irradiation times are used. The efficiency of all initiators parallels the intensity of their absorption in this low-energy region and the length of the irradiation time regardless of the light/dark irradiation sequence used (Table I).

In contrast to organic photochemical initiators, which are consumed in the act of initiation, the complex $W_{10}O_{32}^{4-}$ is regenerated during reaction by eq 4. As a consequence it is better termed a photocatalyst than an initiator, and the reactions in Table I are better called photocatalyzed rather than photoinitiated autoxidations. Importantly, the longer wavelengths of light, $\lambda > 300$ nm, that are effective for inducing autoxidation with $W_{10}O_{32}^{4-}$ do not photodecompose the initial kinetic alkyl hydroperoxide products formed from substrates with tertiary C–H bonds.

Although no concerted effort was made to optimize the substrate conversions for the reactions in Table I, a few reactions were run demonstrating that both high substrate conversion and high selectivity could be achieved without difficulty. In a typical reaction, 0.95 mmol of isobutane, 3.6×10^{-3} mmol of $Q_4W_{10}O_{32}$, and 2.0 mL of acetonitrile solvent were placed in a Pyrex Schlenk flask under an atmosphere of zero grade air (only ppm impurities of H_2O, CO_2, and hydrocarbons) and irradiated 120 min with a 1000-W Xe lamp. TBHP was produced with nearly quantiative selectivity at a conversion of isobutane of 55% (yield of TBHP based on isobutane consumed of ca. 100%). Thus, $W_{10}O_{32}^{4-}/\lambda > 300$ nm/CH_3CN constitutes a system for the efficient and selective photochemical generation of these useful hydroperoxide oxidants via hydrocarbon autoxidation. The polyoxometalates that have redox-active excited states accessible with near-UV and visible light, including $W_{10}O_{32}^{4-}$, should have numerous potential applications in photochemical synthetic transformations.

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Department of Chemistry
Emory University
Atlanta, Georgia 30322

R. Carlisle Chambers
Craig L. Hill*

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Kinetics of the Homolytic Dioxygen Insertion into the Cobalt-Carbon Bond in $(nta)(H_2O)Co^{III}\text{–}CH_3^-$

The dioxygen insertion reaction into metal–carbon σ bonds is relevant to several biological processes.[1] The reaction of several complexes with macrocyclic ligands and a metal–alkyl σ bond with oxygen is known to yield the corresponding organoperoxo derivatives. Experimental results mainly for complexes with a cobalt–alkyl bond[2] (some work was reported also on tin[3] and germanium[3] complexes) leave little doubt that dioxygen insertion, thermally or photochemically, proceeds via a homolytic mechanism. However, to date no complete kinetic analysis of these reactions was carried out.

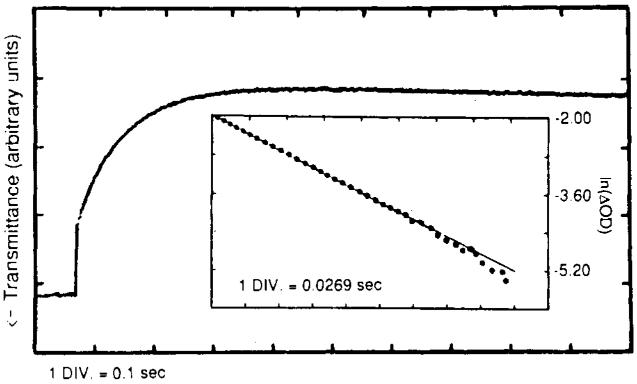

Figure 1. Increase of the absorption (at 310 nm) due to formation of $(nta)(H_2O)Co^{III}\text{–}O_2CH_3^{2+}$ in the presence of oxygen and a first-order plot (insert). $[Co^{II}(nta)(H_2O)_2^-] = 4 \times 10^{-3}$ mol dm^{-3}, $[nta]_{total} = 6 \times 10^{-3}$ mol dm^{-3}, $[(CH_3)_2SO] = 0.1$ mol dm^{-3}, $[O_2] = 5 \times 10^{-5}$ mol dm^{-3}, and pH = 6.5.

Recently it was shown that the reaction of $^\bullet CH_3$ free radicals with $Co^{II}(nta)(H_2O)_2^-$ proceeds via the reaction sequence[4]

$$Co^{II}(nta)(H_2O)_2^- + {}^\bullet CH_3 \overset{K_1}{\rightleftharpoons} (nta)(H_2O)Co^{III}\text{–}CH_3^- + H_2O \tag{1}$$

$$^\bullet CH_3 + (nta)(H_2O)Co^{III}\text{–}CH_3^- \xrightarrow{k_2} Co^{II}(nta)(H_2O)_2^- + C_2H_6 \tag{2}$$

(where nta = $N(CH_2CO_2^-)_3$). From the results $k_1 = 1.6 \times 10^8$ dm^3 mol^{-1} s^{-1} and $2k_2/K_1 = 28$ s^{-1} were derived.[4] These results suggest that methyl free radicals, $^\bullet CH_3$, formed in a solution containing a mixture of $Co^{II}(nta)(H_2O)_2^-$ and O_2, will react mainly with $Co^{II}(nta)(H_2O)_2^-$ if $[Co^{II}(nta)(H_2O)_2^-]/[O_2] > 50$ is maintained, as

$$\begin{gathered} O_2 + {}^\bullet CH_3 \xrightarrow{k_3} {}^\bullet O_2CH_3 \\ k_3 = 4.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1\,5} \end{gathered} \tag{3}$$

Under these experimental conditions $(nta)(H_2O)Co^{III}\text{–}CH_3^-$ is expected to decompose via reactions −1, 3, and 4.

$$^\bullet O_2CH_3 + Co^{II}(nta)(H_2O)_2^- \rightarrow (nta)(H_2O)Co^{III}\text{–}O_2CH_3^- \tag{4}$$

The kinetics of formation of $(nta)(H_2O)Co^{III}\text{–}O_2CH_3^-$ under these conditions are expected to obey the following rate law:

$$-\frac{d[(nta)(H_2O)Co^{III}\text{–}CH_3^-]}{dt} = \frac{k_3k_{-1}[O_2][(nta)(H_2O)Co^{III}\text{–}CH_3^-]}{k_1[Co^{II}(nta)(H_2O)_2^-] + k_3[O_2]} \tag{5}$$

i.e.

$$\frac{1}{k_{obs}} = \frac{K_1[Co^{II}(nta)(H_2O)_2^-]}{k_3[O_2]} + \frac{1}{k_{-1}} \tag{6}$$

Aqueous solutions containing 5×10^{-4}–4×10^{-3} mol dm^{-3} $CoSO_4$, 6×10^{-3} mol dm^{-3} nta, 1×10^{-5}–1×10^{-4} mol dm^{-3} O_2, 0.1 mol dm^{-3} $(CH_3)_2SO$, and $(1.1\text{–}2.0) \times 10^{-2}$ mol dm^{-3} N_2O at pH 6–7 were irradiated by a short, 0.1–1.0-μs, electron pulse (5 MeV, 200 mA) from the linear electron accelerator of the Hebrew University of Jerusalem. The experimental setup was described earlier in detail.[6] Under these conditions, all the primary free radicals are transformed into methyl free radicals which react with $Co^{II}(nta)(H_2O)_2^-$ to form $(nta)(H_2O)Co^{III}\text{–}CH_3^-$ via reaction 1.

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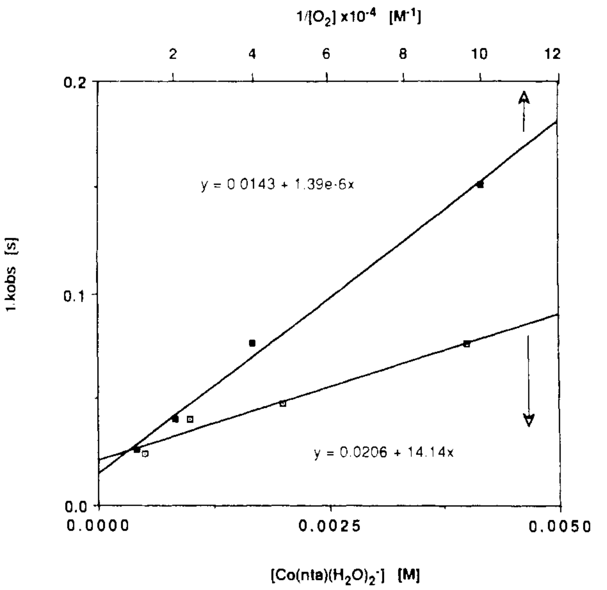


Figure 2. Dependence of $1/k_{obs}$ for the oxygen insertion reaction on $[Co^{II}(nta)(H_2O)_2^-]$ at constant $[O_2] = 5 \times 10^{-5}$ mol dm^{-3} and on $1/[O_2]$ at constant $[Co^{II}(nta)(H_2O)_2^-] = 1 \times 10^{-3}$ mol dm^{-3}. All solutions contained 0.1 mol dm^{-3} $(CH_3)_2SO$ at pH = 6.2–6.5. Wavelength of observation: 310 nm.

Some $(nta)(H_2O)Co^{III}–O_2CH_3^-$ is formed in parallel via reactions 3 and 4. The formation of $(nta)(H_2O)Co^{III}–CH_3^-$ is followed by a process obeying a first-order rate law (Figure 1). The observed rate of reaction increases when the concentration of O_2 is increased or the concentration of $Co^{II}(nta)(H_2O)_2^-$ is decreased. Plots of $1/k_{obs}$ vs $1/[O_2]$ or vs $[Co^{II}(nta)(H_2O)_2^-]$ yield straight lines (Figure 2) as expected. From the intercepts, $k_{-1} = 60 \pm 10$ s^{-1} is calculated. With the reported value for $k_1 = 1.6 \times 10^8$ dm^3 mol^{-1} s^{-1},[4] $K_1 = (2.7 \pm 0.5) \times 10^6$ dm^3 mol^{-1} is calculated. The latter value is smaller by about a factor of 25 than that previously estimated.[4] From the slopes of the lines in Figure 2, $2K_1/k_3 = (1.0 \pm 0.4) \times 10^{-3}$ s^{-1} is calculated, and hence, $k_3 = (3 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1}. The fact that identical values, within the limits of experimental accuracy, for both k_{-1} and k_3 are obtained from both plots supports the suggested mechanism. Furthermore the derived rate constant for the reaction of oxygen with $^\bullet CH_3$ radicals, k_3, is in very good agreement with an analogously derived value from the investigation of the nickel–cyclam system[7] and a literature value,[5] thus giving additional proof for the suggested mechanism. Having determined K_1, one also can calculate the rate constant of reaction 2. An earlier study yielded the ratio $2k_2/K_1 = 28$ s^{-1} [4] and hence $2k_2 = (7.5 \pm 2.0) \times 10^7$ dm^3 mol^{-1} s^{-1}.

The spectrum of the product of this process (Figure 3) ($\lambda_{max} = 325$ nm; $\epsilon_{max} = 7200$ mol^{-1} dm^3 cm^{-1}) differs considerably from that of $(nta)(H_2O)Co^{III}–CH_3^-$ ($\lambda_{max} = 245$ nm; $\epsilon_{max} = 14000$ mol^{-1} dm^3 cm^{-1})[4] and of $(nta)Co^{III}(H_2O)_2$ ($\lambda_{max} \leq 230$ nm; $\epsilon_{max} \geq 12000$ mol^{-1} dm^3 cm^{-1})[4] and resembles that of $(nta)(H_2O)Co^{III}$-$O_2CH_2C(CH_3)_2OH^-$ ($\lambda_{max} = 330$ nm; $\epsilon_{max} = 4200$ mol^{-1} dm^3 cm^{-1}).[8]

Furthermore, the reaction of the methylperoxo radical with $Co^{II}(nta)(H_2O)_2^-$ was studied. The concentrations of the reactants were chosen so that the pulse radiolytically generated $^\bullet CH_3$ radicals reacted mainly with dioxygen to form the methylperoxo radical in the first step ($[O_2] = 7 \times 10^{-4}$ mol dm^{-3}, $[Co^{II}(nta)(H_2O)_2^-] = (2–10) \times 10^{-4}$ mol dm^{-3}, $[N_2O] = 1.1 \times 10^{-2}$ mol dm^{-3}, and pH = 6.3). Under the conditions of excess $Co^{II}(nta)(H_2O)_2^-$, a pseudo-first-order formation of $(nta)(H_2O)Co^{III}–O_2CH_3^-$ according to reaction 4 is observed. The Co^{II} dependence yields a second-order rate constant of $k_4 = (1.0 \pm 0.1) \times 10^8$ dm^3 mol^{-1} s^{-1}. This value can be compared to a previously reported rate constant for the reaction of $^\bullet O_2CH_2C(CH_3)_2OH$ with $Co^{II}(nta)(H_2O)_2^-$, $k = 1 \times 10^8$ dm^3 mol^{-1} s^{-1}, at pH = 5.[8]

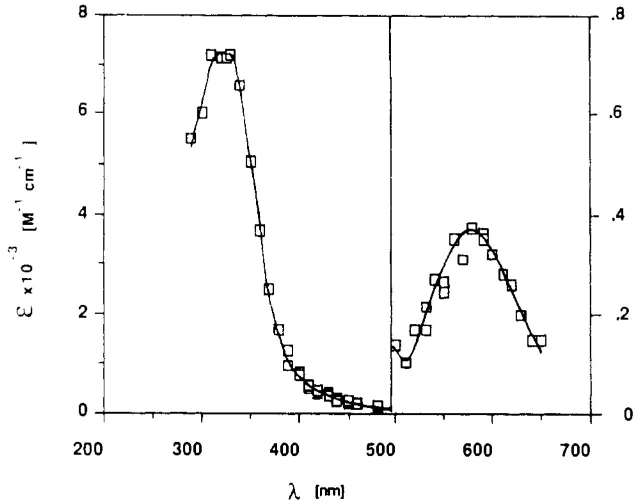
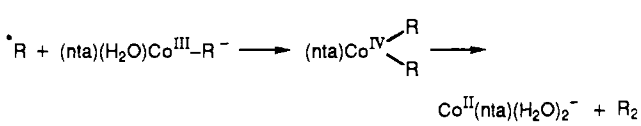


Figure 3. UV/vis spectrum of pulse radiolytically generated $(nta)(H_2O)Co^{III}O_2CH_3^{2+}$ in N_2O-saturated aqueous solutions (pH = 6.7) of $Co^{II}(nta)(H_2O)_2^-$. $[CoSO_4] = 1 \times 10^{-3}$ mol dm^{-3}, $[nta]_{total} = 6 \times 10^{-3}$ mol dm^{-3}, $[O_2] = 7.5 \times 10^{-5}$ mol dm^{-3}, and $[(CH_3)_2SO] = 0.1$ mol dm^{-3}.

Finally it is of interest to note that $2k_2$ for methyl radicals is considerably smaller than that for the corresponding reaction

$$^\bullet R + (nta)(H_2O)Co^{III}\text{–}R^- \xrightarrow{k_{2a}} Co^{II}(nta)(H_2O)_2^- + R_2 \qquad (2a)$$

for R = $^\bullet CH_2OH$ and $^\bullet CH(CH_3)OH$, for which $2k_{2a} = 1.0 \times 10^9$ and 0.6×10^9 dm^3 mol^{-1} s^{-1}, respectively.[4] This result suggests that the detailed mechanism of reaction 2 involves an attack of the free radical on the central cobalt cation, followed by a reductive elimination reaction, i.e.



$$^\bullet R + (nta)(H_2O)Co^{III}\text{–}R^- \longrightarrow (nta)Co^{IV}{<}^{R}_{R} \longrightarrow Co^{II}(nta)(H_2O)_2^- + R_2$$

This conclusion is due to the fact that it is difficult to envisage why $2k_2$ is slower for methyl radicals than for $^\bullet CH_2OH$ and $^\bullet CH(CH_3)OH$ radicals for the alternatively suggested detailed mechanism that involves the attack of the free radical on the carbon atom bound to the central cobalt atom.[4]

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Nuclear Research Centre Negev, R. Bloch Coal Research Center, and Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

Alexandra Sauer*[9]
Haim Cohen[10,11]
Dan Meyerstein*[9,11]

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