Hydroxyl Radical-Induced Oxidation of Ethanol in Oxygenated Aqueous Solutions. A Pulse Radiolysis and Product Study

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**-Radiolysis of N₂O-saturated water or photolysis of aqueous H₂O₂ provided a source of OH radicals. These radicals react with ethanol by preferentially abstracting an H atom at C-1. In the presence of oxygen these radicals are converted into the corresponding peroxy radicals.

The a-hydroxyethylperoxyl radicals decay by first order kinetics (k = k₁ + k₂[OH⁻]); acetaldehyde and HO₂/H + O₂ being the products (k₁ (20 °C) = 5.0 ± 1.0 s⁻¹, Eₐ = 66 ± 7 kJ·mol⁻¹, k₂ = (4 ± 1) × 10⁶ M⁻¹·s⁻¹). In competition (favoured by low pH, low temperature and high dose rate) they also decay by second order kinetics (2k₃ = (7 ± 2) × 10⁸ M⁻²·s⁻¹). The most important route in the bimolecular decay leads to acetaldehyde, acetic acid and oxygen (ca. 75%). This route might largely be concerted (Russell mechanism), but there might also be a contribution from the disproportionation of oxyl radicals within the solvent cage. There is also a concerted route that leads to two molecules of acetic acid and to hydrogen peroxide (ca. 10%). Another pathway (ca. 15%) yields two oxyl radicals and oxygen. The former may either decompose into formic acid and methyl radicals (ca. 5%) or rearrange into 1,1-dihydroxyethyl radicals (ca. 10%). These radicals add oxygen and the resulting peroxy radicals rapidly decompose into acetic acid and HO₂.

The reaction of a-hydroxyethylperoxyl radicals with HO₂/O₂ radicals appears to be slow (kₓ = 10⁷ M⁻¹·s⁻¹).

1. Introduction

The oxidation of ethanol by molecular oxygen following OH radical attack has been investigated by several workers [1-5]. Acetaldehyde, hydrogen peroxide and acetic acid were observed as the major products. A breakthrough was achieved when it became apparent that in aqueous solution a-hydroxalkylperoxyl radicals readily eliminate HO₂ in a type of reaction which is now well documented [6-12]. Such reactions (reactions (1) and (2) in the Scheme) could explain the formation of acetaldehyde at least at low dose rates. However, there was considerable uncertainty about the mechanism leading to the formation of acetic acid. Interpretations based either on pulse radiolysis [3] or on products analysis [4, 5] failed to give a convincing and generally acceptable mechanism. In the meantime the fate of peroxy radicals in aqueous solutions has been better understood [13] and it is now possible to interpret data obtained previously [14, 15].

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2. Results and Discussion

In the radiolysis of N₂O/O₂ (80/20 v/v)-saturated dilute aqueous solutions of ethanol, OH radicals from the radiolysis of water abstract carbon-bound hydrogen atoms from the substrate, preferentially from C-1 (85%) and to a minor extent from both C-2 (13%) and oxygen (2%) [16]. The ethanol-derived radicals so generated add oxygen at diffusion-controlled rates [17] to form the corresponding a-hydroxyethylperoxyl radicals (G* = 5.1) and β-hydroxyethylperoxyl radicals (G = 0.9). H atoms from the radiolysis of water are scavenged by oxygen to give HO₂ (G = 0.55).

In neutral solutions, both HO₂ (pK = 4.7) [18] and acetic acid, one of the other known main products, are largely dissociated. Pulse radiolysis and flash photolysis combined with conductometric measurements are therefore suitable methods to follow instantaneously the formation of HO₂ and acetic acid in irradiated ethanol solutions. Here HO₂ can be readily distinguished from stable acids in neutral solutions since O₂ is only a transient...

* The G value is defined as the number of molecules or radicals formed per 100 eV of energy absorbed.
conducting species which decays by dismutation with HO₂ (reaction (12)) [18] to form the non-conducting H₂O₂.

\[
O_2 + HO_2^* \rightarrow H_2O_2 + O_2
\]

\[k_1 = (9.0 \pm 0.5) \times 10^7 \text{M}^{-1}\text{s}^{-1}\]  

(a) Pulse- and flash-conductometric measurements

First-order elimination reactions

Fig. 1A shows the conductivity change in a N₂O/O₂ (80/20 v/v)-saturated ethanol solution after an electron pulse of 0.43 J kg⁻¹. Immediately after the pulse there is a fast increase in conductivity \([G(H^+)^{\text{min}} = 1.3]\). This increase is the result of the sum of two components. The first is due to the presence of as yet unrecombined H⁺ and OH⁻ ions (produced in the pulse); the second component is due to H⁺/O₂ ions produced by the dissociation of HO₂ (formed from H atoms + O₂). After the initial jump the conductivity signal continues to increase for a few ms with approximately first-order kinetics to a maximum level \([G(H⁺)^{\text{max}} = 5.0]\). From this maximum level the conductivity slowly decays in the course of several hundred ms to a lower and constant level \([G(\text{permanent acid}) = 1.4]\). Conductivity changes were measured at various temperatures, pH values and dose rates. The \(G\) values of acidic products as well as their half-lives of formation are given in Table I. The results shown in Table I demonstrate that at low dose rate, pH 6.8, and 20 °C and above, the major course of the conductivity changes can be explained by the first-order formation (reactions 1 and 2) and the second-order decay of the transient species HO₂/(H⁺ + O₂) (reaction 12).

Fig. 1. Conductivity signals in a 0.1 M ethanol solution (pH = 6.8) saturated with N₂O/O₂ (80/20 v/v) and irradiated with a 1 µs electron pulse at 20 °C. (A) dose 0.4 J kg⁻¹, 20 ms/division; (B) dose 17 J kg⁻¹, 0.5 ms/division; (C) dose 17 J kg⁻¹, 20 ms/division.
In particular at 44 °C the yield of the transient conducting species H+/O₂⁻ approaches the theoretical yield of α-hydroxyethylperoxyl radicals.

At pH > 7 the formation of H⁺/O₂⁻ was observed as a decrease of conductivity due to the replacement of OH⁻ by the less conducting O₂⁻. Also in basic solution the latter is a rather stable species [k(O₂⁻ + O₂) < 0.3 M⁻¹s⁻¹] [18]. At low pulse intensities (around 0.4 J·kg⁻¹), the rate of formation of O₂⁻ was found to increase with increasing OH⁻ concentration (Table II). The hydroxide ion induces an O₂⁻ elimination (reaction (2)) by deprotonating the α-hydroxyethylperoxyl radical. The observed rate of HO₂⁻/O₂⁻ elimination from α-hydroxyethylperoxyl radicals is therefore the sum of the spontaneous elimination (reaction (1)) and the OH⁻-induced elimination (reaction (2)):

\[ k(\text{HO}_2^-/\text{O}_2^-) = k_1 + k_2[\text{OH}^-]. \] (13)

From the data given in Table II a value of

\[ k_2 = (4 \pm 1) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \]

has been calculated.

When the pulse intensity given to the ethanol solution is increased, the buildup of the conductivity following the electron pulse was found to become faster (Fig. 1 B) and to approach second-order kinetics with the reciprocal first half-life times being linearly proportional to the dose rate (Fig. 2). At pH 6.5 and 20 °C the straight line in Fig. 2 intercepts the ordinate at 250 s⁻¹ as a result of the first-order HO₂⁻/O₂⁻ eliminations (reactions (1) and (2)). The corresponding first-order rate constant is thus

\[ k(\text{HO}_2^-/\text{O}_2^-) = 173 \text{ s}^{-1}. \]

Knowing the OH⁻ concentration and using \( k_2 \) given above the rate constant at 20 °C of the spontaneous HO₂⁻ elimination of α-hydroxyethyl-
Table II. Rate constant of HO₂ elimination from α-hydroxyethylperoxyl radicals as function of OH⁻ and phosphate concentrations (a) conductometric measurements, (b) optical measurements (see text).

<table>
<thead>
<tr>
<th>pH</th>
<th>Doses [J kg⁻¹]</th>
<th>[OH⁻] M⁻¹</th>
<th>[HPO₄²⁻] M⁻¹</th>
<th>t₁/₂ s⁻¹</th>
<th>kobs s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.30</td>
<td>0.40</td>
<td>2 × 10⁻⁹</td>
<td>0</td>
<td>2.6 × 10⁻³</td>
<td>266 (a)</td>
</tr>
<tr>
<td>6.80</td>
<td>0.43</td>
<td>5.9 × 10⁻⁸</td>
<td>0</td>
<td>1.7 × 10⁻³</td>
<td>407 (a)</td>
</tr>
<tr>
<td>8.37</td>
<td>0.46</td>
<td>2.3 × 10⁻⁶</td>
<td>0</td>
<td>8.0 × 10⁻⁵</td>
<td>8.7 × 10² (a)</td>
</tr>
<tr>
<td>8.75</td>
<td>0.74</td>
<td>5.6 × 10⁻⁶</td>
<td>0</td>
<td>3.0 × 10⁻⁵</td>
<td>2.3 × 10⁴ (a)</td>
</tr>
<tr>
<td>7.6</td>
<td>20</td>
<td>4 × 10⁻⁷</td>
<td>5.7 × 10⁻⁵</td>
<td>3.0 × 10⁻⁵</td>
<td>2.3 × 10⁴ (b)</td>
</tr>
<tr>
<td>8.0</td>
<td>20</td>
<td>4 × 10⁻⁷</td>
<td>6 × 10⁻⁵</td>
<td>2.4 × 10⁻⁵</td>
<td>2.9 × 10⁴ (b)</td>
</tr>
</tbody>
</table>

The rate constant of HO₂ elimination (k₁) is calculated according to equation 13 to be:

\[ k₁ = 50 ± 10 \text{ s}⁻¹. \]

Bimolecular reactions

From the slope of the straight line in Fig. 2 a second-order rate constant can be obtained which is attributed to the bimolecular self-reaction of the α-hydroxyethylperoxyl radicals:

\[ 2k₃ = (7 ± 2) \times 10⁶ \text{ M}⁻¹\text{s}⁻¹. \]

Together with the observed dose rate dependence of the rate of the formation of acids G (permanent acid) increases significantly at high dose rates (see Table I and Fig. 1 C). To account for these observations the bimolecular self-reaction of the α-hydroxyethylperoxyl radicals with the formation of a tetroxide as intermediate has been proposed. Reaction (3) is the rate determining step assuming the tetroxide formed is short-lived. As the result of its decomposition, stable acids (mainly acetic acid) are formed (reactions (4), (5) and (6)).

Reaction (4) is based on the general mechanism proposed by Russell [19] for the bimolecular self-reactions of primary and secondary alkylperoxyl radicals. There might also be a contribution of its free-radical equivalent (reaction (7)). The high G-value of acetic acid found in product analysis at high dose rates together with the considerable yield of acetaldehyde (see Table III) gives evidence that reaction (4) (or (7)) is the main pathway followed after reaction (3) has occurred.

Analogous of reaction (5) have been reported as the major mode of bimolecular decay of the hydroxymethylperoxyl radicals [20] as well as other alkyl peroxyl radicals [21, 22]. There is some evidence for reaction (5) in the present system since acetic acid was found to have a higher yield (G = 3.1) under high dose rate conditions (Table III) than can be accounted for by reaction (4) with respect to G (acetaldehyde) = 2.0. However, as will be shown below, reaction (5) is not the only reaction pathway responsible for the excess G (G = 1.1) of acetic acid. The contribution of reaction (5) is not more than 10% of the bimolecular decay of the α-hydroxyethylperoxyl radicals.

Table III. Products and their G values in irradiated oxygenated aqueous ethanol solutions (10⁻²–10⁻¹ M) at 20 °C.

<table>
<thead>
<tr>
<th>X-rays</th>
<th>Co-60-γ</th>
<th>e⁻ Pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose rate [W · kg⁻¹]</td>
<td>0.14–0.43</td>
<td>0.15</td>
</tr>
<tr>
<td>Saturated with</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>pH</td>
<td>4–11a</td>
<td>3</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>2.55b</td>
<td>2.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>n. f.</td>
<td>n. d.</td>
</tr>
<tr>
<td>Formic acid</td>
<td>n. d.</td>
<td>n. d.</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>n. d.</td>
<td>0.17</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>3.5b</td>
<td>3.7</td>
</tr>
</tbody>
</table>

a Buffered solutions; b Ref. [1]; c Ref. [4]; d Ref. [5], values give total acids; n. f. not found; n. d. not determined; e considerable errors (see Experimental).
Fragmentation reactions as depicted in reaction (8) are also a well-established decomposition mode of alkylperoxyl radicals through the formation of two oxyl radicals and oxygen [23], followed by β-fragmentation of the oxyl radicals [22, 24, 25]. The methyl radicals formed in reaction (8) will be converted by oxygen into methylperoxyl radicals which may then react further to form among other products, formaldehyde and methanol [26]. Formic acid and formaldehyde are indeed found as minor products in pulse-irradiated ethanol solutions (see below).

Some of the one-carbon fragment products, however, can also come from the bimolecular reactions of the β-hydroxyethylperoxyl radicals (reactions (14) and (15)).

\[
\begin{align*}
\cdot \text{O}_2\text{CH}_2\text{CH}_2\text{OH} + \text{RO}^- & \rightarrow \\
\cdot \text{OCH}_2\text{CH}_2\text{OH} + \text{RO}^+ + \text{O}_2 \\
\cdot \text{OCH}_2\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{O} + \cdot \text{CH}_2\text{OH}
\end{align*}
\]

The hydroxymethyl radicals will be converted again by oxygen into the corresponding hydroxymethylperoxyl radicals, which then react by well documented mechanisms to give formaldehyde and formic acid [8, 20].

At high dose rates there is more \( \text{HO}_2/(\text{H}^+ + \text{O}_2) \) formed (the G value of transient conductivity, corrected for incomplete dissociation, is 1.0 at 24.5 J·kg\(^{-1}\), see Table I) than can be accounted for by the reaction of \( \text{H}^+ + \text{O}_2 \) and by the (negligible) residual contribution of reactions (1) and (2). The excess formation of \( \text{HO}_2/\text{H}^+ + \text{O}_2 \) with \( G \approx 0.5 \) may be explained by reactions (9–11). This type of reaction has recently been observed to play a major role in the decay of diethyl ether-derived peroxyl radicals [27].

**Temperature dependence**

The kinetics of the conductivity change was also investigated by flash photolysis of solutions containing \( 5 \times 10^{-9} \) M \( \text{H}_2\text{O}_2 \) and 1 M ethanol. The 5 µs-UV flash is absorbed by \( \text{H}_2\text{O}_2 \) thus producing OH radicals. The subsequent reactions then proceed in full analogy to those described in the radiolytic experiments. In the flash system neither H atoms nor \( \text{H}^+/\text{OH}^- \) are formed initially, and so there is no conductivity change immediately after the flash. Hence, the kinetics of the buildup can be evaluated with more confidence, particularly at small starting concentrations of the radicals.

In Fig. 3 the results of experiments at two different initial radical concentrations are presented, the dependence of the observed rate constants being plotted as a function of temperature. Competition between reaction (1) and reaction (3) produces curves for the two initial radical concentrations which differ greatly at lower temperatures but approach one another at higher temperatures where reaction (1) predominates. The extrapolated tangent (dashed line) to the experimental points at high temperatures gives a rate constant of \( k_1 = 45 \pm 10 \text{s}^{-1} \) at 20 °C, which agrees well with the value of \( k_1 = 50 \pm 10 \text{s}^{-1} \) obtained by pulse radiolysis. The activation energy calculated from the slope of the dashed line is \( E_a = 66 \pm 7 \text{kJ·mol}^{-1} \) and is assigned to that of reaction (1).
b) Pulse spectroscopic measurements

Because the peroxyl radicals derived from ethanol absorb only weakly above 220 nm, optical measurements were necessarily carried out at higher pulse intensities where the interplay of first- and second-order reactions makes interpretation rather complicated. When an ethanol solution saturated with N₂O/O₂ (80/20 v/v) was irradiated with a 1 µs-electron pulse of 20 J·kg⁻¹, a transient absorption with a maximum at 244 nm was observed immediately after the pulse. This absorbing species can be attributed mainly to the ethanol-derived peroxyl radicals (for simplicity, the α and β radicals are assumed to have identical optical properties), which are formed with G = 5.5. A small amount of O₂ (in equilibrium with HO₂) is also present. The absorption spectrum of the α-hydroxyethylperoxyl radicals thus deduced from the optical signals, is quite similar to the spectrum of O₂ [18] but the extinction coefficients are slightly lower and independent of pH between 4 and 9 [ε max (244 nm) = 1180 M⁻¹·cm⁻¹]. At pH < 7 the rate of bleaching increases with decreasing pH. However, at pH > 7, a further buildup of optical absorption was observed which remained constant for several hundreds of ms. These observations are presented schematically in Fig. 4. At lower pH the α-hydroxyethylperoxyl radicals react predominantly bimolecularly to form non-absorbing species. As the pH increases towards 7, reaction (2) competes more and more effectively with the bimolecular self-reactions. O₂ absorbs more strongly and disappears more slowly [18] than HO₂, hence a slower disappearance of the optical absorption was observed. At pH > 7, reaction (2) becomes predominant. O₂ being a relatively stable species and its extinction coefficient (at 244 nm) being higher than that of the ethanol-derived peroxyl radicals, a secondary buildup of the optical absorption is observed. At still higher pH such as at pH 11, all of the α-hydroxyethylperoxyl radicals are already converted to O₂ at the end of the pulse, thus a higher and constant absorption was observed at the pulse end.

HPO₄²⁻ also induces the HO₂ elimination of α-hydroxyethylperoxyl radicals in a similar but less effective way than OH⁻. Thus at pH 6.7 the optical absorption at 244 nm disappears faster in an unbuffered solution than in the presence of the phosphate buffer (Fig. 3). The contribution of HPO₄²⁻ to the rate of HO₂ elimination according to the relationship

\[ k(H^+ + O_2) = k_1 + k_2[OH^-] + k_{16}[HPO_4^{2-}] \]  

[16]

can be estimated from the rate of O₂ formation in the presence of phosphate-buffer since k₁ and k₃ are already known. From the values in Table II k₁₆ = (4 ± 1) x 10⁸ M⁻¹·s⁻¹ was obtained.

3. Product analysis

For product analysis, irradiations were carried out to a total dose of 100-600 J·kg⁻¹. In all cases, linear yield-dose relationships were observed from which the G values were calculated. In Table III the products and their G values in irradiated oxygenated ethanol solutions under various conditions are compiled together with selected literature values. Although glycolaldehyde and ethylene glycol from the β-hydroxyethylperoxyl radicals have been reported [5] as minor products, they are neglected here for simplicity of discussion.

Under conditions of low dose rates, and in buffered solutions, acetaldehyde and hydrogen peroxide have been found [1] to be the only radiation products (Table III). Their G values can now be accounted for by the first-order HO₂ elimination reactions (reactions (1) and (2)).

The formation of acetic acid was observed at low pH [4], in neutral unbuffered solutions at low temperatures [5] and at high dose rates (see Table III).
Based on the present reaction scheme it becomes apparent that under such conditions the HO₂ elimination reaction is effectively suppressed, and the bimolecular decay route (reaction (3)) gains in importance. The G values for total acidic products obtained by titration of pulse-irradiated solutions (Table III) compare well with those from pulse-conductometric measurements (Table I), after correction for partial dissociation of the acids.

The proposed mechanism [5] for the formation of acetic acid via the α-hydroxyethylhydroperoxide can be ruled out by the following considerations:

i. The formation of a stable acidic species following a second-order kinetics within a few hundred ms after the pulse (see Section I) can be directly related to the bimolecular self-reactions of the ethanol peroxyl radicals (reactions (5) to (7)).

ii. The equilibrium

\[
\begin{align*}
\text{OH} & \leftarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}_2 \\
\text{OH} & \leftarrow \text{CH}_3\text{C} - \text{OH} + \text{HO}_2 \\
\text{CH}_3\text{COOH} + \text{H}_2\text{O} & \rightarrow \text{O}_2
\end{align*}
\]  

(17)

was reexamined by mixing equimolar amounts of H₂O₂ and acetaldehyde in aqueous solution and following the formation of the hydroperoxide by its reaction with acidic KI [28]. The concentrations of both H₂O₂ and the organic hydroperoxide in the mixture can be determined because of their different rates of reaction with this reagent. H₂O₂ reacts instantaneously whereas the organic hydroperoxide reacts with a half-life of ca. 30 s. From the time dependence of the peroxide concentrations \(k_1 = 0.03 \text{ M}^{-1}\text{s}^{-1}\) and the equilibrium constant \(K = 50 \pm 10 \text{ M}^{-1}\) were calculated.

If the hydroperoxide were formed as the precursor of acetic acid [5], it should be in equilibrium with the other two products, acetaldehyde and H₂O₂, and should be detected by the above method. No peroxide other than H₂O₂ was found immediately after irradiation in the N₂O/O₂-saturated ethanol solution irradiated at 0 °C.

iii. Total peroxides in the irradiated oxygenated ethanol solution as determined iodometrically were found not to decrease with post-irradiation time as reported in reference [5].

Another possibility leading to the formation of acetic acid under steady-state irradiation conditions is reaction (18).

Evidence for reactions (18) is the product distribution found in oxygenated ethanol solutions irradiated at pH 3 and dose rate 0.5 W kg⁻¹ (Table III). Taking \(k_2 = 50 \text{ s}^{-1}\) and the rate constant for the bimolecular self-reaction of ethanol-derived peroxyl radicals, \(2k = 7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}\), less than 4% of the ethanol-derived peroxyl radicals should undergo bimolecular reactions at this dose rate, i.e. \(G(\text{acetic acid}) = 0.5 \text{ found [4]}\) under such conditions, with \(k(\text{HO}_2 + \text{HO}_2) = 10^6 \text{ [18]}\) the rate constant for reaction (18) can be estimated to be of the order of \(10^7 \text{ M}^{-1}\text{s}^{-1}\).

3. Conclusion

At low dose rates and favoured by high pH, high buffer concentration and high temperature the α-hydroxylethylperoxyl radicals decompose according to reactions (1) and (2). The ultimate products are then acetaldehyde and hydrogen peroxide (disproportionation of HO₂/O₂⁻ radicals). At high dose rates such as can be reached under pulse radiolysis conditions the α-hydroxyethyl peroxyl radicals decay bimolecularly (starting with reaction (3)). Routes 4 and 7 cannot be distinguished. Together they make up ca. 75% as judged from the acetaldehyde yield. There is a contribution of ca. 10% by route 9-11 as indicated by the intermediate HO₂⁻/(H⁺ + O₂⁻) at high dose rates. In these reactions acetic acid is the main product. A further pathway to acetic acid is reaction (5). The contribution of this type of reaction is considerably smaller in the present system (ca. 10%) than in the case of hydroxymethylperoxyl radicals where this reaction type is the dominant route (≥ 90%) [20]. Assuming equal contributions from the α- and β-hydroxyethylperoxyl radicals to the formic acid yield, small contribution of ca. 5% for route 8 is inferred.

4. Experimental

Ethanol (p.a., Merck) was purified by refluxing with 2,4-dinitrophenylhydrazine followed by fractional distillation. Irradiations were carried out using either a Co-60-γ-source, a 2.8 MeV van de
Graaff generator or a flash photolysis apparatus. The electron pulses were of 1 μs duration with doses of 0.4–29 J·kg⁻¹. The half-life width of the UV-flashes was 5 μs. For flash photolysis, the aqueous solutions contained 5 x 10⁻³ M H₂O₂ and 1 M ethanol and were saturated with oxygen. For γ- and pulse radiolysis, 0.01–0.1 M ethanol solutions saturated either with N₂O/O₂ (80/20 v/v) or with oxygen were used. For product analysis at high dose rates, the N₂O/O₂-saturated solutions were irradiated with repeated electron pulses of 4 J·kg⁻¹ and frequencies of 10–25 s⁻¹. The flash conductometric and pulse radiolysis setups have been described elsewhere [15, 29, 30]. Fricke dosimetry was carried out for product analysis and for pulse spectroscopic measurements. For pulse conductivity measurements a 0.01 M methyl chloride solution at pH 6 previously degassed with argon was used as the dosimeter taking G(HCl) = 2.75 [31].

Acetaldehyde was determined by GC (1.5 m Carbowax M (10%) on Teflon + 3 m P 4000 (15%) on KOH-treated Celite operated at 85 °C) and photometrically with p-hydroxydiphenyl as reagent [32] [ε (20 °C; 540 nm) = 4.6 x 10⁴ M⁻¹·cm⁻¹]. Total acidic products were determined by potentiometric titration with 0.01 N NaOH. Formic acid was separated from formaldehyde by distillation after the addition of 2,4-dinitrophenylhydrazine/HCl to the irradiated solution and was then determined as formaldehyde after reduction with magnesium/HCl [33]. Due to the inherent difficulties of this analytical method, errors can be as high as ±30%. Formaldehyde after reduction with magnesium/HCl and T. W. Davis, J. Phys. Chem. 56, 575 (1952). Total £

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