coupling in the diamine. If one considers the hole of the cation as delocalized on the two nitrogen atoms, then via a coulombic argument the **DA222** cation–neutral pair would have a much lower stabilization than the analogous **222** pair. This idea can be applied mutatis mutandis to the excited electronic states of these compounds.

Finally, it is interesting to compare the photophysics of the cage amines with those of the acyclic tertiary amines. Excimer formation has been observed in only one acyclic amine: the diamine *N,N,N′,N′*-tetramethyl-1,3-propanediamine (TMPD) whose binding energy has been reported to be 11.3 kJ/mol.[26] While no direct evidence of excimer formation has been observed for any other acyclic amines, there is, nevertheless, some interesting behavior. For example, triethylamine (TEA) in *n*-hexane solution has a fluoroescence self-quenching rate constant of 6×10^9 M^{-1} s^{-1}, about one-third the diffusion-controlled value. Due to the similarity in amine geometries, one would expect TEA to have an association with a stability approximately equal to that of TMPD. The fact that excimer fluorescence is not observed in TEA is probably due to steric interactions between the alkyl groups of the planer, excited-state molecule and those of the ground-state monomer. Rapid conformational interconversion of the ground state as discussed by Bushweller et al.[27] would also presumably inhibit excimer formation. As the self-quenching rate constant suggests, a weakly bound excimer may play a role in the fluoresence quenching process.

It is evident from photophysical studies that amine excimer stabilization is decreased as methylene units are added to the bridge of the cage. This observation is explained as arising from an increase in steric hindrance to excimer formation. This hindrance has been determined to be brought about by increases in both the C–N–C angles and the lone-pair N–C–H dihedral angle as methylene units are added. Regarding **DA222**, an argument based on electronic structure can be made to account for the lack of excimer formation. While emissive excimers are found in relatively few amines, it is possible that weak photoassociation occurs in many of the tertiary amines.

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The Rapid Hydration of the Acetyl Radical. A Pulse Radiolysis Study of Acetaldehyde in Aqueous Solution

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Abstract: In aqueous solution acetaldehyde and its hydrate are in a 0.8:1 equilibrium. Hydroxyl radicals generated by the pulse radiolysis of N_2O-saturated water react with this mixture with an overall rate constant of $k = 2.4 \times 10^9$ dm^3 mol^{-1} s^{-1}, the rate of reaction with acetaldehyde being about 3 times faster ($k_5 = 3.6 \times 10^9$ dm^3 mol^{-1} s^{-1}) than with the hydrate ($k_6 = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1}). The predominant radicals formed are the acetyl radical and its hydrated form, H-abstraction at methyl occurring to only about 5–10%. The acetyl radical rapidly hydrates ($k_9 = 2 \times 10^4$ s^{-1}). Thus, its rate of hydration is 2×10^6 times faster than that of the parent compound acetaldehyde. The hydrated acetyl radical has been monitored by its rapid reduction of tetranitromethane ($k_{11} = 2.8 \times 10^9$ dm^3 mol^{-1} s^{-1}), the formation of $O_2^{\bullet-}$ in the presence of oxygen, and its deprotonation at pH 11 ($pK_a \leq 9.5$). The acetyl radical does not oxidize *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) at the pulse radiolysis time scale, but the acetylperoxyl radical (formed in the presence of oxygen) reacts rapidly with TMPD ($k_{15} = 1.9 \times 10^9$ dm^3 mol^{-1} s^{-1}), ascorbate ($k = 8.3 \times 10^8$ dm^3 mol^{-1} s^{-1}), and $O_2^{\bullet-}$ ($k_{16} \simeq 10^9$ dm^3 mol^{-1} s^{-1}) and hence is the most strongly oxidizing peroxyl radical known so far. Data on the rate of water loss from the hydrated acetyl radical are considerably less accurate, but it may well be that this reaction has a rate constant of $k_{10} \simeq 3 \times 10^4$ s^{-1}.

In aqueous solutions acetaldehyde is present in a 0.8:1.0 mixture of the carbonyl form and the hydrate ($K_{1,2} = 1.246$ at 20 °C).[1]

$$CH_3CHO + H_2O \rightleftarrows CH_3CH(OH)_2 \qquad (1, 2)$$

The rate constant of hydration k_1 has been reported to be 9.0×10^{-3} s^{-1} at 25 °C. The establishment of the equilibrium is also proton and base catalyzed ($k(H^+) = 930$ dm^3 mol^{-1} s^{-1}, $k(OH^-) = 8 \times 10^4$ dm^3 mol^{-1} s^{-1}).[2]

Hydroxyl radicals and H atoms are generated by the radiolysis of N_2O-saturated water (reactions 3 and 4). Their radiation-chemical yields (G values) are $G(OH) = 0.57$ μmol J^{-1} and $G(H) = 0.06$ μmol J^{-1}. The radicals OH and H react with acetaldehyde and its hydrate by abstracting carbon-bound H atoms (e.g., reactions 5–8).

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^\bullet OH,\ e^-_{aq},\ H^\bullet,\ H^+,\ H_2O_2,\ H_2 \qquad (3)$$

$$e^-_{aq} + N_2O \rightarrow {}^\bullet OH + N_2 + OH^- \qquad (4)$$

$${}^\bullet OH + CH_3CHO \rightarrow CH_3C^\bullet O\ (\mathbf{1}) + H_2O \qquad (5)$$

$${}^\bullet OH + CH_3CH(OH)_2 \rightarrow CH_3C^\bullet(OH)_2\ (\mathbf{2}) + H_2O \qquad (6)$$

$${}^\bullet OH + CH_3CHO \rightarrow {}^\bullet CH_2CHO\ (\mathbf{3}) + H_2O \qquad (7)$$

$${}^\bullet OH + CH_3CH(OH)_2 \rightarrow {}^\bullet CH_2CH(OH)_2\ (\mathbf{4}) + H_2O \qquad (8)$$

It will be shown that the acetyl radical **1** and its hydrated form **2** can be distinguished by their different redox properties. The acetyl radical **1** is in equilibrium with its hydrated form **2** as is the parent compound acetaldehyde (reactions 9 and 10).

$$CH_3C^\bullet O\ (\mathbf{1}) + H_2O \rightleftarrows CH_3C^\bullet(OH)_2\ (\mathbf{2}) \qquad (9/10)$$

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From a CIDNP experiment it has been suggested that the hydrated acetyl radical loses water very rapidly.[3] In the present study we show that the acetyl radical **1** also hydrates rapidly, about 2×10^6 times faster than acetaldehyde, even though the equilibrium may lie on the side of the acetyl radical.

Experimental Section

Acetaldehyde (Merck) was redistilled prior to use. Tetranitromethane (Serva), KSCN (Merck), *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (Fluka), 2,2-azinobis(3-ethylbenzthiazoline-6-phosphate) (ABTS) (Sigma), and other chemicals were used as received. N_2O-saturated solutions of acetaldehyde were prepared by injecting a chilled sample of acetaldehyde through a serum cap into a flask containing purified (Millipore Milli-Q system) N_2O-saturated water. Since solutions were continuously flushed with O_2-free (Oxysorb) N_2O during measurements, to avoid possible losses of acetaldehyde, the N_2O was bubbled through an acetaldehyde solution of the same concentration as that being investigated.

Pulse radiolysis was carried out at room temperature ($\simeq 20$ °C) by using a 2.8 MeV Van de Graaff electron accelerator. Electron pulses of 0.4-μs duration were given with doses ranging from 1.5–15 Gy, usually ca. 3 Gy. The pulse radiolysis setup together with its most recent improvements have been described elsewhere.[4,5] For pulse-spectrophotometric measurements, dosimetry was performed with N_2O-saturated 0.01 mol dm^{-3} KSCN solutions taking $G(SCN_2^{\bullet -}) = 0.62$ μmol J^{-1} and $\epsilon(480$ nm$) = 7600$ dm^3 mol^{-1} cm^{-1}.[6] For pulse-conductometric measurements 0.01 mol dm^{-3} dimethyl sulfoxide solutions at pH 5 was used taking $G(H^+) = 0.62$ μmol J^{-1}.[7]

^{60}Co-γ-radiolysis experiments were done at a dose rate of 0.9 Gy s^{-1}. For the measurement of the conductivity changes in the steady-state experiments a commercial conductivity meter (Radiometer, CDM 3) was used.

Results and Discussion

The Reaction of OH Radicals with Acetaldehyde. The overall rate constant for the reaction of OH radicals with the equilibrium mixture of acetaldehyde and its hydrate has been redetermined by pulse radiolysis of N_2O-saturated solutions of acetaldehyde (4.5×10^{-3}–1.5×10^{-2} mol dm^{-3} as determined by GC) containing $(1-2) \times 10^{-3}$ mol dm^{-3} KSCN. Under these conditions acetaldehyde, its hydrate, and SCN^- compete for the OH radical. $SCN^\bullet$ complexes with SCN^- and the yield of $(SCN)_2^{\bullet -}$ is measured at 480 nm. On the basis of $k(^\bullet OH + SCN^-) = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1},[8] the overall rate constant for reactions 5–8 was found to be

$$k_{5-8} = 2.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The existing literature value[8] of $k_{5-8} = 5 \times 10^8$ dm^3 mol^{-1} s^{-1} is certainly too low. It has been determined by a less reliable method.

It will be shown below that in the present system about 65% of the radicals formed in reactions 5–8 are acetyl radicals **1**, about 26% hydrated acetyl radicals **2**, whereas the formylmethyl radical **3** and its hydrated form **4** contribute 5–10%. Taking the known percentages of acetaldehyde and its hydrated form and the above yields it is calculated that acetaldehyde reacts 3 times faster with OH radicals than its hydrated form. One can then break down the overall rate constant of $k_{5-8} = 2.4 \times 10^9$ dm^3 mol^{-1} s^{-1} into individual rate constants

$$k_5 = 3.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_6 = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_7 \simeq k_8 \simeq 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

For convenience all rate constants measured in this study are compiled in Table I.

Table I. Compilation of Rate Constants[a]

reaction		rate constant
(5)	$^\bullet OH + CH_3C\mathit{H}O$	3.6×10^9 dm^3 mol^{-1} s^{-1}
(6)	$^\bullet OH + CH_3C\mathit{H}(OH)_2$	1.2×10^9 dm^3 mol^{-1} s^{-1}
(7)	$^\bullet OH + C\mathit{H}_3CHO$	10^8 dm^3 mol^{-1} s^{-1}
(8)	$^\bullet OH + C\mathit{H}_3CH(OH)_2$	10^8 dm^3 mol^{-1} s^{-1}
(9)	$CH_3C^\bullet O + H_2O$	2×10^4 s^{-1}
(10)	$CH_3C^\bullet(OH)_2 - H_2O$	($\simeq 3 \times 10^4$ s^{-1})
(11)	$CH_3C^\bullet(OH)_2 + C(NO_2)_4$	2.8×10^9 dm^3 mol^{-1} s^{-1}
(15)	$CH_3C(O)O_2^\bullet$ + TMPD	1.9×10^9 dm^3 mol^{-1} s^{-1}
	$CH_3C(O)O_2^\bullet$ + ABTS	1.8×10^9 dm^3 mol^{-1} s^{-1}
	$CH_3C(O)O_2^\bullet$ + ascorbate	8.3×10^8 dm^3 mol^{-1} s^{-1}
(16)	$CH_3C(O)O_2^\bullet + O_2^{\bullet -}$	10^9 dm^3 mol^{-1} s^{-1}
(17)	$CH_3C(O)OOH + CH_3CHO$	1.5×10^{-2} dm^3 mol^{-1} s^{-1}
	$^\bullet CH_2CHO$ + ascorbate	7×10^8 dm^3 mol^{-1} s^{-1}

[a] The value in brackets is tentative.

The Hydrated Acetyl Radical 2. Among the four radicals **1–4** which are formed in the reactions 5–8 radical **2** is the only one which is strongly reducing. It can be monitored by its fast reaction with tetranitromethane (TNM) (reaction 11) by measuring the formation of the nitroform anion (NF^-) which exhibits a strong absorption at 350 nm ($\epsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

$$CH_3C^\bullet(OH)_2\ (\mathbf{2}) + C(NO_2)_4 \rightarrow CH_3CO_2^- + C(NO_2)_3^- + NO_2^\bullet + 2H^+ \quad (11)$$

When N_2O-saturated aqueous solutions of acetaldehyde (2×10^{-3} mol dm^{-3}) containing TNM ($0.4-2.1 \times 10^{-4}$ mol dm^{-3}) are subjected to a high-energy electron pulse, reactions 3–8 take place within 1–2 μs. H atoms are partly (30–70%) scavenged by TNM (taking $k(H^\bullet + \text{acetaldehyde}) = 3 \times 10^7$ dm^3 mol^{-1} s^{-1}).[9] Any hydrated acetyl radicals formed in reaction 4 or in a subsequent reaction are oxidized according to reaction 11.

The formation of NF^- follows two kinetically distinguishable steps (Figure 1). The yield ratio of the fast to the slow step is 2:3. The total yield of NF^- decreases somewhat with increasing dose/pulse. Extrapolating to zero dose/pulse yields $G(NF^-) = 0.52$ μmol J^{-1}. The first step follows first-order kinetics, and the observed rate constant is TNM concentration dependent (Figure 2A). This process is attributed to reaction 11 and from the slope in Figure 2A

$$k_{11} = 2.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

is calculated. The reaction of the H atoms with TNM ($k(H^\bullet + \text{TNM}) = 5.5 \times 10^8$ dm^3 mol^{-1} s^{-1})[9] although contributing to a small extent to the NF^- formation, does not influence significantly the measured rate constants of the first and second step, because at the low TNM concentrations this contribution can be fully neglected and at the high TNM concentrations it is only ≤8% of the total NF^- yield.

The rate of NF^- formation in the second step is also kinetically of first-order, but it is independent of the TNM concentration (in the range of 4×10^{-5} to 2.1×10^{-4} mol dm^{-3}, cf. Figure 2B). It is attributed to the rate of hydration of the acetyl radical (reaction 9). From the data in Figure 2B

$$k_9 = 2 \times 10^4 \text{ s}^{-1}$$

is obtained. The rate constant of reaction 9 is independent of pH in the pH range of 1.8–11.4. If the rate constant of the H^+- and OH^--induced hydration is considerably less than diffusion-controlled as found for acetaldehyde, the lack of a pH dependence within this range is to be expected.

In Figure 2A at zero TNM concentration a small intercept ($k = 5 \times 10^4$ s^{-1}) is apparent. This intercept should represent the sum of the rate constants of the hydration (reaction 9) and the dehydration (reaction 10). No unequivocal experiment could be thought of to determine the dehydration rate constant more accurately (see below). Hence

$$k_{10} \simeq 3 \times 10^4 \text{ s}^{-1}$$

must remain a tentative value.

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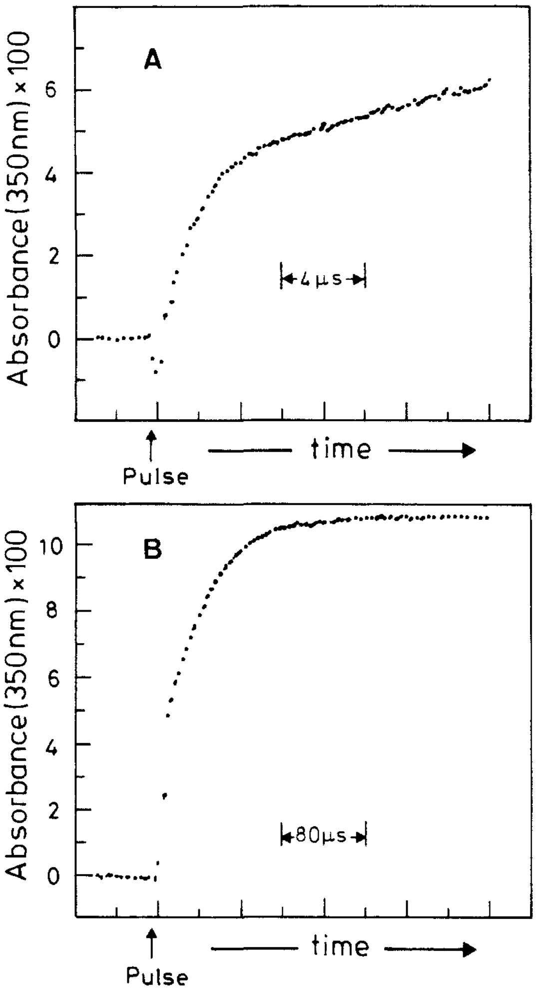

Figure 1. Pulse radiolysis (3 Gy/pulse, pulse length 0.4 µs) of N_2O-saturated aqueous solutions of acetaldehyde (2×10^{-3} mol dm^{-3}) containing tetranitromethane (1.4×10^{-4} mol dm^{-3}) at pH 6.5. Formation of the nitroform anion measured by its absorption at 350 nm as a function of time. (A: initial fast buildup, 2 µs div^{-1}; B: subsequent slow buildup, 40 µs div^{-1}).

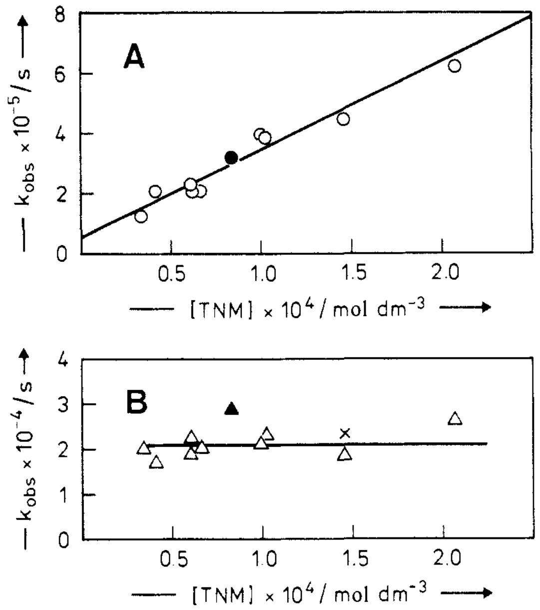

Figure 2. Dependence of the observed first-order rate constant of the fast (A) and the slow (B) buildup of nitroform anion formation as a function of the tetranitromethane (TNM) concentration (cf. Figure 1). Open symbols, pH 6.5; filled symbols, pH 1.8; × pH 11.4. To eliminate the contribution of radical–radical reactions the observed first-order rate constants were measured as a function of dose/pulse and extrapolated to zero dose/pulse.

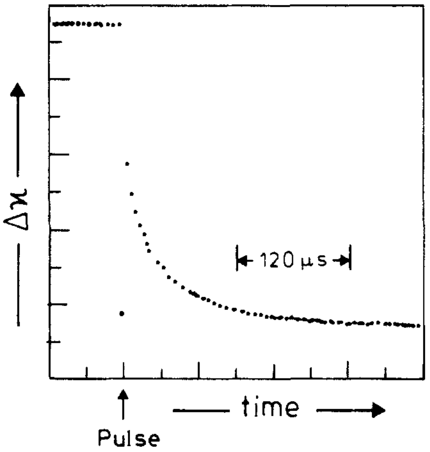

Figure 3. Conductivity change following a 0.4 µs electron pulse of 3 Gy in an N_2O-saturated aqueous solution of acetaldehyde (5×10^{-3} mol dm^{-3}) at pH 10.9.

The rapid hydration of the acetyl radical can be followed in yet another way. α-Hydroxyalkyl radicals have pK_a values 4–6 units below their parent compounds,[10,11] and the pK_a of the hydrated acetyl radical should lie below 10 (cf.[12]). Thus, at pH 11 it must be largely ionized, while in contrast the acetyl radical is not. In pulse conductometric experiments in basic solutions there should be a drop in conductivity due to the replacement of OH^- (λ_0 = 178 Ω^{-1} cm^{-1} equiv^{-1}) by the hydrate radical anion ($\lambda_0 \simeq$ 40 Ω^{-1} cm^{-1} equiv^{-1}). This drop should be followed by a second decrease in conductivity when the acetyl radical hydrates and immediately ionizes. The kinetics of this second drop should be identical with those of the slow component in the TNM experiments. This is indeed the case as shown in Figure 3.

The observed rate constant of this second conductivity decrease was found to be $k_9 = 2 \times 10^4$ s^{-1}, the same as the value reported above.

The radiation chemical yield for the hydrated acetyl radical of $G(\mathbf{2})$ = 0.15$_5$ µmol J^{-1} is obtained from the fast buildup of NF^- after correcting for the contribution of $H^{\bullet}$ + TNM. There is an alternative way of determining this yield. It is known that α-hydroxyalkylperoxyl radicals eliminate $HO_2^{\bullet}$.[13] This $HO_2^{\bullet}$ elimination is especially fast ($t_{1/2} \leq 2$ µs) in the case of the dihydroxymethylperoxyl radical (derived from formaldehyde hydrate)[14] and similar peroxyl radicals.[15] The pK_a value of $HO_2^{\bullet}$ is 4.8.[16] The rapid decay of the hydrated acetylperoxyl radical **5** formed in reaction 12 leads therefore to two protons and two anions (reaction 13).

$$CH_3C^{\bullet}(OH)_2\ (\mathbf{2}) + O_2 \rightarrow CH_3C(OH)_2O_2^{\bullet}\ (\mathbf{5}) \quad (12)$$

$$CH_3C(OH)_2O_2^{\bullet}\ (\mathbf{5}) \rightarrow 2H^+ + CH_3CO_2^- + O_2^{\bullet -} \quad (13)$$

Their formation has been measured by pulse conductometry. In an N_2O/O_2 (4:1 v/v)-saturated 10^{-3} mol dm^{-3} acetaldehyde solution at pH 6.5, the conductivity increase measured 10 µs after the pulse corresponds to G(acid) = 0.34 µmol J^{-1}. Since 0.057 µmol J^{-1} of $H^+/O_2^{\bullet -}$ are produced by the primary H atoms re-

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acting with O_2, the yield of the hydrated acetylperoxyl radical **5** is $G(\mathbf{2}) = 0.14\ \mu\text{mol J}^{-1}$, which is in good agreement with the value obtained above.

The Acetyl Radical 1 and the Acetylperoxyl Radical 6. We found no redox indicator to monitor the acetyl radical. However, its yield can be determined indirectly. In the presence of oxygen, the acetyl radical adds rapidly O_2 to give the acetylperoxyl radical **6** (reaction 14).

$$CH_3C^{\bullet}O\ (\mathbf{1}) + O_2 \rightarrow CH_3C(O)O_2^{\bullet}\ (\mathbf{6}) \qquad (14)$$

In contrast to its parent radical, the acetylperoxyl radical **6** rapidly oxidizes *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) to $TMPD^{\bullet+}$ (reaction 15) which absorbs strongly at 565 nm.[17]

$$CH_3C(O)O_2^{\bullet}\ (\mathbf{6}) + TMPD \rightarrow CH_3C(O)O_2^- + TMPD^{\bullet+} \qquad (15)$$

In N_2O/O_2 (4:1 v/v)-saturated acetaldehyde solutions containing 3.3×10^{-5}–1.7×10^{-4} mol dm^{-3} TMPD at pH 7.6–8.2, the buildup of $TMPD^{\bullet+}$ is observed 20–50 μs after the pulse. The plateau value corresponds to 0.37 μmol J^{-1} (corrected for the contribution of OH radicals) of oxidizing radicals which is attributed to the acetylperoxyl radicals. The observed first-order rate constant of the buildup at 565 nm is linearly proportional to the TMPD concentrations. From the plot of k_{obsd} versus [TMPD] the bimolecular rate constant

$$k_{15} = 1.9 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

is obtained. Compared to other peroxyl radicals the acetylperoxyl radical is the most powerful oxidant found so far (data by S. Steenken, cf.[18]). It is therefore not surprising that the acetylperoxyl radicals reacts with the weaker reductant 2,2'-azinobis(3-ethylbenzthiazoline-6-phosphate) (ABTS) with the same rate constant (our measured value is $k = 1.8 \times 10^9$ dm^3 mol^{-1} s^{-1}) as with TMPD. Both reactions are effectively diffusion-controlled. Oxidation of ascorbate ion by the acetylperoxyl radical also occurs, albeit with a somewhat lower rate constant ($k = 8.3 \times 10^8$ dm^3 mol^{-1} s^{-1}).

The acetylperoxyl radical also oxidizes the superoxide radical formed in reaction 13 and by O_2 scavenging primary H atoms (reaction 16). The peracetic acid formed (cf.[20]) in this reaction

$$CH_3C(O)O_2^{\bullet}\ (\mathbf{6}) + O_2^{\bullet-} \rightarrow CH_3C(O)O_2^- + O_2 \qquad (16)$$

has a pK_a of 8.2. At pH $\leq$ 6.5 reaction 16 is followed by a protonation of the peracetate ion with the net result of a decrease in conductivity. In an O_2-saturated acetaldehyde solution where $G(O_2^{\bullet-}) = 0.41$ and $G(\mathbf{6}) = 0.18\ \mu\text{mol J}^{-1}$ the rate constant of reaction 16 has been estimated from the halflife of the conductivity decay to be

$$k_{16} \simeq 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

In competition the acetylperoxyl radicals decay bimolecularly and react with the formylmethylperoxyl radicals. Details of the complex kinetics have not yet been elucidated. However, in irradiated N_2O/O_2-saturated acetaldehyde solutions the formation of CO_2 can be measured. At pH 10–11 it is slowly converted into the bicarbonate ion, a reaction which can be followed by pulse conductivity.[19] From the net decrease in conductivity $G(CO_2) = 0.16\ \mu\text{mol J}^{-1}$ is calculated. Peracetic acid reacts slowly with acetaldehyde ($k_{17} = 1.2 \times 10^{-2}$ dm^3 mol^{-1} s^{-1})[20] to give 2 equiv of acetic acid (reaction 17). This explains the observed[21] post-irradiation formation of acid in γ-irradiated oxygenated solutions of acetaldehyde.

$$CH_3C(O)O_2H + CH_3CHO \rightarrow 2CH_3C(O)O^- + 2H^+ \qquad (17)$$

We now have repeated such experiments by following the conductivity increase during and after γ-irradiation of O_2-saturated acetaldehyde solutions (0.1 and 0.04 mol dm^{-3})[22] at pH 6.8. During irradiation the conductivity increased linearly with dose due to the formation of acetic acid according to reactions 12 and 13. This was then followed by a slow first-order increase in conductivity with half-lives of 9 and 17 min for the respective acetaldehyde concentrations used. The average value for

$$k_{17} = 1.5 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

calculated from these data is in acceptable agreement with the reported value.

The Formylmethyl Radical 3 and Its Hydrated Form 4. Neither the acetyl radical nor its hydrated form are strongly oxidizing radicals and are unable to oxidize TMPD, ABTS, and ascorbate under pulse radiolysis conditions, but the formylmethyl radical is known to oxidize TMPD with a rate constant of 2.0×10^9 dm^3 mol^{-1} s^{-1}.[23] In an N_2O-saturated acetaldehyde solution (10^{-2} mol dm^{-3}) containing 10^{-4} mol dm^{-3} TMPD at pH 7.6, the formation of $TMPD^{\bullet+}$ reached its maximum level equivalent to 0.05 μmol J^{-1} of $TMPD^{\bullet+}$ at 100 μs after the pulse. Further buildup of the $TMPD^{\bullet+}$ was counteracted by radical–radical reactions so that the absorption of $TMPD^{\bullet+}$ was observed to decrease after reaching its maximum level. The above formation of $TMPD^{\bullet+}$ in the system is fully accounted by the OH radical (4% is scavenged directly by TMPD) and the formylmethyl radical formed in reaction 7. Similar results have been observed with ascorbate ($k = 7 \times 10^8$ dm^3 mol^{-1} s^{-1}). From these data it is concluded that the formylmethyl radical is formed with a G value of 0.03 μmol J^{-1} which is about 5% of the total radical yield. This value may also include the yield of the hydrated formylmethyl radical, if not, then the total yield of these two radicals may be around 10%. Such a value is expected, since in the case of ethanol also 13% of the OH radicals abstract an H atom from the methyl group.[24]

The surprising result of this study is that the rate constant of hydration of the acetyl radical is 6 orders of magnitude faster than that of the parent compound, acetaldehyde. Although we have not been able to measure the dehydration rate constant k_{10} with acceptable accuracy, our estimated value could indicate that the equilibrium 9/10 lies on the side of the acetyl radical confirming the interpretation of some earlier CIDNP experiments.[3]

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