MECHANISM OF THE REACTION OF OZONE WITH PHENOLS

M. L. Konstantinova, S. D. Razumovskii,
and G. E. Zaikov

An investigation has been carried out into the composition of the products of
the O_3 reaction with PhOH in different solvents and into the kinetics of their
build-up. A scheme is proposed for the reaction in which the first stage,
which limits the rate of the entire process, is formation of a complex of O_3
with the PhOH hydroxy group. Formation of muconic acid does not require the
participation of H_2O.

The mechanism of the reaction of ozone with phenols has attracted attention for some
time [1-4]. This interest is explained by special features of the reaction itself [1-3] and
by the use of ozone to break down phenols in waste waters [4].

A scheme has previously been proposed [3] for the formation of the main end and inter-
mediate reaction products. Later, new experimental data were obtained [5] which made it
necessary to introduce certain amendments to Bailey's scheme. Here we discuss these amend-
ments and produce new experimental results supporting the proposed changes.

EXPERIMENTAL

The phenol, pyrocatechol, and hydroquinone used in the experiments were of chemically
pure cp grade. The O_3 was produced by passing O_2 through an electric discharge ($[O_3]$ =
$5 \cdot 10^{-5}$ moles/liter). To determine the structure of the products 3 g PhOH were dissolved in
250 ml H_2O or $CHCl_3$; 50 ml portions were ozonized, to 30% conversion, the portions combined,
evaporated, and the residue separated on a column (silica gel μ 40/100, solvent gradient:
CCl_4:$CHCl_3$). The yield of reaction products was monitored by TLC. The required extent of
PhOH conversion was determined from the difference between added and unreacted PhOH using
GLC in a Tsvet-100 chromatograph (1 m column, chromosorb W, phase E 30.3% helium, 132°C),
and from the amount of O_3 absorbed, allowing for the stoichiometric coefficient of the
reaction [6]. The kinetics of build-up of products were studied in a bubbler system (V_{soln} =
50 ml, [PhOH] = 0.213 moles/liter, $[O_3]$ = 10^{-3} moles/liter). The course of the reaction
was followed by taking samples, treating them with an ethereal solution of diazomethane, and
carrying out a GLC analysis. The O_2 liberated in the process of the reaction was studied
using an O_3—He mixture. The O_2—O_3 was adsorbed on 20 mg silica gel at −100°C and residual
O_2 was stripped with He. The desorbed O_3 in a stream of He was directed into a reactor con-
taining the starting solution of PhOH. The O_2 formed in the reaction process was recorded
using GLC (analytical conditions: catharometer detector, column temperature 20°C, molecular-
sieve carrier 5 Å, 30 μm).

RESULTS AND DISCUSSION

The action of ozone on phenol is accompanied by the formation of a set of products
(Table 1). In their number are hydroxy derivatives of phenol (pyrocatechol and hydroquinone)
bifunctional and multifunctional open-chain compounds (muconic acid, etc.) formed by cleavage
of the aromatic nucleus, and small amounts of quinones and diphenol.

The composition of the products and the kinetics of the reaction [7] indicate that the
reaction mechanism does not vary on passing from water to organic solvents, and the data
obtained in different media may be compared with each other. Bailey's scheme [3] may be
represented by scheme 1:

TABLE 1. Composition of Products of the Reaction of Ozone with Phenol in Different Solvents* (293 K, phenol conversion 30%)

| Compound	Solvent			Identification
	H_2O	$CHCl_3$	C_6H_{14}	
Phenol (I)	70	70	70	—
Muconic acid (VII)	9	9,8	10,4	Mp 305° (C_2H_5OH) [13]
Pyrocatechol (V)	11,2	9,5	9,7	Mp 105° (C_6H_6) [13]
Hydroquinone (VIII)	6,8	7,2	6,2	Mp 170° (H_2O) [13]
4,6-Dioxo-2-hexenoic acid (IX)	2	0,9	1,2	PMR of methyl ester ($CDCl_3$, δ, ppm): 3.4 s (OCH_3), 5.5 d (CH=CH), 3.8m(CH_2), 7,9t (COH)
p-Benzoquinone (XI)	—	1,7	1,5	Mp 116° (H_2O) [13]
Diphenyl-2,2-diol (XII)		0,9	1	Mp 110° (C_7H_8) [13]

*All the substances obtained were chromatographically identical with known specimens and their mixtures gave no melting-point depression.
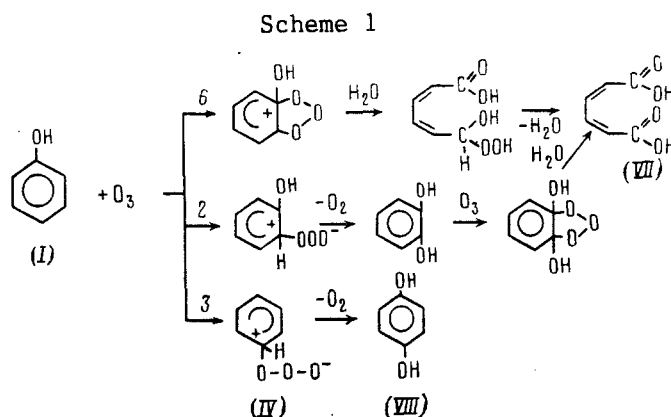
Scheme 1

It is assumed in the scheme that in the first stage of the reaction ozone attacks the aromatic nucleus, the reaction following a mechanism of electrophilic addition of ozone. It may take place at different positions relative to the hydroxy group (routes 2 and 3) and is accompanied by the formation of two series of products: with retention of the aromatic nucleus (route 2) and with its opening (route 6).

The first inconsistency between Bailey's scheme and our data emerged during a study of the kinetics of the reaction of ozone with phenol [7]. It appeared that the first stage of the reaction, which limits the rate of the process when t < 45°C, is formation of a labile short-lived complex with the phenol hydroxy group (II):

Scheme 2
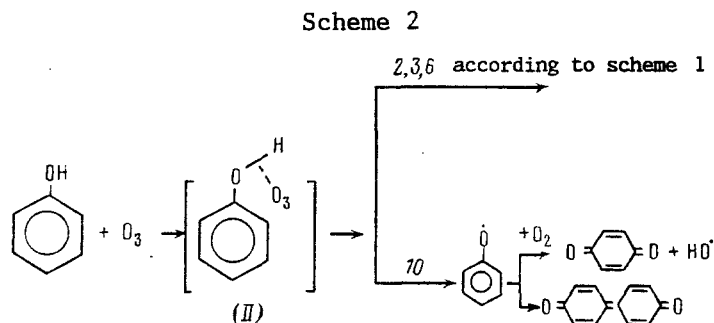
This does not imply that reaction of ozone with the aromatic nucleus does not occur at all, simply that its rate in normal conditions is approximately 50 times slower. Complex (II) may be converted by different routes, both in products (shown in scheme 1) and in compounds, the formation of which cannot be explained by Bailey's scheme. Such compounds must include p-quinone and diphenoquinone, which are present in the reaction mixture in small amounts (Table 1). These products are typical of radical reactions involving phenol [8].
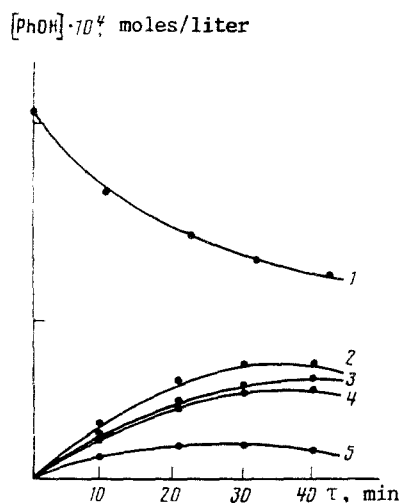
$[PhOH] \cdot 10^4$ moles/liter

Fig. 1. Kinetics of PhOH consumption and of build-up of reaction products from O_3 and PhOH in $CHCl_3$; [PhOH] = 0.213 moles/liter: (1) PhOH; (2) muconic acid; (3) hydroquinone; (4) pyrocatechol; (5) 4, 6-dioxo-2-hexenoic acid.

Another inconsistency between scheme 1 and our data emerged during study of the mechanism of formation of one of the main reaction products, muconic acid. According to the scheme it is formed either as a result of the reaction of ozonides with water, or as a product of further oxidation of pyrocatechol. The two routes were checked experimentally. The first study was of the composition of the products of the ozone reaction with PhOH in the absence of water (Table 1). It turned out that muconic acid is formed when the reaction is carried out in $CHCl_3$ and C_6H_6 solutions. Then a study was undertaken of the kinetics of PhOH consumption and the kinetics of pyrocatechol, muconic-acid, and hydroquinone build-up (Fig. 1). Special attention was paid to the course of the curves for low PhOH conversions. Evidently all the reaction products build up in parallel at a constant rate from the earliest stages of reaction and, consequently, are formed from a common intermediate compound. It is suggested that this product is a complex of ozone with one of the C=C bonds of the aromatic nucleus which is formed with destruction of the ring π-system. Considering that the reaction kinetics are not influenced by the polarity of the medium [9] and that the central oxygen atom in the O_3 molecule has the highest electron affinity [9], this complex is assumed to have the weakly polar structure (IIIa). Complex (IIIa) may be converted into a primary ozonide and then into muconic acid without involving water (IIIa) → (VI) → (VII):
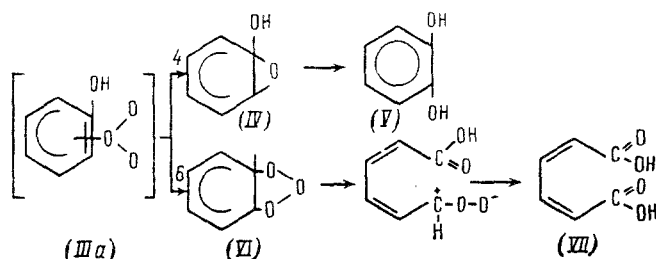
This path is characteristic of aromatic compounds and olefins and its mechanism has been well studied [10]. A second possible direction for conversion of (IIIa) is its decomposition into oxygen and epoxide (IV) with rapid isomerization of the later into pyrocatechol (V). Reactions of this type were discovered by Yakobi [11] who observed the formation of PhOH and cresoles during the action of O_3 on benzene and toluene. Formation of O_2 in amounts equivalent to the sum of (V), (VIII), and (XII) was established by chromatographic analysis of an O_3—He mixture after being in contact with PhOH solutions. Neither compound (IV) nor its analogs in the case of other aromatic compounds were detected experimentally, possibly owing to the speed of their isomerization into (V). However, a similar type of reaction (formation of oxides by the action of O_3 on substituted olefins) has been noted by several authors [12]:
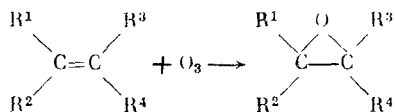

This is an additional argument in support of the proposed intermediate stages during formation of pyrocatechol from PhOH.

To solve the problem of the contribution of the reaction of pyrocatechol with O_3 in formation of muconic acid we determined the reaction rate of O_3 with pyrocatechol and obtained a rate constant k_p equal to $5 \cdot 10^2$ liters/mole·sec ($k_{ph} = 1.8 \cdot 10^2$ liters/mole·sec). When PhOH and pyrocatechol are simultaneously present in the system their reaction rates with O_3 are proportional to the products of concentration by rate constant ($k_p[P]$ and $k_{ph}[Ph]$ respectively). In the initial moments of the reaction when PhOH conversion is 10-15% practically all the muconic acid is formed from PhOH. This is consistent with the course of the curves in Fig. 1.

Hydroquinone (VIII) and 4, 6-dioxo-2-hexenoic acid (IX) are formed in the system as well as pyrocatechol and muconic acid. The mechanism of their formation, apparently, is similar to that discussed above. In this case attention is drawn to the quite significant distance which the ozone molecule travels during isomerization of the primary complex (II).

No appreciable amounts of reaction products corresponding to insertion of O_3 at the meta position relative to the hydroxy group were detected in the system. Evidently this is consistent with the distribution of electron density in the PhOH aromatic nucleus. Taking all this into account, the mechanism of the reaction of O_3 with PhOH is better described by the following scheme:
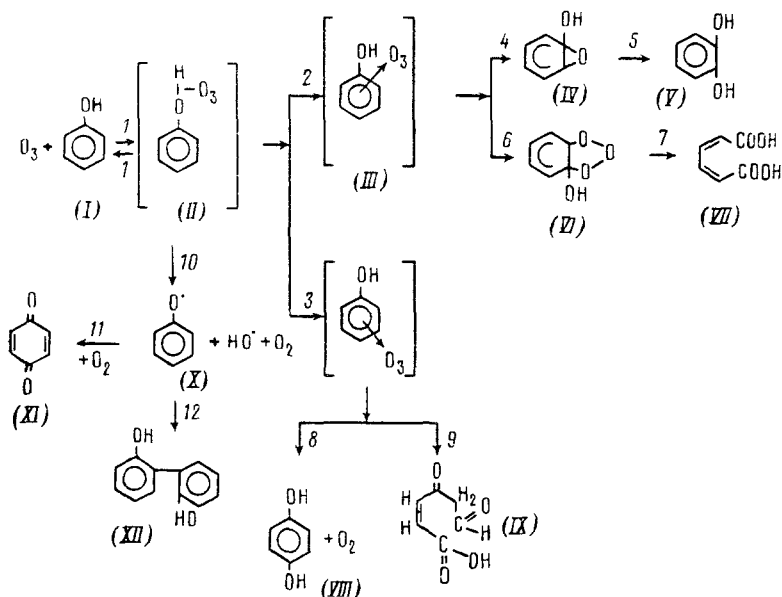
This differs from Bailey's scheme by a different sequence of stages for formation of muconic acid and does not require the participation of water in the reaction. The new stages 1—10—12 and 1—2—2—5 have been introduced into the scheme. The first route leads to formation of diphenols and quinone, and the second route to formation of pyrocatechol (through the epoxide (IV)).

LITERATURE CITED

1. Y. Yamamoto, E. Niki, H. Shiokawa, and Y. Kamiya, J. Org. Chem., 44, 2737 (1979).
2. P. S. Singer and M. D. Gurol, Water Res., 17, 1163 (1983).
3. P. S. Bailey, Ozonation in Organic Chemistry, Vol. 2, Academic Press, New York (1982), p. 31.
4. I. P. Duguet, E. Brodard, B. Dussert, and I. Wallevialle, J. Ozone Sci. Eng., 7, 241 (1985).
5. S. D. Razumovskii, S. K. Rakovskii, D. M. Shopov, and G. E. Zaikov, Ozone and its Reactions with Organic Compounds [in Russian], Izd. Bulg. Akad. Nauk, Sofia (1983), p. 192.
6. S. D. Razumovskii, D. V, Ruban, G. A. Nikiforov, et al., Neftekhimiya, 13, 101 (1973).
7. V. V. Ershov, G. A. Nikiforov, A. A. Volod'kin, Sterically Hindered Phenols [in Russian], Khimiya, Moscow (1972), p. 90.
8. M. L. Konstantinova, S. D. Razumovskii, and G. E. Zaikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1396 (1981).
9. S. D. Razumovskii and G. E. Zaikov, Usp. Khim., 49, 2344 (1980).

10. S. D. Razumovskii and L. V. Berezova, Izv. Akad. Nauk SSSR, Ser. Khim., 223 (1974).
11. V. A. Yakobi, Proceedings of the D. I. Mendeleev Moscow Inst. of Chem. Tech., No. 103, Mezhvuzovskii Sbornik, Moscow (1978), p. 66.
12. F. S. Toby and S. Toby, J. Phys. Chem., 80, 2313 (1976).
13. Dictionary of Organic Compounds [Russian translation], Izd. Inostr. Lit., Moscow (1949).