J. Am. Chem. Soc. **1990**, *112*, 403-407

Hydroxyl Radical Induced Oxidation of Acetaldehyde Dimethyl Acetal in Oxygenated Aqueous Solution. Rapid $O_2^{\bullet -}$ Release from the $CH_3C(OCH_3)_2O_2^{\bullet}$ Radical

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Abstract: The oxidative degradation of acetaldehyde dimethyl acetal in dilute aqueous solutions has been studied kinetically by pulse radiolysis and with respect to product formation by both γ-radiolysis and pulse radiolysis. In N_2O-saturated solutions, H abstraction from the substrate by the OH radical produces the radicals $CH_3CH(OCH_3)OCH_2^{\bullet}$ (**1**), $CH_3C^{\bullet}(OCH_3)_2$ (**2**), and ${}^{\bullet}CH_2CH(OCH_3)_2$ (**3**). Radicals **1** and **2** have reducing properties and react rapidly with tetranitromethane, yielding nitroform anion. Radical **3** is probably inert toward this compound on the pulse radiolysis time scale. While **1** forms an adduct with an observable lifetime (k(dec) = 4.4×10^4 s^{-1}), **2** gives rise to the immediate formation of nitroform anion. It has been estimated that the radicals are formed with G values of $G(\mathbf{1}) = 0.34$, $G(\mathbf{2}) = 0.21$, and $G(\mathbf{3}) \leq 0.02$ μmol J^{-1}. In N_2O/O_2 (4:1, v/v) saturated solutions, the products are (G (μmol J^{-1}) in parentheses) formaldehyde (0.16), methanol (≈0.3), acetaldehyde (0.15), methyl acetate (0.21), formic acid (0.16), hydrogen peroxide (0.14), and organic hydroperoxide (0.19). As shown by pulse radiolysis, oxygen reacts with radicals **1**–**3** with a rate constant of $k \geq 2 \times 10^9$ dm^3 mol^{-1} s^{-1}, yielding (mainly) the peroxyl radicals $CH_3CH(OCH_3)OCH_2O_2^{\bullet}$ (**4**) and $CH_3C(OCH_3)_2O_2^{\bullet}$ (**5**). Peroxyl radical **5** cleaves off $O_2^{\bullet -}$ in a fast reaction ($k = 6.5 \times 10^4$ s^{-1}), which subsequently leads to the formation of methyl acetate and methanol. Besides reacting with $O_2^{\bullet -}$ to form the corresponding hydroperoxide, peroxyl radical **4** undergoes bimolecular termination reactions, yielding acetaldehyde, methanol, formic acid, and hydrogen peroxide. In particular, it appears that the formic acid is not produced instantly but is released from α-methoxyethyl formate upon hydrolysis whose rate constant has been determined ($k_0 = 0.1$ s^{-1}) and found to be remarkably fast compared to other neutral hydrolytic reactions of comparable aliphatic esters. It is shown that the formation of the product acetaldehyde is *not* in consequence of acetal hydrolysis mediated by the proton formed radiolytically.

Molecular oxygen reacts with most organic radicals at practically diffusion-controlled rates, yielding the corresponding peroxyl radicals.[1] Thus, whenever a carbon-centered radical is generated in the natural environment, it will be rapidly converted into its peroxyl radical. Acetaldehyde dimethyl acetal may be taken as a model system for the more complex situation of the acetal function in polysaccharides, which upon free-radical attack can break up into smaller units. This reaction is of some concern in the ozone treatment of drinking water where algae-derived polysaccharides are effectively degraded,[2] thereby providing low molecular weight feed for bacterial regrowth. This ozone-mediated degradation of the polysaccharides is likely to be caused by OH radicals and organic peroxyl radicals, but with the superoxide radical also playing an important role as an intermediate.[3]

Radiation techniques provide a powerful tool for studying the formation and the fate of peroxyl radicals in aqueous solutions (for a review see ref 4). When ionizing radiation is absorbed by water, OH radicals, solvated electrons, and H atoms are formed as reactive intermediates (reaction 1). By saturating the water

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^{\bullet}OH,\ e_{aq}^-,\ H^{\bullet},\ H^+,\ H_2O_2,\ H_2 \tag{1}$$

$$e_{aq}^- + N_2O \rightarrow {}^{\bullet}OH + N_2 + OH^- \tag{2}$$

$$CH_3CH(OCH_3)_2 + {}^{\bullet}OH \rightarrow CH_3CH(OCH_3)OCH_2^{\bullet}\ (\mathbf{1}) + H_2O \tag{3}$$

$$CH_3CH(OCH_3)_2 + {}^{\bullet}OH \rightarrow CH_3C^{\bullet}(OCH_3)_2\ (\mathbf{2}) + H_2O \tag{4}$$

$$CH_3CH(OCH_3)_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2CH(OCH_3)_2\ (\mathbf{3}) + H_2O \tag{5}$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{6}$$

$$CH_3CH(OCH_3)OCH_2^{\bullet}\ (\mathbf{1}) + O_2 \rightarrow CH_3CH(OCH_3)OCH_2O_2^{\bullet}\ (\mathbf{4}) \tag{7}$$

$$CH_3C^{\bullet}(OCH_3)_2\ (\mathbf{2}) + O_2 \rightarrow CH_3C(OCH_3)_2O_2^{\bullet}\ (\mathbf{5}) \tag{8}$$

$${}^{\bullet}CH_2CH(OCH_3)_2\ (\mathbf{3}) + O_2 \rightarrow {}^{\bullet}O_2CH_2CH(OCH_3)_2\ (\mathbf{6}) \tag{9}$$

with a 4:1 (v/v) mixture of N_2O and O_2, the solvated electrons are converted into further OH radicals (reaction 2). The OH radicals do not react with O_2 but react rapidly with the solute (reactions 3–5). The same type of reaction is given by the H atom, but often its reaction with O_2 is much faster and some HO_2 radicals ($H^+ + O_2^{\bullet -}$; $pK_a(HO_2^{\bullet}) = 4.8$)[5] are formed as well (reaction 6). The organic radicals are converted by oxygen into peroxyl radicals (reactions 7–9).

Under such conditions the radical yields are $G(\mathbf{4}\text{–}\mathbf{6}) \approx G({}^{\bullet}OH) \approx 0.6$ μmol J^{-1} and $G(HO_2^{\bullet}) \approx G(H^{\bullet}) \approx 0.06$ μmol J^{-1}. It will be shown that the peroxyl radical **4** (**6** being unimportant quantitatively) decays bimolecularly following a well-established reaction pathway. Peroxyl radical **5**, however, undergoes a unimolcular reaction: It rapidly eliminates $O_2^{\bullet -}$.

The radiolysis of acetaldehyde (diethyl) acetal in oxygenated solution has found some attention already in the past.[6,7] The formation of acetaldehyde was recognized, but it was not clear that this product is formed in the course of peroxyl radical reactions only (see below). The suggestion was made[6] that its formation is due to the hydrolysis of the acetal, mediated by the proton formed in reaction 1. This erroneous view has found entry in textbooks on radiation chemistry[8] and is often cited in the context of biological effects of ionizing radiation (e.g. ref 9–11). One aim of the present work is to eliminate this wrong concept by demonstrating that under these conditions the formation of acetaldehyde from its acetals is fully explained through peroxyl radical reactions.

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0002-7863/90/1512-403$02.50/0

Experimental Section

Acetaldehyde dimethyl acetal (Merck) was fractionally distilled to a GC purity of 99.9%. It contained only traces of acetaldehyde. Triply distilled water was presaturated with a 4:1 (v/v) mixture of N_2O/O_2 and an aliquot of the acetal injected to a concentration of 2×10^{-3} mol dm^{-3}. For product analysis, irradiations were done in a ^{60}Co γ-source at a dose rate of 0.15 Gy s^{-1}. Substrate turnover did not exceed 10%. Products were also determined in pulse-irradiated samples.

Acetaldehyde dimethyl acetal is sufficiently stable against hydrolysis under these conditions (cf. ref 12). The acetaldehyde reading of irradiated solutions did not change noticeably on standing for several days.

Most of the products were analyzed by gas chromatography on a glass capillary column (74 m, CW 20M) whose stationary phase had been cross-linked by γ-irradiation in order to avoid decomposition of the film by the solvent water. The column was operated at 80 °C (carrier gas, N_2; flame ionization detection). Formaldehyde was determined by the acetylacetone method.[13] In the experiments with $Fe(CN)_6^{3-}$, the bleaching of the absorption due to the consumption of $Fe(CN)_6^{3-}$ was taken into account. Formic acid was measured by HPIC (Dionex, column HPIC AS4; eluent 5×10^{-4} mol dm^{-3} $NaHCO_3$, 1.5 cm^3 min^{-1}).

Total acid formation as obtained by titration (Radiometer) matched the yield of formate anion as determined by HPIC. For the measurement of the conductivity change during γ-radiolysis, a commercial conductivity meter (Radiometer, CDM 3) was used.

Total hydroperoxide formation was determined by the iodide method.[14] To differentiate between organic hydroperoxides and hydrogen peroxide, the latter was destroyed with catalase (Boehringer, 0.5 μL cm^{-3}) and the remaining organic hydroperoxide determined. The hydrogen peroxide yield was calculated from the difference of these two values.

The yield of $O_2^{\bullet-}$ formed in the steady-state experiments was determined after irradiation by the tetranitromethane method (cf. reaction 18) from the absorbance of the stable nitroform anion.

Oxygen uptake was measured with an oxygen-sensitive electrode (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany).

Pulse radiolysis was performed at room temperature (20 ± 2 °C) with 0.4–1-μs electron pulses from a 2.8 MeV van de Graaff electron accelerator. Doses per pulse were between 2 and 15 Gy. The pulse radiolysis setup with its recent modifications has been described.[15] For pulse spectrometric experiments the KSCN dosimetry system was used.[16] Pulse conductivity experiments were carried out with a 10-MHz ac bridge,[17] with the dimethyl sulfoxide dosimetry system as a reference.[15]

Results and Discussion

Distribution of OH Attack. The rate constant for the reaction of OH radicals with acetaldehyde dimethyl acetal, relative to the one with KSCN, has been reported to be 0.20.[18] On the basis of $k({}^{\bullet}OH + SCN^-) = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1} (cf. ref 19), the overall rate constant for reactions 3–5 is 2.2×10^9 dm^3 mol^{-1} s^{-1}. Among the three radicals formed upon OH attack on acetaldehyde dimethyl acetal, **1** and **2** have reducing properties and react readily with tetranitromethane (TNM) (reactions 10–12), giving the nitroform anion (NF^-) (cf. ref 20), which is characterized by a strong absorption at 350 nm (ϵ = 15 000 dm^3 mol^{-1} cm^{-1}). In a pulse-irradiated N_2O-saturated solution of acetaldehyde dimethyl acetal (2×10^{-3} mol dm^{-3}) containing TNM, the spectrum taken 200 μs after the pulse agrees with the well-known spectrum of NF^- (Figure 1). Its yield corresponds to essentially the total yield of OH radicals and H atoms. This indicates that the yield of radical **3** corresponds to less than 5% of the total OH radical attack (i.e., $G(\mathbf{3}) \leq 0.02$). The NF^- formation is biphasic. It is known that some types of radical react with TNM by forming an adduct (such as **7**), which then decays to give NF^-.[20] The adducts usually have absorption maxima near 300 nm. From Figure 1 it can be seen that the absorption spectrum 4 μs after the pulse consists of the absorption of NF^- with its maximum at 350 nm, as well

$$CH_3CH(OCH_3)OCH_2^{\bullet}\ (\mathbf{1}) + C(NO_2)_4 \rightarrow CH_3CH(OCH_3)OCH_2ON(O^{\bullet})C(NO_2)_3\ (\mathbf{7}) \quad (10)$$

$$CH_3CH(OCH_3)OCH_2ON(O^{\bullet})C(NO_2)_3\ (\mathbf{7}) + H_2O \rightarrow CH_3CH(OCH_3)OCH_2OH\ (\mathbf{8}) + NO_2^{\bullet} + C(NO_2)_3^- + H^+ \quad (11)$$

$$CH_3{}^{\bullet}C(OCH_3)_2\ (\mathbf{2}) + C(NO_2)_4 + H_2O \rightarrow CH_3C(OCH_3)_2OH\ (\mathbf{9}) + NO_2^{\bullet} + C(NO_2)_3^- + H^+ \quad (12)$$

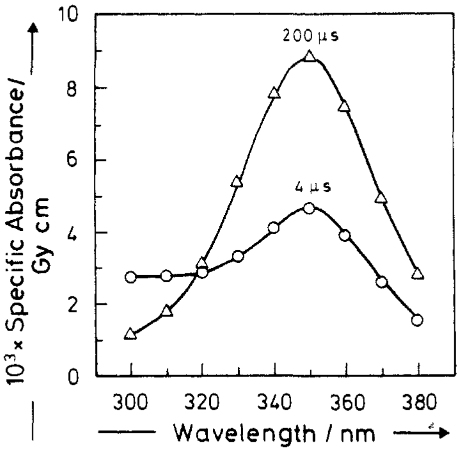

Figure 1. Optical absorption spectra obtained on pulse irradiation of an N_2O-saturated solution of acetaldehyde dimethyl acetal containing 2.3 $\times 10^{-4}$ mol dm^{-3} of TNM at pH 6.5, measured at 4 μs (○) and 200 μs (△) after the pulse (≈4 Gy/pulse).

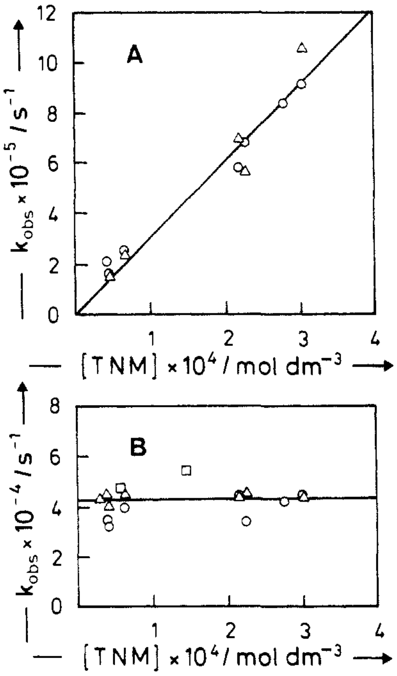

Figure 2. Dependence on TNM concentration of the observed first-order rate constants in N_2O-saturated acetaldehyde dimethyl acetal solutions at pH 6.5, as determined by pulse radiolysis (≈3 Gy/pulse): (A) fast absorption buildup at 300 nm (○) and 350 nm (△); (B) formation of NF^-/H^+ as a consequence of the decay of the TNM adduct measured at 300 nm (absorption decay, ○) and at 350 nm (absorption buildup, △) and by the conductivity buildup (□).

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as of an adduct with its maximum at 300 nm. Due to the overlap of the two absorption spectra, the *yield* of radical **2** cannot be calculated; neither can that of radical **3**. However, this difficulty is surmounted by the use of the conductivity detection method (see below). In Figure 2A the observed rate constant of the buildup at 300 and 350 nm is given as a function of the TNM concentration, from which $k_{10} \approx k_{12} = 3.0 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ is calculated. This rapid buildup is followed by a much slower decay at 300 nm and a concomitant buildup at 350 nm. The observed rate constant, $k_{11} = 4.4 \times 10^4\ \mathrm{s^{-1}}$, is independent of the TNM concentration (Figure 2B). In agreement with a preceding study on the reactions of TNM with the radicals derived from formaldehyde and acetaldehyde dimethyl acetals,[18,20] these results are interpreted as follows: Both radicals **1** and **2** react rapidly with TNM (reactions 10 and 12). While one of them (radical **1**, see below) forms an adduct (reaction 10) sufficiently long-lived to be detected (reaction 11, $k_{11} = 4.4 \times 10^4\ \mathrm{s^{-1}}$), the other (radical **2**) undergoes rapid NF^- formation (reaction 12). In this case too, an adduct might be formed as a first step, but its lifetime must be shorter ($k > 10^6\ \mathrm{s^{-1}}$) than the time of its formation even at the highest TNM concentrations used in these experiments.

The formation of H^+/NF^- in reactions 11 and 12 has been monitored by pulse-conductivity detection as well. Since reaction 10 does not cause any change in conductivity, the conductivity increase ($G(H^+/NF^-) = 0.21\ \mu\mathrm{mol\ J^{-1}}$) observed immediately (4 μs) after the pulse in an N_2O-saturated solution of acetaldehyde dimethyl acetal containing $1.46 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$ TNM at pH 4.0 represents essentially only the yield of radical **2**. After this prompt increase of conductivity, a slower buildup of conductivity to a total value of $G(H^+/NF^-) = 0.6\ \mu\mathrm{mol\ J^{-1}}$ is observed. The reaction of primary H atoms with TNM is sufficiently slow, so as to coincide with the second step of the conductivity increase. Thus the yield of radical **1** $G(\mathbf{1}) = 0.34\ \mu\mathrm{mol\ J^{-1}}$ is obtained. The observed rate constants of this conductivity buildup likewise are independent of TNM concentration and are identical with those observed by the optical method (Figure 2B).

The yield of radical **1** has also been determined with $K_3Fe(CN)_6$ as oxidant and by measurement of the yield of formaldehyde formed according to reactions 13 and 14. In the γ-radiolysis of

$$CH_3CH(OCH_3)OCH_2^{\bullet}\ (\mathbf{1}) + Fe(CN)_6^{3-} + H_2O \rightarrow CH_3CH(OCH_3)OCH_2OH + Fe(CN)_6^{4-} + H^+ \quad (13)$$

$$CH_3CH(OCH_3)OCH_2OH \rightarrow CH_3CHO + CH_2O + CH_3OH \quad (14)$$

an N_2O-saturated solution of acetaldehyde dimethyl acetal containing $10^{-4}\ \mathrm{mol\ dm^{-3}}$ $Fe(CN)_6^{3-}$, $G(CH_2O) = 0.32\ \mu\mathrm{mol\ J^{-1}}$ was found, which agrees well with that determined above for radical **1**. Thus, $G(\mathbf{1}) \approx 0.34$, $G(\mathbf{2}) = 0.21$, and $G(\mathbf{3}) \leq 0.02\ \mu\mathrm{mol\ J^{-1}}$.

Reactions in the Presence of Oxygen. In Figure 3 the composite spectrum of the radicals **1**–**3** taken 2 μs after the pulse in N_2O-saturated solution of acetaldehyde dimethyl acetal (circles) is compared with the corresponding spectrum taken at the same time in N_2O/O_2 (4:1) saturated solution (crosses). It is found that the reactions of radicals **1**–**3** with oxygen are essentially complete within 2 μs after the pulse. At the oxygen concentration used ($2.8 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$) this implies rate constants of $k_7 \approx k_8 \approx k_9 \geq 2 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, which is characteristic for this type of reaction.[1] A more precise determination of the rate constant at lower oxygen concentrations is not feasible due to interference from the subsequent increase in absorption caused by the formation of $O_2^{\bullet -}$, attributed to reaction 15. The spectrum that thus evolves is shown as well in Figure 3 (triangles) and is identical with that of $O_2^{\bullet -}$ (cf. ref 21).

$$CH_3C(OCH_3)_2O_2^{\bullet}\ (\mathbf{5}) \rightarrow CH_3C(OCH_3)_2^{+}(\mathbf{10}) + O_2^{\bullet -} \quad (15)$$

$$CH_3C(OCH_3)_2^{+}\ (\mathbf{10}) + H_2O \rightarrow CH_3C(OCH_3)_2OH\ (\mathbf{11}) + H^+ \quad (16)$$

$$CH_3C(OCH_3)_2OH\ (\mathbf{11}) \rightarrow CH_3C(O)OCH_3 + CH_3OH \quad (17)$$

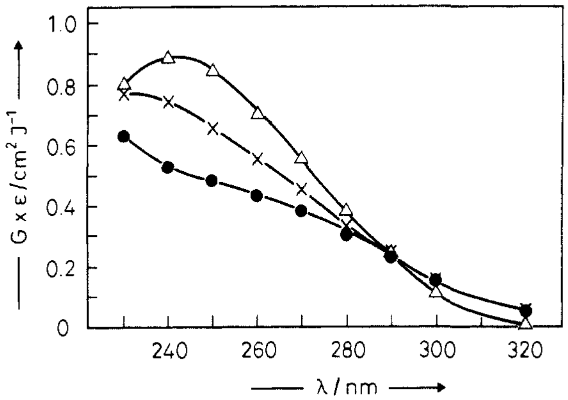

Figure 3. Optical absorption spectra of the transient species in the pulse radiolysis of acetaldehyde dimethyl acetal solutions at pH 6.5 with a dose of 7 Gy/pulse: N_2O-saturated solutions 2 μs after the pulse (●); N_2O/O_2 (4:1) saturated solutions, 2 μs (×) and 15 μs (▲) after the pulse.

The $O_2^{\bullet -}$ elimination reaction is monitored pulse conductometrically: At pH 5 in pulse-irradiated N_2O/O_2 (4:1, v/v) saturated solution of acetaldehyde dimethyl acetal, a conductivity increase is observed immediately following the neutralization reaction between H^+ and OH^- formed during the pulse (cf. reactions 1 and 2). This increase is due to the formation of $O_2^{\bullet -}$ and H^+ from the reaction of the H atoms with O_2 (reaction 6, $pK_a(HO_2^{\bullet}) = 4.8$).[5] This process is followed by a further conductivity buildup, which is kinetically of first order ($k_{15} = 6.5 \times 10^4\ \mathrm{s^{-1}}$). The yield of $H^+/O_2^{\bullet -}$ was measured at pH 6.5 (full dissociation of $HO_2^{\bullet}$) and at pH 10.7. In basic solution the formation of $H^+/O_2^{\bullet -}$ results in a decrease of conductivity, because OH^- ($\lambda^0 = 180\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$) is replaced by $O_2^{\bullet -}$ ($\lambda^{\circ} = 60\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$). From these measurements, $G(O_2^{\bullet -}) = 0.19\ \mu\mathrm{mol\ J^{-1}}$ is calculated for reaction 15. This is in good agreement with $G(\mathbf{2})$ of 0.21.

The observed rate constant of $O_2^{\bullet -}$ formation at pH 5 ($k_{15} = 6.5 \times 10^4\ \mathrm{s^{-1}}$) rules out an OH^--induced reaction; viz. $[OH^-] = 10^{-9}\ \mathrm{mol\ dm^{-3}}$, $k(OH^- + \mathbf{5}) \leq 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, and $k(OH^-\ \text{induced}) \leq 10\ \mathrm{s^{-1}}$. This leaves as an alternative a water-assisted elimination, i.e. reaction 15 and 16 occurring concertedly. But if the process occurs in two steps, then only the assumption that the reaction of the carbocation **10** with water (reaction 16) is much faster than its formation (reaction 15), can be reconciled with the conductivity behavior. We therefore conclude that $k_{16} > 6.5 \times 10^4\ \mathrm{s^{-1}}$. The rate constant of the hydrolysis of mono-α-alkoxyalkyl carbocation is estimated at $> 2 \times 10^7\ \mathrm{s^{-1}}$ while that of trimethoxymethyl cation is $1400\ \mathrm{s^{-1}}$.[22] One would expect k_{16} to lie somewhere in between.

In addition to the conductivity experiments, the formation of $O_2^{\bullet -}$ from reaction 15 has also been monitored by its fast reaction with TNM (reaction 18; $k_{18} = 1.9 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$).[5] At

$$O_2^{\bullet -} + C(NO_2)_4 \rightarrow O_2 + C(NO_2)_3^- + NO_2^{\bullet} \quad (18)$$

sufficiently low concentrations of TNM ($< 3 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$) and sufficiently high O_2 concentration (N_2O/O_2, 1:1, v/v) in acetaldehyde dimethyl acetal solutions, direct scavenging of radical **2** by TNM is negligible. Under these conditions the buildup of NF^- at 350 nm is found to reflect the rate constant of reaction 18; the total yield of NF^- ($0.27\ \mu\mathrm{mol\ J^{-1}}$) is satisfactorily balanced by the yield of $O_2^{\bullet -}$ from reaction 15 and from the H atom ($0.06\ \mu\mathrm{mol\ J^{-1}}$) and again shows good agreement with the value of 0.21 for $G(\mathbf{2})$.

The hemiorthoester **11** formed in reaction 16 hydrolyses into methyl acetate and methanol under the present experimental conditions (reaction 17). Upon γ-irradiation at a dose rate of 0.15 Gy s⁻¹, the yield of methyl acetate is $0.21\ \mu\mathrm{mol\ J^{-1}}$ (Table I), in fair agreement with the foregoing interpretation regarding the fate of radical **2**. The fact that G(methyl acetal) is independent

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Table I. Electron Pulse and γ-Radiolysis (Dose Rate: 0.15 Gy s^{-1}) of N_2O/O_2 (4:1) Saturated Aqueous Solutions of Acetaldehyde Dimethyl Acetal (G, μmol J^{-1})

product	pulse radiolysis	γ-radiolysis
formaldehyde[a]	0.13	0.16
methanol[a]	nd	$\approx$0.3
acetaldehyde[a]	nd	0.15
methyl acetate	0.24	0.21
formic acid	0.14	0.16
hydrogen peroxide	0.13	0.14
organic hydroperoxide(s)	0.14	0.19
superoxide formation	0.28	0.26
oxygen uptake	nd	0.59

[a] All or part of these products are released by the organic hydroperoxide(s) upon analysis.

of the dose rate (electron pulse vs γ-radiolysis) lends further support to this interpretation. It also implies that in this dose rate range this product is exclusively formed from radical **5** in a unimolecular reaction without competition from a bimolecular one and thus *not* from radical **4**, which is capable of undergoing bimolecular termination reactions.

Decay of Peroxyl Radical 4. Since we expect the peroxyl radical **5** to be entirely converted into methyl acetate, and since the yield of radical **3** (and in consequence radical **6**) is relatively small, we must conclude that the other products, i.e. formaldehyde, acetaldehyde, formic acid, and organic hydroperoxide, derive for the most part from peroxyl radical **4**. It is known that peroxyl radicals derived from ethers in a α-position have only a weak tendency to eliminate $O_2^{\bullet-}$ in a manner similar to reaction 15.[23] Even though the possibility of an intramolecular H abstraction at the acetalic carbon atom cannot a priori be discounted, the main reaction of **4**, even at a dose rate of 0.15 Gy s^{-1}, is the bimolecular decay. On the basis of our present knowledge with regard to the behavior of similar peroxyl radicals,[4] we consider reactions 19–23.

$$(4) + (4) \rightarrow CH_3CH(OCH_3)OCH_2OH + CH_3CH(OCH_3)OCHO + O_2 \quad (19)$$

$$(4) + (4) \rightarrow 2CH_3CH(OCH_3)OCHO + H_2O_2 \quad (20)$$

$$(4) + (4) \rightarrow 2CH_3CH(OCH_3)OCH_2O^{\bullet} + O_2 \quad (21)$$

$$CH_3CH(OCH_3)OCH_2O^{\bullet} \rightarrow CH_3CH(OCH_3)OC^{\bullet}(H)OH \quad (22)$$

$$CH_3CH(OCH_3)OC^{\bullet}(H)OH + O_2 \rightarrow CH_3CH(OCH_3)OCHO + HO_2^{\bullet} \quad (23)$$

$$CH_3CH(OCH_3)OCHO + H_2O \rightarrow CH_3CHO + HCO_2H + CH_3OH \quad (24)$$

$$RO_2^{\bullet} + O_2^{\bullet-} + H^+ \rightarrow RO_2H + O_2 \quad (25)$$

$$2O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2 \quad (26)$$

These radical reactions are followed by hydrolytic reactions 14 and 24. Since radical **5** disappears early on via reaction 15, and radical **6** is generated in a relatively small yield, we omit for the sake of simplicity all cross-termination reactions of **4** except the one with $O_2^{\bullet-}$. The latter, which is formed mainly in reactions 6 and 15, will react with radical **4** (reaction 25), yielding organic hydroperoxide, while its self-termination (reaction 26) generates hydrogen peroxide beyond the amount formed in reactions 1 and 20.

We may also attempt to estimate the relative importance of reactions 19–21. As the yield of any product derived from radical **6** cannot exceed $G \approx 0.02$ μmol J^{-1}, we may fairly ascribe all of the organic hydroperoxide production to reaction 25. The yield of formic acid has been determined in three different ways at practically identical values, under conditions where the hydroperoxide remained undegraded. The experimental results thus indicate that formic acid is produced independently, alongside the hydroperoxide, leading to the conclusion that its precursor, the α-methoxyethyl formate, is the only other major product formed in the bimolecular decay of radical **4**. In contrast, formaldehyde may well be produced as a result of the decomposition of the hydroperoxide under the conditions of the analysis. We therefore conclude that reaction 19 should be of little importance. This view is in keeping with what one might expect if one recalls that the prototype of **4**, $HOCH_2O_2^{\bullet}$, mainly reacts with its kind under formation of formic acid and hydrogen peroxide,[24] i.e., in the sense of reaction 20 but not 19 or 21. Incidentally, reaction 21 would be expected to eventually yield the same products as reaction 20 (via reactions 22, 23, and 26).

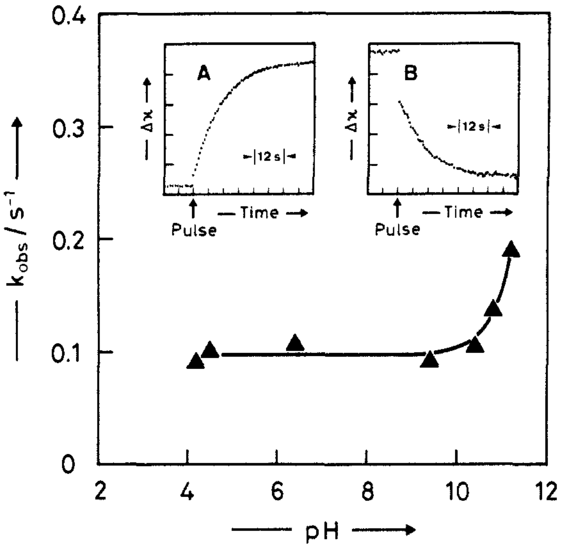

Figure 4. Dependence on pH of the observed first-order rate constant of the slow conductivity change as the result of hydrolysis reaction 24 in pulse-irradiated N_2O/O_2-saturated solutions of acetaldehyde dimethyl acetal. Insets: A, permanent conductivity buildup observed at pH 4.2, 8 Gy/pulse; B, conductivity decrease observed at pH 10.4, 11 Gy/pulse.

A relatively fast decay of the $O_2^{\bullet-}$ has been observed pulse conductometrically both at pH 6.7 and in basic solutions (pH 9.4–11.2); this cannot be explained by its spontaneous disproportionation.[5] At pH 6.7, the conductivity decrease was observed to have a half-life of 1.6 ms at a dose of 6.2 Gy and 0.9 ms at 12 Gy. At pH 10.4 the half-life of the conductivity increase was 1.5 ms at a dose of 14 Gy. This we may ascribe to reaction 25. By computationally modeling the situation within the framework of the above mechanism, which on the millisecond time scale is approximated by reactions 20, 25, and 26, we arrive at a rough estimate of k_{20} and k_{25} (k_{26} being known[5]): Both k_{20} and k_{25} must be near 1×10^8 dm^3 mol^{-1} s^{-1}. If we likewise model the γ-radiolysis with respect to the yields of organic hydroperoxide, formic acid, and H_2O_2, we find that values near 1×10^8 for these rate constants are compatible with the product ratios.

The ease of reaction of $O_2^{\bullet-}$ with organic peroxyl radicals varies significantly with the type of the peroxyl radical. With the (hydroxyethyl)peroxyl radical (derived from ethanol) the bimolecular rate constant has been estimated to be $k \leq 10^7$ dm^3 mol^{-1} s^{-1},[25] whereas with the acetylperoxyl radical (derived from acetaldehyde) $k \approx 10^9$ dm^3 mol^{-1} s^{-1} has been obtained.[26] The value of k_{25} determined in this work lies in between.

Hydrolysis of the Intermediate $CH_3CH(OCH_3)OCHO$. The yield of formic acid as determined by ion chromatography after γ-radiolysis of acetaldehyde dimethyl acetal in N_2O/O_2-saturated solutions is identical with that determined by monitoring the

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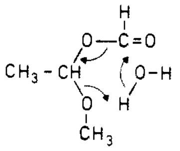
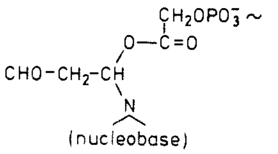
Chart I



A



B

conductivity increase during radiolysis with a conductivity meter. This means that the product $CH_3CH(OCH_3)OCHO$ must hydrolyze relatively fast (reaction 24). This hydrolysis has been followed by pulse conductometric detection of the development of permanent conductivity in acidic and basic solutions (cf. insets in Figure 4). In the pulse-irradiated N_2O/O_2-saturated acetaldehyde dimethyl acetal solution (pH 6.7), this conductivity change is observed once the transient conductivity due to $H^+/O_2^{\bullet-}$ (see above) has subsided. Permanent conductivity corresponding to $G(H^+)$ and 0.15 μmol J^{-1} builds up with a rate constant k_{24} = 0.1 s^{-1} (inset A, Figure 4). The dependence of k_{24} on pH has been plotted in Figure 4. Due to the limitations of the method, the pH range where proton-catalyzed hydrolysis sets in cannot be accessed, while the hydroxide-catalyzed hydrolysis can be followed only up to pH 11.2. From these limited data $k_{24\,\mathrm{OH^-}} \approx$ 60 dm^3 mol^{-1} s^{-1} has been estimated. A rate constant such as $k_{24\,0}$ = 0.1 s^{-1} is remarkably fast for a neutral ester hydrolysis. In the case of the prototype, methyl formate, k_0 cannot be determined since the effect of neutral hydrolysis is smothered by that of base ($k_{\mathrm{OH^-}}$ = 38.4 dm^3 mol^{-1} s^{-1})[27] and acid ($k_{\mathrm{H^+}}$ = 4 × 10^{-3} dm^3 mol^{-1} s^{-1}; cf. ref 28) catalysis that together determine a minimum k_{obsd} $\approx$ 5 × 10^{-8} s^{-1} near pH 5. Chloromethyl chloroacetate is an example of an aliphatic ester with a flat pH dependence ($k_0 \approx$ 10^{-4} s^{-1}) over a broad range; cf. ref 29. In the present case, intramolecular-assisted catalysis (see Chart IA) might help to explain the relatively large value for k_0. The behavior of acetal esters is of special interest in so far as it is commonly assumed that the cancer drug bleomycin produces a DNA lesion,[30,31] which has similar structural elements (see chart IB; cf. ref 4, Chapter 16).

Radiolytic Proton-Catalyzed Hydrolysis of Acetaldehyde Dimethyl Acetal? Aldehyde formation upon radiolysis of acetals has sometimes been ascribed to the hydrolysis of the acetal mediated by the proton formed in reaction 1.[6] However, it can be easily shown that the increase of the proton concentration upon water radiolysis is much too small to have any hydrolytic effect. During γ-radiolysis at a dose rate of 0.15 Gy s^{-1}, the H^+ steady-state concentration rises by about 10^{-11} mol dm^{-3}. In pulse radiolysis at pH 7 during a submicrosecond electron pulse of 10 Gy, the H^+ concentration may for about a microsecond attain 3 × 10^{-6} mol dm^{-3}, but hydrolytic effects are equally minute: A proton concentration equivalent to pH 5.5 is present for only a few microseconds, while the hydrolysis half-life of acetaldehyde diethyl acetal in strong acid at pH 0 is as long as 2.8 s.[12]

Acknowledgment. We thank M. Wurgel for valuable technical assistance. Part of this work has been supported by the German Federal Ministry for Research and Technology in connection with Project 02-WT 8720 (Initiator Professor G. O. Schenck; Coordinator Professor H. Bernhardt).

Registry No. 1, 4617-61-2; **2**, 25748-53-2; **3**, 16828-28-7; **4**, 123676-91-5; **5**, 123676-92-6; **6**, 123676-93-7; **7**, 73239-58-4; **8**, 123676-94-8; **9**, 58982-50-6; **10**, 23012-06-8; $CH_3CH(OCH_3)_2$, 534-15-6; N_2O, 10024-97-2; O_2, 7782-44-7; $O_2^{\bullet-}$, 11062-77-4; $C(NO_2)_4$, 509-14-8; $C(NO_2)_3^-$, 20143-63-9; $NO_2^{\bullet}$, 10102-44-0.

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