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Mechanism of the Reaction of Radicals with Peroxides and Dimethyl Sulfoxide in Aqueous Solution

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Abstract: The reactions of methyl and methylperoxyl radicals derived from dimethyl sulfoxide (DMSO) with hydrogen peroxide, peroxymonocarbonate (HCO_4^-), and persulfate were studied. The major reaction observed for the hydroperoxides was the abstraction of the hydrogen atom by the radicals. The radicals interact with a lone pair of electrons on the peroxide to produce methanol and formaldehyde. Furthermore, the results indicate that in RO_2H and RO_2R', electron-withdrawing groups cause a considerable increase in the reactivity of the peroxides towards the radicals and not only towards nucleophiles. The $HO_2^{\bullet}/O_2^{\bullet -}$ and $CO_3^{\bullet -}$ radicals react with DMSO to produce methyl radicals. Thus, the formation of the $^{\bullet}CH_3$ radicals in the presence of DMSO is not proof of the formation of the $^{\bullet}OH$ radicals in the system. These reactions must be considered when radical processes, such as in biological and catalytic systems, are studied. Especially, the plausible role of HCO_4^- ions in biological systems as a source of oxidative stress cannot be overlooked.

Keywords: dimethyl sulfoxide · hydrogen peroxide · persulfate · radicals · radiolysis

Introduction

It is well known that the chemistry of peroxides (i.e., hydrogen peroxide, organic peroxides, or other peroxides such as peroxodisulfate) in a wide variety of (industrial) chemical or biological systems often involves radical species formed in those solutions. Predominantly, hydroxyl radicals (or high-oxidation-state metal–peroxide or oxo intermediates) are produced through Fenton chemistry in the presence of catalytic amounts of transition-metal ions.[1–9] Peroxides are also known to react with reducing radicals, usually forming $RO^{\bullet}$ radicals.[10]

Hydroxyl radicals in turn react with organic molecules in solution to produce secondary radicals, for example, alkyl radicals.[11,12] Furthermore, in all catalytic processes involving alkyl radicals, alkylperoxyl radicals are formed in the presence of dioxygen.[12–20] These transients are also formed in biological systems usually during oxidative-stress phenomena.[21,22] However, the reactions of alkyl and alkylperoxyl radicals with peroxides were not studied.

Hydroxyl radicals are known to react with dimethyl sulfoxide (DMSO) to produce methyl radicals or peroxomethyl radicals in the presence of oxygen [see reactions (7)–(9) below].[23] Indeed, the formation of methane or ethane (or final products of methyl radicals in aerated solutions) in DMSO-containing aqueous solutions is often taken as evidence that hydroxyl radicals were intermediates in the reaction mechanism and, therefore, DMSO is used as a probe for hydroxyl radicals.[24–26]

Although DMSO is widely used to generate methyl radicals in dilute aqueous solutions by radiation or Fenton chemistry, its interactions with other radicals, which might be formed in the solution, was not fully studied. The reaction of hydroxyl radicals (produced by irradiating N_2O-saturated aqueous solutions or using the Fenton reagent) with DMSO results in the production of methane and ethane, with the respective yields dependent on dose rate (i.e., the steady-state concentration of the methyl radicals) and the concentration of DMSO. Ethane, the major product, is formed by the bimolecular radical reaction of two methyl

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radicals, whereas methane is formed by the abstraction of hydrogen atoms from DMSO or methanesulfinic acid (CH_3SOOH).[27,28] Recently, the rate constant of the reaction of methyl radicals with DMSO, thus contributing towards the formation of methane through abstraction of hydrogen atoms from the methyl group of DMSO, according to reaction (1), was reported.[29]

$$\begin{aligned} &{}^{\cdot}CH_3 + (CH_3)_2SO \rightarrow CH_4 + CH_2S(O)CH_3 \\ &k_1 = 100 \pm 20\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}\ (\mathrm{pH}\,4) \end{aligned} \tag{1}$$

Thus, it was of interest to study the reactions of further radicals with DMSO, for example, those derived from a peroxide/DMSO system.

As hydrogen peroxide is prevalent in biological systems[30] and is also a product of the irradiation of dilute aqueous solutions, it was of interest to study the reaction of hydrogen peroxide with methyl or methylperoxyl (in aerated systems) radicals derived from DMSO.

A variety of bleaching processes employ additives to catalyze the reactions of peroxides, which usually involve transfer reactions of oxygen atoms. Possible additives are carbonates or persulfates. However, as in all systems involving peroxides radical processes often contribute to the reaction mechanism, it was of interest to include peroxide substitutes, such as peroxymonocarbonate (HCO_4^-) and persulfate, and investigate their reactions with methyl or methylperoxyl radicals, or rather the influence of the addition of carbonates on the reaction between hydrogen peroxide and methyl or methylperoxyl radicals. The results may be relevant to radical-induced biological deleterious processes[31,32] and to the catalytic oxidation of various substrates by hydrogen peroxide in the presence of HCO_3^- ions.[33–35]

Experimental Section

General: All the materials used were of analytical-reagent grade and were purchased from Merck, Aldrich, or Fluka. The solutions were prepared using distilled water, which was further purified by using a Millipore Milli-Q system. The final resistance was better than $10\,\mathrm{M\Omega\,cm^{-1}}$. All pH measurements were performed using a Corning 220 or a HANNA HI 9017 pH meter, and the pH value was adjusted by the addition of $HClO_4$ and/or NaOH. N_2O gas was purchased from Maxima. Dioxygen traces were removed by passing the gas (He, Ar, or N_2O) through a wash bottle containing aqueous V^{2+} ions (0.1 M) in dilute H_2SO_4 over zinc amalgam (the aqueous solution of V^{2+} ions was prepared by the reduction of $NaVO_3$ with zinc amalgam) and a wash bottle containing distilled water. All the solutions were saturated with the desired gases by bubbling the gas through the solution in a glass syringe for 15 min.[36,37] Solutions with the desired oxygen content were prepared by mixing degassed solutions with oxygen-saturated solutions by syringe-to-syringe transfer.

Irradiation: A Noratom and a Nordion ^{60}Co-γ source with dose rates of 3.5–8.0 and 38—82 $\mathrm{Gy\,min^{-1}}$ (over the time range of the investigation), respectively, were used for low-dose-rate experiments and analysis of the products. The dose delivered to the vials, identical to those irradiated for the analysis of the final product, was measured using the Fricke dosimeter for low-dose-rate situations (irradiation with the ^{60}Co-γ source); a solution of 1.0×10^{-3} M NaCl, 1.4×10^{-3} M $FeSO_4$, and 0.8 N H_2SO_4 was used with $G(\mathrm{Fe^{III}}) = 15.6$.[38]

GC analysis: GC analyses of methane and ethane were performed on a HP 5890 gas chromatograph with FID and TCD detectors and a Poropak Q column. GC analysis of methanol was performed by using a high-space method on a Varian 3600 gas chromatograph using a MXT-WAX capillary column (0.53 mm × 30 m).

Analysis of formaldehyde: A previously reported procedure was followed[39] in which formaldehyde reacts with a reagent containing 0.050 M acetylacetone, 1.0 M ammonium acetate, and 0.033 M acetic acid to form a yellow complex. The concentration of formaldehyde was determined colorimetrically at the wavelength of maximum absorption ($\lambda = 412$ nm).

Analysis of peroxides: The concentration of peroxides was determined by using the iodide method.[40] A solution containing KI and ammonium heptamolybdate is mixed with a solution containing potassium biphthalate to obtain the following final concentrations: 3.2×10^{-5} M ammonium heptamolybdate, 0.02 M potassium biphthalate, and 0.08 M KI at pH 4. This solution is added the samples to be analyzed, which contain various concentrations of peroxides, and the I_3^- complex is formed according to reactions (2) and (3).

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2\,H_2O \tag{2}$$

$$I_2 + I^- \rightleftharpoons I_3^- \tag{3}$$

The formation of I_3^- ions is followed at the absorption maximum of $\lambda = 352$ nm. This method does not differentiate between hydrogen peroxide and other peroxides in the system.

Analysis of sulfate ions: Detection by ion chromatography on a Dionex DX500 Instrument with an anion specific column (ION PAC AS 4 A-SC 4 mm) and a carbonate buffer as an eluant was carried out.

UV/Vis studies: A Hewlett Packard 8452 A diode array UV/Vis spectrophotometer recorded the UV/Vis spectra.

Formation of radicals with ionizing radiation: Herein, the products of the reaction of methyl or methylperoxyl radicals with hydrogen peroxide, peroxymonocarbonate, or persulfate in aqueous solutions were studied. The radicals were formed by irradiating the solutions with ionizing radiation. When ionizing radiation is absorbed by a dilute aqueous solution the initial products are formed according to reaction (4).[41]

$$H_2O \xrightarrow{\gamma,\,e^-} {}^{\cdot}H\ (0.60),\ {}^{\cdot}OH\ (2.65),\ e^-_{aq}\ (2.65),\ H_2O_2\ (0.75),\ H_2\ (0.45) \tag{4}$$

The G values are given in parentheses (G values are defined as the number of molecules of each product per 100 eV of radiation absorbed by the solution). The distribution of these products in the solution after 1×10^{-7} s is homogeneous.[41]

The reactions of hydroxyl radicals were studied by saturating the solutions with N_2O (0.022 M) to decrease the interference from other initial radicals as a result of the reaction of N_2O with the hydrated electron [e^-_{aq}; reaction (5)].[11]

$$e^-_{aq} + N_2O \rightarrow N_2 + {}^{\cdot}OH + OH^- \quad k_5 = 8.7\times10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1} \tag{5}$$

It is important that [H^+] was kept below 1×10^{-3} M as e^-_{aq} reacts in a diffusion-controlled manner with protons [reaction (6)].[11] Under these conditions, the hydrated electrons all react with N_2O to yield the hydroxyl radical as the major product.

$$e^-_{aq} + H_3O^+ \rightarrow {}^{\cdot}H + H_2O \quad k_6 = 2.2\times10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1} \tag{6}$$

Methyl radicals were formed in aqueous solutions containing DMSO by reactions (7) and (8).[27]

$${}^{\cdot}OH + (CH_3)_2SO \rightarrow (CH_3)_2S^{\cdot}(O)OH \quad k_7 = 7.0\times10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1} \tag{7}$$

$$(CH_3)_2S^{\cdot}(O)OH \rightarrow CH_3S(O)OH + {}^{\cdot}CH_3 \quad k_8 = 1.5\times10^7\,\mathrm{s}^{-1} \tag{8}$$

In solutions containing dioxygen, methyl, or other alkyl radicals ($^{\bullet}R$) are converted into the corresponding peroxyl ($RO_2^{\bullet}$) radicals in reactions approaching the diffusion controlled limit [reaction (9)]; for example:

$$O_2 + {}^{\bullet}CH_3 \rightarrow {}^{\bullet}OOCH_3 \quad k_9 = 4.1 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1\,[42,43]} \tag{9}$$

Results and Discussion

Reaction of hydrogen peroxide with methyl radicals: N_2O-saturated aqueous solutions containing hydrogen peroxide (0.50–1.5×10^{-3} M) and DMSO (0.10 M) at pH 5.5 were irradiated in vials with a ^{60}Co-γ source (230 rad min^{-1}) for a total dose of 6900—100 000 rad. Blank solutions contained only DMSO (0.10 M). The resulting mixtures were analyzed by GC for the gaseous products ethane and methane (Table 1). As expected, N_2O-saturated solutions containing DMSO only result in the production of methane and ethane.[27,28] The relative yields of methane and ethane depend on the concentration of DMSO and the dose rate, as these gases are formed by reactions (1) and (10).

$$2\,{}^{\bullet}CH_3 \rightarrow C_2H_6 \tag{10}$$

Thus, a combined $G(^{\bullet}CH_3)$ value of 6.0 results, that is, all the initially produced hydroxyl radicals during the radiolysis of aqueous solutions are converted into methyl radicals.

On the introduction of hydrogen peroxide into the system, the yield of ethane decreases slightly versus the DMSO blanks, whereas the yield of methane increases dramatically, thus resulting in a combined $G(^{\bullet}CH_3)$ value of up to 10.7 under the above conditions; that is, more methyl radicals were produced relative to the initial radical yield ($G=6.0$). Therefore, the presence of hydrogen peroxide in solution induces the production of additional methyl radicals.

The reaction of methyl radicals with hydrogen peroxide has been studied,[44] but the results given herein differ considerably from those previously reported for a system containing less DMSO[44] (10^{-3}–10^{-2} M vs. 0.10 M in this system). The rate constant of the abstraction of hydrogen atoms from hydrogen peroxide by the methyl radical has been reported [reaction (11)]:[44]

$$^{\bullet}CH_3 + H_2O_2 \rightarrow CH_4 + {}^{\bullet}HO_2 \quad k_{11} = 2.7 \times 10^4\,\text{M}^{-1}\,\text{s}^{-1} \tag{11}$$

whereas the reaction of methyl radicals with hydrogen peroxide to produce the hydroxyl radicals has been ruled out. In the previous study (which used relatively low concentrations of DMSO), the production of methane increased with increasing concentration of hydrogen peroxide, but no catalytic effect had been observed.[44]

The present results indicate that at relatively high concentrations of DMSO and low dose rates reaction (11) is followed by reaction (12) (pK_a value of $HO_2^{\bullet}$ is 4.8[45]).

$$\begin{aligned}(CH_3)_2SO + HO_2^{\bullet}/O_2^{\bullet-} &\rightarrow (CH_3)_2S^{\bullet}O_2H \rightarrow \\ {}^{\bullet}CH_3 + CH_3S(O)OOH/CH_3S(O)OO^{-}&\end{aligned} \tag{12}$$

This behavior is the source of the additional yield of methyl radicals.

It should be pointed out that one cannot rule out the possibility that reaction (13), which is analogous to reaction (31), also occurs.

Table 1. Products from irradiated solutions containing 0.10 M DMSO with/without the addition of hydrogen peroxide at various concentrations and/or the addition of bicarbonate.

$[H_2O_2]$ [M]	G(peroxides)[a]	$G(CH_3OH)$	$G(CH_2O)$	$G(C_2H_6)$	$G(CH_4)$	pH	$[HCO_3^-]$ [M]	G(peroxides)[a]	$G(^{\bullet}CH_3)$[b]
0	–	–	–	1.5	3.0	5.5	–	–	6.0
5.0×10^{-4}	–	–	–	1.2	6.6	5.5	–	–	9.0
1.0×10^{-3}	–	–	–	1.1	8.5	5.5	–	–	10.7
1.5×10^{-3}	–	–	–	0.9	8.9	5.5	–	–	10.7
0	0.4	0	0	1.5	3.0	8.8		0.4	6.0
5.0×10^{-4}	0.2	0.5	0.24	1.2	6.7	8.8	–	0.2	9.8
1.0×10^{-3}	0.1	1.2	0.26	1.1	8.5	8.8	–	0.1	12.2
1.5×10^{-3}	0	1.8	0.28	0.9	9.0	8.8	–	0	12.9
0	0.4	0	0	2.3	5.0	8.8	0.050	0.4	9.6
5.0×10^{-4}	0.1	0.6	0.28	1.2	5.8	8.8	0.050	0.1	9.1
1.0×10^{-3}	0	1.3	0.49	1.1	4.2	8.8	0.050	0	8.2
1.5×10^{-3}	0	1.9	0.70	1.1	3.2	8.8	0.050	0	8.0
0	0.4	0	0	2.6	5.2	8.8	0.10	0.4	10.4
5.0×10^{-4}	0.1	0.6	0.32	1.3	5.6	8.8	0.10	0.1	9.1
1.0×10^{-3}	0	1.6	0.54	1.2	3.7	8.8	0.10	0	8.3
1.5×10^{-3}	0	2.1	0.72	1.2	3.0	8.8	0.10	0	8.2

[a] $G(\text{peroxides}) = G(H_2O_2) + G(CH_3OOH) + G(CH_3S(O)OOH) + G(HO_2CH_2(CH_3SO))$; the analysis of peroxides (see Materials and Methods) does not differentiate between these peroxides. [b] $G(CH_3OH) + G(CH_2O) + 2\,G(C_2H_6) + G(CH_4) = G(^{\bullet}CH_3)$; given under the assumption that all radicals react to produce these products exclusively.

$$(CH_3)_2SO + HO_2^{\cdot} \rightarrow H_2O_2 + {}^{\cdot}CH_2(CH_3)SO \qquad (13)$$

The results suggest that reaction (12) is relatively slow, and therefore the chain reaction is short and observed only at relatively high concentrations of DMSO. The results, thus, indicate that methyl radicals are formed not only by the reaction of the hydroxyl radicals with DMSO, but also by its reaction with the superoxide radicals.

Possible termination reactions are given by reactions (1), (10), and (14)–(16).

$$2\,HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (14)$$

$${}^{\cdot}HO_2 + {}^{\cdot}CH_3 \rightarrow CH_3O_2H \qquad (15)$$

$$\begin{aligned}&{}^{\cdot}CH_2(CH_3)SO + HO_2^{\cdot}/{}^{\cdot}CH_3 \rightarrow\\ &HOOCH_2(CH_3)SO/CH_3CH_2S(CH_3)O\end{aligned} \qquad (16)$$

It should be mentioned that especially under conditions of long irradiation times the oxygen produced in reaction (14) (rather quickly under these pH conditions) would react with the methyl radicals to produce methylperoxyl (${}^{\cdot}OOCH_3$) radicals.

The fact that the production of ethane decreases slightly in samples containing hydrogen peroxide in a concentration-dependent fashion is in accord with the relatively low rate constant of reaction (11), which therefore lowers only slightly the steady-state concentration of the methyl radicals.

The effect of bicarbonate on the reaction of methyl radicals with hydrogen peroxide: In the bleaching industry, peroxymonocarbonate, also called peroxocarboxylic acid, is often employed as a substitute for hydrogen peroxide. It is well known that the addition of carbonate accelerates the reaction of hydrogen peroxide with various reductants as the considerably more reactive peroxycarbonate ion (HCO_4^-) is produced.[46,47] The method for the activation of hydrogen peroxide by bicarbonate developed by Drago and co-workers[48,49] encompasses an intermediate peroxomonocarbonate complex as the oxidizing species in the chain reaction. The reaction between hydrogen peroxide and bicarbonate to form HCO_4^- ions proceeds very quickly at room temperature in aqueous solutions at approximately neutral pH.

Peroxymonocarbonate is formed in the equilibrium reaction (17) and subsequently oxidizes nucleophilic substrates (S) [reaction (18); NHE = normal hydrogen electrode].[46,47,50]

$$H_2O_2 + HCO_3^- \rightleftharpoons HCO_4^- + H_2O \quad k_{17} = 0.33\,\text{M}^{-1} \qquad (17)$$

$$\begin{aligned}&S + HCO_4^- \xrightarrow{k^{18}} SO + HCO_3^- \quad E^{\circ}(HCO_4^-/HCO_3^-) =\\ &1.8 \pm 0.1\,\text{V (vs NHE/25}\,^{\circ}\text{C)}\end{aligned} \qquad (18)$$

The second-order rate constants k_{18} of the oxidizing reaction of HCO_4^- ions are generally several orders of magnitude (200–2000, depending on the substrates) larger than the respective reactions with hydrogen peroxide.[46,47]

In general, peroxocarboxylic acids are formed by the reaction of RC(O)X with hydrogen peroxide [reaction (19)].

$$RC(O)X + H_2O_2 \rightarrow RC(O)OOH + HX \qquad (19)$$

The activation of hydrogen peroxide by bicarbonate has recently been studied intensively as the hydrogen peroxide/bicarbonate system has the potential to replace organic peroxides or peroxo acids in organic syntheses (e.g., epoxidation of olefins), in bleaching processes, and as active ingredients in cleaning agents. The reactive hydrogen peroxide/carbonate complex is also of importance in biological systems in which the HCO_4^- ion is one of the reactive oxygen species (ROS) that contributes to oxidative stress in biological systems.[21,22]

N_2O-saturated aqueous solutions containing hydrogen peroxide ($0.50–1.5\times10^{-3}\,\text{M}$) and DMSO (0.10 M) at pH 8.8, and solutions with added bicarbonate (0.050 or 0.10 M) were irradiated in vials with a ^{60}Co-γ source (230 rad min^{-1}) for a total dose of 6900–100 000 rad. Blank solutions contained only DMSO (0.10 M). The resulting mixtures were initially analyzed by GC for the gaseous products ethane, methane, and, later on, formaldehyde, methanol, and peroxides according to the procedures given above (Table 1, Figure 1, and Figure 2. In the absence of hydrogen peroxide, the addition of bicarbonate had a major influence on the yield of methyl radicals produced in the system. Therefore, it should be concluded that reaction (20) takes place in addition to reactions (1) and (10):

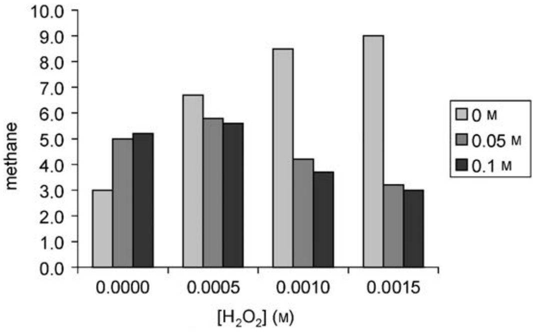


Figure 1. Methane production in irradiated, deaerated aqueous solutions containing DMSO (0.10 M), hydrogen peroxide (0–0.0015 M), and hydrogen carbonate (0–0.1 M) at pH 8.8.

$${}^{\cdot}CH_3 + HCO_3^- \rightarrow CH_4 + CO_3^{\cdot-} \qquad (20)$$

or less probably reactions (21) and (22) occur:

$${}^{\cdot}CH_3 + CO_3^{2-} \xrightarrow{H^+} CH_4 + CO_3^{\cdot-} \qquad (21)$$

$$\begin{aligned}&CO_3^{\cdot-} + (CH_3)_2SO \xrightarrow{H_2O} {}^{\cdot}CH_3 + CH_3S(O)OCO_2^-/\\ &(CH_3S(O)OH + CO_3^{2-})\end{aligned} \qquad (22)$$

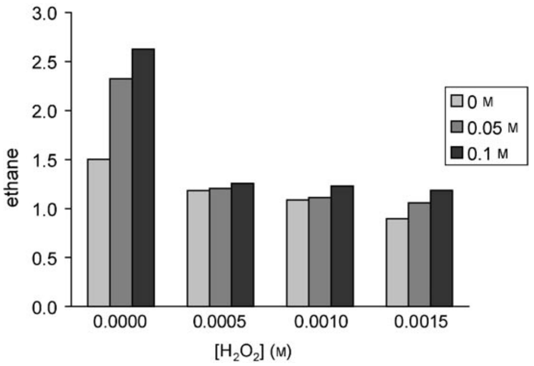


Figure 2. Ethane production in irradiated, deaerated aqueous solutions containing DMSO (0.10 M), hydrogen peroxide (0–0.0015 M), and hydrogen carbonate (0–0.1 M) at pH 8.8.

It is plausible that also the termination reaction (23) plays a role.

$$^{\bullet}CH_3 + CO_3^{\bullet-} \rightarrow CH_3OCO_2^- \quad (23)$$

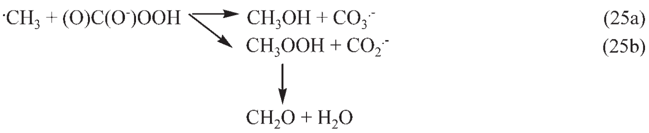
It should be pointed out that the results indicate that reaction (20) is not fast, and therefore the yield of ethane increases with increasing concentration of bicarbonate. The reaction of the methyl radicals with bicarbonate has not been reported so far. It should be noted that probably other alkyl radicals formed in the presence of bicarbonate will react similarly. Likewise, reaction (22) has not been reported and should be taken into account in all systems containing DMSO and bicarbonate.

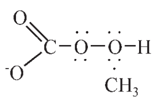
With the introduction of hydrogen peroxide into the bicarbonate-containing system, the total yield of the methyl radicals (initially calculated from the yield of the gaseous products ethane and methane alone) decreases dramatically, even below $G = 6.0$. Thus, it is obvious that additional products besides ethane and methane are formed from the reactions of the methyl radicals in this system. Thus, the search for products was extended to include the plausible products methanol, formaldehyde, and peroxides. The total yield of peroxides was determined without differentiating between them. No other products were observed in any of these analytical techniques.

It is seen that while the addition of hydrogen peroxide or bicarbonate alone increases the total yield of methyl radicals, this yield decreases on the addition of both solutes into the system. This behavior is mainly evident in a drastic decrease in the amount of methane produced in those systems containing hydrogen peroxide and bicarbonate. The decrease in ethane production on changing the concentration of hydrogen peroxide on the other hand is very similar with or without the addition of bicarbonate into the system. These results indicate clearly that the methyl radicals react with the complex anion $OC(O^-)OOH$ as methyl radicals react with excess bicarbonate or hydrogen peroxide through reactions (11) or (20) and eventually reproduce methyl radicals through the chain reactions (22) or (12). Thus, reaction (24) is clearly faster than reactions (20) or (11), though under the experimental conditions $[H_2O_2] = 30[HCO_4^-]$.

$$^{\bullet}CH_3 + (O)C(O^-)OOH \rightarrow \text{products} \quad (24)$$

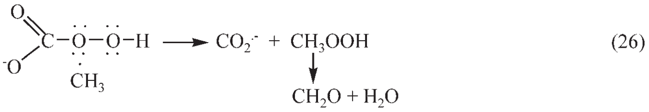
Analysis of the product distribution shows that whereas the yield of methanol is nearly independent of the bicarbonate concentration, the yield of formaldehyde rises with increasing bicarbonate concentration. Both formaldehyde and methanol are formed in parallel reactions [reactions (25a) and (25b)].





A

A conceivable intermediate that leads to the formation of methanol is **A**, whereas formaldehyde is derived by reaction (26).



As the combined yield of methanol and formaldehyde is small relative to the total amount of methyl radicals produced in the system, it is plausible that methane is produced by reaction (27).

$$^{\bullet}CH_3 + (O)C(O^-)OOH \rightarrow CH_4 + (O)C(O^-)OO^{\bullet} \quad (27)$$

It is also plausible that the radical $(O)C(O^-)OO^{\bullet}$ does not react with DMSO to produce further methyl radicals. The fate of the latter radical with DMSO might involve abstraction of a hydrogen atom to form $^{\bullet}CH_2(CH_3)SO$ or oxidation of the sulfoxide to sulfone. It should be noted that in GC analysis of solutions containing bicarbonate and hydrogen peroxide at least one further product, not identified, is observed. The main conclusion to be drawn from the bicarbonate/hydrogen peroxide/DMSO system is that the formation of the $(O)C(O^-)OOH$ complex accelerates and alters the mechanism of reaction of hydrogen peroxide with methyl radicals.

It should be mentioned that the yield of the peroxide products measured under the experimental conditions is not accurate, as the amount of peroxides produced in the system is relatively small compared with the initial concentration of hydrogen peroxide. Moreover, $G(\text{peroxides}) = 0$ indicates that peroxides in those systems disappear. As $G(H_2O_2) = 0.75$ for the irradiation of dilute aqueous solutions, approximately this amount is destroyed in those systems that show $G(\text{peroxides})=0$. This yield is also approximately equal to the yield of formaldehyde produced in those systems, thus supporting the proposed mechanism.

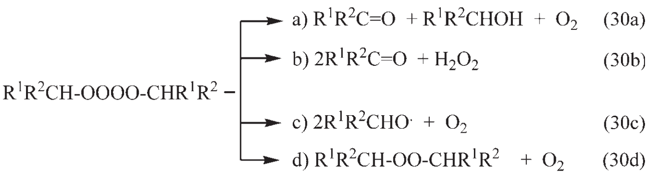
Reaction of hydrogen peroxide with methylperoxyl radicals: Alkyl radicals form peroxoalkyl radicals in the presence of dioxygen, therefore methyl radicals are converted exclusively into methylperoxyl ($^{\bullet}O_2CH_3$) radicals in aerated solutions. In general, these species are relatively strong one-electron oxidants.[10] Moreover, the chemistry of organic peroxyl radicals ROO$^{\bullet}$ is characterized by their biradical reactions, thus leading to the formation of a variety of products, as shown, for example, in reaction (28).

$$2\,(CH_3)_2CHOO^{\cdot} \rightarrow (CH_3)_2CHOOH + (CH_3)_2CO + 1/2\,O_2/{}^1O_2 \quad (28)$$

The chemistry of organic peroxyl radicals in aqueous solution has been intensively studied by von Sonntag and coworkers.[51] In general, the first intermediate formed by bimolecular reactions of two peroxyl radicals is an intermediate of the type given in reaction (29).

$$2\,R^1R^2CH{-}OO^{\cdot} \rightarrow R^1R^2CHOOOOCHR^2R^1 \quad (R^1,\ R^2 = H \text{ or alkyl}) \quad (29)$$

The dimer produced in reaction (29) is short-lived and can decompose according to reactions (30a)–(30d), which often occur in parallel.



$R^1R^2CH\text{-}OOOO\text{-}CHR^1R^2$

a) $R^1R^2C{=}O + R^1R^2CHOH + O_2$ (30a)

b) $2R^1R^2C{=}O + H_2O_2$ (30b)

c) $2R^1R^2CHO^{\cdot} + O_2$ (30c)

d) $R^1R^2CH\text{-}OO\text{-}CHR^1R^2 + O_2$ (30d)

Thus, the final products of the decomposition of $CH_3OO^{\bullet}$ in aqueous solutions are 50% CH_2O, 27% CH_3OH, 14% CH_3OOH, 5% HCO_2H, and 2% CH_3OOCH_3,[51] with the detection of 23% of H_2O_2 (all the given percentages are relative to the yield of the hydroxyl radical). Obviously in this case, 56% of the radicals react by reaction (30a), which is basically a disproportionation reaction.

N_2O/O_2-saturated (70:30) aqueous solutions containing hydrogen peroxide (0.50–1.5×10^{-3} M) and DMSO (0.10 M) at pH 5.5 and 8.8 were irradiated in vials with a ^{60}Co-γ source (230 rad min^{-1}) for a total dose of 6900–100000 rad. Blank solutions contained only DMSO (0.10 M). The resulting mixtures were analyzed for the products methanol, formaldehyde, and peroxides (Table 2).

The results clearly show that in the absence of bicarbonate only the pH of the solution affects the formaldehyde and methanol yields, which is in accord with a previous report.[52] On the other hand, the addition of hydrogen peroxide affects the yield of peroxides. The fact that the production of formaldehyde and methanol is independent of the concentration of hydrogen peroxide indicates that hydrogen peroxide does not react or reacts very slowly with $^{\bullet}O_2CH_3$ radicals, as otherwise at least one of those product yields would have been influenced.

Table 2. The effect of the addition of hydrogen peroxide on the production of methanol, formaldehyde, and peroxides in irradiated, aerated solutions containing 0.10 M DMSO.[a]

$[H_2O_2]$ [M]	$[HCO_3^-]$ [M]	$G(CH_2O)$	pH	$G(CH_3OH)$	G(peroxides)[b]
0	–	2.8	5.5	1.5	2.9
5.0×10^{-4}	–	2.8	5.5	1.5	2.9
1.0×10^{-3}	–	2.8	5.5	1.5	3.7
1.5×10^{-3}	–	2.8	5.5	1.5	4.8
0	–	3.2	8.8	1.1	3.0
5.0×10^{-4}	–	3.2	8.8	1.1	3.0
1.0×10^{-3}	–	3.2	8.8	1.1	3.2
1.5×10^{-3}	–	3.2	8.8	1.1	4.8
0	0	3.2	8.8	1.1	3.0
0	0.050	3.2	8.8	1.1	3.0
0	0.10	3.2	8.8	1.1	3.0
5.0×10^{-4}	0	3.2	8.8	1.1	3.0
5.0×10^{-4}	0.050	2.8	8.8	1.5	1.8
5.0×10^{-4}	0.10	2.4	8.8	1.9	1.4
1.0×10^{-3}	0	3.2	8.8	1.1	3.2
1.0×10^{-3}	0.050	2.8	8.8	1.5	1.7
1.0×10^{-3}	0.10	2.3	8.8	2.0	1.1
1.5×10^{-3}	0	3.2	8.8	1.1	4.8
1.5×10^{-3}	0.050	2.7	8.8	1.6	2.7
1.5×10^{-3}	0.10	2.3	8.8	2.0	0.8

[a] $G(CH_3OH)+G(CH_2O)+2\,G(C_2H_6)+G(CH_4)=G({}^{\bullet}CH_3)$; given under the assumption that all radicals react to produce these products exclusively. [b] $G(\text{peroxides})=G(H_2O_2)+G(CH_3OOH)+G(CH_3S(O)OOH)+G(HO_2CH_2(CH_3SO))$; analysis of the peroxides (see Materials and Methods) does not differentiate between these peroxides.

The increased yield of peroxides can be explained by reactions (31)–(33).

$$CH_3O_2^{\cdot} + (CH_3)_2SO \rightarrow CH_3O_2H + {}^{\cdot}CH_2(CH_3)SO \quad (31)$$

$$^{\cdot}CH_2(CH_3)SO + O_2 \rightarrow {}^{\cdot}O_2CH_2(CH_3)SO \quad (32)$$

$$^{\cdot}O_2CH_2(CH_3)SO + H_2O_2 \xrightarrow{H_2O} HO_2^{\cdot}/(O_2^{-\cdot} + H_3O^+) + HO_2CH_2(CH_3)SO \quad (33)$$

If reaction (34), which is analogous to reaction (12), contributes to the mechanism, it does so also in the absence of hydrogen peroxide and would not influence the yield of any of the measured products.

$$CH_3O_2^{\cdot} + (CH_3)_2SO \rightarrow {}^{\cdot}CH_3 + CH_3S(O)OOCH_3 \quad (34)$$

The main product of the reaction of methylperoxyl radicals ($^{\bullet}O_2CH_3$) with each other is formaldehyde [reaction (30)].[51]

The effect of bicarbonate on the reaction of hydrogen peroxide with methylperoxyl radicals: N_2O/O_2-saturated (70:30) aqueous solutions containing hydrogen peroxide ($0.50–1.5\times10^{-3}$ M) and DMSO (0.10 M) at pH 8.8 and solutions with added bicarbonate (0.050 or 0.10 M) were irradiated in vials with a ^{60}Co-γ source (230 rad min^{-1}) for a total dose of 6900–100 000 rad. Blank solutions contained only DMSO (0.10 M). The resulting mixtures were analyzed for the products methanol, formaldehyde, and peroxides (Table 2).

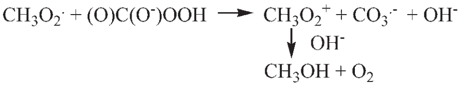
The results show that:

1) The addition of bicarbonate does not influence the yield of the products in the absence of hydrogen peroxide; thus, we conclude that methylperoxyl radicals do not react or react very slowly with bicarbonate.
2) Despite this fact, the yield of the products changes dramatically by the addition of bicarbonate in the presence of hydrogen peroxide (though under the experimental conditions $[H_2O_2]=30[HCO_4^-]$), in particular:

a) the yield of formaldehyde decreases on the addition of bicarbonate;
b) the yield of methanol rises with increasing bicarbonate concentration;
c) the sum of these two products (methanol and formaldehyde) is independent of the concentration of hydrogen peroxide or bicarbonate;
d) the yield of peroxides decreases with increasing bicarbonate concentration in solution.

Therefore, the following conclusions can be drawn:

1) The yield of formaldehyde is reduced to only two thirds of the amount produced in solutions not containing bicarbonate; thus, $k(CH_3O_2^{\bullet}+HCO_4^-)=10\,k(CH_3O_2^{\bullet}+H_2O_2)$.
2) The main reaction in bicarbonate containing solutions is shown in reaction (35).



$$CH_3O_2^{\cdot} + (O)C(O^-)OOH \longrightarrow \underset{\substack{\downarrow\, OH^- \\ CH_3OH\, +\, O_2}}{CH_3O_2^+} + CO_3^{\cdot -} + OH^- \quad (35)$$

This reaction clearly does not proceed by an outer-sphere mechanism, and probably a free $CH_3O_2^+$ ion is not formed, rather a partial positive charge, which results in an attack by an OH^- ion or water. This reaction increases the yield of methanol and decreases the yield of the products, mainly formaldehyde and peroxides, formed in reaction (36).

$$2\,CH_3O_2^{\cdot} \rightarrow \text{products} \quad (36)$$

The methylperoxyl radical acts as a reducing species (formally resulting in a $CH_3O_2^+$ species) in contrast to most of its typical reactions,[51] though disproportionation reactions [e.g., reaction (30a)] are observed.

3) The dramatic decrease in the yield of the peroxide in the presence of bicarbonate shows that $k_{35}=3000\,k_{31}$.

The results discussed above show that the HCO_4^- ion is considerably more reactive toward the $CH_3O_2^{\bullet}$ radicals than hydrogen peroxide. Moreover, the formation of the HCO_4^- ion changes the mechanism of the reaction between the radicals and hydrogen peroxide at least partially and, therefore, the product distribution of the reaction. Thus, it is seen that the addition of bicarbonate to hydrogen peroxide also catalyzes the reaction of bicarbonate with radicals and not just nucleophiles. These findings are in accord with the use of bicarbonate as an enhancer of hydrogen peroxide in industrial oxidations. Furthermore, the above findings might help to shed light on important mechanisms in biological reactions.

The reaction of persulfate with methyl radicals: Many bleaching processes employ peroxide/persulfate ($^-O_3SOOSO_3^-$) systems, and the sulfate radical ($SO_4^{\bullet -}$) has been widely assumed to be the reactive species. Persulfate differs from other peroxide ROOH systems in that the abstraction of a hydrogen atom by methyl radicals [reaction (11)] is not possible in this case.

N_2O-saturated aqueous solutions containing persulfate ($0.10–1.0\times10^{-3}$ M) and DMSO (0.10 M) at pH 4.5 were irradiated in vials with a ^{60}Co-γ source (230 rad min^{-1}) for a total dose of 6900–100 000 rad. Blank solutions contained only DMSO (0.10 M). The resulting mixtures were analyzed by GC for the gaseous products ethane and methane and for the plausible products methanol, formaldehyde, and sulfate ions (Table 3). The yields of ethane and methane decreased with increasing persulfate concentration. That the yield of ethane or methane is not decreased considerably more, indicates that the reaction of persulfate with the methyl radicals is not fast. The addition of persulfate to the system also leads to the formation of methanol (the yield of methanol rises with increasing persulfate concentration), whereas formaldehyde was not formed. These products led to a combined sum of $G=6$ for the yield of the methyl radical (Table 3). Moreover, the formation of sulfate ions was measured, and it is clear that sulfate ions are produced in a catalytic process (Figure 3).

Analysis of the products from the experimental studies suggest a mechanism given in reactions (37)–(39).

Table 3. Irradiation products of solutions containing 0.10 M DMSO with/without the addition of persulfate of varying concentrations.[a]

[persulfate] [M]	pH	$G(CH_4)$	$G(C_2H_6)$	$G(CH_3OH)$	$G(SO_4^{2-})$	$G(^{\bullet}CH_3)$[b]
0	4.5	3.0	1.5	0	0.1	6.0
1.0×10^{-4}	4.5	2.6	1.4	0.6	11	6.0
2.0×10^{-4}	4.5	2.5	1.3	0.9	23	6.0
4.0×10^{-4}	4.5	2.5	1.3	1.0	47	6.1
8.0×10^{-4}	4.5	2.4	1.2	1.2	89	6.0
10.0×10^{-4}	4.5	2.4	1.2	1.3	120	6.1

[a] CH_2O was not detected in these experiments. [b] $G(CH_3OH)+2G(C_2H_6)+G(CH_4)=G(^{\bullet}CH_3)$; given under the assumption that all radicals react to produce these products exclusively.

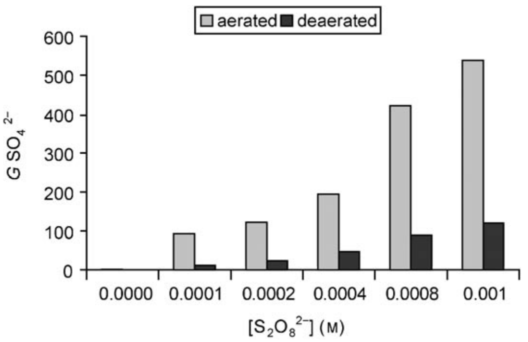


Figure 3. Comparison of sulfate formation in irradiated, deaerated or aerated aqueous solutions containing DMSO (0.10 M) and persulfate (0–0.001 M) at pH 4.5.

$$^{\bullet}CH_3 + S_2O_8^{2-} \xrightarrow{H_2O} (CH_3^+/CH_3OH) + SO_4^{2-} + SO_4^{\bullet -} \qquad (37)$$

$$SO_4^{\bullet -} + (CH_3)_2SO \rightarrow {}^{\bullet}CH_2(CH_3)SO + H^+ + SO_4^{2-} \qquad (38)$$

$$^{\bullet}CH_2(CH_3)SO + S_2O_8^{2-} \xrightarrow{H_2O} SO_4^{\bullet -} + HOCH_2(CH_3)SO + H^+ + SO_4^{2-} \qquad (39)$$

This mechanism explains the catalytic formation of sulfate ions in this system. At high doses slightly more than twice the total amount of persulfate in the system is detected as sulfate ions; therefore, the additional sulfate ions must stem from the oxidation of DMSO. The explanation for this finding is that apparently reaction (40) is faster than reaction (38), which should also hold true for CH(O)S(O)CH$_3$ and the final products in this chain of reactions, the end product of which is sulfate.

$$SO_4^{\bullet -} + HOCH_2(CH_3)SO \rightarrow SO_4^{2-} + H^+ + {}^{\bullet}CH(OH)S(O)CH_3 \qquad (40)$$

The fact that reaction (38) occurs and not reaction (41) is interesting, as it proves that oxidizing radicals with different characteristics react differently with DMSO.

$$SO_4^{\bullet -} + (CH_3)_2SO \rightarrow {}^{\bullet}CH_3 + CH_3S(O)OSO_3^- \qquad (41)$$

Thus, the radicals $^{\bullet}$OH, HO$_2^{\bullet}$, and CO$_3^{\bullet -}$ react predominantly by the pathway that produces methyl radicals, whereas the abstraction of hydrogen atoms from the methyl groups of DMSO probably also plays a role. On the other hand, SO$_4^{\bullet -}$ radicals react exclusively by the pathway of the abstraction of hydrogen atoms from the methyl group, otherwise a yield of $G(^{\bullet}CH_3) > 6$ would have been found.

From the decrease in the concentration of ethane and methane, the radiation dose rate, and the rate constants for reactions (1) and (10) ($k_1 = 100$[29] and $k_{10} = 1.2\text{–}1.6 \times 10^9\,M^{-1}s^{-1}$, respectively),[43] the rate constant for reaction (37) can be estimated as $k_{37} = 500 \pm 250\,M^{-1}s^{-1}$. This value is not very accurate because of the decomposition of persulfate in the chain reaction.

The reaction of persulfate with methylperoxyl radicals: Whereas the sulfate radical (SO$_4^{\bullet -}$) has been widely assumed to be the reactive species in all persulfate-containing radical reactions, a recent report shows that in aerated solutions (under oxidizing conditions) the radical anion O$_2$S$_2$O$_8^{\bullet -}$ is also involved.[53]

N$_2$O/O$_2$-saturated (70:30) aqueous solutions containing persulfate (0.10–1.0 × 10^{-3} M) and DMSO (0.10 M) at pH 4.5 were irradiated in vials with a ^{60}Co-γ source (230 rad min^{-1}) for a total dose of 6900–100000 rad. Blank solutions contained only DMSO (0.10 M). The resulting mixtures were analyzed for the products methanol, formaldehyde, and sulfate ions (Table 4). No peroxide final products were detected; moreover, all the persulfate decomposed during the irradiation at such high doses. The yield of formaldehyde decreases with increasing persulfate concentration, whereas the yield of methanol increases. These results clearly show that formaldehyde is formed by the biradical reaction of two methylperoxyl radicals [reaction (42)].

Table 4. Irradiation products of aerated aqueous solutions containing 0.10 M DMSO with/without the addition of persulfate of varying concentrations.

[persulfate] [M]	pH	G(CH$_2$O)	G(CH$_3$OH)	G(SO$_4^{2-}$)	G($^{\bullet}$CH$_3$)[a]
0	4.5	2.8	1.5	0.7	4.3
1.0 × 10^{-4}	4.5	2.5	1.8	7.2	4.3
2.0 × 10^{-4}	4.5	2.2	2.1	106	4.3
4.0 × 10^{-4}	4.5	1.7	2.6	195	4.3
8.0 × 10^{-4}	4.5	0.7	3.6	422	4.3
10.0 × 10^{-4}	4.5	0.4	3.9	538	4.3

[a] $G(CH_3OH) + G(CH_2O) = G(^{\bullet}CH_3)$; given under the wrong assumption [see reaction (31)] that all radicals react to produce these products exclusively.

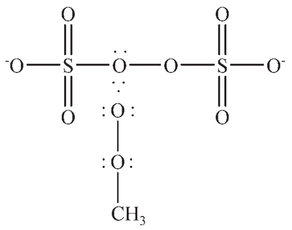
$$2\,CH_3O_2^{\bullet} \rightarrow \text{products} \qquad (42)$$

Clearly the reaction of methylperoxyl radicals with persulfate yields only methanol [reaction (43)].

$$CH_3O_2^{\bullet} + S_2O_8^{2-} \rightarrow \text{products} \qquad (43)$$

In aerated solutions (reaction of persulfate with methylperoxyl radicals), a high yield of sulfate is detected that is considerably higher than from the reaction of persulfate with methyl radicals. The increase in the concentration of sulfate ions is independent of dose rate and only dependent on the persulfate concentration. The long chain reaction suggests that under our experimental conditions SO$_4^{\bullet -}$ is the chain carrier and not S$_2$O$_8^{\bullet}$O$_2^{\bullet -}$ or SO$_6^{\bullet -}$.

It is suggested that in reaction (43) an intermediate (**B**) is formed in which the methylperoxyl radical is bound to one oxygen atom of the peroxo group of the persulfate. This intermediate can then decompose into CH$_3$O$_2^+$ + SO$_4^{\bullet -}$ + SO$_4^{2-}$, which will be followed by reaction (44).



B

$$CH_3O_2^+ \rightarrow CH_3^+ + O_2 \rightarrow CH_3OH + H^+ \qquad (44)$$

The formed sulfate radical anion reacts as above (in deaerated solutions) by reaction (36) with DMSO. In the case of aerated solutions, reaction (37) is possibly replaced by reaction (43), which gives reaction (45).

$$^{\bullet}CH_2(CH_3)SO + O_2 \rightarrow {}^{\bullet}O_2CH_2(CH_3)SO \qquad (45)$$

The $^{\bullet}O_2CH_2(CH_3)SO$ radical reacts further with persulfate in a manner analogous to reaction (44). Thus, it is obvious that in aerated solutions DMSO is oxidized to a greater extend (and therefore more sulfate product is formed) than in solutions not containing dioxygen. It should be pointed out that in reaction (45) the methylperoxyl radical acts as a reducing agent and not as oxidizing agent as in common reactions. Thus, alkylperoxyl radicals can act as reducing agents with suitably strong oxidants.

Conclusion

The reactions of methyl and methylperoxyl radicals derived from DMSO with hydrogen peroxide, peroxymonocarbonate (HCO_4^-), and persulfate were studied and led to the following general conclusions:

1) The formation of methyl radicals in the presence of DMSO is not a proof of the formation of hydroxyl radicals in the system. The results show that $HO_2^{\bullet}/O_2^{\bullet-}$ and $CO_3^{\bullet-}$ radicals react with DMSO to produce methyl radicals as well [reaction (46)].

$$HO_2^{\bullet}/CO_3^{\bullet-}+(CH_3)_2SO \rightarrow {}^{\bullet}CH_{3+}CH_3S(O_2H)O/ CH_3S(OCO_2^-)O \qquad (46)$$

   Thus, DMSO cannot be used as a hydroxyl radical probe compound, even in biological systems.[24–26]

2) In the reaction of radicals with peroxides, the major reaction observed for hydroperoxides is the abstraction of hydrogen atoms by the radicals. However, the radicals also interact with a lone pair of electrons on the peroxide, thus producing methanol and formaldehyde. This reaction becomes considerably slower when ROOR species (e.g., persulfate) are involved, as the abstraction of a hydrogen atom is not available in these systems. Furthermore, the results point out that RO_2H or RO_2R' electron-withdrawing groups considerably increase the reactivity of the peroxides towards radicals and not only towards nucleophiles [reactions (47) and (48)].

$$^{\bullet}CH_3 + RO_2H \rightarrow CH_4/CH_3OH/CH_2O + RO_2^{\bullet}/\text{products} \qquad (47)$$

$$^{\bullet}O_2CH_3 + RO_2H \rightarrow CH_3OH/CH_2O + RO_2^{\bullet}/\text{products} \qquad (48)$$

3) In the reaction of radicals with CO_4H/CO_4^- three different mechanisms seem to prevail: a) the abstraction of hydrogen atoms; b) attack on the near oxygen atom; c) attack on the far oxygen atom of the peroxide group.

Each of these mechanisms yields a different product. These reactions have to be considered in biological systems in which HCO_3^- ions are always present. Finally, in any radical-induced process, including in biological systems, the reactions of secondary radicals (alkyl or alkylperoxyl species) with peroxides in the presence of peroxides have to be considered.

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