

Hydroxyl-radical-induced Oxidation of Cyclohexa-1,4-diene by O₂ in Aqueous Solution. A Pulse Radiolysis and Product Study

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Hydroxyl radicals have been generated radiolytically in N₂O/O₂ (4:1)-saturated aqueous solutions. They react with cyclohexa-1,4-diene by H-abstraction and by addition to a double bond yielding equal amounts of cyclohexadienyl **1** and 6-hydroxycyclohex-3-enyl radicals **2**. As shown by pulse radiolysis, **1** and **2** react with O₂ with an overall rate constant of $k = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Radical **1** yields two isomeric peroxy radicals: **4** (cyclohexa-1,3-diene structure) and **5** (cyclohexa-1,4-diene structure). Since the C–H...O–O distance in **4** is only *ca.* 1.8 Å, it is suggested that **4** is the radical which rapidly eliminates HO₂[•] ($k \geq 8 \times 10^5 \text{ s}^{-1}$ as measured by pulse radiolysis) yielding benzene (*ca.* 60% of **4** + **5**). The peroxy radical **5** which has a longer C–H...O–O distance (*ca.* 3.8 Å) might not undergo this reaction. Instead it undergoes intramolecular cyclization thereby forming endoperoxidic intermediates which are believed to be the precursors of products which upon reduction with NaBH₄ yield trihydroxycyclohexenes.

In the presence of superoxide dismutase to remove O₂^{•-} radicals and at low cyclohexa-1,4-diene concentration ($4 \times 10^{-4} \text{ mol dm}^{-3}$), the 6-hydroxycyclohex-3-enyl-peroxy radicals **6** and **7** derived from **2** decay bimolecularly yielding equal amounts of 4,5-dihydroxycyclohexene, 6-hydroxycyclohex-3-enone and oxygen ($k = 1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). At high cyclohexa-1,4-diene concentration ($10^{-2} \text{ mol dm}^{-3}$) **6** and **7** abstract H-atoms from the substrate ($k = 820 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) yielding the corresponding 6-hydroxycyclohex-3-enyl hydroperoxides. In competition with these bimolecular reactions, **6** and **7** also undergo intramolecular cyclization similar to radical **5**. In subsequent reactions endoperoxidic products are formed which have been identified as tetrahydroxycyclohexanes after reduction with NaBH₄.

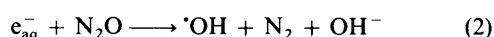
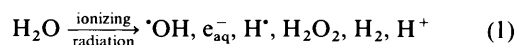
A number of fragment products with one to three carbon atoms have also been found which may result from the degradation of some of the endoperoxidic intermediates derived from the radicals **5**, **6** and **7**.

A material balance is presented which accounts for the oxygen consumed in this system.

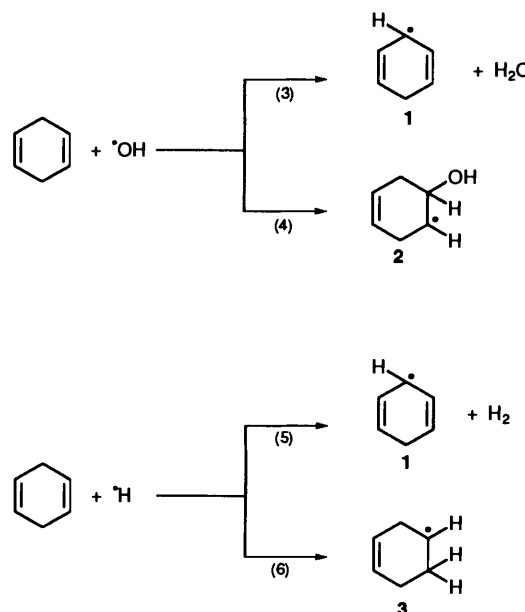
Bisallylic hydrogen atoms are only weakly bound ($73 \pm 5 \text{ kcal mol}^{-1}$ in the case of cyclohexa-1,4-diene).^{1,2} Hence they are a preferred site for free-radical attack. A typical example is the autoxidation of polyunsaturated fatty acids which proceeds as a chain reaction involving pentadienyl radicals and their corresponding peroxy radicals (for a review see Ref. 3).

Cyclic cyclohexadienyl radicals are generated when radicals abstract an H-atom from cyclohexa-1,4- or -1,3-diene^{4,5} or add to aromatic compounds such as benzene. Again, such cyclohexadienyl radicals may be of some biological relevance, and in the biodegradation (detoxification) of benzene one line of thought is that the enzymatic degradation may lead to a hydroxy-substituted cyclohexadienyl radical in the first step.⁶ Thus the fate of such intermediates is of great interest. We have taken up this subject recently (see Refs. 7, 8), as well as the study of unsubstituted cyclohexadienyl peroxy radicals presented here, in the hope that the results from each system would complement the other as is indeed the case.

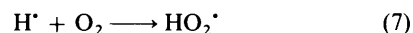
Radiation techniques provide powerful tools for the study of the formation and fate of peroxy radicals in aqueous solution.^{3,9} In the radiolysis of N₂O-saturated aqueous solutions, hydroxyl radicals are formed, as shown in reactions (1) and (2). The OH radicals react with added cyclohexa-1,4-

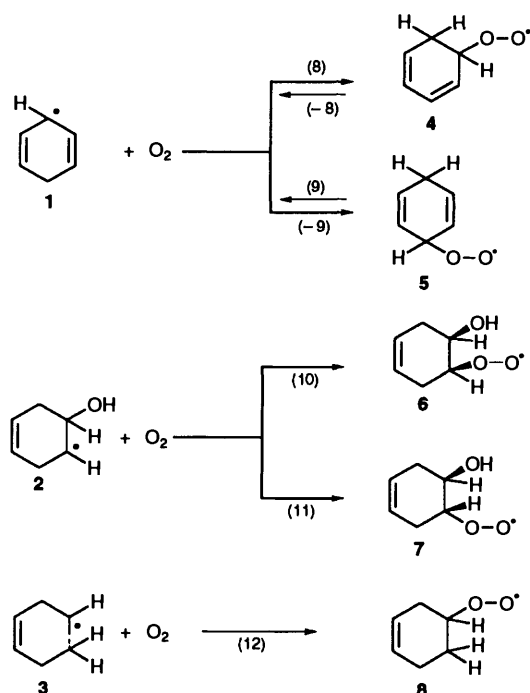


diene by H-abstraction [reaction (3)] and addition to a C=C double bond [reaction (4); $k_{3,4} = 7.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$].⁴



These two reactions occur with about equal probability.⁵ At high cyclohexa-1,4-diene concentrations the H-atoms react mainly with the substrate [reactions (5) and (6), $k_{5,6} = 4.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_5/k_6 = 0.28$]^{4,5} and only a minor fraction is scavenged by the oxygen [reaction (7);

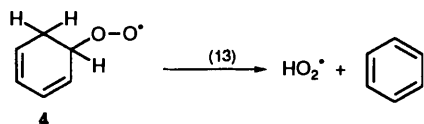




$k_7 = 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.¹⁰ In the presence of oxygen (*i.e.*, in N₂O/O₂ (4:1 v/v)-saturated solutions), oxygen converts the substrate radicals into the corresponding peroxy radicals [reactions (8)–(12)].

In the bimolecular termination reactions the cyclohexadienyl radicals **1** react from their cyclohexa-2,4-dienyl as well as their cyclohexa-2,5-dienyl structure yielding the corresponding dimers.⁵ Similarly, in their reaction with oxygen two different peroxy radicals (**4** and **5**) must be formed. Also two isomers (*cis* and *trans*) are produced (the radicals **6** and **7**) when the 6-hydroxycyclohex-3-enyl radical **2** reacts with oxygen.

In the autoxidation of cyclohexa-1,4-diene in a *non-aqueous medium*, it has been suggested that the major product benzene is formed by an elimination of the HO₂ radical from the cyclohexadienylperoxy radicals in a chain process involving the HO₂ radical as the chain-propagating and terminating species.¹¹ It will be shown in this work that only the peroxy radical **4** can eliminate HO₂ [reaction (13)].



The present study was carried out in *aqueous solutions* using ionizing radiation to produce the radicals. This has two advantages: the yields of the primary radicals are known { $G(\cdot\text{OH}) = 5.8 \times 10^{-7} \text{ mol J}^{-1}$, hence $G(\mathbf{1}) = G(\mathbf{4} + \mathbf{5}) = 2.9 \times 10^{-7} \text{ mol J}^{-1}$ and $G(\mathbf{2}) = G(\mathbf{6} + \mathbf{7}) = 2.9 \times 10^{-7} \text{ mol J}^{-1}$;⁵ $G(\text{H}\cdot) = 0.57 \times 10^{-7} \text{ mol J}^{-1}$, $G(\mathbf{3}) = G(\mathbf{8}) \leq 0.44 \times 10^{-7} \text{ mol J}^{-1}$ depending on $[\text{O}_2]/[\text{1,4-CHD}]$ } on which a product material balance can be based, and kinetic studies can be done in pulse radiolysis experiments by applying the ionizing radiation as a submicrosecond pulse and monitoring the formation and subsequent decay of the peroxy radicals either by photometry or conductimetry. The latter technique is especially useful whenever HO₂· radicals [$\text{H}^+ + \text{O}_2^{\cdot-}$; $\text{p}K_a(\text{HO}_2\cdot) = 4.8$]¹² are released from neutral peroxy radicals. The combination of product studies and pulse radiolysis has already yielded a large body of data that has enabled us to give

a detailed picture of the different pathways by which organic peroxy radicals can decay in an aqueous environment.^{3,9}

In the present study it will be shown that the cyclohexadienylperoxy radical **4** indeed rapidly eliminates HO₂·, but that the chemistry of its isomer **5** is very different. Some data concerning the fate of the peroxy radicals **6** and **7** will also be given.

Experimental

Cyclohexa-1,4-diene (1,4-CHD) (Merck) was redistilled under reduced pressure after which it contained <0.1% benzene. *trans*-4,5-Dihydroxycyclohexene **20** and 1,2,4,5-tetrahydroxycyclohexanes **16** were synthesized by reacting 1,4-CHD with 30% hydrogen peroxide in 98% formic acid. The identity of **20** was confirmed by IR, ¹H NMR [$\delta(270 \text{ MHz}; \text{D}_2\text{O})$ 2.1 (4 H, ddd, *J* 3, 5 and 15, CH₂), 3.6 (2 H, m, CHOD) and 5.5 (2 H, d, *J* 3, CH)] and GC-MS. The mass spectrum of the trimethylsilyl derivative of **20** ($M = 258$) is characterized by m/z (%) 258 (2.5), 243 (2.3), 204 (64), 168 (37), 155 (45), 147 (54) and 73 (100). The mass spectra of the trimethylsilyl derivatives of **16** ($M = 436$) are characterized by m/z (%): 421 (0.13), 346 (1.6), 331 (6.2), 256 (4.3), 241 (1.7), 230 (3.6), 217 (100), 191 (5.3), 167 (5.9), 147 (26), 133 (5.9), 103 (10.5) and 73 (72). 3,4,6-Trihydroxycyclohexenes **12** were independently synthesized by steady-state γ -radiolysis of an N₂O-saturated cyclohexa-3,5-diene-1,2-diol solution in the presence of 1,4-dithiothreitol (DDT) (*cf.* Ref. 5). The mass spectra of the trimethylsilyl derivatives of **12** thus generated are characterized by m/z (%): 331 ($M - 15; 0.5$), 256 ($M - 90; 0.5$), 230 (100), 204 (1), 147 (20) and 73 (75).

Solutions were made up in Millipore Milli-Q filtered water. Typically, prior to addition of the necessary amount of 1,4-CHD the water was saturated with a 4:1 mixture of N₂O and O₂ (Messer Griesheim). Oxygen concentrations deviating from these standard conditions were made up by using a Brooks gas-mixing device.

Benzene and phenol were determined by HPLC on Nucleosil 5C18 reversed-phase columns (benzene: 2.5 cm column, water as the eluent, retention time 4 min; phenol: 12 cm column, 5×10^{-3} phosphate buffer pH 7 as the eluent, retention time 25 min). Hydrogen peroxide and organic hydroperoxides were determined using the potassium iodide method (Allen's reagent).¹³ Low-molecular-weight aldehydes were converted with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (Fluka) at pH 3 into the corresponding oximes, and after addition of acid and salt the oximes were extracted into cyclohexane. Their yields were determined by GC (20 m, OV-225, 50–220 °C, 8 °C min⁻¹) using cyclohexanone as an internal standard. 4,5-Dihydroxycyclohexenes (**20** and **21**) and 6-hydroxycyclohex-3-enone **19** were determined by GC by injecting the irradiated sample directly into a 20 m FFAP column (60–230 °C) with its stationary phase cross-linked by γ -irradiation in order to prevent its destruction by water. Endoperoxides and hydroperoxides which cannot be determined in this way were reduced with NaBH₄ (or with NaBD₄) to the corresponding alcohols. Of the NaBH₄-reduced products only 4-hydroxycyclohexene (extracted into cyclohexane) could be analysed directly by GC (30 m CW-20M, 70–200 °C). The other NaBH₄-reduced products were trimethylsilylated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Fluka) and trimethyl(chloro)silane (TMCS) in pyridine and analysed by GC-MS on a Hewlett-Packard 5971A mass selective detector coupled with an HP 5890 Series II gas chromatograph using a 50 m PS-240 column operating at 50–240 °C. In some cases the irradiated samples before and after NaBH₄ reduction were analysed by HPLC on a 12 cm Nucleosil 5C18 reversed-phase column eluted with water and detected at 200 nm.

For pulse radiolysis a 2.8 MeV van de Graaff electron accelerator delivering pulses of 0.4–4 μs duration was used. The

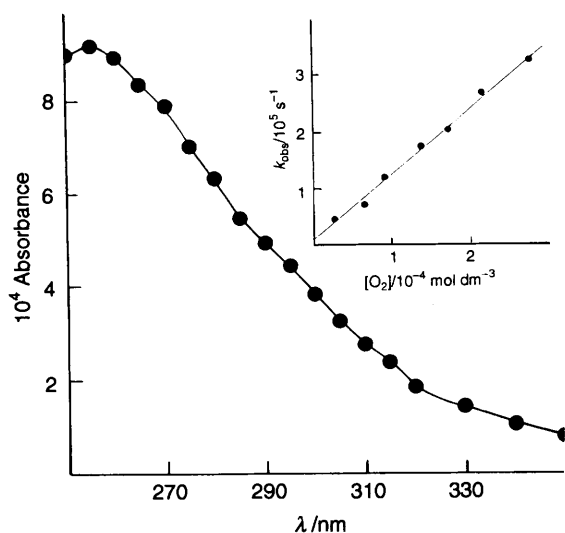


Fig. 1 Transient UV absorption spectrum (normalized to 1 Gy) of pulse-irradiated N_2O/O_2 -saturated aqueous solution of cyclohexa-1,4-diene measured 30 μs after the pulse. Inset: plot of k_{obs} vs. $[O_2]$

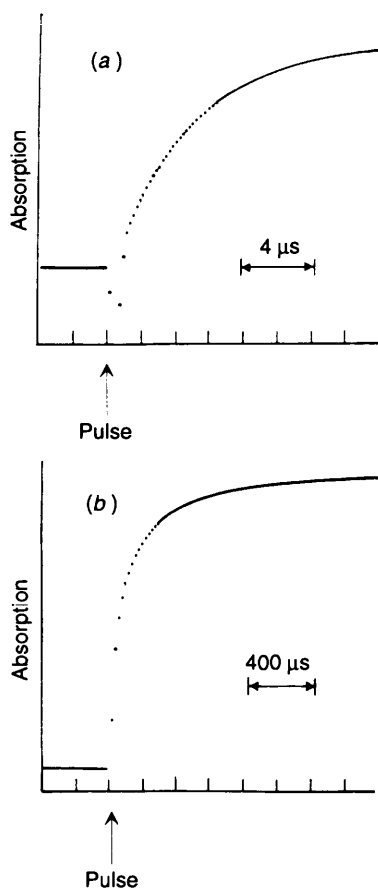


Fig. 2 Build-up of nitroform anions monitored at 350 nm in the pulse radiolysis (4 Gy pulse $^{-1}$, pulse length 0.4 μs) of N_2O/O_2 -saturated aqueous solutions of cyclohexa-1,4-diene (10^{-2} mol dm $^{-3}$) containing tetranitromethane (3×10^{-4} mol dm $^{-3}$) at pH 6.5: (a) initial fast component, 2 μs per time division; (b) 200 μs per time division

set-up in its most recent version has been described.¹⁴ The dosimetry was done as reported earlier.¹⁵ Tetranitromethane (TNM) reacts noticeably with 1,4-CHD when the latter is present at high concentrations. For this reason in steady-state experiments using TNM the 1,4-CHD concentrations were kept at $\leq 3 \times 10^{-4}$ mol dm $^{-3}$, and in pulse radiolysis experiments solutions containing TNM and 1,4-CHD were kept in two

different bottles and were only mixed just before being placed in the pulse radiolysis cell.

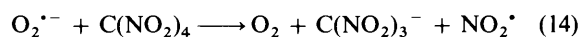
Results and Discussion

1. *Pulse radiolysis.*—1.1. *Formation of peroxy radicals.* The cyclohexadienyl radical **1** formed in reaction (3) is well characterized by a UV absorption maximum at 310 nm^{4,16} with an absorption coefficient of 4400 dm 3 mol $^{-1}$ cm $^{-1}$ redetermined in our preceding study.⁵ The absorption maximum of radical **2** is expected¹⁷ to lie below 240 nm and cannot be observed under our experimental conditions.

In N_2O/O_2 -saturated solutions of 1,4-CHD immediately following the electron pulse, the absorption of radical **1** with the maximum at 310 nm was observed to decay rapidly as the radicals **1**, **2** and **3** were converted into the corresponding peroxy radicals **4–8** [reactions (8)–(12)]. The resulting composite absorption spectrum is shown in Fig. 1. The rate constant of oxygen addition was determined by following the decay of **1** at 310 nm in 1,4-CHD-containing solutions which had been saturated with N_2O/O_2 of varying composition ($[O_2] \leq 20\%$ v:v). The observed rate constant of the decay of **1** was a linear function of the oxygen concentration (*cf.* inset in Fig. 1). From the slope of the k_{obs} vs. $[O_2]$ plot the overall rate constant for oxygen addition [reactions (8)–(12)] was obtained, $k = 1.2 \times 10^9$ dm 3 mol $^{-1}$ s $^{-1}$.

In a previous study we have shown that hydroxycyclohexadienyl radicals and oxygen are in equilibrium with the corresponding peroxy radicals.⁷ This is, in principle, also expected for the unsubstituted cyclohexadienyl radicals **1** and its corresponding peroxy radicals **4** and **5**. However, as will be shown below, the radicals **4** and **5** undergo rapid unimolecular decay reactions. For this reason it has not been possible in this case to observe the reversibility of the oxygen addition [*i.e.*, the equilibria (8)/(–8) and (9)/(–9)] at the oxygen concentrations achievable at ambient pressure. The small intercept shown in the inset of Fig. 1 is not necessarily an indication of such reversibility, since some contribution from the bimolecular decay of the radicals must be taken into account here (about 10^4 s $^{-1}$ at the given doses).

1.2. *Unimolecular formation of HO_2^* .* Following oxygen addition, the rapid formation of $HO_2^*/O_2^{*-} + H^+$ was observed through the reaction of O_2^{*-} with tetranitromethane (TNM) [reaction (14), $k_{14} = 1.9 \times 10^9$ dm 3 mol $^{-1}$ s $^{-1}$].^{12,18} This gives rise to the strongly absorbing nitroform anion NF^- [$\epsilon(350 \text{ nm}) = 15000$ dm 3 mol $^{-1}$ cm $^{-1}$].¹⁸ Other peroxy radicals, which have oxidizing rather than reducing properties, do not react with TNM. Even the (potentially reducing) HO_2^* radical does not react with TNM on the pulse radiolysis timescale ($k < 10^5$ dm 3 mol $^{-1}$ s $^{-1}$).¹²



The build-up of the nitroform anion in the pulse radiolysis of an N_2O/O_2 (4:1)-saturated 1,4-CHD solution containing 3×10^{-4} mol dm $^{-3}$ TNM consists of two steps as shown in Fig. 2 over two time ranges. It can be seen from Fig. 2(a) that the major event is a very fast build-up with $k_{obs} = 3.0 \times 10^5$ s $^{-1}$ and $G(NF^-) = 1.7 \times 10^{-7}$ mol J $^{-1}$. Both of these values are independent of dose rates (3–22 Gy/pulse). This is followed by a smaller and much slower build-up with $k_{obs} = 5.4 \times 10^3$ s $^{-1}$ and $G(NF^-) = 0.4 \times 10^{-7}$ mol J $^{-1}$. Since this second step is of such low yield and slow rate, no attempt has been made to investigate it further.

The first-order rate constant of this fast NF^- build-up [*cf.* Fig. 2(a)] has been measured as a function of the TNM concentration in a solution saturated with N_2O/O_2 (4:1) (Fig. 3). At low TNM concentrations k_{obs} increases

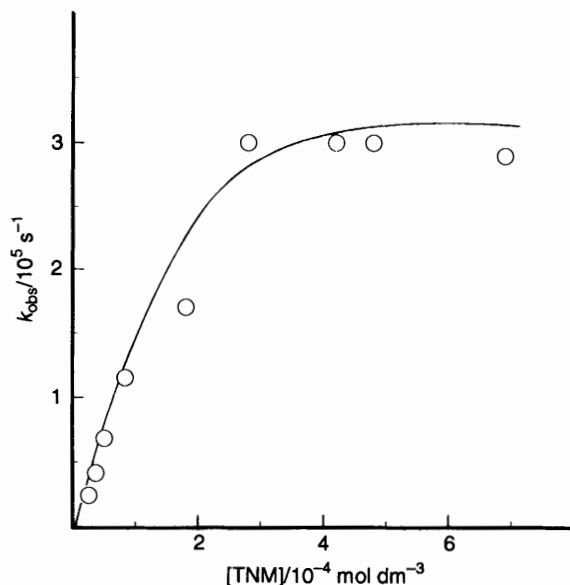


Fig. 3 Pulse radiolysis (3 Gy pulse⁻¹) of N₂O/O₂-saturated aqueous solutions of cyclohexa-1,4-diene (10⁻² mol dm⁻³) containing tetra-nitromethane at pH 6.5. Dependence of the observed first-order rate constant of the fast build-up of nitroform anions on the TNM concentration.

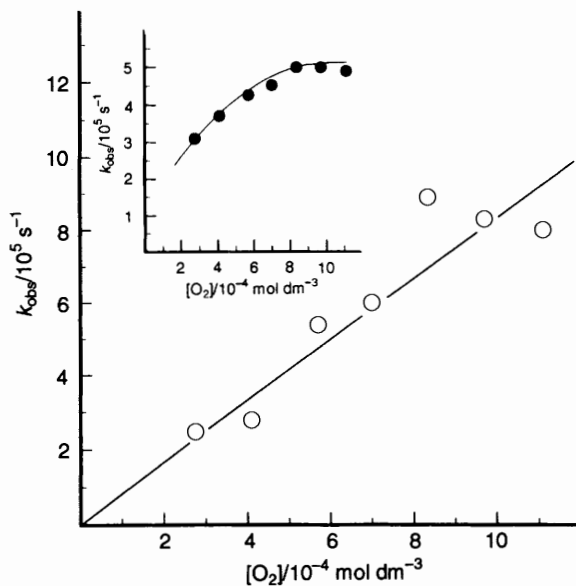


Fig. 4 Pulse radiolysis (3 Gy pulse⁻¹) of N₂O/O₂-saturated aqueous solutions of cyclohexa-1,4-diene (10⁻² mol dm⁻³) containing tetra-nitromethane (5 × 10⁻⁴ mol dm⁻³). Dependence of the observed first-order rate constant of the fast build-up of nitroform anions on the oxygen concentrations at pH 10.3. Inset: k_{obs} vs. [O₂] at pH 6.5.

proportionally to the increasing TNM concentration as determined by the rate of reaction (14). However, at TNM concentrations higher than 3×10^{-4} mol dm⁻³, k_{obs} reaches a plateau value of 3.0×10^5 s⁻¹. Since this is the limiting rate of oxygen addition [reactions (8)–(12)] at 20% oxygen (2.7×10^{-4} mol dm⁻³), further experiments were carried out in solutions saturated with mixtures of N₂O/O₂ containing up to 80% oxygen to overcome this limitation (Fig. 4).

At pH 6.5 and with a TNM concentration of 5×10^{-4} mol dm⁻³ where reaction (14) is not rate-limiting, k_{obs} of NF⁻ build-up increases with oxygen concentration to about 40% O₂. At still higher oxygen concentrations it reaches a plateau (inset of Fig. 4). This could mean that the plateau now represents the rate constant for the unimolecular decay of a cyclohexadienylperoxyl radical. On the other hand, it is known that the HO₂[•] radical

reacts only very slowly with TNM (see above) and the plateau value of 5×10^5 s⁻¹ is very close to the rate constant expected for the deprotonation of the HO₂[•] radical.

In order to distinguish between these two possibilities the same experiments were repeated at pH 10.3 instead of at pH 6.5 where the high OH⁻ concentration speeds up the deprotonation of the HO₂[•] radical (Fig. 4). Under these conditions k_{obs} of the fast NF⁻ build-up continues to increase with oxygen concentration above 60% O₂ (8×10^{-4} mol dm⁻³) to above 8×10^5 s⁻¹ (here the time resolution of our experimental method reaches its limit, *cf.* substantial experimental errors). From these results it follows that the plateau value at 5×10^5 s⁻¹ obtained at pH 6.5 (inset in Fig. 4) represents the rate of the deprotonation of the HO₂[•] radical. We therefore conclude that O₂ adds to the cyclohexadienyl radical and HO₂[•] is subsequently eliminated. The HO₂[•]-elimination must at least be as fast as the oxygen addition at $\geq 60\%$ O₂ (*i.e.* $k_{13} \geq 8 \times 10^5$ s⁻¹). The alternatives, direct electron transfer from the cyclohexadienyl radical to O₂, or oxygen addition followed by O₂⁻ release, can be ruled out (with the concomitant formation of a cyclohexadienyl carbonation: reactions of this kind have been found in the rapid formation of O₂⁻ from the reactions of the dimethylaminomethyl radical¹⁹ and the 1,1-dimethoxyethyl radical²⁰ with oxygen).

The *G* value of benzene formation in an N₂O/O₂-saturated 1,4-CHD solution under pulse radiolysis conditions (2.5–25 Gy/pulse) has been determined to be 1.6×10^{-7} mol J⁻¹ (Table 2). This is in good agreement with *G*(HO₂[•]) observed in the first step of NF⁻ build-up. This finding excludes the possibility that the second (slow) step of NF⁻ build-up is due to further benzene formation. The cyclohexadienylperoxyl radicals **4** and **5** are formed with a *G* value of 2.9×10^{-7} mol J⁻¹ (see the Introduction). This means that only a fraction (*ca.* 60%) of the cyclohexadienylperoxyl radicals formed in this system eliminates HO₂[•].

The question now arises as to which of the two conceivable radicals **4** or **5** gives rise to this reaction. Since this reaction occurs by H-transfer (*i.e.*, HO₂[•]-elimination as shown above), one would expect that the distance between the oxygen which carries the odd electron and a bisallylic H atom must play an important role. If one may assume that the carbon skeleton of radical **4** retains the structure of cyclohexa-1,3-diene (radical **5** that of cyclohexa-1,4-diene) (for the structures of cyclohexa-1,3- and -1,4-diene see Ref. 21), and that the angle at the central oxygen of the COO[•] group is between 90° and 120°,²² it can be calculated that in **4** this distance is only 1.4–2.2 Å, compared with 3.5–4.2 Å in **5**.

Stereoelectronic factors such as a suitable alignment of the accepting oxygen orbital and the C–H σ-bond to be cleaved influence the readiness of the HO₂[•]-elimination. The orbital overlap decreases exponentially with the distance. The difference between these two distances in **4** and **5** is considerable. We therefore believe that the fast HO₂[•]-elimination is due to the reaction involving the much shorter distance, *i.e.*, is due to reaction (13). This conclusion is supported by results of a detailed study on the decay of hydroxycyclohexadienylperoxyl radicals.⁸ There it has been shown that the peroxyl radical with the cyclohexa-1,3-diene structure (corresponding to **4**) also undergoes fast HO₂[•]-elimination. At the high dose rates of a pulse radiolysis its bimolecular decay product, catechol, has not been observed, whereas hydroquinone, which is the bimolecular decay product of the other hydroxycyclohexadienylperoxyl radical with the cyclohexa-1,4-diene structure (corresponding to **5**), has been found as a major product.

A list of the rate constants determined in this work is given in Table 1.

2. Steady-state γ-Radiolysis.—2.1. Studies at high 1,4-CHD

Table 1 Compilation of the rate constants determined in the present study

Reactions	Rate constants	
(8), (9), (10), (11), (12)	$k(\text{O}_2 \text{ addition})$	$1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
(13)	$k(4 \rightarrow \text{benzene} + \text{HO}_2)$	$\geq 8 \times 10^5 \text{ s}^{-1}$
(15)	$k(6, 7 + 6, 7)$	$1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1 a}$
(26), (27)	$k(6, 7 + 1,4\text{-CHD})$	$820 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1 a}$

^a Obtained by computer simulation.

Table 2 γ -Radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated aqueous solutions of cyclohexa-1,4-diene ($10^{-2} \text{ mol dm}^{-3}$) at a dose rate of 0.14 Gy s^{-1} : products and their G values. Benzene and phenol were also determined under the high dose rate (25 Gy/pulse) of pulse radiolysis.

Products	Precursors	Determined as TMS-derivatives after reduction with NaBH_4	$G/10^{-7} \text{ mol J}^{-1}$	
			γ	e^- -beam
Benzene	4		2.8	1.6
<i>cis</i> -6-Hydroxycyclohex-3-enyl hydroperoxide 18	7	<i>cis</i> -4,5-Dihydroxycyclohexene 21	1.3	
<i>trans</i> -6-Hydroxycyclohex-3-enyl hydroperoxide 17	6	<i>trans</i> -4,5-Dihydroxycyclohexene 20	1.5	
Cyclohexene endoperoxidic hydroperoxides 11	5	Trihydroxycyclohexenes 12	0.4	
Hydroxycyclohexane endoperoxidic hydroperoxides 15	6, 7	1,2,4,5-Tetrahydroxycyclohexanes 16	0.2	
Cyclohex-3-enyl hydroperoxide	8	4-Hydroxycyclohexene ^a	0.3	
Phenol	5		Absent	0.1
Lactic acid	5, 6, 7		0.32	
Glyoxal	5, 6, 7		0.15	
Acetaldehyde	5, 6, 7		0.44	
Formaldehyde	5, 6, 7		0.7	
Hydrogen peroxide			2.3	
Total organic hydroperoxides			3.5	
Superoxide radicals			4.6 ^b	
Oxygen uptake			7.5	

^a Not trimethylsilylated. ^b Determined at $[1,4\text{-CHD}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$.

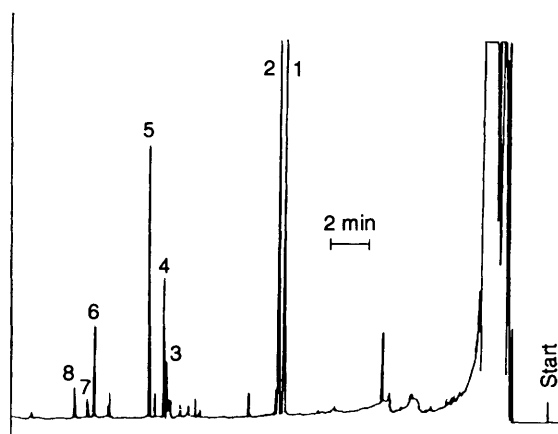


Fig. 5 Gas chromatogram of trimethylsilylated NaBH_4 -reduced products in the γ -radiolysis of an $\text{N}_2\text{O}/\text{O}_2$ -saturated cyclohexa-1,4-diene solution: 1, *cis*-4,5-dihydroxycyclohexene **21**; 2, *trans*-4,5-dihydroxycyclohexene **20**; 3–5, trihydroxycyclohexenes; 6–8, 1,2,4,5-tetrahydroxycyclohexanes

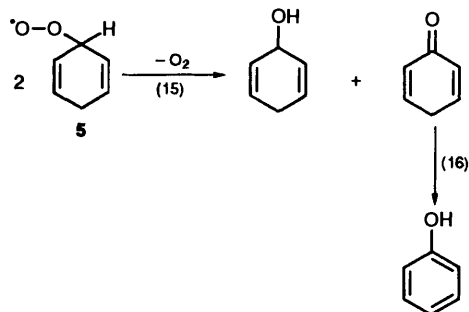
concentrations. In the γ -radiolysis of $\text{N}_2\text{O}/\text{O}_2$ -saturated 1,4-CHD ($10^{-2} \text{ mol dm}^{-3}$) solutions benzene is the major product (*cf.* Table 2). Its yield is even higher than under pulse radiolysis conditions. There is also a large amount of organic hydroperoxides formed. To identify these peroxidic products the irradiated samples were reduced with NaBH_4 and the resulting products were trimethylsilylated. After this treatment a number of polyhydric alcohols were identified by GC-MS. These are the *cis*- and *trans*-isomers of dihydroxycyclohexenes, at least three isomers of trihydroxycyclohexenes (the exact positions of the

OH-groups are not yet established), and three isomers of 1,2,4,5-tetrahydroxycyclohexanes (see Fig. 5). Although small amounts of dihydroxycyclohexenes have been observed in the irradiated and silylated samples without the NaBH_4 reduction, these were actually decay products of the unstable hydroperoxides during the work-up procedures for silylation. When the irradiated samples were analysed directly by HPLC, the dihydroxycyclohexenes were absent. Furthermore, when the reduction was carried out with NaBD_4 instead of with NaBH_4 and the resulting products trimethylsilylated, the mass spectra of these polyhydric alcohols showed no incorporation of deuterium. These results indicate that the precursors of these polyhydric alcohols did not contain any carbonyl function, but instead hydroperoxidic and/or endoperoxidic functions. Since the sum of the G values of these polyalcohols determined by GC matches the G value of total organic hydroperoxides determined by the iodimetric method (see Table 2), we conclude that these polyhydric alcohols derive exclusively from the corresponding hydroperoxides and endoperoxyhydroperoxides as the result of NaBH_4 reduction.

2.2. The fate of peroxy radical 5. An oxygen-carbon binding energy of $\leq 15 \text{ kJ mol}^{-1}$ may be estimated for **4** and **5**.²³ Thus reactions (8) and (9) are likely to be reversible at room temperature on the timescale we are concerned with in the pulse radiolysis experiments. We have shown that reaction (13) is very fast. If radical **5** breaks up into **1** and O_2 [reaction (–9)], eventually all radicals **1** should be converted into HO_2^{\cdot} and benzene by following reaction route (13). Since this is not the case, one may conclude that there are other faster decay routes for radical **5** than the reverse reaction (–9).

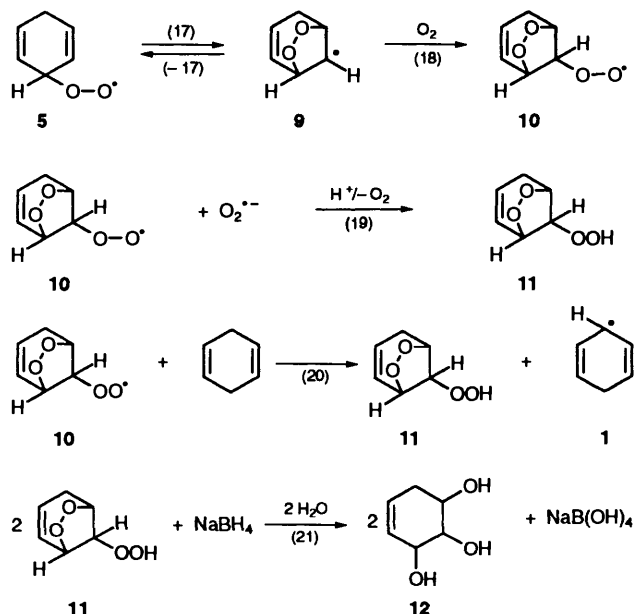
Phenol would be the key product [*via* the unstable cyclohexa-2,5-dieneone,^{24,25} *cf.* reaction (16)] if peroxy radicals **5** decay

bimolecularly according to the Russell mechanism [reaction (15)] or other well-known bimolecular decay routes for peroxy radicals with an H atom at the α -position to the peroxy function as in **5** (cf. Refs. 3, 9). However, under the conditions of γ -



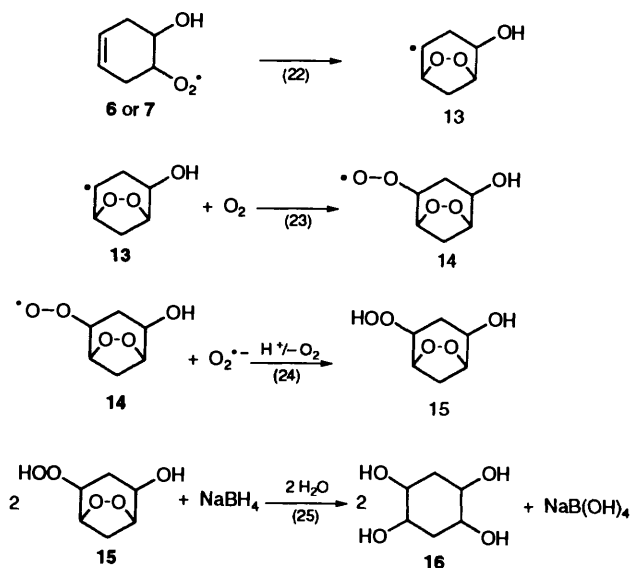
radiolysis phenol is not among the products (Table 2) and at the much higher dose rates of pulse radiolysis it is a very minor product [$G(\text{phenol}) = 0.03 \times 10^{-7} \text{ mol J}^{-1}$ at $2.5 \text{ Gy pulse}^{-1}$ and $0.1 \times 10^{-7} \text{ mol J}^{-1}$ at 25 Gy pulse^{-1}]. These results indicate that radical **5** decays mainly *via* some fast unimolecular reaction except under extremely high dose rate conditions where its bimolecular decay reactions can start to compete.

One such fast unimolecular decay route available to radical **5** is the intramolecular addition of the peroxy radical to one of the double bonds [reaction (17)] to give an endoperoxidic radical **9**. Such reactions are well documented, both as intramolecular and as intermolecular reactions.²⁶⁻³¹ Although this type of reaction is endothermic by $\leq 15 \text{ kcal mol}^{-1}$ and hence reversible,²³ radical **9** can be scavenged by oxygen [reaction (18)] to give the corresponding peroxy radical **10**. Two reductants are available in this system, $O_2^{\cdot-}$ and 1,4-CHD, to convert radical **10** into the corresponding endoperoxidic hydroperoxide **11** [reactions (19) and (20)]. After reduction with NaBH_4 **11** is converted into the trihydroxycyclohexenes [reaction (21)].



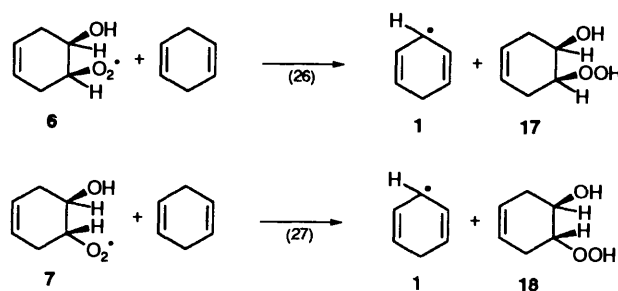
2.3. Unimolecular decay reactions of the peroxy radicals **6 and **7**.** The identification of 1,2,4,5-tetrahydroxycyclohexanes **16** (see Fig. 5 and Table 2) after reduction of the radiation products with NaBH_4 points to the formation of a product with a hydroxy group in addition to an endoperoxidic function and a hydroperoxidic group. In the peroxy radicals **6** and **7** there is a

hydroxy group as well as an unsaturated bond for intramolecular addition by the peroxy radical function. In a similar fashion to the reactions of radical **5** we suggest that radicals **6** and **7** also decay unimolecularly to form a new radical **13** with an endoperoxidic function [reaction (22)]. In a route similar to that depicted for radical **9**, radical **13** will eventually be converted into **16** [reactions (23)–(25)].



2.4. 1,4-CHD concentration dependence. At the 1,4-CHD concentration of $10^{-2} \text{ mol dm}^{-3}$ the sum of products listed in Table 2 exceeds the total peroxy radical yields by about 20%. This is accompanied by a high oxygen uptake of $G = 7.5 \times 10^{-7} \text{ mol J}^{-1}$. When the concentration of 1,4-CHD was reduced to $4 \times 10^{-4} \text{ mol dm}^{-3}$, $G(O_2 \text{ uptake})$ decreased to $5.6 \times 10^{-7} \text{ mol J}^{-1}$ (Fig. 6 inset). As shown in Fig. 6, the yields of benzene and of the hydroperoxides **17** and **18** are also lower at lower 1,4-CHD concentrations. In contrast, the yields of the diols **20** and **21**, which are absent at high 1,4-CHD concentrations, become more and more prominent at lower 1,4-CHD concentrations. These results indicate that some chain reactions involving 1,4-CHD, which has four readily abstractable bisallylic hydrogens, may take place at high concentrations of 1,4-CHD.

At $10^{-2} \text{ mol dm}^{-3}$ 1,4-CHD, essentially all of radicals **6** and **7** end up as the hydroxycyclohexene hydroperoxides **17** and **18** (see Table 2). These are formed when **6** and **7** abstract one of the four bisallylic hydrogens from 1,4-CHD [reactions (26) and (27)]. Concomitantly radical **1** is regenerated.



2.5. Studies at low 1,4-CHD concentrations: bimolecular decay reactions of the peroxy radicals **6 and **7**.** Since there is a relatively high steady-state concentration of $O_2^{\cdot-}$ present in the system due to reactions (7) and (13) and its relatively slow rate

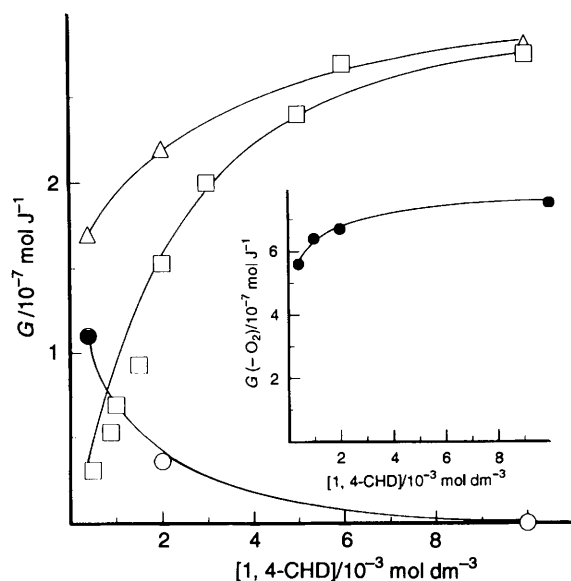
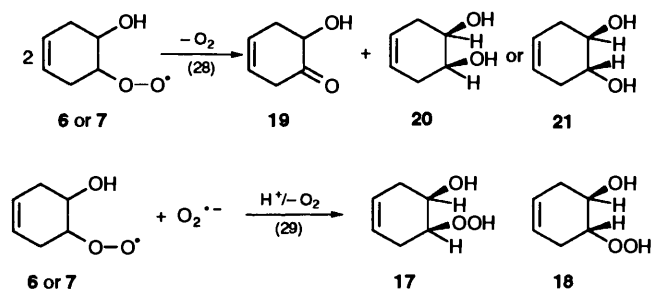


Fig. 6 Dependence of the G values of products in the γ -radiolysis of N_2O/O_2 -saturated 1,4-CHD solutions on 1,4-CHD concentrations: Δ , benzene; \square , hydroperoxides **17** and **18** in 1,4-CHD solutions containing SOD; \circ , dihydroxycyclohexenes **20** and **21**; \bullet , **20** and **21** in a 1,4-CHD solution containing SOD. Inset: G (oxygen uptake) as a function of 1,4-CHD concentrations.

of dismutation, some fractions of radicals **6** and **7** may react with $O_2^{\cdot -}$ and lead to the formation of **17** and **18** [reaction (29)]. In order to study the products of the bimolecular decay of radicals **6** and **7**, superoxide dismutase (SOD) was added to the 1,4-CHD solution to remove $O_2^{\cdot -}$ and the concentration of 1,4-CHD was reduced to $4 \times 10^{-4} \text{ mol dm}^{-3}$.

The products and their G values are compiled in Table 3. As expected at this low 1,4-CHD concentration where H-abstraction of the substrate by the peroxy radicals **6**, **7** and **10** [reactions (26), (27) and (20)] are unlikely, the G value of benzene is identical with that observed under pulse radiolysis conditions (see above). It represents the primary yield of radical **4**. It can be seen in Table 3 that the sum of the G values of *trans*- and *cis*-4,5-dihydroxycyclohexenes (**20** and **21**) is about equal to that of 6-hydroxycyclohex-3-enone (**19**). Their combined yields account for $> 80\%$ of their precursor radicals **6** and **7** [$G(\mathbf{6}, \mathbf{7}) = G(\mathbf{2}) = 2.9 \times 10^{-7} \text{ mol J}^{-1}$]. These results indicate that under these conditions radicals **6** and **7** decay essentially bimolecularly according to reaction (28). Most likely for steric reasons the formation of peroxy radical **6** (*trans* configuration) is favoured over that of peroxy radical **7** (*cis* configuration). This explains the preference of the formation of *trans*-4,5-dihydroxycyclohexene **20** over that of its *cis* isomer **21** (cf. Table 3).



2.6. The rate constants of H-abstraction of the substrate by radicals **6 and **7**.** In order to estimate the rate constants of reactions (26) and (27), the formation of organic hydroperoxides at a dose rate of 0.14 Gy s^{-1} was measured in the presence of

SOD as a function of the 1,4-CHD concentrations ($4 \times 10^{-4} - 10^{-2} \text{ mol dm}^{-3}$). The G values of the hydroperoxides **17** and **18** have also been determined independently by GC after $NaBH_4$ reduction (see above) at the lowest and the highest 1,4-CHD concentrations. Since the increase in the yields of **17** and **18** account for 85% of the increase in total hydroperoxide yields over the range of the 1,4-CHD concentration used, one may make a reasoned estimate of $G(\mathbf{17}, \mathbf{18})$ from $G(\text{total hydroperoxides})$ over the whole range of 1,4-CHD concentrations. The results are plotted in Fig. 6. As can be seen from this figure, the yield of the hydroperoxides **17** and **18** increases with increasing 1,4-CHD concentrations reaching, at high 1,4-CHD concentrations, a plateau value near $G(\mathbf{17}, \mathbf{18}) = 2.8 \times 10^{-7} \text{ mol J}^{-1}$.

The behaviour displayed in Fig. 6 is consistent with the above-mentioned competition. The G value of hydroperoxide formation is given by expression (30).

$$G(\mathbf{17}, \mathbf{18}) = \frac{G(\mathbf{6}, \mathbf{7}) \times k_{26,27} \times [1,4\text{-CHD}]}{k_{26,27} \times [1,4\text{-CHD}] + k_{28}[\mathbf{6}, \mathbf{7}]} \quad (30)$$

The values $k_{28} = 1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{26,27} = 820 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ have been obtained by computer simulation whereby $G(\mathbf{17}, \mathbf{18})$ was the entity to be simulated. The value for k_{28} is within the wide spread of values found for the bimolecular decay of peroxy radicals.⁹ The value for $k_{26,27}$ appears to be a reasonable value judged by the value of $362 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reported for the reaction of peroxy radicals derived from polyunsaturated fatty acids with 1,4-CHD.³²

2.7. Fragment products. Besides these products with intact carbon-skeletons, there are a number of fragment products with one to three carbon atoms as listed in Table 2. Those fragment products with four or more carbon atoms seem to have negligible yields and no attempt has been made to characterize them in detail. Excessive fragmentation has also been observed in the case of the $\cdot OH/\text{benzene}/O_2$ system.⁸ In the present case they are by no means straightforward bimolecular fragmentations as are known to occur with simpler peroxy radicals.^{3,9} For example it is noted that two products, lactic acid and acetaldehyde carry methyl groups, a structural element which does not exist in 1,4-CHD. Concomitant with the breakdown of the six-carbon ring structure, 1,2-H shifts must have occurred. Similar types of reaction have been observed in the decay of five-membered cyclic peroxides.²⁹ The endoperoxidic intermediates derived from radicals **5**, **6** and **7** discussed above do have the structural elements of a five-membered cyclic peroxide. It is conceivable that the degradation of these intermediates leads, in part, to the fragment products observed here.

2.8. Material balance. It has been shown above that under pulse-radiolysis conditions $G(\text{benzene})$ is only $1.6 \times 10^{-7} \text{ mol J}^{-1}$ and that it can be related to the fast HO_2^{\cdot} -elimination of radical **4**. At high 1,4-CHD concentration and at the low dose rate of γ -radiolysis (Table 2), the yield of radical **1** is considerably higher owing to reactions (20), (26) and (27). Hence $G(\text{benzene})$ and $G(O_2^{\cdot -})$ also increase. Concomitantly all primary radicals **2** are converted into *cis*- and *trans*-6-hydroxycyclohex-3-enyl hydroperoxides **18** and **17**, and endoperoxides **15** (which upon reduction with $NaBH_4$ give rise to the 1,2,4,5-tetrahydroxycyclohexanes **16**). The total yield of these products ($G = 3.06 \times 10^{-7} \text{ mol J}^{-1}$) agrees well with the yield of **2** determined earlier at $G = 2.9 \times 10^{-7} \text{ mol J}^{-1}$.⁵

Although a detailed mechanism for the fragmentation routes cannot be given, an overall oxygen material balance can be put forward. It can be shown that such a value agrees to $\leq 10\%$ with the value for oxygen uptake given in Table 2. Hence we conclude that not much material has escaped our detection, although it is quite possible that it is distributed among a large number of minor products.

Table 3 γ -Radiolysis of N_2O/O_2 (4:1 v:v)-saturated aqueous solutions of cyclohexa-1,4-diene (4×10^{-4} mol dm $^{-3}$) in the presence of superoxide dismutase (SOD) at pH 6.5: products and their *G* values

Products	Precursors	<i>G</i> /10 $^{-7}$ mol J $^{-1}$
Benzene	4	1.7
6-Hydroxycyclohex-3-enone 19	6, 7	1.3
<i>trans</i> -4,5-Dihydroxycyclohexene 20	6, 7	0.7
<i>cis</i> -4,5-Dihydroxycyclohexene 21	6, 7	0.4
<i>cis/trans</i> -6-Hydroxycyclohex-3-enyl hydroperoxides 17, 18	6, 7	0.3
Formaldehyde	5, 6, 7	1.4
Total organic hydroperoxide		0.6
Oxygen uptake		5.6

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