

iron complexes with oxo and carboxylate bridges having distinct iron sites. The only other unsymmetric complex is $[\text{N}_5\text{FeOFeCl}_3]^+$, a singly bridged diiron complex with a six-coordinate and a four-coordinate metal center.²³ However, neither of these complexes adequately mimic the asymmetry found in methemerythrin and its anion complexes.

The UV-vis spectrum of **1** (Figure 2) exhibits absorption features with maxima near 330, 400, 490, and 650 nm. These have also been observed for methemerythrin,²⁴ ribonucleotide reductase,²⁵ and the synthetic (μ -oxo)bis(μ -carboxylato)diiron(III) complexes,¹⁰ but their precise nature is not yet understood. That these spectral features are found for oxo-bridged diiron(III) complexes with either one or two bridging carboxylates suggests that they are associated with the presence of the bent oxo bridge and that the carboxylates do not directly contribute to the spectral features.

The number of carboxylate bridges does not appear to affect the magnetic properties of these oxo- and carboxylato-bridged complexes (Table I). SQUID magnetic susceptibility data on **1** from 4 to 200 K are shown in Figure 3 and can be fit with the standard Boltzmann distribution equation for an antiferromagnetically coupled diferric complex.²⁶ With g fixed at a value of 2.0, the fit yielded $2J = -234 \text{ cm}^{-1}$ ($\mathcal{H} = -2JS_1 \cdot S_2$), TIP = $2.2 \times 10^{-5} \text{ emu/mol}$, and 0.04% high-spin ferric impurity ($F = 4.00$).²⁷ An improved fit can be obtained with the following parameters: $g = 2.04$, $2J = -238 \text{ cm}^{-1}$, TIP = 0, and 0.06% high-spin ferric impurity ($F = 2.89$, Figure 3). The J value for **1** compares favorably with those found for other (μ -oxo)bis(μ -carboxylato)diiron(III) complexes,^{10,11,12,28} and this similarity emphasizes the fact that the strength of the antiferromagnetic coupling interaction is determined almost solely by the oxo bridge.

A third property that characterizes the presence of the oxo bridge is the large quadrupole splitting observed in the Mössbauer spectrum of the complex. **1** and **2** exhibit quadrupole doublets with ΔE_Q values of ca. 1.5 mm/s, comparable to those observed for other synthetic complexes (Table I). The doublets are somewhat broadened ($\Gamma = 0.32 \text{ mm/s}$), probably reflecting the differences in the iron sites. It is clear, however, that these structural differences do not translate into large differences in the quadrupole splittings. The challenge thus remains for synthetic inorganic chemists to design molecules that mimic the large differences in ΔE_Q values as found in ribonucleotide reductase⁷ and the purple acid phosphatases.^{29,30}

In summary, we have synthesized a new family of (μ -oxo)(μ -carboxylato)diiron(III) complexes using tetradentate tripodal ligands such as TPA and HDP,²⁰ which have structural, spectroscopic, and magnetic properties comparable to those of the (μ -oxo)bis(μ -carboxylato)diiron complexes. The similarities emphasize the point that both (μ -oxo)diiron(III) units with one or two carboxylate bridges are suitable candidates for the active sites of enzymes such as ribonucleotide reductase and purple acid phosphatase, which as yet have not been crystallographically characterized.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

(31) (a) Visiting scientist from Nankai University, Tianjin, People's Republic of China. (b) Gray Freshwater Biological Institute, University of Minnesota.

Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Shiping Yan^{31a}
David D. Cox
Linda L. Pearce
Carlos Juarez-Garcia^{31b}
Lawrence Que, Jr.*

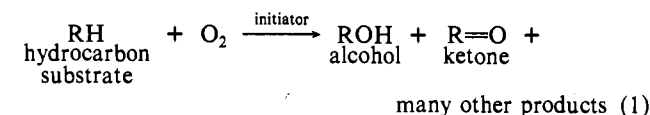
Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70122

Jian H. Zhang
Charles J. O'Connor

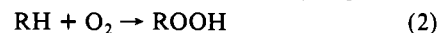
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Excited States of Polyoxometalates as Oxidatively Resistant Initiators of Hydrocarbon Autoxidation. Selective Production of Hydroperoxides

Some of the largest scale industrial processes such as autoxidation of the hydrocarbons, cyclohexane, and *p*-xylene (eq 1) as well as a myriad of small scale halogenation and other reactions carried out in industrial and academic laboratories are radical-chain processes.^{1,2} For alkanes, these processes are generally not



very selective and nearly all depend on initiators to start and sustain reaction. Alkane autoxidation reactions are as messy as they are important. The autoxidation of cyclohexane in conjunction with the Du Pont nylon process produces over 120 products!² Both the thermal and photochemical conditions used for autoxidation initiation generally do not permit selective production of the useful hydroperoxides, ROOH, the usual initial nonradical kinetic products in alkane reactions (eq 2). Indeed, the hydroperoxides



themselves readily initiate chains under typical thermal and photochemical free-radical reaction conditions.¹ In massive and miniscule scale reactions alike, the initiators in the above reactions are consumed. In context with our goal of developing thermodynamically stable yet experimentally tractable catalysts for the selective functionalization of alkanes and other kinetically difficult transformations,³ we report here a polyoxometalate-based system that efficiently initiates hydrocarbon autoxidation with unusually

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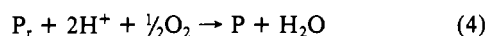
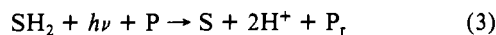
Table I. Photoinitiated Autoxidation of Isobutane with Near-UV and Visible Light^a

| reacn no. | initiator | initiator concn, mM | irradiation time, h | product yields ^b | |
|-----------|---|---------------------|---------------------|-----------------------------|-------------------|
| | | | | ROOH = TBHP ^c | ROOR ^c |
| 1 | AIBN | 0.36 | 0.5 | 0 | 0 |
| 2 | (PhCOO) ₂ | 0.36 | 0.5 | 0 | 0 |
| 3 | (t-BuO) ₂ | 0.38 | 0.5 | 0 | 0 |
| 4 | H ₃ PW ₁₂ O ₄₀ | 0.36 | 0.5 | 0 | 0 |
| 5 | Q ₄ W ₁₀ O ₃₂ | 0.37 | 0.5 | 100 (12) [4.50] | 0 |
| 6 | Q ₄ W ₁₀ O ₃₂ | 0.37 | 1.0 | 97 (32) [1.15] | 3 (1) [0.38] |
| 7 | Q ₄ W ₁₀ O ₃₂ | 0.37 | 0.33 ^d | 100 (10) [3.78] | 0 |
| 8 | Q ₄ W ₁₀ O ₃₂ | 0.37 | 0.20 ^e | 100 (4) [1.44] | 0 |
| 9 | Q ₄ W ₁₀ O ₃₂ | 0.37 | 0.0 | 0 | 0 |
| 10 | Q ₄ W ₁₀ O ₃₂ | 0.29 | 0.5 | 100 (18) [5.15] | 0 |
| 11 | Q ₄ W ₁₀ O ₃₂ | 0.22 | 0.5 | 100 (22) [4.76] | 0 |
| 12 | Q ₄ W ₁₀ O ₃₂ | 0.15 | 0.5 | 100 (31) [4.58] | 0 |
| 13 | Q ₄ W ₁₀ O ₃₂ | 0.073 | 0.5 | 100 (39) [2.83] | 0 |
| 14 | Q ₄ W ₁₀ O ₃₂ | 0.037 | 0.5 | 100 (64) [2.35] | 0 |
| 15 | Q ₄ W ₁₀ O ₃₂ | 0.029 | 0.5 | 100 (78) [2.28] | 0 |
| 16 | Q ₄ W ₁₀ O ₃₂ | 0.022 | 0.5 | 100 (51) [1.11] | 0 |

^aAll reactions run under an atmosphere of zero grade air (21% O₂) with initiator and 7.0 × 10⁻³ mol substrate dissolved in 10.0 mL CH₃CN. Samples were magnetically stirred and thermostated at 21 °C during irradiation by 1000-W Xe arc lamp equipped with infrared and UV (λ > 280 nm) cutoff filters. ^bReactions analyzed by withdrawing aliquots from the reaction vessel for gas chromatography; products were quantified by coinjection of authentic samples with an internal standard (bromobenzene). ^cPercent of total moles of organic products detected (mol product/mol initiator) [mmol product × 10²]. ^dA 5-min irradiation followed by 10 min of dark; sequence repeated for 1.0 h. ^eA 1-min irradiation followed by 4 min of dark; sequence repeated for 1.0 h.

low-energy light and at room temperature, which, in turn, permits the selective production of hydroperoxide at tertiary C-H bonds even at high conversions of substrate. Furthermore, the initiator is not consumed in the process of initiation.

The photooxidation of organic compounds by polyoxometalates, P (eq 3), and the subsequent oxidation of the photoreduced forms, P_r (eq 4), have been described by several investigators.⁴ Although



SH₂ = organic substrate = alcohols, ethers, amides, others

it appeared more than reasonable to us that radical-chain autoxidation of the substrates initiated by intermediate organic radicals and oxygen-derived radicals could be important in these aerobic oxidations, this possibility heretofore had not been mentioned. There is now good experimental evidence that polyoxometalate-catalyzed functionalization of hydrocarbons under anaerobic conditions generates radicals at some point in the reaction,³ and it is reasonable that these radicals, or those generated as intermediates in eq 4, could initiate radical-chain autoxidation for at least this class of substrates. In this work, we have examined the product distributions resulting from irradiation of acetonitrile solutions of polyoxometalates and representative hydrocarbons. The product distributions generated from isobutane (*tert*-butyl hydroperoxide = TBHP), cyclohexane (alcohol and ketone), cyclohexene (allylic alcohol, allylic ketone, and some epoxide), and ethylbenzene (acetophenone) are typically those seen upon autoxidation of these substrates, suggesting that autoxidation is likely an important component of these complex redox processes and that the predominant substrate oxidation step likely involves hydrogen abstraction by the usual alkyl peroxy chain carrying radical intermediates rather than reaction with the polyoxometalate excited states involved in eq 3.

Table I compares the product distributions derived from autoxidation of the alkane, isobutane, initiated photochemically with conventional organic as well as polyoxometalate compounds. The

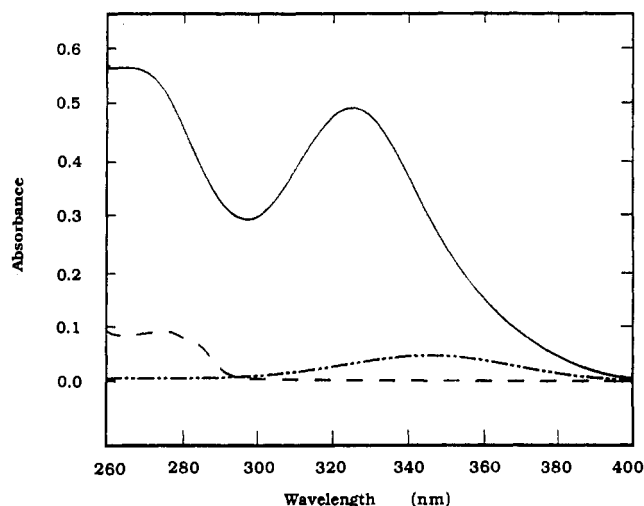


Figure 1. Electronic absorption spectra (λ = 260–400 nm) of autoxidation initiators in CH₃CN: [(C₄H₉)₄N]₄W₁₀O₃₂ (3.65 × 10⁻⁵ M), —; benzoyl peroxide (3.65 × 10⁻⁵ M), - - -; AIBN (3.60 × 10⁻³ M), - · - ·. All spectra were obtained by using 1.0-cm path length quartz cells.

light source used purposely in these experiments is not that often used for such applications (e.g. Hg lamp/quartz reaction vessel, λ > 190 nm) but rather near-UV and visible light from a 1000-W Xe lamp filtered through the Pyrex glass of a typical reaction vessel (λ > 270 nm with maximum irradiance > 310 nm). For all initiators there is no detectable reaction in the absence of light. Only Q₄W₁₀O₃₂ (Q = tetra-*n*-butylammonium cation) is an effective initiator with this low-energy light. The electronic absorption spectra in Figure 1 largely explain the relative efficiencies of the different photochemical initiators in Table I. The diacyl and dialkyl peroxide functions do not absorb appreciably at λ > 300 nm and show no activity. Both α,α'-azobis(isobutyronitrile) (AIBN) and α-H₃PW₁₂O₄₀, a Keggin heteropolyanion (T_d symmetry), absorb weakly in the λ > 300-nm region. Note that the spectrum of AIBN in Figure 1 is for a solution 100 times more concentrated than that for the spectrum of Q₄W₁₀O₃₂. Typical solvent-dependent values for λ_{max} (ε) of the n-π* transition of the azo function are 346 nm (~15 M⁻¹ cm⁻¹). In contrast, the solvent-dependent values for λ_{max} (ε) for W₁₀O₃₂⁴⁻ in organic solvents are 325 ± 3 nm (~1.3 × 10³ M⁻¹ cm⁻¹). Although AIBN and α-H₃PW₁₂O₄₀ show no ability to initiate autoxidation under the conditions in Table I, they do facilitate production of low yields of TBHP when higher concentrations of initiator and/or longer

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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 quantitative 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 $(nta)(H_2O)Co^{III}-CH_3^-$

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 bond² (some work was reported also on tin³ and germanium³ 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.

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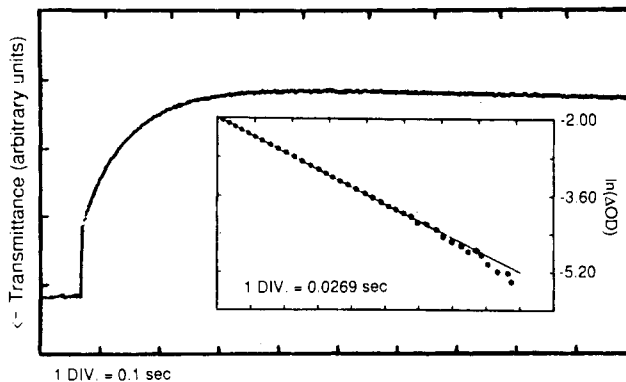
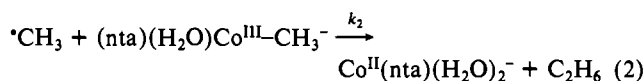
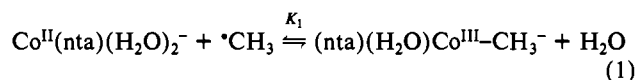
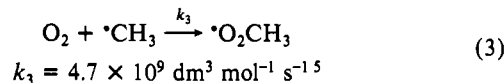


Figure 1. Increase of the absorption (at 310 nm) due to formation of $(nta)(H_2O)Co^{III}-O_2CH_3^{2+}$ in the presence of oxygen and a first-order plot (insert). $[Co^{II}(nta)(H_2O)_2^-] = 4 \times 10^{-3}$ mol dm^{-3} , $[nta]_{total} = 6 \times 10^{-3}$ mol dm^{-3} , $[(CH_3)_2SO] = 0.1$ mol dm^{-3}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

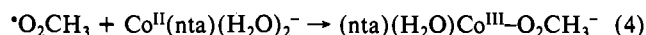
Recently it was shown that the reaction of $\cdot CH_3$ free radicals with $Co^{II}(nta)(H_2O)_2^-$ proceeds via the reaction sequence⁴



(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, $\cdot CH_3$, 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



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



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

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

i.e.

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

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 $(1.1$ – $2.0) \times 10^{-2}$ 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 $(nta)(H_2O)Co^{III}-CH_3^-$ via reaction 1.

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