

Ozonolysis of phenols in aqueous solution

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In the ozonolysis of phenol in aqueous solution at pH 3, 7 and 10 the following products were quantified: catechol, hydroquinone, 1,4-benzoquinone, *cis,cis*-muconic acid, H₂O₂, 2,4-dihydroxybiphenyl and 4,4'-dihydroxybiphenyl. At pH 10, material balance (products vs. phenol consumption) is obtained. Singlet dioxygen, O₂(¹Δ_g), and [•]OH are formed as short-lived intermediates. The precursor of the latter, O₃^{•-}, and a phenoxyl radical is suggested to arise from electron transfer from phenol/phenolate to ozone. Addition of [•]OH to phenol gives rise to dihydroxycyclohexadienyl radicals which add dioxygen and eliminate HO₂[•] thereby forming catechol/hydroquinone. In competition and catalysed by H⁺ and OH⁻, the dihydroxycyclohexadienyl radical eliminates water yielding a phenoxyl radical. At pH 10, they readily oxidise catechol and hydroquinone. This reforms phenol (accounting for the low phenol consumption) and yields higher-oxidised products, eventually 1,4-benzoquinone. *cis,cis*-Muconic acid can be accounted for by the Criegee mechanism, while O₂(¹Δ_g) is released on the way to (some of the) catechol and hydroquinone.

Similar reactions proceed with hydroquinone (products: 1,4-benzoquinone, 2-hydroxy-1,4-benzoquinone and H₂O₂, with high yields of O₂(¹Δ_g) and [•]OH) and with catechol (products: 2-hydroxy-1,4-benzoquinone, *cis,cis*-muconic acid, H₂O₂ with high yields of O₂(¹Δ_g) and [•]OH). Material balance is not obtained for these two systems.

Pentachlorophenolate, pentabromophenolate and 2,4,6-triiodophenolate ions give rise to halide ions, O₂(¹Δ_g) (58%/48%/10%) and [•]OH (27%/2%/0%). It is suggested that together with O₂(¹Δ_g) the corresponding *ortho*- and *para*-quinones plus a halide ion are formed. Further halide ion is released upon the hydrolysis of these and other products. For pentachlorophenolate the material balance with respect to the short-lived intermediates is 85%. With the bromo- and iodophenolates the O₂(¹Δ_g) yields are substantially lowered, most likely due to release of triplet (ground state) dioxygen induced by the heavy atom effect.

Introduction

Ozonation is widely used in drinking-water processing for disinfection^{1,2} as well as for the removal of unwanted contaminants.³ There is an increasing concern about potential unwanted by-products. Phenol and its derivatives often pose a problem. Moreover, the omnipresent natural organic matter (NOM) may contain phenolic groups. The aim to degrade phenols with ozone has led to a large number of studies, in particular of its parent,⁴⁻¹⁶ but a detailed mechanistically-oriented study is still missing. For a better understanding of the underlying processes, especially also for an assessment of potential by-product formation, such a study is urgently needed.

Upon deprotonation of phenol (pK_a = 10), the ozone rate constant increases as much as six orders of magnitude (*cf.* Table 2). Due to this large difference in rates, ozone reacts practically only with the phenolate in equilibrium in neutral and slightly acidic solutions. For studying the reactions specific to phenol, the pH has to be lowered to <4.

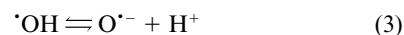
Upon the ozonolysis of phenol, [•]OH is formed.¹⁵⁻¹⁷ We have recently suggested that this is due to an electron transfer from phenolate/phenol to ozone [*E*⁷(phenol) = 0.86 V¹⁸; *E*⁷(ozone) = 1.03 V] [reaction (1)],¹⁷ and this will be substantiated in the present paper.



In reaction (1), a phenoxyl radical is formed either directly or *via* the phenol radical cation which is a strong acid (pK_a = -2)¹⁹ and readily deprotonates. In the ozonolysis of phenol, the

dimerisation products of phenoxyl radicals have, in fact, already been reported.^{8,9}

The ozonide radical, O₃^{•-}, is only stable at high pH. It is in equilibrium with O₂ and O^{•-} [reaction (2), pK = 6.26],²⁰ and O^{•-} is in equilibrium with [•]OH [reaction (3), pK_a = 11.8].²¹ At all pH values relevant for water processing, equilibria (2) and (3) are fully shifted towards [•]OH.



As a consequence, the reactions of [•]OH with phenol must be taken into account. There is also the intriguing observation⁸ that the consumption of phenol is low despite its high rate of reaction with ozone. Thus, it is expected that the reaction of ozone with phenol is much more complex than has been thought before. In the present paper, some of these complexities are disentangled. Although the main thrust of the paper is directed to the elucidation of the ozonolysis of phenol, data on the ozonolysis of hydroquinone, catechol and highly halogenated phenols will also be presented. The chemistries of the latter are mechanistically quite interesting.

Experimental

Phenol, hydroquinone, catechol, pentachlorophenol, pentabromophenol and 2,4,6-triiodophenol were commercially available in high purity and used as received. For the quantification of the products, *cis,cis*-muconic acid, 1,2,4-trihydroxybenzene, 1,4-benzoquinone (resublimed) and 4,4'-dihydroxybiphenyl were also available as reference material. For the calibration of

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2-hydroxy-1,4-benzoquinone, 1,2,4-trihydroxybenzene was oxidised with 1,4-benzoquinone,²² a reaction which proceeds quantitatively.²³

Solutions were made up in Milli-Q-filtered (Millipore) water. A dioxygen-fed ozonator (Philaqua, Gladbeck) was used to produce the ozone stock solutions. Their ozone content was determined spectrophotometrically using $\epsilon(260)^{24,25} = 3300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. When the ozonation was carried out at pH 10, the pH was lowered to pH 4 immediately after ozonation in order to minimise the autoxidation of phenolic products and the degradation of 1,4-benzoquinone.

Ozone rate constants were determined directly by stopped flow by following the decay of ozone at 260 nm at a more than ten-fold substrate concentration or with fast ozone reactions by competition²⁶ using buten-3-ol ($k = 7.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)^{27,28} as competitor. Stopped-flow experiments were carried out with the help of a Biologic (SF3) instrument equipped with a diode array system (Tidas-16, J&M, Aalen) for optical detection.

Formaldehyde yields were determined using the Hantzsch method.²⁹ Organic (hydro)peroxides and H_2O_2 were quantified with molybdate-activated iodide,³⁰ either by following the kinetics of this reaction or by post-column derivatisation.^{17,27,31}

The products were separated by HPLC on a reversed phase column (RP18, 25 cm) using 25% methanol and 0.1% phosphoric acid in water as eluent at a flow rate of 1 ml min^{-1} [retention times (min): 1,2,4-trihydroxybenzene (3), hydroquinone (7.5), 2-hydroxy-1,4-benzoquinone (9), 1,4-benzoquinone (10), catechol (13), *cis,cis*-muconic acid (16.8), *cis,trans*-muconic acid (17.5) and phenol (25)]. Under these conditions, 2-hydroxy-1,4-benzoquinone and 1,4-benzoquinone peaks were not well resolved. A better separation was obtained with 10% methanol and 0.1% phosphoric acid in water as eluent [2-hydroxy-1,4-benzoquinone (14), 1,4-benzoquinone (16)] or water as an eluent [2-hydroxy-1,4-benzoquinone (4), 1,4-benzoquinone (45)]. 4,4'-Dihydroxybiphenyl (10.5) and 2,4'-dihydroxybiphenyl (14) were separated using 30% acetonitrile in water as eluent. Upon standing, *cis,cis*-muconic acid partially isomerises into *cis,trans*-muconic acid, and this has been accounted for whenever *cis,cis*-muconic acid yields are reported.

Halide ions were determined by ion chromatography (Dionex DX100) on a AS9-HC column (with Ion Pac AG9-HC as pre column); eluent: $1.8 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ – $1.7 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaHCO}_3$ at 1 ml min^{-1} for chloride (10 min) and bromide (25 min); $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ – $0.75 \times 10^{-3} \text{ mol dm}^{-3} \text{ NaHCO}_3$ for iodide (30 min). Methanesulfinic acid (5.8) and methanesulfonic acid (6.8) were separated on the AG14/AS14 column; eluent: $4.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ – $4.25 \times 10^{-4} \text{ mol dm}^{-3} \text{ NaHCO}_3$.

Singlet dioxygen, $\text{O}_2(^1\Delta_g)$, yields were determined by measuring its fluorescence as has been described elsewhere.¹²

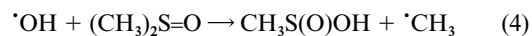
Kinetic simulations were carried out with the help of the Chemical Kinetics SimulatorTM software, version 1.01 (from IBM, Almaden Research Center).

Results and discussion

Scavenging experiments

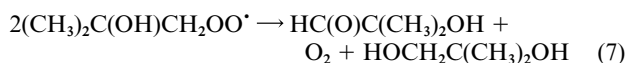
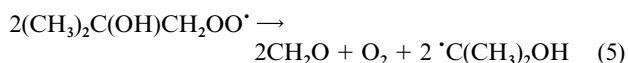
It has been mentioned in the Introduction that $\cdot\text{OH}$ is formed in the reaction of ozone with phenol. This conclusion is based on $\cdot\text{OH}$ -scavenging experiments with DMSO and tertiary butanol (Bu^tOH). This approach has been discussed in detail in recent studies,^{17,32} and only a brief account will be given here for a better understanding of the results presented below.

Compared to phenol, DMSO and Bu^tOH react with ozone at negligible rates even if present at reasonable excess (*cf.* Table 2). The DMSO assay is superior, since scavenging of $\cdot\text{OH}$ yields immediately the detected product, methanesulfinic acid which is formed in 92% yield³³ [reaction (4)].



Subsequent oxidation of methanesulfinic acid to methanesulfonic acid by some oxidising species does not materially alter the assay as long as both are measured. Methanesulfinic acid is known to undergo a very efficient $\cdot\text{OH}$ -induced autoxidation,³⁴ but this seems not to be the reason for the formation of methanesulfonic acid here, since the methanesulfinic acid to methanesulfonic acid ratio does not depend on the DMSO concentration.¹⁷ From the data shown in Table 1 (see below), it is estimated that in the ozonolysis of phenol the $\cdot\text{OH}$ radical yield must be ~22% at pH 10 and close to that at pH 7. It is recalled that at both pH values the reacting species is the phenolate ion.

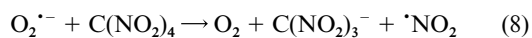
In the Bu^tOH assay, the measured products, formaldehyde and 2-hydroxy-2-methylpropionaldehyde, result from the bimolecular decay of the Bu^tOH -derived peroxy radicals [*e.g.*, reactions (5)–(7)].³⁵



To arrive at the $\cdot\text{OH}$ yield in this assay in ozone reactions, the formaldehyde yield has to be approximately doubled; the yield of 2-hydroxy-2-methylpropionaldehyde is typically 1.3–1.4 times that of formaldehyde.¹⁷

In the presence of other radicals or reducing agents such as hydroquinone, they may undergo additional reactions, *i.e.* not only self-termination reactions. This seems to have occurred in the phenol system as well. The hydroquinone yield is reduced and the 1,4-benzoquinone yield enhanced with respect to the unscavenged system (see below). Thus, besides concluding that $\cdot\text{OH}$ must play an important role, its quantification is not as precise as with the DMSO system.

The yield of $\text{O}_2^{\cdot-}$ may be determined with tetranitromethane [TNM, reaction (8)].



In peroxy radical chemistry, the TNM assay is a very common procedure,^{36,37} but in ozone reactions this assay is not as straightforward (for the special requirements see ref. 17).

Products of phenol ozonolysis

In the ozonolysis of phenol, the major products are hydroquinone, catechol, 1,4-benzoquinone and *cis,cis*-muconic acid. At low phenol conversions, their yields increase nearly linearly with increasing ozone concentration (Fig. 1).

Similar catechol (12.4%) and hydroquinone (8.6%), but higher muconic acid (12.3%) yields were reported before.⁸ There are also low yields of the dimers of the phenoxyl radicals, such as 2,4'-dihydroxybiphenyl and 4,4'-dihydroxybiphenyl (determined at pH 10, *cf.* Table 1).

Using only the small guard column for chromatography to speed up the elution of phenol and of the dihydroxybiphenyls gave no evidence for the formation of high-molecular-weight material.

Phenol consumption

For measuring the destruction of phenol as a function of the ozone concentration, lower phenol concentrations have to be used. Under these conditions and at pH ~7, only 0.48 mol phenol are destroyed per mol ozone consumed (Fig. 2).

An even more pronounced deviation from stoichiometry (0.33) has been reported before.⁸ The value of such measure-

Table 1 Ozonolysis of phenol. Products and their yields in % of ozone consumed. When more than one value is given, further runs at four or five different ozone concentrations were carried out. Some experiments were carried out in the presence of scavengers ($\cdot\text{OH}$: Bu $\cdot\text{OH}$, and DMSO; $\text{O}_2^{\cdot-}$: tetranitromethane, TNM; see text)

Product (Scavenger)	$\leq \text{pH } 3$	pH 6–7	pH 10
Hydroquinone	1.6/1.1 ^a	13.3/16	0.8
Hydroquinone (Bu $\cdot\text{OH}$)	—	< 1	—
Catechol	4.8/1.8 ^a	13.6	20
Catechol (Bu $\cdot\text{OH}$)	—	2	—
1,4-Benzoquinone	9.6/10.4/6.1 ^a	4.6/4.6	32
1,4-Benzoquinone (Bu $\cdot\text{OH}$)	—	13	—
<i>cis,cis</i> -Muconic acid	4.8/4.0/3 ^a	2.8	1
<i>cis,cis</i> -Muconic acid (Bu $\cdot\text{OH}$)	—	2.0	—
4,4'-Dihydroxybiphenyl	—	—	~1
2,4'-Dihydroxybiphenyl	—	—	~1
Singlet dioxygen, $\text{O}_2(^1\Delta_g)^{12}$	Absent	5.6	8
Formaldehyde (Bu $\cdot\text{OH}$)	10/11	14/13/12	11
2-Hydroxy-2-methylpropionaldehyde (Bu $\cdot\text{OH}$)	—	15.4	—
Methanesulfinic acid (DMSO)	—	—	16
Methanesulfonic acid (DMSO)	—	—	4
Nitroform anion (TNM)	3	—	—
Organic (hydro)peroxide	—	Absent	—
Organic (hydro)peroxide (Bu $\cdot\text{OH}$)	—	2.6	—
Hydrogen peroxide	8.5	4.8	2
Hydrogen peroxide (Bu $\cdot\text{OH}$)	—	16	—
Hydrogen peroxide (DMSO)	—	13	—
Phenol consumption	33 ^a	48 ^a	59 ^a
Phenol consumption (Bu $\cdot\text{OH}$)	—	42 ^a	—

^a At [phenol] = 2.5×10^{-4} mol dm $^{-3}$; —: not determined.

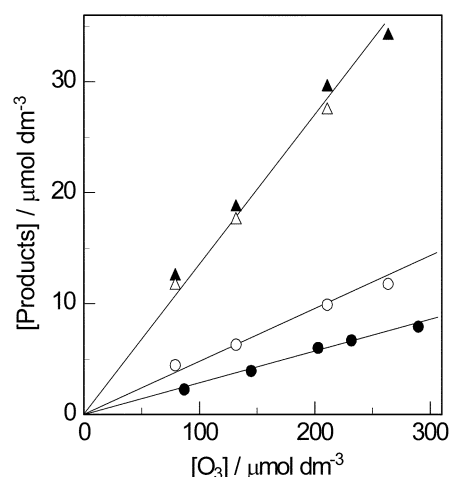


Fig. 1 Ozonolysis of phenol (3×10^{-3} mol dm $^{-3}$) in aqueous solution at pH 7. Yields of hydroquinone (Δ), catechol (\blacktriangle), 1,4-benzoquinone (\circ) and *cis,cis*-muconic acid (\bullet) as a function of the ozone concentration.

ments is debatable. In general, consumption yields can only be measured at a reasonable turnover of the substrate, otherwise the deviation from the untreated sample is too small. As a consequence, at a low turnover large errors are involved, because small changes of a large value have to be measured. At high conversions, which yield a reasonable decrease of the substrate concentration that can be measured with confidence, the competition of the products for the reagent (here: ozone) consumes the reagent and hence results in a low substrate consumption yield. At pH 3, the yields of the major products are indeed all much lower than when the experiments were carried out at a ~10-fold higher phenol concentration (Table 1). Thus, the competition in the reactions between phenol plus ozone and ozone plus products must have been effective. At this pH, the rate constant of ozone with phenol is only 1.3×10^3 dm 3 mol $^{-1}$ s $^{-1}$, while those of the potential products are all one to two orders of magnitude higher (Table 2). Thus, they readily interfere leading to a low consumption value, *i.e.* this value is of no significance as far as the mechanism is concerned.

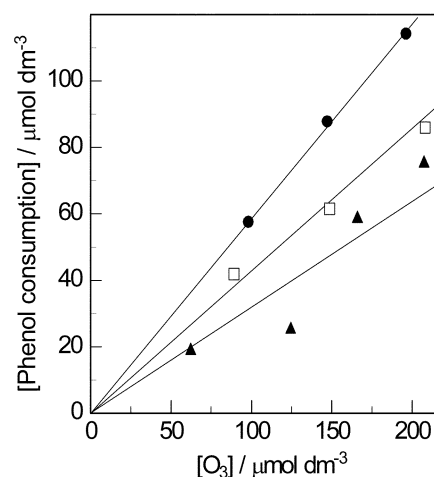


Fig. 2 Ozonolysis of phenol (2.5×10^{-4} mol dm $^{-3}$) in aqueous solution. Consumption of phenol as a function of the ozone concentration at pH 3 (\blacktriangle), 7 (\square) and 10 (\bullet).

At pH 7, the consumption value is higher, in agreement with a now higher k_{obs} for the reaction of ozone with phenol ($k_{\text{obs}} \approx 10^6$ dm 3 mol $^{-1}$ s $^{-1}$), but major aspects that were discussed for the situation at pH 3 persist.

At pH 10, the rate of reaction of phenol and that of all phenolic products is about the same ($k_{\text{obs}} \approx 10^9$ dm 3 mol $^{-1}$ s $^{-1}$), and the rate constants of *cis,cis*-muconic acid and of 1,4-benzoquinone are now lower. Under such conditions, the competition of phenol and its products is now "on equal terms", and the consumption value, although still somewhat too low, is now meaningful. The fact that it is below unity is of importance as far as mechanistic aspects are concerned.

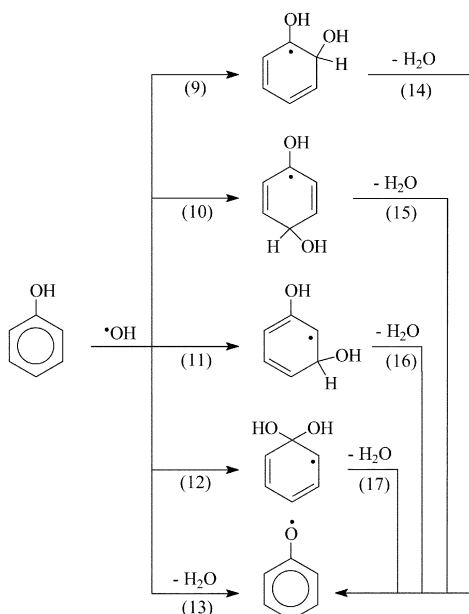
Mechanistic considerations

While in the case of olefins the Criegee mechanism⁵⁰ dominates and free-radical pathways are typically absent,^{27,51} free radicals play an important role in the ozonolysis of phenol, since $\cdot\text{OH}$ is formed in ~22% yield. The reactions of $\cdot\text{OH}$ with phenol are well known. The electrophilic $\cdot\text{OH}$ adds preferential to the *ortho*- (48%) and *para*-positions (36%) [reactions (9) and (10)].⁵²

Table 2 Compilation of rate constants (unit: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) relevant for the present study. These values were used for modelling

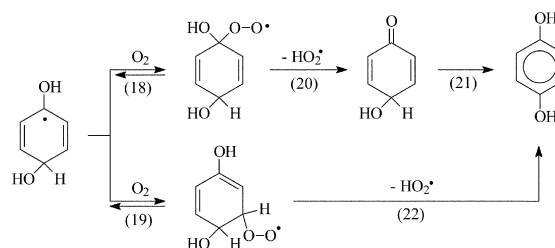
Reaction	Rate constant	Reference
Phenol + $\text{O}_3 \rightarrow$ products	1.3×10^3	38
Phenolate + $\text{O}_3 \rightarrow$ products	1.4×10^9	38
Catechol + $\text{O}_3 \rightarrow$ products	3.1×10^5	39
Hydroquinone + $\text{O}_3 \rightarrow$ products	5.2×10^5 at pH 7	This work
	1.5×10^6	39
	2.3×10^6 at pH 7	This work
	1.8×10^6 at pH 3	This work
Pentachlorophenolate + $\text{O}_3 \rightarrow$ products	1.2×10^6	This work
Pentabromophenolate + $\text{O}_3 \rightarrow$ products	1.7×10^6	This work
2,4,6-Triiodophenolate + $\text{O}_3 \rightarrow$ products	6.8×10^6	This work
1,4-Benzoquinone	2.5×10^3	This work
<i>cis,cis</i> -Muconic acid	4×10^4	40
$\text{O}_2^{\cdot-} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_3^{\cdot-}$	1.6×10^9	41
$\cdot\text{OH} + \text{Phenol} \rightarrow \text{OH-adduct radicals}$	$\sim 1 \times 10^{10}$	21
$\cdot\text{OH} + \text{Phenolate ion} \rightarrow \text{OH-adduct radicals}$	$\sim 1 \times 10^{10}$	21
2 OH-Adduct radicals \rightarrow products	2×10^8 (2k)	42
OH-Adduct radicals + $\text{O}_2 \rightarrow \text{OH-adduct-peroxyl radicals}$	1.2×10^9	42
OH-Adduct-peroxyl radicals $\rightarrow \text{HO}_2^{\cdot} +$ products	$1.3 \times 10^5 \text{ s}^{-1}$	42
<i>p</i> -OH-Adduct radical \rightarrow Phenoxy + H_2O	$1.8 \times 10^3 \text{ s}^{-1}$	42
<i>o</i> -OH-Adduct radical \rightarrow Phenoxy + H_2O	Very slow	42
<i>p</i> -OH-Adduct radical \rightarrow Phenoxy + H_2O (H^+ -catal.)	1.7×10^9	42
<i>o</i> -OH-Adduct radical \rightarrow Phenoxy + H_2O (H^+ -catal.)	$(1.1\text{--}2.1) \times 10^8$	42
2 Phenoxy \rightarrow Products	2.6×10^9 (2k)	43
	2.3×10^9 (2k)	44
Phenoxy + $\text{O}_2^{\cdot-} \rightarrow$ products	$\geq 1 \times 10^9$	cf. ref. 45
2 Semiquinone \rightarrow hydroquinone + 1,4-benzoquinone	3.1×10^8	46
Cyclohexadienone \rightarrow Phenol	$3.8 \times 10^3 \text{ s}^{-1}$	47
$\text{O}_3 + \text{Bu}^t\text{OH} \rightarrow$ products	$\sim 1 \times 10^{-3}$	48
$\text{O}_3 + \text{DMSO} \rightarrow$ products	8	48
$\cdot\text{OH} + \text{Bu}^t\text{OH} \rightarrow$ products	6×10^8	21
$\cdot\text{OH} + \text{DMSO} \rightarrow$ products	7×10^9	21
$\text{O}_2^{\cdot-} + \text{C}(\text{NO}_2)_4 \rightarrow \text{O}_2 + \text{C}(\text{NO}_2)_3^{\cdot-} + \cdot\text{NO}_2$	2×10^9	49

Addition to the *meta*-position [reaction (11), 8%] and phenoxy radical formation [reactions (12)/(17) and (13), 8%] are of lesser importance. In acidic and basic solutions, the dihydroxycyclohexadienyl radicals rapidly eliminate water giving rise to further phenoxy radicals [reactions (14)–(16)].⁵³

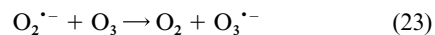


Ozone is generated from dioxygen, and dioxygen is always present in excess over ozone. Therefore, one has to take into account that the dihydroxycyclohexadienyl radicals react with dioxygen [e.g., reactions (18) and (19)], and release $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ [$\text{p}K_a(\text{HO}_2^{\cdot}) = 4.8$]⁴¹ [reactions (20) and (22)] (for rate constants see Table 2).⁴² The main products from these reactions are hydroquinone and catechol (the analogous routes to the latter are not shown). There are competing reactions, but they are

minor in comparison (for potential additional decay pathways see ref. 54).⁴²



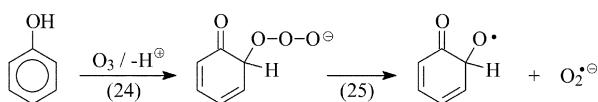
The formation of $\text{O}_2^{\cdot-}$ in these reactions may, in principle, induce a chain reaction, since $\text{O}_2^{\cdot-}$ readily reacts with ozone giving rise to $\text{O}_3^{\cdot-}$ [reaction (23)] and hence to $\cdot\text{OH}$.⁴⁸



However at pH 10, the reaction of ozone with phenolate is so fast that this reaction can be neglected at the phenol concentrations used ($[\text{phenol}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$). Even at pH 7 the rate of reaction of ozone with phenol is too fast ($\sim 3 \times 10^3 \text{ s}^{-1}$) to allow reaction (23) to compete effectively ($\leq 2\%$ of total ozone reaction). At pH 3, its contribution is $\sim 3\%$ as has been determined with the help of the TNM assay ($[\text{TNM}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$). This assay can only be carried out with confidence at this low pH, because the hydroquinone anion reacts too rapidly with TNM, even at the low concentrations in equilibrium present at pH ~ 7 . At pH 3, however, this reaction is sufficiently slow, and the nitroform anion yield is significant. The low value observed under these conditions is due to the rapid H^+ -catalysed water elimination which prevents dioxygen from reacting with the dihydroxycyclohexadienyl radicals.⁴²

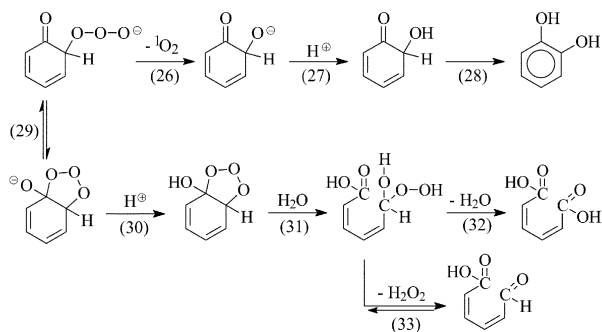
These data now allow us to distinguish between $\cdot\text{OH}$ formation by an electron transfer [reactions (1)–(3)] or *via* an $\text{O}_2^{\cdot-}$ -induced reaction as favoured in a study on methoxylated benzenes.^{55,56} There, it has been suggested that the ozone adducts of

the type formed according to reaction (24) may decompose into two radicals one of which being $O_2^{\cdot-}$ [reaction (25)].



At pH 3, the $HO_2^{\cdot}/O_2^{\cdot-}$ yield is 3% (see above), while the $\cdot OH$ yield at this pH is about the same as that at the higher pH values, *i.e.* ~22%, as is evident from the very similar formaldehyde yields in the presence of BuOH under these three conditions. We, therefore, exclude the superoxide pathway [reactions (25), (23), (2) and (3)] as a major contribution to $\cdot OH$ formation.

At pH 7, the water elimination reactions (14) and (15) are too slow (*cf.* Table 2) to compete with the addition of dioxygen [*cf.* reactions (18) and (19)]. Due to some competing reactions, the yield of catechol is 40% and that of hydroquinone is 30% of the $\cdot OH$ yield, *i.e.* lower than that of their precursors, the corresponding dihydroxycyclohexadienyl radicals.⁴² From these data, we calculate that a catechol yield of ~9% and a hydroquinone yield of ~7% is formed *via* $\cdot OH$. The much higher catechol (~14%) and hydroquinone yields (~15%, Table 1) clearly show that there must be further routes to these products. The observation that $O_2(^1\Delta_g)$ is among the products¹² strongly indicates that reactions (24), (26)–(28) take place. A similar reaction sequence leading to hydroquinone can be written for an ozone attack at the *para* position.



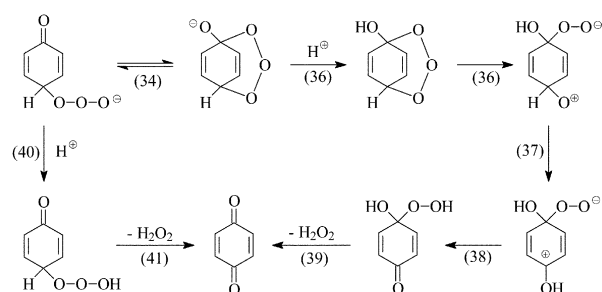
In competition, the ozone adduct may close the ring yielding the Criegee intermediate [reactions (29) and (30)]. Ring opening and water elimination gives rise to *cis,cis*-muonic acid [reactions (31) and (32)]. In all other systems that have been investigated thus far, the α -hydroxyhydroperoxide eliminated H_2O_2 [*cf.* reaction (33)],^{27,51} and a water elimination has never been observed. In the present system, however, the elimination of H_2O_2 seems not to occur. The high molar absorption coefficients of muonic systems would have allowed us to detect the aldehyde in the HPLC chromatogram. Interestingly, *cis,cis*-muonic acid is even observed in basic solutions, conditions that normally favour the elimination of H_2O_2 . Reactions such as (33) are reversible, and this could account for the formation of *cis,cis*-muonic acid despite the fact the k_{33} is very likely much larger than k_{32} [reaction (32) is irreversible].

The yield of *cis,cis*-muonic acid strongly depends on the pH. It is highest at low pH and low at high pH (Table 1). The inverse has been observed for the $O_2(^1\Delta_g)$ yields. This can be accounted for by equilibrium (29). At high pH, the hydrotrioxide anion will have a longer lifetime allowing a more efficient elimination of $O_2(^1\Delta_g)$ [reaction (26)]. Concomitantly, the yield of catechol (and hydroquinone) are increased [*cf.* reactions (27) and (28)]. The present system seems to be related to the ozonolysis of pyrimidines, where $O_2(^1\Delta_g)$ is only released, when ozone is reacted with the anion.^{12,57}

Although the $O_2(^1\Delta_g)$ yield often matches that of the corresponding product, there are cases, where release of triplet (ground state) dioxygen takes place. This process is lower in

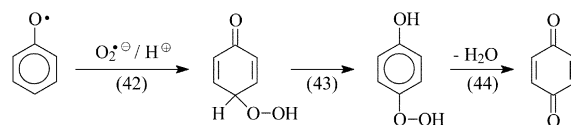
energy by 105 kJ mol^{-1} but violates the spin conservation rule. Spin orbit coupling (heavy atom effect) as in the halide ions bromide [54% $O_2(^1\Delta_g)$] and iodide [14% $O_2(^1\Delta_g)$] are typical examples.¹² Long lifetimes of the ozone adduct may also allow the release of triplet dioxygen.⁵⁸ A case in point may be the triethylamine system.⁵⁹ Thus, it is possible that in basic solutions the $O_2(^1\Delta_g)$ yield does not necessarily fully reflect the yield of reactions such as (26).

At pH 7, the yields of 1,4-benzoquinone and H_2O_2 match. This may be accidental (*cf.* the low H_2O_2 yield at pH 10, where hydroquinone is expected to autoxidise quite fast autocatalytically^{60,61} to these products). If not, reactions (34)–(39) should be considered which are, in major aspects, analogous to the established Criegee mechanism. The 1,4-addition pathway is supported by products observed in the ozonolysis of methoxylated benzenes.⁶²



Protonation of the *para*-adduct gives rise to a hydrotrioxide [reaction (40)]. Hydrotrioxides are common intermediates in the ozonolysis of aliphatic compounds, *e.g.*, of alcohols.^{63–69} They yield the corresponding carbonyl compound, often with very few side reactions. Mechanistic details are not yet fully elucidated. Reaction (41), assisted by a water molecule as a relay to allow for a six-membered transition state, could also be a route to 1,4-benzoquinone and H_2O_2 , but this must remain a tentative suggestion.

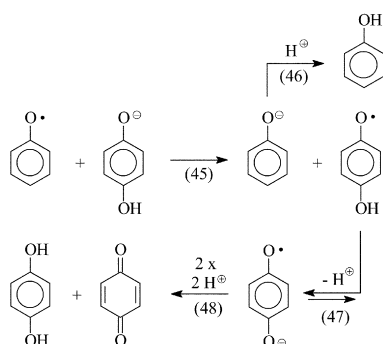
In the context of the formation of 1,4-benzoquinone and H_2O_2 , the fate of $HO_2^{\cdot}/O_2^{\cdot-}$ must be discussed. Its yields are abundant at pH 7 (~70% of the $\cdot OH$ yield,⁴² *i.e.* ~15% of reacted ozone). At pH 10 it is lower because of the competition of the OH^- -induced water elimination and dioxygen addition. It can undergo two radical–radical reactions, self-termination and a reaction with the phenoxyl radical. The self-termination is slow at pH ~7 ($k_{obs} < 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$),⁴¹ but its reaction with phenoxyl radicals is fast.⁴⁵ Reduction by electron transfer has been considered^{70,71} (this would contribute to the low value of phenol consumption), but addition seems to be an even more important pathway.^{45,72} In the present system, this could contribute to 1,4-benzoquinone formation [reactions (42)–(44)].



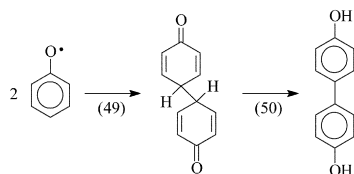
The analogous reaction, addition to the *ortho* position, would lead to 1,2-benzoquinone. There is no evidence for its formation. This is not surprising, since it is a stronger oxidant than 1,4-benzoquinone and would oxidise hydroquinone, *i.e.* the final product of this reaction would again be 1,4-benzoquinone. Since other reactions compete for the phenoxyl radicals as well, some $O_2^{\cdot-}/HO_2^{\cdot}$ will remain and slowly⁴¹ decay forming H_2O_2 and dioxygen.

At pH 10 (to some extent also at pH 7), catechol and hydroquinone are largely dissociated. Their monoanions react readily with the phenoxyl radicals [*e.g.*, reaction (45)]. This reaction consumes phenoxyl radicals and reforms phenol [reaction (46)]. It mainly accounts for the low consumption of phenol at this pH. The semiquinone radicals [$pK_a = 4$, equilibrium (47)]⁷³

disproportionate yielding 1,4-benzoquinone and hydroquinone [reaction (48)].



At pH 10, phenoxyl radicals are formed in ~22% yield *via* reaction (1). Further phenoxyl radicals are generated upon the OH⁻-induced water elimination from the dihydroxycyclohexadienyl radicals [reactions (14)–(16)]. These reactions compete with the addition of dioxygen [*e.g.*, reactions (18) and (19)]. The dioxygen concentration in the ozone stock solution was close to $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ (saturation), while the phenol solution which was reacted with the ozone stock solution was air-saturated ($[\text{O}_2] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$). If the OH⁻-induced water elimination is as fast as the fast H⁺-induced reaction ($\sim 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) only a fraction of the dihydroxycyclohexadienyl radicals are converted into phenoxyl radicals, the major part (>50%) still reacts with dioxygen, *i.e.* the phenoxyl radical yield is ~30% at pH 10. The dimer yields formed under these conditions, *e.g.* 4,4'-dihydroxybiphenyl [reactions (49) and (50)], are low in comparison, altogether a few percent including the other dimers, 2,2'-dihydroxybiphenyl, 2-phenoxyphenol and 4-phenoxyphenol. The latter were not quantified in the present study, but according to a detailed study on the dimerisation of phenoxyl radicals,⁴⁴ the ones measured here represent 70% of the total dimer yield. High dimer yields have been reported in earlier studies,^{8,9} but they were not related to ozone consumption



The substituted phenols that make up the dimers have also lower reduction potentials than phenol and are readily oxidised by the phenoxyl radical.⁴⁴ The rearrangement of cyclohexadienones [*cf.* reactions (21), (28) and (50)] is speeded up by proton catalysis^{74,75} (and likely also by base catalysis). In neutral solution, it occurs at the sub-millisecond time scale (Table 2). At the phenol concentration used here ($3 \times 10^{-3} \text{ mol dm}^{-3}$), the intrinsic half-life of the ozone reaction is ~0.25 ms at pH 7 and < 1 μs at pH 10. Of course, the time required for complete mixing is much higher, but these values indicate the time scale of the reaction during the mixing procedure. At a typical ozone concentration of $1 \times 10^{-4} \text{ mol dm}^{-3}$, the phenoxyl yield is $\sim 3 \times 10^{-5} \text{ mol dm}^{-3}$. They decay with a (first) half-life of 150 μs. Thus in the batch experiment, the time scale of all these reactions may be at least similar. This will be different upon continuous ozonation. As the ozonation proceeds, the cyclohexadienones have plenty time to rearrange. Upon continuous ozonation this may eventually lead to the formation of high-molecular-weight products, especially at high turnovers, but with our batch system and with low turnovers significant amounts of oligomerisation products were not observed.

Material balance

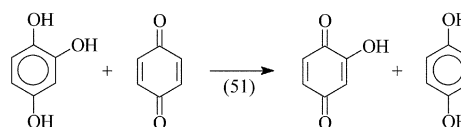
From the above discussion, it is obvious that at low pH and

similarly at pH 7 it is impossible to put up a material balance based on the observed products. The best condition for trying a material balance is pH 10. At this pH, we observe ~1% hydroquinone, 20% catechol, 32% 1,4-benzoquinone and 2% dimers (3% correcting for the missing ones). The dimers contain two phenol units, and their yield has to be doubled for a material balance. The sum of this is ~59%. A few percent, *e.g.* products derived from [•]OH addition to the *meta*-position and reactions competing with the HO₂⁻-elimination (together ~3%), must remain undetected. It has been discussed above that the consumption value determined with a low phenol concentration is always on the low side. Thus, product yields (~62%) and phenol consumption (~59%) are in reasonable agreement.

Hydroquinone and catechol

The quantifiable products of the ozonolysis of hydroquinone and catechol at pH ~7 are given in Table 3.

It is seen from this table that the material balance is incomplete, and it is not adequate to discuss the chemistries of hydroquinone and catechol ozonolysis in detail. In many aspects, they follow similar lines as depicted above for their parent, phenol. Hydroxyl radicals are major intermediates in both systems (hydroquinone: ~33%; catechol: ~22%). Their formation is connected with that of semiquinone radicals, and further semiquinone radicals may be formed upon the reaction of [•]OH with hydroquinone/catechol (detailed studies as for phenol are not available). The 1,4-semiquinone radicals disproportionate into hydroquinone and 1,4-benzoquinone. Correspondingly, the 1,2-semiquinone radicals could disproportionate into catechol and 1,2-benzoquinone (not detected, possibly unstable under our conditions). Another major intermediate is O₂(¹Δ_g) (hydroquinone: 16%, catechol: 14%). The corresponding product could be 1,2,4-trihydroxybenzene if ozone adds preferentially to the *ortho*-positions of these substrates [*cf.* reactions (26)–(28)]. This product is not observed. This is not surprising, because it is readily oxidised to 2-hydroxy-1,4-benzoquinone by 1,4-benzoquinone,²² whereby 1,4-benzoquinone is reduced to hydroquinone, the educt [reaction (51), for the kinetics of this reaction see ref. 23].



2-Hydroxy-1,4-benzoquinone is a major product in both systems. Yet in the presence of Bu^tOH which does not interfere with O₂(¹Δ_g) formation, it is practically no longer present as shown for the hydroquinone system. Under these conditions, the yield of 1,4-benzoquinone is strongly enhanced, *i.e.* the Bu^tOH-derived peroxy radicals certainly interfere at one stage. Quinones are good radical scavengers. Whether 2-hydroxy-1,4-benzoquinone, which is deprotonated under these conditions⁴⁶ and combines the properties of a quinone and an enolate, is capable of scavenging the Bu^tOH-derived peroxy radicals has not yet been studied.

In the ozonolysis of catechol, the Criegee-type product, *cis,cis*-muconic acid, is formed in a ~10% yield. The corresponding products that might have been formed in the ozonolysis of hydroquinone (potentially a complex mixture of non-muconic compounds) were not detected.

Halogenated phenols

Pentachlorophenol has been used in many countries, *e.g.* in China, for years in large quantities as a herbicide and to fight snail fever. Although discontinued, some drinking-water resources are still contaminated due to its slow biodegradation. Its ozonolysis has already found some attention.^{76,77} Here, we

Table 3 Ozonolysis of hydroquinone and catechol (3×10^{-3} mol dm $^{-3}$). Products and their yields in % of ozone consumed. Some experiments were carried out in the presence of \cdot OH scavengers, Bu t OH and DMSO

Product	Hydroquinone	Catechol
1,4-Benzoquinone	13/12	Absent
1,4-Benzoquinone (Bu t OH)	36/32	Absent
1,4-Benzoquinone (DMSO)	30	Absent
2-Hydroxy-1,4-benzoquinone	11	7.4
2-Hydroxy-1,4-benzoquinone (Bu t OH)	<1	—
2-Hydroxy-1,4-benzoquinone (DMSO)	<1	—
1,2,4-Trihydroxybenzene	Absent	Absent
Singlet dioxygen, O $_2$ ($^1\Delta_g$)	16	14
Hydrogen peroxide	5.6	5.1
Hydrogen peroxide (Bu t OH)	14	—
Hydrogen peroxide (DMSO)	10.4	7.2
Organic (hydro)peroxides	Absent	Absent
Organic (hydro)peroxides (Bu t OH)	1.9	—
Formaldehyde	Absent	Absent
Formaldehyde (Bu t OH)	21/20	11
2-Hydroxy-2-methylpropionaldehyde	Absent	—
2-Hydroxy-2-methylpropionaldehyde (Bu t OH)	23	—
Methanesulfinic acid (DMSO)	6	Absent
Methanesulfonic acid (DMSO)	27	22
Substrate consumption	47 a	47 a
Hydroquinone consumption (Bu t OH)	48 a	—

a At [substrate] = 2.5×10^{-4} mol dm $^{-3}$; —: not measured.

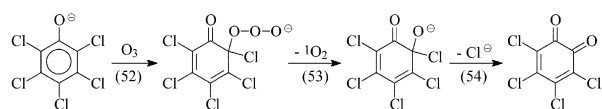
Table 4 Yields of halide ions, O $_2$ ($^1\Delta_g$),¹² formaldehyde in the presence of Bu t OH, and \cdot OH calculated¹⁷ from the latter data, expressed as % of ozone consumed, in the ozonolysis of some halogenated phenolates. Some experiments were carried out in the presence of the \cdot OH scavenger Bu t OH

Phenolate	Halide ion	O $_2$ ($^1\Delta_g$)	CH $_2$ O (Bu t OH)	\cdot OH
Pentachlorophenolate	235	58	13	27 \pm 4.5
Pentabromophenolate	340	48	1	2
2,4,6-Triiodophenolate	106	10	Absent	Absent

have included pentabromophenol and 2,4,6-triiodophenol, because in our study on the \cdot OH-induced reactions of this class of compounds we had noticed most interesting substituent effects (addition to the ring vs. electron transfer).⁷⁸ These halogenated phenols have low pK $_a$ values (ranging from 4.5 to 6.6).⁷⁸ While the phenolates are reasonably soluble in water, the phenols are not. Hence, only the ozonolysis of the phenolates was studied. Their rate constants with ozone, realised to be high but unknown,⁷⁷ were determined by competition against buten-3-ol for which a rate constant of 7.9×10^4 dm 3 mol $^{-1}$ s $^{-1}$ is reported.²⁷ It yields formaldehyde in 100% yield,²⁷ and since formaldehyde is not a product of the ozonolysis of the halogenated phenolates, the competition can be based on this product. The rate constants obtained from these data (not shown) are compiled in Table 2.

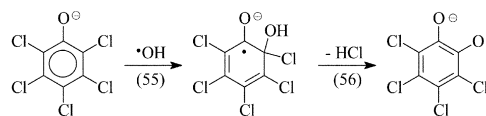
In Table 4, the yields of halide ion, O $_2$ ($^1\Delta_g$)¹² and of \cdot OH are shown. In the case of pentachlorophenolate, the chloride yield increased with time. For obtaining quasi-stable conditions, halide ion yields were therefore measured one day after ozonolysis. No attempt has been made to follow the kinetics of halide ion release. The \cdot OH yields were calculated from the formaldehyde yields in the presence of a large excess of Bu t OH.

For pentachlorophenolate, a reasonable ozone balance (~85%) with respect to the short-lived intermediates, \cdot OH and O $_2$ ($^1\Delta_g$), is obtained. As an example, the process that must occur, when the *ortho*-ozone-adduct releases O $_2$ ($^1\Delta_g$) are shown in [reactions (52)–(54)].

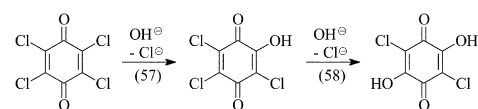


The resulting product is tetrachloro-1,2-benzoquinone, and tetrachloro-1,4-benzoquinone (chloranil) is formed, when ozone adds to the *para* position. The reaction of \cdot OH has been

shown to be two-fold, addition to the ring [47%, e.g. reaction (55)] and electron transfer (53%).⁷⁸ The sequence of reactions for the *ortho*- \cdot OH-adduct is shown in reactions (55) and (56).



In reaction (55), a geminal chlorohydrin is formed. Geminal chlorohydrins lose HCl within less than a few μ s [cf. reaction (56)].^{79,80} Kinetic details (decay of the intermediates formed in these reactions including that of the pentachlorophenoxy radical, release of HCl at short and long times) have been measured, but mechanistic suggestions remained tentative.⁷⁸ However, a typical feature of these reactions is the release of more than one chloride ion per \cdot OH, and this feature is also reflected in the ozonation data shown in Table 4. Furthermore, tetrachloro-1,4-benzoquinone is well known to hydrolyse quite rapidly in two distinct steps [reactions (57) and (58)].⁸¹



In the case of pentabromophenolate, the ozone balance vs. O $_2$ ($^1\Delta_g$) plus \cdot OH seems to be much poorer. However as in the case of the bromide and iodide ions,¹² the heavy atom effects are likely to have broken the spin conservation rule, and the O $_2$ ($^1\Delta_g$) yield reflects the ozone addition/dioxygen elimination pathway only to some extent. In the case of the 2,4,6-triiodophenolate, this must be *a fortiori* so, and a substantial drop in the O $_2$ ($^1\Delta_g$) yield is indeed observed (Table 4). We, therefore, tentatively suggest that with the latter two practically only the ozone addition/dioxygen elimination pathway occurs. This now raises the question, why with 2,4,6-triiodophenolate the iodide yield is

stoichiometric with respect to ozone consumption, while with pentabromophenolate ~3 mol bromide are released per mol ozone reacted. Considering the dramatic drop in the rate of hydrolysis of tetrachloro-1,4-benzoquinone to 2-hydroxytrichloro-1,4-benzoquinone,⁸¹ it is possible that the quinones derived from 2,4,6-triiodophenolate do not yet hydrolyse on the time scale that we are concerned with here.

Conclusion

Natural waters always contain some organic matter (NOM). This material, often related to lignin, may contain phenolic groups. As shown in the present study, ozonolysis of phenols in aqueous solution gives rise to large amounts of [•]OH. This now explains, why [•]OH formation is observed³ at the early stages of an ozone treatment in drinking-water processing.

Acknowledgements

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