The Case of (2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)(H_2O)$Co^{III}-OOR^{2+}$ (R = CH_2OH, CH_2CN, CCl_3) and Reactions with the Methylperoxyl Radical[‡]

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The long-lived transient complexes (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclo-tetradeca-1,3,8,10-tetraene)(H_2O)-Co^{III}–OOR^{2+}, $[(tim)(H_2O)Co^{III}–O_2R]^{2+}$ (R = CH_2OH, CH_2CN, CCl_3) were prepared from the reaction of $[Co^{II}(tim)(H_2O)_2]^{2+}$ with the corresponding peroxyl radicals, applying radiation chemistry techniques. The resultant transient complexes, which are relatively stable (lifetime of days), were subsequently treated with methylperoxyl ($CH_3O_2^{\cdot}$) radicals to form $[Co^{III}(tim)(H_2O)_2]^{3+}$ and formaldehyde. The results point out that the $CH_3O_2^{\cdot}$ radicals rapidly oxidize MOOR peroxides.

Introduction

Peroxyl radicals are key intermediates in a large variety of oxidation processes that include, amongst others, catalytic oxidations by peroxides, which proceed via radical mechanisms[1] (for example processes which involve the Fenton reaction[2]), catalytic oxidations by dioxygen,[3] and radical processes, involving organic radicals, in oxygenated solutions.[4] Of special importance here are deleterious radical processes in biological systems.[5] It is therefore not surprising that the properties of peroxyl radicals have been studied by many research teams and summarized in several comprehensive reviews.[6]

Surprisingly enough the kinetics and reaction mechanisms of peroxyl radicals with different types of peroxides have not been studied — no rates of such reactions are reported in the compilation of the rates of reaction of peroxyl radicals.[4] This is surprising as peroxides are formed in many of the reactions of peroxyl radicals and might therefore participate in the processes studied and thus affect the nature of the final products in a variety of catalytic oxidations and biological processes. Of special importance are systems where one of the reactants is a transition metal peroxo complex, as intermediates of this type are formed in most catalytic — including enzymatic — processes.[1−3]

Recently, while studying the properties of the relatively long lived peroxide $[L^1(H_2O)Co^{III}-OOCH_3]^{2+}$ (L^1 = tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) it was noted that the $CH_3OO^{\cdot}$ radical reacts with it via reaction (1):[7]

$$[L^1(H_2O)Co^{III}-OOCH_3]^{2+} + CH_3OO^{\cdot} \rightarrow [L^1Co^{II}(H_2O)_2]^{2+} + CH_2O + CH_3OH + O_2$$

$$k = 1.5 \times 10^{9}\ \mathrm{M}^{-1}\mathrm{s}^{-1}\ [7] \qquad (1)$$

i.e. via a mechanism which yields the same products as one of the possible mechanisms for the decomposition of $CH_3OOOOCH_3$,[8] and thus results in the same products as the dimerization of the peroxyl radical. However, the formation of the dimer $CH_3OOOOCH_3$ in this reaction seems unlikely. It is therefore of interest to note that the same products would also be expected if the peroxyl radical acts as a reducing agent towards the $[L^1(H_2O)Co^{III}-OOCH_3]^{2+}$ peroxide. {The CH_3OO^+ formed will decompose in aqueous solutions, maybe synchronously, into dioxygen and methanol and the $[L^1(H_2O)Co^{II}-OOCH_3]^+$ into $[L^1Co^{II}(H_2O)_2]^{2+}$ and CH_3OOH which yields CH_2O}. In principle, the same products will also be formed if the peroxyl radicals oxidize the $[L^1(H_2O)Co^{III}-OOCH_3]^{2+}$ peroxide forming $[L^1(H_2O)Co^{IV}-OOCH_3]^{3+}$ and CH_3OO^-. {$[L^1(H_2O)$-

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[‡] On the Chemical Properties of the Transient Complexes L_mM^{n+1}-OOR, Part 2. Part 1: Ref.[7]

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$Co^{IV}-OOCH_3]^{3+}$ has then to decompose into $[L^1Co^{II}(H_2O)_2]^{2+} + CH_3^+ + O_2$ in order to form the observed products.} However, as L^1 stabilizes low-valent complexes due to the four imine ligating groups, the formation of a Co^{IV} transient complex seems unlikely. However, the results of this study point out that the peroxyl radicals oxidize the peroxide bound to the central cation.

The reaction of the peroxyl radical with $[L^1(H_2O)Co^{III}-OOCH_3]^{2+}$ is extremely fast,[7] even faster than the dimerization reaction of the radical ($CH_3OO^{\cdot} + CH_3OO^{\cdot}$ = products, $k = 4 \times 10^8$ $M^{-1}s^{-1}$).[9] This observation is of special interest as the reactions of peroxyl radicals with many transition metal complexes yield transient complexes of the type $L_mM^{n+1}-OOR$,[5b] and complexes of this type are also formed in a variety of biological and catalytic processes involving oxidation by peroxides or dioxygen.[1−3] Recent reports suggest that these transient complexes are relatively stable in some systems.[10] In some cases for transient complexes of the type $L_mM^{n+1}-OOH$ the reversible, pH dependent, switching of the hydro-peroxide complex and the peroxide complex has been demonstrated.[11] Reactions of the $L_mM^{n+1}-OOR$ complexes with peroxyls are therefore mechanistically of similar importance to the reaction of high-valent iron-oxenes with peroxides.[12]

It therefore seemed of crucial importance to study the mechanisms and rates of reactions of a variety of peroxyl radicals with a variety of peroxides in order to elucidate the detailed mechanisms of these reactions and the factors that affect them and their rates. For the present study radiation chemistry techniques were chosen.[13,14] In order to obtain a better understanding of the mechanisms of the reactions studied it was decided to prepare relatively stable $[L(H_2O)Co^{III}-OOR]^{2+}$ ($R \neq CH_3$) complexes and react them with $CH_3O_2^{\cdot}$ radicals. Such a study was expected to yield different final products depending on whether the $CH_3O_2^{\cdot}$ radical reacted as an oxidizing or as a reducing agent. The results demonstrate that the complexes with R = CH_2OH, CH_2CN, CCl_3 are indeed stable enough.

Results

Formation of the Transients $[(tim)(H_2O)Co^{III}-OOR]$

The following solutions were irradiated by a short electron pulse from the linear accelerator. *MeOH/CH_3CN system:* 70% N_2O and 30% O_2 saturated solutions containing 0.3 M MeOH or CH_3CN and $[Co(tim)(H_2O)_2]^{2+}$ (0.5−2.0) $\times 10^{-4}$ M at pH = 3.0.
CCl_4 system: 70% Helium or Argon and 30% O_2 saturated solutions containing 0.1% CCl_4, 10% 2-propanol and $[Co(tim)(H_2O)_2]^{2+}$ (0.5−2.0) $\times 10^{-4}$ M at pH = 3.0.

Under these conditions more than 90% of the primary radicals are converted into the desired $^{\cdot}OOR$ (R = CH_2OH, CH_2CN, CCl_3) radicals during the pulse (see Exp. Sect.). In all the systems studied a formation reaction was observed after conversion of the initially formed radicals into the peroxyl radicals. A typical reaction is shown in Figure 1. The formation of the transients obey pseudo first order rate laws, under conditions of excess $[Co(tim)(H_2O)_2]^{2+}$, and the observed rates are proportional to the initial $[Co(tim)(H_2O)_2]^{2+}$ concentration (see Figure 2). The rates are independent of the concentration of all other components of the solution, pH, pulse intensity and wavelength of observation. The kinetics of the formation of the transient complexes indicate that they are produced from a reaction between $[Co(tim)(H_2O)_2]^{2+}$ and the specific peroxyl radical formed by the radiation, as in the reaction of $[Co(tim)(H_2O)_2]^{2+}$with methylperoxyl radicals.[7] Thus it is proposed that the reaction observed is:

$$[Co(tim)(H_2O)_2]^{2+} + RO_2^{\cdot} \rightarrow [(tim)(H_2O)Co^{III}-OOR]^{2+} \qquad (2)$$

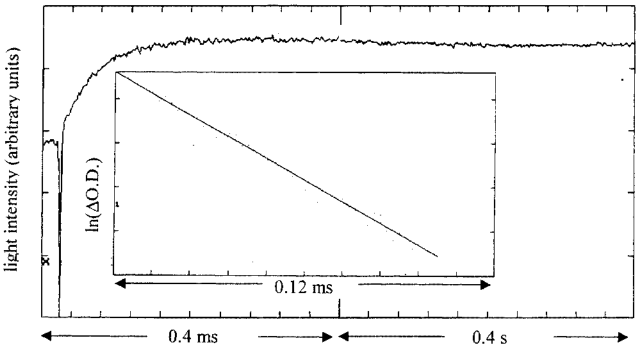


Figure 1. Increase of the absorption (at 314 nm) due to the formation of $[(tim)(H_2O)Co^{III}-OOCH_2CN]^{2+}$ in the presence of oxygen (30% O_2, 70% N_2O) and first order plot (insert); conditions: 0.3 M CH_3CN, 5×10^{-5} M $[Co(tim)(H_2O)_2]^{2+}$

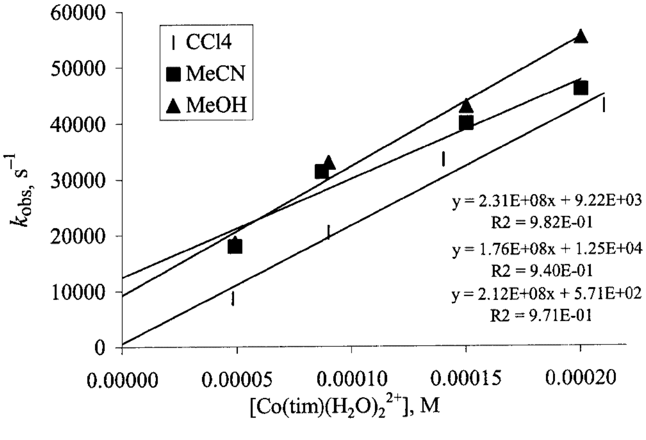


Figure 2. Dependence of k_{obs} for the transients formation on $[Co(tim)(H_2O)_2]^{2+}$

The derived second order rate constants, i.e. the specific rate constants of the cobalt peroxo complex formation, are calculated as (1.8−2.3) $\times 10^8$ $M^{-1}s^{-1}$, in good agreement with the value measured for the formation of the methylperoxo complex,[7] see Table 1.

Table 1. Formation rate constants of the complexes $[(tim)(H_2O)Co^{III}-OOR]$

R	$k_f \times 10^{-8}$ $M^{-1}s^{-1} \pm 0.3$
CH_2OH	2.3
CH_2CN	1.8
CCl_3	2.1
CH_3	1.8 [7]

Decomposition of the Transients $[(tim)(H_2O)Co^{III}-OOR]$

The transient complexes are relatively long lived. The transient complexes absorb in the UV region similar to $[(tim)(H_2O)Co^{III}-O_2CH_3]^{2+}$,[7] and they do not absorb around 520 nm where the absorption spectrum of $[Co(tim)(H_2O)_2]^{2+}$ has a maximum. The complex with R = CH_2CN is the longest lived one — it decomposes within about eight days — followed by R = CH_2OH, decomposing within 2.5 days, and R = CCl_3, decomposing within 1.5 days under the experimental conditions. Figure 3 shows a typical decomposition sequence. In comparison to these $[(tim)(H_2O)Co^{III}-O_2CH_3]^{2+}$ has a half life time of only approximately ten minutes at pH = 3.0 under the experimental conditions.[7] The final product of the decomposition in all cases is $[(tim)Co(H_2O)_2]^{3+}$ as verified by comparison of its spectrum with the spectra obtained after several days (see Figure 3).

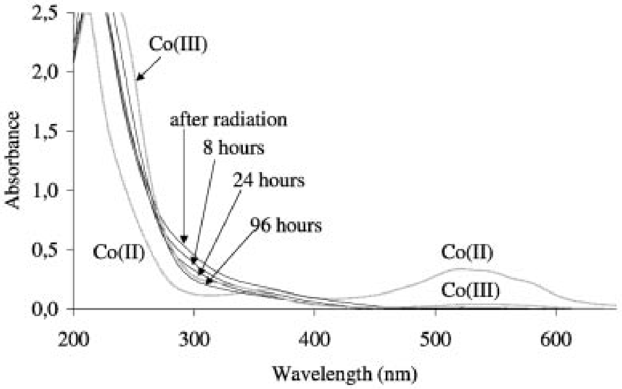


Figure 3. Decomposition sequence of the transient $[tim(H_2O)Co^{III}-OOR]$ (R = CH_2OH) over a period of four days after irradiation of an aqueous solution (70% N_2O and 30% O_2 saturated) containing $[Co(tim)(H_2O)_2]^{2+}$ (9.6×10^{-5} M) and CH_3OH (0.3 M) for 45 min in a ^{60}Co γ-source

Reaction of the Transients $[(tim)(H_2O)Co^{III}-OOR]$ (R = CH_2CN, CH_2OH) with the $^{\cdot}OOCH_3$ Radical

As the resulting peroxo complexes proved to be so stable, although experiments to purify them by ion exchange failed, these complexes were considered ideal candidates to investigate their reaction with a different peroxyl radical (reaction 3).

$$[(tim)(H_2O)Co^{III}-OOR]^{2+} + R'O_2^{\cdot} \rightarrow \text{products} \quad (3)$$

Initially, the simplest peroxyl radical, methylperoxyl, was chosen as we had previously investigated its reaction with the $[Co(tim)(H_2O)_2]^{2+}$ complex.[7] For these experiments the solutions were irradiated twice: during the first irradiation the relatively stable peroxo cobalt complex was formed and in the second irradiation the methylperoxyl radical was formed in the presence of the long-lived metal peroxy complex. The reaction of the peroxo cobalt complex with the methylperoxyl radical was monitored by recording UV/Vis spectra and measuring the amount of formaldehyde produced in the systems.

Solutions prepared as above to yield the peroxo cobalt complexes, for two different cobalt complex concentrations for each system (7.5×10^{-5} and 9.6×10^{-5} M for R = CH_2CN and 9.7×10^{-5} and 1.2×10^{-4} M for R = CH_2OH), were irradiated in the ^{60}Co γ-source for 35 and 45 minutes for R = CH_2CN and 40 and 55 minutes for R = CH_2OH. These times were calculated to yield a slight excess of the peroxyl radical over the $[(tim)Co(H_2O)_2]^{2+}$ complex and thus a radiation dose sufficient to convert all the $[(tim)Co(H_2O)_2]^{2+}$ complex into the specific peroxo cobalt complex, as verified by the absence of the specific absorbance of $[(tim)Co(H_2O)_2]^{2+}$ at 520 nm. The yield of the peroxo cobalt complex was calculated accordingly by the disappearance of the absorbance at 520 nm. Before the second radiation two thirds (8 mL) of the derived solution had N_2O bubbled through it; DMSO was then added to achieve a final concentration of 1 M, and distilled water saturated with O_2 added to give a final volume of 12 mL and a final concentration of 30% dioxygen and 70% N_2O. These solutions were then irradiated in the ^{60}Co γ-source by an additional dose producing $CH_3O_2^{\cdot}$ radicals so that

Table 2. Formaldehyde produced during the reaction of the complexes $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ with the methylperoxyl radical

R	$[(tim)Co(H_2O)_2{}^{2+}]_{init}$ M	$[(tim)(H_2O)Co^{III}-OOR]$[a] M	$[H_2CO]$ M
CH_2CN	7.5×10^{-5}	5.0×10^{-5}	5.1×10^{-5}
CH_2CN	9.6×10^{-5}	6.4×10^{-5}	5.9×10^{-5}
CH_2OH	9.7×10^{-5}	6.1×10^{-5}	5.8×10^{-5}[b]
CH_2OH	1.2×10^{-4}	8.2×10^{-5}	7.4×10^{-5} [b]

[a] Approximately 2/3 of the derived concentration after the first irradiation as measured by the disappearance of the UV/Vis band due to $[(tim)Co(H_2O)_2]^{2+}$. [b] These values were corrected for those derived in blank solutions.

$[CH_3O_2^{\cdot}] = 1.1[(tim)(H_2O)Co^{III}-OOR^{2+}]$. The UV/Vis spectra of these solutions were recorded. The spectra demonstrated that the $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ complexes were consumed during the second irradiation and transformed into $[Co^{III}(tim)(H_2O)_2]^{3+}$; no $[Co^{II}(tim)(H_2O)_2]^{2+}$ was formed during the second irradiation.

The yields of formaldehyde found in the two systems after the second irradiations are tabulated in Table 2. It should be noted that no formaldehyde was produced for R = CH_2CN after the first irradiation, i.e. during the formation of the $[(tim)(H_2O)Co^{III}-OOCH_2CN]^{2+}$ complex. For R = CH_2OH a slight amount of formaldehyde, similar to a blank solution containing only methanol, was produced after the first irradiation, probably due to the reaction of $^{\cdot}O_2CH_2OH$ radicals with each other.

Discussion

Formation of the Transients $[(tim)(H_2O)Co^{III}-OOR]^{2+}$

The rate constants of the reactions of $[Co(tim)(H_2O)_2]^{2+}$ with the peroxyl radicals $^{\cdot}OOR$ (R = CH_2OH, CH_2CN, CCl_3) to form $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ obtained in this work, $k = (1.8-2.3) \times 10^8$ $\text{M}^{-1}\text{s}^{-1}$ agree well with the value of $k = (1.8 \pm 0.3) \times 10^8$ $\text{M}^{-1}\text{s}^{-1}$ reported earlier for R = CH_3 [7] (see Table 1). These rates are in agreement with the known rates of ligand exchange of cobalt(II) in such complexes,[15] and indicate that the rate-determining step in these reactions is the ligand exchange, in agreement with reports for a variety of radical reactions with transition metal complexes.[15b]

The very long lifetime of the $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ transient complexes suggests that k_{-2} is very low, otherwise the transient complexes would decompose much faster via 2 $RO_2^{\cdot} \rightarrow$ products or via $RO_2^{\cdot} + [(tim)(H_2O)Co^{III}-OOR]^{2+}$.

$$[Co(tim)(H_2O)_2]^{2+} + RO_2^{\cdot} \underset{k_{-2}}{\rightleftarrows} [(tim)(H_2O)Co^{III}-OOR]^{2+} \quad (2)$$

The lifetimes of the transient complexes are relatively long, in the range of days at pH = 3.0 under the experimental conditions. As the transient complexes are strong oxidizing agents, such long lifetimes suggest that reactions of transients of this type with different substrates might play a crucial role both in catalytic systems and in deleterious biological processes.

Reaction of the Transients $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ (R = CH_2CN, CH_2OH) with the $^{\cdot}OOCH_3$ Radical

The reaction of $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ (R = CH_2CN, CH_2OH) with $^{\cdot}OOCH_3$ radicals was followed and shown to produce formaldehyde and $[Co^{III}(tim)(H_2O)_2]^{3+}$ in all cases. The amount of formaldehyde produced is equal to the concentration of the peroxometal complex reacted with the methylperoxyl radical.

The observation that all the transient complexes $[(tim)(H_2O)Co^{III}-OOR]^{2+}$ decomposed during the second irradiation suggests that under the experimental conditions the rate of reaction (4) is relatively fast, competing with reaction (5).

$$[(tim)(H_2O)Co^{III}-OOR]^{2+} + CH_3O_2^{\cdot} \rightarrow \text{products} \quad (4)$$

$$2CH_3O_2^{\cdot} \rightarrow \text{products } (k_5 = 4 \times 10^8\ \text{M}^{-1}\text{s}^{-1}) \quad (5)$$

From the dose rate of the ^{60}Co source and k_5 one can calculate (see Exp. Sect.) that $k_4 \geq 2 \times 10^5$ $\text{M}^{-1}\text{s}^{-1}$.

The fact that CH_2O is quantitatively formed in reaction (4), and no CH_2O is formed when the solutions are irradiated without the addition of DMSO, proves that the $CH_3O_2^{\cdot}$ radicals react as an oxidizing agent in this reaction. As the redox potential of the $CH_3O_2^{\cdot}$ radicals, 0.77 V vs. NHE,[8] is probably too low to oxidize the central Co^{III} cation, it is proposed that the reaction observed is:

$$[(tim)(H_2O)Co^{III}-OOR]^{2+} + CH_3O_2^{\cdot} \rightarrow [(tim)(H_2O)Co^{III}-OOR]^{3+} + CH_3O_2^{-} \quad (6)$$

followed by

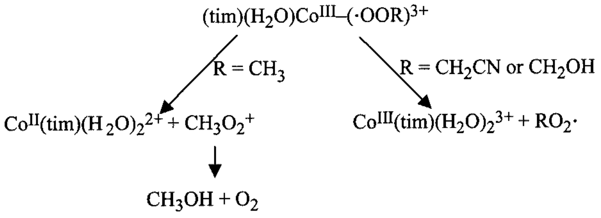
$$CH_3O_2^{-} + H_3O^{+}/H_2O \rightarrow CH_3OOH + H_2O/OH^{-} \quad (7)$$

$$CH_3OOH \rightarrow CH_2O + H_2O \quad (8)$$

and as the other final product is $[Co^{III}(tim)(H_2O)_2]^{3+}$ by

$$[(tim)(H_2O)Co^{III}-(^{\cdot}OOR)]^{3+} \rightarrow [Co^{III}(tim)(H_2O)_2]^{3+} + {}^{\cdot}OOR \rightarrow \text{products} \quad (9)$$

It is of interest to note that the final product of reaction (1), which is analogous to reaction (6), is $[Co^{III}(tim)(H_2O)_2]^{2+}$ and not $[Co^{II}(tim)(H_2O)_2]^{3+}$. If reaction (1) proceeds via an analogous mechanism to reaction (6) one has to conclude that the mechanism of decomposition of the transient complexes $[(tim)(H_2O)Co^{III}-(^{\cdot}OOR)]^{3+}$ depends on the redox potentials of the $ROO^{+}/ROO^{\cdot}$ couples. Electron-withdrawing substituents such as -CN and -OH are expected to shift this potential anodically and therefore these transient complexes decompose via the right pathway in the scheme whereas the transient with R = CH_3 decomposes via the left pathway.



In order to verify this hypothesis other stable complexes of the type $[(L)(H_2O)Co^{III}-OOR]$ have to be found where R is an electron-donating substituent.

Concluding Remarks

The results obtained in this study suggest that transient complexes of the type $L_mM^{n+1}-OOR$ might be relatively stable, at least for $M^{n+1} = Co^{III}$, even in aqueous solutions.

The results demonstrate that $RO_2^{\cdot}$ radicals react by fast reactions with complexes of the type $L_mM^{n+1}{-}OOR$. It is suggested that these reactions proceed via $R'O_2^{\cdot} + LM^{n+1}{-}(^{-}OOR) \rightarrow R'O_2^{-} + LM^{n+1}{-}(^{\cdot}OOR)$.

These reactions might be of crucial importance in a variety of catalytic and biological processes.

Experimental Section

Materials: All solutions were prepared from A.R. grade chemicals and from distilled water further purified by passing through a Milli Q Millipore setup, final resistivity >10 MΩ/cm.

$[Co(tim)Cl_2]PF_6$ was prepared according to literature methods[16] and characterized by NMR spectroscopy and UV/Vis spectrophotometry. Solutions of $[Co(tim)Cl_2]^+$ at pH = 2 were reduced by the introduction of the Adams catalyst, PtO_2, and bubbling dihydrogen for ca. 1 h. The spectrum of $[Co(tim)(H_2O)_2]^{2+}$ thus obtained is identical to that reported in the literature.[16]

Techniques: Solutions were handled by syringe techniques. pH values were measured with a Hanna HI 9017 pH meter and adjusted with $HClO_4$ and/or NaOH.

Irradiations: Pulse-radiolysis experiments were carried out with the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem. The pulse duration was 0.1−1.5 μs with a 200 mA current of 5 MeV electrons. The dose per pulse was 3−30 Gray. Irradiations were carried out in a 4 cm spectrosil optical cell, the analyzing light passing three times through the cell. A 150-W Xenon arc provided the analyzing light. The experimental setup was identical to that described earlier in detail.[17a]

For dosimetry, an N_2O-saturated solution containing 1×10^{-3} M KSCN was used. The yield of $(SCN)_2^{\cdot-}$ was measured by using $\varepsilon_{475} = 7600\ \text{M}^{-1}\text{cm}^{-1}$ and the dose per pulse was calculated assuming $G(SCN)_2^{\cdot-} = 6.0$[17] (the G value is defined as the number of molecules of each product/100 eV radiation absorbed by the solution) and an optical path of 12.3 cm. The dose per pulse was set so that the initial radical concentration was 2−20 μM. The value of the molar extinction coefficients calculated from the dosimetry measurements carry an error limit of 15% due to the scatter of the pulse intensity and uncertainties in G values.

A ^{60}Co source, Noratom, with a dose rate of 4 Gray/min was used for low dose-rate experiments and product analysis.

Simulation of k_4: The rate constant was estimated with the help of the Pro-K global analysis/simulation software by Applied Photophysics. The γ-source irradiation was mimicked by formally adding a reaction forming the radicals at the appropriate rate over the course of the reaction.

Production of Radicals: The radiolysis of water in dilute aqueous solutions can be summarized by:[17]

$$H_2O \xrightarrow{e^-,\gamma} e^-_{aq}\ (2.65),\ \ldots \qquad (10)$$

$$\ldots\ OH^{\cdot}\ (2.65),\ H^{\cdot}\ (0.60),\ H_2\ (0.45),\ H_2O_2\ (0.75)$$

(G value in parentheses). In concentrated solutions, the yields of the primary radicals are somewhat higher and those of H_2O_2 and H_2 are somewhat lower.[17]

In neutral N_2O-saturated solutions ($[N_2O] = 0.022$ M) the hydrated electron is converted into the hydroxyl radical via:

$$e^-_{aq} + N_2O \xrightarrow{H_2O} N_2 + OH^- + {}^{\cdot}OH \qquad (11)$$

$$k_{11} = 8.7 \cdot 10^9\ \text{M}^{-1}\ \text{s}^{-1}\ [18]$$

In acidic solutions the reaction of e^-_{aq} with H^+, which produces $H^{\cdot}$ atoms, becomes important:

$$e^-_{aq} + H^+ \rightarrow H^{\cdot}\ (k_{12} = 2.2 \times 10^{10}\ \text{M}^{-1}\text{s}^{-1}) \qquad (12)\ [18]$$

however at pH > 3 the contribution of $H^{\cdot}$ atoms to the total radical yield is less than 10%.

Methyl radicals were prepared by the reaction of $^{\cdot}OH$ radicals with $(CH_3)_2SO$:

$$(CH_3)_2SO + {}^{\cdot}OH \rightarrow (CH_3)_2{}^{\cdot}S(O)OH \quad (k_{13} = 7.0 \times 10^9\ \text{M}^{-1}\text{s}^{-1}) \qquad (13)[19]$$

$$(CH_3)_2{}^{\cdot}S(O)OH \rightarrow {}^{\cdot}CH_3 + CH_3S(O)OH \quad (k_{14} = 1.5 \times 10^7\ \text{M}^{-1}\text{s}^{-1}) \qquad (14)[19]$$

$^{\cdot}CH_2OH$ and $^{\cdot}CH_2CN$ radicals were formed by hydrogen abstraction:

$$CH_3OH + {}^{\cdot}OH \rightarrow {}^{\cdot}CH_2OH + H_2O \quad (k_{15} = 9.7 \times 10^8\ \text{M}^{-1}\text{s}^{-1}) \qquad (15)\ [18]$$

$$CH_3OH + {}^{\cdot}H \rightarrow {}^{\cdot}CH_2OH + H_2 \quad (k_{16} = 2.6 \times 10^6\ \text{M}^{-1}\text{s}^{-1}) \qquad (16)\ [18]$$

$$CH_3CN + {}^{\cdot}OH \rightarrow {}^{\cdot}CH_2CN + H_2O \quad (k_{17} = 2.2 \times 10^7\ \text{M}^{-1}\text{s}^{-1}) \qquad (17)\ [20a]$$

$$CH_3CN + {}^{\cdot}H \rightarrow {}^{\cdot}CH_2CN + H_2\ (k_{18} = 3.6 \times 10^6\ \text{M}^{-1}\text{s}^{-1}) \qquad (18)\ [20b]$$

$^{\cdot}CCl_3$ radicals were prepared from solutions containing 2-propanol and CCl_4 via the reactions below (these reactions were performed in solutions containing argon or helium instead of N_2O):

$$CCl_4 + e^-_{aq} \rightarrow {}^{\cdot}CCl_3 + Cl^-\ (k_{19} = 1.3 \times 10^{10}\ \text{M}^{-1}\text{s}^{-1}) \qquad (19)\ [21]$$

$$(CH_3)_2CHOH + {}^{\cdot}OH/{}^{\cdot}H \rightarrow {}^{\cdot}C(CH_3)_2OH + H_2O/H_2 \quad (k_{20} = 1.9 \times 10^9/7.4 \times 10^7\ \text{M}^{-1}\text{s}^{-1}) \qquad (20)\ [18]$$

$${}^{\cdot}C(CH_3)_2OH + CCl_4 \rightarrow CH_3COCH_3 + {}^{\cdot}CCl_3 + Cl^- + H^+ \quad (k_{21} = 1 \times 10^8\ \text{M}^{-1}\text{s}^{-1}) \qquad (21)\ [22]$$

For experiments performed in this work the N_2O or Ar/He saturated solutions were mixed with identical O_2 saturated solutions in the ratio 70:30 prior to irradiation. Under these conditions the $^{\cdot}R$ radicals react with dioxygen to form the desired peroxyl radicals:

$${}^{\cdot}R + O_2 \rightarrow RO_2^{\cdot} \qquad (22)$$

These reactions are very fast and approach the diffusion controlled limit, e.g.: $k_{22} = 4.7 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$ for R = $CH_3^{\cdot}$.[4,23]

Product Analysis: UV/Vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

Analysis of formaldehyde was performed according to a literature procedure.[24] Formaldehyde reacts with a reagent containing 0.05 M acetylacetone, 1 M ammonium acetate and 0.033 M acetic acid, to form a yellow complex. The concentration of formaldehyde was determined colorimetrically at the wavelength of maximum absorption (412 nm).

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