

On the Mechanism of Phenol Ozonolysis

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Abstract—The mechanisms of liquid-phase phenol ozonation are revised. A new mechanism in which a significant role is played by free-radical reactions is suggested for this process.

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The reactions of ozone with phenol and its derivatives have long been the subject of numerous studies (see, e.g., [1–5] and references therein). The kinetics of these reactions has been investigated, and the product composition has been determined. Reaction mechanisms [2, 4, 5] have been derived from the results of these studies. According to these mechanisms, most of the oxidation products form via molecular pathways and the stoichiometric coefficient S (which is equal to the amount of ozone reacted per mole of substrate) is close to unity at the initial stages of the reaction. However, it has been demonstrated by the examples of phenol, 2,6-dimethylphenol, and 2,6-dichlorophenol that, even at a small extent of reaction, S differs significantly from unity and varies with time [6]. Furthermore, the mechanisms suggested in [2, 4, 5] raise other questions requiring an answer.

This is the reason why we decided to revise the mechanism of phenol ozonation. Since the most comprehensive data presently available on the product composition and product accumulation rate refer to unsubstituted phenol (PhOH) [2, 4, 5], it is pertinent to discuss the ozonolysis mechanism using this compound as the example.

We will proceed from the following facts:

(1) The ozonolysis of PhOH [2, 4, 5] first yields muconic acid (**1**); pyrocatechin (**2**); hydroquinone (**3**); and small amounts of 4,6-dioxo-2-hexenoic acid (**4**), *p*-benzoquinone (**5**), and diphenyl-2,2-diol (**6**). The later stages of ozonolysis yield glyoxal and glyoxalic, maleic, oxalic, and formic acids (these stages are not considered here).

(2) It was found that, at 293 K and pH ~6, products **1–4** accumulate simultaneously at the initial stages of the reaction [5].

(3) Under these conditions, S varies between ~0.3 and 2.5 [6].

Bailey [2] and Razumovskii et al. [4, 5] suggested two different mechanisms to explain the observed product composition.

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According to Bailey [2], the reaction proceeds by the mechanism of an electrophilic attack of ozone on the aromatic ring, yielding products **1–3**. However, this mechanism was questioned in a later work [5]. Firstly, it does not account for the formation of products **4–6**. Secondly, it involves water in the formation of **1**, while it was found that **1** forms in nearly the same yield in nonaqueous media, namely, chloroform and *n*-hexane [5]. Thirdly, Bailey's mechanism disregards the complexation between ozone and phenol.

It is interesting that it was Bailey and his colleagues who discovered complexes between ozone and aromatic compounds [7, 8]. The stability constants of some of these complexes were determined in more recent works [9, 10].

Furthermore, Bailey's mechanism ignores the formation of free phenoxyl radicals, which were detected by ESR in a 2,4,6-tri-*tert*-butylphenol–ozone mixture at 153–293 K [11].

In the alternative mechanism suggested by Razumovskii et al. [4, 5], the key element is a labile intermediate complex between ozone and the hydroxyl group of phenol. It is assumed that most of the reaction products (91% in chloroform, 92% in *n*-hexane, and 97% in water), with the exception of **5** and **6**, result from the molecular decomposition of this complex via various parallel reactions [5].

An analysis of the mechanisms suggested in the literature has demonstrated that Razumovskii's mechanism [4, 5] accounts for most of the experimental data concerning phenol ozonolysis. However, like Bailey's mechanism, it provides no answer to a number of serious questions and, therefore, needs to be refined and supplemented. Pay attention to the following significant circumstances:

(1) The stoichiometric coefficient S is fixed in both Bailey's [2] and Razumovskii's [4, 5] mechanisms: in the former, $S = 1$; in the latter, S is nearly equal to unity but is slightly smaller. However, it was found in a later study [6] that S is variable even at a small extent of reac-

tion, when the primary products react with ozone at a negligibly low rate.

(2) In both mechanisms, the formation of rather large proportions of **2** and **3** per phenol consumed (53–60% in the aggregate, depending on the solvent [5]) is explained by the hydroxylation of phenol with ozone. As was demonstrated by a study of benzene ozonolysis products and kinetics [12], ozone indeed shows some hydroxylating properties. However, the phenol yield in this reaction is very low and decreases from 0.9 to 0.2% as the reaction temperature is lowered from 347 to 323 K, the main reaction product being an ozonide. Calculations using data from [12] demonstrate that the phenol yield at 293 K will be ~0.03%. Therefore, the hydroxylation of an aromatic ring is a very slow process. In order to explain the formation of **2** and **3** in the framework of Bailey's or Razumovskii's mechanism, one has to assume that the hydroxylation rate increases by a factor of $(1.8\text{--}2.0) \times 10^3$ in passing from benzene to phenol. This seems to be unlikely. With better reason, it should be assumed that the diatomic phenols result from free-radical reactions.

Below, we present a mechanism that is seemingly free from the above contradictions.

Initially, we will briefly consider the state of the reactants in the reaction mixture. Phenol and the free-radical intermediates HO^\bullet , HO_2^\bullet , and HO_3^\bullet in an aqueous solution are involved in the following equilibria:

Reaction	$\text{p}K_a$	a (pH 3–6)
$\text{PhOH} \rightleftharpoons \text{PhO}^- + \text{H}^+$	9.99 [13]	$10^{-7}\text{--}10^{-4}$
$(\text{PhO}^\bullet)\text{H}^+ \rightleftharpoons \text{PhO}^\bullet + \text{H}^+$	–1.95 [14]	$10\text{--}10^4$
$\text{HO}^\bullet \rightleftharpoons \text{O}^\bullet + \text{H}^+$	11.9 [15]	$10^{-9}\text{--}10^{-6}$
$\text{HO}_2^\bullet \rightleftharpoons \text{O}_2^\bullet + \text{H}^+$	4.8 [16]	$2 \times 10^{-2}\text{--}20$
$\text{HO}_3^\bullet \rightleftharpoons \text{O}_3^\bullet + \text{H}^+$	8.2 [17]	$10^{-5}\text{--}10^{-2}$

Here,

$$a = \frac{[\text{A}^-]}{[\text{AH}]},$$

where $[\text{A}^-]$ and $[\text{AH}]$ are the concentrations of the base A^- and the conjugate acid AH (PhO^- and PhOH , PhO^\bullet and $(\text{PhO}^\bullet)\text{H}^+$, etc.).

It is clear from the calculated a data that, at the given pH values, all reactants except the hydroperoxyl radical will exist in the solution in their neutral (uncharged) forms, namely, PhOH , PhO^\bullet , HO^\bullet , and HO_3^\bullet . At pH 3, the hydroperoxyl radical will mainly be present as HO_2^\bullet ; at pH 6, as the oxygen anion radical. At pH 4–5, the concentrations of these species will be comparable.

For a simpler analysis of the reaction mechanism, which is very complicated in the general case, we will

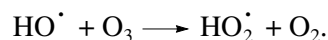
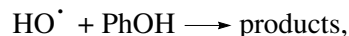
limit our consideration to the case of all intermediate radicals being in nonionic form in the solution. As has just been demonstrated, this is the case at pH 3. We will consider only the initial stage of ozonolysis (see scheme).

As in Razumovskii's mechanism [4, 5], the first step is the formation of a phenol–ozone complex. However, as was ascertained by Shereshovets et al. [9, 10], this is a charge-transfer complex rather than a complex between ozone and the hydroxyl group of phenol, contrary to Razumovskii's statement [4, 5]. An equation correlating the stability constant (K) of complexes in *n*-hexane with the nature of the substituents in the aromatic ring [10] leads to $K = 0.12$ l/mol for the $\text{PhOH}\text{--}\text{O}_3$ complex at 293 K.

Next, the phenol–ozone complex is converted via reactions (II)–(IV).

With the above reservation, reactions (II) and (III) are quite similar to their counterparts in Razumovskii's mechanism [5]. Reaction (IV) yields hydroxyl and phenoxyl radicals. It is possible that the precursor of HO^\bullet is HO_3^\bullet , which decomposes rapidly according to the following scheme: $\text{HO}_3^\bullet \longrightarrow \text{HO}^\bullet + \text{O}_2$.

The HO^\bullet radical can then react with phenol and ozone (no reactions of this radical are considered in [5]):

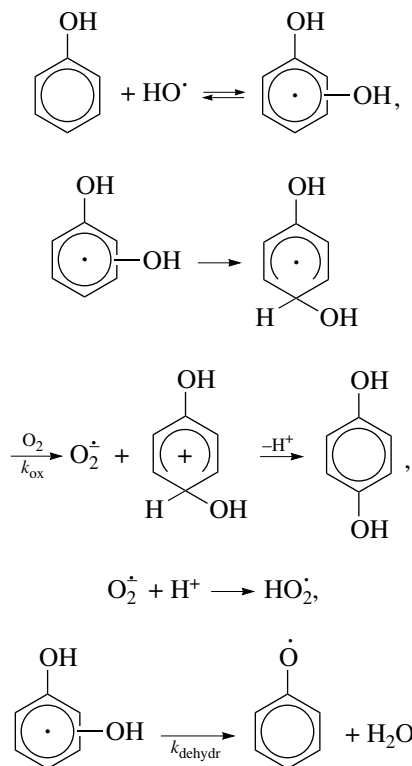


As will be demonstrated below, the first of these reactions occurs through the "sticking" of the radical to the aromatic ring and, as consequence, its rate constant $k(\text{HO}^\bullet + \text{PhOH})$ is similar to the diffusion-controlled rate constant ($10^8\text{--}10^9$ l mol^{–1} s^{–1} [18]). The rate constant of the reaction $\text{HO}^\bullet + \text{O}_3$ in the gas phase at room temperature is 3×10^7 l mol^{–1} s^{–1} [19]; apparently, it will not take a very different value for an aqueous solution. Since $k(\text{HO}^\bullet + \text{PhOH}) \gg k(\text{HO}^\bullet + \text{O}_3)$ and always $[\text{PhOH}] \gg [\text{O}_3]$, HO^\bullet reacts only with phenol under the conditions examined.

This reaction, which was studied in detail by Raghavan and Steenken [20] at 293 K and pH \approx 3–6, proceeds simultaneously via three pathways ((V)–(VII)). The reactions involving an oxidizer ((V) and (VI)) are reported to yield ultimate products **2** and **3** in a 1.4 : 1 ratio [20]. This result is in good agreement with our product ratios of 1.32 : 1 (in chloroform), 1.56 : 1 (in *n*-hexane), and 1.65 : 1 (in water) [5]. Therefore, there is reason to believe that reactions (V) and (VI) are the main sources of these products.

Raghavan and Steenken [20] added various benzoquinones (including *p*-benzoquinone) as oxidizers to the reaction mixture. In our case, the most likely oxidizer is oxygen (see below).

The mechanism of the reaction between HO^\bullet and PhOH includes the formation of an intermediate active complex between the free radical and the substrate and a rapid conversion of this complex [20]:

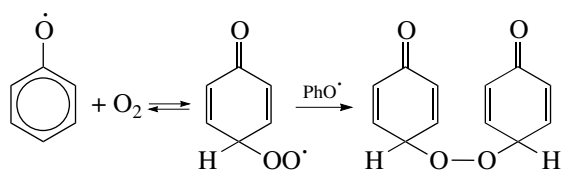


The rate constants of intermediate complex oxidations with benzoquinones are very large ($k_{\text{ox}} = 3.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) and depend only slightly on the benzoquinone structure [20]. It can therefore be assumed that the rate constant of the reaction involving O_2 will be nearly the same. The standard oxidation potential of oxygen ($E_0(\text{O}_2) = +0.682 \text{ V}$) differs only slightly from that of *p*-benzoquinone ($+0.699 \text{ V}$). The standard oxidation potential of ozone is much higher ($E_0(\text{O}_3) = +2.07 \text{ V}$), but the ozone concentration in the solution is several orders of magnitude lower than the oxygen concentration. Therefore, ozone is unlikely to play a significant role in this reaction.

The dehydration rate constant k_{dehydr} depends strongly on the structure of the intermediate dihydrocyclohexadienyl radical, the reactant that eliminates water. For the radical with a *para* structure (as in the above scheme), $k_{\text{dehydr}} \sim 1 \times 10^9 \text{ s}^{-1}$; for the radical with an *ortho* structure, k_{dehydr} takes much smaller values of $\sim 1 \times 10^8 \text{ s}^{-1}$ [20].

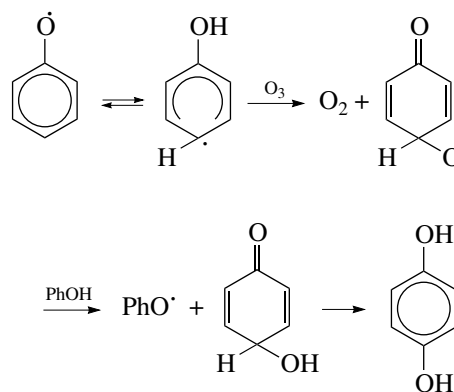
The phenoxyl radical resulting from reactions (IV) and (VII) can react with oxygen, ozone, another phenoxyl radical, or HO_2^\bullet .

The reaction between PhO^\bullet and O_2 , which proceeds according to the scheme [21]

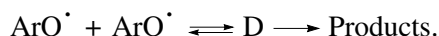


does not play any significant role, as judged from the material balance for the overall process [5]. This is due to the fact that the equilibrium in this reaction is strongly shifted to the initial reactants. The stability constant of the intermediate peroxy radical is estimated to be as low as $K \sim 10^{-5} \text{ l/mol}$ [21].

Ozone is known to be rather reactive toward free radicals [1]. The reaction between PhO^\bullet and O_3 can be fast if it proceeds not via the above addition mechanism but via the abstraction of an O atom from the ozone molecule by a mesomeric carbon-centered radical:



According to the literature [14, 21, 22], aroxyl radicals recombine via the reversible formation of a ketonic dimer D:



For the phenoxyl radical, this equilibrium is completely shifted to the products, so their recombination is irreversible. In polar solvents, the primary molecular product of the decomposition of the dimer is diphenoquinone [14], which is rapidly converted into diphenyl-2,2-diol via the enolization reaction (VIII). In an aqueous acid solution at room temperature, the rate constant of the recombination of PhO^\bullet radicals is $1.3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ [14].

It can be assumed that the reaction between PhO^\bullet and HO_2^\bullet (reaction (IX)), which is similar to the recombination reactions between phenoxyl and alkyl peroxy radicals, is also rather fast. The free-radical decomposition of the intermediate hydroperoxide by the cleavage of the O–O bond is thermodynamically much less favorable.

Along with participating in reaction (IX), the hydroperoxyl radical can react with ozone (reaction (X)), phenol (reaction (XI)), or another hydroperoxyl radical. The rate constant of reaction (X) in the gas phase at room temperature is $2 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ [23]. The rate

constant of reaction (XI) is 2–3 orders of magnitude lower: for aqueous solutions, its value is known for hydroquinone ($1.7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ at 295 K and $\text{pH} \approx 0.4\text{--}3.5$) and 2,6-di-*tert*-butylphenol ($2.4 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ at 273 K).

When comparing the rates of reactions (X) and (XI), it is necessary to take into account the following. At the initial stages of ozonolysis, when the process is nearly diffusion-controlled, the steady-state ozone concentration in the solution is extremely low and, as a consequence, reaction (XI) can proceed at a much higher rate than reaction (X).

The recombination of hydroperoxyl radicals in aqueous solutions,



is a comparatively slow reaction: at 273–296 K and $\text{pH} \approx 2\text{--}6$, its rate constant is $(0.8\text{--}3.0) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ [24, 25]; that is, it is comparable with the rate constant of reaction (X). Since it is obvious that $[\text{O}_3] \gg [\text{HO}_2^\cdot]$, the hydroperoxyl recombination should be neglected.

Below, we present the mechanism of the early stages of phenol ozonolysis that is based on the results of this and other studies and accounts both for the formation of main products and for the stoichiometric coefficient S being variable (see scheme).

Let us analyze this mechanism. The following initial assumption will be made in order to significantly simplify the kinetic analysis: the rate of the cross recombination of PhO^\cdot and HO_2^\cdot (reaction (IX)) will be taken to be negligible. Indeed, reaction (IX) is likely to be rather slow because of the low steady-state phenoxyl and hydroperoxyl concentrations in the solution. This deduction is supported to some extent by a low yield of *p*-benzoquinone, the product of reaction (IX) [5].

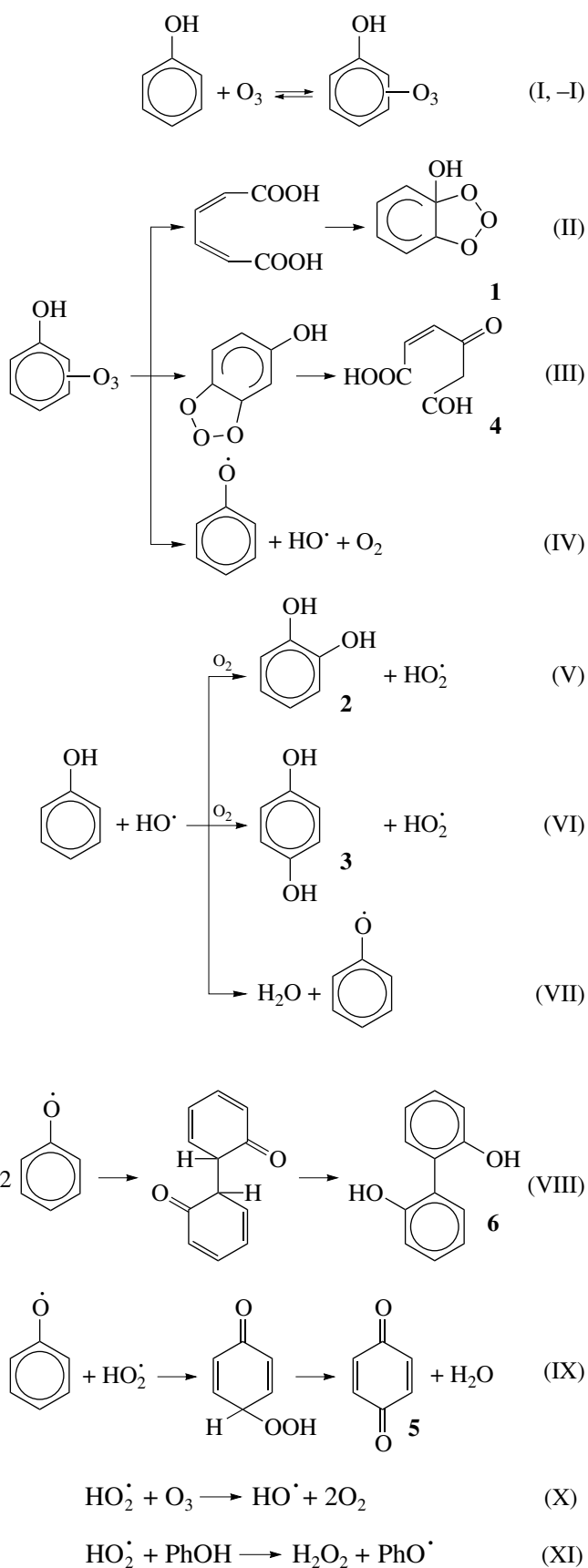
Based on the above scheme, the following equation can be written for the phenol–ozone complex in the steady state:

$$-\frac{d[\text{PhOH}]}{dt} = \alpha k_1 [\text{PhOH}] [\text{O}_3] \quad (1)$$

$$+ (k_5 + k_6 + k_7) [\text{PhOH}] [\text{HO}^\cdot] + k_{11} [\text{PhOH}] [\text{HO}_2^\cdot],$$

where $\alpha = \frac{k_2 + k_3 + k_4}{k_{-1} + k_2 + k_3 + k_4}$ is the probability of the irreversible decomposition of the complex to reaction products. Applying quasi-stationarity conditions to HO_2^\cdot and HO^\cdot and substituting the concentrations of these radicals into Eq. (1), we obtain the following final expression for the phenol consumption rate:

$$-\frac{d[\text{PhOH}]}{dt} = (\alpha + \gamma\delta) k_1 [\text{PhOH}] [\text{O}_3]. \quad (2)$$



Scheme.

Here, $\gamma = \frac{k_4}{k_{-1} + k_2 + k_3 + k_4}$ is the probability of the irreversible decomposition of the complex to radicals;

$\delta = \frac{(k_5 + k_6 + k_7) + \beta(k_5 + k_6)}{k_7 + \beta(k_5 + k_6)}$ is a combination of

kinetic constants, whose physical meaning is the efficiency of the chain pathway of phenol consumption;

and $\beta = \frac{k_{11}[\text{PhOH}]}{k_{10}[\text{O}_3] + k_{11}[\text{PhOH}]}$ is the probability of an

HO_2^\cdot radical being lost through the reaction with a phenol molecule.

Likewise, applying the quasi-steady-state approximation to the concentrations of the phenol-ozone complex, HO_2^\cdot , and HO^\cdot leads to the following equation for the ozone consumption rate:

$$-\frac{d[\text{O}_3]}{dt} = [\alpha + (1 - \beta)\gamma(\delta - 1)]k_1[\text{PhOH}][\text{O}_3]. \quad (3)$$

Dividing Eq. (3) by Eq. (2) gives

$$\frac{d[\text{O}_3]}{d[\text{PhOH}]} = \frac{\alpha + (1 - \beta)\gamma(\delta - 1)}{\alpha + \gamma\delta}. \quad (4)$$

Equation (4) provides an explanation for much of the above experimental data. Indeed, if the free-radical pathway of phenol ozonation is neglected ($\gamma = 0$), Bailey's scheme leads to

$$\frac{d[\text{O}_3]}{d[\text{PhOH}]} = \frac{\Delta[\text{O}_3]}{\Delta[\text{PhOH}]} = 1.$$

If, conversely, the free-radical pathway is significant and the probability α is rather low, then the following relationships may take place: $\alpha \ll \gamma\delta$ and $\alpha \ll (1 - \beta)\gamma(\delta - 1)$. The stoichiometric coefficient for the initial stage of the process will then be equal to

$$S = \frac{d[\text{O}_3]}{d[\text{PhOH}]} = \frac{(1 - \beta)(\delta - 1)}{\delta}.$$

Since the $\frac{\delta - 1}{\delta}$ ratio is less than unity, S is determined by the probability β :

$$S \approx \frac{k_{10}[\text{O}_3]}{k_{10}[\text{O}_3] + k_{11}[\text{PhOH}]} \frac{\delta - 1}{\delta};$$

that is, S depends on the ratio of the initial ozone and phenol concentrations and can be a rather small fraction.

Thus, the mechanism presented in the scheme, which can be regarded as a refined and supplemented Razumovskii's mechanism [4, 5], accounts for all regularities in phenol ozonation, specifically, the formation of major and minor molecular products of the reaction and the low and variable ratio of consumed ozone to reacted phenol.

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