Hydroxyl Radical-Induced Oxidation of Diisopropyl Ether in Oxygenated Aqueous Solution. A Product and Pulse Radiolysis Study

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Diisopropyl Ether, Hydroxyl Radicals, Peroxyl Radicals, Pulse Radiolysis

Introduction

Radiation techniques have proved to be most powerful tools for studying the reactions of peroxy radicals in aqueous solutions. Hydroxyl radicals from the radiolysis of water are allowed to react with a given substrate, thus producing substrate radicals which in the presence of oxygen are usually converted rapidly (k = 2 x 10^9 dm^3 mol^-1 s^-1) [1] into the corresponding peroxy radicals. Since the yield of OH radicals per absorbed dose of ionizing radiation is well known, product studies can be easily put on a quantitative basis. Furthermore, with the use of pulse radiolysis techniques peroxy radicals can be produced within a few microseconds and their decay followed by optical and conductivity detection. In our preceding studies (cf. Ref. [2–6] and references cited in Ref. [6]) we have studied the fate of primary and secondary peroxy radicals. In the present study we investigate a system which mainly yields tertiary peroxy radicals. The incentive to study diisopropyl ether comes from another branch of our research interest: The tertiary peroxy radical of diisopropyl ether is a model for the peroxy radical at C(4') of DNA which has been implicated as a major precursor of DNA strand breakage induced by ionizing radiation and also by the anticancer drug bleomycin (for reviews see [7] [8]).

Experimental

Diisopropyl ether was purified by fractional distillation (GC>99.5%). Solutions were prepared by addition of the ether to triply distilled water presaturated with N_2O/O_2 (4:1 v/v) or pure oxygen. When pure N_2O was required, the gas was passed through another diisopropyl ether solution before reaching the solution to be irradiated. Irradiations were carried out at room temperature with a 56Co-γ source (dose rate 0.035 and 0.39 Gy s^-1) or a 2.8 MeV van de Graaff electron generator for pulse radiolysis experiments. The electron pulses were of a duration between 0.4–2 μs with doses ranging from 5 to 30 Gy. The pulse-radiolytic setup as well as the dosimetry have been described elsewhere [9]. The conductivity change was monitored by an AC-operated (10 MHz) two-cell bridge described by Asmus and Janata [10].
GC analysis of the products was carried out with a 140 m Carbowax 400 glass capillary column operated at 60 °C with H₂ as carrier gas. Formaldehyde was determined colorimetrically with chromotropic acid [11]. Total peroxide in the irradiated sample was determined iodometrically [12] allowing 1 h for complete reaction. After hydrogen peroxide had been removed by the addition of catalase, the remaining organic peroxides were determined similarly. Acidic products were determined by the conductivity increase in the irradiated solutions using a conductivity meter (Radiometer CDM 3).

Because of a lack of authentic reference material, 2-isopropanoxypropanol in the irradiated solutions was reduced by NaBH₄ (2 mg/10 cm³), after 1 h the excess reagent was destroyed with 1 mol dm⁻³ formic acid by bringing the pH to 4.5) to isopropanoxy-2-propanol, which was analysed by GC. Isopropanoxy-2-propanol was prepared from 1,2-propylene oxide and isopropanol in the presence of concentrated sulfuric acid and was identified by GC-MS. Isopropenyl isopropyl ether was prepared from 2-isopropanoxypropyl chloride by alkoxide-catalysed elimination of HCl. The ether was then purified by preparative GC (97.8% pure) and identified by GC-MS and ¹H NMR. Oxygen consumption was determined by an oxygen-specific electrode (Wiss. Techn. Werkstätten, Weilheim).

Results and Discussion

Pulse radiolysis

In the radiolysis of N₂O-saturated aqueous solutions OH radicals are generated according to reactions (i) and (ii).

\[
\text{H}_2\text{O} \xrightarrow{\text{ionizing radiation}} '\text{OH}, \text{H}, \text{H}^+, \text{OH}^-, \text{H}_2\text{O}_2, \text{H}_2
\]

(i)

\[
e^- + \text{N}_2\text{O} \rightarrow '\text{OH} + \text{OH}^- + \text{N}_2
\]

(ii)

Under such conditions the major radical species is the OH radical G(OH) ≈ 5.4 (molecules/100 eV) while the H atom contributes only about 10% (G(H) = 0.55). These radicals rapidly react with added diisopropyl ether (DIPE) (2 × 10⁻³ mol dm⁻³). The rate constant of the reaction of OH radicals with DIPE has been determined by competition with SCN⁻ (1-10) × 10⁻³ mol dm⁻³, k(OH + SCN⁻) = 1.1 × 10¹⁰ dm³ mol⁻¹s⁻¹ [13]) to be

\[
k(\text{OH} + \text{DIPE}) = (3.7 ± 0.4) \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}.
\]

Hydroxyl radicals will react (cf. Ref. [14]) with DIPE by abstracting H atoms both from the α and the β position of the ether function (reactions (1) and (2)).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
'\text{OH} + \text{H} - & \rightarrow '\text{C-O-C-H} + \text{H}_2\text{O} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

1

2

α-Alkoxyalkyl radicals such as radical 1 (cf. reaction (1)) are known to be rapidly oxidized in aqueous solution by tetra-nitromethane (TNM) (reaction (3)), while radicals of the type 2 are considerably less reactive [14].

\[
\begin{align*}
1 + \text{C(NO}_2)_4 & \rightarrow \text{H}_2\text{O} \\
& \rightarrow \text{HO-C-O-C-H} + \text{C(NO}_2)_3 + '\text{NO}_2 + \text{H}^+
\end{align*}
\]

(3)

On pulse radiolysis of an N₂O-saturated 2 × 10⁻³ mol dm⁻³ DIPE solution containing TNM, the nitroform anion (NF⁻) with its maximum at 350 nm was produced within a few μs after the pulse and there was no further increase of [NF⁻] up to 1 ms. The rate of NF⁻ formation was directly proportional to the TNM concentration between 4 × 10⁻³ and 1.2 × 10⁻⁴ mol dm⁻³. The rate constant, thus obtained, of the oxidation of radical 1 by TNM was

\[
k_3 = (4 ± 0.5) \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}.
\]

There was no evidence of the formation of an intermediate adduct between radical 1 and TNM at about 300 nm as found in some instances with other α-alkoxyalkyl radicals [14]. From the absorbance of NF⁻ at 350 nm the yield of radical 1 was calculated to be 78% of total OH radical attack (H atoms from the radiolysis of water react mainly with TNM). Thus only 22% of the OH radicals abstract hydrogen atoms at the methyl groups (reaction (2)). This value is close to the corresponding value observed with isopropanol [15].

The radicals 1 and 2 derived from DIPE do not have very characteristic absorptions at λ > 240 nm. The
The composite absorption spectrum of radicals 3 (G = 4.3) and 4 (G = 1.2) is also included in Fig. 1 (triangles). The transient absorption at 250 nm decays with $2k = 6 \times 10^7 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ up to the first half-life. The rest of the absorption then decays more slowly, $2k = 2 \times 10^7 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

The conductivity change of an aqueous $\text{N}_2\text{O}/\text{O}_2$-saturated $2 \times 10^{-3} \text{mol dm}^{-3}$ DIPE solution following a 1 $\mu$s electron pulse at pH 6.5 was found to consist of a prompt increase at pulse end corresponding to $G(FP + \text{anion}) = 0.6$ which was followed by a second-order buildup to $G(\text{acid}) = 1.3$ (3–10 Gy) with $2k = 6 \times 10^7 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. This conductivity buildup was followed by a decay process whose rate depended on the dose per pulse. The net permanent conductivity increase of the diisopropyl ether solution measured 10 s after the pulse corresponded to $G(\text{acid}) = 0.5$.

Basic solutions (pH 9–11) of $\text{N}_2\text{O}/\text{O}_2$-saturated DIPE solutions showed analogous results in the form of conductivity decrease as the neutral solution. Here formation of acids results in the removal of $\text{OH}^-$ by neutralisation with $\text{H}^+$ of the acids leaving anions with much lower equivalent conductivity than the $\text{OH}^-$ in the solution. The prompt formation of primary $\text{HO}_2$ ($\text{H}^+ + \text{O}_2$) was observed which was followed by a second-order conductivity decrease ($2k = 5 \times 10^7 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) to a plateau level corresponding to $G(\text{anion} - \text{OH}^-) = 1.3$. This conductivity change disappeared to a large extent 10 s after the pulse (85% at pH 9.0 and 50% at pH 10.9).

To confirm our observation that the bimolecular decay of the peroxyl radicals results mainly in the formation of a permanent acid in neutral solutions but a transient acid ($\text{HO}_2^-$) in basic solutions, we have undertaken to monitor the formation of $\text{O}_2^-$ by its reduction of TNM to the nitroform anion ($\text{NF}^-$) [17]. Indeed, in the pulse radiolysis of $\text{N}_2\text{O}/\text{O}_2$-saturated DIPE solutions containing $\approx (2–3) \times 10^{-5} \text{mol dm}^{-3}$ TNM, $G(\text{NF}^-) = G(\text{O}_2^-) \leq 0.2$ was obtained in the course of the bimolecular decay of the peroxyl radicals (10 ms, 10–15 Gy) at pH 6.5 whereas $G(\text{NF}^-) = G(\text{O}_2^-) = 0.5$ was obtained at pH 11.3.

**Product analysis**

GC analysis of $\gamma$-irradiated $\text{N}_2\text{O}/\text{O}_2$-saturated DIPE solutions showed the products isopropyl acetate,
acetone, isopropanol and traces of methanol and acetaldehyde (G < 0.05). Table I summarizes the G values of the products under various irradiation conditions. There was also an unknown product which disappeared completely upon treatment with NaBH₄ and was replaced by a new peak with the retention time of 2-isopropoxypropanol. We therefore conclude that the unknown product is 2-isopropoxypropanal. 2-Isopropoxypropanol and isopropenyl isopropyl ether were not found among the products.

Organic peroxodic material was detected in the irradiated diisopropyl ether solutions which is distinguishable from H₂O₂ by its slower reaction with the KI reagent (half-life = 6 min). TLC on silica gel in acetone/CCl₄ (1:2) of the γ-irradiated DIPE solutions, which had been concentrated in vacuo, visualized with the amine-naphthol reagent [18] showed three peroxide spots with Rᵣ = 0.34 (intensive), 0.47 (faint) and 0.53 (very faint) apart from the H₂O₂ spot with Rᵣ = 0.13. Attempts to synthesize authentic 2-isopropoxyhydroperoxide from isopropenyl isopropyl ether and H₂O₂ by the method of Milas et al. [19] failed. However, because of the relative ease with which this peroxidic material reacts with KI it is quite probable that it is of a hydroperoxide nature, and not a peroxide (cf. Ref. [20]). Further evidence supporting this assignment comes from the fact that the reduction of 2-isopropoxyhydroperoxide by KI would give equal amounts of acetone and isopropanol. Indeed, in the radiolysis of N₂-saturated DIPE solutions the G values of both these products increase by an equal amount approximately equivalent to the G value of the organic peroxidic product (see Table I). At the same time G(isopropyl acetate) decreases by a similar amount upon KI treatment. This would be the case if the unknown peroxidic decomposes on GC analysis into isopropyl acetate. 1-Ethoxethylhydroperoxide was also found to decompose under GC conditions, albeit only partly, into ethyl acetate [20]. Therefore we consider G(isopropyl acetate) determined after the KI treatment to be its true G value.

**Reaction mechanism**

From the list of products shown in Table I it can be seen that the carbon skeleton of DIPE is conserved in products like 2-isopropoxypropanal, but it is also fragmented into two complementary couples, isopropyl acetate/formaldehyde and isopropanol/acetone.

The G value of 2-isopropoxypropanal is close to the yield of its precursor, radical 4, as determined by the percentage of OH attack at the methyl groups (reaction (2)). A likely route to 2-isopropoxypropanal is discussed below.

In the product study (Table I) four different experimental conditions have been investigated. Comparing the data for N₂-saturated solutions one can see that under the high dose rate conditions of pulse radiolysis there is a 1:1 ratio of isopropanol and acetone. On going to lower dose rates G(isopropanol) is not significantly changed, but G(acetone) rises substantially. Concomitantly G(oxygen uptake) and G(hydrogen peroxide) increase. This is an indi-

<table>
<thead>
<tr>
<th>Dissolved gas</th>
<th>Dose rate (Gy s⁻¹)</th>
<th>N₂O/O₂ (4:1)</th>
<th>O₂</th>
<th>e⁻ pulses</th>
<th>Hydrogen peroxide</th>
<th>Organic peroxides</th>
<th>Formic acid</th>
<th>Formamide</th>
<th>Isopropanol</th>
<th>Isopropyl acetate</th>
</tr>
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<tr>
<td></td>
<td>0.035</td>
<td>0.39</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl acetate</td>
<td>1.6ₐ</td>
<td>1.8ₐ (2.5ₐ)</td>
<td>2.6ₐ (2.9ₐ)</td>
<td>0.2ₐ (1.0ₐ)</td>
<td></td>
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</tr>
<tr>
<td>Acetone</td>
<td>3.6ₐ</td>
<td>2.2ₐ (3.0ₐ)</td>
<td>1.1ₐ (1.5ₐ)</td>
<td>1.2ₐ (1.7ₐ)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>1.3ₐ</td>
<td>1.2ₐ (1.8ₐ)</td>
<td>1.1ₐ (1.4ₐ)</td>
<td>0.7ₐ (1.2ₐ)</td>
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<tr>
<td>Formaldehyde</td>
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<td>1.8</td>
<td>2.0</td>
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<td></td>
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<tr>
<td>2-Isopropoxypropanal</td>
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<td>1.4ₐ</td>
<td>n.d.</td>
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<tr>
<td>Organic peroxides</td>
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<td>0.9</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>3.5</td>
<td>2.4</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Acids</td>
<td>0.6</td>
<td>0.5</td>
<td>0.5ₐ</td>
<td></td>
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<td></td>
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<tr>
<td>Oxygen consumption</td>
<td>7.5</td>
<td>5.1</td>
<td>n.d.</td>
<td></td>
<td></td>
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</table>

a Direct GC determination; b GC determination after KI reduction; c GC determination as 2-isopropoxy-1-propanol after NaBH₄ reduction; d obtained from pulse conductometric measurements; e a series of 1 μs-pulses with an average dose rate of 2.6 Gy/pulse delivered at 1 s⁻¹ frequency to give total doses from 100 to 320 Gy; n.d. not determined.

**Table I.** Radiolysis of oxygenated aqueous diisopropyl ether solutions (10⁻³ mol dm⁻³, pH = 6.5). Products and their G values.
cation that “excess” acetone comes from first order or pseudo-first order reactions of the primary peroxyl radicals and not from their bimolecular decay. They will be discussed later.

Another complementary couple is isopropyl acetate and formaldehyde. The percursor of formaldehyde is the CH$_3$O$_2$ radical 5, which is the result of a fragmentation reaction involving radical 3 to give isopropyl acetate and the CH$_3$ radical (reaction (11)). Although radical 5 will decay to form mainly formaldehyde, depending on the dose rate conditions it will also give rise to other products such as formic acid [2]. Therefore the ratio of isopropyl acetate to formaldehyde yields has been found to be >1 under pulse radiolysis conditions.

In the present system, radicals 4 and 5 are primary peroxyl radicals, whereas the most abundant peroxyl radical 3 is a tertiary peroxyl radical. Primary peroxyl radicals in the systems that we have studied (see Introduction) tend to decay in water bimolecularly with rate constants of $2 k > 5 \times 10^8$ dm$^3$mol$^{-1}$s$^{-1}$. Data for tertiary peroxyl radicals (in non-aqueous media) indicate that their decay might be considerably slower [21]. The cross-termination of a primary and a tertiary peroxyl radical should fall in between.

It then follows that under steady-state conditions there is a preponderance of the cross-termination between the primary peroxyl radicals 4 and 5, and the tertiary peroxyl radical 3 whereas under pulse radiolysis conditions the reaction between two tertiary peroxyl radicals 3 will gain in importance once most of radical 4 are consumed by 3, while radical 5 is still being formed from 2-(2-propoxy)propoxyl radicals (reaction (11)) in the course of the bimolecular decay of 3 + 3.

It is now generally accepted that in the bimolecular decay of peroxyl radicals a tetroxide is formed (reaction (6)) as an intermediate which is short-lived at room temperature. According to our present knowledge (see Introduction) the decay of the tetroxide intermediate proceeds via a number of competing reactions, concerted reactions such as the Russell mechanism (reaction (8)) and the formation of oxyl radicals (reaction (9)). Reaction (8) accounts for the equal yields of isopropanol and acetone (cf. reaction (10)) under pulse radiolysis conditions and also explains the formation of some of the aldehyde yield (formaldehyde and 2-isopropoxypropanal). The oxyl radical route (reaction (9)) leads to the formation of (some of) the isopropyl acetate (reaction (11)) and the methylperoxyl radicals 5 (cf. reaction (12)). In analogy to many other more straightforward examples we believe that the transient conductivity (H$^+$ + O$_2$) formed during the bimolecular decay of the peroxyl radical arises from the sequence of reactions (13)–(15). The rapid 1,2-H-shift of oxyl radicals in aqueous solutions (reaction (13)) is a well-established process [22–24], as is the elimination of HO$_2$ (reaction (15)) from the subsequently formed $\alpha$-hydroxyalkytoperoxyl radical (for a review see [25]). However, HO$_2$-elimination reactions of $\alpha$-hydroxyalkytoperoxyl radicals are often fast only in basic solutions where they are catalysed by OH$^-$. Hence in neutral solutions and at the high dose rates of pulse radiolysis such peroxyl radicals tend to decay bimolecularly to form acids (reaction (16), cf. [26]). This explains our pulse radiolysis results, i.e. that for the most part permanent acid is formed in neutral solutions while in basic solutions O$_2$ formation is preferred.

Since radical 3 is by far the most abundant species, most of the isopropyl acetate must come from the bimolecular decay of two peroxyl radicals 3 (reaction (17)).
The bimolecular reactions of methylperoxyl radicals will yield mainly formaldehyde as has been shown by a detailed study on this species [2]. The bimolecular decay of O$_2$ in neutral solution is slow (under neutral conditions taking place by the reaction of the small equilibrium concentration of HO$_2$ (pK$_a$(HO$_2$) = 4.7 with k(O$_2$ + HO$_2$) = 1.0 x 10$^8$ dm$^3$ mol$^{-1}$s$^{-1}$) [17]). The reactions of the organic peroxyl radicals with O$_2$ lead to hydroperoxides (reaction (18)).

$$\text{RO}_2^+ + O_2 + H^+ \rightarrow \text{RO}_2H + O_2$$

These reaction are generally quite slow. A value of $k_{18} \approx 10^7$ dm$^3$ mol$^{-1}$s$^{-1}$ has been estimated for R=CH$_3$CHOH [27] or less for other systems (cf. [4]). With the use of thin-layer-chromatography, three organic hydroperoxides have been revealed after $\gamma$-radiolysis. These organic hydroperoxides are preferentially formed at high O$_2$ steady-state concentrations such as are attained in low-dose-rate experiments, especially with the solutions saturated with oxygen at atmospheric pressure.

Although we are unable to derive more than an overall bimolecular decay rate constant of $2k = 5 \times 10^7$ dm$^3$ mol$^{-1}$s$^{-1}$ from our pulse radiolysis data, a computer simulation based on the reaction mechanism given in Scheme 1 with a rate constant of $8 \times 10^6$ dm$^3$ mol$^{-1}$s$^{-1}$ for each of the cross-termination reactions (3 + 4, 3 + 5), $8 \times 10^5$ dm$^3$ mol$^{-1}$s$^{-1}$ for each of the termination reactions of the primary peroxyl radicals (4 + 4, 4 + 5, 5 + 5), and $10^5$ dm$^3$ mol$^{-1}$s$^{-1}$ for reactions (17) and (18) together with $k_{11} = 10^5$ s$^{-1}$ gives a picture of the relative abundance of the radicals in the course of one second after an electron pulse of 10 Gy (Fig. 2).

When this simulation procedure is applied to the case of the steady-state irradiation, the above set of reactions gives a product distribution very close to that obtained under the very high dose rate of electron pulses but not at the low dose rates of the $\gamma$-irradiation, where acetone has been found with much higher yields than isopropanol. In order to obtain the product distribution found under $\gamma$-irradiation an additional intramolecular reaction of radical 3 (reaction (19)) with a rate constant of about 1 s$^{-1}$ must be introduced. This reaction leads to a increase in the acetone and hydrogen peroxide yields at the expense of the isopropyl acetate yield. It also implies an increase in the oxygen uptake. An analogous reaction has been shown to play a role in the decay mechanism of the peroxyl radicals derived from diethyl ether [20]. Whether there is any intermolecular H-abstraction by radical 3 has not been investigated in this work. However, it is known for the case of diethyl ether that such reactions are insignificant compared to the intramolecular ones.
One set of experiments has been carried out in O₂-saturated solutions. Under such conditions G(3) = 2.2 and G(4) = 0.6 while G(O₂) rises to 3.2. Hence the participation of O₂ in the formation of products (reaction (18)) will be enhanced. This is in accordance with the substantially higher yield of organic hydroperoxide found, compared with the case of N₂O/O₂-saturated solutions. At the same time G(isopropyl acetate) drops to a disproportionately low value of 0.2 and G(isopropanol) is also disproportionately higher than expected on the basis of the yield of radical 3. These results could be explained if an alternative decay reaction of radical 3 (reaction (25)) is admitted with a rate constant k₂5 of the order of 1 s⁻¹. We derive some additional encouragement to consider this reaction (4)
(22) and G(3) = 3.0 shows that O₂-elimination is a major process in this system. It may partly account for the observed first-order decay of the poly(U) peroxy radicals [29, 30]. Unpublished pulse radiolysis data by Bothe and Schulte-Frohlinde confirm our observation of O₂-release from poly(U) peroxy radicals, but in addition show that most of this O₂ is released in the millisecond to second time regime. This would be in fair agreement with our estimate that such reactions might be quite slow indeed, and since this reaction has to compete with the bimolecular decay of the peroxy radicals, it would only play a role if the life time of the peroxy radicals is rather long such as with small molecules at low dose rates or with high molecular weight material, e.g. nucleic acids, even at elevated dose rates.

We would like to thank Mrs. R. Paulini for skillful technical assistance.

Conclusion

The present work had been undertaken to understand better some of the principles that might govern the fate of tertiary peroxy radicals located at the sugar moiety of nucleic acids. There are two aspects that seem worth mentioning. With poly(U) it has been observed that base peroxy radicals abstract H atoms from the sugar moiety with a rate constant of about 0.2 s⁻¹[29]. This reaction is an intramolecular reaction. A similar rate constant for the intramolecular H abstraction of the tertiary peroxy radical from the other side of the ether function (reaction (19)) has been estimated in this study. In addition there is evidence from the present work and from unpublished results on the fate of the peroxy radicals derived from acetaldehyde dimethylacetal that ether and acetal peroxy radicals may eliminate in aqueous solutions O₂ (cf. reaction (25)). This has led us to measure the release of O₂ from poly(U) using the formation of the nitroform anion from tetrinitromethane as a monitor [17]. The high yield of G(O₂) = 3.0 shows that O₂-elimination is a major process in this system. It may partly account for the observed first-order decay of the poly(U) peroxy radicals [29, 30]. Unpublished pulse radiolysis data by Bothe and Schulte-Frohlinde confirm our observation of O₂-release from poly(U) peroxy radicals, but in addition show that most of this O₂ is released in the millisecond to second time regime. This would be in fair agreement with our estimate that such reactions might be quite slow indeed, and since this reaction has to compete with the bimolecular decay of the peroxy radicals, it would only play a role if the life time of the peroxy radicals is rather long such as with small molecules at low dose rates or with high molecular weight material, e.g. nucleic acids, even at elevated dose rates.

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