The reaction of methyl radicals with hydrogen peroxide

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Methyl radicals (plus methanesulfinic acid) were generated radiolytically in N_2O-saturated aqueous solutions by reacting the OH radicals thus formed with dimethyl sulfoxide. Upon addition of hydrogen peroxide the methyl radicals abstract an H-atom from hydrogen peroxide. With increasing hydrogen peroxide concentrations the methane yield increases while that of ethane drops. The yield of methanesulfinic acid remains unaffected. At constant hydrogen peroxide concentration, the ethane yield increases with increasing dose rate. The system has been successfully modelled using $k(^{\bullet}CH_3 + H_2O_2) = 2.7 \times 10^4$ dm^3 mol^{-1} s^{-1}. As the corresponding rate constant in the gas phase is reported to be 3.3×10^7 dm^3 mol^{-1} s^{-1}, the water solvent appears to have a dramatic effect. Some aspects of the mechanism of H-abstraction from H_2O_2 are briefly discussed.

Hydrogen peroxide and other peroxides such as peroxodisulfate are known to react with reducing radicals,[1–7] for example α-hydroxyalkyl radicals,[1–4,7] thereby producing OH or sulfate radicals, respectively. This reaction may be due to either an electron transfer reaction [reaction (1)] or a radical substitution

$$^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_2O + H^+ + {}^{\bullet}OH + OH^- \quad (1)$$

reaction [reaction (2)]. In addition, it has been recently shown

$$^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_2(OH)_2 + {}^{\bullet}OH \quad (2)$$

that such radicals can also abstract an H atom from hydrogen peroxide [reaction (3)].[7]

$$^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_3OH + HO_2^{\bullet} \quad (3)$$

The rate constants of these reactions are moderate, typically in the order of 10^4 dm^3 mol^{-1} s^{-1}, and it is thus surprising that the methyl radical has been reported[8] to react with hydrogen peroxide with a rate constant of 3.5×10^7 dm^3 mol^{-1} s^{-1} (for a cautionary remark see, however, ref. 9).

Hydrogen peroxide is used to inactivate cells, *e.g.* micro-organisms.[10] It can pass through the cell's membrane and reach the DNA. It there reacts with adventitious transition metal ions yielding OH radicals *via* a Fenton-type reaction.[11] Surprisingly, the product ratios that are formed under such conditions differ from those formed by OH radicals that were generated by ionising radiation[12] (compare also data given in ref. 13 with those in ref. 14). The reason for this may be due to a reaction of the OH-radical-induced DNA radicals with the transition metal ion still being in close proximity or with the large amount of H_2O_2 typically used for the inactivation of cells. Thus, there is a considerable demand for a better understanding of the reactions of free radicals with H_2O_2.

The hydroxymethyl radical is generally a poor hydrogen abstractor, and since the rate constant of its reaction with H_2O_2 by H-abstraction is 8×10^3 dm^3 mol^{-1} s^{-1}, a more reactive radical such as the methyl radical may indeed react considerably faster. Moreover, in the case of the hydroxymethyl radical it was not possible to distinguish between routes (1) and (2). In either case, an OH radical would be formed. The methyl radical cannot undergo an electron-transfer reaction, and if it was capable of undergoing a radical substitution reaction [reaction (5)]

$$^{\bullet}CH_3 + H_2O_2 \longrightarrow CH_4 + HO_2^{\bullet} \quad (4)$$

$$^{\bullet}CH_3 + H_2O_2 \longrightarrow CH_3OH + {}^{\bullet}OH \quad (5)$$

an OH radical would be formed. This can be tested, and the corresponding experiments will be presented in this paper.

Experimental

All the chemicals were of highest available purity and were used as received. Dimethyl sulfoxide (10^{-3}–10^{-2} mol dm^{-3}) solutions containing varying amounts of H_2O_2 were made up with Milli-Q-filtered (Millipore) water. Prior to irradiation, solutions were saturated with N_2O purified by an Oxisorb column (Messer-Griesheim).

Samples were irradiated in a panorama ^{60}Co-γ-source, where positioning of the samples at different distances from the source allowed variation of the dose rate. Except for the dose-rate-dependence measurements, γ-irradiation was carried out at a dose rate of 0.11 Gy s^{-1}.

Methane and ethane were determined by gas chromatography using a system described earlier.[15] Methanesulfinic acid was determined by ion chromatography (Dionex DX-100). Reference material was commercially available (Fluka).

Simulations were performed on a standard PC computer with a Chemical Kinetics Simulator™ software, version 1.01, developed by IBM at the Almaden Research Center.

Results and discussion

The methyl radical generating system

Hydroxyl radicals and some H atoms are formed in the radiolysis of N_2O-saturated aqueous solutions [reactions (6) and (7),

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H^+, H_2O_2, H_2 \quad (6)$$

$$e_{aq}^- + N_2O + H_2O \longrightarrow {}^\bullet OH + OH^- + N_2 \quad (7)$$

$G({}^\bullet OH) = 5.8 \times 10^{-7}$ mol J^{-1}, $G(H^\bullet) = 0.6 \times 10^{-7}$ mol J^{-1}].[16] In the presence of dimethyl sulfoxide the OH radicals are scavenged by the solute yielding 92% methyl radicals and 8% ${}^\bullet CH_2S(O)CH_3$ radicals [reactions (8)–(10)].[17] In reactions (8)

$${}^\bullet OH + (CH_3)_2S{=}O \longrightarrow (CH_3)_2S(OH)O^\bullet \quad (8)$$

$$(CH_3)_2S(OH)O^\bullet \longrightarrow {}^\bullet CH_3 + CH_3S(O)OH \quad (9)$$

$${}^\bullet OH + (CH_3)_2S{=}O \longrightarrow {}^\bullet CH_2(CH_3)S{=}O + H_2O \quad (10)$$

and (9) methanesulfinic acid is formed as well. Hydrogen atoms are scavenged according to reaction (11).

$$H^\bullet + (CH_3)_2S{=}O \longrightarrow (CH_3)_2S(H)O^\bullet \quad (11)$$

Product studies and modelling

Methyl radicals may react with one another yielding ethane [reaction (12)] or recombine [reaction (13)] with the small amounts of ${}^\bullet CH_2S(O)CH_3$ radicals formed in reaction (10).

$$2{}^\bullet CH_3 \longrightarrow C_2H_6 \quad (12)$$

$${}^\bullet CH_3 + {}^\bullet CH_2(CH_3)S{=}O \longrightarrow CH_3CH_2(CH_3)S{=}O \quad (13)$$

Already in the absence of hydrogen peroxide, small amounts of methane are formed [$G(CH_4) \approx 0.5 \times 10^{-7}$ mol J^{-1}]. In principle, this could be formed by an H-abstraction from dimethyl sulfoxide (${}^\bullet CH_3 + (CH_3)_2S{=}O \rightarrow CH_4 + {}^\bullet CH_2(CH_3)S{=}O$), but this yield is independent of the dimethyl sulfoxide concentration (10^{-3} to 10^{-2} mol dm^{-3}). It is concluded that it results from a disproportionation of methyl radicals with the dimethyl sulfoxide H-adduct radicals [reaction (14)]. There are two potential

$${}^\bullet CH_3 + (CH_3)_2S(H)O^\bullet \longrightarrow CH_4 + (CH_3)_2S{=}O \quad (14)$$

positions of addition: addition at sulfur or at oxygen. As the OH radical, the H atom is an electrophilic radical, and since the former adds to sulfur it is inferred that addition to sulfur is also the preferred reaction of the H atom.

In the presence of hydrogen peroxide, the yield of methane increases (Fig. 1, inset). This effect has to be attributed to an increasing contribution of reaction (4). The addition of hydrogen peroxide has no effect, however, on the yield of methanesulfinic acid indicating that no further OH radicals are generated. Thus, reaction (5) does not take place.

The data shown in Fig. 1 can be used to arrive at the rate constant of reaction (4), since the rate of radical formation is exactly known and the rate constants of the most relevant reactions are well established (Table 1). Where these have not yet been determined, they can be assumed to be approximately 2×10^9 dm^3 mol^{-1} s^{-1}, since practically all small radicals recombine at close to diffusion-controlled rates. Termination rates of $HO_2^\bullet/O_2^{\bullet-}$ radicals [reactions (15) and (16); $k_{15} =$

$$2\,HO_2^\bullet \longrightarrow H_2O_2 + O_2 \quad (15)$$

$$HO_2^\bullet + O_2^{\bullet-} + H^+ \longrightarrow H_2O_2 + O_2 \quad (16)$$

8.3×10^5 dm^3 mol^{-1} s^{-1}, $k_{16} = 9.7 \times 10^7$ dm^3 mol^{-1} s^{-1}][18] depend on pH, but since the formation of methanesulfinic acid rapidly lowers the pH, the rate constant close to the maximum value (at pH 4.8) has been taken. The self-termination of $HO_2^\bullet/O_2^{\bullet-}$ radicals produces molecular oxygen [reactions (15) and (16)] which readily reacts with the methyl radicals [reaction (17)] (for the reactions of methylperoxyl radicals see ref. 19).[20]

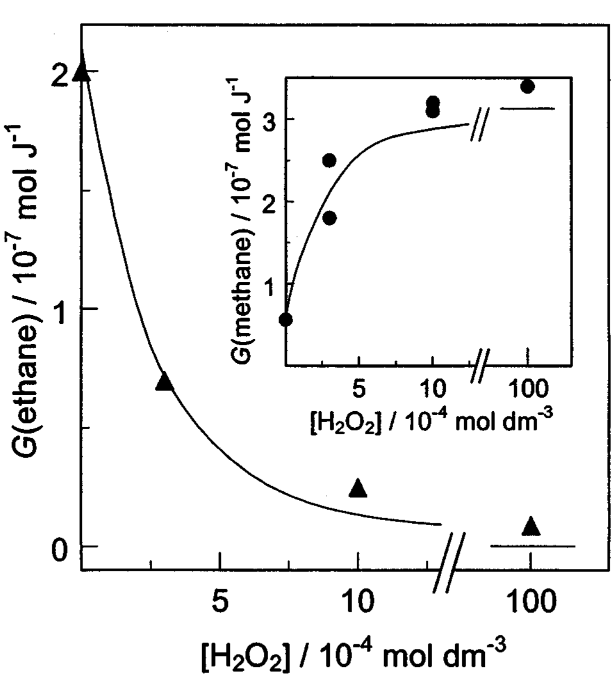

Fig. 1 γ-Radiolysis of N_2O-saturated aqueous solutions of dimethyl sulfoxide. G(ethane) as a function of the H_2O_2 concentration. Inset: G(methane) as a function of the H_2O_2 concentration. Dose rate: 0.11 Gy s^{-1}. The solid lines have been calculated using the rate constants listed in Table 1.

$${}^\bullet CH_3 + O_2 \longrightarrow CH_3OO^\bullet \quad (17)$$

Using the rate constants compiled in Table 1, the data shown in Fig. 1 can be simulated taking $k_4 = 2.7 \times 10^4$ dm^3 mol^{-1} s^{-1} (solid line in Fig. 1). Any deviation (10%) from this value leads to an unacceptable fit. The panoramic ^{60}Co-γ-source used in these experiments allows irradiation of the samples at different dose rates; *i.e.* the rate of initiation can be varied very accurately. An increase in the dose rate favours the bimolecular decay of radicals compared to reactions that are kinetically (pseudo) first order. In order to be in the sensitive region for the ethane yield to vary significantly as a function of dose rate, a hydrogen peroxide concentration of 3×10^{-4} mol dm^{-3} has been chosen. As can be seen from Fig. 2, G(ethane) increases with increasing dose rate, as expected. The solid line in this figure has been calculated based on the rate constants given in Table 1. Thus, the dose rate experiments give further (internal) evidence for the value of the rate constant of reaction (4) obtained above by modelling the data shown in Fig. 1.

On the reactivity of H_2O_2 with hydrogen-abstracting radicals

In the gas phase, the rate constant of reaction (18) is 1.0×10^9 dm^3 mol^{-1} s^{-1}.[22] In contrast, the corresponding rate constant in water is merely 2.7×10^7 dm^3 mol^{-1} s^{-1},[21] implying a thirty-fold rate decrease by the water solvent.

$${}^\bullet OH + H_2O_2 \longrightarrow H_2O + HO_2^\bullet \quad (18)$$

Even more dramatic is the effect of water on the rate constant of reaction (4). In the gas phase, k_4 is reported[23] as 3.3×10^7 dm^3 mol^{-1} s^{-1}, suggesting a thousand-fold rate suppression by water. How are these findings to be rationalised? The rate of H-abstraction from the O–H group of a substrate is strongly influenced by the solvent,[24] and the variation of the rate constant of H-abstraction from phenols and *tert*-butylhydroperoxide and by the cumyloxyl radical with the solvent was interpreted in terms of hydrogen-bonding between phenol and solvent,[25–27] *i.e.* the stronger the hydrogen bonding the lower the rate constant. It is reasonable to interpret the low values of $k({}^\bullet OH + H_2O_2)$ and $k({}^\bullet CH_3 + H_2O_2)$ in water in the light of these findings. On

Table 1 Compilation of rate constants (in units of $dm^3\ mol^{-1}\ s^{-1}$ unless specified) used for the simulation

No.	Reaction	Rate constant	Reference
(4)	${}^{\bullet}CH_3 + H_2O_2 \rightarrow CH_4 + HO_2{}^{\bullet}$	2.7×10^4	This work
(8)	${}^{\bullet}OH + (CH_3)_2SO \rightarrow (CH_3)_2S(OH)O^{\bullet}$	6.4×10^9	ref. 17
(9)	$(CH_3)_2S(OH)O^{\bullet} \rightarrow {}^{\bullet}CH_3 + (CH_3)_2S(O)OH$	$1.5 \times 10^7\ s^{-1}$	ref. 17
(10)	${}^{\bullet}OH + (CH_3)_2SO \rightarrow {}^{\bullet}CH_2(CH_3)SO + H_2O$	5.6×10^8	ref. 17
(11)	${}^{\bullet}H + (CH_3)_2SO \rightarrow (CH_3)_2S(H)O^{\bullet}$	6×10^6	ref. 21
(12)	$2\ {}^{\bullet}CH_3 \rightarrow C_2H_6$	$3.2 \times 10^{9\,a}$	ref. 20
(13)	${}^{\bullet}CH_3 + {}^{\bullet}CH_2(CH_3)SO \rightarrow CH_3CH_2(CH_3)SO$	2×10^9	assumed
(14)	${}^{\bullet}CH_3 + (CH_3)_2S(H)O^{\bullet} \rightarrow CH_4 + (CH_3)_2SO$	2×10^9	assumed
(16)	$HO_2{}^{\bullet} + O_2{}^{\bullet -} + H^+ \rightarrow H_2O_2 + O_2$ (see text)	2×10^7	ref. 18
(17)	${}^{\bullet}CH_3 + O_2 \rightarrow CH_3OO^{\bullet}$	3.7×10^9	ref. 20
	$2\ {}^{\bullet}CH_2(CH_3)SO \rightarrow (CH_2(CH_3)SO)_2$	2×10^9	assumed
	$HO_2{}^{\bullet} + {}^{\bullet}CH_3 \rightarrow CH_3OOH$	2×10^9	assumed
	$HO_2{}^{\bullet} + {}^{\bullet}CH_2(CH_3)SO \rightarrow HOOCH_2(CH_3)SO$	2×10^9	assumed
	$H^{\bullet} + {}^{\bullet}CH_3 \rightarrow CH_4$	5×10^9	assumed
	$2\ {}^{\bullet}OH \rightarrow H_2O_2$	5.5×10^9	ref. 21
	$2\ H^{\bullet} \rightarrow H_2$	5×10^9	ref. 21
	$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O$	7×10^9	ref. 21
	$CH_3OO^{\bullet} + {}^{\bullet}CH_3 \rightarrow CH_3OOCH_3$	2×10^9	assumed
(18)	${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2{}^{\bullet}$	2.7×10^7	ref. 21

[a] $2k$.

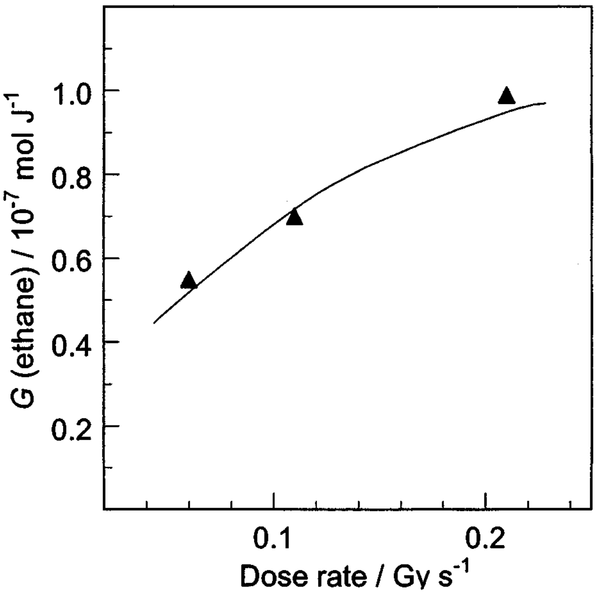

Fig. 2 γ-Radiolysis of N_2O-saturated aqueous solutions of dimethyl sulfoxide in the presence of 3×10^{-4} mol dm^{-3} H_2O_2. *G*(ethane) as a function of dose rate. The solid line has been calculated using the rate constants listed in Table 1.

average, the effect of hydrogen-bonding appears as a strengthening of the O–H bond. Obviously, this energy increment must impact the reactivity of the methyl radical much more strongly than that of the OH radical (*cf.* the factors of 1000 and 30, respectively).

We note in passing that the rate constant in water of reaction (19) is 10^7 $dm^3\ mol^{-1}\ s^{-1}$,[28] *i.e.* almost the same as with H_2O_2.

$$ {}^{\bullet}OH + (CH_3)_3COOH \longrightarrow H_2O + (CH_3)_3COO^{\bullet} \quad (19)$$

The H-abstraction from hydrogen peroxide by the methyl radical is only about ten times faster than the corresponding reaction by the hydroxymethyl radical, despite the fact that the former reaction is more exothermic by as much as *ca.* 38 kJ mol^{-1}.[29–31] The relatively small effect of the thermochemistry on the rate can be rationalized by invoking the polar effect in the transition state.[32–34] Thus, the lower the oxidation potential of the alkyl radical, the more important the contribution of the charge transfer state at the transition state geometry is expected to be, resulting in a lowering of the latter's energy. Therefore, this effect is expected to compensate for the rate reduction due to poorer exothermicity. A similar trend is observed for the rate of H-abstraction from thiols by alkyl radicals.[35] In this case the polar effect overrides thermochemistry, and the rates increase with decreasing exothermicity. However, in the case of thiols, this observation may be also rationalised in terms of an addition–elimination mechanism.[16]

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