The OH radical-induced chain reactions of methanol with hydrogen peroxide and with peroxodisulfate

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Hydroxymethyl radicals, $^{\bullet}CH_2OH$, were generated radiolytically in the reaction of OH radicals with methanol. In the presence of H_2O_2 they yield formaldehyde *via* a chain reaction which regenerates an OH radical [reaction (2)]. $G(CH_2O)$ first increases with increasing H_2O_2 concentration and with the inverse of the square root of the dose rate, eventually reaching a plateau near $G(CH_2O) \approx 65 \times 10^{-7}$ mol J^{-1}. This indicates that besides the bimolecular termination of the CH_2OH radicals there must be an additional termination reaction of (pseudo-)first-order kinetics which is attributed to an H-abstraction from H_2O_2 by CH_2OH [reaction (12)].The data have been fitted using $k_2 = 6 \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_{12} = 2.75 \times 10^3$ dm^3 mol^{-1} s^{-1}. In basic solution the chain length first becomes longer because the anion of the $^{\bullet}CH_2OH$ radical, $^{\bullet}CH_2O^-$ [pK_a($^{\bullet}CH_2OH$) = 10.7] rapidly transfers an electron to H_2O_2 ($k = 4 \times 10^5$ dm^3 mol^{-1} s^{-1}). Upon further increasing the pH, *i.e.* when the anion of H_2O_2 starts to become of importance [pK_a(H_2O_2) = 11.6] the chain length drops again. The data can be fitted assuming that $^{\bullet}CH_2O^-$ is not capable of transferring an electron to HO_2^- at an appreciable rate and that the H-abstraction reaction from HO_2^- is considerably faster ($k = 2.9 \times 10^4$ dm^3 mol^{-1} s^{-1}) than from H_2O_2.

It is well-known that in aqueous solutions of methanol OH radicals generate hydroxymethyl radicals which react with hydrogen peroxide yielding formaldehyde (hydrate) (or formaldehyde and water) and a new OH radical [reactions (1) and (2)]. This sequence leads to a chain reaction.[1,2] Mechanistically,

$$^{\bullet}OH + CH_3OH \longrightarrow H_2O + {}^{\bullet}CH_2OH \qquad (1)$$

$$^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_2O + H^+ + OH^- \,[CH_2(OH)_2] + {}^{\bullet}OH \qquad (2)$$

two possibilities can be envisaged: an electron transfer which would result in the formation of formaldehyde, a proton and a hydroxide ion, or a radical substitution reaction with formaldehyde hydrate as the product. At present it is not yet possible to distinguish between these two possibilities.

The termination of the chain reaction has been thought to occur by the bimolecular decay of hydroxymethyl radicals [reactions (3) and (4)]. The latter reaction has been reinvestigated

$$2\,{}^{\bullet}CH_2OH \longrightarrow (CH_2OH)_2 \qquad (3)$$

$$2\,{}^{\bullet}CH_2OH \longrightarrow CH_2O + CH_3OH \qquad (4)$$

recently.[3] The overall rate constant of this reaction is $2k_{3,4} = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}, whereby predominantly ethylene glycol (83%) and to a lesser extent formaldehyde and methanol (17%) are formed (for earlier studies see ref. 3).

The rate constant of reaction (1) is 9.7×10^8 dm^3 mol^{-1} s^{-1},[4] and that of reaction (5) only 2.7×10^7 dm^3 mol^{-1} s^{-1},[4] *i.e.* at

$$^{\bullet}OH + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet} \qquad (5)$$

elevated methanol concentrations and low H_2O_2 concentrations reaction (5) does not contribute effectively to the chain termination. Assuming that no reaction other than reactions (3) and (4) contributes to the chain termination, reaction (2) must be the rate-determining propagation step. With the set of equations (1)–(4) the rate constant of reaction (2) has been calculated at 4×10^4 dm^3 mol^{-1} s^{-1} using ionizing radiation as a source of OH radicals,[2] and 2.3×10^4 dm^3 mol^{-1} s^{-1} using Ti(III)–H_2O_2 to start the reaction.[1] In the present paper it will be shown that an additional termination reaction has to be taken into account. This results in a somewhat higher value for k_2.

Experimental

All the chemicals were of highest available purity and were used as received. Solutions were made up with Milli-Q-filtered (Millipore) water. The pH was adjusted with H_2SO_4 or NaOH. Prior to irradiation, solutions were saturated with N_2O purified by an Oxisorb column (Messer-Griesheim). In order to reduce the background levels of formaldehyde formed by a slow oxidation of methanol by hydrogen peroxide or peroxodisulfate in the absence of ionizing radiation, aliquots of N_2O-purged methanol were added to the reaction vessel through a rubber septum directly before irradiation.

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-irradiations were done at a dose rate of 8.2×10^{-2} Gy s^{-1}.

Formaldehyde was derivatized with dinitrophenylhydrazine in acidic acetonitrile solution and the resulting dinitrophenylhydrazone was determined by HPLC (Nucleosil C18 column, eluent: acetonitrile–water 1/1 v/v, optical detection at $\lambda = 360$ nm). For each sample a separate blank was run, and the background readings, usually not exceeding 10% of the measured signal, were subtracted.

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

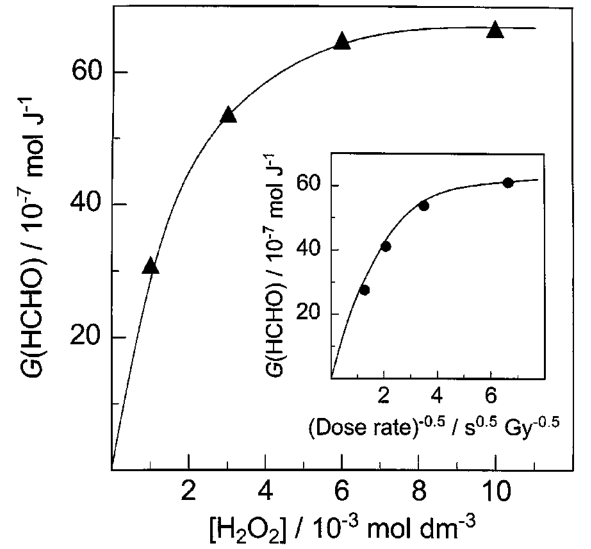

Fig. 1 γ-Radiolysis of N_2O-saturated solutions of methanol (1 mol dm^{-3}) in the presence of H_2O_2 at pH 3. Dependence of $G(CH_2O)$ as a function of the H_2O_2 concentration at a dose rate of 8.2×10^{-2} Gy s^{-1}. Inset: $G(CH_2O)$ as a function of the inverse of the square root of the dose rate; $[H_2O_2] = 3 \times 10^{-3}$ mol dm^{-3}. The curves were calculated using the rate constants compiled in Table 1.

Results and discussion

The radical-generating system

In the present study OH radicals have been generated radiolytically in N_2O-saturated solutions [reactions (6) and (7)].[5] Their

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

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

radiation-chemical yield is $G({}^{\bullet}OH) = 5.6 \times 10^{-7}$ mol J^{-1}. In addition, some H-atoms are formed $[G(H^{\bullet}) = 0.6 \times 10^{-7}$ mol $J^{-1}]$ which also generate hydroxymethyl radicals by H-abstraction [reaction (8), $k_8 = 2.6 \times 10^6$ dm^3 mol^{-1} s^{-1}].[4] The fact that

$$H^{\bullet} + CH_3OH \longrightarrow H_2 + {}^{\bullet}CH_2OH \qquad (8)$$

OH radicals also abstract to a minor extent oxygen-bound H-atoms[6] [reaction (9)] is of little consequence, because in

$${}^{\bullet}OH + CH_3OH \longrightarrow H_2O + CH_3O^{\bullet} \qquad (9)$$

aqueous solutions methoxyl radicals are rapidly converted into hydroxymethyl radicals [reaction (10)].[7] The reaction of the

$$CH_3O^{\bullet}\ (\text{in water}) \longrightarrow {}^{\bullet}CH_2OH \qquad (10)$$

H-atom with H_2O_2 [reaction (11), $k_{11} = 5 \times 10^7$ dm^3 mol^{-1} s^{-1}]

$$H^{\bullet} + H_2O_2 \longrightarrow H_2O + {}^{\bullet}OH \qquad (11)$$

leads to the formation of OH radicals and thus does not terminate the chain either.

Thus, ionizing radiation provides a clean source of hydroxymethyl radicals. Using this technique has the great advantage that the steady-state concentration of the radicals can be varied upon varying the dose rate, *i.e.* by positioning the samples to be irradiated at different distances from the center of the panorama ^{60}Co-γ-source.

Chain propagation and termination in acid and neutral solutions

If the above reactions were the only ones occurring in this system one would expect that no plateau should be observed in the plot of $G(CH_2O)$ *vs.* the H_2O_2 concentration (Fig. 1), and that a plot of $G(CH_2O)$ *vs.* the inverse of the square root of the dose rate should also be a straight line under the conditions of the inset of Fig. 1. However, as is readily seen from these figures, the formaldehyde yields reach a plateau at higher hydrogen peroxide concentrations and also at low dose rates. This requires some efficient chain-terminating process not considered thus far. The data can be simulated if it is taken into account that the hydroxymethyl radicals not only undergo electron transfer/substitution [reaction (2)] but in competition H-abstraction [reaction (12)], albeit with a considerably lower efficiency. Reaction (12) is exothermic by only 21 kJ mol^{-1} [BDH(H–CH_2OH)[8] = (395 ± 8) kJ mol^{-1}, BDH(H–OOH)[9] = 374 kJ mol^{-1}] and hence it is quite feasible. The terminating processes in question consist of reactions (12)–(14).

$${}^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_3OH + HO_2^{\bullet} \qquad (12)$$

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (13)$$

$$HO_2^{\bullet} + {}^{\bullet}CH_2OH \longrightarrow HO_2CH_2OH \qquad (14)$$

The computed lines in these figures have been obtained by taking $k_2 = 6 \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_{12} = 2.75 \times 10^3$ dm^3 mol^{-1} s^{-1}. In this computation, the self-termination of the $HO_2^{\bullet}$ radical [reaction (13), $2k_{13} = 1 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 3,[10] where the majority of experiments have been done] and the cross-termination [reaction (14), $k_{14} \approx 2 \times 10^9$ dm^3 mol^{-1} s^{-1}, assumed] have been included. Due to the slow self-termination rate constant of the $HO_2^{\bullet}$ radical reaction (13) plays a very minor role in this system, and hence the involvement of O_2 and the subsequent peroxyl radical chemistry[11] can be neglected. In reaction (14) hydroxymethylhydroperoxide is formed. This is in equilibrium with formaldehyde and H_2O_2. Under the conditions of the determination of formaldehyde (formation of its 2,4-dinitrophenylhydrazone and subsequent HPLC) it is also determined as formaldehyde (*cf.* ref. 11).

In order to test this suggestion, the hydroxymethyl radical was reacted with peroxodisulfate which is known[12] to undergo a similar chain reaction [reactions (15) and (16)] but lacks the possibility to donate a hydrogen atom.

$${}^{\bullet}CH_2OH + S_2O_8^{2-} \longrightarrow CH_2O + H^{+} + SO_4^{2-} + SO_4^{\bullet-} \qquad (15)$$

$$SO_4^{\bullet-} + CH_3OH \longrightarrow {}^{\bullet}CH_2OH + H^{+} + SO_4^{2-} \qquad (16)$$

Upon substituting hydrogen peroxide by peroxodisulfate under otherwise identical conditions a straight line is obtained when the formaldehyde yield is plotted *vs.* the peroxodisulfate concentration (Fig. 2), *i.e.* no saturation effect is observed in this system. Since the rate constant of the sulfate radical with methanol is not very fast ($k_{16} = 9 \times 10^6$ dm^3 mol^{-1} s^{-1}) a high methanol–peroxodisulfate ratio is required in order to avoid complications due to a reaction of the sulfate radical with peroxodisulfate.[12]

From the data shown in Fig. 2 the rate constant of reaction (15) is calculated at 1.5×10^5 dm^3 mol^{-1} s^{-1} which is in reasonable agreement with the values of 1.3×10^5 dm^3 mol^{-1} s^{-1} (ref. 13) and 7×10^4 dm^3 mol^{-1} s^{-1} (ref. 12) reported in the literature. We take the similarity of the rate constants of reactions (2) and (12) and the very different behaviour of H_2O_2 and $S_2O_8^{2-}$ with respect to the chain termination as additional support (beyond the good fitting) for our suggestion that in the case of H_2O_2 reaction (12) is the most important chain-terminating step at low steady-state radical concentrations.

Chain propagation and termination in basic solution

In basic solutions the hydroxymethyl radical deprotonates

Table 1 Compilation of rate constants used in the present study

No.	Reaction	Rate constant/ $dm^3\ mol^{-1}\ s^{-1}$	Reference
(1)	${}^{\bullet}OH + CH_3OH \longrightarrow H_2O + {}^{\bullet}CH_2OH$	9.7×10^8	Ref. 4
(2)	${}^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_2O + OH^- + {}^{\bullet}OH$	6×10^4	This work
(12)	${}^{\bullet}CH_2OH + H_2O_2 \longrightarrow CH_3OH + HO_2{}^{\bullet}$	2.75×10^3	This work
(17)	${}^{\bullet}CH_2O^- + H_2O_2 \longrightarrow CH_2O + {}^{\bullet}OH + OH^-$	4×10^5	This work
(18)	${}^{\bullet}CH_2O^- + H_2O_2 \longrightarrow CH_3O^- + HO_2{}^{\bullet}$	2.75×10^3	This work
(19)	${}^{\bullet}CH_2O^- + HO_2{}^- \longrightarrow CH_2O + {}^{\bullet}O^- + OH^-$	0	This work
(20)	${}^{\bullet}CH_2O^- + HO_2{}^- \longrightarrow CH_3O^- + O_2{}^{\bullet -}$	2.9×10^4	This work
(3)	$2\ {}^{\bullet}CH_2OH \longrightarrow (CH_2OH)_2$	$1.6 \times 10^{9\,a}$	Ref. 3
(4)	$2\ {}^{\bullet}CH_2OH \longrightarrow CH_2O + CH_3OH$	$2.4 \times 10^{8\,a}$	Ref. 3
	${}^{\bullet}CH_2OH + {}^{\bullet}CH_2O^- + H_2O \longrightarrow CH_2O + CH_3OH + OH^-$	8.5×10^8	Ref. 3
	$2\ {}^{\bullet}CH_2O^- + H_2O \longrightarrow CH_2O + CH_3OH + 2\ OH^-$	$1.9 \times 10^{9\,a}$	Ref. 3
(5)	${}^{\bullet}OH + H_2O_2 \longrightarrow H_2O + HO_2{}^{\bullet}$	2.7×10^7	Ref. 4
	$2\ HO_2{}^{\bullet} \longrightarrow H_2O_2 + O_2$	$1.6 \times 10^{6\,a}$	Ref. 10
	${}^{\bullet}CH_2OH + HO_2{}^{\bullet} \longrightarrow CH_2O + H_2O_2$	2×10^9	This work
(15)	${}^{\bullet}CH_2OH + S_2O_8{}^{2-} \longrightarrow CH_2O + SO_4{}^{2-} + SO_4{}^{\bullet -}$	1.5×10^5	This work
(16)	$SO_4{}^{\bullet -} + CH_3OH \longrightarrow {}^{\bullet}CH_2OH + H^+ + SO_4{}^{2-}$	8×10^6	Ref. 12

[a] 2*k*.

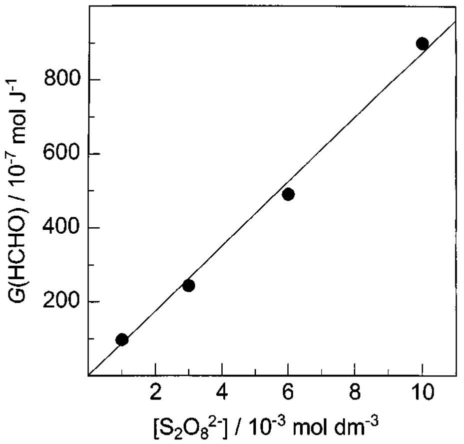

Fig. 2 γ-Radiolysis of N_2O-saturated solutions of methanol (1 mol dm^{-3}) in the presence of $S_2O_8{}^{2-}$ at pH 3. Dependence of $G(CH_2O)$ as a function of the $S_2O_8{}^{2-}$ concentration at a dose rate of 8.2×10^{-2} Gy s^{-1}. The line was calculated using the rate constants compiled in Table 1.

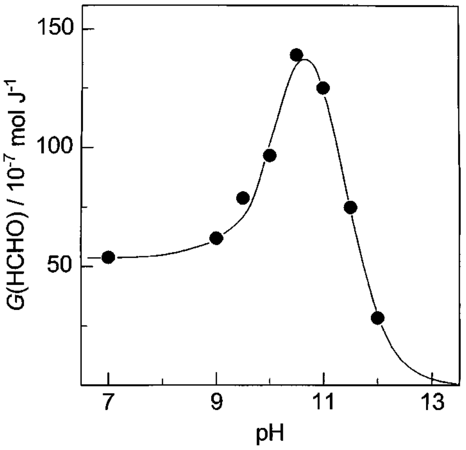

Fig. 3 γ-Radiolysis of N_2O-saturated solutions of methanol (1 mol dm^{-3}) in the presence of 3×10^{-3} mol dm^{-3} H_2O_2 at a dose rate of 8.2×10^{-2} Gy s^{-1} as a function of pH. The curve was calculated using the rate constants compiled in Table 1.

[$pK_a({}^{\bullet}CH_2OH) = 10.7$].[14,15] Upon deprotonation its reductive power is increased, and the ${}^{\bullet}CH_2O^-$ is even capable of donating an electron to N_2O.[3] One would therefore expect that in basic solutions an electron transfer from the ${}^{\bullet}CH_2O^-$ radical to H_2O_2 [reaction (17)] should enhance the chain length as compared to

$$ {}^{\bullet}CH_2O^- + H_2O_2 \longrightarrow CH_2O + {}^{\bullet}OH + OH^- \quad (17)$$

acidic or neutral solutions as long as the rate of the corresponding chain-breaking reaction (18) is not equally enhanced. In the

$$ {}^{\bullet}CH_2O^- + H_2O_2 \longrightarrow CH_3O^- + HO_2{}^{\bullet} \quad (18)$$

pH range 7–10.5 increased formation of formaldehyde is indeed observed (Fig. 3).

However, at high pH H_2O_2 also deprotonates [$pK_a(H_2O_2) = 11.6$]. As a consequence of this, upon further increasing the pH the ${}^{\bullet}CH_2O^-$ radical will have to react with the conjugate base of H_2O_2, $HO_2{}^-$ [reactions (19) and (20)].

$$ {}^{\bullet}CH_2O^- + HO_2{}^- \longrightarrow CH_2O + {}^{\bullet}O^- + OH^- \quad (19)$$

$$ {}^{\bullet}CH_2O^- + HO_2{}^- \longrightarrow CH_3O^- + O_2{}^{\bullet -} \quad (20)$$

Now the situation is reversed. In reaction (19) electron transfer from ${}^{\bullet}CH_2O^-$ to the negatively charged $HO_2{}^-$ is strongly impeded, $HO_2{}^-$ no longer being a good electron acceptor. On the other hand, $HO_2{}^-$ is a much better H-donor [*cf.* reaction (20)] than H_2O_2 [*cf.* reactions (12) and (18)]. For example, upon deprotonation the rate constant of H_2O_2 with the OH radical is enhanced by a factor of about 300.[4] Taking these two effects into account, one can model the pH dependence of the chain length (solid curve in Fig. 3) by assuming the rate constants shown in Table 1.

In the alkaline range, there are now more reactions that have to be considered than under acid to neutral conditions, and a reasonable simulation may be obtained by assuming different sets of rate constants. In order to keep the assumptions to a minimum, it has been assumed that the rate of reaction (18) equals that of reaction (12). The dramatic drop at very high pH can only be accounted for when the rate constant of reaction (20) is set much higher than that of reaction (18). The data shown in Fig. 3 suggest that beyond pH 13 the chain reaction should cease. Thus, it is reasonable to assume that reaction (19) is very slow, and the data can be adequately fitted when its rate constant is set zero, but any very low value would equally accommodate the data.

Comparison with previous data

In one of the previous studies the rate constant of reaction (2) was determined by a product study using ionizing radiation to initiate the reaction.[2] This study was carried out in the high-dose-rate range where in the yield *vs.* the inverse of the dose rate plot the deviation from the linearity is not yet apparent. Thus, there was no need to consider reaction (12) as an additional termination reaction. This also holds for the EPR study.[1] The values of k_2 obtained in these two studies, $(4 \pm 0.4) \times 10^4$ and $(2.3 \pm 0.8) \times 10^4$ dm^3 mol^{-1} s^{-1}, respectively, are somewhat lower than the value of 6×10^4 dm^3 mol^{-1} s^{-1} reported here. A lower value is expected, since the additional termination step (12) had not been included in the evaluation of their data.

Further values for k_2 have been obtained by following, in the radiolysis of N_2O-saturated aqueous methanol solutions, the degradation of low concentrations of H_2O_2 at a given dose rate and by measuring the final steady-state concentration of H_2O_2.[16] These two methods yielded values of 2.2×10^5 and 1.75×10^5 dm^3 mol^{-1} s^{-1}, respectively. These values have come out higher than the present one, because it had not been realized that H_2O_2 peroxide is destroyed in a chain reaction.

Our value for the peroxodisulfate reaction, $k_{15} = 1.5 \times 10^5$ dm^3 mol^{-1} s^{-1}, is very close to the value of 1.3×10^5 dm^3 mol^{-1} s^{-1} (ref. 13) and only higher by a factor of two compared to our earlier value of 7×10^4 dm^3 mol^{-1} s^{-1},[12] where this reaction has been studied at much lower methanol concentrations. In the low methanol concentration range additional reactions (*e.g.* the reaction of $SO_4^{\bullet -}$ with $S_2O_8^{2-}$ and $S_2O_8^{\bullet -}$ with methanol) play a role that has to be considered at the high methanol concentration used here. The earlier value[12] was a fit to accommodate all these various reactions best. Considering this, the agreement between these two data sets also is acceptable.

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