Oxidation of Benzene by the OH Radical. A Product and Pulse Radiolysis Study in Oxygenated Aqueous Solution

Xian-Ming Pan, Man Nien Schuchmann and Clemens von Sonntag*
Max-Planck-Institut für Strahlenchemie, Stiftstraße 34-36, D-4330 Mülheim/Ruhr, Germany

---

Hydroxyl radicals [generated radiolytically in N_2O/O_2 (4:1 v/v)-saturated aqueous solutions] have been reacted with benzene. The major product is phenol. At low dose rate (γ-radiolysis) it is formed in 53% yield with respect to the OH radical yield. This value increases to 93% in alkaline solution (pH 12.3). With deuteriated benzene it is reduced to 39%. In addition, more than fifteen different ring-opened and fragment products are formed. A good material balance (based on primary OH radical yield and oxygen consumption) was obtained.

At high dose rate (pulse radiolysis) the major products are phenol, hydroquinone and cyclohexa-2,5-diene-1,4-diol. An important intermediate is the $HO_2^•/O_2^{•-}$ radical. Its rate of formation (k_{obsd} = 800 s^{-1}) has been followed by pulse radiolysis using tetranitromethane as a scavenger as well as conductimetrically (build-up of $H^+/O_2^{•-}$).

The results have been interpreted as follows: in their reaction with benzene, hydroxyl radicals yield the hydroxycyclohexadienyl radical **1**. In the presence of oxygen, radical **1** undergoes reversible oxygen addition yielding four different hydroxycyclohexadienylperoxyl radicals: the *cis*- and *trans*-isomers of 6-hydroxycyclohexa-2,4-dienylperoxyl radical **3** and the *cis*- and *trans*-isomers of 4-hydroxycyclohexa-2,5-dienylperoxyl radical **4**. As reported previously, in the equilibrium mixture of the radicals **1**, **3** and **4** the concentration of radical **3** represents only a few per cent of the total. It is suggested that **3** eliminates $HO_2^•$ thereby yielding phenol. In basic solution deprotonation of **4** is followed by an $O_2^{•-}$-elimination which opens up an additional route to phenol. The fact that phenol formation is not quantitative and its yield is reduced in the case of deuteriated benzene is due to another unimolecular decay route. The competing reaction is the intramolecular addition of the peroxyl radical function to a double bond (and subsequent fragmentation of the ring system). Since the $HO_2^•$-elimination is not very fast, bimolecular decay of the radicals **1**, **3** and **4** (mainly of **4**, $2k$ = 8.9 × 10^8 dm^3 mol^{-1} s^{-1}) plays an increasingly important role under the conditions of pulse radiolysis. As a consequence, the hydroquinone and cyclohexa-2,5-diene-1,4-diol yields increase with increasing dose rates under pulse radiolysis conditions (2–25 Gy $pulse^{-1}$) as those of phenol and $HO_2^•$ decrease.

The gas-phase reactions of OH radicals with benzene and its derivatives in the presence of oxygen have been the subject of numerous studies (see Ref. 1 and references therein) because of their involvement in the atmospheric degradation of aromatic hydrocarbons emitted into the troposphere from vehicle use. Benzene and its derivatives also play an increasing role as pollutants of ground water (from industrial accidents) and often threaten drinking-water resources. For the degradation of such pollutants OH radicals [from ozone,[2] photolysis of hydrogen peroxide,[3] ozone/hydrogen peroxide (peroxon)[4,5] and ionizing radiation[6]] are generally used. A large number of studies dealing with the OH-radical-induced degradation of benzene in oxygenated aqueous solution have been reported, but the resulting products have mostly not been quantitatively determined, and even qualitative assignments are controversial.[7-17]

Also in the biodegradation (detoxification) of benzene, one line of thought is that enzymatic degradation may lead to a hydroxy-substituted cyclohexadienyl radical in the first step.[18] Thus the fate of such intermediates is of much general interest.

Radiation techniques provide powerful tools to study OH-radical-induced peroxyl radical reactions both by allowing detailed product studies as well as by elucidating the kinetics with the help of pulse radiolysis.[19] In the present paper use is made of these techniques. For the first time a full material balance will be presented and kinetic data will be given which clearly demonstrate various aspects of the very complex reaction mechanism.

Experimental

Benzene (Merck) and C_6D_6 (Janssen) and D_2O (99.8%, Merck) were used as supplied. As reference materials, phenol (Merck), catechol (Merck), hydroquinone (Merck), cyclohexa-2,5-diene-1,4-diol and *cis*-cyclohexa-3,5-diene-1,2-diol (Sigma) were commercially available. *trans,trans*-Mucondialdehyde was a gift from Prof. G. Witz.[20] Upon reduction with $NaBH_4$ it yielded the *trans,trans*-hexadiene-1,6-diol. The mass spectrum of its trimethylsilyl ether is characterized by the ions *m*/*z* (%): 258 (0.9; M^+), 256 (0.5; M^+ − 2), 243 (0.6; M^+ − 15), 168 (18; M^+ − 90), 155 (14), 147 (16), 103 (9), 75 (74), 73 (100)

Solutions were made up in Millipore Milli-Q filtered water presaturated with N_2O/O_2 (4:1 v/v) (Messer Griesheim) prior to the addition of the required amount of benzene (2 × 10^{-3}–2 × 10^{-2} mol dm^{-3}). In some cases where different N_2O/O_2 ratios were required, the gas mixture was prepared with the help of a Brooks gas mixer.

γ-Radiolysis was carried out in a ^{60}Co-γ-source at a dose rate of 0.14 Gy s^{-1}. Total absorbed doses were less than 300 Gy. Pulse radiolysis was carried out with a 2.8 MeV Van de Graaff electron generator delivering 0.4–2 μs electron pulses of 1–25 Gy. The pulse radiolysis set-up with the optical and conductimetric detection techniques as well as the data processing procedures have been described elsewhere.[21,22]

Hydrogen peroxide was determined with potassium iodide method (Allen's reagent).[23] Since iodine formed in the reaction of hydrogen peroxide with Allen's reagent is consumed slowly

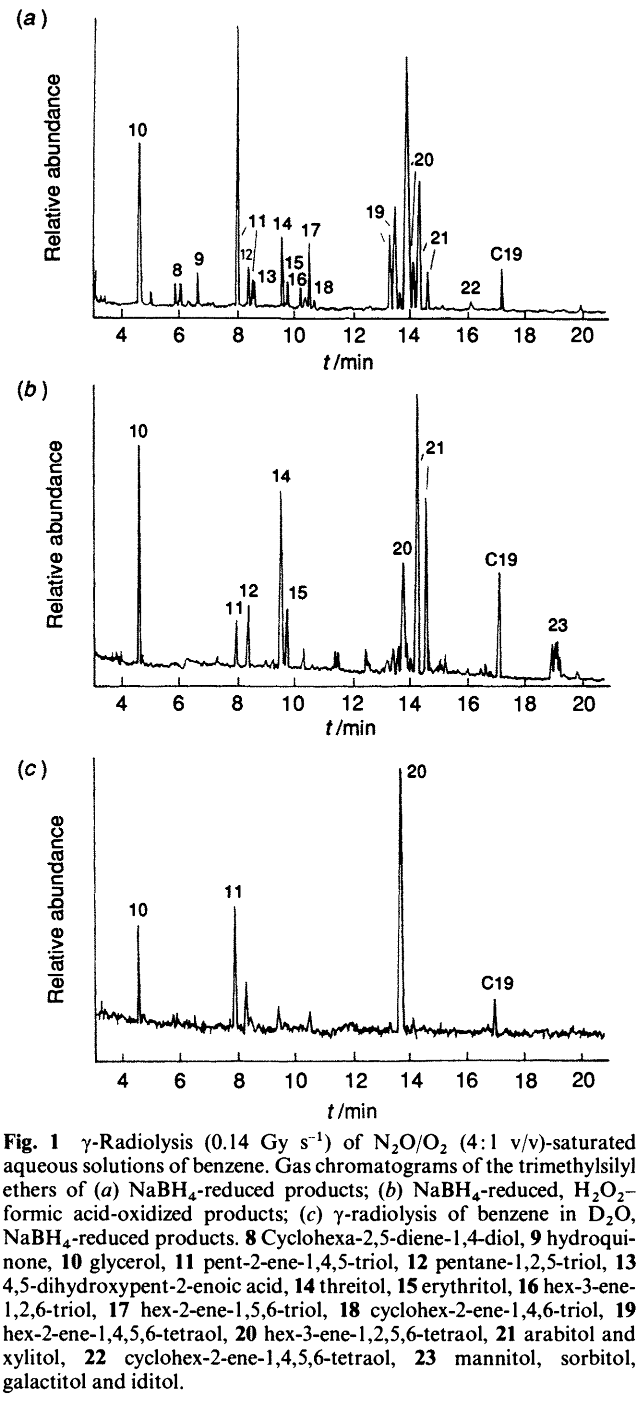


Fig. 1 γ-Radiolysis (0.14 Gy s^{-1}) of N_2O/O_2 (4:1 v/v)-saturated aqueous solutions of benzene. Gas chromatograms of the trimethylsilyl ethers of (*a*) $NaBH_4$-reduced products; (*b*) $NaBH_4$-reduced, H_2O_2–formic acid-oxidized products; (*c*) γ-radiolysis of benzene in D_2O, $NaBH_4$-reduced products. **8** Cyclohexa-2,5-diene-1,4-diol, **9** hydroquinone, **10** glycerol, **11** pent-2-ene-1,4,5-triol, **12** pentane-1,2,5-triol, **13** 4,5-dihydroxypent-2-enoic acid, **14** threitol, **15** erythritol, **16** hex-3-ene-1,2,6-triol, **17** hex-2-ene-1,5,6-triol, **18** cyclohex-2-ene-1,4,6-triol, **19** hex-2-ene-1,4,5,6-tetraol, **20** hex-3-ene-1,2,5,6-tetraol, **21** arabitol and xylitol, **22** cyclohex-2-ene-1,4,5,6-tetraol, **23** mannitol, sorbitol, galactitol and iditol.

by the benzene solution, analysis was carried out immediately (within one minute) after the addition of the reagent. Oxygen concentrations were measured with an oxygen-sensitive electrode (Wissenschaftlich-Technische Werkstätten, Weilheim). Formic acid was determined by ion chromatography (Dionex 2010 i, Dionex Ion-Pac column HPIC-AS4 with precolumn HPIC-AG4, eluent 5 × 10^{-4} mol dm^{-3} $NaHCO_3$, flow rate 1.5 cm^3 min^{-1}, retention time 7.3 min). Carbon monoxide was determined by GC on a 2 m molecular sieve (5 Å) column (FID, 60 °C, H_2 as carrier gas) after on-line catalytic reduction to methane. The low-molecular-weight aldehydes (formaldehyde, acetaldehyde and glyoxal) were converted into the corresponding oximes at pH 3 with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (Aldrich). The oximes formed were then extracted with cyclohexane and measured by gas chromatography on an 18 m SE-54 column.

Some of the radiation products were quantitatively determined by HPLC using a 12 cm Nucleosil 5C18 column with 5 × 10^{-3} mol dm^{-3} phosphate buffer at pH 7, flow rate 1.5 cm^3 min^{-1}, as the eluent (retention time: cyclohexa-2,5-diene-1,4-diol, 2 min; hydroquinone, 3 min; catechol, 10 min; phenol, 22 min; and mucondialdehyde 25 min).

The less volatile products were determined as trimethylsilyl ethers after reduction with $NaBH_4$ ($NaBD_4$), elimination of boric acid by evaporation in acidified (with formic acid) methanol, and trimethylsilylation with BSTFA and TMCS in pyridine.[24] The trimethylsilylated derivatives were analysed by GC–MS on a Hewlett-Packard 5971A Mass Selective Detector coupled with a HP 5890 Series II Gas Chromatograph using a 12 m HP-1 (cross-linked methyl silicone gum) column. For the quantitative determination of the trimethylsilylated derivatives, a 25 m PS-345 column was used with sorbitol as an internal standard.

Upon $NaBD_4$ reduction a carbonyl function is converted into an alcohol function labelled with one deuterium. Thus from the mass spectrum of such a partially deuteriated polyhydric alcohol the position of the former carbonyl group can be recognized.[24] Fig. 1(*a*) shows the gas chromatogram of the trimethylsilylated and $NaBH_4/NaBD_4$-reduced products from the γ-radiolysis of benzene in N_2O/O_2-saturated solution. The peaks **8** (two stereoisomers of cyclohexa-2,5-diene-1,4-diol) and **9** (hydroquinone) have been identified by comparison with authentic materials. These are also original radiation products (unchanged by the $NaBD_4$-reduction) as determined by HPLC (see above). The identification of glycerol (peak **10**, precursor: CHO–CO–CHO), threitol and erythritol (peaks **14** and **15**, their common precursor: tetros-3-ulose), arabitol and xylitol (the two peaks **21**, their common precursor: pentodialdose) based on their mass spectra for the positions of incorporated deuterium atoms have been reported earlier (see Refs. 24–26) and are not shown here. For simplicity the identification of the products glycolic acid and 2-hydroxypropionic acid as trimethylsilylated derivatives and butenedial as the $NaBD_4$-reduced, trimethylsilylated derivative by GC–MS are also not shown here. The assignments of the other products by comparing the *m*/*z* values of their mass spectra obtained under three different work-up conditions are compiled in Table 1. The TMS-derivatives of these polyhydric alcohols are labelled either with (*a*) no deuterium ($NaBH_4$-reduced), (*b*) one deuterium for each carbonyl function ($NaBD_4$-reduced), or (*c*) many deuteriums (C_6D_6, $NaBD_4$-reduced).

To facilitate the identification of products with unsaturated C=C bonds, an additional derivatisation method was employed. After $NaBH_4$ reduction, products were treated with H_2O_2 (30%) and formic acid (98%) at 70 °C for 2 h followed by hydrolysis with 20% NaOH at 100 °C for 2 h to convert an unsaturated C=C group into a diol group[27] before they were trimethylsilylated and analysed by GC–MS. Fig. 1(*b*) shows that, compared with Fig. 1(*a*), the saturated polyhydric alcohols **10**, **12**, **14**, **15** and **21** either remain unchanged or may even be enhanced. All the other polyhydric alcohols with one or more unsaturated C=C groups either disappeared or were diminished significantly in yield. **11** is largely converted into the pentitols **21**, whereas **19** and **20** are converted into four hexitols **23** (mannitol, sorbitol, galactitol and iditol).

When benzene was irradiated in D_2O instead of H_2O and the products were reduced with $NaBH_4$ and trimethylsilylated, of the ring-opened products with three or more carbon atoms obtained under normal conditions [irradiation in H_2O, *cf.* Fig. 1(*a*)], only glycerol **10**, pent-2-ene-1,4,5-triol **11** and hex-3-ene-1,2,5,6-tetraol **20** were observed [Fig. 1(*c*)].

Results

In the radiolysis of N_2O-saturated aqueous solutions, hydroxyl

Table 1 Identification of products as TMS derivatives by GC–MS [*cf.* Fig. 1(*a*)] under three different work-up conditions: (*a*) reduction with $NaBH_4$, (*b*) reduction with $NaBD_4$ and (*c*) C_6D_6, reduction with $NaBD_4$

Peak	Identified as TMS derivative	*M*	*m*/*z* Values (relative abundance)
11	Pent-2-ene-1,4,5-triol (precursor: CH_2OH-CO-CH=CH-CHO)	334	(*a*) 73 (100), 103 (10), 133 (10), 147 (45), 155 (10), 231 (71), 244 (2) (*b*) 73 (100), 103 (10), 133 (8), 147 (45), 157 (5), 233 (60), 246 (2) (*c*) 73 (100), 105 (15), 133 (10), 147 (77), 161 (10), 236 (85), 250 (2)
12	Pentane-1,2,5-triol (precursor: 2-oxopentanedial CHO-CH_2-CH_2-CO-CHO)	336	(*a*) 73 (75), 103 (3), 143 (100), 147 (25), 233 (8) (*b*) 73 (95), 105 (4), 146 (100), 147 (43), 236 (15) (*c*) 73 (95), 105 (2), 147 (40), 148 (100), 149 (80), 239 (17)
13	4,5-Dihydroxypent-2-enoic acid (precursor: COOH-CH=CH-CO-CHO)	348	(*a*) 73 (100), 103 (20), 129 (20), 147 (40), 156 (25), 217 (10), 245 (12), 318 (15), 333 (5) (*b*) 73 (100), 104 (20), 129 (10), 147 (30), 156 (20), 157 (15), 217 (3), 245 (10), 246 (4), 320 (10), 335 (2) (*c*) 73 (100), 105 (20), 132 (17), 147 (38), 159 (36), 220 (3), 248 (15), 321 (20), 338 (5)
16	Hex-3-ene-1,2,6-triol (precursor: CHO-CH_2-CH=CH-CO-CHO)	348	(*a*) 73 (100), 103 (80), 147 (33), 155 (30), 245 (30), 258 (4) (*b*) 73 (100), 104 (95), 147 (28), 157 (27), 247 (44), 261 (8) (*c*) 73 (100), 105 (80), 147 (30), 160 (18), 251 (25), 266 (3)
17	Hex-2-ene-1,5,6-triol (precursor: CHO-CH=CH-CH_2-CHOH-CHO)	348	(*a*) 73 (90), 103 (7), 117 (20), 133 (10), 147 (35), 155 (21), 205 (100), 245 (5) (*b*) 73 (90), 104 (2), 118 (15), 133 (8), 147 (50), 157 (10), 206 (100), 247 (5) (*c*) 73 (100), 105 (5), 120 (20), 133 (10), 147 (60), 160 (7), 208 (100), 250 (2)
18	Cyclohex-2-ene-1,4,6-triol (possible precursor: 4-hydroxy-5,6-epoxycyclohex-2-enone)	346	(*a*) 73 (36), 147 (20), 204 (6), 230 (100) (*b*) 73 (65), 147 (25), 204 (12), 231 (100) (*c*) 73 (34), 147 (11), 206 (2), 234 (100)
19	Two stereoisomers of hex-2-ene-1,4,5,6-tetraol (precursor: CH_2OH-CHO-CHO-CH=CH-CHO)	436	(*a*) 73 (100), 103 (2), 117 (12), 142 (28), 147 (40), 205 (45), 231 (15), 243 (10), 333 (3), 346 (6) (*b*) 73 (100), 103 (3), 118 (18), 144 (25), 147 (44), 206 (40), 233 (15), 245 (10), 335 (6), 349 (7) (*c*) 73 (100), 120 (15), 105 (5), 120 (15), 147 (90), 208 (50), 236 (15), 248 (10), 338 (5), 353 (6)
20	Two stereoisomers of hex-3-ene-1,2,5,6-tetraol (precursor: CHO-CHOH-CH=CH-CHOH-CHO)	436	(*a*) 73 (100), 103 (12), 129 (100), 147 (20), 155 (6), 205 (5), 217 (7), 229 (2), 243 (15), 333 (5), 346 (2) (*b*) 73 (100), 104 (15), 129 (68), 147 (36), 156 (6), 206 (5), 218 (4), 230 (5), 244 (15), 334 (6), 348 (2) (*c*) 73 (76), 105 (15), 133 (100), 147 (35), 161 (7), 208 (5), 220 (7), 235 (3), 248 (10), 339 (11)
22	Cyclohex-2-ene-1,4,5,6-tetraol (possible precursor: 5,6-hydroxycyclohex-2-ene-1,4-dione)	434	(*a*) 73 (40), 147 (17), 191 (6), 204 (5), 230 (100) (*b*) 73 (50), 147 (20), 191 (6), 204 (5), 205 (6), 231 (100), 232 (56) (*c*) 73 (54), 147 (16), 192 (16), 206 (7), 234 (100)

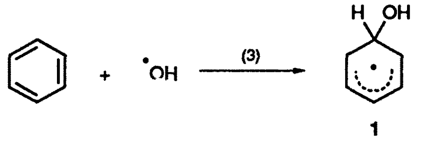
radicals are formed [reactions (1) and (2)]. The radiation chemical yields (*G* values) of the primary radicals are known [$G(^{\bullet}OH) = 5.8 \times 10^{-7}$ mol J^{-1} and $G(H^{\bullet}) = 0.57 \times 10^{-7}$ mol J^{-1}].

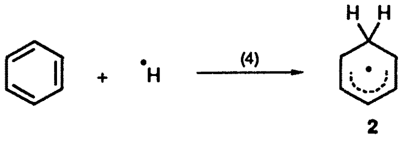
$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^{\bullet}OH, e^-_{aq}, H^{\bullet}, H_2O_2, H_2, H^+ \quad (1)$$

$$e^-_{aq} + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^- \quad (2)$$

The OH radicals react with benzene to give the hydroxycyclohexadienyl radical **1** [reaction (3)]. This addition is fast and irreversible at room temperature ($k_3 = 7.8 \times 10^9$ dm^3 mol^{-1} s^{-1}).[28] In the presence of oxygen, radical **1**, for which two mesomeric forms may be written, is converted into the *cis*- and *trans*-isomers of the hydroxycyclohexadienyl peroxyl radicals **3** and **4** [reactions (5) and (6), $k_{5,6} = 3.1 \times 10^8$ dm^3 mol^{-1} s^{-1}].[29] In a previous paper of ours it has been shown that in oxygenated solutions, radical **1** is in equilibrium with radicals **3** and **4** [reactions (5/−5) and (6/−6)], whereby radical **3** is the minor component, contributing no more than a few per cent of the total radical concentration.[29]

The H atom plays only a minor role. It reacts both with benzene [reaction (4), $k_4 = 9.1 \times 10^8$ dm^3 mol^{-1} s^{-1}] and with oxygen [reaction (7), $k_7 = 2.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}).[28] At a





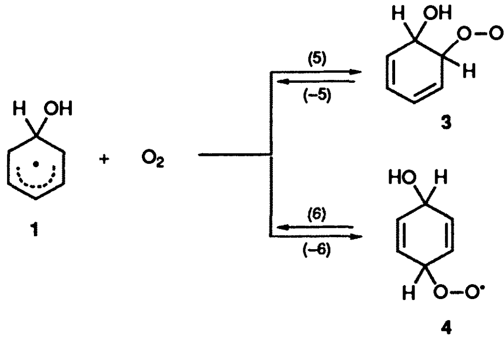


Table 2 γ-Radiolysis of N_2O/O_2 (4 : 1 v/v)-saturated aqueous solutions of benzene and C_6D_6 (both 2×10^{-3} mol dm^{-3}) at pH 6.5. Products and their G values (in units of 10^{-7} mol J^{-1}) at a dose rate of 0.14 Gy s^{-1}. Also included are the results of benzene irradiated in D_2O under otherwise identical conditions

Products	Identified as	G[a] C_6H_6	C_6D_6	C_6H_6/D_2O
Phenol		3.1	2.3	3.4
Cyclohexa-2,5-diene-1,4-diol **8**		0.1	0.07	n.d.
Hydroquinone **9**		0.1	0.07	n.d.
Catechol		0.05	$\leqslant$0.03	n.d.
Mucondialdehyde		n.f.	n.f.	n.f.
5,6-Epoxy-4-hydroxycyclohex-2-enone	**18**	0.02	0.03	n.f.
CHO–CH=CH–CHO–CHO–CH_2OH	**19**	0.15	0.2	n.f.
CHO–CHOH–CH=CH–CHOH–CHO **26**	**20**	0.5	0.6	0.9
5,6 Dihydroxycyclohex-2-ene-1,4-dione	**22**	0.01	0.01	n.f.
CHO–CH_2–CH=CH–CO–CHO	**16**	0.03	0.04	n.f.
CHO–CH=CH–CH_2–CHOH–CHO	**17**	0.1	0.1	n.f.
CHO–$(CHOH)_3$–CHO	**21**	0.2	0.4	n.f.
CHO–CO–CH=CH–COOH	**13**	0.04	0.06	n.f.
CHO–CH=CH–CO–CH_2OH **27**	**11**	0.5	0.7	0.7
CHO–CH_2–CH_2–CO–CHO	**12**	0.1	0.05	n.f.
CHO–CHO=CH–CHO		0.2	0.3	n.d.
CHO–CHOH–CO–CH_2OH	**14/15**	0.1	0.2	n.f.
CH_3–CHOH–COOH		0.2	0.2	n.d.
CHO–CO–CHO	**10**	0.3	0.5	0.4
CH_2OH–COOH		0.2	0.2	n.d.
Glyoxal		0.2	n.d.	n.d.
Acetaldehyde		0.3	n.d.	n.d.
Formaldehyde		0.7	0.9	n.d.
Formic acid		0.9	1.4	n.d.
Carbon monoxide		n.d.	n.d.	$\approx$0.2
Oxygen consumption		5.6	9.0	n.d.
Hydrogen peroxide		1.7	1.4	1.6
Organic hydroperoxide		n.f.	n.f.	n.d.
$HO_2^{\bullet}$ (by TNM)		4.0	n.d.	n.d.

[a] n.f. Not found; n.d. not determined.

Table 3 γ-Radiolysis of N_2O/O_2-saturated aqueous solution of benzene. G(Phenol) in units of 10^{-7} mol J^{-1} at different O_2-concentration at a dose rate of 0.14 Gy s^{-1}

O_2(%)	G(phenol)
5	3.7
10	3.85
15	3.5
20	3.1
50	2.5

typical benzene concentration of 2×10^{-3} mol dm^{-3} the contribution of radical **2** and hence that of the corresponding cyclohexadienyl peroxyl radicals is only a fraction of the primary H atom yield (*ca.* 20% of $H^{\bullet}$). In addition, cyclohexadienyl peroxyl radicals re-form benzene in 60% yield by $HO_2^{\bullet}$-elimination.[30] Thus, only radicals **3** and **4** (and some $HO_2^{\bullet}/O_2^{\bullet -}$) have to be considered as precursors of the observed products.

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \qquad (7)$$

In neutral-to-basic solutions, $HO_2^{\bullet}$ ($pK_a = 4.8$)[31] is fully dissociated ($H^+ + O_2^{\bullet -}$). The formation of $O_2^{\bullet -}$ can be monitored by its fast reaction with tetranitromethane (reaction 8, $k_8 = 1.9 \times 10^9$ dm^3 mol^{-1} s^{-1}),[31] which gives the strongly absorbing nitroform anion [ε(350 nm) = 15 000 dm^3 mol^{-1} cm^{-1}].[32] In pulse radiolysis its build-up can also be measured by following the conductivity changes due to the concomitant formation of H^+.

$$O_2^{\bullet -} + C(NO_2)_4 \longrightarrow O_2 + C(NO_2)_3^- + {}^{\bullet}NO_2 \qquad (8)$$

γ-Radiolysis.—In the γ-radiolysis of benzene in N_2O/O_2-saturated solutions phenol is the major final product, in agreement with previous studies (see the introduction). In addition to small amounts of cyclohexa-2,5-diene-1,4-diol, hydroquinone and catechol, there is a large number of ring-opened and fragment products with one to six carbon atoms which contain carbonyl and/or hydroxy and/or acidic groups. Their identification is presented in the Experimental section (*cf.* Table 1). their yields (G values) are given in Table 2.

When C_6D_6 is irradiated instead of benzene, identical (but deuteriated) products are formed albeit with a different distribution of their yields (see Table 2). In particular the yield of the main product phenol is considerably reduced. This reduction is compensated by a corresponding increase in the yield of the ring-opened and fragment products. Since ring-opening and fragmentation consume more oxygen than phenol formation, $G(O_2$-consumption) is correspondingly higher with deuteriated benzene than with benzene itself. As can be readily calculated there is a good material balance between the OH radical yield, the oxygen consumed and the oxygen incorporated in the products. Hence, not much material could have escaped our attention. Irradiation carried out in D_2O instead of in H_2O has very little influence on the phenol yield, but it reduces the number of ring-opened and fragment products to only three with enhanced yields [*cf.* Table 2 and Fig. 1(*c*)].

In addition to deuteriation (C_6D_6 *vs.* C_6H_6) and solvent (D_2O *vs.* H_2O) there are further factors which determine the product distribution. As can be seen from Table 3, G(phenol) increases considerably when the oxygen concentration is reduced. While G(phenol) remains the same in acidic as in neutral solutions, it increases strongly in alkaline solutions. At pH 12.3, G(phenol) = 5.5×10^{-7} mol J^{-1} has been found (Fig. 2), *i.e.*, nearly all (93%) primary OH-adduct radicals are converted into

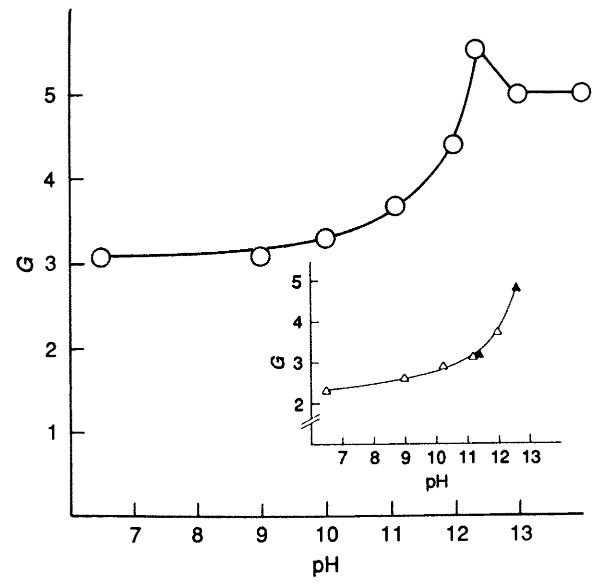


Fig. 2 G values (in units of 10^{-7} mol J^{-1}) of phenol in the γ-radiolysis of N_2O/O_2 (4:1 v/v)-saturated solutions of benzene as function of pH. Inset: pH-dependence of $G(O_2^{\bullet -})$ in the pulse radiolysis (*ca.* 2 Gy per pulse) of N_2O/O_2-saturated solutions of benzene; (△) determined as NF^- (conditions as given in Fig. 4); (▲) determined by conductivity detection.

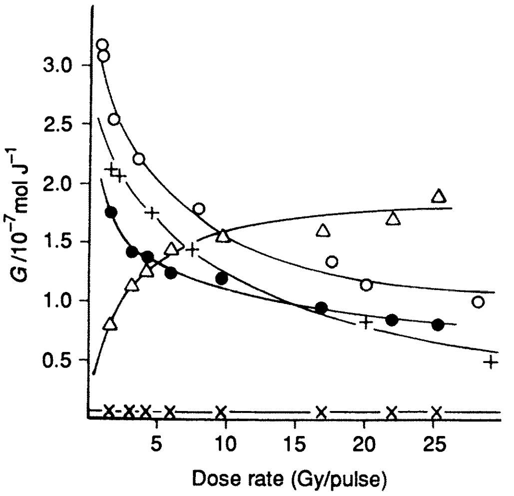


Fig. 3 Pulse radiolysis of N_2O/O_2 (4:1 v/v)-saturated aqueous solutions of benzene (2×10^{-3} mol dm^{-3}) at pH 6.5. G values of acid (+) ($H^+ + O_2^{\bullet -}$ determined by pulse-conductivity detection) and of phenol (●), cyclohexa-2,5-diene-1,4-diol **8** or hydroquinone **9** (identical yields) (△), catechol (×) (determined by HPLC), and of $O_2^{\bullet -}$ (○) (determined as NF^- in a benzene solution containing 2×10^{-4} mol dm^{-3} TNM) as a function of dose rate.

this single product [at still higher pH, G(phenol) drops due to dissociation of the OH radical, $pK_a(^{\bullet}OH) = 11.9$, and scavenging of $O^{\bullet -}$ by O_2]. There is also a noticeable effect of temperature on G(phenol), which increases from 3.1×10^{-7} mol J^{-1} at 20 °C, to 3.8×10^{-7} mol J^{-1} at 40 °C and to 4.2×10^{-7} mol J^{-1} at 70 °C.

In Table 2 the high yield of phenol is accompanied by the formation of an equivalent amount of $HO_2^{\bullet}/O_2^{\bullet -}$ ($G = 4.0 \times 10^{-7}$ mol J^{-1} which includes *ca.* 0.5×10^{-7} mol J^{-1} from the primary H atoms) which was determined by its reaction with TNM [reaction (8)]. However, the H_2O_2 yield ($G = 1.7 \times 10^{-7}$ mol J^{-1} which includes the primary H_2O_2 yield of 0.72×10^{-7} mol J^{-1} from the radiolysis of water) is much less than expected if all of the $HO_2^{\bullet}/O_2^{\bullet -}$ formed simply decayed into H_2O_2 and O_2. Some of the superoxide radicals must have decayed by cross-termination with other long-lived peroxyl radicals in the system such as the endoperoxide peroxyl radicals (see the Discussion section). Indeed, when the enzyme superoxide dismutase (SOD) was added to accelerate, the dismutation of $O_2^{\bullet -}$, $G(H_2O_2)$ increased to 2.7×10^{-7} mol J^{-1}.

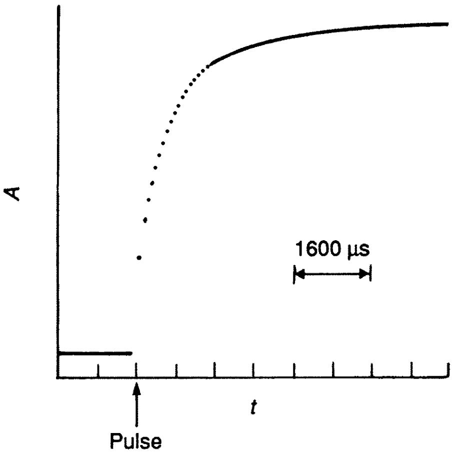


Fig. 4 Pulse radiolysis (3 Gy $pulse^{-1}$, pulse length 0.4 μs) of N_2O/O_2 (4:1 v/v)-saturated aqueous solution of benzene (2×10^{-3} mol dm^{-3}) containing tetranitromethane (5×10^{-4} mol dm^{-3}) at pH 6.5. Formation of the nitroform anion measured by its absorption at 350 nm as a function of time.

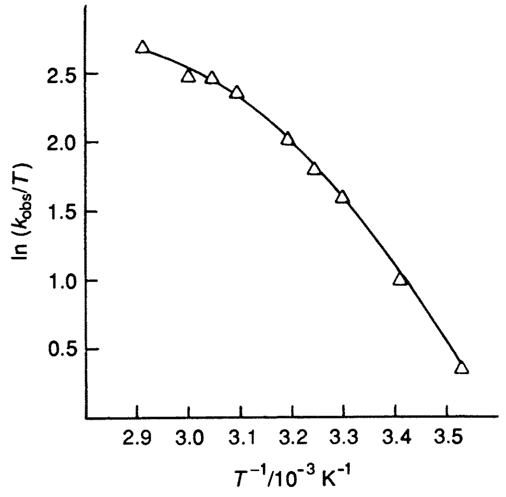
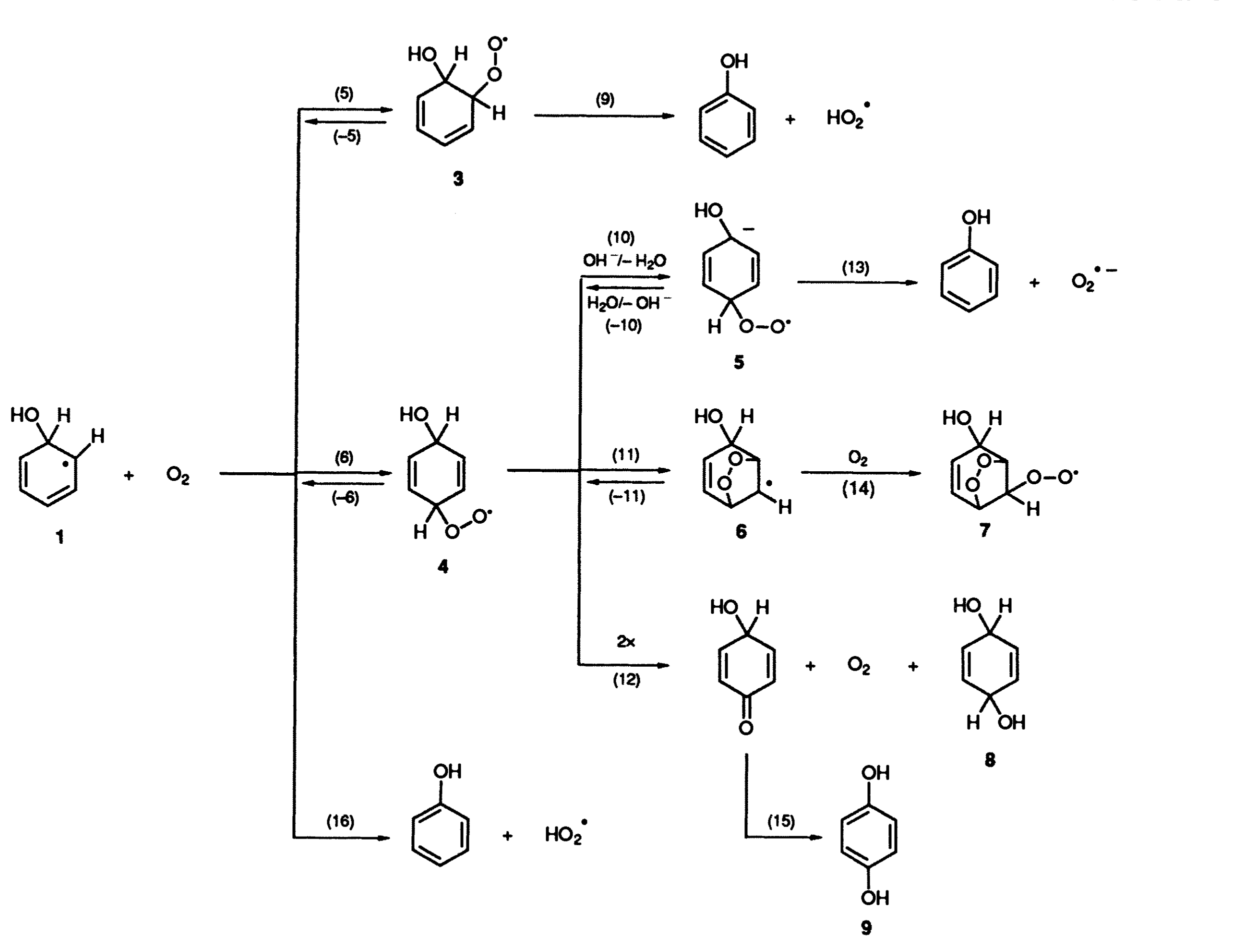


Fig. 5 Arrhenius plot of the observed rate constant k_{obsd} of $O_2^{\bullet -}$-formation in the pulse radiolysis of benzene in N_2O/O_2-saturated solutions containing tetranitromethane (conditions as given in Fig. 4).

Pulse Radiolysis.—When the irradiation of N_2O/O_2-saturated benzene solution was carried out at the very high dose rates delivered by the electron accelerator, the product distribution changed dramatically compared with γ-radiolysis. Hydroquinone **9** and cyclohexa-2,5-diene-1,4-diol **8** which are formed in very low yields ($G = 0.1$) at the low dose rate of γ-radiolysis (Table 2) now become major products. In Fig. 3 their G values are plotted against the dose per pulse. As G(**8** and **9**) increase with increasing dose rates, G(phenol) follows the opposite trend.

Also included in Fig. 3 are data concerning the yield of $HO_2^{\bullet}/O_2^{\bullet -}$. This intermediate has been monitored by conductimetry (formation of H^+ plus $O_2^{\bullet -}$) as well as optically by its reaction with TNM [reaction (8)]. Parallel to the phenol yield, $G(O_2^{\bullet -})$ determined by these two independent methods also decreases with increasing dose rates.



Scheme 1

An example of the build-up kinetics of $O_2^{\bullet -}$ formation as monitored at 350 nm of the NF^- absorption resulting from the reaction of $O_2^{\bullet -}$ with TNM is shown in Fig. 4. At sufficiently low dose rates (1–4 Gy per pulse) the build-up kinetics can be approximated by first-order kinetics. The observed first-order rate constant k_{obsd} obtained at 1 Gy per pulse is 800 s^{-1} at room temperature. The value of k_{obsd} increases with increasing temperature. An Arrhenius plot is shown in Fig. 5.

In the pulse radiolysis of benzene in basic solutions $G(O_2^{\bullet -})$, as monitored by its reaction with TNM [reaction (8)], is observed to increase with increasing OH^- concentration similar to the trend observed under γ-radiolysis conditions (*cf.* Fig. 2 inset). The pK_a value of phenol is 10.0. The formation of phenolate (λ_{max} = 287 nm) has been observed at 287 nm and by a decrease in conductance (removal of two equivalents of OH^- by phenol and $HO_2^{\bullet}$ as acids) in benzene solution at pH > 10. The observed first-order rate constant of phenolate formation is very similar to that of NF^- (*i.e.* $O_2^{\bullet -}$) formation under the same pH and dose rate conditions. However, under the high dose rates of pulse radiolysis, the bimolecular decay of the peroxyl radicals still plays an important role even at high OH^- concentrations. *G*(phenolate) and $G(O_2^{\bullet -})$ show strong dose-rate dependence up to pH 12.6. The observed rate constants of phenolate and $O_2^{\bullet -}$ build-up also show dose-rate dependence (k_{obsd} increases from 1600 s^{-1} at 2 Gy per pulse to 3000 s^{-1} at 10 Gy per pulse at pH 12.6).

Discussion

The Phenol and $HO_2^{\bullet}$*-formation.*—Phenol will be formed if the hydroxycyclohexadienylperoxyl radicals eliminate $HO_2^{\bullet}$. In Fig. 3 the *G* values of ($H^+ + O_2^{\bullet -}$) and NF^- together with *G*(phenol) are plotted as functions of dose rate. After subtraction of $G(HO_2^{\bullet}) \approx 0.5 \times 10^{-7}$ mol J^{-1} from the primary H atoms, the *G* values of $O_2^{\bullet -}$ determined as NF^- by the TNM method agree well with *G*(phenol). The values for $H^+/O_2^{\bullet -}$ obtained by conductivity detection are slightly lower than those obtained with TNM, since during its slow build-up (see below) part of the $O_2^{\bullet -}$ will have disappeared by dismutation with $HO_2^{\bullet}$.[31] These results clearly show that the formation of phenol is accompanied by an $HO_2^{\bullet}$-formation reaction. However, at most the phenol yield observed in γ-radiolysis accounts only for 53% of the total peroxyl radical yield (see Table 2). Evidently not all of the hydroxycyclohexadienylperoxyl radicals decay into phenol.

In the unsubstituted cyclohexadienyl radical/O_2 system, very rapid formation of $HO_2^{\bullet}$ has been observed ($k \geq 8 \times 10^5$ s^{-1}).[30] It has been argued that this rapid $HO_2^{\bullet}$-formation can only result from the peroxyl radical with the cyclohexa-1,3-diene structure but not from the one with the cyclohexa-1,4-diene structure. In the former the distance between the -OO• function and the H-atom at the α-position to the -OH group is shorter (1.8 ± 0.4 Å) than the corresponding distance in the latter (3.85 ± 0.35 Å).[30] In the present system the peroxyl radical **3** has the cyclohexa-1,3-diene structure and is therefore more likely to undergo $HO_2^{\bullet}$-elimination to give phenol as depicted in reaction (9) (see Scheme 1) than radical **4** which has the longer C–H • • • •O–O distance.

In the liquid-phase autoxidation of cyclohexa-1,4-diene, it has been reported that the key step is the reaction of the cyclohexadienyl radical with oxygen to give benzene and $HO_2^{\bullet}$ radicals directly.[33] An analogous reaction can be written for radical **1** with oxygen [reaction (16)] as an alternative (or parallel) pathway to reactions (5/−5) followed by reaction (9).

The only difference between these two routes is the existence of the peroxyl radical **3** as an intermediate in the latter. In a previous report of ours[29] it has been shown that the oxygen addition reaction of the hydroxycyclohexadienyl radical **1** is reversible and the resulting peroxyl radicals exist predominantly as radical **4**. It has been argued that radical **3**, if it exists, can only have a very low steady-state concentration compared with radical **4** owing to the fast reverse reaction (-5). There is then no strong evidence to exclude the possibility that the radical **1** reacts with oxygen by H-transfer to give phenol and $HO_2^{\bullet}$ directly without first forming a peroxyl radical.

As shown in Fig. 3 the yields of phenol and of $HO_2^{\bullet}/O_2^{\bullet -}$ decrease strongly with increasing radical concentrations (*i.e.* dose rates). $HO_2^{\bullet}$-formation [reactions (9) and/or (16)] is relatively slow (Fig. 4). Thus at high dose rates of pulse radiolysis bimolecular radical–radical reactions not only of radical **1**, which compete with its reaction with oxygen, but also of radicals **3** and **4**, which compete with $HO_2^{\bullet}$-elimination, effectively reduce the yields of phenol and $HO_2^{\bullet}$. Only at very low dose rates (dose per pulse) do the G values approach those of the steady-state experiment (Table 2).

The kinetics of the $HO_2^{\bullet}/O_2^{\bullet -}$-formation is not of simple first order under pulse radiolysis conditions owing to the presence of the reversible intramolecular reactions (see below) as well as to the competition of the bimolecular decay. However, as a useful parameter we have determined the first-order rate constant, k_{obsd}, of the absorption build-up at 350 nm (NF^- formation in the presence of TNM) (*cf.* Fig. 4) and of the conductivity build-up in pulse-irradiated benzene solutions at very low dose rates (≤ 3 Gy per pulse) where first-order kinetics are a good approximation. At 1 Gy per pulse, $k_{obsd} = 800\ s^{-1}$ was obtained. This value is much smaller than the value of $\geq 8 \times 10^5\ s^{-1}$ obtained for the corresponding $HO_2^{\bullet}$-formation in the cyclohexadiene system.[30] This difference explains the fact that in the benzene system at an oxygen concentration as high as 2.5×10^{-4} mol dm^{-3} the equilibria ($5/-5$), ($6/-6$) are established before any noticeable $HO_2^{\bullet}$-elimination occurs and are therefore observable.[29] In contrast, in the cyclohexadiene system, the reversibility of the oxygen addition reaction has not been observed.[30]

Since $HO_2^{\bullet}$-formation is rather slow, the value of k_{obsd} increases with increasing dose rate as the contribution from the bimolecular reactions increases. It also increases with temperature. Fig. 5 shows the Arrhenius plot of the k_{obsd} obtained at a range of temperatures. It is evident that the relationship between $\ln(k_{obsd}\ T^{-1})$ and T^{-1} is not a linear function. Such deviation from the Arrhenius relationship is typical for reactions preceded by an equilibrium.[34] For this reason we cannot obtain the values of the enthalpy and entropy of activation for reaction (9) from Fig. 5. Nevertheless, the phenol data (see the Results section) confirm the trend that k_9 and/or k_{16} increases with increasing temperature.

As can be seen from reactions (9) and/or (16), no ^{18}O should be incorporated into the phenol when the molecular oxygen carries the ^{18}O label. Experiments to confirm this have been carried out[15] and it has indeed been found that under γ-radiolysis conditions no ^{18}O label was found in the phenol, in agreement with the above interpretation. However, when the Fenton reagent was used as a source of OH radicals some ^{18}O became incorporated into the product phenol. The reason for this has not been investigated. It may partly be due to reduction of the intermediate peroxyl radicals such as **4** by Fe^{II}. Although compounds such as dihydroxycyclohexadiene are stable, they can yield phenol under certain working conditions. In addition, in the Fenton reaction, the steady-state concentration of radicals is usually much higher than that in ^{60}Co γ-radiolysis experiments. Thus bimolecular processes such as reaction (12) may also play a role. This may, in part, explain the differences between these two systems.*

The formation of phenol is not affected in acidic solutions. $G(\text{phenol}) = 2.8 \times 10^{-7}$ mol J^{-1} was found at pH 3. However, in basic solutions of benzene we have observed a marked increase in the yields of both phenol and $O_2^{\bullet -}$ with pH (Fig. 2), and at pH 12.3, 93% of the radicals **3** plus **4** decay into these products. We attribute this finding to an OH^--induced $O_2^{\bullet -}$-elimination reaction of radical **4** [reactions (10) and (13) in Scheme 1]. An estimate of the rate constant is given below.

Other Unimolecular Reactions of Radicals **3** *and* **4**.—Reaction (9) is an $HO_2^{\bullet -}$-elimination reaction and reaction (16) an H-transfer reaction both of which should show a noticeable isotope effect when H is substituted by D. In fact when benzene is substituted by C_6D_6, G(phenol) drops from 3.1×10^{-7} to 2.3×10^{-7} mol J^{-1} under otherwise identical experimental conditions (see Table 2). At the same time the yields of the fragmentation products and of oxygen consumption increase noticeably. Such a kinetic isotope effect which results in changes in product yields reveals the presence of competing reactions. This we believe to be the intramolecular radical addition reaction (11) (see Scheme 1) and subsequent oxygen addition which lead to the peroxyl radical **7**. The decay of this radical would lead to considerable alteration and/or fragmentation of the carbon skeleton of the benzene ring as shown in the products listed in Table 2 (identified as **10**–**23** as well as the smaller fragments with one to three carbon atoms). The C–O binding energies of α,α′-endoperoxyalkyl radicals such as radical **6** are very weak (*ca.* 12 kcal mol^{-1}),[35] thus reaction (11) must also be reversible [reaction (-11)]. Hence, as can be seen from Scheme 1, an additional equilibrium is involved, with one more exit, reaction (14). When radical **6** reverts to radical **4** [reaction (-11)], the latter can subsequently decay *via* radical **3** and reaction (9) to yield phenol. Alternatively, the other C–O bond in radical **6** can also open to yield radical **3** and *vice versa*. However, for the sake of simplicity, this reversible reaction between radicals **6** and **3** is not shown in Scheme 1. When radical **6** reverts to radical **3**, this also leads to the formation of phenol. These two (indistinguishable) routes to phenol are blocked when radical **6** is scavenged by oxygen [reaction (14)]. Such a reaction is irreversible on the timescale of our experiments owing to the stronger $C\text{–}O_2^{\bullet}$ binding energy of the resulting peroxyl radical **7**.

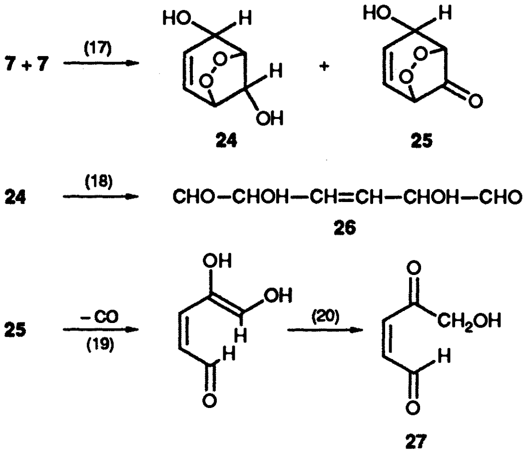
If this reasoning is correct, G(phenol) should increase with decreasing oxygen concentration. This is indeed the case as shown in Table 3. As much as it can reasonably be varied, G(phenol) should not depend on dose rate at low dose rates of γ-radiolysis (at a given oxygen concentration). This has also been observed in experiments using a tenfold lower dose rate than that given in Table 2.

The type of reaction depicted in reaction (11) is well-documented, both intramolecular and intermolecular.[36-41] In the case of polyunsaturated fatty acids, the rate constant of the cyclization reaction (here: endoperoxide formation) has been given as 800 s^{-1}.[40] For the hydroxycyclohexadienylperoxyl radicals **3** and **4** the corresponding rate constants (*e.g.* k_{11}) are probably of a similar order of magnitude. Since the equilibrium concentration of radical **3** is only a small percentage of that of radical **4**, endoperoxide formation from radical **3**, although also possible, must be negligible compared with reactions (9) and (11). It is therefore not included in Scheme 1.

At present it is premature to come up with a detailed

---

* When the photolysis of an aromatic α-azohydroperoxide was used as a source of OH radicals in benzene (as the solvent) again some ^{18}O was incorporated into the product phenol (see Ref. 14). How fast $HO_2^{\bullet}$ is eliminated from the radicals **3** and **4** in benzene is not yet known, and further studies are required to elucidate this non-aqueous system.



Scheme 2

fragmentation mechanism, but it is noted that among the products, lactic acid, acetaldehyde and formaldehyde are formed (Table 2). Benzene does not contain any carbon carrying more than one hydrogen atom, thus in the processes leading to these products H-shift reactions must have occurred. Such reactions have indeed been reported for the decay of endoperoxides.[39] However, the results obtained for benzene irradiated in D_2O [see Fig. 1(*c*) and Table 2] indicate that the two main ring-opened products, **26** and **27**, could indeed derive from the bimolecular decay of the endoperoxyl radical **7** (*cf.* Scheme 2). The unstable endoperoxides **24** and **25** formed in reaction (17) subsequently undergo ring scission to give the end products **26** and **27** and carbon monoxide, respectively, as depicted in reactions (18) and (19).* A larger number of fragment products are formed in water than in D_2O. Thus water (or the OH groups in **7** and other intermediates such as **24** and **25**) must play a role in their degradation. Details are not known at present.

Bimolecular Decay of Peroxyl Radicals **3** *and* **4**.—The rate constant, $2k = 8.9 \times 10^8$ dm^3 mol^{-1} s^{-1}, of the overall bimolecular decay of the peroxyl radicals **3** and **4** has been determined by monitoring the absorption decrease at 300–315 nm in pulse-irradiated N_2O/O_2-saturated benzene solutions at high dose rates. This value is identical with the literature value.[12] Since radical **3** is only the minor component, bimolecular decay must take place mainly between two radicals of **4** yielding 4-hydroxycyclohexa-2,5-dienone, oxygen and cyclohexa-2,5-diene-1,4-diol **8** [reaction (12)]. Cyclohexadienones such as 4-hydroxycyclohexa-2,5-dienone, are known to isomerize rapidly into the corresponding phenols,[42] in this case yielding hydroquinone **9** [reaction (15)].

The yields of **8** and **9** are quite low at the low dose rate of γ-radiolysis (see Table 2). Under pulse radiolysis conditions they become the major products. Fig. 3 shows that with the increasing dose rate (dose per pulse) *G*(**8**) and *G*(**9**) increase, and at the highest dose used they reach a value of 1.9×10^{-7} mol J^{-1}. On the other hand, the yield of catechol is very low [at a dose of 25 Gy pulse^{-1} *G*(hydroquinone)/*G*(catechol) = 33] and independent of dose rate. Bimolecular decay between **3** and **4** in reactions analogous to reactions (12) and (15) would yield catechol or cyclohexa-3,5-diene-1,2-diol. The latter has not been found among the products even under pulse radiolysis conditions. Its absence together with the low yield of catechol as shown in Fig. 3 would suggest that **3** must have a very low steady-state concentration. Although this is in agreement with our preceding conclusion, we are not certain whether there is not another as yet unidentified source of catechol [note that the same low *G*(catechol) is found at low dose rates of γ-radiolysis, *cf.* Table 2]. However, the hydroquinone results clearly indicate that **4** must be the major peroxyl radical in the very early stages. Since radical **1** is also present in equilibrium with radical **4**, bimolecular decay between these two radicals may also take place, albeit to a minor extent. We have not been able so far to detect and identify any product that could result from such a cross-termination reaction.

Mucondialdehyde.—The biodegradation of benzene is thought by some researchers to involve the hydroxycyclohexadienyl radical and its corresponding peroxyl radicals.[43] In this context it has been suggested that the toxic mucondialdehyde, which is among the products when benzene is degraded by liver microsomes, may involve these ring-precursors.[20] This conclusion is based on the experiments using the Fenton system to generate OH radicals where mucondialdehyde was found.[16] In the present work no mucondialdehyde was found either by HPLC or by GC–MS after reduction with $NaBH_4$. The precursor of mucondialdehyde would have to be radical **3** which in a *bimolecular* reaction could then yield an oxyl radical which would subsequently undergo ring-opening. Subsequent oxygen addition and $HO_2^{\cdot}$-elimination could, in principle, yield this product (*cf.* the general routes of peroxyl radical decay in aqueous solutions compiled in Ref. 19). However, as has been shown above in connection with the formation of catechol, the equilibrium concentration of radical **3** is extremely low and it eliminates $HO_2^{\cdot}$ so fast that it stands no chance of undergoing bimolecular reactions.

It has been mentioned above that under the conditions of the Fenton reaction and in the presence of $^{18}O_2$ some ^{18}O became incorporated into the phenol but this does not take place under the less complex conditions of γ-radiolysis as a source of OH radicals.[15] We believe that mucondialdehyde formation must also be a side route introduced by the various components of the Fenton reagent.

Estimates of the Actual Rate Constants.—The presence of a number of equilibria and competing reactions for the decay of radicals **3** and **4** as shown in Scheme 1 renders the kinetic measurements in this work rather difficult to interpret. We have therefore applied computer simulation of the kinetic and yield data to obtain an estimation of the actual rate constants involved in Scheme 1. The following assumptions and simplifications were made:

1. Oxygen addition to radical **1** to yield **3** or **4** is equally fast. Since the overall rate constant has been measured to be 3.1×10^8 dm^3 mol^{-1} s^{-1},[29] k_5 and k_6 should be half of this value.
2. As for the reverse reactions (−5) and (−6), the values $k_{-5} = 8.0 \times 10^5$ s^{-1} and $k_{-6} = 10^4$ s^{-1} appear best to fit the observation that the overall reverse rate constant is 1.2×10^4 s^{-1},[29] and that the concentration of **3** is only a few per cent of that of **4**.
3. For simplicity, an overall rate constant for endoperoxide formation [reactions (11/−11)] is taken as 500 s^{-1}, close to the literature value of 800 s^{-1} for a similar type of reaction (see above).
4. The OH^--induced superoxide-elimination [reactions (10/−10) and (13)] is simplified to one overall reaction.

---

* The discrepancy between the *G* values of **27** and carbon monoxide may be the result of the different work-up conditions for the analyses of these products. Thus their yields might reflect different stages of the post-irradiation decomposition of the endoperoxide **25**. Carbon monoxide, which was determined directly as a free gas in the irradiated solutions, may be present in low yield as its complementary product **27** immediately after irradiation. But in order to determine **27**, the irradiated samples were reduced with $NaBH_4$ and then silylated, during which **25** could completely have decomposed.

Table 4 Compilation of the rate constants obtained in the $^{\bullet}OH$–benzene–O_2 system by pulse radiolysis (*a*) and by computer simulation of experimental data (*b*) (for assumptions see the text)

Reactions		Rate constants
(5)	$\mathbf{1} + O_2 \longrightarrow \mathbf{3}$	1.5×10^{8} dm^{3} mol^{-1} s^{-1} (*a*, *b*)
(6)	$\mathbf{1} + O_2 \longrightarrow \mathbf{4}$	1.5×10^{8} dm^{3} mol^{-1} s^{-1} (*a*, *b*)
(−5)	$\mathbf{3} \longrightarrow \mathbf{1} + O_2$	8.0×10^{5} s^{-1} (*b*)
(−6)	$\mathbf{4} \longrightarrow \mathbf{1} + O_2$	1.0×10^{4} s^{-1} (*b*)
(9)	$\mathbf{3} \longrightarrow HO_2^{\bullet}$ + Phenol	2.0×10^{4} s^{-1} (*b*)
(10/−10, 13)	$\mathbf{4} + OH^{-} \longrightarrow O_2^{\bullet-}$ + Phenol + H_2O	1.2×10^{5} dm^{3} mol^{-1} s^{-1} (*b*)
(11/−11)	$\mathbf{4} \longrightarrow \mathbf{6}$	5.0×10^{2} s^{-1} (*b*)
(12)	$\mathbf{4} + \mathbf{4}$	8.0×10^{8} dm^{3} mol^{-1} s^{-1} (*a*, *b*)
(16)	$\mathbf{1} + O_2 \longrightarrow HO_2^{\bullet}$ + Phenol	6.0×10^{6} dm^{3} mol^{-1} s^{-1} (*b*)

5. Phenol and $HO_2^{\bullet}$-formation *via* reaction (9) and *via* reaction (16) are assumed to be of equal importance. [It is noted that if these two reaction routes are assumed to be mutually exclusive, the estimated value for the rate constant of either reaction (9) or reaction (16) would increase by a factor of two].

With these assumptions we have obtained a set of values for the individual rate constants involved in Scheme 1 which best describe the experimental rate of build-up and yield of the superoxide anion as well as the final yields of the products phenol and hydroquinone at a given dose rate at neutral pH and at pH 12.3. The results are summarized in Table 4. These rate constants are neither the unique nor the absolute values, given the complexity of the present system. However, they may provide a general impression of the relative importance of the individual reactions.

References

1 R. Atkinson, S. M. Aschmann, J. Arey and W. P. L. Carter, *Int. J. Chem. Kinet.*, 1989, **21**, 801.
2 J. Hoigne, in *Process Technologies for Water Treatment*, ed. S. Stucki, Plenum, New York, 1988, p. 121.
3 S. Lunak and P. Sedlak, *J. Photochem. Photobiol., A: Chemistry*, 1992, **68**, 1.
4 E. Gilbert, *Vom Wasser*, 1991, **77**, 263.
5 C. von Sonntag, G. Mark, R. Mertens, M. N. Schuchmann and H.-P. Schuchmann, *J. Water Supply Res. Technol.—Aqua*, 1993, in the press.
6 M. G. Nickelsen, W. J. Cooper, C. N. Kurucz and T. D. Waite, *Environ. Sci. Technol.*, 1992, **26**, 144.
7 M. Daniels, G. Scholes and J. Weiss, *J. Chem. Soc.*, 1956, 832.
8 I. Loeff and G. Stein, *J. Chem. Soc.*, 1963, 2623.
9 T. K. K. Srinivasan, I. Balakrishnan and M. P. Reddy, *J. Phys. Chem.*, 1969, **73**, 2071.
10 L. I. Kartasheva and A. K. Pikaev, *High Energy Chem.*, 1972, **6**, 76.
11 I. Balakrishnan and M. P. Reddy, *J. Phys. Chem.*, 1972, **76**, 1273.
12 G. Ramanan, *J. Indian Chem. Soc.*, 1976, **53**, 957.
13 L. Castle, J. R. Lindsay Smith and G. V. Buxton, *J. Mol. Catal.*, 1980, **7**, 235.
14 N. Narita, and T. Tezuka, *J. Am. Chem. Soc.*, 1982, **104**, 7316.
15 G. Cohen and S. E. Ofodile, in *Oxy Radicals and their Scavenger Systems, Vol. I: Molecular Aspects*, eds. G. Cohen and R. A. Greenwald, Elsevier, New York, 1983, p. 74.
16 L. Latriano, A. Zaccaria, B. D. Goldstein and G. Witz, *J. Free Radicals Biol. Med.*, 1985, **1**, 363.
17 S. Das, O. J. Mieden, X.-M. Pan, M. Repas, M. N. Shuchmann, H.-P. Schuchmann, C. von Sonntag and H. Zegota, in *Oxygen Radicals in Biology and Medicine*, eds. M. G. Simic, K. A. Taylor, J. F. Ward and C. von Sonntag, Plenum, New York, 1988, p. 55.
18 I. Johansson and M. Ingelman-Sundberg, *J. Biol. Chem.*, 1983, **258**, 7311.
19 (*a*) C. von Sonntag, *The Chemical Basis of Radiation Biology*, Taylor and Francis, London, 1987, p. 57; (*b*) C. von Sonntag and H.-P. Schuchmann, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1229.
20 L. Latriano, B. D. Goldstein and G. Witz, *Proc. Natl. Acad. Sci. USA*, 1986, **83**, 8356.
21 S. Steenken, J. Buschek and R. A. McClelland, *J. Am. Chem. Soc.*, 1986, **108**, 2808.
22 A. J. S. C. Vieira and S. Steenken, *J. Am. Chem. Soc.*, 1987, **109**, 7441.
23 A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, 1952, **56**, 575.
24 M. Dizdaroglu, D. Henneberg and C. von Sonntag, *Org. Mass Spectrom.*, 1974, **8**, 335.
25 M. N. Schuchmann and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1958.
26 C. von Sonntag and M. Dizdaroglu, *Carbohydr. Res.*, 1977, **58**, 21.
27 A. Roebuck and H. Adkins, *Org. Synth., Coll. Vol. III*, Wiley, New York, 1955, p. 217.
28 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.
29 X.-M. Pan and C. von Sonntag, *Z. Naturforsch., Teil B*, 1990, **45**, 1337.
30 X.-M. Pan, M. N. Schuchmann and C. von Sonntag, to be published.
31 B. H. J. Bielski, D. E. Cabelli, R. L. Arudi and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1985, **14**, 1041.
32 K.-D. Asmus, H. Möckel and A. Henglein, *J. Phys. Chem.*, 1973, **77**, 1218.
33 D. G. Hendry and D. Schuetzle, *J. Am. Chem. Soc.*, 1975, **97**, 7123.
34 M. S. Akhlaq, C. P. Murthy, S. Steenken and C. von Sonntag, *J. Phys. Chem.*, 1989, **93**, 4331.
35 S. W. Benson, *J. Am. Chem. Soc.*, 1965, **87**, 972.
36 F. R. Mayo, *J. Am. Chem. Soc.*, 1958, **80**, 2497.
37 F. R. Mayo, A. A. Miller and G. A. Russell, *J. Am. Chem. Soc.*, 1958, **80**, 2500.
38 F. R. Mayo, *Acc. Chem. Res.*, 1968, **1**, 193.
39 A. Fish, In *Organic Peroxides, Vol. I*, ed. D. Swern, Wiley-Interscience, New York, 1970, p. 181.
40 N. A. Porter, L. S. Lehman, B. A. Weber and K. J. Smith, *J. Am. Chem. Soc.*, 1981, **103**, 6447.
41 H.-P. Schuchmann, C. von Sonntag and R. Srinivasan, *J. Photochem. Photobiol., A: Chemistry*, 1988, **45**, 49.
42 R. Benn, H. Dreeskamp, H.-P. Schuchmann and C. von Sonntag, *Z. Naturforsch., Teil B*, 1979, **34**, 1002.
43 D. M. Jerina, *Chem. Technol.*, 1973, **3**, 120.

Paper 2/06357C
Received 27*th November* 1992
Accepted 16*th December* 1992