

Kinetics of Phenol Oxidation with Ozone in a Thin Layer on a Solid Surface

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Abstract—Ozone has been reacted with phenol in thin supported layers, and the dynamics of this reaction has been investigated. The stoichiometry of this reaction coincides with the stoichiometry of the same reaction in solution. Specific reaction rate (β) has been determined for various phenol conversions. The effective rate constant of the reaction, estimated by extrapolating β to zero reaction time, is significantly higher than the rate constant of the reaction in solution. The reaction between ozone and phenol is diffusion-controlled. The reaction products form a barrier layer, which protects the deeper phenol layers against ozone. The barrier layer is as thick as 8–15 phenol monolayers.

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Reactions between ozone and various compounds on the surface or in surface layers are frequent in nature and technology. Well-known examples are rubber cracking [1], leaf growth suppression in agricultural plants under the action of ozone [2], and graft copolymer preparation [3]. Reactions of ozone with various mineral-supported hydrocarbons are used to convert these hydrocarbons into more valuable compounds [4]. Corona discharges have widely been used in the modification of polymer films and fibers in order to improve the adhesion of dyes to these materials [5]. However, this treatment often alters the totality of physicochemical properties of the solid support, including its hygroscopicity and mechanical strength [6]. In most cases, the properties of a material as a function of the ozone treatment time and other reaction parameters pass through an extremum [7]. However, such an extremum is difficult to find because of the lack of information about the details of the reaction between ozone and the surface or the supported thin reactant layer [8, 9] and about the relation between the reaction kinetics and mechanisms on the surface and the behavior of molecules in nanosized layers on solid surfaces. It has recently been demonstrated that thin layers differ markedly from large volumes in terms of molecular mobility, an important property of a reacting system [10]. Here, we report the reaction between ozone and glass-supported phenol and suggest approaches to the estimation of reaction dynamics. Using these approaches, we demonstrate that the reaction rate is significantly higher in the thin layers than in solution.

EXPERIMENTAL

Phenol (reagent grade) and CCl_4 (reagent grade) were treated with an ozone–oxygen mixture for 20 min in order to decompose reactive impurities. Ozone was prepared by passing oxygen at a flow rate of 10–100 ml/min through an electric discharge (~4 kV). Ozone concentration was measured spectrophotometrically as a change in the gas extinction coefficient at $\lambda = 254$ nm [11]. Phenol was applied on the inner surface of the reactor by wetting the surface with phenol solutions of different concentrations in CCl_4 for obtaining layers of various thicknesses. The layer thickness varied from 9 to 25 monolayers. The range of concentrations used was from 8.57×10^{-3} to 1.37×10^{-7} mol/l. The initial number of phenol layers formed on the reactor surface was calculated from the working surface of the reactor, the amount of phenol applied, and the geometry of the phenol molecule. The area occupied by one phenol molecule on the reactor surface is 7.2 Å in length and 4.6 Å in width (in the SI system, 7.2×10^{-10} and 4.6×10^{-10} m, respectively). These dimensions were derived from the bond lengths in the phenol molecule (C–C 1.3, C–O 1.1, and O–H 1.08 Å) and were then optimized. Hence, the area occupied by one phenol molecule is 33.12×10^{-20} m². The phenol content of one monolayer on the whole reactor surface was 1.58×10^{-8} mol. The reactor was a molybdenum glass cylinder 0.6 cm in diameter and 20.7 cm in length. The amount of phenol left on the inner reactor surface was determined as the difference between the phenol weights before and after wetting. The total number of layers was equal to the total number of phenol moles (Q_{ph}) divided by the number of phenol moles in one monolayer. The extent and rate of the reaction were judged from the difference

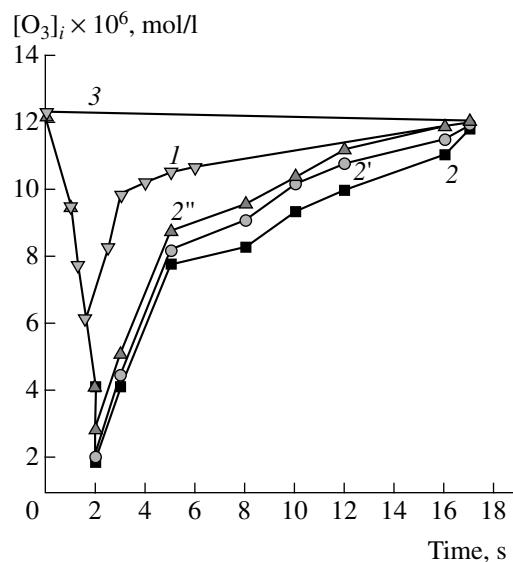


Fig. 1. Time dependence of the ozone concentration (3) at the reactor inlet, (1) at the outlet of the empty reactor, and (2, 2', 2'') at the outlet of the reactor with a thin phenol layer on its surface ((2) 8, (2') 16, and (2'') 24 monolayers). For further explanation, refer to the main text.

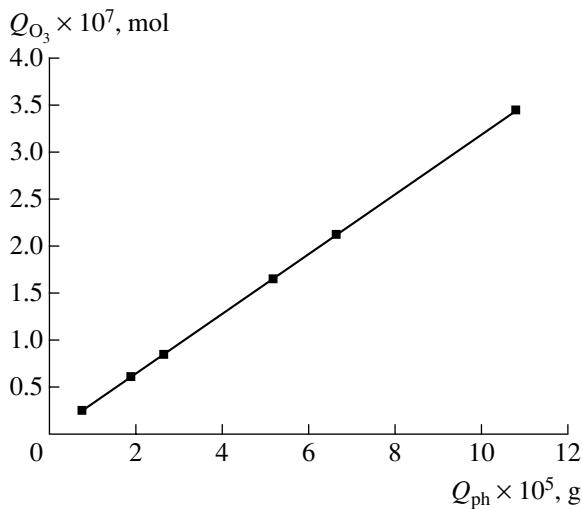


Fig. 2. Reacted ozone versus reacted phenol.

between the inlet and outlet ozone concentrations: $\Delta[O_3] = [O_3]_0 - [O_3]_g$.

RESULTS AND DISCUSSION

The reaction between ozone and phenol supported on the mineral surface is rather fast. Figure 1 shows the time dependences of the ozone concentration in the gas phase at the reactor inlet (curve 3), at the outlet of the empty reactor (curve 1), and at the outlet of the reactor with various numbers of monolayers supported on its surface (curves 2, 2', 2''). The descending branch common to all curves, which is due to a decrease in the outlet oxygen concentration, arises from the specific fea-

tures of our experimental technique (the reactor is switched over to a preliminarily established ozone–oxygen flow). The area between curve 1 and line 3 corresponds to the amount of ozone required to fill the empty reactor, and the area between curves 2–2'' and line 3 corresponds to the amount of reacted ozone plus the amount of ozone filling the reactor. The difference between these areas is equal to the amount of reacted ozone. As is clear from Fig. 1, as the ozone–oxygen mixture ($[O_3] = 1.65 \times 10^{-7} \text{ mol/l}$, $v_g = 1.67 \text{ cm}^3/\text{min}$, 20°C) passes over the phenol layer, a noticeable part of the ozone fed into the reactor is absorbed. This adsorption can be caused by a chemical reaction or by the catalytic decomposition of ozone on reactor walls, substrate, or the products of the O_3 –substrate reaction.

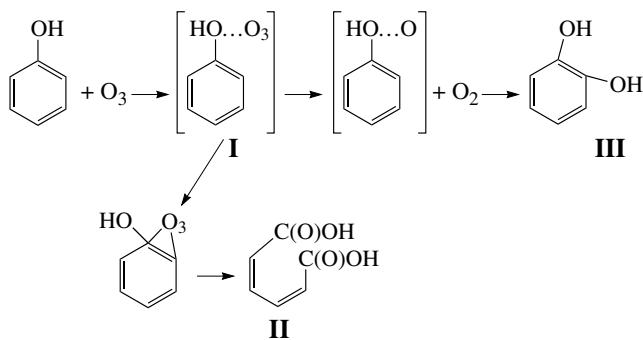
The assumption that ozone decomposes on reactor walls is disproved by the fact that the loss of ozone in the empty reactor is small. The reaction products do not take part in ozone decomposition either. This was verified by a replica passing of the $O_2 + O_3$ mixture through the reactor containing reaction products after the relaxation of the system for 1–18 h. In both runs, only ozone losses due to reactor filling were observed and the experimental curves were similar to line 1 in Fig. 1. Furthermore, our experiments proved that supported phenol reacts with ozone fed into the reactor and is thus consumed. A comparison between the ozone flow rate Q_{O_3} and the amount of reacted phenol enabled us to calculate the stoichiometric coefficient of the reaction. The molar consumption of ozone exceeded the molar amount of supported phenol reacted by a factor of 3 (Fig. 2), and, therefore, the stoichiometric coefficient was equal to 3, as in ozone–phenol reactions in solution [12–14]. This large stoichiometric coefficient testifies that the reaction proceeds in several steps. The first step is the formation of labile primary complex between O_3 and the phenolic OH group (I) [14]. Subsequent rearrangements in this complex results mainly in muconic acid (II) and pyrocatechin (III), which are the products of ozone incorporation into the C–H bond and into the aromatic ring in the immediate vicinity of the phenolic hydroxyl (scheme). Both products react with ozone as rapidly as, or even more rapidly than, the starting phenol [14]. It is these secondary reactions that are responsible for the large stoichiometric coefficient of the reaction. The muconic acid/pyrocatechin ratio in the reaction products has an effect on the overall process stoichiometry (the stoichiometric coefficient varies between 3 and 4, taking fractional intermediate values). The ultimate products of the reaction—glyoxylic and oxalic acids—react slowly with ozone. Under the experimental conditions examined, they act as an inert barrier layer making it difficult for ozone to access the surface layers of unreacted phenol. This view is in agreement with the data presented in Fig. 1. At the earlier stages of the process, ozone is absorbed rather efficiently (up to 88%). At later stages, as reactive groups in the surface layer (8–15 monolayers, 1.52×10^{-7}

3.16×10^{-7} mol/m²) are consumed, the ozone absorption rate decreases and, accordingly, the outlet ozone concentration in the gas phase increases. Raising the amount of phenol supported on the reactor surface did not lead to any substantial increase in ozone consumption, confirming the above view that the reaction products act as a barrier layer.

The data presented in Fig. 1 enable us to calculate basic kinetic features of the chemical reaction, namely, its specific rate and effective rate constant. This calculation is based on the comparison between the rate of ozone absorption from the gas phase and the reaction rate in the accessible substrate layer. For any arbitrary point in an ozone absorption curve (Fig. 1), the observed change in $[O_3]_g$ is related to variations of the specific absorption rate and reactant concentrations. These time variations are described in terms of simple relationships under the following assumptions.

(1) The gas is perfectly mixed when moving in the reactor, and $[O_3]_g$ is the same throughout the reactor cross section. This assumption is based on the view that mass transfer in the gas phase is usually rather intensive. This assumption is experimentally supported by the fact that replacing the phenol layer with a thin polybutadiene film, whose C=C bonds react with ozone three orders of magnitude more rapidly than phenol, leads to efficient ozone absorption [9].

Mechanism of the reaction between phenol and O₃



(2) The variation of the phenol concentration along the length of the reactor (l) at any time point is not large. Indeed, the gas stream and supported phenol are in contact for ~ 3.4 s. This time is sufficient for the phenol concentration in the accessible layer to change by 2–4%.

(3) The O₃ solubility in the phenol layer was assumed to be equal to the ozone solubility in ethylbenzene ($\alpha = [O_3]_0/[O_3]_g = 2$) because of the lack of published data.

As the gas mixture moves along the phenol layer, its ozone content decreases. The variation of ozone concentration is described by a monomolecular rate equation:

$$d[O_3]_v/d\tau = B[O_3]_v \quad (1)$$

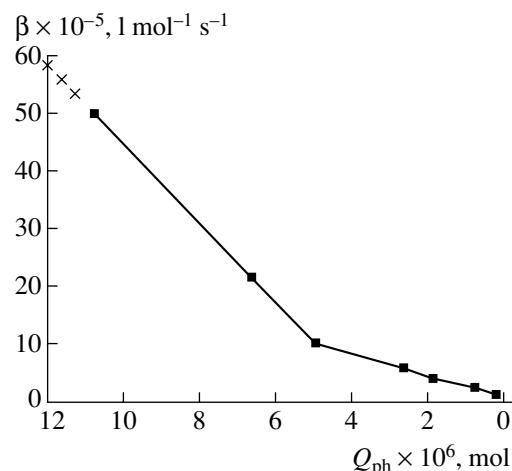


Fig. 3. Specific reaction rate as a function of the amount of reacted phenol. The crosses extrapolate the straight line to the initial phenol concentration.

where $[O_3]_v$ is the current ozone concentration in an arbitrarily cross section of the reactor and B is the complex multiplier that models the reaction rate coefficient and is equal to

$$B = [\Phi]\alpha\gamma\beta. \quad (2)$$

Here, $[\Phi]$ is the average phenol concentration in the chosen cross section of the accessible layer, α is the ozone solubility, γ is the volume of the layer (cm³), and β is the specific reaction rate (1 mol⁻¹ s⁻¹).

Transform expression (1) to

$$-d[O_3]_v/[O_3]_v = B d\tau. \quad (3)$$

Integrating Eq. (3) yields

$$[O_3]_v/[O_3]_0 = (1 - e^{-B\tau}), \quad (4)$$

where $[O_3]_0$ is the inlet ozone concentration and τ is the gas-reactor wall contact time. From Eq. (4),

$$e^{-B\tau} = 1 - [O_3]_v/[O_3]_0,$$

$$e^{B\tau} = 1/(1 - [O_3]_v/[O_3]_0).$$

Hence, the complex multiplier is

$$B = \{\ln 1 - \ln(1 - [O_3]_v/[O_3]_0)\}/\tau \quad (5)$$

and the specific reaction rate is

$$\beta = \{\ln 1 - \ln(1 - [O_3]_v/[O_3]_0)\}/\tau\alpha[\Phi]_v \quad (6)$$

This method enabled us to calculate the specific reaction rate at several time points during the process and to plot β versus phenol conversion (Fig. 3). The plot of β versus phenol conversion shows that, early in the process, when only a small fraction of the phenol is reacted (<10% or $< 1.08 \times 10^{-5}$ g), the reaction pro-

ceeds at a high rate. At the end of the process, the reaction rate decreases notably. This is possible only for a diffusion-controlled process. At its initial stages, the reaction proceeds rapidly because the phenol concentration in the layer accessible to ozone is high. At these stages, the accessible layer is one phenol monolayer thick [15], there are no diffusion limitations, the reaction is governed by chemical mechanisms [11, 16], and the specific reaction rate is nearly equal to the effective rate constant: $\lim(\beta)_{\tau \rightarrow 0} = k_{ph}$.

In our experiments, we could measure the ozone absorption rate ~ 20 s after the beginning of the reaction (Fig. 1) because the ozone concentration front smeared out on its way to the measuring cell. That is why the β limit at $\tau \rightarrow 0$ was found by extrapolating the $\beta = f(Q_{ph})$ curve to the initial Q_{ph} value. In our experiments, k_{ph} was equal to 5×10^6 l mol⁻¹ s⁻¹. As ozone is consumed and less reactive products build up, the reaction rate begins to be determined by the diffusion of ozone through the barrier layer of reaction products to underlying phenol layers [17, 18] and the reaction slows down, as is shown in Fig. 3.

A comparison between the k_{ph} data for the thin-layer reaction and the reaction rate data reported for phenol–ozone reactions in solution has demonstrated that, under equal conditions, the thin-layer reaction is appreciably more rapid than the same reaction in solutions and the specific rate constant of the thin-layer reaction ($k_{ph} = 5 \times 10^6$ l mol⁻¹ s⁻¹) is approximately four orders of magnitude higher than the rate constant of the same reaction in carbon tetrachloride ($k_{ph,sol} = 2.3 \times 10^2$ l mol⁻¹ s⁻¹) [16].

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