PERKIN 2

Hydroxyl-radical-induced reactions of the poly(vinyl methyl ether) model 2,4-dimethoxypentane in the absence and presence of dioxygen: a pulse radiolysis and product study

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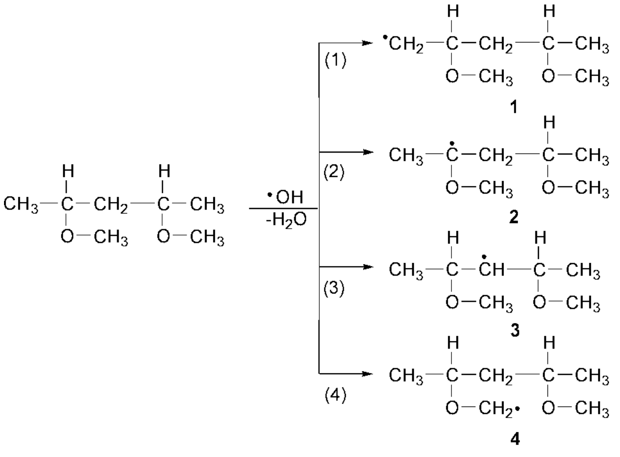
Hydroxyl radicals were generated radiolytically and reacted with 2,4-dimethoxypentane, a low-molecular-weight model of poly(vinyl methyl ether). Using the pulse radiolysis technique and specific radical scavengers, it has been shown that OH radicals react by H-abstraction ($k = 3.7 \times 10^9$ dm^3 mol^{-1} s^{-1}), generating primary (**4**, ~45%) and tertiary (**2**, ~35%) α-alkoxyalkyl radicals as well as secondary and primary β-alkoxyalkyl radicals (**3** and **1**). In the absence of dioxygen, radicals **1**–**4** decay ($2k = 1 \times 10^9$ dm^3 mol^{-1} s^{-1}) by recombination and disproportionation yielding dimers and vinyl ethers in nearly equal amounts. In the presence of dioxygen, four different peroxyl radicals (**5**–**8**) are formed. They decay bimolecularly by non-uniform kinetics (initially, $2k \approx 7 \times 10^7$ dm^3 mol^{-1} s^{-1}). Especially at low dose rate, they also undergo (mainly) intramolecular H-abstraction. This leads to an increased autoxidation, *e.g.* dioxygen uptake reaches values more than three-times the initial radical yield. Based on these data, the major reaction pathways as well as some side- and consecutive reactions are discussed.

It has been shown previously that the complex free-radical chemistry of even simple synthetic polymers can only be understood when their low-molecular-weight models have been investigated in some detail. For example, the OH-radical-induced transformations of poly(vinyl alcohol)[1] and poly(acrylic acid)[2,3] could be explained on the basis of the corresponding reactions of their low molecular equivalents pentane-2,4-diol[1] and 2,4-dimethylglutaric acid,[4] respectively. These models allowed detailed product studies that were not possible with the polymers.

Aqueous solutions of poly(vinyl methyl ether) have unusual solubility behaviour, *i.e.* it precipitates upon heating to about 34–37 °C.[5,6] The main application of this polymer is its use as an additive in dispersion-type pressure-sensitive adhesives and heat-sensitive composites are made from its aqueous dispersions with natural rubber. Hydrogels made from poly(vinyl methyl ether) are also heat-sensitive, and may be used as a recyclable separation system[7] or a chemomechanical valve.[8] There is also a growing interest in their biomedical application, *e.g.*, in the search for an artificial muscle.[9]

The treatment of the polymer with ionizing radiation in aqueous solution is the most convenient method for preparing and sterilizing hydrogels for medical applications.[10,11] This treatment is, of course, connected with chemical changes, and hence some studies of the influence of ionizing radiation on poly(vinyl methyl ether) have already been undertaken.[12–14] However, data on the reactions of the poly(vinyl methyl ether) free-radical intermediates and detailed product studies are still missing. The aim of the present work was to study the mechanism of the radiolysis, *i.e.* the OH-radical-induced reactions, of the poly(vinyl methyl ether) model 2,4-dimethoxypentane in aqueous solution. Hydroxyl radicals are known to show little selectivity in their H-abstraction reactions [*cf.* reactions (1)–(4)], although abstraction of hydrogens bound to α-alkoxyalkyl positions will dominate,[15,16] and one has to assume that more than one type of radical is formed not only in the model system but also with the polymer. These radicals will have different reactivities, and it is the aim of this study to elucidate some of their properties.



Some of the free-radical chemistry of ethers in aqueous solution is already known,[15–19] and this gives a good entry into the present study.

Experimental

2,4-Dimethoxypentane and 4-methoxypentan-2-ol were synthesised according to ref. 20. 4-Methoxypentan-2-one was formed in 80% yield upon the oxidation of 2-methoxypentan-4-ol with potassium dichromate in concentrated sulfuric acid.[21] The mixture of D,L- and *meso*-2,4-dimethoxypentane was separated by distillation (HMS 1000, Fischer Technik) to a GC purity of >99.7%. 3-Methoxy-1-methylbutyl formate was obtained in 75% yield upon refluxing 13.1 ml 2-methoxypentan-4-ol, 3.23 ml formic acid and 0.5 g Amberlite IR-120P

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ion exchange resin (Sigma) in 20 ml chloroform for 3 hours using a water separator.[21]

D,L-2,4-Dimethoxypentane solutions (10^{-4}–10^{-2} mol dm^{-3}) were made up in Milli-Q-filtered (Millipore) water after having the water saturated with N_2O, N_2O–O_2 or O_2. Irradiations were carried out at room temperature in a panoramic ^{60}Co-γ-source (Nuclear Engineering Ltd.) at dose rates ranging from 0.0014 to 0.14 Gy s^{-1}. Conversions were always kept <25%. The pulse radiolysis setup (a 2.8 MeV Van-de-Graaff electron generator delivering 3 to 40 Gy electron pulses of 0.4 µs duration) has been described.[22] Dose rates were determined by Fricke dosimetry in γ-radiolysis and thiocyanate[23] in pulse radiolysis experiments.

Formaldehyde was determined after derivatization with 2,4-dinitrophenylhydrazine in acidic (0.1 M perchloric acid) acetonitrile solution by HPLC (Nucleosil C18 column, acetonitrile–water 1 : 1 v/v).[24] The yields of H_2O_2 and organic hydroperoxides were determined by reaction with molybdate-activated iodide.[25] Iodine formation *via* H_2O_2 reduction occurs during mixing, while organic hydroperoxides react much more slowly (*cf.* ref. 26). The yield of 2,4-dihydroperoxy-2,4-dimethoxypentane was determined by converting it in acid solution (2 h at pH 1) into acetylacetone which was measured by making use of the strong UV absorbance of its enolate moiety in alkaline solutions [ε(294 nm) = 2.14×10^4 dm^3 mol^{-1} cm^{-1}].[27]

After their hydrolyses at pH > 11, 3-methoxy-1-methylbutyl formate and methyl acetate were determined as formate and acetate ion by ion chromatography (Dionex 2010i, AS9; eluent 9×10^{-3} mol dm^{-3} Na_2CO_3).

The organic products were identified by GC-MS (30 m Carbowax) after extraction from the irradiated solutions into diethyl ether using a Ludwig extractor. Quantitative analyses of the extracts were done by GC (Hewlett-Packard 5980, 30 m Stabilwax S-42). Since the reference material for some of the products to be analysed was not available, response factors have been estimated by assuming equal mass response for *meso*-2,4-dimethoxypentane added as an internal standard.

Typical mass spectra (*m*/*z*; abundance in parentheses; molecular weights were obtained by chemical ionisation): dimers (M_r = 262, a selected typical spectrum): 131 (24), 101 (6), 85 (5), 59 (100); 2,4-dimethoxy-2,4-dimethyloxetane (M_r = 146): 115 (31), 99 (38), 75 (48), 73 (19), 72 (19), 43 (100), 42 (37), 41 (20), 39 (10); 2,4-dimethoxypentan-3-one (M_r = 146): 117 (14), 71 (11), 59 (100), 31 (10), 29 (12); 3-methoxy-1-methylbutyl formate (M_r = 146): 85 (26), 59 (100), 45 (13), 43 (10), 29 (10); 2,4-dimethoxypentane (M_r = 132): 100 (10), 85 (12), 59 (100); 2,4-dimethoxypent-1-ene (M_r = 130): 98 (6), 59 (100), 41 (7), 31 (13); 4-methoxypentan-2-ol (M_r = 118): 59 (100), 45 (31), 43 (16), 42 (14), 33(12), 31 (11), 29 (12); 4-methoxypentan-2-one (M_r = 116): 101 (29), 69 (11), 59 (61), 43 (100), 42 (10), 41 (12), 31 (13), 29 (12).

Dioxygen consumption was determined by a dioxygen-sensitive membrane electrode (Wissenschäftlich Technische Werkstätten, Weilheim).

Results and discussion

The radical-generating system

In a dilute deoxygenated aqueous solution of 2,4-dimethoxypentane (10^{-4}–10^{-2} mol dm^{-3}), the radiation energy is largely absorbed by water leading to OH radicals, hydrated electrons (e_{aq}^-) and H atoms as reactive intermediates [reaction (5)]. Saturating the solution with N_2O converts e_{aq}^- to further $^\bullet OH$ [reaction (6), solvated electrons do not react with saturated ethers[28]]. Under these conditions, the radiation-chemical yields (*G* values) are $G(^\bullet OH) = 5.8 \times 10^{-7}$ mol J^{-1} and $G(H^\bullet) = 0.6 \times 10^{-7}$ mol J^{-1}.[29] The OH radical reacts with 2,4-dimethoxypentane with a rate constant of 3.7×10^9 dm^3 mol^{-1} s^{-1} as determined by pulse radiolysis using the SCN^- competition method.[30] With 2,4-dimethoxypentane, the H atom will undergo the same reactions as $^\bullet OH$, albeit at a slower rate (*cf.* ref. 30). If diethyl ether is a good model, H atoms may react with 2,4-dimethoxypentane with a rate constant of about 4×10^7 dm^3 mol^{-1} s^{-1}.[30]

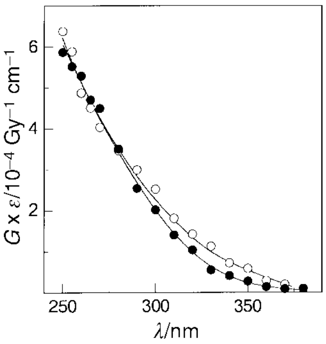


Fig. 1 Pulse radiolysis of N_2O-saturated (○) and N_2O–O_2 (4 : 1 v/v)-saturated (●) solutions of 2,4-dimethoxypentane (1×10^{-3} mol dm^{-3}); 10 Gy per pulse. Absorption spectra measured 6 µs after the pulse.

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} e_{aq}^-, {}^\bullet OH, H^\bullet, H^+, H_2O_2, H_2 \qquad (5)$$

$$e_{aq}^- + N_2O \longrightarrow {}^\bullet OH + N_2 + OH^- \qquad (6)$$

In the presence of O_2, (typically N_2O–O_2-(4 : 1)-saturated solutions were used), the OH radicals still react with the substrate while the H atom is scavenged by O_2 [reaction (7)]. The pK_a of $HO_2^\bullet$ is 4.8,[31] and at around pH 7 its conjugate base, $O_2^{\bullet -}$, predominates.

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

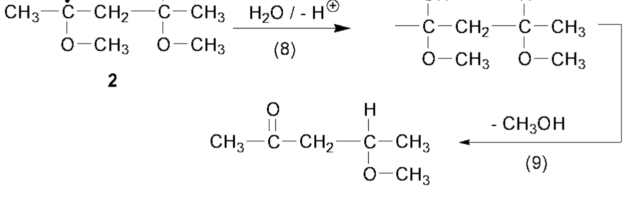
Reactions in the absence of O_2

Radicals **1**–**4** do not have characteristic absorptions at λ > 250 nm (Fig. 1). As expected, the spectrum resembles not only that obtained from poly(vinyl methyl ether)[14] but also those from diisopropyl ether[16] and 1,4-dioxane.[19]

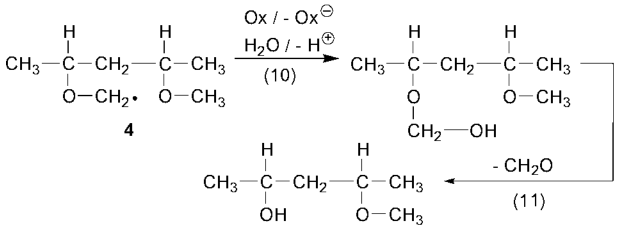
The second-order rate constant of the decay of radicals **1**–**4** (as monitored at 280 and 320 nm) is $2k = 1 \times 10^9$ dm^3 mol^{-1} s^{-1}, a value typical for small alkyl radicals.

Hydroxyl radical attack produces *mainly* three kinds of radicals, the tertiary and primary α-alkoxyalkyl radicals **2** and **4**, as well as the secondary radical **3**. H-Abstraction from methyl groups, here forming radical **1**, is usually of little (≤15%) importance,[32] and thus in this system radical **1** should play only a minor role.

The α-alkoxyalkyl radicals such as radicals **2** and **4** are known to be rapidly oxidized in aqueous solution by oxidants (Ox = *e.g.* $[Fe(CN)_6]^{3-}$, $IrCl_6^{3-}$, tetranitromethane or 4-nitrobenzonitrile, the latter two *via* an adduct, *cf.* refs. 17–19). The intermediate cations react very rapidly with water, but in favourable cases can be sufficiently long-lived to be monitored.[18]



In the present system, radicals **2** and **4** are rapidly oxidised by $Fe(CN)_6^{3-}$ [reactions (8) and (10); $k_8 = k_{10} = 3.9 \times 10^9$ dm^3 mol^{-1} s^{-1}] as has been shown in a pulse radiolysis experiment by



following the bleaching of $Fe(CN)_6^{3-}$ at 420 nm. The total yield of α-alkoxyalkyl radicals based on $Fe(CN)_6^{3-}$ bleaching is $G = 5.1 \times 10^{-7}$ mol J^{-1}, *i.e.* ~80% of the initial yield of $^{\bullet}OH$ plus $H^{\bullet}$. The H atom reacts very rapidly ($k = 6.3 \times 10^9$ dm^3 mol^{-1} s^{-1})[30] with $Fe(CN)_6^{3-}$, and at the given 2,4-dimethoxypentane concentration of 1×10^{-2} mol dm^{-3} could have contributed directly to the bleaching of $Fe(CN)_6^{3-}$. Thus, the yield of the sum of **2** + **4** may be somewhat lower (*ca.* ~78% of $^{\bullet}OH$).

The hemiacetals formed after the reaction of the carbocation with water are unstable and decompose into the alcohol and the carbonyl compound [reactions (9) and (11)]. Thus, formaldehyde results from the oxidation of **4**. In presence of an oxidant (10^{-4} mol dm^{-3}, $IrCl_6^{3-}$ or tetranitromethane), formaldehyde concentrations increase linearly with dose (γ-radiolysis) yielding in both cases $G(CH_2O) = 2.7 \times 10^{-7}$ mol J^{-1}, *i.e.* ~45% of the total $^{\bullet}OH$ plus $H^{\bullet}$ yield. The yield per $^{\bullet}OH$ could be somewhat higher, because, as mentioned above, the oxidants scavenge some H-atoms. From these data it is concluded that radical **4** is ~45% of the OH radical yield and taking into account the fact that the total bleaching of $Fe(CN)_6^{3-}$ was ~80% of the OH-radical yield, the yield of radical **2** must be around 35% of the OH-radical yield.

Somewhat intriguing is the behaviour of $Fe(CN)_6^{3-}$. With this oxidant, $G(CH_2O)$ is only 1.8×10^{-7} mol J^{-1}. We have followed this aspect using dimethyl ether as a probe which gives rise to only one kind of (reducing) radical. With $IrCl_6^{2-}$ (2×10^{-4} mol dm^{-3}) as oxidant we find $G(CH_2O) = 5.74 \times 10^{-7}$ mol J^{-1}, identical to the yield of $^{\bullet}OH$, but with $Fe(CN)_6^{3-}$ formaldehyde yields were markedly lower [$G(CH_2O) = 2.3 \times 10^{-7}$ mol J^{-1}]. A similar situation has been found for poly(vinyl methyl ether), where formaldehyde yields are also lower than those with other oxidants.[33] Weakly oxidizing radicals react with $IrCl_6^{2-}$ by chlorine transfer.[34] Attempts to observe similar reactions with $Fe(CN)_6^{3-}$ remained unsuccessful, and it has been assumed that α-alkoxyalkyl radicals undergo merely electron transfer to this oxidant as α-hydroxyalkyl radicals do. However, the present results indicate that although the $Fe(CN)_6^{3-}$ absorption is completely bleached, this process is only partly due to one-electron transfer.

In the absence of an oxidant, the primary stable products can only be vinyl ethers and dimers [*cf.* reactions (12)–(14)]. Indeed, 2,4-dimethoxypent-1-ene and twenty-six distinct dimer peaks were detected by GC-MS (Fig. 2).

This large number of dimers with up to four chiral centres results from the various possibilities of recombination of radicals **1**–**4**. Surprisingly, 4-methoxypentan-2-one (b in Fig. 2) was also produced in considerable yield. Since 2,4-dimethoxypent-2-ene [*cf.* reaction (13)] was missing, this vinyl ether must have hydrolysed into 4-methoxypentan-2-one [reaction (15)] during the rather long work-up period. The much higher rate of hydrolysis of 2,4-dimethoxypent-2-ene as compared to 2,4-dimethoxypent-1-ene is in agreement with similar behaviour of 1-ethoxybut-1-ene and 2-ethoxypropene.[35]

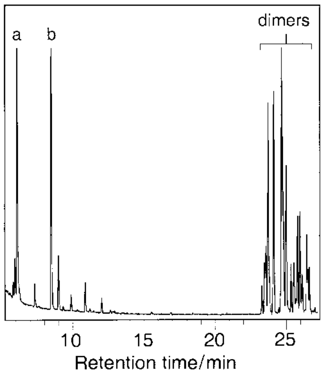
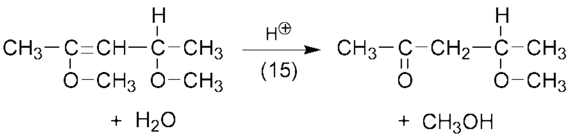


Fig. 2 γ-Radiolysis of N_2O-saturated aqueous solutions of 2,4-dimethoxypentane. Gas chromatogram of a diethyl ether extract of the products; a = 2,4-dimethoxypent-1-ene, b = 4-methoxypentan-2-one. Diethyl ether and 2,4-dimethoxypentane elute earlier, the dimer fraction elutes between 23 and 27 min.



All products show a linear yield *vs.* dose relationship, and from these data (not shown) *G* values were calculated (Table 1). Since two radicals are required for the formation of these products [*cf.* reactions (12)–(14)], the total product yield of 2.94×10^{-7} mol J^{-1} is in good agreement with the initial radical yield, *i.e.* material balance is found.

Oxygenated solutions

In the presence of O_2, radicals **1**–**4** are rapidly converted into the corresponding peroxyl radicals **5**–**8** [reactions (16)–(19)].

In the present system, this reaction cannot be followed by pulse radiolysis, because of the spectral similarities of the parent radicals and their corresponding peroxyl radicals (Fig. 1). However, from other systems, where this reaction can be measured, it is inferred that the reaction must be very fast, typically 2×10^9 dm^3 mol^{-1} s^{-1}.[36] Thus this process is much faster than the recombination of the primary radicals and, therefore, dimers are no longer formed. Instead, a series of new products is observed (Fig. 3).

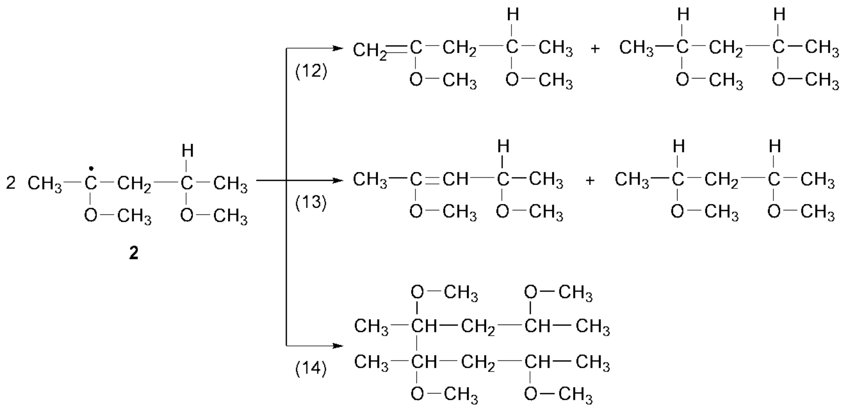
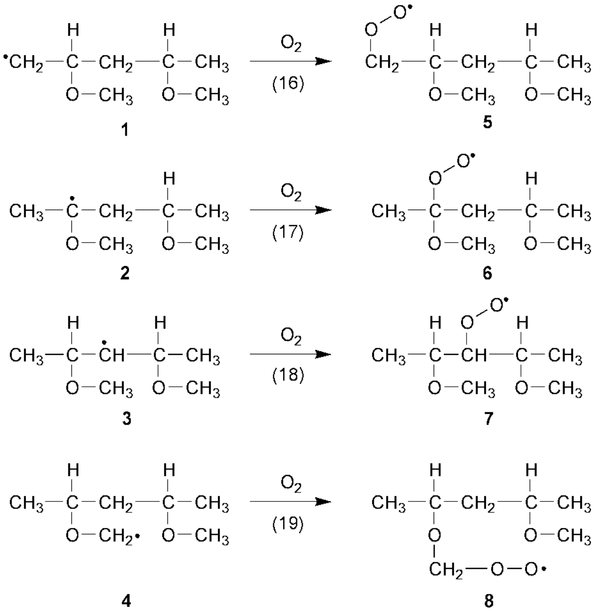


Table 1 Products and their G values in the γ-radiolysis of N_2O-saturated solutions of 2,4-dimethoxypentane

Product	G value/10^{-7} mol J^{-1}
2,4-Dimethoxypent-2-ene	0.86
4-Methoxypentan-2-one	0.53
Dimers	1.55



In the presence of O_2, the transient at 260 nm decays much slower than in its absence, and the decay does not follow simple second-order kinetics. Although fraught with a large error, one estimates up to the first half-life a rate constant of $2k \approx 7 \times 10^7$ dm^3 mol^{-1} s^{-1}. The rest of the absorption decays even more slowly. This decay is much slower than is found for many other alkylperoxyl radicals, where values as high as 2×10^9 dm^3 mol^{-1} s^{-1} are not uncommon,[36] but a similarly low rate constant and overall behaviour have been observed with diisopropyl ether[16] which is closely related to our system. There, it has been tentatively suggested that the slowness of the reaction is mainly due to the presence of tertiary peroxyl radicals which have a lower number of routes for bimolecular decay than primary and secondary peroxyl radicals. The build-up of $O_2^{\bullet-}$ in some of the decay processes that will be discussed below will certainly add to this effect. The self-termination of $O_2^{\bullet-}/HO_2^{\bullet}$ is very slow at around pH 7 as is the reaction of $O_2^{\bullet-}$ with moderately oxidizing peroxyl radicals[37] such as those formed in the present system (for a review on peroxyl radical reactions in water see ref. 38).

From radiolysis in anoxic conditions, it follows that α-alkoxyalkyl radicals **2** and **4** make up *ca.* 80% of the total yield of peroxyl radicals. Therefore, the α-alkoxyalkylperoxyl radicals **6** and **8** should be the main precursors of the final products listed in Table 2.

Besides the bimolecular termination reactions of the peroxyl radicals **5**–**8**, one has to consider reactions with $O_2^{\bullet-}/HO_2^{\bullet}$, and intramolecular as well as intermolecular H-abstraction reactions. The competition between these three types of reaction will be responsible for the dose rate and dioxygen concentration dependence of the product distribution shown in Table 2.

Bimolecular decay of peroxyl radicals. According to our present knowledge of the bimolecular decay of peroxyl radicals, a tetraoxy compound is formed [reaction (20)] as an intermediate which is very short lived at room temperature.[38] Three major decay processes of this tetraoxy compound are shown for a primary or secondary peroxyl radical in reactions (21)–(23). While tertiary peroxyl radicals can undergo the same kind of reactions in their cross-termination reactions with primary and secondary peroxyl radicals, only channel (23) is available for their self-termination.

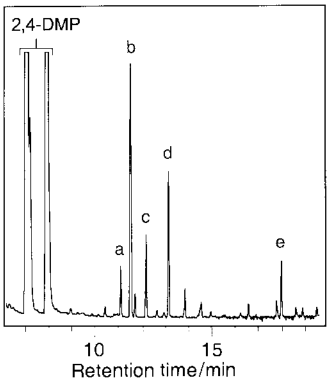


Fig. 3 γ-Radiolysis of N_2O–O_2-saturated aqueous solutions of a mixture of *meso*- and D,L-2,4-dimethoxypentane (2,4-DMP). Gas chromatogram of a diethyl ether extract of the products; a = 4-methoxypentan-2-one, b = 2,4-dimethoxy-2,4-dimethyloxetane, c = 3-methoxy-1-methylbutyl formate, d = 4-methoxypentan-2-ol, e = 2,4-dimethoxypentan-3-one.

$$2\,R_2CHOO^{\bullet} \longrightarrow R_2CH\text{-}O_4\text{-}CHR_2 \qquad (20)$$

$$R_2CH\text{-}O_4\text{-}CHR_2 \longrightarrow R_2C{=}O + R_2CHOH + O_2 \qquad (21)$$

$$R_2CH\text{-}O_4\text{-}CHR_2 \longrightarrow 2\,R_2C{=}O + H_2O_2 \qquad (22)$$

$$R_2CH\text{-}O_4\text{-}CHR_2 \longrightarrow 2\,R_2CHO^{\bullet} + O_2 \qquad (23)$$

Reactions (21) and (22) are often written as concerted reactions. In water, they contribute in varying amounts, depending on the system.[38]

More interesting is the fate of the oxyl radical formed in reaction (23). In water, primary and secondary alkoxyl radicals undergo a very fast 1,2-H-shift, whereby an α-hydroxyalkyl radical is formed [reaction (24)].[39–42] This kind of reaction can occur with oxyl radicals derived from peroxyl radicals **5**, **7** and **8**. This reaction is often faster than a β-fragmentation[38] which is typically undergone by tertiary oxyl radicals. Here, one has to take into account that in asymmetrically substituted radicals there is a preference for breaking the weaker C–C bond, *i.e.* typically the bond to the larger substituent [*cf.* reactions (35) and (36)].[43–45]

This general aspect of oxyl radical chemistry has some bearing on the present system. The α-hydroxyalkyl radicals react rapidly with dioxygen and the α-hydroxyalkylperoxyl radicals thus formed eliminate $HO_2^{\bullet}$ [reactions (26) and (27)]. The rate of $HO_2^{\bullet}$ elimination is especially fast when one of the substituents in the α-position is an alkoxyl group.[38] This increases the $HO_2^{\bullet}/O_2^{\bullet-}$ yield beyond that formed in reaction (7).

$$R_2CHO^{\bullet} \longrightarrow {}^{\bullet}CR_2OH \qquad (24)$$

$$R_3CO^{\bullet} \longrightarrow R^{\bullet} + R_2C{=}O \qquad (25)$$

$${}^{\bullet}CR_2OH + O_2 \longrightarrow {}^{\bullet}OOCR_2OH \qquad (26)$$

$${}^{\bullet}OOCR_2OH \longrightarrow HO_2^{\bullet} + R_2C{=}O \qquad (27)$$

The yield of $O_2^{\bullet-}$ can be quantified with the help of tetranitromethane.[46] Among the peroxyl radicals, $O_2^{\bullet-}$ is the only one that has reducing properties. Thus, no other peroxyl radical interferes with reaction (28). The nitroform anion which is

Table 2 Products and their G values (in units of 10^{-7} mol J^{-1}) in the γ-radiolysis of N_2O–O_2 and O_2-saturated aqueous solutions of 2,4-dimethoxypentane (10^{-3} mol dm^{-3}) at pH 6.5

Dose rate/Gy s^{-1}	0.0014	0.014	0.14	0.14	0.14	0.14
Dioxygen concentration (%)	20	20	20	9	50	100
Products	$G/10^{-7}$ mol J^{-1}					
Formaldehyde	3.6	2.5	1.9	2.8	2.8	1.0
Methyl acetate	nd	nd	2.3	nd	nd	nd
3-Methoxy-1-methylbutyl formate	2.1	1.9	1.8	2.0	2.4	1.3
4-Methoxypentan-2-ol	0.11	0.11	0.14	0.12	0.09	0.03
4-Methoxypentan-2-one	0.25	0.14	0.13	0.18	0.21	0.07
2,4-Dimethoxy-2,4-dimethyloxetane	1.1	0.75	0.68	0.74	0.53	0.07
2,4-Dimethoxypentan-3-one	0.2	0.15	0.12	0.16	0.02	0.02
Superoxide radicals	nd	nd	2.9	nd	nd	nd
Hydrogen peroxide	2.2	1.9	1.7	1.5	2.4	1.5
Organic hydroperoxides	5.0	3.3	2.6	2.3	3.5	2.2
Dioxygen uptake[a]	19	12	10	nd	nd	nd
Dioxygen uptake[b]	22	15	10	nd	nd	nd

[a] Substrate concentration 10^{-4} mol dm^{-3}. [b] Substrate concentration 10^{-2} mol dm^{-3}.

formed in this reaction can be readily determined due to its strong absorption at 350 nm.

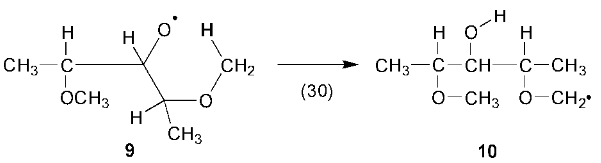
$$O_2^{\bullet -} + C(NO_2)_4 \longrightarrow O_2 + C(NO_2)_3^- + {}^{\bullet}NO_2 \quad (28)$$

Using this approach, the total $O_2^{\bullet -}$ yield was determined at 2.9×10^{-7} mol J^{-1}. Taking $G(O_2^{\bullet -}) = 0.6 \times 10^{-7}$ mol J^{-1} from reaction (7), this leaves $G(O_2^{\bullet -}) = 2.3 \times 10^{-7}$ mol J^{-1} for the release of further $HO_2^{\bullet}/O_2^{\bullet -}$ due to reaction (27).

The peroxyl radicals can be reduced by $O_2^{\bullet -}$ [reaction (29)], but there is also the possibility that other reactions occur *via* an intermediate tetraoxy compound.[47]

$$ROO^{\bullet} + O_2^{\bullet -} + H^+ \longrightarrow ROOH + O_2 \quad (29)$$

Intra- and intermolecular H-abstractions. Both alkoxyl and peroxyl radicals can undergo intramolecular H-abstraction reactions, preferably *via* a six-membered transition state [*cf.* reactions (30) and (31)].



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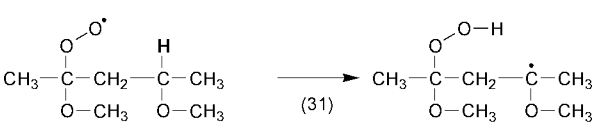
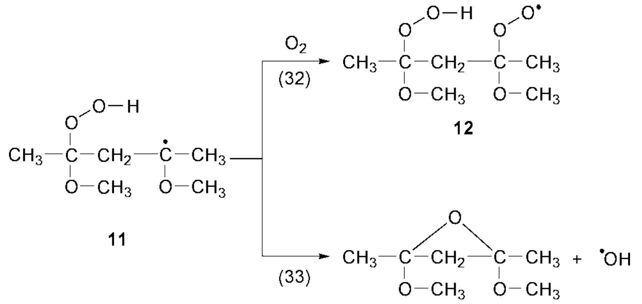


6 11

The alkoxyl radicals are much more reactive, but, in competition, they undergo the rapid unimolecular 1,2-H-shift and β-fragmentation reactions (24) and (25) discussed above. These reactions are so fast ($k \approx 10^6$ s^{-1}) that they are not sensitive to dose rate effects. If there are no specific products formed in reactions such as (30) it is practically impossible to trace this intramolecular H-transfer of an intermediate oxyl radical.

On the other hand, the peroxyl radicals undergo H-abstraction reactions [*e.g.* reaction (31)] much more slowly, but they are long-lived which can compensate for the slowness of the reaction. Because this intramolecular H-transfer competes with the bimolecular decay, there must be a strong dose rate effect. In competition with the *intra*molecular H-transfer, there is always also an *inter*molecular H-transfer. The rate of this process, however, depends on the substrate concentration. Both processes lead to an increased formation of hydroperoxides [*cf.* reaction (31)] and an enhancement of the dioxygen-uptake caused by further addition of O_2 to the new radical site. Under similar conditions, this has already been observed with diethyl ether,[15] but the present ether is much more prone to this kind of reaction (*cf.* its ready autoxidation[20]). Inspection of Table 2 shows that even at the highest dose rate used G(dioxygen uptake) considerably exceeds the values typical for systems which do not undergo such reactions readily,[48,49] *i.e.* the range of (3–6) × 10^{-7} mol J^{-1}, *i.e.* even under these conditions intra- and intermolecular H-abstractions occur to a noticeable extent. As expected, G(dioxygen uptake) increases further with decreasing dose rate. However, increasing the substrate concentration ten-fold further increases G(dioxygen uptake) only slightly (*cf.* Table 2). It is hence concluded that *inter*molecular H-transfer is of little importance compared to *intra*molecular H-transfer.

At first sight, 2,4-dimethoxy-2,4-dimethyloxetane is a surprising product. However, due to the ease of reaction (31), the second-generation radical **11** must be quite abundant. This radical carries an hydroperoxyl function in close proximity. It is well-established that β-alkylperoxide species may undergo rapid radical-induced cleavage of the peroxide function yielding the epoxide and an alkoxyl radical.[50,51] Here, we formulate a similar process [reaction (33)] which might be even more favourable, since a less-strained four-membered ring is formed. In the presence of O_2, the formation of the oxetane [reaction (33)] is in competition with an addition of O_2 to the alkyl radical [reaction (32)]. Thus the oxetane yield should decrease upon increasing the dioxygen concentration. On the other hand, its yield should increase upon lowering the dose rate, because this will favour the formation of its precursor **11** [*cf.* reaction (31)]. Both effects are indeed observed (*cf.* Table 2; note that under 100% O_2 the OH radical yield is halved compared to N_2O–O_2-saturated solutions).



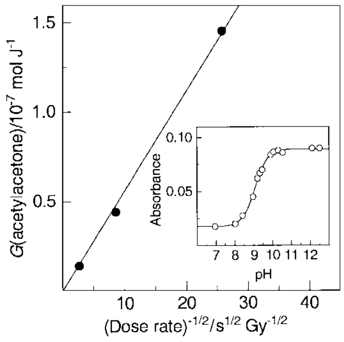
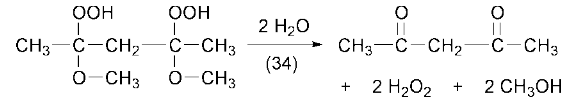


Fig. 4 γ-Radiolysis of 2,4-dimethoxypentane. *G*(Acetylacetone) (after acidification) as a function of (dose rate)$^{-\frac{1}{2}}$. Inset: spectral changes at 290 nm as a function of pH. The pK_a of acetylacetone is 9.1.

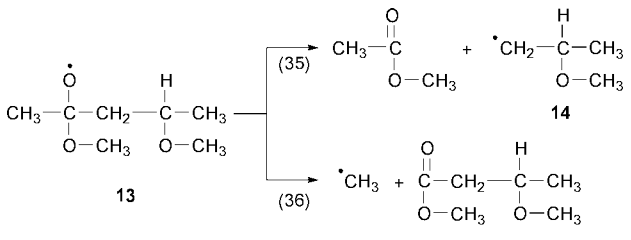
The peroxyl radical **12** formed in reaction (32) can be reduced by $O_2^{\bullet -}$ or by intermolecular H-transfer, and a dihydroperoxide is formed. This is unstable and hydrolyses under acid conditions yielding acetylacetone [reaction (34)] whose identity was confirmed by its spectral properties and its pK_a value[27] (*cf.* inset in Fig. 4).



The precursor of acetylacetone is a second-generation peroxyl radical (**12**) resulting from the intramolecular H-abstraction reaction (31). Hence, it should behave similarly to the chain products of autoxidation reactions, *i.e.* its yield should be linearly related to (dose rate)$^{-\frac{1}{2}}$. Fig. 4 shows that such a plot indeed yields a straight line, supporting the above suggestion.

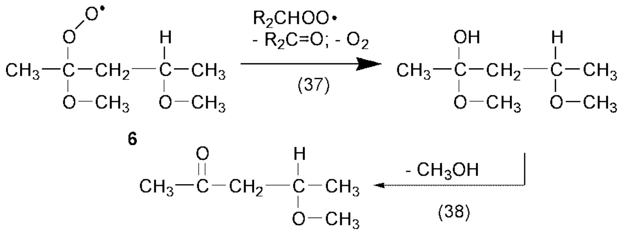
Some further mechanistic aspects. As a consequence of these H-transfer reactions and the large number of first- and second-generation peroxyl radicals, it is practically impossible to come up with any detailed scheme for the reactions of the individual first-generation peroxyl radicals **5**–**8**. It is important to keep this in mind when we discuss some possible mechanisms. These are very likely to occur, but the quantitative aspects should not be stressed.

When in the bimolecular decay of the peroxyl radicals **6** oxyl radical **13** is formed, it will preferentially decay according to reaction (35) rather than reaction (36) (*cf.* the effects of substituents on alkoxyl radical fragmentation).[43–45]

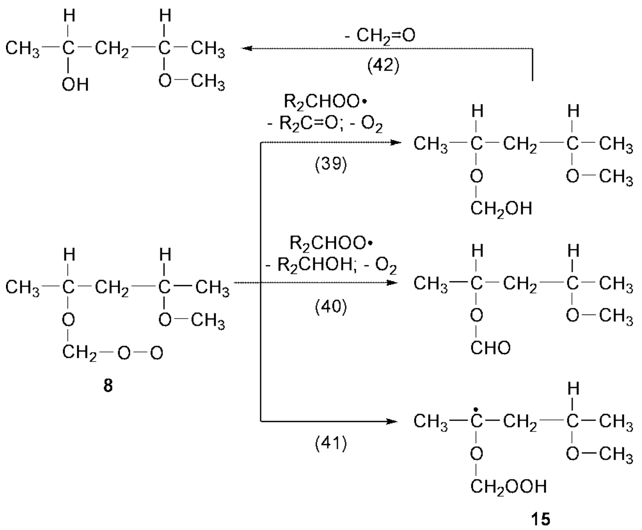


As can be seen from Table 2, *G*(methyl acetate) = 2.3 and methyl 2-methoxybutyrate was not detected (it should have eluted after 2,4-dimethoxypentane, but no reference material was available for its definitive identification making this statement rather tentative), and it seems likely that reaction (36), where a stronger C–C bond has to be broken, is indeed of minor importance.

In competition with oxyl radical formation, peroxyl radical **6** may undergo bimolecular termination according to reaction (37), and the resulting hemiacetal can be the precursor of 4-methoxypentan-2-one [reaction (38)].



Of similar importance to peroxyl radical **6** is peroxyl radical **8**. Decay route (21) in the general scheme leads to the formation of 4-methoxypentan-2-ol and 3-methoxy-1-methylbutyl formate [reactions (39) and (40) plus (42)]. At the highest dose rate used, their combined yield is $G = 1.9 \times 10^{-7}$ mol J^{-1}, somewhat lower but not far from the estimated yield of the precursor radical **4**. One also must consider an intramolecular H-transfer [reaction (41)] which contributes to the hydroperoxide yield.



The product formed in reaction (39) will lose formaldehyde [reaction (42)]. Based on the fact that the yield of 4-methoxypentan-2-ol is very low and that it can be reasonably well determined (reference material was available), it is concluded that reaction (39) is of minor importance. Thus the high yields of formaldehyde observed in this system must have further sources. Upon lowering the dose rate, the formaldehyde yield nearly doubles as do the yields of the organic hydroperoxides. This is taken as an indication that it is largely formed in the further breakdown of the material due to intramolecular autoxidation. Among others, a potential precursor could be the radical of the hydroperoxide **15** (note that the formaldehyde determination is done in acid media which would hydrolyse the α-alkoxyhydroperoxide).

Relevance to the poly(vinyl methyl ether) system

There is some disagreement in the literature[12–14] as to the absorption spectra of poly(vinyl methyl ether)-derived radicals and the possible interpretation of the reported[12] maximum at 310 nm. Since such a spectral feature is absent in the case of the model compound (*cf.* Fig. 1) and also in purified poly(vinyl methyl ether),[14,33] it seems that the maximum reported[12] for poly(vinyl methyl ether) is probably due to impurities present in a commercial sample used in that study.

The model compound data indicate that the carbon atoms in the position α to the alkoxyl groups are preferentially attacked by $^{\bullet}$OH (~80% attack compared to 50% abundance of H-atoms available for abstraction from these positions), and thus it is expected that a similar preference will be observed with the polymer (*cf.* ref. 33).

Product analysis for the model compound following irradiation in anoxic conditions allowed determination of the proportions of disproportionation reactions and recombination of radicals. Since recombination occurs with *ca.* 50% probability, it is expected that no more than half of the polymer radicals would recombine. This limits the maximum possible yield of intermolecular crosslinks to *ca.* 1.5×10^{-7} mol dm^{-3}, a relatively high value when compared to the other water-soluble polymers [*ca.* 15% recombination has been found in the poly(vinyl alcohol) system[1] and *ca.* 40% in poly(acrylic acid)[4]]. This is an important parameter for the radiation-induced formation of poly(vinyl methyl ether) hydrogels.

In the presence of dioxygen, dimer formation is suppressed, and hence also in the polymer no crosslinking can take place under such conditions. This simplifies the analysis of changes in molecular weight, since only one process (chain scission) is involved. The model study also provides evidence that the main pathway leading to chain scission is the fragmentation of oxyl radicals formed as short-lived intermediates in the decay of the peroxyl radicals.

Product studies on the model indicate the presence of chain autoxidation processes. Since the autoxidation chain reaction is terminated by radical recombination, and the latter is expected to be slower for polymer radicals, one expects that the autoxidation of the polymer will be even more efficient than that of 2,4-dimethoxypentane. In the model compound the autoxidation chain reaction occurs to a large extent by *intra*molecular H-abstraction, and in the polymer this is indeed the major autoxidation pathway.[33]

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