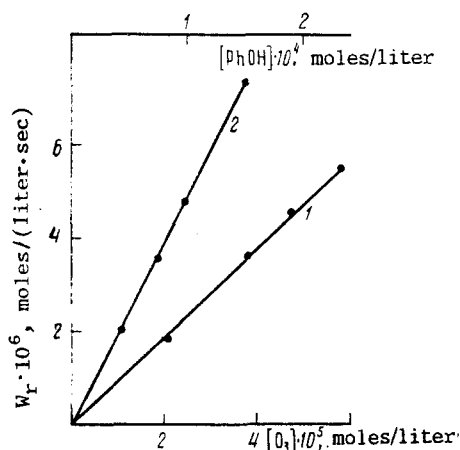


Fig. 2

Fig. 2. Dependence of reaction rate on concentration of: ozone (1), $[\text{PhOH}]_0 = 10^{-4}$ M; phenol (2), $[\text{O}_3] = 5 \cdot 10^{-5}$ M.

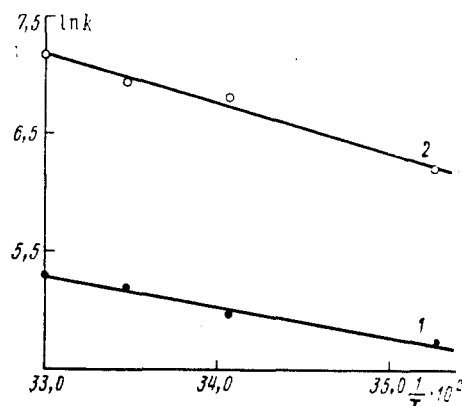
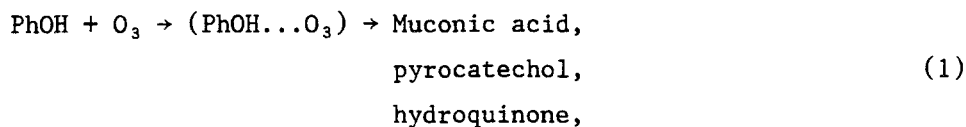


Fig. 3

Fig. 3. The dependence $\ln k = f(1/T)$: (1) for the reaction of O_3 with PhOH in aqueous solution; (2) in the presence of alkali, $[\text{NaOH}] = 10^{-4}$ M.



but in an alkaline medium new paths may emerge for PhOH consumption:



The rate constants $k_1 = 160$ liters/(mole·sec) [10] and $k_2 = 0.02$ liters/(mole·sec) [11] were determined previously. In the conditions of the experiments with maximum alkali concentration the product $k_2[\text{OH}^-][\text{O}_3]$ gas α provides less than a 1% addition to the reaction rate (α is the Henry coefficient). On the other hand, stage (5) provides a simple explanation of the increase in oxidation rate, since PhO^- is a more reactive species with respect to O_3 than PhOH [4].

During investigation of the dependence of reaction rate on concentrations of O_3 and PhOH in conditions where there was excess alkali and all the PhOH was present as phenolate ion, first orders with respect to each component were found (Fig. 2):

$$W_r = k_5 [\text{PhO}^-] [\text{O}_3] \quad (8)$$

The value $k_5 = 9 \cdot 10^2$ liters/(mole·sec) is appreciably higher than that of k_1 and k_2 , in agreement with the above.

The temperature dependence of the reaction rate (Fig. 3) obeys the following equations:

$$k_1 = (2.1 \pm 0.2) \cdot 10^6 \exp\left(\frac{5500 \pm 230}{RT}\right)$$

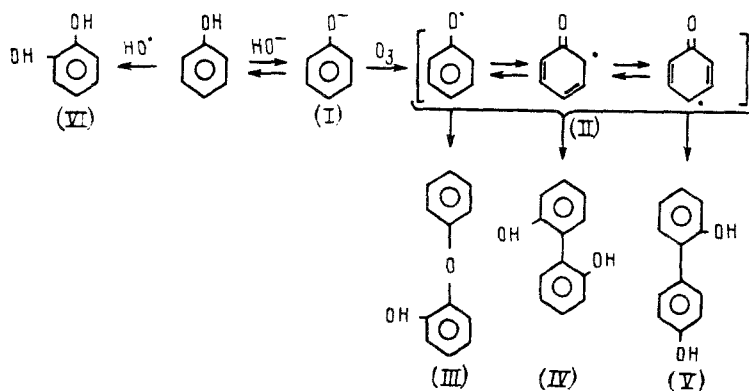
$$k_3 = (5.1 \pm 0.4) \cdot 10^8 \exp\left(-\frac{7700 \pm 300}{RT}\right)$$

Study of the composition of the products of the O_3 reaction with PhOH for different alkali concentrations in the system gives additional scope for choosing between routes for the reaction.

If in alkaline medium O_3 initially reacts with hydroxyl ion to form an oxy radical which then adds on to the PhOH aromatic nucleus (reactions (2) and (3)), then the main reaction product should be pyrocatechol. According to the published data [12, 13] the yield of pyrocatechol is about 80%. When reactions (4) and (5) predominate, the main products of the process will be products from the dimerization of intermediate phenoxyl radicals [14].

Analysis of the data given in Table 1 shows the muconic acid, hydroquinone, and pyrocatechol are formed in neutral medium. When the alkali concentration in the system is increased, pyrocatechol is retained and 2,2- and 2,4-dihydroxydiphenyls and other dimerization and oligomerization products appear in significant amounts. Dimers and oligomers of pyrocatechol decrease.

All this suggests that in the reaction of O_3 with PhOH in alkaline medium the phenolate ion (I) is formed first and then is oxidized to the phenoxyl radical (II). The reaction products were found to contain three types of dimers, (III), (IV), and (V), formed from different tautomers of the phenoxyl radical. The pyrocatechol (VI) accompanying the dimers is formed by route (2):



The greater the amount of alkali present in the system, the higher is the stoichiometric coefficient of the reaction. Increase in the stoichiometric coefficient of O_3 indicates formation of phenolate ions from radical-condensation products and their multiple involvement in the reaction with O_3 to form oligomers of phenol.

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