

Homogeneous Catalytic Photochemical Functionalization of Alkanes by α -Dodecatungstophosphate. Rate Behavior, Energetics, and General Characteristics of the Processes

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Abstract: The photochemical functionalization of saturated hydrocarbons catalyzed by the heteropolytungstate α -dodecatungstophosphate in acetonitrile solution has been examined in detail. Under anaerobic conditions, the net processes involve oxidation of alkane, RH, and evolution of hydrogen ($\text{RH} \rightarrow \text{R} + \frac{1}{2}\text{H}_2$) with conversion of light into chemical energy ($\Delta H^\circ > +30$ kcal/mol of RH oxidized in some cases). The processes are catalytic in the polyoxotungstate with or without Pt(0) or other hydrogen evolution catalyst, but Pt(0) greatly accelerates the reoxidation of the photoreduced polyoxotungstate, the slow step, resulting in increased turnover rates. Two oxidative titration procedures adapted for these hydrophobic media, and the sizes and shapes of the electronic absorption chromophores generated as a function of time upon irradiation in the near-UV of $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$ (**1**) in acetonitrile solutions of representative alkanes, establish that the principal form of the photoreduced catalyst is the one-electron heteropoly blue species $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$, in contrast to the case for photooxidation of alcohols and other organic substrates by **1**. The product distributions have been established for the functionalization of representative branched alkanes and cycloalkanes. The relative yields of the initial alkane-derived oxidation products in these processes, alkene, *N*-alkylacetamide, alkylalkane dimer, and alkyl methyl ketone, vary with the alkane substrate, the form of the polyoxotungstate, and the reaction conditions. All these organic products are remarkably stable under the reaction conditions. Alcohols are not produced in these polyoxotungstate-based systems. The highest selectivities (ca. 100% for alkene production) are seen with **1** in the absence of Pt(0). Quantum yields average 0.1 but vary with the form of the polyoxotungstate and the reaction conditions and can be considerably higher. For the exemplary system, substrate = cyclooctane and catalyst = **1**, production of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ is a one-photon process that is first order in alkane, inverse order in water for low concentrations of water, and zero order in **1** for high concentrations of **1**. A rate law that involves the substrate, solvent, initial products, catalyst, and light intensity in accord with substantial kinetic data is derived. The relative observed rate constants for the production of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ under optically dense conditions by photooxidation of several normal, branched, and cyclic alkanes by **1** are unlike those seen in radical, hydride abstraction, electrophilic, or any type of alkane activation process documented for homogeneous liquid-phase reactions. These relative rates, the primary kinetic isotope effects, $k_{\text{cyclohexane-}h_{12}}/k_{\text{cyclohexane-}d_{12}} = 1.38$ and $k_{\text{cis-Decalin-}h_{12}}/k_{\text{cis-Decalin-}d_{12}} = 1.39$, and the product distribution studies are most compatible with electron transfer as the principal alkane activation process in the mechanism. These data also allow an analysis of some of the steps in the mechanism that follow the substrate activation process and a rationale for production of the various alkane-derived byproducts.

The development of methods for the selective conversion of alkanes into oxygenated compounds, higher molecular weight alkanes, and other classes of organic products continues to be a great challenge to the chemical community.¹⁻³¹ Although alkane

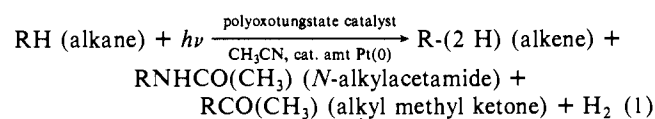
activation by organometallic compounds¹⁻⁷ and alkane hydroxylation by metalloporphyrin and related complexes⁸⁻²² now con-

- (1) References 2-7 are reviews of alkane C-H bond activation by organometallic systems, each with a different mandate or orientation.
- (2) Shilov, A. E. *Activation of Saturated Hydrocarbons Using Transition Metal Complexes*; Reidel: Dordrecht, 1984.
- (3) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902.
- (4) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
- (5) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.
- (6) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.
- (7) Ephritikhine, M. *Nouv. J. Chim.* **1986**, *10*, 9.
- (8) References 9-16 list alphabetically, by investigator's last name, representative papers that address alkane oxygenation or functionalization catalyzed by metalloporphyrins.
- (9) (a) Breslow, R. S.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400. (b) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728. (c) Svastits, E. W.; Dawson, J. H.; Breslow, R.; Gellman, S. H. *Ibid.* **1985**, *107*, 6427.
- (10) (a) Nee, M. W.; Bruce, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123. (b) Dicken, C. M.; Lu, F.-L.; Nee, M. W.; Bruce, T. C. *Ibid.* **1985**, *107*, 5776.
- (11) Chang, C. K.; Ebina, F. *J. Chem. Soc., Chem. Commun.* **1981**, 778.
- (12) (a) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243.
- (13) (a) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 2920. (b) Smegal, J. A.; Hill, C. L. *Ibid.* **1983**, *105*, 3515. (c) Hill, C. L.; Smegal, J. A.; Henly, T. J. *J. Org. Chem.* **1983**, *48*, 3277. (d) Brown, R. B., Jr.; Williamson, M. M.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 1602 and references cited therein. See also ref 18.
- (14) (a) Mansuy, D.; Fontecave, M.; Bartoli, J.-F. *J. Chem. Soc., Chem. Commun.* **1983**, 253. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *Ibid.* **1984**, 1161. (c) Battioni, P.; Renaud, J.-P.; Bartoli, J. F.; Mansuy, D. *Ibid.* **1986**, 341. (d) Battioni, P.; Bartoli, J. F.; Leduc, P.; Fontecave, M.; Mansuy, D. *Ibid.* **1987**, 791.
- (15) Nappa, N.; Tolman, C. A. *Inorg. Chem.* **1985**, *24*, 4711.
- (16) (a) Suslick, K. S.; Cook, B.; Fox, M. *J. Chem. Soc., Chem. Commun.* **1985**, 580. (b) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281. (c) Suslick, K. S.; Acholla, F. V.; Cook, B. R. *Ibid.* **1987**, *109*, 2818.

- (17) Recent review on metalloporphyrin-catalyzed oxygenation: Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578.
- (18) Review: Hill, C. L. "New Methodology for the Catalytic Functionalization of Hydrocarbons". *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; in press.
- (19) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
- (20) Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908.
- (21) (a) Herron, N.; Stucky, G. D.; Tolman, C. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1521. (b) Herron, N.; Tolman, C. A. *Ibid.* **1987**, *109*, 2837.
- (22) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536.
- (23) (a) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1497. (b) Hill, C. L.; Renneke, R. F.; Faraj, M. K.; Brown, R. B., Jr. *Proceedings from the International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidations*; Ando, W., Ed.; Elsevier: New York, 1988; p 155.
- (24) (a) Barton, D. H. R.; Göktürk, A. K.; Morzycki, J. W.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1* **1985**, 583. (b) Balavoine, G.; Barton, D. H. R.; Boivin, J.; Gref, A.; Ozbalik, N.; Rivière, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1727. (c) Barton, D. H. R.; Boivin, J.; Le Coupance, P. *Ibid.* **1987**, 1379, and earlier references cited in each.
- (25) (a) Olah, G. A.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 2726. (b) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *Ibid.* **1971**, *93*, 1251. (c) Olah, G. A.; Olah, J. A. *Ibid.* **1971**, *93*, 1256, and many other papers by this group.²⁶
- (26) Olah, G. *Acc. Chem. Res.* **1987**, *11*, 422.
- (27) Brown, S. H.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1987**, 970.
- (28) Parshall, G. W. *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley-Interscience: New York, 1980; Chapter 10 and references cited therein.
- (29) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; Chapter 2 and references cited therein.
- (30) Weissmehl, K.; Arpe, H.-J. *Industrial Organic Chemistry*; Verlag Chemie: New York, 1978; p 212.
- (31) References 32-34 cite recent studies of alkane activation and/or oxidation in the gas or solid phases.

stitute major areas of research, alkane functionalization by the Gif and Gif-Orsay systems,²⁴ superacid electrophilic species,^{25,26} photosensitized Hg vapor,²⁷ and other systems collectively have also substantially broadened our base of knowledge regarding the least reactive but most abundant class of organic compounds. Most of the energetic and mechanistic characteristics of these saturated hydrocarbon functionalization processes are distinct from industrial alkane autoxidation or other free-radical chain hydrocarbon oxidation processes.²⁸⁻³⁰

The early-transition-metal polyoxometalate complexes attracted our attention in context with the oxidation of hydrocarbons and other difficult organic transformations by virtue of their *thermodynamic* resistance to oxidation, numerous structural and electronic features, and experimental tractability. Transition-metal-substituted polyoxometalate complexes can function as inorganic porphyrins in that they catalyze the oxo transfer and other metalloporphyrin-catalyzed processes for tens of thousands of turnovers without the apparent oxidative degradation seen for metalloporphyrins and other complexes containing organic ligands.^{22,23} The stability and tractability characteristics of polyoxometalates also led us to assess the use of this class of complexes for catalytic photochemical processes. The catalytic photochemical functionalization of alkanes as exemplified in eq 1 and the



modification of this chemistry to produce only alkenes and hydrogen have both been reported recently.^{23b,35,36} These photochemical processes warrant serious attention for two principal reasons: They display energetic and mechanistic features that are distinct from all thermal hydrocarbon functionalization processes including those catalyzed by polyoxometalate derivatives, and they constitute the fairly efficient conversion of light into chemical energy (for example, the production of alkene and hydrogen from alkane, the reverse of conventional olefin catalytic hydrogenation, can be as endothermic as +35 kcal/mol).³⁶ This paper reports the results of a fairly comprehensive examination of the photochemical and photosynthetic functionalization of saturated hydrocarbons by α -dodecatungstophosphate in acetonitrile solution.

Experimental Section

Materials. The acetonitrile was Burdick and Jackson glass-distilled grade and was stored under argon in Aldrich Sure-Seal bottles or in

Schlenk flasks. All manipulations involving acetonitrile solutions were carried under an inert atmosphere. The alkane substrates were either glass-distilled grade from Burdick and Jackson or reagent grade from Aldrich, Wiley, or Fluka. All alkanes used in these experiments had purities of greater than 99+% by gas chromatography after passage through a column of neutral activity grade I alumina. The catalyst α -H₃PW₁₂O₄₀·nH₂O (**1**) was prepared by literature procedures and crystallized twice from aqueous HCl or H₂O to produce needles.^{37,38} The purity of the catalyst, **1**, was checked by infrared, UV-visible, and ¹⁸³W NMR spectroscopy, and the degree of hydration was approximately 11 (*n* ~ 10.7). Glass spatulas were used to manipulate **1**, since metal spatulas rapidly reduced the complex. All other reagents and deuteriated solvents were reagent grade and were used without purification.

Methods. The ¹⁸³W nuclear magnetic resonance spectra were recorded on a IBM WP-200-SY spectrometer using a probe specifically designed and fabricated for this application for us by Cryomagnetic Systems, Inc. The ¹⁸³W spectra were recorded at 8.34 MHz in Wilmad 515-7PP 15-mm-i.d. NMR tubes with a probe temperature of 25 °C. ¹H NMR spectra were recorded on a Nicolet NB-360 operating at 361 MHz in 5-mm-i.d. NMR tubes with a probe temperature of approximately 25 °C. Chemical shifts were relative to a 2.0 M solution of sodium tungstate in D₂O external standard (¹⁸³W) and TMS internal standard (¹H). The infrared spectra of samples were recorded on a Perkin-Elmer Model 1430 infrared spectrophotometer, most as KBr pellets (2-4 wt % of compound in KBr). The electronic absorption spectra were obtained on a Hewlett-Packard Model 8451A multidiode array instrument. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA (carbon, hydrogen, nitrogen), and by Galbraith Laboratories, Knoxville, TN (phosphorus, tungsten).

The gas chromatographic analyses of the organic oxidation products were carried out on a Hewlett-Packard 5890 instrument equipped with flame ionization detectors and a 25 m × 0.2 mm (i.d.) 5% phenyl methyl silicone fused-silica capillary column with a variety of temperature programs. Nitrogen was used as the carrier gas, and products were quantified on a Hewlett-Packard 3390A electronic integrator. Gas chromatographic/mass spectrometric analyses of organic products were carried out on a Finnigan 4000 or a VG 70S instrument. Hydrogen gas was quantified either on a Varian gas chromatograph equipped with a molecular sieve 5A column operated at 50 °C and an integrating strip chart recorder or on a Hewlett-Packard 5890 gas chromatograph equipped with a similar column operated at 50 °C and a Hewlett-Packard 3390A electronic integrator. Product yields in all cases were determined by internal standard techniques.

Quantum yields for the formation of the reduced polyoxotungstates with cyclooctane as the organic substrate were determined at 320 nm by ferrioxalate actinometry^{39,40} using the improved method of Baxendale and Bridge.⁴¹ A 320-nm interference filter (fwhm = 9.6 nm, transmission maximum at 320 nm = 21%), a 1.0-cm cell, and optically dense solutions at 320 nm were used in these quantum yield measurements. In addition, the approximate quantum yields were measured for conditions in which the entire charge-transfer absorption manifold of the polyoxotungstate was irradiated simultaneously with the full spectrum of the ozone-free xenon lamp. The different shapes of the absorption envelopes of the polyoxotungstate and the actinometer were taken into account to calculate the full lamp quantum yields. The quantum yields were also found to be comparable to those determined at 320 nm (approximately 0.1), suggesting that they may be relatively invariant over the entire charge-transfer absorption manifold of the polyoxotungstate. The quantum yields in this paper are defined specifically as the moles of electrons represented in the photoreduced product complex divided by the einsteins of photons absorbed by the reactant polyoxotungstate complex.

Oxidative Titration of the Reduced Heteropolytungstates in Alkane/Acetonitrile. Reproducible values for the number of electrons per PW₁₂O₄₀⁶⁻ moiety in the photoreduced heteropolytungstates (heteropoly blues or HPBs)⁴²⁻⁴⁴ were obtained with standard solutions of dichromate

(32) Recent investigations of alkane activation in the gas phase: (a) Baseman, R. J.; Buss, R. J.; Casavecchia, P.; Lee, Y. T. *J. Am. Chem. Soc.* **1984**, *106*, 4108. (b) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Bowers, M. T. *Ibid.* **1985**, *107*, 1788. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1985**, *107*, 7399. (d) Busca, G.; Centi, G.; Trifiro, F. *Ibid.* **1985**, *107*, 7757. (e) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *Ibid.* **1986**, *108*, 1120. (f) Freas, R. B.; Campana, J. E. *Ibid.* **1986**, *108*, 4659. (g) Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *Ibid.* **1986**, *108*, 5675. (h) Cassidy, C. J.; Freiser, B. S. *Ibid.* **1986**, *108*, 5690. (i) Kang, H.; Beauchamp, J. L. *Ibid.* **1986**, *108*, 7502. (j) Tolbert, M. A.; Beauchamp, J. L. *Ibid.* **1986**, *108*, 7509. (k) Tonkyn, R.; Weisshaar, J. C. *Ibid.* **1986**, *108*, 7128. (l) Mandich, M. L.; Steigerwald, M. L.; Reents, W. D., Jr. *Ibid.* **1986**, *108*, 6197. (m) Magnera, T. F.; David, D. E.; Michl, J. *Ibid.* **1987**, *109*, 936. (n) Tews, E. C.; Freiser, B. S. *Ibid.* **1987**, *109*, 4433 and references cited in each.

(33) (a) Cogen, J. M.; Maier, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 7752. (b) Lebrilla, C. B.; Maier, W. F. *Ibid.* **1986**, *108*, 1606. (c) Maier, W. F. *Nature (London)* **1987**, *329*, 531.

(34) Recent studies of methane dehydrogenation over metal oxides: (a) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4117. (b) Otsuka, K.; Liu, Q.; Morikawa, A. *J. Chem. Soc., Chem. Commun.* **1986**, 586. (c) Aika, K.; Moriyama, T.; Takasaki, N.; Iwamatsu, E. *Ibid.* **1986**, 1210. (d) Sofranko, J. A.; Leonard, J. J.; Jones, C. A. *J. Catal.* **1987**, *103*, 302. (e) Jones, C. A.; Leonard, J. J.; Sofranko, J. A. *Ibid.* **1987**, *103*, 311. (f) Hutchings, G. J.; Scurrell, M. S.; Woodhouse, J. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1388. (g) Martin, G.-A.; Mirodatos, C. *Ibid.* **1987**, 1393. (h) Anderson, J. R.; Tsai, P. *Ibid.* **1987**, 1435. (i) Lin, C.-H.; Ito, T.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4808 and references cited in each.

(35) Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528.

(36) Renneke, R. F.; Hill, C. L. *New J. Chem.* **1987**, *11*, 763.

(37) (a) Wu, H. *J. Biol. Chem.* **1920**, *43*, 189. (b) Rocchioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

(38) Small differences in the reactivities of initially prepared acetonitrile/alkane solutions of α -H₃PW₁₂O₄₀·nH₂O (**1**) were observed as a function of the exact protocols used to prepare this complex despite the fact that both the ¹⁸³W and ³¹P NMR spectra of several preparations indicated that all contained only this particular complex. As a result of these small changes, one specific preparation and batch of the complex only was used in all the experiments reported here.

(39) Parker, C. A. *Proc. R. Soc. London, A* **1953**, *220*, 104.

(40) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, A* **1956**, *235*, 518.

(41) Baxendale, J. H.; Bridge, N. K. *J. Phys. Chem.* **1955**, *59*, 783. These authors used NH₄F to catalyze the formation of the spectroscopically observed iron(II) tris(1,10-phenanthroline) reduction product.

or ceric ion. Since the accurate determination of these values was important to the studies described in this paper, some effort was spent to optimize the conditions for oxidative titration of the HPB complexes. Permanganate has been the oxidative titrant of choice for the HPB titrations in the literature.⁴⁵ Nearly all these literature studies have been in aqueous media. In the aprotic and fairly hydrophobic acetonitrile/alkane media employed in catalytic alkane functionalization studies reported here, however, permanganate did not prove to be as satisfactory an oxidative titrant for the reduced polyoxotungstates as either dichromate or ceric ion. Two factors arose in selecting an optimal oxidative titrant for these studies. First, unlike the aqueous HPB oxidative titrations, the HPB titrations here were complicated by the presence of olefin and, in some cases, other alkane oxidation products that were potentially susceptible to further oxidation under the titration conditions. The rates of olefin oxidation by permanganate are substantially faster than for either dichromate or ceric ion, and usually quite rapid at 25 °C.⁴⁶ Second, the oxidative titrants based on MnO_4^- were unstable. Under anaerobic conditions both aqueous solutions of KMnO_4 and acetonitrile solutions of either KMnO_4 or $(n\text{-Bu}_4\text{N})\text{MnO}_4$ ⁴⁷ decomposed to produce insoluble finely divided MnO_2 complicating the titrations. The dichromate and ceric solutions do not lose oxidative titer with time.⁴⁸ Titrations with $(n\text{-Bu}_4\text{N})\text{MnO}_4$ in acetonitrile generally gave poorer and less reproducible results than titrations with aqueous KMnO_4 .

The actual titrations in this work were carried out by adding a degassed standard solution of potassium dichromate or ceric ammonium nitrate in water by gas-tight syringe to the reaction vessel containing the reduced polyoxotungstate and alkane oxidation products under an argon atmosphere. The end points in both cases were readily detected. The values of electrons per reduced polyoxotungstate molecule from these titrations were very reproducible and agreed well with the total yield of organic oxidation products.

In addition to oxidative titrations based on Cr^{VI} and Ce^{IV} , titrations based on O_2 were also satisfactory. The consumption of O_2 was readily monitored by gas chromatography using a molecular sieve 5A column with N_2 as the internal standard. The molar response factor, O_2 to N_2 , was evaluated with known volumes of pure O_2 and N_2 contained in 250-mL Schlenk flasks at 25 °C and atmospheric pressure. O_2 was reduced cleanly to H_2O , and independent experiments demonstrated that any intermediate H_2O_2 generated in the titrations was rapidly reduced by the heteropoly blue species present to H_2O . The value of the number of electrons per polyoxotungstate molecule derived from the O_2 titrations agreed well with the values derived from the titrations discussed above.

Apparatus and Methods for Product Distribution and Kinetics Studies. Most of the product distribution as well as the kinetics studies were carried out in the same type of reaction vessel, a long-necked cylindrical 2.0-mm path length quartz cuvette equipped with a micro magnetic stirring bar, a high-vacuum Teflon stopcock, and a side arm terminating in a standard-taper ground-glass joint. A few of the reactions were run in similar vessels but configured with 1-cm path length rectangular quartz cuvettes rather than the cylindrical ones. These reaction vessels were designed to permit the following: (1) ready introduction of reactant liquids and gases and removal of product liquids or gases for analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) while an inert atmosphere was maintained in the vessel, (2) facile degassing of the contents of the vessel through a dual-manifold vacuum line, (3) sealing of the degassed reactant solutions under inert atmosphere such that no stopcock grease or other chemicals were in contact with the reactants at any time, (4) direct irradiation of the solution with UV in addition to visible light, (5) efficient magnetic stirring of the contents of the cuvette during irradiation, and (6) monitoring of the photochemical reactions directly by electronic absorption spectroscopy. Most of the rate measurements involved following the

distinct blue chromophores of the photoreduced polytungstates via the cuvette portion of the reaction vessel using the rapid-scanning Hewlett-Packard UV-visible spectrophotometer cited above. Some of the rate measurements also involved recording the evolution of hydrogen or organic products with time (see Results).

Some reactions were run in rectangular Pyrex cuvettes (1-cm path length) for comparison with the reactions run in the quartz cuvette reaction vessels described above. For a few experiments that assessed the polyoxometalate reduction products, hydrogen, or organic oxidation products for representative reactions using sunlight as the light source, 25-mL Pyrex reaction vessels were used. These vessels were equipped with grease-free high-vacuum Teflon stopcocks and side arms terminating in standard-taper ground-glass joints to permit facile interfacing with dual-manifold vacuum lines. Reactions in these vessels were generally run with 10.0 mL of alkane/polyoxotungstate/acetonitrile solutions, which were magnetically stirred during gas/degas cycles.

The principal light sources for this work were Oriol ozone-free ($\lambda > 245$ nm) 1000-W Xe arc lamp assemblies equipped with infrared and other filters (specified in the individual experiments) and a series of lenses to focus the beam on the quartz cuvette portion of the reaction vessels. The housing for the reaction vessel maintained the orientation of the cuvette relative to the incident light beam and permitted magnetic stirring of the reaction solution during irradiation. The temperature of all photochemical reactions was approximately 25 °C. Control experiments established that both the rates of production of the reduced polyoxotungstate and the distributions of organic products for the alkane/ $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$ /acetonitrile systems were nearly independent of temperature. For example, over a range of -4 to $+67$ °C, cyclooctane gave only cyclooctene as a product with no detectable *N*-cyclooctylacetamide or other cyclooctyl-containing compounds.

Rate Studies. The following conditions and factors first had to be met before adequately rigorous kinetics measurements could be made on the complex homogeneous systems constituted by polyoxometalates, alkanes, solvent, and light:

(1) The polyoxometalate for these studies had to be readily purified and characterized in solution and had to exhibit reasonably high quantum yields for photooxidation of saturated hydrocarbons when irradiated in its charge-transfer absorption manifold. Many polyoxometalates of Mo and W fulfilled these criteria. Complex 1 was chosen since its absorption and photochemical action spectra had been characterized reasonably thoroughly in earlier catalytic photochemical investigations from our laboratory and because the rates of reoxidation of its reduced form could be systematically controlled by altering the reaction conditions.

(2) The solvent for these studies had to display the ability (a) to dissolve both alkane and the polyoxometalate 1, (b) to resist oxidation under conditions where the alkane had a finite and readily quantified reactivity, (c) not to absorb far into the visible, permitting selective irradiation of the polyoxometalate chromophore in the presence of a large excess of solvent and alkane substrate, and (d) to be obtained in a highly purified state. Although several solvents since our initial work have now been found that fulfill all four criteria above to a reasonable degree, acetonitrile is perhaps the best solvent given all these features and was chosen for the studies here.

The requirements for the kinetics studies and control studies concerning the actual rate and redox behavior are discussed subsequently in the Results.

In a typical rate study, 2.50 mL of a stock solution of 3.3×10^{-3} M 1 and 4.8×10^{-1} M alkane in acetonitrile was placed in the reaction vessel described above, degassed thoroughly (at low temperatures when necessary so as not to lose any solvent or alkane), and then placed in the photochemical apparatus described above. The rates of production of polyoxotungstate reduction products along with hydrogen and alkane oxidation products were monitored by UV-visible spectroscopy and by the chromatographic methods as described above, respectively.

Results

There are both similarities and some differences between the catalytic photochemical dehydrogenation of alkanes by polyoxometalates and the catalytic photochemical dehydrogenation of alcohols by these same complexes. The latter reactions have been investigated by several groups, and similar behavior has been observed for many different alcohol substrates and polyoxometalates.⁴⁹⁻⁵⁷ Both the alkane and alcohol photochemical ox-

(42) Review on heteropoly blues: Pope, M. T. In *Mixed Valence Compounds*; Brown, D. B., Ed.; Reidel: Boston, 1980; pp 365-386.

(43) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983; Chapter 6.

(44) Review of electrochemical reductions of heteropoly compounds: Alimarin, I. P.; Dorokhova, E. N.; Kazanski, L. P.; Prokhorova, G. V. *Zh. Anal. Khim.* **1980**, 35, 2000; *J. Anal. Chem. USSR (Engl. Transl.)* **1980**, 35, 1300.

(45) Exemplary paper citing permanganate titration of heteropoly blues generated by photoreduction of polyoxotungstates in the presence of alcohols: Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 793.

(46) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 5 and references cited therein.

(47) Sala, T.; Sargent, M. V. *J. Chem. Soc., Chem. Commun.* **1978**, 253.

(48) The yellow color of fresh Ce^{IV} solutions, lost during a period of several days due to hydrolysis, could be fully restored by addition of H_2SO_4 . See: Day, R. A., Jr.; Underwood, A. L. *Quantitative Analysis*, 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1980; p 283.

(49) References 50-57 address the catalytic photochemical oxidation of alcohols by polyoxometalates. The references are cited in alphabetical order by the principal investigator's last name.

(50) (a) Darwent, J. R. *J. Chem. Soc., Chem. Commun.* **1982**, 798. (b) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, 395.

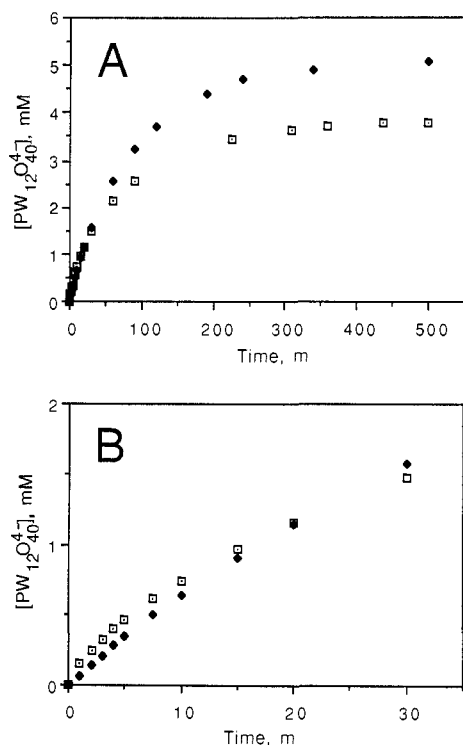
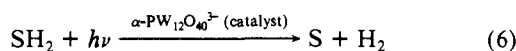
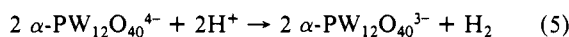
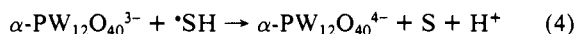
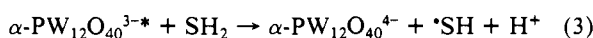
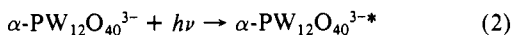


Figure 1. Rates of photochemical production of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ by 2-butanol (\blacklozenge) and cyclooctane (\square) in acetonitrile solution from **1** as a function of time. An expanded plot at early times (**B**) is shown at the bottom. $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]_0 = 3.3$ mM for both substrates. Other conditions are described in the Experimental Section.

idations by heteropoly- and isopolytungstates involve absorption of light (eq 2), oxidation of the substrate by the excited poly-



$\text{SH}_2 =$ organic substrate = alkane, alcohol, others

oxometalate, generating reduced polyoxometalate (eq 3 followed by eq 4), and a slower dark reaction involving reoxidation of the reduced polyoxometalate (eq 5), completing a net catalytic cycle (eq 6). Several points regarding the photochemical dehydrogenation of alkane substrates versus alcohol substrates are illustrated in Figures 1 and 2. The plots of the concentration of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ under conditions where the rate of eq 5 is very slow (no Pt(0),

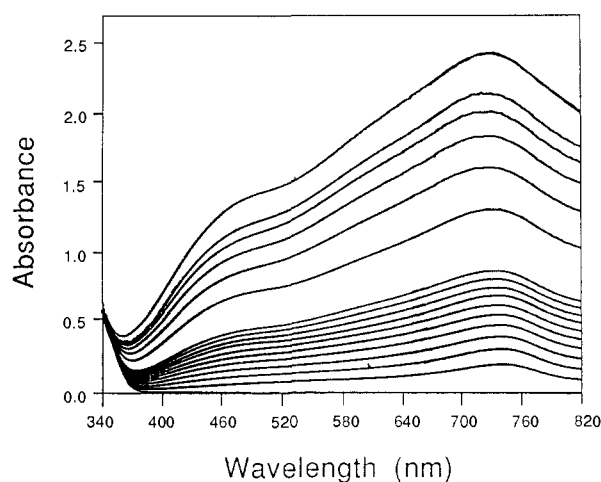


Figure 2. Absorption spectra of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ produced upon irradiation of cyclooctane/acetonitrile solutions of **1** at 2-min intervals ($t = 0\text{--}20$ min) and at 20-min intervals ($t = 20\text{--}120$ min). The top spectrum corresponds to $t = 240$ min, the time after which there is no further increase in absorbance. $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]_0 = 3.3$ mM; a 2-mm path length cell was used. Other conditions are described in the Experimental Section.

25 °C) as a function of irradiation time in polyoxometalate photooxidations of alkanes are nearly always more curved than the corresponding plots for the alcohols. Figure 1 displays plots using the same polyoxometalate catalyst ($\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40} \cdot 10.7\text{H}_2\text{O}$, **1**), reaction vessel, solvent, light source, reaction temperature, and analysis conditions for cyclooctane, an exemplary alkane, and 2-butanol, an exemplary alcohol. Figure 2 illustrates the time dependence for generation of the reduced polyoxotungstate chromophore during irradiation of a cyclooctane/acetonitrile solution of **1**. In the case of the alcohol photochemical dehydrogenations by **1**, we and others have shown that the final steady-state spectrum corresponds to the presence of three or more electrons per $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ moiety, implying that the initial less reduced polyoxotungstate species is susceptible to further reduction.⁴⁹⁻⁵⁷ In other words, the initially produced less reduced polyoxotungstate species is still photochemically active. A more photochemically active reduced polyoxotungstate would lead to an apparently smaller inner-filter effect and thus to a smaller curvature in the [reduced polyoxotungstate] versus irradiation time plot, as is observed (Figure 1).⁵⁸ The difference in these curves and the shape of reduced polyoxotungstate spectra as a function of irradiation time for alkane versus alcohol reactions became apparent once methods had been found to adequately quantitate the degree of reduction of the polyoxometalates in the aprotic fairly hydrophobic reaction media required for the alkane functionalization chemistry.

Aqueous dichromate or ceric ion titrations of photoreduced polyoxotungstates in alkane/acetonitrile solutions under anaerobic conditions gave reasonable and reproducible values for the number of electrons per polyoxotungstate molecule. Permanganate, the oxidative titrant of choice in the literature titrations of heteropoly blues in conventional aqueous media, could not be used to titrate the photoreduced polyoxometalates in the alkane dehydrogenation reactions. Permanganate titrations suffered from two problems that the dichromate and ceric solutions did not (see the Experimental Section). Anaerobic oxidative titration with either dichromate or ceric ion established that in the final steady-state absorption spectra achieved under constant irradiation with a 1000-W ozone-free Xe lamp using quartz vessels ($\lambda > 245$ nm), the value for A_∞ in all alkane reactions examined where **1** was the catalyst was approximately one electron per PW_{12} moiety. This is in marked contrast to all the alcohol photooxidations by polyoxometalates where the reduced polyoxometalate chromophore

(51) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347.

(52) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148.

(53) (a) Nomiya, K.; Sugie, Y.; Miyazaki, T.; Miwa, M. *Polyhedron* **1986**, *5*, 1267. (b) Nomiya, K.; Miyazaki, T.; Maeda, K.; Miwa, M. *Inorg. Chim. Acta* **1987**, *127*, 65.

(54) (a) Papaconstantinou, E.; Dimotikali, D.; Politou, A. *Inorg. Chim. Acta* **1980**, *46*, 155. (b) Papaconstantinou, E. *J. Chem. Soc., Chem. Commun.* **1982**, 12. (c) Dimotikali, D.; Papaconstantinou, E. *Inorg. Chim. Acta* **1984**, *87*, 177. (d) Ioannidis, A.; Papaconstantinou, E. *Inorg. Chem.* **1985**, *24*, 439. (e) Argitis, P.; Papaconstantinou, E. *Inorg. Chem.* **1986**, *25*, 4386.

(55) Savinov, E. N.; Saidkhanov, S. S.; Parmon, V. N.; Zamaraev, K. I. *Dokl. Phys. Chem. (Engl. Transl.)* **1983**, *272*, 741.

(56) Ward, M. D.; Brazdil, J. F.; Grasselli, R. K. *J. Phys. Chem.* **1984**, *88*, 4210.

(57) (a) Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 793. (b) Yamase, T.; Watanabe, R. *J. Chem. Soc., Dalton Trans.* **1986**, 1669.

(58) For a discussion of the inner filter effect see: Demas, J. N. *Creation and Detection of the Excited State*; Ware, W. R., Ed.; Dekker: New York, 1976; Vol. 4, pp 11-12.

at A_{∞} corresponds to three or more electrons per polyoxometalate. Thus, the only reduced polyoxotungstate species present in appreciable concentrations in the alkane reactions using **1** is α -PW₁₂O₄₀⁴⁻. These results explain in part the greater curvature in the [product] vs time plots in Figure 1 for alkanes relative to alcohols and the nearly isosbestic behavior and the constancy of the reduced polyoxotungstate spectra in Figure 2.

The presence of a Pt(0) hydrogen evolution catalyst (e.g., colloidal Pt(0) or powdered Pt(0) on carbon) can increase the rate of the reoxidation process (eq 5) considerably. As a consequence, the optimal turnover rates for the overall catalytic reaction (eq 6) usually require the presence of such a hydrogen evolution catalyst. Maximal turnover rates are achieved with low concentrations of **1**, high concentrations of alkane, and high light intensities with continuous removal of hydrogen as it is formed. With the faster alkanes such as cyclooctane, 30 or more turnovers can be achieved in a day with no apparent decomposition of the catalyst. Although the photochemical functionalization of alkanes is clearly catalytic based on α -dodecatungstophosphate, this polyoxometalate is far from the most efficient polyoxotungstate with respect to turnover rates. For the polyoxometalate alkane functionalization system examined in detail here, alkane/**1**/CH₃CN/light ($\lambda > 245$ nm), the absence of Pt(0) renders eq 5 2–3 orders of magnitude slower than the production of the reduced polyoxotungstate (eq 2–4). The presence of only α -PW₁₂O₄₀⁴⁻ in these photochemical reactions and the slow rate of reoxidation of this species by hydrogen evolution simplify the subsequent kinetic behavior and its interpretation. The quantum yields for production of reduced polyoxotungstates vary with the polyoxotungstate used and the reaction conditions. An exemplary quantum yield for production of α -PW₁₂O₄₀⁴⁻ in the cyclooctane/**1**/CH₃CN system evaluated at 320 nm (9-nm band-pass) is 0.1. Similar quantum yields were obtained with only 320-nm and full lamp ($\lambda > 245$ nm) radiation, suggesting that the quantum yields for production of this compound may be fairly constant throughout the charge-transfer absorption envelope of α -PW₁₂O₄₀³⁻. Nearly constant quantum yields as a function of the wavelength of the incident light for photooxidation of alcohol and other substrates by polyoxotungstates have been documented.^{54,57,59}

The next aspect of the kinetics of the cyclooctane/**1**/CH₃CN/light ($\lambda > 270$ nm) system that needed to be addressed was the nature of all the organic products derived from photooxidation of the alkane. These products not only had to be identified, but their stability under the reaction conditions, during both irradiation and postirradiation, including their ability to react with either α -PW₁₂O₄₀³⁻ or α -PW₁₂O₄₀⁴⁻ had to be determined. An unusual but important point concerning this hydrocarbon photooxidation chemistry noted earlier is that the relative reactivities of the alkane substrates and the alkene, *N*-alkylacetamide, and other products are remarkably similar.³⁶ As a consequence, effectively no further oxidation of these products under the pseudo-first-order conditions used here (150 equiv of alkane/equiv of **1**) could be observed in either rate or product distribution studies. Conditions were found, those given in the Experimental Section, where eq 3 and 4 were irreversible as written and α -PW₁₂O₄₀⁴⁻, the only reduced polyoxotungstate present, did not undergo subsequent reactions with any of the starting materials or products under the reaction conditions. Independently it was shown that the absorption of light by α -PW₁₂O₄₀⁴⁻ and subsequent photooxidation of alkanes by the excited states of this species proceeded at negligible rates in alkane/acetonitrile media with the same light source ($\lambda > 270$ nm) relative to the analogous processes for α -PW₁₂O₄₀³⁻. In Figures 3 and 4 are plotted the concentrations of both the reduction product, α -PW₁₂O₄₀⁴⁻, and the alkane-derived oxidation products with time for reaction of cyclooctane and *cis*-1,2-dimethylcyclohexane, respectively, in the absence of a hydrogen evolution catalyst. The following four points are noted. First, the reaction slows down as the α -PW₁₂O₄₀³⁻ is converted into α -PW₁₂O₄₀⁴⁻. Second, the only appreciable organic

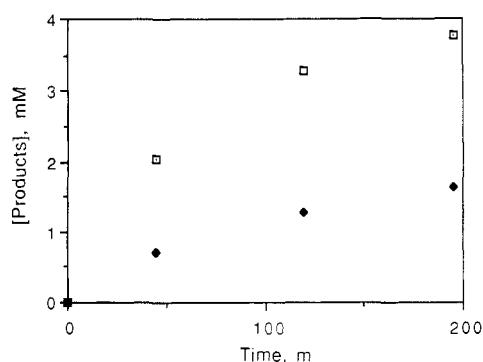


Figure 3. Generation of polyoxotungstate reduction product, α -PW₁₂O₄₀⁴⁻ = P_r (□), and organic oxidation product, cyclooctene (◆), upon irradiation of **1** in acetonitrile/cyclooctane as a function of time. No other products are observed in this reaction. A redox balance is maintained since two molecules of P_r are produced for each molecule of cyclooctene. [α -PW₁₂O₄₀³⁻]₀ = 3.3 mM; other conditions are described in the Experimental Section.

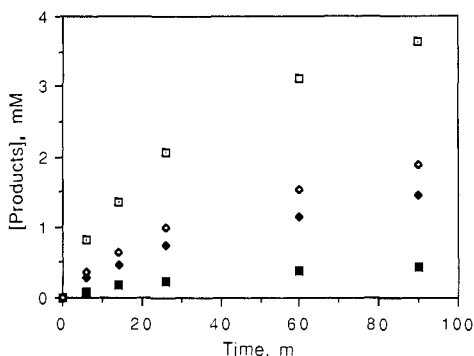


Figure 4. Generation of polyoxotungstate reduction product, α -PW₁₂O₄₀⁴⁻ = P_r (□), and organic oxidation products, 1,2-dimethylcyclohexene (◆), 1,6-dimethylcyclohexane (■), and total alkene (◇), upon irradiation of **1** in acetonitrile/*cis*-1,2-dimethylcyclohexane as a function of time. A redox balance is maintained between all the products at all times during the course of the reaction. [α -PW₁₂O₄₀³⁻]₀ = 3.3 mM; other conditions are described in the Experimental Section.

products are the corresponding alkenes in these systems, cyclooctene in the former case and the isomeric dimethylcyclohexenes in the latter case. Third, for some of the alkane substrates there is good balance between alkane oxidation products and the α -PW₁₂O₄₀⁴⁻ reduction product (stoichiometry: 2 equiv of the one-electron product α -PW₁₂O₄₀⁴⁻/equiv of the two-electron product alkene). In the reactions where there is a poor product balance (the organic oxidation products substantially lower in concentration than α -PW₁₂O₄₀⁴⁻), we have searched systematically for other oxidation products, including nonvolatile carboxylic acids, and have failed to find any. Fourth, the product balances in these reactions are maintained throughout the reactions. These and other data indicate that the observed product distributions are, in most cases, kinetically controlled. Experiments such as these under stoichiometric or low-turnover conditions render an examination of the product distributions from several representative alkane photochemical dehydrogenation reactions more useful (Table I).

Several points are apparent on inspection of the organic product distributions in Table I: (1) The principal alkane-derived oxidation products in most cases are the maximally substituted alkenes. (2) The selectivity with respect to generation of the organic products varies with the alkane substrate, with the highest selectivities for alkene seen with some cycloalkanes and acyclic alkanes capable of forming the trisubstituted and tetrasubstituted products. (3) The presence of the hydrogen evolution catalyst, Pt(0), has little effect on the product distribution for oxidation of some substrates (e.g., *cis*-1,2-dimethylcyclohexane) but has marked effects on the product distributions with most substrates (e.g., cyclooctane and others not listed in Table I). (4) The distributions of products in the systems containing Pt(0) vary as a function of irradiation

(59) Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. M.; Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.*, following paper in this issue.

Table I. Representative Product Distributions from the Homogeneous Photochemical Functionalization of Alkanes by α -Dodecatungstophosphate^a

P ^b	conditions ^c	$h\nu$ time ^d	organic product yields, ^{b,e} %		
			alkene	RNHAc	RR
Cyclooctane Oxidation Reactions					
1	no Pt(0), closed	45	100 (71) {0.22}	0	0
		120	100 (78) {0.39}	0	0
		195	100 (86) {0.49}	0	0
1	Pt(0), closed	262	91 [60] {0.96}	0	9 [6] {0.10}
		545	82 [65] {1.3}	1.2 [0.9] {0.02}	17 [13] {0.27}
		1297	68 [62] {3.6}	11 [10] {0.57}	15 [13] {0.78} ^f
1	no Pt(0), purged with Ar	120	100 (85) {0.42}	0	0
1	Pt(0), purged with Ar	120	91 {0.69}	0	9 {0.07}
		260	86 [1.7]	0	14 {0.26}
		370	88 [2.9]	0	12 {0.40}
2	no Pt(0), closed	131	77 (103) {0.19}	0	23 (31) {0.06}
2,3-Dimethylbutane Oxidation Reactions					
1	no Pt(0), closed	205	100 (93) {0.60}	0	0
Cyclohexane Oxidation Reactions					
1	no Pt(0), closed	233	100 (65) {0.10}	0	0
2	no Pt(0), closed	120	68 (86) {0.10}	0	32 (41) {0.05}
Methylcyclohexane Oxidation Reactions					
1	no Pt(0), closed	90	100 (111) {0.29}	0	0
1	Pt(0), closed	500	95 [108] {1.2} ^g	0	0
		1200	57 [60] {2.3}		
<i>cis</i> -1,2-Dimethylcyclohexane Oxidation Reactions					
P ^b	conditions ^c	$h\nu$ time ^d	1,2-dimethylcyclohexene	1,6-dimethylcyclohexene	
1	no Pt(0), closed	6	77 (68) {0.08}	23 (21) {0.03}	
		14	72 (69) {0.14}	28 (28) {0.06}	
		26	76 (73) {0.23}	24 (23) {0.07}	
		60	76 (74) {0.35}	24 (24) {0.11}	
		90	77 (81) {0.44}	23 (23) {0.13}	
1	Pt(0), closed	140	78 [76] {0.66}	20 [19] {0.17}	
		327	80 [73] {1.3}	20 [18] {0.31}	
		495	81 [79] {1.8}	19 [18] {0.41}	

^aAll reactions run under optically dense conditions at 25 °C with the procedures and reactant quantities indicated in the Experimental Section. Product distributions were quantified by GC or GC/MS after approximately 0.5% alkane conversion for the reactions without Pt(0) hydrogen evolution catalyst and 1–4% alkane conversion for the reactions with Pt(0). ^bP = polyoxometalate catalyst; 1 = α -H₃PW₁₂O₄₀·*n*H₂O; 2 = (*n*-Bu₄N)₃(α -PW₁₂O₄₀); P_r = α -PW₁₂O₄₀⁴⁻. ^cConditions described in the Experimental Section. The second, tenth, and twelfth (last) reactions were run in Pyrex Schlenk flasks with a reactant volume of 10 mL. ^dTime of irradiation in minutes using light source and apparatus described in the Experimental Section. ^eYields before parentheses are equivalents of that organic product divided by total equivalents of all detectable organic products generated \times 100. Yields in parentheses are equivalents of electrons represented by organic oxidation products divided by equivalents of reduced polyoxometalate α -PW₁₂O₄₀⁴⁻ generated \times 100. These yields are only reported for the systems lacking Pt(0). Yields in brackets are equivalents of electrons based on organic oxidation products divided by equivalents of hydrogen generated \times 100. These yields are only reported for the systems that contain Pt(0). The yields in braces are turnovers of catalyst = moles of organic product divided by moles of polyoxometalate. RNHAc is the *N*-alkylacetamide and RR the alkylalkane, derived from reactant alkane. Alkyl methyl ketone (RCOMe) is seen as a byproduct in some reactions. ^fTrace amounts of alcohol and ketone were also found after 1297 min. ^gSeveral unidentified organic products were present.

time. Independent experiments have established clearly that the Pt(0) is not simply an innocent catalyst for hydrogen evolution (eq 5) and this process only but that Pt(0) enhances production of all types of byproducts, *N*-alkylacetamide (RNHAc), alkyl-alkane dimer (RR), and alkyl methyl ketone (RCOMe) and that the generation of these byproducts increases with time. Control studies have established that the *N*-alkylacetamides and the alkyl methyl ketones are not formed to an appreciable degree from the initially produced alkenes under the reaction conditions. (5) Not surprisingly, when these photochemical functionalizations are run as one-pot reactions in closed vessels such that H₂ accumulates, the effects of the Pt(0) on the catalytic formation of the byproducts are enhanced. (6) The inherent selectivities for production of the organic products in the absence of Pt(0) vary markedly with the polyoxotungstate. For example, the formation of dimers is far more pronounced when W₁₀O₃₂⁴⁻ as opposed to α -PW₁₂O₄₀³⁻ is used as the catalyst.^{23b}

With the control and product studies above at hand, determination of the major features of the rate law for the exemplary system cyclooctane/1/CH₃CN/light ($\lambda > 245$ nm) was relatively straightforward. The most quantitative method for following most of the rate processes was to monitor the blue chromophore of α -PW₁₂O₄₀⁴⁻ with time. The rate of production of this species as a function of the concentration of alkane substrate is shown

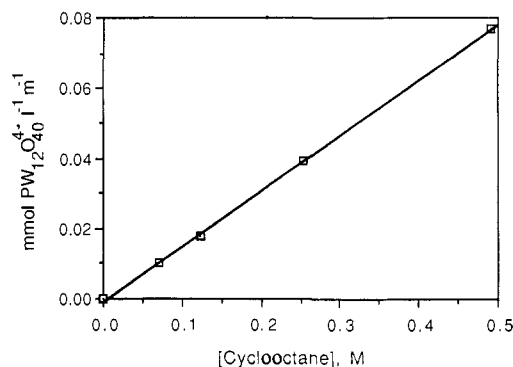


Figure 5. Initial rate of formation of α -PW₁₂O₄₀⁴⁻ as a function of the concentration of cyclooctane in the α -PW₁₂O₄₀³⁻/cyclooctane/CH₃CN/ $h\nu$ ($\lambda > 245$ nm) system. [α -PW₁₂O₄₀³⁻]₀ = 0.41 mM in acetonitrile; other conditions are described in the Experimental Section.

in Figure 5. The plot is rigorously first order over a wide range in cyclooctane concentration. The rate of production of α -PW₁₂O₄₀⁴⁻ is also first order in light intensity (Figure 6), indicating that one-photon processes dominate the observed photochemistry for this system. The rate behavior as a function of the initial

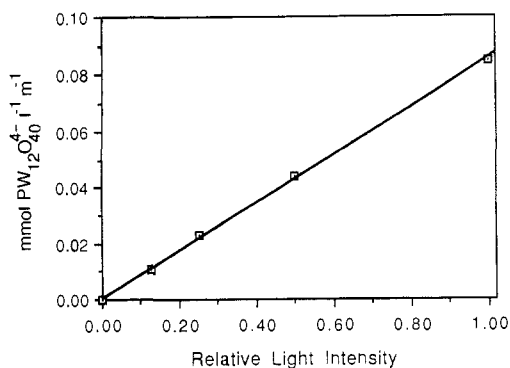


Figure 6. Initial rate of formation of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ as a function of light intensity in the $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ /cyclooctane/ $\text{CH}_3\text{CH}/h\nu$ ($\lambda > 245$ nm) system. Transmittance UV neutral-density filters (12.5%, 25%, 50%) were used. 100% transmittance corresponds to full irradiance of the xenon arc lamp without any filter. $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]_0 = 0.41$ mM and $[\text{cyclooctane}] = 0.48$ M in acetonitrile; other conditions are described in the Experimental Section.

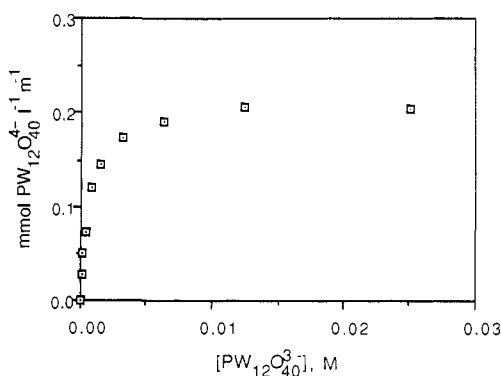


Figure 7. Initial rate of formation of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ as a function of the concentration of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ in the $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ /cyclooctane/ $\text{CH}_3\text{CN}/h\nu$ ($\lambda > 245$ nm) system. $[\text{Cyclooctane}] = 0.48$ M; other conditions are described in the Experimental Section.

concentration of the heteropolytungstate $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ is more complex. In Figure 7 is illustrated the change in the dependence from approximately first order at low concentrations of catalyst to zero order at approximately 6.6 mM. To establish whether or not the curvature in Figure 7 was a consequence of saturation kinetics, saturation with respect to absorption of incident light, or other factors, two lines of experimentation were explored. The first experiments involved irradiation of two 1.0-cm path length quartz cuvettes each containing the same solution of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ and alkane in acetonitrile, placed back to back in the light beam of the photochemical apparatus. Subsequent to irradiation, the photochemical products in both the front and back cuvettes were quantified. This procedure was followed on several stock solutions that varied only in the concentration of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$. These experiments indicated that at high concentrations of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ effectively all the light was being absorbed by the contents of the front cell and that the curvature in the rate vs $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]$ plot (Figure 7) could be explained principally by light absorption effects. Second, the calculated curves for $+d[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}]/dt$ as a function of the concentration of the catalyst **1** matched the experimental curves quite well for both irradiation with 320-nm light only and irradiation with the full lamp ($\lambda > 245$ nm).⁶⁰ These two lines of experimental evidence for limiting light absorption effects do not preclude a component of kinetic saturation with respect to $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ to account for the curvature in the rate vs $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]$ plot, however. Finally an examination of

(60) Theoretical curves were constructed for irradiation at a single wavelength (320 nm) with the equation $(+d[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}]/dt)_\lambda = I_{0\lambda}(1 - 10^{-A(\lambda)})\phi_\lambda$, where λ , $I_{0\lambda}$, $A(\lambda)$, and ϕ_λ are the wavelength, the intensity of the incident light beam, the absorbance, and the quantum yield at wavelength λ , respectively. For irradiation over the complete spectrum of the lamp, an integration over all wavelengths (treating ϕ_λ as a constant) was performed.

Table II. Initial Rates for Organic Substrate Oxidations

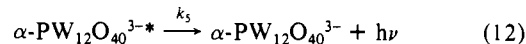
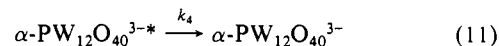
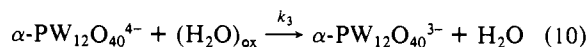
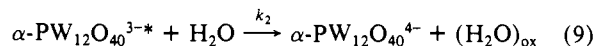
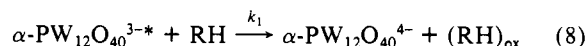
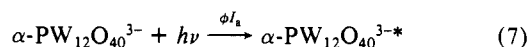
organic substrate	initial rate, $\text{mM}\cdot\text{m}^{-1}$
<i>n</i> -pentane	3.6×10^{-4}
<i>n</i> -hexane	6.1×10^{-4}
<i>n</i> -heptane	8.7×10^{-4}
<i>n</i> -octane	1.0×10^{-3}
<i>n</i> -nonane	1.1×10^{-3}
cyclopentane	1.6×10^{-3}
cyclohexane- <i>h</i> ₁₂	2.1×10^{-3}
cyclohexane- <i>d</i> ₁₂	1.5×10^{-3}
cycloheptane	4.0×10^{-3}
cyclooctane	9.6×10^{-3}
cyclodecane	1.4×10^{-2}
2,3-dimethylbutane	1.9×10^{-3}
2,2-dimethylbutane	2.4×10^{-4}

$+d[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}]/dt$ as a function of the concentration of small quantities of H_2O and D_2O added to the system established not only that there was an inhibition by H_2O (D_2O) but also that there was a demonstrable and reproducible inverse solvent kinetic isotope effect, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.80$.

The observed rate constants at early reaction times under optically dense conditions for production of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ upon irradiation of **1** as a function of the alkane are summarized in Table II. The relative rates in this table are unusual. Such kinetic selectivities and primary kinetic isotope effects, $k_{\text{cyclohexane-}h_{12}}/k_{\text{cyclohexane-}d_{12}} = 1.38$, are not seen in C-H bond oxidation processes involving three-membered-ring, hydride abstraction or even classical radical-atom abstraction transition states (see Discussion).

Discussion

Rate Behavior and General Characteristics of the Photochemical Alkane Functionalization Reactions. Equations 7–12 represent the minimal mechanism that explains not only the rate behavior but also the relevant control experiments described above. This mechanism (eq 7–12) is derived for the Pt(0)-free system.



Analysis of the polyoxotungstate-catalyzed photochemical functionalization of alkanes begins with formation of the polyoxometalate excited state (eq 7) and subsequent substrate oxidation by this excited state (eq 8). The quantity of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}$ is dictated by ϕI_a , where I_a is the intensity of the light absorbed by $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ and ϕ is the quantum yield for production of the excited state(s) that are competent to oxidize alkane, RH, from the initially produced excited state(s). For the systems examined in detail here, the latter process (eq 8) is represented in simplest terms as oxidation of alkane by the excited polyoxotungstate, $\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}$, producing reduced polyoxotungstate, $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$, and oxidized alkane, represented for the moment as $(\text{RH})_{\text{ox}}$. Limited experimental^{61,62} and theoretical⁶³ data are now available on the electronic structure of polyoxometalates, including the d⁰

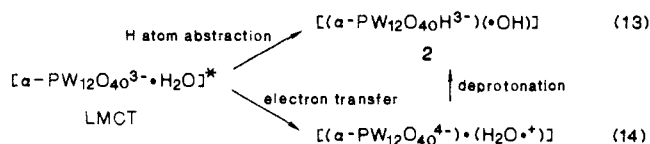
(61) Some general discussions of the electronic structure of polyoxometalates in both oxidized and reduced forms are in: Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

(62) Nomiya, K.; Sugie, Y.; Amimoto, K.; Miwa, M. *Polyhedron* **1987**, *6*, 519.

(63) (a) Taketa, H.; Katsuki, S.; Eguchi, K.; Seiyama, T.; Yamazoe, N. *J. Phys. Chem.* **1986**, *90*, 2959. (b) Moffat, J. B. *J. Mol. Catal.* **1984**, *26*, 385. (c) Klemperer, W. G., unpublished results.

T_d symmetry $\alpha\text{-XM}_{12}\text{O}_{40}^{n-}$ structure. The $X\alpha$ calculation of Katsuki, Yamazoe and co-workers of the T_d phosphomolybdate, $\alpha\text{-PMO}_{12}\text{O}_{40}^{3-}$, a species isoelectronic and isostructural to **1**, would ascribe the ligand to metal charge-transfer (LMCT) excited states of P^* primarily to transfer of electron density from the lone-pair electrons on the doubly bridging oxygens to the adjacent $d^0 \text{W}^{\text{VI}}$ ions.^{63a} Until more data on the electronic structure of polyoxometalates, and in particular **1**, are available, however, we prefer not to speculate regarding the relationship of the possible features of the frontier orbitals of P^* and the observed redox and photo-redox activity exhibited by these species in solution. Previous work from our laboratory documenting the substantial effects of medium on the photochemical action spectrum for P reduction/organic substrate oxidation testifies to the marked effect that solvation can have on polyoxometalate frontier orbitals involved in redox processes.^{59,64,65} Since there is very little if any perturbation of the electronic absorption spectrum of P or the photochemical redox action spectra for P reduction and alkane oxidation by the presence of alkane substrate in solution, it is reasonable to assign the excited state, P^* , involved in these alkane oxidation processes as arising primarily from intramolecular oxide ligand to tungsten metal charge-transfer (LMCT) character rather than intermolecular electron donor (alkane) to acceptor (P) charge-transfer character (Mulliken EDA behavior). Recent investigations of heteropoly anions in dipolar aprotic organic media appear to exhibit at least a component of the latter behavior.^{59,64,65} The collective data now available, of course, do not preclude attack on alkane by more than one LMCT excited state of P. It will doubtless be difficult, however, to distinguish spectroscopically or kinetically between two or more such states generated simultaneously upon excitation, when all are capable of oxidizing alkane.

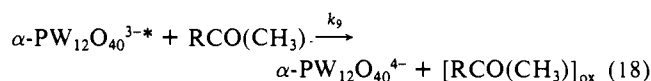
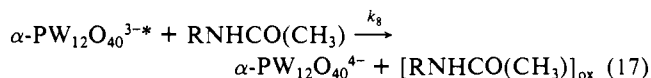
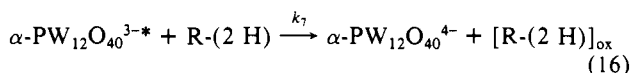
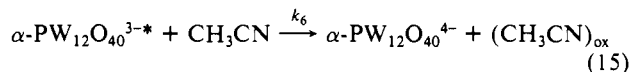
The inverse dependence of the rate of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ production by water and the inverse solvent isotope effect, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.80$, argue strongly that a water-dependent process is depleting the excited state(s), i.e. $\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}$, that is (are) competent to oxidize alkane. This is most simply represented by eq 9. In principle, the initially generated LMCT state could produce hydroxyl radical specie(s) **2** either by hydrogen abstraction or by electron transfer followed by deprotonation of hydrogen-bonded or proximal water molecules of solvation (eq 13 and 14, respectively), two kinetically indistinguishable pathways. Any hydroxyl



radical or peroxide species produced proximal to $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ would likely reoxidize the latter back to $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ at rates at least competitive with oxidation of alkane substrate. These processes are collectively represented by eq 10. Such reoxidation processes would effectively decrease the quantum yield with respect to production of the alkane functionalization products. Independent experiments showing a rapid rate of oxidation of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ by H_2O_2 , a far less reactive oxidant than hydroxyl radical, are fully in accord with the water oxidation/ $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ reoxidation hypothesis. Yamase and co-workers have invoked the intermediacy of hydroxyl radicals in photoinduced redox processes involving the isopoly compounds of Mo with alkylammonium or related organic cations.⁶⁶

The remaining processes that constitute the minimal mechanism are eq 11 and 12. Since the quantum yields of fluorescence are

very small under the reaction conditions (k_5 very small) and the overall quantum yields for production of $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ only average approximately 0.1, this requires that the collective radiationless decay processes, represented in simplest terms by eq 11 (k_4), are substantial. The dissipation of the kinetically productive excited state(s), $\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}$, by oxidation of the solvent, acetonitrile (eq 15), is nil ($k_6 \sim 0$), and oxidation of the initial kinetic products



from alkane oxidation, alkene (eq 16), *N*-alkylacetamide (eq 17), and alkyl methyl ketone (eq 18) at early reaction times is also effectively zero. Although quenching of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}$ by ground-state $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ or $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ is, in principle, possible, it is difficult to garner experimental evidence for such processes in the particular system investigated here, $\text{RH}/1/\text{CH}_3\text{CN}/h\nu$. As a consequence and for the sake of simplicity, we have not written equations for these processes that would require inclusion in the rate law expression.

It is clear from the relative sizes of the observed rate constants in Table II that the rate-determining activated complex contains alkane. All 13 alkanes examined give distinct reproducible rates, and the rate for each alkane is outside experimental error of the rate for any other alkane (a possible exception is *n*-pentane relative to 2,2-dimethylbutane). Although the relative rates do not preclude the possibility that there may be two or more processes with similar rates that are co-rate-limiting, a reasonable hypothesis at the moment given all the data is that a single irreversible step involving alkane and P^* is rate limiting. The reverse of reactions 15–18 is not likely to be important (excited-state generation from the thermal reaction of the products in any of these reactions is likely to encounter a fairly substantial activation barrier defined in part by the exothermicities of the forward reactions).

The rate for the overall alkane functionalization processes, monitored by production the one-electron-reduced form of **1**, $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$, based on the mechanism given above would be eq 19, where steady-state expressions have been substituted for $\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}$ and $(\text{H}_2\text{O})_{\text{ox}}$.

$$\begin{aligned} \text{rate} = & +d[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}]/dt = (\phi I_a/k_1[\text{RH}] + k_2[\text{H}_2\text{O}] + \\ & k_4 + k_5 + k_6[\text{CH}_3\text{CN}] + \sum_{i=7-9} k_i[\text{organic products}]_i)(k_1[\text{RH}] \\ & + k_2[\text{H}_2\text{O}] - k_2k_3[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}][\text{H}_2\text{O}]/k_3[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}]) \quad (19) \end{aligned}$$

$\text{PW}_{12}\text{O}_{40}^{3-*}$ and $(\text{H}_2\text{O})_{\text{ox}}$. Canceling factors and terms and accounting for the relative effective sizes in the terms for $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}]$ as discussed above, this complex expression simplifies to eq 20 for early reaction times. Since $(k_2[\text{H}_2\text{O}] + k_4) \gg$

$$+d[\alpha\text{-PW}_{12}\text{O}_{40}^{4-}]/dt = \frac{\phi I_a k_1[\text{RH}]}{[k_1[\text{RH}] + k_2[\text{H}_2\text{O}] + k_4]} \quad (20)$$

$k_1[\text{RH}]$, we have a limiting expression in accord with all the rate data: first-order dependence on alkane concentration, the inverse dependence on H_2O concentration, the first-order dependence on light intensity, and saturation with respect to the concentration of the catalyst, $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$. The concentration of the latter is included in ϕI_a term, as is the usual convention. The photochemistry becomes zero order in $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ in large part if not entirely as a consequence of light absorption effects. A linear plot of the rate as a function of cyclooctane (RH) concentration indicates that $k_1[\text{RH}]$ is small. In contrast to the literature studies where the alcohol photooxidations have been investigated, however,

(64) Prosser-McCartha, C. M.; Kadkhodayan, M.; Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1747.

(65) Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *Inorg. Chem.* **1987**, 26, 1436.

(66) (a) Yamase, T.; Ikawa, T. *Bull. Chem. Soc. Jpn.* **1977**, 50, 746. (b) Yamase, T. *J. Chem. Soc., Dalton Trans.* **1978**, 238. (c) Yamase, T.; Sasaki, R.; Ikawa, T. *J. Chem. Soc., Dalton Trans.* **1981**, 628. (d) Ohashi, Y.; Yanagi, K.; Sasada, Y.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1982**, 55, 1254. (e) Yamase, T. *Inorg. Chim. Acta* **1982**, 64, L155. (f) Yamase, T. *J. Chem. Soc., Dalton Trans.* **1982**, 1987. (g) Yamase, T. *Inorg. Chim. Acta* **1983**, 76, L25 and references cited therein.

the studies of alkane photooxidation reported here are hampered by the limited solubility of alkanes in the solvent (CH₃CN), making quantification of k_1 difficult for these systems. A modified steady-state expression in which $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-*}]$ is replaced by the total absorption, $I_{0\lambda}(1 - 10^{-\epsilon_{\lambda}b(P)})$, where $P = \alpha\text{-PW}_{12}\text{O}_{40}^{3-}$, integrated over all λ , accounts for a plateau in rate at high $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]$ where optically dense conditions have been attained at practically all the wavelengths in the charge-transfer absorption envelope of the complex.

Nature of the Substrate Activation Process. The information now available from rate measurements and kinetic product distributions allows us to address the nature of the substrate oxidation process (eq 8) with respect to the substrate moiety and the nature of the initial alkane oxidation product, $(\text{RH})_{\text{ox}}$ in eq 8. Four possible transition states for the alkane activation process exist: a carbonium ion, **3** (R^+), produced by hydride abstraction; a carbanion, **4** (R^-), produced by deprotonation; a radical, **5** (R^\cdot), produced by hydrogen atom abstraction; and an alkane cation radical, **6** ($\text{RH}^{+\cdot}$), produced by electron transfer.⁶⁷ Although thermochemical calculations have led to the speculation that hydride abstraction might be operable in at least one alkane oxidation reaction, combustion,⁶⁸ experimental evidence for this process, or transition state **3**, is not compelling for any homogeneous reaction involving the oxidation of alkanes by metal complexes. The principal argument for carbonium ion-hydride character vs radical-hydrogen atom character in the C-H cleavage transition state is the high primary to secondary to tertiary C-H attack selectivities. These selectivities for hydride abstraction from alkanes are not known with certainty from experiment, but they have been approximated as 1:10⁴:10⁸, based on the ease of carbonium formation from alkyl halides.⁶⁹ The data in Table II show clearly that although the C-H cleavage selectivities favor tertiary C-H bonds, the primary to secondary to tertiary C-H attack selectivities are far less pronounced and in the range of hydrogen atom abstraction processes (vide infra). The fact that carbonium ion is not generated directly in the rate-determining substrate activation process does not, of course, preclude the generation of carbonium ions in subsequent steps of the mechanism. Indeed, as discussed below, many of the experimental data presented in this paper are compatible with the presence of carbonium ions in some processes. Transition state **4** is most unlikely for the substrate activation step in the mechanism. Alkanes are some of the least acidic compounds known⁷⁰ while many polyoxometalate anions, including **1**, are weak bases.⁷¹

Substrate activation by radical hydrogen abstraction, transition state **5**, and electron transfer, transition state **6**, are most compatible with the data. Five facts, however, argue against a classical atom abstraction. First, there is a monotonic increase in the relative reactivities of the C₅-C₁₀ cycloalkanes. Three other types of other radical processes that reflect the relative stabilities of the C₅-C₈ cycloalkyl radicals all indicate that C₆ is less reactive than both C₅ and C₇.⁷²⁻⁷⁴ Second, the ratios of attack on primary vs

secondary vs tertiary C-H bonds are quite constant in most if not all investigated liquid-phase and gas-phase reactions between conventional radicals and alkanes. For example, the primary vs secondary vs tertiary selectivities for Cl[·] (1:3.5:4.2; 25 °C, liquid phase),⁷⁵ Br[·] (1:80:1700; 150 °C, gas phase),⁷⁶ and *tert*-butoxy radicals (1:12:44; 40 °C, liquid phase)⁷⁷ with respect to attack on alkanes are relatively constant over a range of structurally diverse alkanes.⁷⁸ The primary vs secondary vs tertiary selectivities, defined per C-H bond, for reaction of photoexcited **1** with alkanes as calculated are not constant. Third, the *n*-alkanes all react at different rates, and rates increase with chain length at least up to *n*-nonane. The relative concentrations of C-H bonds for all these reactions were very similar. Alkyl radicals unlike carbonium ions are quite localized and the reactivities correlate closely with bond strengths. The average bond strength among the more reactive secondary C-H bonds in the *n*-alkanes particularly for the larger *n*-alkanes should be nearly identical, yet reactivity increases linearly with chain length up to C₈ and C₉ normal alkanes (Table II). Fourth, on the basis of bond energies and typical rates of reaction with radicals, the cycloalkanes should not be much more reactive than the *n*-alkanes. Yet, for the photooxidation of alkanes by **1**, cyclodecane is 15 times more reactive than *n*-nonane, a molecule with a molecular formula differing by only one carbon atom. Fifth, the observed primary kinetic isotope effects, $k_{\text{cyclohexane-}h_{12}}/k_{\text{cyclohexane-}d_{12}} = 1.38$, $k_{\text{cis-Decalin-}h_{12}}/k_{\text{cis-Decalin-}d_{12}} = 1.39$, are quite small given that the rate-determining transition state clearly contains alkane. Primary kinetic isotope effects seen in rate-limiting radical abstraction of hydrogen atoms from alkanes and other molecules with sp³-hybridized C-H bonds are usually severalfold higher than this value and can be over 10.^{12b,78,79}

We reported in our preliminary communication on the catalytic photochemical functionalization of alkanes that there was some correlation between the ionization potentials of the alkanes and their relative reactivities with respect to P*.³⁵ This information in conjunction with that given above leads us to postulate that the substrate activation process (eq 8) is principally electron transfer in character (transition state **6**) rather than radical abstraction in character (transition state **5**). It is not inconceivable that there may be a change in mechanism as a function of the alkane substrate, and therefore at this time, we do not exclude completely the applicability of transition state **5** for some reactions. Changes in the mechanism of alkane functionalization as a function of the substrate itself have been noted in other homogeneous alkane oxidation systems.^{13b,15} Furthermore, different polyoxometalates may photooxidize alkanes by different mechanisms.

Steps Subsequent to C-H Cleavage. Formation of Products. The catalytic photochemical oxidation of alkanes by polyoxotungstates always produces alkenes; the principal byproducts are the *N*-alkylacetamides, the alkylalkane dimers, and the alkyl methyl ketones. The data suggest that more than one type of organic intermediate is important in these catalytic hydrocarbon functionalization reactions. Although the five points cited above argue against the formation of alkyl radicals in the alkane activation step, radicals are doubtless generated subsequent to this step in the mechanism. If the initial oxidized form of the alkanes ((RH)_{ox} in eq 8) is the cation radical, radicals can and probably will be generated by deprotonation of this intermediate (eq 21).

(67) Another transition state that could, in principle, be involved in the substrate activation process of homogeneous photochemical alkane functionalization by polyoxotungstates is a three-membered-ring transition state involving the oxygen of an oxotungsten group and the C-H bond. Although concerted oxo transfer and compact triangular transition states may well be involved in the insertion of singlet manifold oxygen atoms in the gas phase into alkane C-H bonds, there is no *strong* experimental evidence to the best of our knowledge that this process occurs in any liquid-phase alkane oxidation reaction by metal complexes. Furthermore, the selectivities exhibited in alkane C-H bond activation by organometallic systems and the high-spin Co^{III} and related electrophilic systems investigated earlier, that probably proceed by three-membered-ring transition states involving C-H and M, are distinct from the C-H cleavage selectivities seen in the photochemical alkane functionalizations catalyzed by polyoxometalates. Finally, a concerted insertion of an oxygen into a C-H bond would lead to an alcohol, and control experiments indicate that alcohols do not convert to the observed products under the reaction conditions nor are they appreciably consumed.

(68) Benson, S. W.; Nangia, P. S. *Acc. Chem. Res.* **1979**, *12*, 223.

(69) Hamilton, G. A. In *Molecular Mechanisms of Oxygen Activation*; Hayaishi, O., Ed.; Academic: New York, 1974; Chapter 10.

(70) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, Part A; Plenum: New York, 1984; pp 373-382 and many references cited therein.

(71) See numerous references in ref 43.

(72) Overberger, C. G.; Bilech, H.; Finestone, A. B.; Liker, J.; Herbert, J. *J. Am. Chem. Soc.* **1953**, *75*, 2078.

(73) Danen, W. C.; Rose, K. A. *J. Org. Chem.* **1975**, *40*, 619. See also: Danen, W. C.; Winter, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 716.

(74) Rogers, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217 and references cited therein.

(75) Russell, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1955**, *77*, 4031.

(76) Tedder, J. M. *Q. Rev., Chem. Soc.* **1960**, *14*, 336.

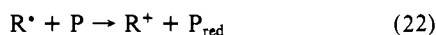
(77) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69.

(78) Good discussion of temperature and polar effects on cleavage selectivities in hydrogen atom abstraction from alkanes: Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 7.

(79) Wiberg, K. B.; Motell, E. L. *Tetrahedron* **1963**, *19*, 2009.



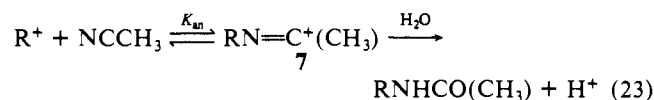
Deprotonation is a dominant decomposition pathway for organic radical cations generated either chemically and electrochemically in solution.⁸⁰ Unfortunately, the often used diagnostic probe for freely diffusing alkyl radical intermediates, the ratio of disproportionation products to coupling products,⁸¹ cannot readily be applied to the catalytic photochemical alkane functionalization systems reported here. The facile oxidation of the radicals to the corresponding carbonium ions (eq 22) appears to be important



$\text{P} = \mathbf{1}$, $\text{W}_{10}\text{O}_{32}^{4-}$, or other polyoxotungstate

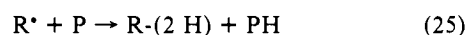
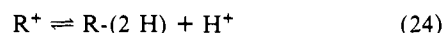
in at least some reactions. Processes analogous to eq 22 are well precedented and thoroughly investigated for several organometallic systems (P in eq 22 \neq polyoxometalate).⁸² Furthermore, Papaconstantinou recently reported that primary and secondary organic radicals derived from alcohols by pulse radiolysis reduce heteropolytungstates of the Keggin structure at nearly diffusion-controlled rates in aqueous media.⁸³

Some lines of evidence are consistent with the presence of carbonium ions, and other lines of evidence are not consistent with these intermediates. The *N*-alkylacetamide byproducts, although produced exclusively under conditions where the hydrogen evolution catalyst $\text{Pt}(0)$ is present, are the major organic oxidation products in some cases. These byproducts are more than likely produced by eq 23. Namely the nitrilium ion, **7**, formed reversibly



from carbonium ion and acetonitrile (with association constant K_{an}) is captured irreversibly by water, in a process directly analogous to the well-known Ritter reaction.⁸⁴ Instead of classical Ritter reactions, however, in which the carbonium ions are generated by $\text{S}_{\text{N}}1$ reactions of ionizable functional groups, or protonation of olefins by mineral acids, carbonium ions are derived in the transformations reported here from unfunctionalized hydrocarbon skeletons. In contrast to the precedence for carbonium ion involvement in *N*-alkylacetamide formation, it has been demonstrated experimentally that alkyl radicals do not react with acetonitrile to give amide products.^{85,87} Carbonium ions could, in principle, be involved in generation of the main product, alkene,

by the deprotonation equilibrium in eq 24. Such processes have



been proposed to occur in acetonitrile solution.⁸⁰ Alternatively, however, alkene could be formed by hydrogen atom abstraction from the alkyl radical by other organic radicals, analogous to the common bimolecular disproportionation of alkyl radicals, or by polyoxometalate species (P) (eq 25). There are two main arguments against the intermediacy of carbonium ions in the pathway(s) leading to the principal products, alkenes. The first is that the products generated from the catalytic photochemical functionalization of a number of alkanes (Table I) show a complete lack of carbocyclic skeletal rearrangements common to most carbonium ion processes. The counter argument to this point is that the principal C-H cleavages are those at the most substituted carbon atoms. The carbonium atoms at these centers, usually tertiary, are those least prone to C-C and C-H rearrangements. The second argument against the involvement of carbonium ions on the pathway(s) leading to alkene is that they should be trapped in a fairly rapid and exothermic reaction by the proximal hydrogen-bonded water molecules, analogous to the studied Ritter processes addressed above (eq 23), yielding alcohols. After all, the 10.7 equiv of H_2O /equiv of $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ in **1** is likely proximal to the location where the alkane-derived intermediates will be generated. No alcohols are produced in the alkane functionalization reactions, however (Table I). In recent control experiments, it was established that even though alcohols are readily oxidized by $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$, the relative oxidation rates ($k_{\text{ROH}}/k_{\text{RH}}$) are such that small quantities of alcohols present in the reaction are not appreciably consumed by further oxidation to the corresponding aldehydes or ketones under the alkane functionalization reaction conditions used here (0.48 M alkane); thus, the complete absence of alcohol at all times during the reaction suggests that alcohol is never formed.⁸⁶

Conclusions

The photochemical functionalization of alkanes by the exemplary polyoxotungstate α -dodecatungstophosphate proceeds principally, but not necessarily exclusively, by a complex redox process in which a charge-transfer excited state(s) of the complex oxidizes the alkanes by a path that involves electron transfer. Water molecules of hydration in the hydrated free acid form of the complex, $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (**1**), interact with the key excited state(s) competent to functionalize alkane and decrease the overall rate and quantum yields for formation of the reduced complex, $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$, and the alkane oxidation products. The presence of $\text{Pt}(0)$ increases the turnover rates but greatly increases the complexity of the net processes. Several lines of evidence indicate the presence of alkyl radicals and carbonium ions in the steps subsequent to alkane substrate activation process.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8715322), the Petroleum Research Fund, administered by the American Chemical Society, and ARCO Chemical Co. for support. Grants from the National Science Foundation were used in part to purchase the 200- and 360-MHz spectrometers.

(80) Becker, J. Y.; Miller, L. L.; Siegel, T. M. *J. Am. Chem. Soc.* **1975**, *97*, 849.

(81) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 2.

(82) Excellent review: Kochi, J. K. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 11.

(83) Papaconstantinou, E. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 2769.

(84) Review: Krimen, L. I.; Cota, D. J. *Organic Reactions*; Dauben, W. G., Ed.; Wiley: New York, 1969; Vol. 17, Chapter 3.

(85) Becker, J. Y.; Byrd, L. R.; Miller, L. L.; So, Y.-H. *J. Am. Chem. Soc.* **1975**, *97*, 853.

(86) We have established in a recent study that **1** functions as an acid catalyst for the hydration of alkene under conditions for catalytic photochemical functionalization of alkanes in acetonitrile.³⁶

(87) For example see: Sosnovsky, G. *Free Radical Reactions in Preparative Organic Chemistry*; Macmillan: New York, 1964; pp 400-401.