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Polyoxometalate Systems for the Catalytic Selective Production of Nonthermodynamic Alkenes from Alkanes. Nature of Excited-State Deactivation Processes and Control of Subsequent Thermal Processes in Polyoxometalate Photoredox Chemistry

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Abstract: The photooxidations of exemplary branched acyclic alkanes and cycloalkanes by a range of polyoxotungstates varying in charge density, ground-state redox potential, acidity, and other properties were examined in detail. The organic products generated in these reactions depend on the polyoxometalate used, and in particular on the ground-state redox potential of the complex. Under anaerobic conditions acyclic branched alkanes yield principally alkenes, while cycloalkanes yield principally alkenes and dimers. Alkyl methyl ketones, derived in part from reaction with acetonitrile solvent, and isomerized alkanes are produced with some alkane substrates. Under aerobic conditions, autoxidation, initiated by radicals generated in the photoinduced redox chemistry, is observed. Under anaerobic conditions the polyoxotungstates with formal redox potentials more negative than −1.0 V vs $Ag/AgNO_3(CH_3CN)$, such as $W_{10}O_{32}^{4-}$ and $W_6O_{19}^{2-}$, photochemically dehydrogenate branched acyclic alkanes in high selectivity to α-olefins and the least substituted alkenes, products heretofore undocumented in photooxidation reactions catalyzed by polyoxometalates. In contrast, the polyoxotungstates, regardless of structural family, with ground-state formal redox potentials less negative than −1.0 V vs $Ag/AgNO_3(CH_3CN)$, such as $\alpha\text{-}PW_{12}O_{40}^{3-}$ and $\alpha\text{-}P_2W_{18}O_{62}^{6-}$, photodehydrogenate these alkanes in high selectivity to the thermodynamic or most substituted alkenes. The ratio of the most substituted alkenes to other alkenes is higher in the latter reactions than the ratio seen under conditions of acid equilibration. Several lines of evidence confirm the importance of alkyl radicals as intermediates and/or implicate hydrogen abstraction as the dominant mode of attack of the excited state of $W_{10}O_{32}^{4-}$ on the alkane substrate: the ratio of alkenes to dimers at early reaction times, the relative rates of polymerization of the various alkenes generated in the reaction (a heretofore undocumented reaction of polyoxometalate excited states), the suppression of all alkene and other organic products generated under anaerobic conditions in favor of the most substituted (tertiary) hydroperoxide upon addition of O_2 to the reaction, the primary kinetic isotope effect, $k_{\text{cyclohexane-}h_{12}}/k_{\text{cyclohexane-}d_{12}}$, of 2.5 for oxidation by the excited state of $W_{10}O_{32}^{4-}$, the relative reactivities of different alkanes, the relative reactivities of tertiary vs primary C–H bonds, the regiochemistry of the alkyl fragments in the dimeric byproducts, and other data. The rate law established for photooxidation of alkanes by $W_{10}O_{32}^{4-}$ (approximately first order in alkane, first order in light intensity, and variable order in $W_{10}O_{32}^{4-}$) coupled with the constancy of the ratios of olefinic to dimeric products over a wide range of both light intensity and $W_{10}O_{32}^{4-}$ concentration and other data establish that the major factor determining the regiochemistry in production of the nonthermodynamic alkenes is bimolecular radical disproportionation while the major factor in determining the regiochemistry in production of the thermodynamic or more substituted alkenes is deprotonation of carbonium ions generated by oxidation of the intermediate radicals by ground-state polyoxotungstates.

Introduction

Stable and selective catalysts for the functionalization of alkanes are rare.[1-14] The chemoselectivities and regioselectivities exhibited under catalytic conditions by the heavily investigated biological systems cytochrome P-450[15] and methane monooxygenase[16] have

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yet to be realized by totally abiological systems. The organometallic systems first developed in the early 1980s provided nonradical and nonclassical regioselectivities for substrate attack (CH_4 and primary C–H most reactive > secondary C–H > tertiary C–H) but to date efforts to render such systems both catalytic and highly stable have met with minimal success.[2,3] Research on several fronts has recently addressed the issue of finding homogeneous catalysts with adequate stability to permit the sustained functionalization of *saturated* hydrocarbons.[1,2g,3,8,9,12-14] Three recent methods for the functionalization or oxidation of alkanes that involve catalysts that are completely inorganic yet homogeneous are thermal oxo transfer oxidation by transition-metal-substituted polyoxometalates ("inorganic metalloporphyrins"),[9] photochemical coupling by Hg vapor (homogeneous gas phase),[12] and photochemical dehydrogenation and/or functionalization by heteropolytungstates, for example, eq 1 (alkane substrate, RH; catalyst, α-$H_3PW_{12}O_{40}$).[13] The products generated in the latter three systems exhibit classical radical substrate attack selectivities: tertiary C–H most reactive.

net reaction:

$$\underset{\text{alkane}}{\mathrm{RH}} + h\nu \xrightarrow[\substack{\mathrm{CH_3CN,\ Ar,\ 25\ °C} \\ \lambda > 280\ \mathrm{nm}}]{\alpha\text{-}\mathrm{PW_{12}O_{40}}^{3-}} \underset{\text{alkene}}{\mathrm{R[-H]}} + \mathrm{H_2} + \text{other organic oxidation products (dependent on conditions)} \qquad (1)$$

Although reactions 2–4 or analogous reactions with other substrates in place of alkane, RH, are generally accepted to sum to the net process, e.g., eq 1, the detailed features of these component reactions have only been experimentally addressed in a few systems; they are not generally understood to a high level of molecular resolution. We report here the further experimental resolution of key features of the general processes, eqs 2–4. We show the relative rates of the photoredox phenomenon (the initial phase of eq 3) and subsequent thermal processes including the rate of oxidation of intermediate organic radicals can be used to produce the less substituted or nonthermodynamic alkenes from branched alkanes directly in high selectivity and catalytically with some systems. The mechanism for production of these α-olefins and less-substituted alkenes is distinct from the mechanisms operable in alkane photodehydrogenation by the organorhodium[3] and organoiridium[11] systems recently reported.

general processes in mechanism summing to eq 1:[17]

$$\alpha\text{-PW}_{12}\text{O}_{40}^{3-} + h\nu \rightarrow \alpha\text{-PW}_{12}\text{O}_{40}^{3-*} \qquad (2)$$

$$\alpha\text{-PW}_{12}\text{O}_{40}^{3-*} + \text{RH} + \alpha\text{-PW}_{12}\text{O}_{40}^{3-} \rightarrow 2\alpha\text{-PW}_{12}\text{O}_{40}^{4-} + \text{R[-H]} + 2\text{H}^+ \qquad (3)$$

$$2\alpha\text{-PW}_{12}\text{O}_{40}^{4-} + 2\text{H}^+ \rightarrow 2\alpha\text{-PW}_{12}\text{O}_{40}^{3-} + \text{H}_2 \qquad (4)$$

Experimental Section

Materials. The polyoxometalates, $Q_4W_{10}O_{32}$ (1),[18] α-$Q_3PW_{12}O_{40}$ (2),[19] α-$H_3PW_{12}O_{40}$,[20] $Q_2W_6O_{19}$,[21] and α-$(NH_4)_6P_2W_{18}O_{62}$,[22] where Q in all cases equals tetra-*n*-butylammonium ion, were prepared by literature methods. A preparation for $Na_4W_{10}O_{32}$ is given below. The purity of all complexes was checked by infrared, UV-visible, ^{183}W and, where applicable, ^{31}P NMR. The acetonitrile solvent (Burdick and Jackson glass-distilled grade) was used as received and stored under extra-dry nitrogen. Burdick and Jackson H_2O was also used. The alkanes were reagent grade from Wiley, Fluka, Aldrich, and Air Products & Chem. Inc. and had purities of >99.9% by gas chromatography (GC). Some alkanes were passed through a column of neutral-activity grade I alumina. *All* the products shown in Table I with the exception of 2,3-dimethyl-2-hydroperoxybutane and dicyclooctyl were commercially available in high purity (>97%).

Synthesis of $Na_4W_{10}O_{32}\cdot xH_2O\cdot yCH_3CN$. A procedure modified from one described by Chauveau[23] for the synthesis of $K_4W_{10}O_{32}\cdot 4H_2O$ was employed. Solutions of 100 g of $Na_2WO_4\cdot 2H_2O$ in 600 mL of water and 600 mL of 1.0 M HCl both at reflux were mixed in a 2-L beaker. After the resulting green solution had refluxed for 20 s, excess solid NaCl (300 g) was added. The mixture was allowed to boil for an additional 20 s, then rapidly cooled, and maintained in a freezer (−10 °C) overnight. The next day the liquid was decanted off the mixture of NaCl and crude $Na_4W_{10}O_{32}$. CH_3CN (300 mL) was added. The mixture was heated and allowed to reflux for ca. 5 min selectively dissolving the more soluble decatungstate and leaving the insoluble NaCl as a white mass. The CH_3CN solution of $Na_4W_{10}O_{32}$ was then filtered at ambient temperature to produce a clear green supernatant. This solution was gently heated in a 500-mL recrystallization dish until the first yellow-green crystals began to form. After three such recrystallizations, approximately 20 g of crystalline $Na_4W_{10}O_{32}$ was collected and allowed to air dry for 15 min. $Na_4W_{10}O_{32}$: ^{183}W NMR (CH_3CN, δ in ppm relative to 2.0 M Na_2WO_4 in H_2O) δ −21.2 (s, equatorial, 8 W), −166.5 (s, cap, 2 W), [Compare to $Q_4W_{10}O_{32}$ in CH_3CN: −16.7 (s, equatorial, 8 W), −160.2 (s, cap, 2 W)][24]; IR (cm^{-1}) 1010 (w), 978 (s), 930 (s), 800 (vs), 600 (m), 430 (s), 355 (m). Anal. Calcd for $Na_4W_{10}O_{32}\cdot 24H_2O$: Na, 3.20; W, 63.97. Found: Na, 3.36; W, 63.95.

The electronic absorption spectrum in CH_3CN of $Na_4W_{10}O_{32}$ for λ > 240 nm was identical in shape with that of $Q_4W_{10}O_{32}$ for both the oxidized and photochemically reduced species. UV–visible spectroscopic measurements (λ > 240 nm) made throughout the entire sample preparation and purification procedure indicated that no polyoxotungstate impurities, which absorbed light in this region, were ever present in appreciable quantities (≤3 mol %) after the initial reaction of sodium tungstate with HCl.

Methods. All the reactions in Table I, except where indicated, were irradiated by using a Xe arc lamp assembly described previously,[13] with a Pyrex cutoff filter (λ > 280 nm) under an argon atmosphere in acetonitrile solvent at 25 °C; the concentration of polyoxometalate and alkane were ~3 mM and ~0.5 M, respectively, throughout. Reactions 17 and 18 unlike the others were run at 0 and 30 °C, respectively. The procedures for monitoring the alkane oxidation and polyoxometalate reduction products as well as the quantum yield measurements were described previously.[13] The most effective GC conditions for the rapid quantitation of products for the reactions of the branched acyclic alkanes involved the use of a 5% phenyl methyl silicone fused-silica capillary column, nitrogen as the carrier gas, and temperature programming. The alkane products were unambiguously identified through the use of GC, gas chromatography–mass spectrometry (GC–MS), and NMR. For the latter, CD_3CN was used as the solvent instead of CH_3CN. Care was taken to ensure that the alkenes were not thermally isomerized, alcohols not dehydrated, nor other side reactions effectuated in the hot (200 °C) GC injector port. Additional confirmation of the alkene products was done through titrations of the photolyte solutions using dilute CCl_4 or CH_3CN solutions of bromine. Addition of bromine resulted in the rapid and complete disappearance of all the alkene product peaks in both the GC traces and the ^{1}H NMR spectra. Addition of strong acid and heat ($T \geq 40$ °C) resulted in the rapid isomerization of alkenes to a distribution of alkenes identical with the one established when acid was added to authentic alkene samples. Small quantities of alcohol (<5%), derived from the hydration of alkenes with the trace quantities of water present,

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also formed under these conditions. In reaction 3, Table I, the major product was determined to be 2,3-dimethyl-2-hydroperoxybutane by spectroscopic and chemical methods: ^{1}H NMR (300 MHz, CD_3CN) δ 1.85–2.00 (m, 1 H), 1.087 (s, 6 H), 0.871 (d, 6 H), and production of the tertiary alcohol, 2,3-dimethyl-2-butanol, upon reduction by stoichiometric quantities of triphenylphosphine. Triphenylphosphine and the sole observed oxidation product, triphenylphosphine oxide, were quantified by GC and ^{1}H NMR. The ^{1}H NMR spectrum of the tertiary alcohol is similar to that of the hydroperoxide, with corresponding peaks shifted slightly: ^{1}H NMR (300 MHz, CD_3CN) δ 1.5–1.7 (heptet, 1 H), 1.072 (s, 6 H), 0.874 (d, 6 H).

Control reactions involving the irradiation of $Na_4W_{10}O_{32}$ (1.8 mM) and tetrasubstituted *alkene* substrate, 2,3-dimethyl-2-butene (3 mM) in CD_3CN, monitored by ^{1}H NMR indicated the production of several peaks from 1–1.8 ppm, which may be attributed to a polymer: ^{1}H NMR (300 MHz, CD_3CN) δ 1.77 (br s, rel intensity 3 H), 1.54 (s, rel intensity 1 H), 1.09 (s, rel intensity 5 H), 1.03 (br s, rel intensity 5 H). The lack of the alkane peaks (present in the regular reactions) facilitated observation of the broad resonances due to polymer. The alkenes generated in the alkane photodehydrogenation reactions are consumed to some extent under the reaction conditions (see Results).

Kinetic Measurements. The apparatus and techniques described elsewhere[13] were followed with some modifications. The most quantitative and experimentally straightforward method to obtain the rate data involved monitoring the distinct chromophores of the reduced forms of the polyoxotungstate catalysts. The principal rate data collected involved one of the systems that could be used to produce nonthermodynamic alkenes from alkanes in high selectivity, the neutral decatungstate salt, **1**, in acetonitrile containing alkane substrate. All the reactions examined herein, except the aerobic reaction, (number 3, Table I) were approximately stoichiometric in polyoxometalate since the rate of reoxidation of the reduced complex by hydrogen evolution was negligible under these conditions [no Pt(0) or other H_2 evolution catalyst present]. The presence of competing or consecutive processes to affect the interpretation of the kinetics data was assessed and found to be minimal at early reaction times. The photooxidation of the cycloalkanes could be carried out to 20% conversion with no evidence for any appreciable side reaction. In contrast, the photooxidation of the branched alkanes by **1** lead to alkenes that in turn began to be consumed by radical polymerization at conversions of alkane as low as 2%. Alkene polymerization was the principal side reaction involving the organic products in the reactions investigated in this study generally (vide infra). The rate data in Figures 2–4 were obtained with a 322-nm interference filter (FWHM = 9.6 nm; percent transmission at maximum, 21%). Optically dense conditions were employed except at low concentrations of polyoxometalate when the concentration was varied (Figure 4). Typical kinetics runs involved irradiation for ca. 20 min. The reactions with **1** and **2** remained homogeneous at all times, but a small quantity of polyoxometalate precipitated in the reactions with $Na_4W_{10}O_{32}$ and α-$(NH_4)_6P_2W_{18}O_{62}$.

Electrochemical Measurements. A single-compartment cell in a three-electrode configuration was used. Cyclic voltammograms were obtained with a PAR Model 173 potentiostat equipped with a Model 176 current follower and monitored by a Model 175 universal programmer. The voltammograms were recorded with a Omnigraphic Series 100 X-Y recorder (Houston Instruments). The reference electrode was Ag/$AgNO_3$ in CH_3CN containing n-$Bu_4N^+PF_6^-$ [(TBA)PF_6], the counter electrode was a platinum wire, and the working electrode was a glassy carbon disk (BAS) with a surface area of 0.07 cm^2. The working electrode was polished with alumina before each experiment. The solutions were thoroughly degassed with argon and all voltammetric measurements recorded under a positive pressure of this gas. All determinations were made at least three times. The potentials were reported relative to Ag/$AgNO_3$(CH_3CN) rather than relative to the ferrocene/ferrocenium couple as per the Gritzner-Kuta IUPAC recommendation,[25] because all measurements involved the use of only CH_3CN in both the cell and the reference electrode reservoir and liquid junction potential differences between samples were minimal. The formal potentials, E^f, were estimated as the average of the anodic and cathodic peak current potentials.

Results

The product distributions resulting from the photochemical oxidation of six branched and cyclic alkanes by the neutral tetra-n-butylammonium salts of decatungstate, $Q_4W_{10}O_{32}$ (**1**), and dodecatungstophosphate, α-$Q_3PW_{12}O_{40}$ (**2**), and other representative neutral and acidic heteropoly and isopoly tungstates are summarized in Table I. All the reactions were run in acetonitrile as it is one of the most inert solvents with respect to the excited states of a range of polyoxometalates. The alkane-derived products vary considerably with the polyoxometalate used.

A number of experiments were conducted in conjunction with the reactions in Table I to clarify various points. First, the reaction conditions in the table (except reaction 3) were chosen so that reoxidation of the photoreduced polyoxometalate, as illustrated in eq 4 for the particular case of reduced dodecatungstophosphate, was minimal in all reactions, allowing the redox balance between the organic oxidation products and the polyoxometalate reduction product(s) to be quantified. This redox balance was quite high (>85% in most cases) for the reactions containing **1** and **2**. With the systems containing **1**, a 1:4 mol ratio of the one- and two-electron-reduced complexes, $W_{10}O_{32}^{5-}$ and $W_{10}O_{32}^{6-}$, respectively, was present at all stages of reaction. With the α-$PW_{12}O_{40}^{3-}$ systems, the one-electron-reduced species, α-$PW_{12}O_{40}^{4-}$, was the major polyoxometalate reduction product. Second, control experiments conducted with all the polyoxotungstate catalysts in Table I indicated that photooxidation of the acetonitrile solvent or the tetra-n-butylammonium (Q) cations (for the complexes with this countercation) were minor side reactions.[26] Photooxidation with $Na_4W_{10}O_{32}$, lacking the potentially oxidizable quaternary ammonium counterions, showed similar behavior in the absence and presence of alkane substrate. The solvent acetonitrile, and not the quaternary ammonium counterions, was mainly responsible for the photoreduction of decatungstate when no alkane substrate was present. The majority of these solvent-derived products under these conditions were not detected. The alkane-containing reactions run in CD_3CN for ^{1}H NMR analysis showed no apparent increase in the intensity of the CD_2HCN resonance (quintet, 1.93 ppm). Third, a thorough investigation of the stabilities of the initial alkene products in the reactions containing **1** and **2** under the reaction conditions (Table I) was conducted to determine whether or not the observed alkene product distributions reflected only the process(es) generating them or additional processes as well. Although at low conversion the alkenes in the reactions containing **2** did not appreciably react further, the alkenes in the reactions containing **1** did.

In the alkane photochemical dehydrogenations catalyzed by **1**, the alkene products are susceptible to three different processes. First, a loss of alkene product accompanied by formation of polymer is observed in the photochemical dehydrogenation of branched alkanes by **1**.[27] An examination of each of the six isomeric 2,3-dimethylpentenes under the conditions for alkane dehydrogenation established that alkene polymerization is likely radical in nature—the relative reactivities of mono-, di-, tri-, and tetrasubstituted alkenes are 1:1.67:10:40. Two lines of evidence indicate, however, that polymerization for even the most reactive tetrasubstituted alkenes is not a major pathway and not one greatly complicating quantitation of the alkenes derived from alkane. First and foremost, the reasonable redox balance of alkene oxidation products vs polyoxometalate reduction products (>85%) observed in reactions 1, 10, and 15 can only be rationalized if the majority of the alkene products initially formed are still unpolymerized at the time the measurement was made. Since the alkene products are not subject to a significant amount of isomerization under these reaction conditions, the ratios of alkenes formed must resemble the initial kinetic product distribution obtained directly from the alkane. Second, the ratios of alkene products obtained as a function of time are reasonably constant for all photo-

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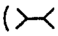
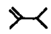
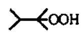
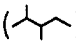
[26] Traces of succinonitrile were detected in the decatungstate reactions conducted in the absence of the reactive alkanes. The principal products derived from the quaternary ammonium cation, n-Bu_4N^+ (Q), for those polyoxotungstates present in this form, were 1-butene + tri-n-butylamine. These products have been noted before (Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 793). They do not represent a net redox reaction inasmuch as both substrate quaternary ammonium cation and the two products together are in the same overall oxidation state. Decomposition of detectable quantities of the Q was only observed in reactions of $Q_4W_{10}O_{32}$. The majority of oxidation equivalents represented by solvent oxidation upon irradiation of **1** based on the quantity of reduced decatungstate was not detectable by gas chromatography.

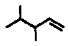
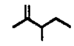
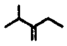
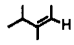
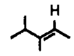
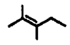
[27] While alkene (<3 mM) was being consumed by polymerization under the reaction conditions, no dimers were being produced. At higher alkene concentrations (~0.5 M) dimers are also observed.

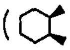
Table I. Organic Product Distributions from Functionalization of Alkanes by Various Polyoxometalate Systems[a]

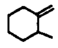
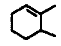
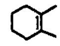
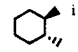
Substrate = 2,3-dimethylbutane ()

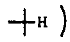
	System[b]	Organic Products,[c] as % of detected products (based on Pred) 		
(1)	1	85(85)	<5(<5)	0(0)
(2)	$Na_4W_{10}O_{32}$	85(85)	<5(<5)	0(0)
(3)	$Na_4W_{10}O_{32}$ / O_2[d]	0^e	0^e	80(f)
(4)	2	0^e	-100(92)	0(0)
(5)	α-$H_3PW_{12}O_{40}$	<5	>95(-90)	0(0)
(6)	$Q_2W_6O_{19}$	85	<5	0
(7)	α-$(NH_4)_6P_2W_{18}O_{62}$	8	80	0
(8)	1 / 2 Mixture[h]	0^e	-100	0
(9)	H^+ equilibrated distribution of alkenes:	<5	>95	

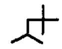
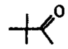
Substrate = 2,3-dimethylpentane ()

	System[b]						
(10)	1	10(10)	61(61)	9(9)	$<2(<2)^g$	5(5)	0^e
(11)	2	0^e	22(20)	0^e	$<2(<2)^g$	17(15)	-59(-53)
(12)	$Q_2W_6O_{19}$	7	66	7	$<2^g$	10	0^e
(13)	1 / 2 Mixture[h]	0^e	31	0^e	$<2^g$	18	41
(14)	H^+ equilibrated distribution of alkenes:	0^e	9	3	7	26	55

Substrate = *cis*-1,2-dimethylcyclohexane ()

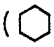
	System[b]				 [i]
(15)	1	19(42)	12(26)	4(11)	55(0)
(16)	2	0^e	12(11)	73(69)	$0^e(0)$
(17)	α-$H_3PW_{12}O_{40}$[j]	0^e	9(8)	91(-87)	$0^e(0)$
(18)	α-$H_3PW_{12}O_{40}$[j]	0^e	23(22)	-77(-73)	$0^e(0)$
(19)	1 / 2 Mixture[h]	<2	13	75	<2
(20)	1 / $Q_2W_6O_{19}$ Mixture[h]	10	7	2	81(0)
(21)	H^+ equilibrated distribution of alkenes:	<5	22	73	

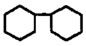
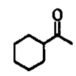
Substrate = isobutane ()

	System[b]				
(22)	1	-90	6	<1	3

Substrate = cyclooctane ()

	System[b]		
(23)	1	57(51)	-43(-39)
(24)	2	77(69)	-23(-21)

Substrate = cyclohexane ()

	System[b]			
(25)	1	25(23)	$32(29)^k$	$37(-)^l$
(26)	2	68(61)	$32(29)^m$	0^e

[a] Acetonitrile solutions of polyoxotungstate (~3 mM) and alkane (~0.5 M). All reactions except the third run under an argon atmosphere. All reactions except 17 and 18 run at 25 °C. Pyrex cutoff filters (λ = 280 nm) were employed. Product distributions were generally independent of the wavelength of irradiation. Other conditions described in the Experimental Section. [b] Q in all cases was the tetra-*n*-butylammonium cation. [c] Percentages calculated from moles of alkane-derived oxidation product detected by GC divided by the total moles of all such products. Yields in parentheses, where given, are based on equivalents of electrons in the reduced polyoxotungstate, P_{red}. GC peaks with high retention times constitute the remaining alkane-derived products. In addition, small quantities of 1-butene and tributylamine were detected in the decatungstate reactions containing this counterion (see text). [d] One atmosphere of O_2 present. [e] Below detectable limit (~1 μM). [f] Reduced decatungstate did not accumulate appreciably due to its rapid reoxidation by O_2. [g] Traces of *cis*-3,4-dimethyl-2-pentene (0.05% of the 2,3-dimethylbutane GC peak area) were initially present in the alkane, increasing the uncertainty in the measurement of its production in the photochemical reactions, especially at low concentrations. This alkene had negligible effects on the photochemistry of the alkane at this concentration. [h] [1] ≈ [2] = 1.8 mM in reactions 8, 13, and 19. [1] ≈ [$Q_2W_6O_{19}$] = 1.8 mM in reaction 20. **1** selectively irradiated with λ > 395 nm light in these "mixed" systems. Control experiments using λ > 395 nm and λ > 280 nm light gave identical organic product distributions for "pure" **1** systems. [i] The formation of this molecule, *trans*-1,2-dimethylcyclohexane, is not accompanied by net polyoxotungstate reduction; hence, the yields based on reduced decatungstate are 0. The concentration of this species increases relative to that of the associated alkene products as the photoreaction progresses. Traces of trans impurity (0.07% of the *cis*-alkane area by GC) were initially present in the cis-alkane substrate but had no effect on the photochemistry. [j] Temperature was 0 °C in reaction 17 and 30 °C in reaction 18. [k] Dimeric product with one double bond accounted for 6% of the detected organic products at the time the measurement was made. This species does not form at early times and apparently is derived from subsequent thermal reactions of the initially generated cyclohexene. It does not arise from the dehydrogenation of dicyclohexyl. [l] Methyl ketone formation is not accompanied by net polyoxometalate reduction. This species does not form at early times and its concentration increases relative to that of the other organic products as the photoreaction progresses. [m] Concentration of dimeric product noted in footnote *k* below detectable limit.

dehydrogenations of the branched alkanes in reactions effected by either **1** or **2** under the reaction conditions. Given the fact that the polymerization rate constants are a function of the nature of the alkene, the constant ratios can be obtained only if this side reaction is minimal.

The two other reactions involving the alkene(s) once they are formed are cis–trans isomerization of these products and production of unsaturated dimers. Additional experiments demonstrated that the cis–trans isomerization of an exemplary alkene, 3,4-dimethyl-2-pentene, can be effected by direct absorption of light and more efficiently via photosensitization with **1**, but that both processes are significantly slower than alkene generation and hence do not appreciably alter the alkene product distributions. No alkene isomerization occurred between species that were not cis–trans isomers of one another. Control experiments indicated that both the polymerization and cis–trans isomerization reactions were effected principally by the excited state of **1** or species derived directly therefrom and not by the ground-state reduced or oxidized complexes. An examination of the product distributions at long reaction times indicated that for some substrates, e.g., cyclohexane, small quantities of unsaturated dimers are produced. Additional experiments indicated that the unsaturated dimers were derived from the initial alkene (e.g., cyclohexene) product and not from dehydrogenation of any saturated dimer generated by radical–radical coupling in situ.

The photooxidations of the branched alkanes (the first four substrates in Table I) under anaerobic conditions yield alkenes and reduced polyoxotungstate with very high selectivity, while the cycloalkanes, cyclohexane and cyclooctane (the last two substrates in Table I), yield principally alkenes, saturated dimers, and the reduced complexes. For these reactions, the ratios of alkene to dimer products are consistent with bimolecular radical coupling (recombination) and disproportionation being the dominant mode of production of these compounds. Disproportionation becomes more favorable relative to coupling as the degree of substitution at the radical center increases. Typical ratios for disproportionation and coupling rate constants, k_d/k_c, are ~0.2, ~1, and ~5 for primary, secondary, and tertiary radicals, respectively.[28] When the photooxidation of 2,3-dimethylbutane by **1** was conducted under an O_2 atmosphere to trap alkyl radical intermediates (reaction 3, Table I), the tertiary hydroperoxide constituted >80% of the organic products detected by both GC and ^1H NMR.[29] The

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(28) Values for k_d/k_c can vary considerably with solvent polarity, viscosity, and other experimental parameters: (a) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441. (b) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.

quantum yields for the production of the tertiary hydroperoxide were similar to those associated with the production of the alkenes in the absence of dioxygen, indicating that the radical chain component was small. Hence, the majority of alcohol product generated is not derived from the usual autoxidation processes—formation and then breakdown of alkyl hydroperoxide. The primary hydroperoxide, if present, constituted less than $^1/_{20}$ of the amount of the tertiary hydroperoxide. The latter is produced at the expense of alkene—no alkenes and only small quantities ($<^1/_{20}$ of the amount of tertiary hydroperoxide) of alcohols were detected under aerobic conditions. The ratio of tertiary to primary alcohols was ~10. Finally, no dimers or other organic oxidation products were detected with reactions of **1** and neopentane, an alkene containing only primary hydrogens.[30]

Three types of highly unusual products are formed from the alkanes: alkyl methyl ketones (reactions 22 and 25, Table I), isomerized alkanes (reactions 15 and 20), and nonthermodynamic alkenes (reactions 1, 2, 6, 10, 12, 15, 20). The alkyl methyl ketones are generated in moderate yields in some of the reactions reported here. Their formation is highly dependent on the concentration of reduced polyoxometalate.[13d] The mechanism of production of the methyl ketones likely involves generation of small quantities of carbanion subsequent to C–H bond cleavage and rapid capture of the carbanion by the nitrile carbon of acetonitrile. The mechanism of this C–C forming reaction has been investigated and reported.[31] The carbanion is derived from the reduction of intermediate alkyl radicals by the reduced **1** species, which are highly reducing. The absence of this product in the reactions containing **2** vs those containing **1** follows from two points. First, the reduced forms of **2** are less reducing than those of **1**; thus, less radical reduction to carbanion will be observed in reactions containing **2** relative to **1**. Second, radical oxidation to carbonium ion is more facile for reactions containing **2**; thus fewer secondary radicals are available for reduction to carbanion in the former reactions.

The major product resulting from the reaction of *cis*-1,2-dimethylcyclohexane with the excited state of **1** (reactions 15 and 20, Table I) is the trans isomer, a product resulting from epimerization at one of the tertiary saturated carbon centers. Although this process can be induced by direct absorption of higher energy light by alkane ($\lambda < 280$ nm), this particular route was completely precluded under the reaction conditions, where **1** absorbed ~100% of the incident light ($\lambda > 360$ nm). The mixed **1**/**2** experiments described below demonstrate that the production of the trans isomer is almost totally suppressed by the addition of **2** and thus that the isomerization is dependent on freely diffusing radicals and not on the nature of the excited state. The high conversion selective production of *trans*-2-decalone from *cis*-2-decalone by irradiated **1** in acetonitrile[32] illustrates that radicals may be involved in reactions other than radical–radical coupling and disproportionation. These may include abstraction of a hydrogen atom from a form of reduced **1** or other processes.

The phenomenon of perhaps the greatest significance in the alkane photooxidation reactions examined, including those in Table I, is the nature of the alkene regioisomers produced upon dehydrogenation of branched alkanes as a function of the polyoxometalate at parity of all other reaction conditions. When the heteropolytungstates **2** and the Wells–Dawson complex α-$(NH_4)_6P_2W_{18}O_{62}$ are used as the photosensitizer–catalyst, the most substituted or thermodynamic alkenes are produced in high selectivity. In contrast, when the isopolytungstates, $W_{10}O_{32}^{4-}$ and $W_6O_{19}^{2-}$, are used, the least substituted or nonthermodynamic alkenes are produced in very high selectivity! The distribution of alkene products obtained upon equilibration of authentic alkene samples with strong acids is given for the first three alkane substrates in Table I (reactions 9, 14, and 21). These equilibrated product distributions are independent of the regioisomerism of the starting alkene and the acid used.[33,34] Importantly, note that the alkene product distributions generated either with **2** or with **1** do not reflect thermodynamic control. While the use of **1** leads to the least substituted alkenes, the use of **2** leads to the most substituted alkenes in selectivities higher than those observed under

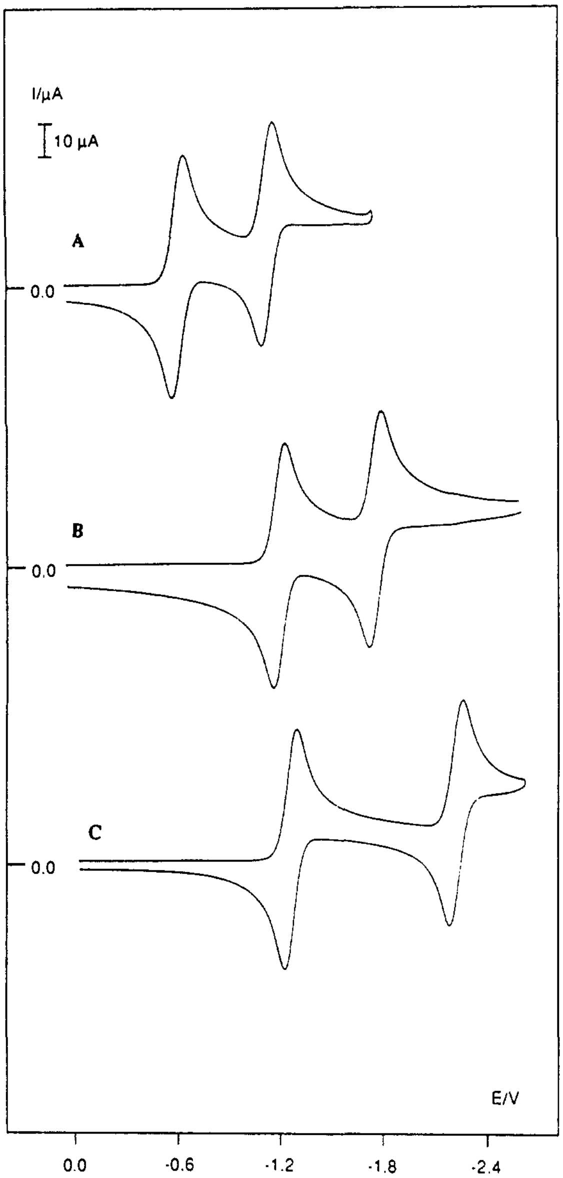

Figure 1. Cyclic voltammograms at a glassy carbon electrode in CH_3CN of (A) α-$Q_3PW_{12}O_{40}$ (**2**; 1.8 mM), (B) $Q_4W_{10}O_{32}$ (**1**; 1.85 mM), and (C) $Q_2W_6O_{19}$ (1.86 mM). Q = tetra-*n*-butylammonium cation. Supporting electrolyte, 0.1 M $(TBA)PF_6$; scan rate, 100 mV/s; room temperature.

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[29] Chambers, R. C.; Hill, C. L. *Inorg. Chem.* **1989**, *28*, 2509.

[30] In this case, however, the relatively high ratio of solvent to alkane reactivity may have precluded significant reaction of this alkane.

[31] Prosser-McCartha, C. M.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 3671.

[32] Hill, C. L.; Renneke, R. F.; Combs, L. A. *New J. Chem.* **1989**, *13*, 701.

[33] The strong acids triflic acid and α-$H_3PW_{12}O_{40}$ themselves, in the dark, equilibrate the isomeric alkenes without producing any other detectable products in appreciable yield (<5%).

[34] The acid-catalyzed alkene isomerizations are much more sensitive to temperature than are the alkane photooxidations. At ~30 °C, the rates of the two types of reactions are comparable. In contrast, at 0 °C there is negligible isomerization over the time scale of reaction execution and product analysis (ca. 20–40 min). The photochemical dehydrogenation of *cis*-1,2-dimethylcyclohexane by α-$H_3PW_{12}O_{40}$ is illustrative: at 0 °C the product distribution is very similar to that produced by the neutral quaternary ammonium salt of this polyoxometalate, **2**, (the ratio of tetrasubstituted alkene to trisubstituted alkene is 10:1); at 30 °C, this ratio has changed to 3.3:1, the same within experimental error as that seen under conditions of complete acid equilibration. The other effect of acids, including α-$H_3PW_{12}O_{40}$ as reported earlier, is the catalyzed hydration of alkenes, a reaction that alters product distributions if many equivalents of water are present. The alcohol/alkene ratio is typically low (0–0.05) at early times but can increase over longer periods of time.

Table II. Redox Potentials from Cyclic Voltammetry of Photoredox-Active Polyoxotungstates Capable of Alkane Dehydrogenation/Functionalization[a]

	first wave		second wave	
polyoxometalate[b]	E^f/V (peak width)[c]	ip_c/ip_a	E^f/V (peak width)[c]	ip_c/ip_a
α-$H_3PW_{12}O_{40}$	−0.630 (120 mV)	*d*	−0.850 (120 mV)	*d*
α-$Q_3PW_{12}O_{40}$ (**2**)	−0.670 (65 mV)	1.10	−1.190 (75 mV)	0.99
α-$(NH_4)_6P_2W_{18}O_{62}$	−0.780[e]		−0.870[e]	
$Q_4W_{10}O_{32}$ (**1**)	−1.270 (65 mV)	1.04	−1.830 (65 mV)	0.94
$Q_2W_6O_{19}$	−1.330 (70 mV)	1.00	−2.290 (75 mV)	0.97

[a] Working electrode, glassy carbon; reference electrode, Ag/0.01 M $AgNO_3$ in CH_3CN; supporting electrolyte, 0.1 M $(TBA)PF_6$; solvent, CH_3CN; polyoxotungstate concentration, 1.8–1.9 mM; $T = 23 \pm 2$ °C; scan rate, 100 mV/s. [b] Q = *n*-Bu_4N^+. [c] The formal redox potentials, E^f, are estimated as the average of the anodic and cathodic peak potentials. Peak width, difference in anodic and cathodic peak potentials. [d] Baseline not easily detected. [e] Only the reduction peak potentials are reported because the system is irreversible.

conditions of acid equilibration (compare reactions 4 and 9, 16 and 21, Table I). Control experiments established that the differences in the organic product distributions for the reactions containing **1** and **2** were not caused by thermal or photochemical side reactions of initial products induced by either the oxidized or reduced forms of the complexes.

Much of the data on these alkane photodehydrogenation processes catalyzed by polyoxotungstates indicates that the redox potentials of the complexes in their ground states as well as their excited states play key roles in various aspects of the mechanism. This compelled us to determine the redox potentials of five key complexes under conditions similar to those seen in the alkane photodehydrogenation processes. The pertinent cyclic voltammetric data are presented in Table II. Clearly the dramatic difference in the regiochemistry of the alkenes produced upon catalytic photochemical dehydrogenation of alkanes by polyoxotungstates does correlate with formal potential, E^f,—the complexes with the more anodic or positive ground-state potentials, i.e., α-$PW_{12}O_{40}^{3-}$ and α-$P_2W_{18}O_{62}^{6-}$, produce the most substituted alkenes while the complexes with the more cathodic or negative ground-state potentials, i.e., $W_{10}O_{32}^{4-}$ and $W_6O_{19}^{2-}$, produce the least substituted alkenes. Representative voltammograms of the tetra-*n*-butylammonium salts of α-$PW_{12}O_{40}^{3-}$, $W_{10}O_{32}^{4-}$, and $W_6O_{19}^{2-}$ are shown in Figure 1.

Using 2,3-dimethylbutane as the alkane substrate, reactions of **1** and **2** were conducted in dry and wet (15% H_2O by weight) acetonitrile. Reactions of **1** showed no alcohol or any changes in the organic oxidation product ratios upon the addition of H_2O. Reactions of **2**, however, showed formation of the tertiary alcohol upon the addition of H_2O. This product accounted for ~25% of the total detected organic products. A quasi thermodynamic alkene distribution was still present. The primary alcohol did not form. The tertiary alcohol was stable under the reaction conditions for the reactions containing both **1** or **2** with or without water.

Reactions were conducted in which a 50:50 molar mixture of a decatungstate, **1**, and a dodecatungstophosphate, **2**, was used in place of just one of the polyoxotungstates (reactions 8, 13, and 19, Table I). In all three reactions incident light ($\lambda > 395$ nm) capable of exciting only **1** was used, yet the product distributions generated were not those characteristic of **1** or the equilibrium distribution of alkenes, but those characteristic of **2**. The maximally substituted olefin was the major product, and for *cis*-1,2-dimethylcyclohexane (reaction 19) the cis–trans alkane isomerization side reaction was almost totally suppressed upon addition of the more oxidizing heteropolytungstate, **2**. A similar reaction with a 50:50 molar mixture of **1** and $Q_2W_6O_{19}$ using *cis*-1,2-dimethylcyclohexane as the substrate (reaction 20), on the other hand, led to the same organic product distribution obtained with pure **1**.

In mixed **1**/**2** systems with *cis*-1,2-dimethylcyclohexane as substrate, where **1** was selectively irradiated, the concentration of added **2** was varied from 0.09 (5% of the concentration of **1** is 1.8 mM) to 1.8 mM. Organic product distributions tending toward those exhibited when only **2** was present were obtained when this complex was present in concentrations from 5 to 30% (0.54 mM) that of **1**.

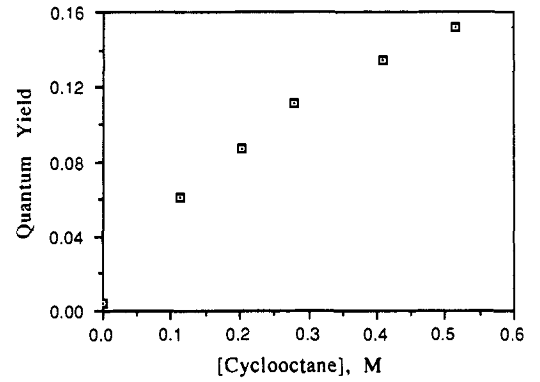

Figure 2. Quantum yields of photoreduction of **1** by cyclooctane as a function of the concentration of cyclooctane in the **1**/cyclooctane/$CH_3CN/h\nu$ system. Values obtained at 322 nm under optically dense conditions with an interference filter (FWHM = 9.6 nm, transmission$_{max,322nm}$ = 21%). Irradiation with an Oriel 1000-W Xe arc lamp assembly. [**1**] = 1.8 mM; $T = 25$ °C; 2.0 mL of solution in a 1.0-cm path length rectangular quartz cuvette was irradiated under an inert atmosphere. Quantum yield defined as the equivalents of electrons reducing the oxidized form of **1** per photon absorbed. The nonzero value of this quantity at [cyclooctane] = 0 M is due to the reactivity of the CH_3CN solvent. Other conditions are described in the Experimental Section.

For the system consisting of **1**, **2**, and *cis*-1,2-dimethylcyclohexane substrate, containing a 95:5 mol ratio of **1** to **2**, the organic oxidation and polyoxometalate reduction products were monitored as a function of time. At early times **2** was photoreduced while the "thermodynamic" organic product distribution was observed. At later times, when oxidized **2** had been consumed, **1** was photoreduced and a shift to a nonthermodynamic alkene distribution and the cis–trans isomerization resulted.

For the mixed **1**/**2** systems under the reaction conditions, additional experiments indicated that energy transfer from the excited state of **1** (or **1***) to **2**, resulting in the generation of **2***, was at most a minor pathway. The importance of this route was evaluated as it could, in principle, produce the changes noted in the organic product distributions when **2** is added. The quantum yields for the photoreduction of **1** and **2** utilizing cyclooctane as the organic substrate are 0.14 and 0.02, respectively.[13c,d] Depending on the amount of energy transferred from **1** to **2**, the quantum yield is expected to decrease from 0.14 to a value between 0.14 and 0.02. Irradiation of the mixed systems with $\lambda > 395$ nm light resulted in rates of polyoxometalate reduction/alkane oxidation slightly higher than the systems with only **1**, a result contrary to that expected if energy transfer was significant. This experiment is compatible, instead, with the increased rate of polyoxometalate reduction expected to arise from the higher radical oxidation rates associated with the presence of the more strongly oxidizing complex **2**. Additional experiments in which the quantum yields of two-component mixed-polyoxometalate systems were studied at different wavelengths of incident light and for which the quantum yield of one component differed by up to a factor of 100 from the other component also provided no evidence for energy transfer.[13d,35]

The kinetics of the photooxidation of cyclooctane by **1** using 322-nm light were examined. The reactions proved to be approximately first order in alkane (Figure 2) and first order in light intensity (Figure 3). The reaction approached first order in **1** at very low concentrations of **1** and zero order at high concentrations (Figure 4). The rates were directly proportional to the quantity of light absorbed by **1** at this wavelength. A primary kinetic isotope effect, $k_{cyclohexane\text{-}h_{12}}/k_{cyclohexane\text{-}d_{12}}$, of 2.5 was obtained with **1**. For reactions consisting of a 50:50 molar mixture of

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(35) Alkene isomerization and other thermal side reactions were not associated with the presence of reduced **2** in the mixed systems (the systems containing **1** and **2**). This new variable, therefore, does not produce the changes noted in these systems.

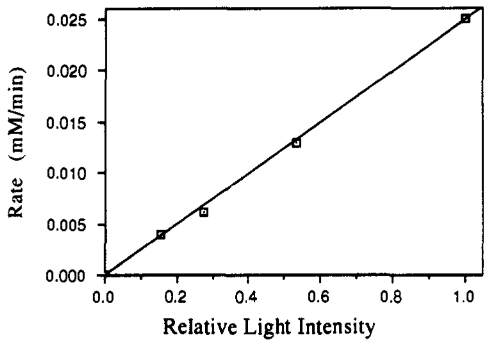

Figure 3. Initial rate of photoreduction of **1** as a function of light intensity in the **1**/cyclooctane/$CH_3CN/h\nu$ system. Values obtained at 322 nm under optically dense conditions with an interference filter (FWHM = 9.6 nm, $\text{transmission}_{\max,322\text{nm}} = 21\%$) in alignment with transmittance UV-neutral density filters (15.5, 27.3, and 53.4% at 322 nm). Irradiance with only the 322-nm interference filter corresponds to a value of 1.00 for the relative light intensity. An Oriel 1000-W Xe arc lamp assembly was employed. [1] = 1.8 mM; [cyclooctane] = 0.48 M; $T = 25$ °C; 2.0 mL of solution in a 1.0-cm path length rectangular quartz cuvette was irradiated under an inert atmosphere. Other conditions are described in the Experimental Section.

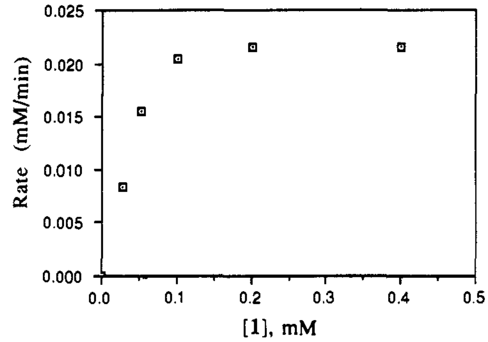

Figure 4. Initial rate of photoreduction of **1** as a function of the concentration of **1** in the **1**/cyclooctane/$CH_3CN/h\nu$ system. Values obtained at 322 nm with an interference filter (FWHM = 9.6 nm, $\text{transmission}_{\max,322\text{nm}} = 21\%$). Irradiation with an Oriel 1000-W Xe arc lamp assembly [cyclooctane] = 0.48 M; $T = 25$ °C; 2.0 mL of solution in a 1.0-cm path length rectangular quartz cuvette was irradiated under an inert atmosphere. Other conditions are described in the Experimental Section.

cyclohexane-h_{12} and cyclohexane-d_{12}, the isotopic distributions observed in the cyclohexene, cyclohexyl methyl ketone, and dicyclohexyl products were consistent with this primary kinetic isotope effect and with freely diffusing radical intermediates.[13d]

The photooxidation of cyclooctane by **1** (reaction 23, Table I) was studied in more detail since it produces only one alkene and one dimer, allowing for any variations in their ratios to be conveniently monitored. When the concentration of **1** was varied by a factor of 169 (13.2–0.078 mM), there was no change in the alkene/dimer ratio of 1.3. Here the rate of reduction of **1** was kept as nearly constant as possible by utilizing an assembly of neutral density filters to attenuate the light impinging upon the more absorptive solutions, those with high concentrations of **1**. When the light intensity was varied by a factor of ~150 at a constant concentration of **1** of 3.1 mM, again, there was no change in the alkene/dimer ratio of 1.3. This same ratio was also obtained when the concentration of cyclooctane was varied at constant concentration of **1** and light intensity.

Analogous experiments with **2** (reaction 24, Table I) yielded results notably distinct from these. When the concentration of **2** was increased by a factor of 46, the alkene/dimer ratio increased from 1.9 (0.55 mM) to 16 (25.5 mM). When the light intensity was varied by a factor of ~150 at a constant concentration of **2** of 5.8 mM, the alkene/dimer ratio increased from 5.8 (high intensity) to ~40 (low intensity).

Addition of a trace of the hydrogen evolution catalyst 10% Pt(0) on carbon (5×10^{-4} mg·atom) to the reactions in Table I renders the reactions catalytic in polyoxometalate. These are not ideal conditions for mechanistic studies but were pursued nevertheless to check if preparative alkene reactions were feasible without altering the reaction conditions further. The photooxidation of cyclooctane by **1** could routinely be carried out to 10–20% conversion of the alkane within 2 h with only small changes in the organic product distribution. In contrast, the photooxidation of branched alkanes by **1** led to significant side reactions, including polymerization at conversions ≤5%.

Discussion

Alkyl Radical Intermediates. Although organic radicals have been proposed as intermediates in nearly all papers that address the photochemical oxidation of organic substrates by polyoxometalates, the evidence for their existence has been less than compelling.[13,17] Several lines of evidence in this study establish that alkyl radicals are generated in the photodehydrogenation of alkanes by polyoxotungstates. First, not only the presence of both alkene and dimer products but also the relative quantities of these products are consistent with radical–radical coupling and disproportionation.[28] The most substituted radicals, tertiary in the cases of the first four substrates in the Table I, would be expected to produce at least 6–10 times the quantity of disproportionation products (alkane + alkene) as coupling products (dimer) while the secondary radicals would be expected to produce comparable quantities of the two types of products.[28] This is what is observed (Table I). With the yields of dimer so low and the alkane produced in the disproportionation returning to the alkane substrate pool, the alkene is the dominant net product for the branched alkanes. Second, the polymerization of alkene products under the reaction conditions and, more significantly, the relative rates of loss of these products (mono-, di-, tri-, and tetrasubstituted alkene reacting in a ratio of 1:1.67:10:40) are in accord with radical-initiated polymerization.[36] Third, the production of 2-hydroperoxy-2,3-dimethylbutane upon photooxidation of 2,3-dimethylbutane by **1** in the presence of O_2 and production of this product at the expense of alkene and all other products strongly implicates the intermediacy of the tertiary radical. More lines of evidence discussed in the next section are not only consistent with alkyl radicals but provide evidence for the nature of the step involving attack on the alkane substrates.

Mechanism of Attack on Alkane Substrate. Two basic mechanisms for the initial substrate attack process involving the excited state of **1** in the alkane photodehydrogenation reactions catalyzed by this complex can be excluded with some certainty at the outset. First, hydride abstraction to generate carbonium ion directly is inconsistent with the negligible levels of Ritter products, the *N*-alkylacetamides, and the lack of skeletal rearrangements seen in the reactions. In addition, the lack of alcohols when the reactions containing **1** are run anaerobically in the presence of water also argues against the direct generation of carbonium ions as the dominant substrate oxidation process. There is evidence, however, for the generation of carbonium ions via oxidation of initially generated radicals (vide infra). Second, a concerted insertion of an oxygen of the excited polyoxotungstate into the alkane bonds, a mechanism analogous to those in some electrophilic[4] and organometallic[2] systems involving a triangular three-membered-ring transition state, is inconsistent with the observed products (no alcohols or ethers) and the minimal degradation of polyoxometalate that is observed after many turnovers under catalytic conditions (i.e., in the presence of a hydrogen evolution catalyst). Furthermore, both hydride abstraction and oxygen insertion mechanisms are sufficiently unprecedented for alkane oxidation under mild conditions in condensed media that considerable data in favor of such mechanisms would need to be acquired before a reasonable argument could be made for the existence of either.[1,2g]

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[36] Although allylic C–H hydrogen abstraction competes with radical addition to the double bond and the polymerization processes are, as a consequence, not clean, the relative rates of loss of the different hydrocarbon alkenes are consistent with the dominance of radical processes, cf.: Tedder, J. M. *Reactivity, Mechanisms, and Structure in Polymer Chemistry*; Wiley: New York, 1974; Chapter 2.

Two additional limiting mechanisms for the attack of the polyoxotungstate excited state, generated by light absorption (eq 5) need to be considered: atom abstraction (or atom transfer, AT)

$$W_{10}O_{32}^{4-} + h\nu \xrightarrow{\phi I_a} W_{10}O_{32}^{4-*} \quad (5)$$

$$W_{10}O_{32}^{4-*} + RH \xrightarrow{k_1} W_{10}O_{32}H^{4-} + R^{\bullet} \quad (6)$$

$$W_{10}O_{32}^{4-*} + RH \rightarrow W_{10}O_{32}^{5-} + (RH)^{\bullet+} \quad (7)$$

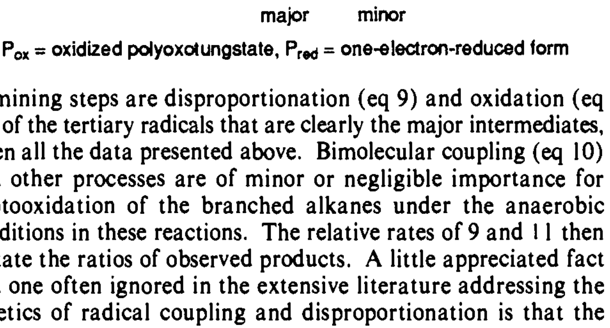
$$(RH)^{\bullet+} \rightarrow R^{\bullet} + H^{+} \quad (8)$$

(eq 6) and electron transfer (ET) followed by deprotonation of the cation radical (eqs 7 and 8). The first mode, AT, is a common one for C–H bond cleavage in a myriad of reactions involving the oxidation of alkanes and other organic substrates with C–H bonds by transition-oxometal and other inorganic species. It is operable in free-radical chain reactions such as industrial chlorination[37] and aerobic oxidation,[38] radical cage processes such as alkane oxygenation by cytochrome P-450[15] and other systems exhibiting hydroxylation by the "atom rebound" mechanism,[39] and other oxidations.[40] Furthermore ASED-MO calculations that have just appeared by Awad and Anderson on alkane photooxidation by $W_{10}O_{32}^{4-}$ conclude that attack on substrate involves a process that is principally AT in nature and not ET.[41] (These investigators also predicted methyl radicals would rather couple to yield ethane than reduce the oxidized $W_{10}O_{32}^{4-}$ species, a point in accord with the data presented here with secondary and tertiary radicals.) At the same time, oxidation of alkanes by the ET process, eqs 7 and 8, under mild conditions in solution is very rare. Both AT and ET mechanisms ultimately produce the organic radical, R$^{\bullet}$, and a proton. The latter may or may not be protonating the polyoxometalate in acetonitrile solution, depending on the conditions.[13d,18]

There are four lines of evidence that atom abstraction, eq 6, is operable in our reactions. First, the primary kinetic isotope effect, $k_{\text{cyclohexane-}h_{12}}/k_{\text{cyclohexane-}d_{12}}$, for photooxidation of cyclohexane by **1** is 2.5. Although this value is significantly higher than the value of 1.4 previously reported for the photooxidation of cyclohexane by the α-$H_3PW_{12}O_{40}$,[13b] it is consistent with a mid-transition-state radical abstraction. The principal caveat here is that although one can argue from basic principles that the isotope effect would be considerably different and possibly negative for the ET process, no bona fide examples of a system that oxidizes unstrained alkanes by ET in condensed media by chemical (vs physical) means has yet been documented; thus, there are no pertinent data available for purposes of comparison. Second, the relative reactivities of various alkanes including neopentane (unreactive), a hydrocarbon with all primary C–H bonds, are compatible with AT. The caveat here is that such data are compatible in principle with ET as well. A correlation of the relative reactivities of alkanes in photochemical oxidation by α-$H_3PW_{12}O_{40}$ with the ionization potentials of alkanes has been reported,[13a] but correlations with ionization potentials just as those with liquid-phase redox potentials are marginally informative. A number of mechanisms including the limiting AT and ET processes exemplified by eqs 6 and 7, respectively, are consistent with such correlations. Third, the ratios of tertiary to primary hydroperoxides and alcohols that are formed when 2,3-dimethylbutane is photooxidized by **1** in the presence of O_2 are consistent with AT. This ratio is at least 20:1 or higher leading, after statistical correction for the numbers of hydrogens, to an apparent kinetic tertiary–primary partitioning selectivity, $k_{\text{tertiaryC-H}}/k_{\text{primaryC-H}}$ of 120:1. A fourth and related point concerns the regiochemistry of the alkyl fragments in the dimers derived from photooxidation of isobutane (reaction 22, Table I)—the predominant dimeric product is that derived from the coupling of two *tert*-butyl radicals.

The principal rationale for invoking the ET mechanism for substrate attack by the polyoxometalate excited state derives from the preferential production of the least substituted alkenes upon dehydrogenation of branched alkanes. There is sufficient experimental evidence now available to indicate that the radicals produced by deprotonation of cation radicals, i.e., those from ET, eqs 7 and 8, are distinct from those produced in all conventional radical abstraction processes, e.g., eq 6. A number of studies by Iwasaki and co-workers in which the cation radicals of *unstrained*[42] alkanes are generated by pulse radiolysis in matrices and in the narrow channels of a ZSM-5 zeolite show that cation radicals deprotonate to give the least substituted or terminal radicals.[43] In contrast, atom abstraction yields the most substituted, often tertiary, radicals. Nonthermodynamic alkenes could then be rationalized to result from subsequent oxidation and deprotonation of the least substituted radicals. To further address the origin of these unusual products, the various steps subsequent to radical generation must be examined.

Product- and Regiochemistry-Determining Steps in the Mechanism. A rationale consistent with all the experimental data that explains both preferential production of the nonthermodynamic and least substituted alkenes when the less oxidizing polyoxotungstates (e.g., $W_{10}O_{32}^{4-}$) are used as the photocatalysts and preferential production of the thermodynamic and most substituted alkenes when the more oxidizing polyoxotungstates (e.g., α-$PW_{12}O_{40}^{3-}$) are used is illustrated using 2,3-dimethylbutane as an exemplary substrate (eqs 9–12). The principal product-determining steps are disproportionation (eq 9) and oxidation (eq 11) of the tertiary radicals that are clearly the major intermediates, given all the data presented above. Bimolecular coupling (eq 10) and other processes are of minor or negligible importance for photooxidation of the branched alkanes under the anaerobic conditions in these reactions. The relative rates of 9 and 11 then dictate the ratios of observed products. A little appreciated fact and one often ignored in the extensive literature addressing the kinetics of radical coupling and disproportionation is that the kinetic products from such disproportionations are often the less substituted alkenes plus alkane. Although the ratios of terminal to internal alkenes in literature studies are generally not as high as those observed in the branched alkane photodehydrogenations



P_{ox} = oxidized polyoxotungstate, P_{red} = one-electron-reduced form

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[37] Poutsma, M. In *Free Radicals* Kochi, J. K., Ed.; Wiley: New York, 1973; Vol II, Chapter 15.

[38] For example, see: Sheldon, R. A., Kochi, J. K., Eds. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapters 2 and 11, and references cited therein.

[39] (a) Mansuy, D.; Battioni, P. In: Reference 1, Chapter VI. (b) Hill, C. L. In: Reference 1, Chapter VIII.

[40] *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum: New York, 1986; and references therein. See also several chapters in ref 38.

[41] Awad, M. K.; Anderson, A. B. *J. Am. Chem. Soc.* **1990**, *112*, 1603.

[42] Cation radicals of strained alkanes unlike unstrained alkanes have been generated by photochemical, radiolytic, and electrochemical means in a number of studies. Exemplary photochemical/radiolytic studies: (a) Qin, X.-Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640. (b) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343. (c) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456. (d) Knight, L. B., Jr.; Arrington, C. A.; Gregory, B. W.; Cobranchi, S. T.; Liang, S.; Paquette, L. *Ibid.* **1987**, *109*, 5521. Exemplary electrochemical study: Gassman, P. G.; Yamaguchi, R. *Ibid.* **1979**, *101*, 1308.

[43] (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1981**, *103*, 3591. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Phys. Chem.* **1986**, *90*, 6836. (c) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Am. Chem. Soc.* **1987**, *109*, 4496.

by $W_{10}O_{32}^{4-}$ and $W_6O_{19}^{2-}$ reported here, ratios of terminal to internal alkenes as high as 9 upon reaction between a tertiary radical and a secondary radical have been reported.[28,44] In view of the fact that steric hindrance is a major factor in determining which hydrogen is abstracted in a disproportionation reaction,[28a] an even higher ratio of terminal to internal alkene, in line with the data presented here, would be expected if two tertiary radicals reacted with each other. The most defensible counterargument as to why the least substituted alkenes are rarely produced in other processes in which radicals are generated in the presence of alkanes is that in virtually all other such processes tertiary radicals are scavenged by neutrals (including solvent) or they are subject to oxidation before they can react with each other.

The production of the more substituted alkenes in alkane photodehydrogenation by the more oxidizing heteropolytungstates, α-$PW_{12}O_{40}^{3-}$ and α-$P_2W_{18}O_{62}^{6-}$, and the lower ratio of dimeric coupling products to alkene products in these reactions vs those containing the less oxidizing isopolytungstates derives from the fact that, with the former complexes, oxidation of alkyl radicals to the corresponding carbocations by the oxidized ground states of these polyoxotungstates, k_{ox} (eq 11), is faster than k_d (eq 9). The rates of thermal oxidation of alcohol-derived organic radicals, generated by pulse radiolysis, by heteropoly tungstates of the Keggin structure, e.g., α-$H_3PW_{12}O_{40}$, in alcohol solution have been independently measured and they are nearly diffusion limited.[45] Carbonium ions resulting from radical oxidation then deprotonate to yield the most substituted alkenes (Zaitsev's rule).[46] These species were trapped by H_2O in the reactions containing **2** and 2,3-dimethylbutane substrate in wet acetonitrile, resulting in the production of the tertiary alcohol. Analogous reactions with **1** yielded no alcohol, as expected from the proposed mechanism. In contrast, k_d is at least 1 order of magnitude greater than k_{ox} for the isopolytungstate complexes, $W_{10}O_{32}^{4-}$ and $W_6O_{19}^{2-}$. The potential data in Table II buttress these arguments. Radical oxidation (eq 11) approaches the diffusion limit for the polyoxotungstates, with first reduction potentials less negative than −1.0 V vs $Ag/AgNO_3(CH_3CN)$ (the α-$PW_{12}O_{40}^{3-}$ and α-$P_2W_{18}O_{62}^{6-}$ complexes). It is substantially slower for the polyoxytungstates, with potentials more negative than this value ($W_{10}O_{32}^{4-}$ and $W_6O_{19}^{2-}$). For the latter complexes, radicals undergo eq 9 predominantly.

This rationale also explains the change from the least substituted alkenes to the most substituted alkenes upon addition of the neutral heteropoly compound **2** to the reaction containing **1**. The addition of **2** causes radicals generated by hydrogen atom transfer to the excited states of **1** to become oxidized significantly faster than they disproportionate. The organic product distributions obtained with different concentrations of **2** illustrate the sensitivity of the branched alkane reactions to the presence of oxidized **2**. When these reactions are followed as a function of time, biphasic behavior is also observed. At early times, when oxidized **1** and **2** are simultaneously present, **2** is reduced preferentially due to its higher reduction potential. It becomes reduced by freely diffusing alkyl radicals or by the initially photogenerated reduced **1**. While there is still a small quantity of oxidized **2** in solution, radicals can be oxidized to carbocations. During this time a quasi thermodynamic distribution of alkenes is obtained and the cis–trans alkane isomerization is suppressed. At later times, when oxidized **2** is depleted by its reduction, only oxidized **1** remains and radical oxidation becomes a minor pathway. At these later stages of reaction, the nonthermodynamic alkenes are produced preferentially and the cis–trans isomerization reaction commences. The wealth of polyoxometalates with varying ground-state redox potentials and susceptibilities to photoredox processes and the numerous methods by which these and other properties of the polyoxotungstates can be modulated[13d,17c] indicate potential for this rich redox chemistry.

A final corroboration of the importance of disproportionation (eq 9) vs oxidation (eq 11) or other processes follows from the kinetics. A simple rate law invoking the steady-state approximation (eq 13) is compatible with the kinetic data described above.

$$\frac{+\mathrm{d}[P_{red}]}{\mathrm{d}t} = \frac{\phi I_a k_1[RH]}{k_1[RH] + k_{nr}} \qquad (13)$$

Here $+\mathrm{d}[P_{red}]/\mathrm{d}t$ represents the rate of photoreduction of **1**, ϕ the quantum efficiency at 322 nm for production of the photoredox active excited state of the complex (eq 5), I_a the quantity of light absorbed (eq 5), k_1 the rate constant for the bimolecular reaction of the excited state of **1** with alkane (eqs 6 and 7), and k_{nr} the rate constant for nonradiative and nonredox deactivation of the excited state. For cyclooctane, the value of ϕ is equal to 0.14 at ~0.5 M (Figure 1), and $k_1[RH] < k_{nr}$. Equation 13 is similar to the one describing the α-$H_3PW_{12}O_{40}$/cyclooctane system previously reported.[13b]

With cyclooctane as the substrate, three distinct lines of evidence, regarding variations in the terms of eq 13, indicate the ground state of **1** is not effectively reduced by freely diffusing radicals (eq 11) under these reaction conditions for alkane photooxidation. First, when the concentration of **1** is varied over a considerable range (a factor of 169), no changes in the relative proportion of dialkyl dimer to alkene products result. This indicates **1** is not competing with radicals for radicals, otherwise the alkene/dimer ratio of 1.3 would increase because carbonium ion intermediates lead overwhelmingly to alkenes only. Second, altering the steady-state concentration of radicals by varying the light intensity has no effect on the alkene/dimer ratio. The rate of formation of dimers is given in eqs 10 and 14, and the rate of

$$\mathrm{d}[RR]/\mathrm{d}t = k_c[R^\bullet][R^\bullet] \qquad (14)$$

$$\mathrm{d}[R^+]/\mathrm{d}t = k_{ox}[R^\bullet][\mathbf{1}] \qquad (15)$$

reaction of radicals with **1** is given in eqs 11 and 15. The second-order dependence on the $[R^\bullet]$ in eq 14 and the first-order dependence in eq 15 indicates at low light intensities, where $[R^\bullet]$ is low, the ratio alkene/dimer should increase if **1** oxidizes radicals. That the competition for free radicals between other radicals and oxidized polyoxometalate can be skewed in favor of the polyoxometalate by lowering the light intensity is physically reasonable, since by lowering the concentration of excited states the radical derived from such a state would have a longer distance to traverse to encounter another radical while the distance to polyoxometalate species would remain constant. But this phenomenon is not observed experimentally; the alkene/dimer ratio of 1.3 is maintained when the light intensity is varied by a factor of ~150. Third, if reduction of **1** was significant, an increase in the observed photoreduction of **1**, $+\mathrm{d}[P_{red}]/\mathrm{d}t$, would be expected to occur when the concentration of **1** was increased since the subsequent thermal reduction would be superimposed to a greater extent on the initial photochemical reduction. In the optically dense region, where this phenomenon can be conveniently monitored, large variations in the concentration of **1** clearly lead to no such increases in the quantum yield.

Analogous experiments with **2**, on the other hand, indicate the ground state of **2** is reduced by freely diffusing radicals. The alkene/dimer ratio increases considerably (see Results) when either the concentration of **2** is increased or the light intensity is decreased. Additionally, the rate of photoreduction of **2** appeared to increase slightly as the concentration of **2** was increased.

The reactivity of the acetonitrile solvent clearly evident in the absence of the alkane substrate indicates that a similar side reaction may be occurring in the presence of the alkane and perhaps contributing toward the alkane oxidation via acetonitrile radical intermediates. Hydrogen atoms are not incorporated into the CD_3CN solvent (see Results) in the presence of alkane substrate, however, indicating this indirect alkane functionalization route is at most of minor significance.

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[44] Larson, C. W.; Rabinovitch, B. S. *J. Chem. Phys.* **1969**, *51*, 2293.

[45] (a) Papaconstantinou, E. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 2769. (b) Lerat, O.; Chauveau, F.; Hickel, B. *New J. Chem.* **1990**, *14*, 37.

[46] The Zaitsev criterion states that a carbonium ion intermediate in an E1 elimination will produce alkenes in approximately a thermodynamic distribution when there is a choice of more than one type of β-hydrogen to eliminate, cf.: March, J. *Advanced Organic Chemistry* 3rd ed.; Wiley: New York, 1985; p 889.

Conclusions

(1) At parity of reaction conditions, the products in alkane dehydrogenation by polyoxometalates depend on both polyoxometalate and substrate. Branched alkanes undergo predominantly dehydrogenation to the corresponding alkenes.

(2) A contention with little substantiation to date, that organic radicals are intermediates in the catalytic photochemical oxidation of organic substrates by polyoxometalates, has been firmly established for the reactions investigated here. Several lines of evidence indicate conclusively that freely diffusing alkyl radicals are intermediates in the anaerobic dehydrogenation of saturated hydrocarbons.

(3) Product distribution and kinetics data are compatible with hydrogen atom abstraction (atom transfer) as the dominant pathway for attack of the polyoxotungstates excited states on alkane. Deprotonation of alkane cation radicals generated by electron transfer to yield nonthermodynamic radicals followed by subsequent oxidation and deprotonation can constitute at most a minor pathway for attack of the polyoxometalate excited state on alkane substrate.

(4) The relative rates of radical–radical disproportionation (k_d) and radical oxidation (k_{ox}) dictate the regiochemistry of the observed alkene products. Inasmuch as these relative rates can be controlled by judicious choice of the polyoxotungstate catalyst(s) and reactions conditions, the regiochemistry of alkane photochemical dehydrogenation can be controlled to a great extent.

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Synthesis and Subsequent Rearrangement of Chloro(pentafluorophenyl)-1,5-cyclooctadienepalladium(II), an Illustrative Example of Endo Attack to a Coordinated Double Bond

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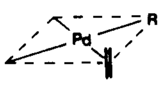
Abstract: $Pd(C_6F_5)Cl$(1,5-cyclooctadiene) has been prepared in high yield and characterized crystallographically: monoclinic space group $P2_1/c$, $a = 8.313$ (1) Å, $b = 7.7800$ (6) Å, $c = 22.292$ (4) Å, $\beta = 95.77$ (1)° ($Z = 4$), final R of 0.024 for 2080 independent reflections. The X-ray structure reveals a high trans influence of the C_6F_5 groups that weakens the opposite palladium–olefin bond. This complex rearranges slowly in solution by intramolecular double bond insertion into the Pd–C_6F_5 bond to give an allyl complex $Pd_2(\mu\text{-}Cl)_2(6\text{-}C_6F_5\text{-}1\text{–}3\text{-}\eta^3\text{-}C_8H_{12})_2$ and σ,π-complex $Pd_2(\mu\text{-}Cl)_2(8\text{-}C_6F_5\text{-}1\text{:}4\text{-}5\text{-}\eta^3\text{-}C_8H_{12})_2$. A derivative of the latter, $Pd(8\text{-}C_6F_5\text{-}1\text{:}4\text{-}5\text{-}\eta^3\text{-}C_8H_{12})$(F6-acac), has been characterized crystallographically: triclinic space group $P\bar{1}$, $a = 10.360$ (3) Å, $b = 11.051$ (2) Å, $c = 11.084$ (4) Å, $\alpha = 73.70$ (2)°, $\beta = 61.41$ (2)°, $\gamma = 66.08$ (2)°, final R of 0.036 for 3341 independent reflections. The rearrangement of $Pd(C_6F_5)Cl$(1,5-COD) is catalyzed by its products and slowed down in coordinating solvents. Both products are the result of an endo attack of C_6F_5 to COD and are formed competitively from a common intermediate.

Introduction

The migratory insertion of olefins into metal–carbon bonds is an important reaction in transition-metal organometallic chemistry.[1] Palladium is perhaps the transition metal most widely used to induce this kind of reaction, as exemplified by the Heck reaction and related processes.[2-4] Whatever the method used to introduce R and the olefin on the palladium, eventually both groups must acquire a mutually cis arrangement as in **1** for the insertion to occur; this cis arrangement followed by olefin rotation to an "in plane" coordination allows evolution to the four-center transition state which leads to insertion.[5]



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Since the intramolecular migration of R to an olefin is very facile in palladium, it is very rare to meet complexes of the type **1** which are isolable or at least detectable and yet reactive enough to undergo insertion. The very few cases reported are all of a special type in which the σ and π bonds to palladium are provided by the same organic moiety, thus forming a palladacycle which confers some extra stability to the molecule.[6-9]

We have reported recently that synthons of "$Pd(C_6F_5)Br$" react with diolefins to give palladium allyls as the result of an insertion of the diene into the Pd–C_6F_5 bond; the assumed intermediates

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(1) See, for example: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Sections 6.3 and 11.3. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley, New York, 1986; Sections 6.3.c, 6.3.d.

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