Reaction of Dihydroxymethyl Radical with Molecular Oxygen in Aqueous Solution

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Dihydroxymethyl radical (1) was found to react with oxygen diffusion controlled (k = 4.5 × 10^10 M⁻¹s⁻¹). The final products of the reaction are formic acid and 1/2 hydrogen peroxide. The precursor of H₂O₂ was shown to be O₂⁻ which is formed with G(O₂⁻) = 0.3 (a value which includes the O₂⁻ formed by H atoms and oxygen (G(H) = 0.55)). If it is assumed that dihydroxymethylperoxyl radicals are formed as intermediates the rate constant of O₂⁻ formation must be ≥ 10⁹s⁻¹. A bimolecular reaction of two dihydroxymethylperoxyl radicals forming tetroxides does not occur at the dose rates used.

The rate constants for the establishment of the equilibrium

\[
CH_2(OH)_2 + H_2O_2 \overset{k_3}{\rightarrow} CH_2OH(OOH) + H_2O
\]

have been determined at pH 5.7 and 19 °C to be \(k_3 = 1.9 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}\) and \(k_3 = 1.5 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}\) in aqueous solution.

Introduction

The decay of aliphatic α-hydroxyperoxyl radicals in aqueous solution has been studied extensively during the past decade [1-12]. If present in high concentrations these radicals decompose in second order reactions. At low radical concentrations the first order reactions are predominant leading to aldehydes (or ketones) and O₂⁻ radicals. In the first order reactions an OH⁻-induced reaction, equation (1), has been distinguished from a spontaneous decay, equation (2).

\[
\begin{align*}
H_2C(OH)OH + OH^- & \rightarrow H_2CO + O_2^- + H_2O \\
H_2C(OH)OH^- & \rightarrow H_2CO + H^+ + O_2^- 
\end{align*}
\]

The spontaneous first order elimination rate constant increases with increasing methyl substitution, e.g. \(k_{el} = 6.5, 50 \) and 600 s⁻¹ for the decay of α-hydroxyperoxyl radicals derived from methanol, ethanol and isopropanol, respectively [3].

In the present work the influence of an additional OH as substituent on the decay rate, on the formation of O₂⁻ and on the final products was studied. The influence of a second OH or alkoxy group on the elimination rate is of interest since an unusual high rate for the formation of O₂⁻ (\(k ≥ 7.0 \times 10^6 \text{s}^{-1}\)) was observed with a similar radical derived from glucose [4].

Experimental

Aqueous solutions of formaldehyde hydrate (10⁻³ - 10⁻² M) were irradiated with 1 or 2 µs electron pulses (0.1-2 krad) from a van de Graaf accelerator (2.8 MeV). Solutions containing H₂O₂ (10⁻² M) and formaldehyde hydrate (5 × 10⁻³ M) were photolyzed with UV flashes (half width of the flash ~ 5 µs, λ > 250 nm). The experimental set up employed has been described earlier [13]. The solutions were prepared from formaldehyde which was freshly produced by heating paraformaldehyde and dissolving the released gaseous formaldehyde in argon saturated water. It should be emphasized that this procedure was found to be necessary in order to obtain formaldehyde hydrate free of polymers. Distillation of aqueous solutions of formaldehyde did not give solutions free of polymers. The hydrate of formaldehyde in aqueous solution is formed spontaneously from the aldehyde within one second at room temperature [14]. pH Values were adjusted with NaOH or HClO₄. Unless otherwise stated the solutions were saturated with a mixture of NO₂/O₂ (80/20 v/v) for electron irradiation and with oxygen for flash photolysis. With one exception all measurements were performed at 21 ± 5°C. The yield of formic acid was determined conductometrically or by titration with NaOH and the yield of H₂O₂ and organic peroxides was measured iodometrically as described by Allan et al. [15]. The yield of H₂O₂ radicals was determined by time dependent conductivity measurement after the electron pulse.

Results

1. Flash photolysis

Solutions containing H₂C(OH)₂ (5 × 10⁻³ M) and H₂O₂ (5 × 10⁻² M) at pH 1.5 showed a fast initial
increase of conductivity within flash duration. After the flash the conductivity decayed within some hundred ms to a constant value which was higher than the level prior to the flash, i.e. transient and permanent conductivity changes were produced (Figure 1). The ratio of the yields of permanent to transient conductivity was observed to decrease with decreasing pH (range 4.4–6.5) and with increasing flash intensity (range varied within a factor 5). An upper limit of unity was reached with small flash intensities, i.e. at low radical concentrations, and at a pH-value of 6.5. The half-life of the decay of the transient conductivity was found to decrease with increasing flash intensity. A bimolecular rate constant of approximately $2 \times 10^7 \text{M}^{-1} \text{s}^{-1}$ at pH = 6.5 was calculated from this dependence assuming homogeneous distribution of the decaying ions. This rate constant is similar to that found for the decay of H$^+$ and O$_2^-$ at pH = 6.5 [16].

2. Pulse radiolysis

In aqueous solutions of H$_2$C(OH)$_2$ (5 $\times$ 10$^{-3}$ M) at pH 3.5–6.5 an increase in conductivity with a half-life of a few $\mu$s is observed after the decay of H$^+$ and OH$^-$ produced by the electron pulse. The kinetics of the build up was of first order with a rate constant which was smaller when the concentration of oxygen in the solution was lowered. A straight line was obtained when the reciprocal half-life of the build up (0.55 $\leq$ t$_{1/2}$ $< 6.5 \mu$s) was plotted versus the oxygen concentration ($2 \times 10^{-3} \leq [\text{O}_2] \leq 2.7 \times 10^{-4}$ M). From the slope of the line a rate constant of $4.5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ $\pm$ 15% was calculated for the reaction of an intermediate with oxygen leading to a conducting species. Experiments at $+1.5 \, ^\circ\text{C}$ showed that the rate determining step for the formation of the conductivity is still the reaction of the radicals with oxygen. From the value reached after the end of this reaction the conductivity decayed to a permanent level that was higher than the value prior to the pulse, i.e. a permanent and a transient conductivity change are produced by the pulse with G values $G_{\text{end}}$ and $G_{\text{trans}}$. The G values were calculated from the conductivity changes using 323 and 55 cm$^2$ Ω$^{-1}$ equivalent$^{-1}$ for the equivalent conductivity of H$^+$ and the anion respectively. Figure 2 shows $G_{\text{end}}$ (curve B), $G_{\text{trans}}$ (curve C) and $G_{\text{max}} = G_{\text{end}} + G_{\text{trans}}$ (curve A) as determined from the results of our conductivity measurements in the pH range 3.5 $<$ pH $<$ 6.5 (errors $\pm 10\%$).

The decay of the transient conductivity was predominantly of second order with a rate constant of $2k \sim 2 \times 10^7 \text{M}^{-1} \text{s}^{-1}$ at pH = 6.5. This constant was derived from the slope of the linear plot of $t_{1/2}$ versus dose rate (0.2 krad pulse$^{-1}$ $<$ dose rate $<$ 2 krad pulse$^{-1}$), neglecting a small first order contribution of the decay. Similar results have been observed previously for the decay of transient conductivity caused by H$^+$ and O$_2^-$ [17]. Thus we
Because only the dissociated forms of the acids are detected in conductivity measurements, the G-values in Fig. 2 have to be corrected for the undissociated forms in order to obtain the total yield of the acids formed. The corrected values (obtained on the basis of pK (HCOOH) = 3.7 and pK (HO₂⁻) = 4.75) are shown in Fig. 2, curve D. The fact that the corrected yields are independent of pH-value (Fig. 2) provides further evidence that the assignment of the conductivity change to the formation of HO₂⁻ and HCOOH is correct.

3. Product analysis

For product analysis irradiations have been performed with solutions containing N₂O/O₂ (80/20 v/v) and formaldehyde hydrate (2 × 10⁻³) at pH = 6.5. The irradiations were carried out either with repetitive pulses from the accelerator (frequency of pulses 1 Hz, dose rate 1 krad µs⁻¹) or at the ⁶⁰Co-γ-source (dose rate 2.5 krad min⁻¹). The total absorbed dose in both cases varied from 15 to 50 krad. Both methods gave the same G values within the limits of experimental errors which shows the absence of dose rate effects. From the linear yield/dose diagrams we obtained the G-values G(HCOOH) = 5.5 and G(H₂O₂) = 3.6 (errors ± 10%).

4. Formation of organic peroxides

In the iodometrical test a fast (t₁/₂ ≤ 10 sec) and a slow (t₁/₂ ~ 2.8 min) build up of I₃⁻ were observed in the irradiated solutions. The fast build up is attributed to H₂O₂ and the slow build up to the presence of organic hydroperoxides or peroxides. However, also unirradiated solutions containing H₂O₂ (10⁻⁴) and formaldehyde (2 × 10⁻³ to 1.4 × 10⁻² M) showed both, the fast and the slow formation of I₃⁻ when the iodometric test for peroxides was carried out after a period of storage of the solution. The following results show that the slow build up found in H₂O₂/CH₂(OH)₂ solutions is due to the presence of hydroperoxides formed in a thermal process:

i. At constant concentration of H₂O₂, the yield of the fast build up decreases with increasing concentration of formaldehyde and with increasing time after preparing the solutions.

ii. A constant value for the yield of the fast build up was reached after 5 h standing of the solution. This value remained constant within the limits of experimental error (15%) for 10 h.
iii. The sum of the yields of the fast build up and the slow build up was approximately constant, neglecting a 15% decrease observed more than 10 h after preparing the solutions at the highest concentration of formaldehyde used.

These observations are explained by assuming the establishment of the equilibrium (3).

\[
\text{CH}_2(\text{OH})_2 + \text{H}_2\text{O}_2 \xrightleftharpoons{\text{k}_3}{\text{k}_-3} \text{CH}_2\text{OH}(\text{OOH}) + \text{H}_2\text{O} \quad (3)
\]

The rate constants determined were \( k_3 = 1.9 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \pm 30\% \) and \( k_3 = 1.5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1} \pm 30\% \) at pH 5.7. These values are considerably higher than those reported earlier (\( k_3 = 1.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \) and \( k_3 = 7.2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1} \)) [19]. This difference could be due to the fact that the authors prepared their solutions by dilution of 36% A.R. grade aqueous stock solution of formaldehyde which is usually not free of polymers.

Since the yield of the slow build up in the irradiated solutions was found to be identical with that of unirradiated solutions with appropriate concentrations, we conclude that no organic hydroperoxides and peroxides are formed by irradiation of aqueous formaldehyde solutions under our conditions.

**Discussion**

The reactive species produced in the radiolysis of \( \text{N}_2\text{O} \) containing aqueous solutions are \( \text{OH} \) radicals (\( G = 5.6-6.0 \)) and hydrogen atoms (\( G = 0.55 \)). Photolysis of hydrogen peroxide in dilute aqueous solutions gives rise to \( \text{OH} \) radicals. The quantum yield for \( \text{OH} \) formation is approximately one [20]. Formaldehyde is present in freshly prepared dilute aqueous solutions predominantly in the form of monomeric methylene-glycol, \( \text{CH}_2(\text{OH})_2 \). The \( \text{OH} \) radicals react with \( \text{CH}_2(\text{OH})_2 \) to give dihydroxymethyl radicals \( 1 \), equation (4). The rate constant [21] for the reaction of \( \text{OH} \) with formaldehyde in aqueous solution was measured to be \( k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \).

\[
\text{CH}_2(\text{OH})_2 + \text{OH} \rightarrow \text{CH}(\text{OH})_2 \times \text{H}_2\text{O} \quad (4)
\]

From this it follows that at concentrations of \( \text{CH}_2(\text{OH})_2 \) higher than \( 10^{-3} \text{ M} \), reaction (4) is practically complete within 1 \( \mu \text{s} \) after pulse or flash. Hydrogen atoms react under our experimental conditions at a diffusion controlled rate with oxygen and form \( \text{HO}_2^- \), equation (5). Due to the pK value of the hydroperoxyl radical (pK = 4.75) \( \text{HO}_2^- \) dissociates within \( \sim 1 \mu\text{s} \) into \( \text{H}^+ \) and \( \text{O}_2^- \), equation (6), thus resulting in a conductivity increase with \( G = 0.55 \) which is complete within 1 \( \mu\text{s} \).

\[
\begin{align*}
\text{H}^- + \text{O}_2 & \rightarrow \text{HO}_2^- \quad (5) \\
\text{HO}_2^- & \rightarrow \text{H}^+ + \text{O}_2^- \quad (6)
\end{align*}
\]

Since \( 1 \) has a pK value of 9.5 [22], it cannot give rise to conductivity changes in the \( \mu\text{s} \) time range under our conditions at pH values \(< 7 \). In the presence of oxygen \( 1 \) reacts with \( \text{O}_2 \). This reaction which is responsible for conductivity has a rate constant of \( 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) (see previous section). Since the half-life for the build up of the conductivity is 0.55 \( \mu\text{s} \) with pure \( \text{O}_2 \) independent of dose, no bimolecular reactions involving two peroxyl radicals (2) can contribute to the formation of conductivity. Hence the formation of conductivity via tetroxides is excluded and the conducting species are expected to be the product of the reaction of \( \text{O}_2 + 1 \) only. The rate of \( \text{O}_2^- \) formation from \( \text{CH}_2(\text{OH})_2 + \text{O}_2 \) is unusual large in comparison with that from the reaction of \( \text{O}_2 \) with \( \text{CH}_2\text{OH} \). In the latter case a peroxy radical is formed as an intermediate which decomposes slowly (eq. (2)) with a rate constant of \(< 5 \text{ s}^{-1} \). If also for the production of \( \text{O}_2^- \) from \( 1 + \text{O}_2 \) the formation of a peroxy radical as an intermediate is assumed (eq. (7)) a rate constant of \( > 10^9 \text{ s}^{-1} \) for its decay follows from the smallest half-life of 0.55 \( \mu\text{s} \) for the conductivity build-up.

\[
1 + \text{O}_2 \rightarrow \text{HC}(\text{OH})_2\text{OO}^- \quad (7)
\]

The reason for this big increase is neither a favourable conformation due to the presence of the substituents, nor release of sterical strain due to elimination since the \( \alpha \)-peroxyl radical of isopropanol produces \( \text{O}_2^- \) with a rate constant at least three orders of magnitude smaller than the rate constant for the \( \text{O}_2^- \) formation from \( \text{O}_2 + 1 \). A very fast formation of \( \text{O}_2^- \) has also been observed from a reaction of \( \text{CH}_2\text{OHCH}((\text{CHOH})_3\text{COH} \) (glucose C-1 radical) with \( \text{O}_2 \) (\( k \geq 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \)) [6]. This shows that the second \( \text{OH} \) group can be replaced by an alkoxy group without significant alteration in the unusual high rate of \( \text{O}_2^- \) formation. The mechanism favoured at present which may explain the fast rate constants is based on the assumption that the second \( \text{OH} \) or \( \text{OR} \) group strongly increases the stability of
the transition state due to a better stabilization of positive charge produced by charge separation during elimination of $O_2^{2-}$ from the peroxyl radical. The proton may be eliminated from the transition state simultaneously or subsequently. The strong stabilization power of two adjacent methoxy groups for a positive charge has recently been demonstrated by the observation that the radical cation $(\text{CH}_3\text{O})_2\text{O}$ in aqueous solution does react surprisingly slowly with water. This radical cation disappears mainly bimolecularly.

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