The Mechanism of Decay of the Radical HO-CH-CH2-OCOCH3 in Aqueous Solutions. A Conductometric Pulse Radiolysis Study

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From conductivity changes following a 1 µs electron pulse applied to N2O saturated H2O or D2O solutions of acetic acid 2-hydroxyethyl ester the rate constants of the monomolecular decay of the radical HO-CH-CH2-OCOCH3 (1) in H2O and of DO-CH-CH2-OCOCH3 in D2O were derived, reaction (1).

HO-CH-CH2-OCOCH3 → CH2CHO + CH3COO⁻ + H⁺ (1)

A value of k1 of 5.5 · 10⁵ s⁻¹ ± 25%, at 22 to 24 °C, independent of the above solvents and of pH (or pD) was obtained. It is concluded that the rate determining step of reaction (1) is the heterolytic fragmentation of the carbon acetate bond in 1 followed by formation of H⁺.

1. Introduction

In a recent paper we described the fast elimination of acetic acid from acetic acid 2-hydroxyethyl ester 2-yl (1) to yield the formylmethyl radical (2) according to the overall reaction (1).

HO-CH-CH2-OCOCH3 → CH2CHO + CH3COO⁻ + H⁺ (1)

1 is produced from acetic acid 2-hydroxyethyl ester (3) as the main radical by OH attack on 3 in aqueous solution.

Reaction (1) seems to be an example of a more general type of radical decay reactions, cf. reaction (2),

R₁-COH-CHR₂R₃-X → HX + R₁-CO-CHR₂R₃ (2),

[R₁, R₂, R₃ = H, alkyl, hydroxylalkyl; X = OH, O-alkyl, O-acyl, phosphate, halide, NR₃⁺] which also occur with radicals derived from glycols, monoalkyglycols, sugars, nucleosides, 2-hydroxyethyl phosphate, glycerophosphate, ribose-5-phosphate, halogenated alcohols, halouracils and β-ammonio alcohols. Similar decay processes might be involved in the degradation of acetyl cellulose or of diglycerides following radical attack or irradiation. In view of this background it seemed of interest to study the detailed mechanism with a suitable example. In this paper conductivity measurements are described that permitted the determination, with reasonable accuracy, of k₁ in H₂O and of the rate constant for decay of DO-CH-CH₂-OCOCH₃ in D₂O.

2. Experimental

The purification of water and of N₂O, and the preparation of 3 have been described earlier. D₂O, 99.75%, 2-propanol and acetic acid were obtained from Merck, Darmstadt, and used as received. The procedure of conductivity measurements following pulsed irradiation has been described elsewhere. Irradiation cells with gold or platinum electrodes were used. Electron pulses of 2.8 MeV and of one microsecond duration delivering ~300 rad to the solution inside the cell were employed.

PH-values were calculated from the measured conductances using the known ion mobilities at pertinent temperatures. Due to an impurity of acetic acid a 10⁻² M solution of 3 in H₂O showed a pH of 5.85. In the other cases the pH was adjusted by adding calculated amounts of acetic acid the degree of dissociation of which was taken into account. Calculated and measured values agreed
within two percent. With solutions in D₂O the procedure was similar. In order to avoid an undesirable isotopic dilution a rather concentrated solution of acetic acid in H₂O (7 · 10⁻² M) was used to adjust the D° concentrations. As measured by conductance these were 1.20 · 10⁻⁵ M for the solution containing 3 and 1.23 · 10⁻⁵ M for the solution containing 2-propanol. The concentrations of 2-propanol used were chosen in order to match the rate of reaction of OH + 2-propanol to that of OH + 3, using \( k(\text{OH} + 3) = 8.5 · 10^{8} \text{M}^{-1}\text{s}^{-1} \) and \( k(\text{OH} + \text{2-propanol}) = 2.0 · 10^{9} \text{M}^{-1}\text{s}^{-1} \).

With regard to the D₂O solutions it was assumed that
\[
\frac{k(\text{OD} + 3)}{k(\text{OD} + \text{2-propanol})} = \frac{k(\text{OH} + 3)}{k(\text{OH} + \text{2-propanol})}.
\]
Since the dose rate varied from pulse to pulse (differences up to 25% were observed) dose rate corrections were applied to the curves obtained from the 2-propanol solutions using the factor (rel. dose rate with 2-propanol solution). The slower overall decay is due to the recombination of D© with OD© which is occurring over a longer time scale. The rate with 2-propanol solution is
\[
\frac{\text{rel. dose rate with 3 solution}}{\text{rel. dose rate with 3 solution}} = \left( \frac{\text{rel. dose rate with 2-propanol}}{\text{rel. dose rate with 2-propanol}} \right)^{1/2}.
\]

### 3. Results and Discussion

During the radiolysis of water OH radicals, H atoms, solvated electrons (\( e^{\circ}_{\text{aq}} \)), H₂, H₂O₂ and H° and OH° are produced. In N₂O saturated aqueous solutions the solvated electrons are scavenged in a very fast reaction to yield N₂, OH radicals and OH° ions, reaction (3).

\[
\text{N}_2\text{O} + e^{\circ}_{\text{aq}} \rightarrow \text{N}_2 + \text{OH} + \text{OH}°.
\]

Since \( k_3 = 8.7 · 10^8 \text{M}^{-1}\text{s}^{-1} \), at [N₂O] \( \sim 3 · 10^{-2} \text{M} \) reaction (3) is almost finished at the end of a one microsecond electron pulse. The reaction of the OH radicals with the substrate (3) reaction (4), occurs with a rate constant \( k_1 = 8.5 · 10^8 \text{M}^{-1}\text{s}^{-1} \).

\[
\text{OH} + 3 \rightarrow \text{radicals} + \text{H}_2\text{O}.
\]

The radicals produced in reaction (4) consist mainly of 1. This radical subsequently decays according to the overall reaction (1) into formylmethyl (2) and acetic acid (1) which is present in form of its conducting ions H° and CH₃COO°.

The conductivity change, \( \Delta \kappa \), as a function of time on irradiation of a N₂O saturated solution containing 10⁻² M 3 at pH = 5.85 is shown in Fig. 1, curve A. In a time interval of about 0.5–2.5 \( \mu \text{s} \) after the pulse there was an increase of conductivity followed by a decrease until \( \sim 80 \mu \text{s} \) when a finite value \( \Delta \kappa_{\text{eq}} \) was reached.*

* From this value a G value for the formation of acetic acid from reaction (4) followed by reaction (1) of 4.5 was obtained, which is slightly lower than the one reported earlier. From the lower value a a for the percent of OH attack at the 2' position of 3 of \( \sim 75\% \) is derived. Other conclusions drawn earlier remain unaffected.

The signal was independent of the concentration of 3 from \( 5 · 10^{-3} \) to \( 3 · 10^{-2} \text{M} \) indicating that reaction (4) is not rate determining for the appearance of conductance. The observed conductivity change after pulse may be understood as an overlap of two competing processes, a fast decay and a first order build up. The fast decay of conductivity immediately after pulse end is mainly due to the recombination of H° and OH° (\( k = 1.4 · 10^{11} \text{M}^{-1}\text{s}^{-1} \)) produced during the pulse.

In more acidic solutions this decay becomes faster, actual rates and the reaction order depending on pH. Decreasing the pH of the solutions of 3 from 5.85 to 5.13 caused a remarkable change in the shape of the curve. The conductivity maximum of curve A, Fig. 1, disappeared, a decay curve reaching a finite value after \( \sim 60 \mu \text{s} \) appeared instead, see curve A, Fig. 2.

Changing the solvent to D₂O and using concentrations of D° comparable to those of the experiments yielding curve A, Fig. 2, the conductivity curve A, Fig. 3 was obtained which is similar in shape to curve A in Fig. 2, however occurring over a longer time scale. The slower overall decay is due to the recombination of D° with OD° which is
slower, \( k_{\text{recomb}} = 8.4 \times 10^{10} \), than the neutralization reaction in light water. In order to separate the two processes of decay and build up a subtraction method was used.

The fast decay process was simulated using solutions of 2-propanol the radicals of which under our conditions do not give rise to conducting species. Curves B in Fig. 1 to 3 thus obtained were subtracted from corresponding curves A to yield curves C depicting the first order build up of conductivity from a species X which decays into ions.

An attempt was also made to separate the fast decay from the build up of conductivity by further decreasing the pH and thus increasing the recombination rate between \( H^\circ \) and \( OH^\circ \). Experimentally this approach was limited by the decreasing sensitivity of such measurements caused by a back ground conductivity increase and by the decrease of the degree of dissociation of acetic acid. This approach is therefore considered to yield less accurate data than the above procedures. In Fig. 4 the oscilloscope trace of a conductivity signal after pulse obtained from a solution of 3 in \( NaOH \) saturated \( H_2O \) of \( pH = 4.26 \) is depicted, apparently showing the build up of conductivity from decaying X.

In Fig. 5, \( \log (\Delta x_{\infty} - \Delta x) \) versus time is plotted using curve C, Fig. 1. A straight line is obtained ranging over 5 half lives, \( t_{1/2} \) being 1.04 ms.

From a larger series of experiments, at 22.2 to 24.4\(^\circ\), we obtained a half life of 1.25 ms \( \pm 25\% \) independent of \( pH \) (from 5.85 to 4.26) and independent of \( H_2O \) or \( D_2O \) as solvent; this half life corresponds to a rate constant for decay of X of \( 5.5 \times 10^5 \) s\(^{-1} \) \( \pm 25\% \). Within the limits of accuracy of this procedure we may state, therefore, the absence of a deuterium isotope effect and of a pH effect on the build up of conductivity. The observed rate of decay is close to the minimum rate of formation of 2 determined earlier\(^1\) spectroscopically.

The above rate constant lies within the range of rate constants determined experimentally by a variety of methods\(^33\) for the dissociation of acetic acid in \( H_2O \), \( k_s \), reaction (5).

\[
CH_3COOH \rightarrow H^\circ + CH_3COO^\circ \quad (5)
\]

\( k_s \) ranges from \( 2.1 \times 10^8 \) to \( 1.4 \times 10^6 \) s\(^{-1} \) including the most accepted value from Eigen and Schoen\(^34\) of \( 8.0 \times 10^8 \) s\(^{-1} \), at 20\(^\circ\). The ratio of the equilibrium constants\(^35,36\) of \( CH_3COOH \) in \( H_2O \) and of \( CH_3COOD \) in \( D_2O \), \( K_{H_2O}/K_{D_2O} \) is equal to 3.3. Assuming \( k_{\text{recomb}} \) to be diffusion controlled and therefore smaller in \( D_2O \) than in \( H_2O \) on account of lower ion mobilities in \( D_2O \) \( \mu_{D_2O}/\mu_{H_2O} = 1.39 \) and \( \mu_{D_2O}/\mu_{H_2O} \) \((CH_3COOO^\circ)/\mu_{D_2O}(CH_3COO^\circ) = 1.17 \), both at 24.5\(^\circ\)\] and taking \( K = k_{\text{diss}}/k_{\text{recomb}} \), \( k_{\text{diss}} \) of \( CH_3COOD \) in \( D_2O \) is estimated to be 4-5 times smaller than \( k_s \).

The measured rate constant of the decay of X, is the same in \( H_2O \) and in \( D_2O \). This rate constant cannot be attributed to the dissociation of acetic acid, and is, therefore, assigned to the ionic fragmentation of the radical I. From this assignment some conceivable mechanism of the decay of I are already excluded, e.g. fast formation of undisassociated acetic acid via a cyclic transition state or by acetoxy migration (reaction (6)), followed by formation of undisassociated acetic acid. A solvolytic reaction of I with water leading to undisassociated acetic acid is also excluded.

In this context acetoxy migrations deserve consideration if they lead to \( H^\circ \) and \( CH_3COO^\circ \) directly. From what is known about such reactions\(^37\) it seems rather unlikely that a process like reaction (6)

\[
CH_3COO \quad I \rightarrow CH-C=CH_2 \quad (6)
\]

followed by elimination of \( H^\circ \) and \( CH_3COO^\circ \) will occur at all, since reaction (6) requires the conversion of a radical centered on secondary carbon into a radical centered on primary carbon, which was never observed\(^37,38\); the opposite direction of an acetoxy migration has been observed instead\(^37,38\) in a few cases different from the one discussed here.

![Fig. 5. Logarithmic plot of \((\Delta x_{\infty} - \Delta x)\) against time, cf. text.](image-url)
A solvolysis of 1 leading immediately to ions, reaction (7), would lead to the ethanediol radical as intermediate that subsequently decays into water and formylmethyl, reaction (8).

\[ \text{H}_2\text{O} \rightarrow \text{HO}^+ + \text{CH}_2\text{CHO} \]  

This reaction sequence is excluded because it is not in accord with conclusions drawn from transient UV spectra and from ESR measurements, according to which the ethanediol radical is no intermediate of the decay of 1. An earlier report, stating the intermediacy of HOCHCH\textsubscript{2}OH and of (HO)\textsubscript{2}CHCH\textsubscript{2} as intermediates of the decay of the 2-chloroethanol radical, HOCHCH\textsubscript{2}Cl (4) a close analogue of 1, was not confirmed. ESR studies in our laboratory on aqueous solutions of 3 as well as on 2-chloroethanol solutions at pH 4–7 gave no evidence for the intermediacy of ethanediol radicals under conditions where HOCHCH\textsubscript{2}OH radicals are obviously stable with respect to reaction (8). Also from transient UV spectra obtained from N\textsubscript{2}O saturated aqueous solutions of 2-chloroethanol (Fig. 1, curve B in reference 1) the intermediacy of the ethanediol radical is to be denied. The measurement of conductivity changes following electron pulses using N\textsubscript{2}O saturated aqueous solutions containing 10\textsuperscript{-3} M 2-chloroethanol, at pH \textasciitilde 6, and employing the procedure, described above, of subtraction of a \( \Delta \) curve obtained with matching 2-propanol solutions an almost horizontal difference curve was obtained which indicated that the decay of 4 occurred mainly already during the electron pulse. The decay of 4 and the decay of 1 are, therefore, regarded as entirely analogous, 4 however, decays about one order of magnitude faster than 1.

The absence of a solvent isotope effect now permits the exclusion of two of the following three conceivable modes of the heterolytic decay of 1. We first consider the simultaneous fragmentation of 1 into H\textsuperscript{+}, CH\textsubscript{3}COO\textsuperscript{-} and 2, as symbolized by reaction (9).

\[ 1 \rightarrow \text{H}^+ + \text{CH}_3\text{COO}^- \]  

For reaction (9) an H/D solvent isotope effect of the order of the one discussed above for the dissociation of acetic acid is expected. From the absence of a solvent isotope effect reaction (9) is excluded.

We now consider a two step mechanism comprising reactions (10) and (11) for the decay of 1.

\[ 1 \rightarrow \text{H}^+ + \text{CH}_3\text{COO}^- \]  

\[ 5 \rightarrow \text{CH}_2\text{CHO} + \text{CH}_3\text{COO}^- \]  

Reaction (10) would become feasible if the radical 1 had a pK-value as low as 5 which would approximately be required for a deprotonation reaction with \( k \sim 5 \times 10^5 \text{s}^{-1} \). We assume that the pK value of 1 is larger than 5. The pK value of the ethanol radical, HOCHCH\textsubscript{3}, in comparison is 11.6. Furthermore, for reaction (10) a strong solvent isotope effect is expected. On the basis of the absence of such an isotope effect and the pK value consideration this case is excluded.

The radical anion 5 should be the intermediate of a base catalysed decay of 1, reaction (13) followed by reaction (11).

\[ \text{1} + \text{OH}^- \rightarrow 5 + \text{H}_2\text{O} \]  

The expected base catalysis was not checked because of the sensitivity of the substrate (3) towards alkali. In neutral and in acidic solutions this mechanism of the decay of 1 may be neglected.

We are now left with a mechanism in which the rate determining step is heterolytic cleavage of the carbon acetate bond. No large solvent isotope effect is to be expected in such a case.

As shown by ESR measurements the decay of 1 according to reaction (1) is slower by a factor of \( \sim 10^3 \) in organic solvents as compared to aqueous solutions. It is therefore concluded that the transition state of reaction (1) is more polar than radical 1.

The transition state is symbolized by formula 6.

\[ \delta+ \quad \delta^- \]  

\[ \text{[(HOCHCH}_2\text{)_3]} \quad \text{--- (OCOCH}_3\text{)]} \]  

Dipolar transition states have frequently been assumed in the formation of ion pairs in SN1 or E1 type reactions. The ion pair to be considered in our case (7)

\[ \text{(HOCHCH}_2\text{)}\textsuperscript{+}(\text{OCOCH}_3\textsuperscript{-}) \]  

probably undergoes a very fast deprotonation. The conjugate base of the radical cation in 7, the formylmethyl radical 2, is assumed to be a very weak base, perhaps even less basic than acetophenone, for which a pK\textsuperscript{00} value of \(-4\) was determined. It can not be excluded that the deprotonation of the developing radical cation starts soon after passing through the transition state 6.
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