

transfer reactions of polar groups (e.g., of phosphate residues), the release of the products from the active site would automatically be initiated, because as soon as the link between the polar group and the hydrophobic site is broken, the distance between them

(57) (a) A similar "cooperative mechanism" between hydrogen-bonding and hydrophobic interactions has very recently been suggested^{57b} for the complexes formed by peptides and the glycopeptide antibiotics, vancomycin and ristocetin. It was concluded "that addition of a hydrophobic group not only allows hydrophobic bonding but also strengthens existing hydrogen bonds" and that the "increased hydrogen bond strength can be an important factor in determining the overall binding energy". (b) Williamson, M. P.; Williams, D. H. *Eur. J. Biochem.* **1984**, *138*, 345-348.

will (at least slightly) increase and the cooperativity will disappear. In this way, the active site would become accessible for another substrate molecule, and a perpetual turnover would be guaranteed.

Acknowledgment. The computer was made available by the Rechenzentrum der Universität Basel (Univac 1100/81). This support, a research grant from the Swiss National Science Foundation, and a fellowship to U.K.H. from the Stipendienfonds der Basler Chemischen Industrie are gratefully acknowledged.

Registry No. BzOH, 100-51-6; ethanol, 64-17-5; dioxane, 123-91-1.

Catalytic Photochemical Dehydrogenation of Organic Substrates by Polyoxometalates

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Abstract: The photochemical behavior of the polyoxometalates based on W, Mo, V, Nb, and Ta in the presence of water or one of a variety of organic substrates including alcohols, amides, ethers, aldehydes, carboxylic acids, nitriles, ketones, and ureas is examined. Irradiation of the charge-transfer bands of polyoxometalates dissolved in organic media at 25 °C leads in most cases to the oxidation of the organic substrate and reduction of the polyoxometalate. The polyoxometalates fall into three categories defined by their thermal and photochemical redox chemistry in the presence of organic substrates. Type I complexes exemplified by those of Nb and Ta do not appear to photooxidize any organic substrate upon irradiation. Type II complexes, exemplified by decavanadate and most heteropoly- and isopolytungstates, and type III complexes, exemplified by most heteropoly- and isopolytungstates, do oxidize a wide range of organic substrates upon irradiation. Reoxidation of the reduced forms of the type II complexes either by reaction with O₂ or by evolution of H₂ is kinetically or thermodynamically unfavorable; reoxidation of the reduced forms of the type III complexes either by reaction with O₂ or by evolution of H₂ is not. Several factors affecting the quantum yields for production of reduced polyoxometalates are outlined, and the energetic features regarding hydrogen evolution are discussed. The infrared, electronic, ³¹P NMR, ¹⁸³W NMR, and ¹⁷O NMR spectral properties of α-H₃PW₁₂O₄₀·6H₂O, **1**, and other polyoxometalates remain the same before and after catalytic photochemical dehydrogenation of representative alcohol, ether, or amide substrates. These results indicate that little if any polyoxometalate decomposition occurs during the photoredox chemistry. Interactions between organic substrates and polyoxometalates have profound effects on the electronic structure of the polyoxometalates. The charge-transfer transitions of polyoxometalate **1** display different sensitivities to medium in the low-energy (λ > 300 nm) vs. the high-energy region of the ultraviolet-visible spectral range. The highest sensitivities of the quantum yields for photoredox chemistry involving organic substrates and **1** to medium are observed in the low-energy or absorption tail region of the spectrum. One possible model explaining the wavelength dependence of the absorption and photochemical action spectra is discussed. A general mechanism in agreement with all the experimental data is proposed for organic substrate oxidation and the effective capture of light energy in these polyoxometalate-organic substrate systems.

Polyoxometalates or polyoxoanions have been known for well over a century, yet it has been only in the last few years that scientific interest in these materials began to increase dramatically.^{2,3} Two reasons for the recent surge in popularity of polyoxometalate chemistry are that only recently have many of the potential applications for these materials become well defined and the analytical methodology for adequately characterizing these complex molecules become well developed.^{2,4-10} Since 1977,

polyoxometalates and, in particular, heteropoly acids have received increasing attention as reagents or catalysts for redox processes involving organic substrates.¹¹⁻¹⁴ Most of these polyoxo-

(1) Some of the preliminary research on this chemistry was executed at the University of California, Berkeley, by C.L.H. Approximately 60% of this work was presented at the Joint NSF-CNRS Polyoxoanion Workshop, St. Lambert des Bois, France, July 11-13, 1983, and written up in the proceedings of that meeting.

(2) The most recent and definitive review on polyoxometalates: Pope, M. T. In "Heteropoly and Isopoly Oxometalates"; Springer-Verlag: Berlin, 1983.

(3) Other reviews: (a) Weakley, T. J. R. *Struct. Bonding (Berlin)* **1974**, *18*, 131. (b) Tsigdinos, G. *Top. Curr. Chem.* **1978**, *76*, 1. (c) Evans, H. T., Jr. *Perspect. Struct. Chem.* **1971**, *4*, 1; (d) Kepert, D. L. *Prog. Inorg. Chem.* **1962**, *4*, 199. (e) Tytko, T.-H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239.

(4) The application of ¹⁷O₆ NMR largely by Klemperer and co-workers⁵ and ¹⁸³W NMR by the groups of Baker,⁶ Brevard, and Schimpf,⁷ Finke,⁸ and Domaille⁹ to polyoxometalates is noteworthy as is the very recent report of fast atom bombardment mass spectrometry (FABMS) for polyoxometalate characterization by Finke, Suslick, and co-workers.¹⁰

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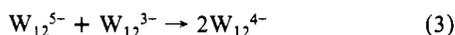
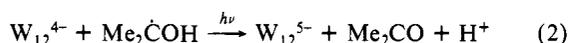
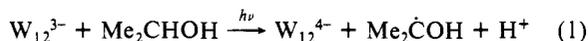
(10) Finke, R. G.; Droegge, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750.

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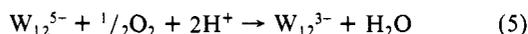
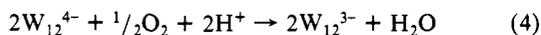
(12) (a) Davison, S. F.; Mann, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1223. (b) Urabe, K.; Kimura, F.; Izumi, Y. 7th International Congress on Catalysis, Tokyo, 1980, Part B, p 1418. (c) Ogawa, H.; Fujinami, H.; Taya, K.; Teratani, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1274. (d) Mateev, K. I. *Kinet. Katal.* **1977**, *18*, 716. (e) Rudenkov, A. I.; Mennenga, G. U.; Rachkovskaya, L. N.; Mateev, K. I.; Kozhevnikov, I. V. *Ibid.* **1977**, *18*, 758. (f) Pachkovskaya, L. N.; Mateev, K. I.; Il'ich, G. N.; Eremenko, N. K. *Ibid.* **1977**, *18*, 854. (g) Taraban'ko, V. E.; Kozhevnikov, I. V.; Mateev, K. I. *Ibid.* **1978**, *19*, 937. (h) Kozhevnikov, I. V.; Taraban'ko, V. E.; Mateev, K. I. *Ibid.* **1980**, *21*, 679, 685. (i) Mennenga, G. U.; Rudenkov, A. I.; Mateev, K. I.; Kozhevnikov, I. V. *React. Kinet. Catal. Lett.* **1976**, *5*, 401. (j) Rachkovskaya, L. N.; Mateev, K. I.; Rudenkov, A. I.; Mennenga, G. U. *Ibid.* **1977**, *6*, 73. (k) Taraban'ko, V. E.; Kozhevnikov, I. V.; Mateev, K. I. *Ibid.* **1978**, *8*, 77.

metalate-facilitated redox processes are oxidations, and the majority involve the use of heteropolyacids as heterogeneous catalysts.¹⁴ The polyoxometalates in the processes that are homogeneous usually function as catalysts for Pd reoxidation in organic oxidations related to the Wacker reaction.^{12,13} As rich as the thermal redox chemistry of polyoxometalates may prove to be, it is apparent from the existing literature that these species, upon irradiation with visible or near-ultraviolet light, facilitate a number of oxidations that are thermodynamically or kinetically unfavorable in the dark.

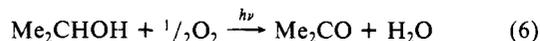
The photosensitivity of polyoxometalates was reported as early as 1914.¹⁵ Yamase has investigated the photoreduction of alkylammonium isopoly compounds of molybdenum and tungsten in aqueous solutions and H₂ evolution from photogalvanic cells based on these photoreductions.¹⁶ Savinov and co-workers have examined the evolution of hydrogen gas from acidic aqueous solutions of SiW₁₂O₄₀.⁶⁻¹⁷ The catalytic photooxidation of alcohols to the corresponding aldehydes or ketones by heteropoly compounds has been reported by several groups.^{1,18-23} Papaconstantinou was the first to examine these processes in detail¹⁸ and demonstrated that the reduced polyoxometalates could be reoxidized by air, thereby completing a cycle catalytic in polyoxometalate.^{21,24} With PW₁₂O₄₀³⁻ as an exemplary heteropoly compound and 2-propanol as an exemplary organic substrate, Papaconstantinou offered eq 1-5 to describe this chemistry.²¹ These processes sum to the catalytic photochemical oxidation in eq 6.



followed by



where $\text{W}_{12} \equiv \text{PW}_{12}\text{O}_{40}$



We and others have demonstrated that the reduced heteropoly

(13) Review of homogeneous Wacker-type heteropolyacid-dependent oxidations: Mateev, K. I.; Kozhevnikov, I. V. *Kinet. Katal.* **1980**, *21*, 855.

(14) Representative recent papers addressing heteropolyacids as heterogeneous catalysts: (a) Akimoto, M.; Ikeda, H.; Okabe, A.; Echigoya, E. *J. Catal.* **1984**, *89*, 196. (b) Mamoru, A. *Ibid.* **1981**, *71*, 88. (c) Akimoto, M.; Tsuchida, Y.; Sato, K.; Echigoya, E. *Ibid.* **1981**, *72*, 83. (d) Konishi, Y.; Sakata, K.; Misono, M.; Yoneda, Y. *Ibid.* **1982**, *77*, 169 and references cited in each.

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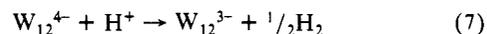
(21) Papaconstantinou, E. *J. Chem. Soc., Chem. Commun.* **1982**, 12.

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(23) Darwent, J. R. *J. Chem. Soc., Chem. Commun.* **1982**, 798.

(24) Most investigators have referred to these alcohol photooxidations by heteropoly compounds summing to either eq 6 or 8 as "photocatalytic" processes. We prefer the terms "catalytic photochemistry" or "photoassisted catalysis" to describe this chemistry. The reason for this is that the term "photocatalytic" is ambiguous and can also refer to processes that are catalytic in photons; i.e., quantum yields in excess of 100% are observed. This is not the case with all polyoxometalate photochemistry documented to date.

compounds, "heteropoly blues", can also be oxidized by protons producing hydrogen gas (eq 7) and defining a new cycle for the



catalytic dehydrogenation of primary and secondary alcohols (eq 8).^{1,19,22-24} Most of the mechanistic details of processes 1-8 remain



unknown as do many of the critical relationships between the electronic and structural properties of the reactants and the observed photochemical and thermal reactivities.

In this paper, we outline for the first time the truly broad scope of polyoxometalate-catalyzed photooxidation and photo-dehydrogenation of organic compounds and demonstrate heretofore unrecognized photophysical and photochemical phenomena associated with these highly complex redox processes.

Experimental Section

Physical Measurements. ³¹P and ¹⁷O NMR spectra were obtained on an IBM WP-200SY spectrometer, and ¹⁸³W NMR spectra were obtained at the NSF regional NMR facility, University of South Carolina, on a Bruker WM400 NMR spectrometer. Infrared spectra of samples 2-4 wt % in KBr were obtained by using a Perkin-Elmer Model 1430 infrared spectrophotometer. The samples were pulverized with KBr by using a "Wig-L-Bug" apparatus by shaking for ca. 60 s. The electronic spectra (250-800 nm) were recorded on a Hewlett-Packard (H/P) Model 8451A diode array UV-visible spectrometer.

The principal photochemical apparatus used for all experiments was an Oriol Corp. 1000-W high-pressure Xe arc lamp. The beam was used either collimated or focused and passed through a circulating water infrared filter and the specified band-pass or interference filters. Quantum yields were determined by using Reinecke's salt actinometry.²⁵

Organic substrates and products were detected and quantified by using either a Perkin-Elmer Sigma 3 or Hewlett-Packard Model 5710 A gas chromatograph equipped with flame ionization detectors and a Hewlett-Packard 3390A electronic reporting integrator. Analyses for hydrogen, oxygen, and nitrogen gases were carried out by using a Varian Model A-90-P gas chromatograph fitted with a molecular sieve 5-Å column and a thermal conductivity detector. Argon was used as the carrier gas, and a Linear Instruments Corp. Model 252 integrating strip chart recorder was used for quantitation of products. Corroboration of product assignments was made by gas chromatography-mass spectrometry (GCMS) analysis by using a Finnegan 4000 GCMS system.

Materials $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$,²⁶ $\text{K}_7\text{HfNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$,²⁷ $\text{K}_8\text{Ta}_6\text{O}_{19}\cdot 17\text{H}_2\text{O}$,²⁸ $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$,²⁹ $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$,²⁶ $\alpha\text{-(Bu}_4\text{N)}_3\text{PMo}_{12}\text{O}_{40}$,^{26,5} $\alpha\text{-(Bu}_4\text{N)}_3\text{PW}_{12}\text{O}_{40}$,^{26,5} $(\text{Bu}_4\text{N)}_2\text{W}_6\text{O}_{19}$,³⁰ and $\alpha\text{-(Bu}_4\text{N)}_{11}\text{H(P}_2\text{W}_{18}\text{O}_{62})_2$,^{26,5} were prepared and purified by literature methods. Water isotopically enriched in ¹⁷O was purchased from DOE/Monsanto or Cambridge Isotope Laboratories. The organic substrates or solvents were Burdick & Jackson glass-distilled grade or reagent grade and used without further purification. Hygroscopic organic solvents were stored in Schlenk flasks and manipulated by using inert atmosphere techniques. Water was freshly deionized and then fractionally distilled from KMnO₄. Colloidal aqueous suspensions of Pt(O) were prepared by the method of Wilenzick et al.³¹ Suspensions of Pt(O) in the dipolar aprotic solvents were prepared by photoreducing 0.2 mM stirred solutions of either H₂PtCl₆ (ALFA) or K⁺[Pt^{IV}Cl₃(CH₂CH₂)⁻ (ALFA) in the presence of the appropriate polyoxometalate.

Polyoxometalates isotopically enriched in ¹⁷O were prepared by methods similar to those of Klemperer and co-workers.⁵ The following preparation of the Bu₄N⁺ form of 1, (Bu₄N)₃PW₁₂O₄₀, is typical. To a 25-mL Schlenk flask was added 3.5 g (10.6 mmol) of Na₂WO₄·2H₂O. The flask was charged with a stirring bar, fitted with a septum stopper, and then heated in vacuo to ca. 300 °C for 30 min. When the dehydration was complete, the flask was allowed to cool and 3.0 mL of 23 atom % ¹⁷O-enriched H₂O was added. The slurry was stored for 24 h at 23 °C. The resulting mixture was then heated to ca. 80 °C to aid in

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dissolution. To the flask was then added 2.3 mL of 12 N HCl via syringe followed by ^{17}O -enriched H_3PO_4 . The latter was prepared by addition of 0.1 mL of ^{17}O -enriched water to 0.1 g of PCl_5 . The temperature was then raised to 95 °C for 1 h, the solution allowed to cool, and the crystalline precipitate collected on a frit. The crystalline solid was dissolved in 4.0 mL of 23 atom % ^{17}O -enriched H_2O and then acidified with 1.4 mL of HCl. Diethyl ether (2.45 mL) was added, and three liquid phases were formed. The lowest phase was removed quickly and dissolved in 4.0 mL of H_2O , and then 0.90 g of $(n\text{-C}_4\text{H}_9)_4\text{NBr}$ dissolved in 2.0 mL of H_2O was added. The product precipitated immediately as an amorphous white solid. Crystalline material (1.7 g) was obtained by recrystallization from hot acetonitrile.

General Procedure for Polyoxometalate Photoreductions and Hydrogen Evolution Studies. The same procedure was used for those reactions specifically addressing the rate of polyoxometalate photoreduction as exemplified by the data in Table I and for those reactions specifically addressing the rate of hydrogen evolution as exemplified by the data in Table II except that the latter reactions contained Pt(O) as a hydrogen evolution catalyst and the former reactions did not.

In a typical reaction, 8 mL of organic substrate, the appropriate quantity of the particular polyoxometalate to make a 1.0 mM solution, and a 0.25-in. magnetic stirring bar were placed in a 25-mL Schlenk flask. The flask was capped with a septum stopper and then the contents degassed either by successive freeze-thaw cycles or by successive gas/degas cycles with a dual manifold vacuum line. After the degassed polyoxometalate solution was placed under ca. 1.05 atm of argon, the flask was placed in the light beam for the specified time. All irradiated samples were stirred magnetically at a constant rate. Reaction times varied from 2 s to several hours depending on both the polyoxometalate and the organic substrate used (*vide infra*). In the hydrogen evolution reactions, 1 mL of the Pt(O) suspension in the particular organic substrate and 7 mL of the polyoxometalate solution in the same organic substrate were placed in the Schlenk flask. The rest of the procedure was the same. The reactions were analyzed by GC for both H_2 and organic products immediately after the irradiations had been terminated. If GCMS product analysis could not be done immediately on a particular sample, then that sample was kept in the dark until the analysis could be performed. The polyoxometalates $\text{K}_7\text{HfNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$, $\text{K}_8\text{Ta}_6\text{O}_{19}\cdot 17\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{V}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$ were insoluble in most or all organic solvents; therefore, aqueous solutions of the water-miscible organic substrates were used for the photochemical experiments. The photochemistry of the water-immiscible organic substrates with the Nb, Ta, or V polyoxometalates was not examined in detail. Several photooxidations of solid organic substrates by polyoxometalates were carried out, although none appear in Tables I, II, or III. These reactions were carried out by dissolving the substrates in either water or acetonitrile, two solvents that have little effect on photoinduced polyoxometalate redox chemistry.

Monitoring Polyoxometalate-Catalyzed Photoredox Processes by NMR. Changes in the nuclear magnetic resonance characteristics of polyoxometalates induced by stoichiometric or catalytic photoredox processes can be monitored most effectively by carrying out the reactions directly in specially adapted NMR tubes rather than in Schlenk flasks. Carrying out the photochemical reactions in the same NMR tubes used for determining the ^{31}P , ^{17}O , and ^{183}W NMR spectra minimized problems resulting from adventitious chemical contaminants including dioxygen and obviated problems associated with transferring polyoxometalate solutions between Schlenk flasks and NMR tubes through metal cannulae that in many cases rapidly reduce polyoxo species.

In a typical study, the polyoxometalate was placed in a 9-in. 10-mm NMR tube along with 1–2 mL of CD_3CN to provide for an internal deuterium lock, 1–3 mL of organic substrate, and 5 mg of $\text{K}^+[\text{Pt}^{\text{II}}\text{Cl}_3(\text{CH}_2\text{CH}_2)]^-$ (ALFA) as a Pt(O) precursor. The actual quantity of polyoxometalate needed to obtain high-quality NMR spectra depends on the polyoxometalate, the viscosity of the organic solvent, and greatly on the particular nucleus being examined. Actual reactant quantities and reaction conditions are specified in Figures 1 and 2. Control experiments demonstrated that neither the diamagnetic d^8 Pt^{II} precursor nor the Pt(O) suspensions resulting from photoreduction of the Pt^{II} complex had any demonstrable effect on the NMR spectra of the polyoxometalates whatsoever. Klemperer has succinctly outlined the advantages of acetonitrile over other organic solvents as a solvent for polyoxometalate NMR studies.⁵ Whereas the NMR spectra had to be determined in the absence of a magnetic stirring bar, the remainder of the protocol, including irradiation and hydrogen evolution, had to be conducted in the presence of one. A 65-mg, 8-mm Teflon-coated magnetic stirring bar was used in all cases. After the addition of solvent, substrate, and stirring bar, the NMR tube was capped with a snugly fitting air-tight septum stopper. The contents of the NMR tube were stirred magnetically and taken through several gas/degas cycles by using a dual manifold vacuum line equipped with a 22-gage needle that was inserted through the septum

stopper. The sample was then irradiated for a specified time with near-ultraviolet and visible light ($\lambda > 290$ nm), the blue paramagnetic reduced species was allowed to discharge completely, giving hydrogen, and then the gaseous and liquid organic contents of the tube were analyzed by GC or GCMS as described above. The stirring bar was then removed as carefully as possible and the NMR spectra recorded. This procedure was repeated sequentially until the desired number of turnovers with respect to polyoxometalate had been achieved.

Determination of Areas under Absorption Curves and Rate Constants (k_{obsd}) for Production of Reduced Polyoxometalates. The area under the absorption curves for polyoxometalates in various photoactive organic media in the low-energy regime ($\lambda = 340\text{--}500$ nm) parallel the degree of substrate-to-polyoxometalate charge transfer or intermolecular electron-donor-acceptor character in these complex solutions; hence several parameters have been plotted against these absorption areas. The absorption areas or integrated absorptions from $\lambda = 340$ to 500 nm were determined by summing all the individual absorptions at each diode over this defined wavelength range.

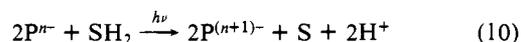
A method was needed for quantifying the relative rates of various photochemical reactions. This, in principal, could be done in a number of ways including measurement of the quantum yields of reduced polyoxometalates after a set irradiation time or the measurement of hydrogen gas after set irradiation times, if the reduced polyoxometalate was allowed to discharge completely to give hydrogen gas. The method of choice was to do kinetics on the production of the reduced polyoxometalates under conditions where the rate of reoxidation of the reduced species by hydrogen evolution or other modes was negligible. Plots of reduced polyoxometalate concentration as a function of irradiation time were first order for most organic substrates provided a hydrogen evolution catalyst was absent. However, we and others have observed that for several substrates under certain reaction conditions, more than one distinct reduced polyoxometalate is formed upon irradiation.^{17–19} These substrates did not yield reliable rate data. The substrates which did yield reliable infinite absorbances were fitted to eq 9. Observed infinity absorbances agreed with the calculated values ($\pm 6\%$).

$$A = A_\infty + (A_0 - A_\infty) \exp(-kt) \quad (9)$$

In a typical kinetics run, 2.0 mL of a 3 mM solution of the polyoxometalate in organic substrate was placed in a Schlenk quartz cuvette containing a small magnetic stirring bar. The contents of the cuvette were degassed and placed under an argon atmosphere by using the method discussed above for degassing the samples in NMR tubes. The electronic spectra were recorded rapidly on the diode array spectrometer after 0.5- or 1.0-min irradiation intervals depending on the substrate. The λ_{max} values of the reduced polyoxometalate were slightly solvent dependent; however, the values for $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$, **1**, the compound used for the data in Table III and Figures 3–5, were within the range of 740–760 nm. The observed rate constants, k_{obsd} , were calculated on an HP-85 microcomputer by using the IKIN3 algorithm.³³

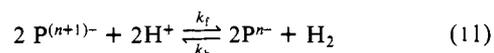
Results and Discussion

Photooxidation of Organic Compounds by Polyoxometalates—Scope of Reaction. Prior to our work, studies of the photooxidation of organic compounds by polyoxometalates had been effectively limited to oxidations of alcohols and carboxylic acids by heteropoly compounds of molybdenum and tungsten.^{18–23} We have investigated the photooxidation of a large number of organic substrates of widely differing reactivity and polarity by polyoxometalates of vanadium, niobium, and tantalum, as well as by the isopoly and heteropoly compounds of molybdenum and tungsten. There is a distinct photochemical process summarized for most substrates by eq 10 followed by a thermal process, which



P^{n-} = polyoxometalate; SH_2 = organic substrate

in the absence of dioxygen is summarized by eq 11. Neither eq



10 nor 11 implies mechanism. We have examined both these

(32) Abbreviations: HPT = heteropolytungstate; THF = tetrahydrofuran; DMF = *N,N*-dimethylformamide; DMA = *N,N*-dimethylacetamide; NMP = methylpyrrolidinone; Me_2SO = dimethyl sulfoxide; HMPA = hexamethylphosphoramide; TMU = tetramethylurea; NMF = *N*-methylformamide.

(33) DeTar, D. F. *Comput. Chem.* (1978) 2, 99.

Table I. Photooxidation of Organic Substrates by Polyoxometalates^a

substrate ^b	polyoxometalate (P _{ox}) ^b				
	type I ^c		type II		type III
	Nb ₆ O ₁₉ ⁸⁻	Ta ₆ O ₁₉ ⁸⁻	V ₁₀ O ₂₈ ^{6-d}	PMo ₁₂ O ₄₀ ³⁻	PW ₁₂ O ₄₀ ³⁻
(1) alcohols					
(a) primary	1	1	3	4	4
(b) secondary	1	1	3	4	4
(c) tertiary	1	1	2	2	2
(2) ethers					
THF	1	1	3	4	4
(3) amides					
formamide	1	1	3	<i>f</i>	<i>f</i>
DMF	1	1	3	4	4
NMP	1	1	3	4	4
(4) aldehydes					
PhCHO	I ^e	I ^e	I ^e	4	4
<i>i</i> -C ₃ H ₇ CHO	I	I	I	<i>f</i>	<i>f</i>
(5) carboxylic acids					
CH ₃ COOH	<i>f</i>	<i>f</i>	1	2	2
(6) ketones					
(CH ₃) ₂ CO	1	1	1	2	2
(7) nitriles					
PhCN	I	I	I	2	2
C ₂ H ₅ CN	I	I	I	<i>h</i>	2
(8) others					
Me ₂ SO	1	1	2	2	2
HMPA	<i>g</i>	<i>g</i>	<i>g</i>	4	4
TMU	1	1	3	4	4
H ₂ O	1	1	1	1	2

^aSamples irradiated in Schlenk flasks under an Ar atmosphere by using a 1000-W Xe lamp and Pyrex cutoff filter ($\lambda > 290$ nm). P_{ox} ca. 1.0 mM in solvent substrate unless otherwise noted. Reactivity: 1 = no reduced polyoxometalate after 1 h; 2 = reduced polyoxometalate after 1 h; 3 = reduced polyoxometalate after 5 min; 4 = reduced polyoxometalate in less than 15 s. ^bAbbreviations for substrates and polyoxometalates are summarized in ref 32. ^cDue to insolubility of Nb and Ta polyoxometalates in organic solvents, all Nb₆O₁₉⁸⁻ and Ta₆O₁₉⁸⁻ reactions were run in aqueous solutions with substrate present from 5 to 40 vol %. ^dStock aqueous solution of (NH₄)₆V₁₀O₂₈ diluted in each case by organic substrate. ^eP_{ox} was either insoluble or formed separate liquid phase from one containing organic substrate. ^fRapid thermal reaction. ^gValue not determined. ^hSlow thermal oxidation of substrate.

Table II. Catalytic Photochemical Production of Hydrogen from Organic Substrates by Heteropolytungstate (HPT) Compounds in Solution^a

	catalysts present ^b			solv-substr ^c	light ^d (λ in nm)	rate of H ₂ production, cm ³ h ⁻¹
	HPT	Pt(0)	H ₂ SO ₄			
(1) 1		yes	yes	NMP	>340	2.3
(2) none		yes	yes	NMP	>340	0
(3) 1		yes	yes	none ^e	>340	~0
(4) 1		yes	yes	NMP	none	0
(5) 1		no	no	NMP	>340	0.20
(6) 1		no	yes	NMP	>340	0.20
(7) 1		yes	no	NMP	>340	1.05
(8) (Bu ₄ N) ₃ PW ₁₂ O ₄₀		yes	no	NMP	>340	0.01
(9) (Bu ₄ N) ₃ PW ₁₂ O ₄₀		yes	yes	NMP	>340	2.3
(10) 1		yes	yes	NMP	>400	0.30
(11) 1		no ^f	no	THF	>340	0.06
(12) 1		yes	no	EtOH	>340	0.38
(13) 1		yes	no	EtOH	>400	<0.01
(14) 1		yes	no	EtOH	>320	1.40
(15) H ₄ SiW ₁₂ O ₄₀ ·7H ₂ O		yes	no	NMP	>340	0.60
(16) (Bu ₄ N) ₁₁ H(P ₂ W ₁₈ O ₆₂) ₂		yes	no	NMP	>340	0.05

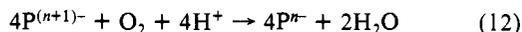
^aReactions run at 27 °C. Reactions executed and analyzed as described in the Experimental Section. ^bConcentration of HPT = 0.64 mM in all cases, concentration of Pt(0) when present = 0.2 mM, concentration of H₂SO₄ when present = 10 mM. The free acid form of PW₁₂O₄₀³⁻ was used to avoid competing photooxidation of quaternary ammonium or other organic counterions. The sample was a hexahydrate as accurately as could be determined (H₃PW₁₂O₄₀·6H₂O, 1). ^cAbbreviations in ref 32. ^dCutoff filters for $\lambda > 320, >340, >400$ nm are Corning No. 4602, 4308, and 3391, respectively. ^e0.64 mM aqueous solution of 1. ^fH₂Pt(IV)Cl₆ inactivates H₃PW₁₂O₄₀ in THF.

processes, and exemplary data are summarized in Tables I and II. The data in Table I were obtained in the absence of Pt(O) or other hydrogen evolution catalyst, which renders hydrogen evolution (eq 11) far slower than polyoxometalate photoreduction (eq 10) in nearly all cases. Consequently the data in Table I illustrate primarily the relative rates of eq 10. In contrast, the data in Table II for the most part were obtained in the presence of Pt(O) and focus on the relative rates of hydrogen evolution. Since quaternary ammonium and other organic cations are susceptible to photooxidation by polyoxometalates,¹⁹ the free acid forms of the polyoxo species were used whenever possible. All the reactions summarized in Tables I and II except reactions 8, 9, and 16 in Table II employed polyoxometalates free of organic

counterions. The free acid forms of the polyoxometalates are generally more soluble in organic media of moderate or low polarity than the corresponding quaternary ammonium forms, and it is this solubility of the free acid forms that renders possible much of the homogeneous chemistry reported in this paper.

Examination of over 100 reactions, most of which are summarized in Tables I and II, indicates that there are three distinct types of behavior with regard to the photochemistry of polyoxometalates in organic media. For purposes of simplicity and organization, we will refer to the polyoxometalates as types I, II, or III, depending on behavior. Type I polyoxometalates exemplified by those of niobium and tantalum, M₆O₁₉⁸⁻, M = Nb or Ta, are species that do not appear to be photoreduced by any

organic material even with ultraviolet light ($\lambda < 290$ nm). Type II polyoxometalates are readily photoreduced by a wide variety of organic substrates, but the reduced species are relatively stable and thermodynamically incapable of evolving hydrogen. That is, eq 10 is very facile at 25 °C, but k_f , eq 11, is not and $k_f/k_b = K_H \ll 1$. Nearly all heteropoly- and isopolymolybdates as well as polyvanadates are in this category. Uranyl ion, UO_2^{2+} , although not considered a polyoxometalate by most investigators, also behaves as a type II material in that it photooxidizes a wide variety of organic substrates but the reduced forms do not evolve hydrogen. In dramatic contrast to the situation with the true polyoxometalates, however, there is a very substantial literature that addresses the photochemistry of uranyl complexes in the presence of organic materials.³⁴ Thermal reoxidation of the reduced forms of the type II polyoxometalates with O_2 (eq 12) is usually ki-



netically slow and sometimes thermodynamically unfavorable. A simple consequence of the fact that the two principal polyoxometalate regeneration processes, hydrogen evolution or air oxidation (eq 11 and 12 respectively), are unfavorable for type II polyoxometalates renders these materials of low or questionable value for formulating catalytic redox cycles that necessitate reduction of the polyoxometalate.

Type III compounds as exemplified by nearly all the heteropoly and isopoly compounds of tungsten undergo both facile photoreduction at 25 °C by a variety of organic substrates, and the reduced forms undergo facile hydrogen evolution or air (O_2) reoxidation. Table II focuses on the catalytic photochemical production of hydrogen gas from three organic substrates, *N*-methylpyrrolidinone (NMP), ethanol, and tetrahydrofuran by polytungstates.

Both the rate of polyoxometalate photoreduction and subsequent hydrogen evolution (for the type III compounds) for any given polyoxometalate varies greatly with the organic substrate. Primary and secondary alcohols, secondary and tertiary amides and ureas, aldehydes, ethers, and phosphoramides are the most reactive organic functions; tertiary alcohols, carboxylic acids, ketones, nitriles, sulfoxides, and water itself are far less reactive. The ordering of substrate reactivities as outlined in Table I cannot be rationalized by any one simple classical model for the initial substrate oxidation process. Indeed it would be unlikely if all the electronically and structurally diverse organic substrates enumerated in Table I were oxidized by the same mechanism (vide infra). All products for all the organic photooxidations summarized in Table I have not yet been identified and quantified. It will require substantial work to rigorously obtain product distributions and to establish which compounds represent kinetic products and which do not. The oxidation of primary alcohols to aldehydes and secondary alcohols to ketones, however, goes in high yield with high selectivity unlike the ether and amide oxidations that produce a number of products. The principal feature with regard to the scope of the photooxidations of organic substrates by polyoxometalates is one of reactivity. Organic compounds normally far more difficult to oxidize than alcohols including amides, ureas, phosphoramides and ethers are photooxidized by polyoxo species under very mild conditions and oxidized as easily as the most reactive alcohols.

In some cases, there are rapid thermal reactions between the polyoxometalates and the organic substrates. Sometimes these are redox processes such as the rapid reduction of $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ by aliphatic aldehydes; sometimes these are nonredox reactions such as the condensation of *i*- $\text{C}_3\text{H}_7\text{CHO}$ induced by $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$, complex 1. Yamase has established that the quantum yields for photooxidation of Bu_4N^+ by $\text{W}_{10}\text{O}_{32}^{4-}$ vary with irradiation time,¹⁹ while the groups of Papaconstantinou²² and Yamase¹⁹ have both reported that the reduced isopoly-

and heteropolytungstates are not photosensitive in alcohol or acetonitrile solutions. We find that the decrease in quantum yields as a function of irradiation time is a fairly general phenomenon observed during the photoredox chemistry of polyoxometalates in organic media. We also find that the photoreduced polyoxometalates, although not completely inactive photochemically, do nevertheless exhibit quantum yields for further reduction that are substantially lower than the quantum yield for the first reduction. The difference in quantum yields for the first reduction and subsequent reductions appears to be a function of several parameters, the most important of which are the nature of organic substrates and the size and redox characteristics of the particular polyoxometalate. For example, the heteropolytungstates and -molybdates of the Dawson structure $[(\text{X}^{n+})_2\text{M}_{18}\text{O}_{62}]^{(16-2n)-}$ tend to take up more electrons than those of the Keggin structure $[\text{X}^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)-}$, and the difference in quantum yields between the first and second electron photoreductions is smaller for the former than the latter. One exemplary absolute quantum yield is for the production of $\text{PW}_{12}\text{O}_{40}^{4-}$, the one-electron heteropoly blue, from 1 in the usually unreactive dipolar aprotic tertiary amide, *N*-methylpyrrolidinone (NMP). This quantum yield is 0.1 at 350 nm. A critical and heretofore unappreciated factor influencing both the absolute quantum yields at any given wavelength and the photochemical action spectra for polyoxometalate photoreduction by organic substrates is the specific interactions between the polyoxometalate and the organic substrate. These interactions, discussed subsequently, have a profound effect on the electronic structure of the reactants.

The hydrogen evolution process, eq 11, is influenced by several factors. Colloidal or finely divided Pt(O) is a true catalyst, accelerating both the rate of polyoxometalate thermal reduction by hydrogen, k_b in eq 11, and hydrogen evolution, k_f in eq 11, equally ($K_H = k_f/k_b$ is unaffected). The value for K_H depends on the solvent as well as the polyoxometalate. Solvents of high polarity and strong hydrogen-bonding ability stabilize the reduced forms of the polyoxometalates more than solvents of low polarity and weak hydrogen-bonding ability. The largest values of K_H seen thus far have been in ether solvents, the smallest values in the secondary amide, *N*-methylformamide (NMF). The difference in K_H values for type III polyoxometalates between these extremes in solvent polarity is usually at least an order of magnitude.

Nature of the Oxidizing Species in Polyoxometalate Photoredox Chemistry. Two questions pertaining to the nature of the active oxidizing species in polyoxometalate photoredox chemistry must be answered before the mechanisms and the structure-reactivity relationships operable in these processes are definitively elucidated. First, are the intact polyoxometalates themselves functioning as the oxidizing species, or are isomers or fragments in equilibrium with the intact polyoxometalates the kinetically active species? Second, what is the nature of the charge-transfer excited states that lead to organic substrate oxidation?

There are only two pieces of data that bear in an important way on the above two questions; both deal with the relationship between the absorption spectra of polyoxometalates and their photochemical reactivity. The first of these data, from the laboratory of Yamase and co-workers, is that the anodic photocurrent for decomposition of $(\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ at a Pt electrode parallels albeit is somewhat out of phase with the absorption spectrum of this complex.¹⁹ The second line of evidence is from the laboratory of Papaconstantinou and co-workers who demonstrated that the photochemical action spectra for the photoreduction of molybdenum heteropoly compounds by alcohols parallels the absorption spectra of these materials.¹⁸ These lines of evidence suggest strongly that charge-transfer excited states of the intact polyoxometalates are the photoactive species responsible for organic substrate oxidation. This evidence, however, constitutes necessary but not sufficient conditions for the above to be true. The evidence would be much stronger if it was rigorously established that the polyoxometalates remained intact during catalysis.

We present here five lines of evidence, not all equally direct or compelling, that the polyoxometalates may stay intact during all the thermal and photochemical processes encountered in the

(34) (a) Jorgensen, C. K.; Reisfeld, R. *Struct. Bonding (Berlin)* **1982**, 50, 121. (b) Rabinowitch, E.; Belford, R. L. "Spectroscopy and Photochemistry of Uranyl Compounds"; Pergamon Press: Oxford, 1964; references cited in each.

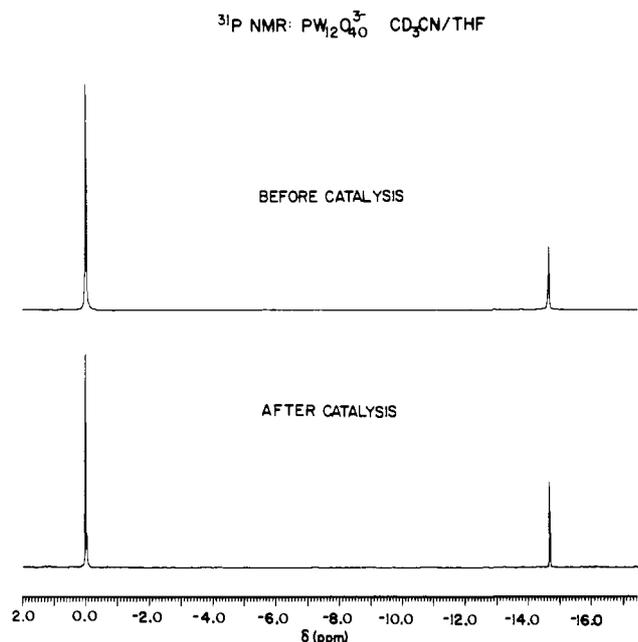


Figure 1. ^{31}P NMR spectra of **1** before and after four turnovers in the photochemical production of hydrogen gas from THF. Conditions: 0.163 g of $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$, **1**, and 5 mg of $\text{Pt}(\text{O})$ precursor in 1 mL of THF and 2 mL of CD_3CN . Sample prepared, irradiated, and analyzed as described in the Experimental Section. Negative chemical shifts are reported in parts per million upfield from an 85% H_3PO_4 external standard. NMR parameters: 25.5- μs pulse width; 0.62 Hz per point resolution; 5-s relaxation delay; 100 acquisitions. Both spectra were recorded at 25 $^\circ\text{C}$.

catalytic photochemical dehydrogenation of organic substrates. Subsequently and in conjunction with this, we provide evidence regarding the nature of the charge-transfer excited states of the polyoxometalates that are the actual oxidants. We have focused our experimental investigations on **1**, an exemplary tractable highly active type III polyoxometalate. It is probable but hardly certain that the following experimental evidence and conclusions will prove applicable to other polyoxo compounds. The data in Figures 1–4 and Table III like the data in Table II pertain to the heteropolytungstate, **1**.

The first line of evidence, quite indirect, is that monomeric tungstate, WO_4^{2-} , the synthetic precursor of **1** and a likely candidate for a lower nuclearity form in equilibrium with **1**, displays no detectable photochemistry in most organic media. In some organic media, photoreduction occurs, but with quantum yields that are orders of magnitude lower than those for **1** and other polytungstates. Second, three catalytic photodehydrogenation reactions were run with **1** and the complex reisolated and examined by infrared spectroscopy after reaction. In all three cases, **1** in 100% NMP, **1** in 100% ethanol, and **1** in 100% THF, the infrared spectrum of the complex was unchanged after 30 turnovers (30 equiv of H_2 produced per equivalent of **1**). Third, the ^{31}P NMR spectra of **1** was unchanged after catalytic photochemical dehydrogenation. An exemplary experiment with an ether, THF, as the organic substrate is illustrated in Figure 1. The chemical shift for the phosphorus atom in **1** on both spectra is -14.7 ppm.³⁵ Fourth, the ^{183}W NMR spectrum of **1** was unchanged after photochemical production of hydrogen gas from the tertiary amide NMP. As in the case with the ^{31}P NMR spectra, the ^{183}W NMR spectrum for **1** after reaction demonstrates the complete absence of any tungstate species except starting material, **1**. The two-bond tungsten–phosphorus coupling constant $^2J(\text{W}–\text{O}–\text{P})$ is identical in both ^{183}W spectra (0.72 Hz), and the ^{183}W chemical shifts are consistent with literature values.⁴⁰ Fifth, the ^{17}O NMR spectra

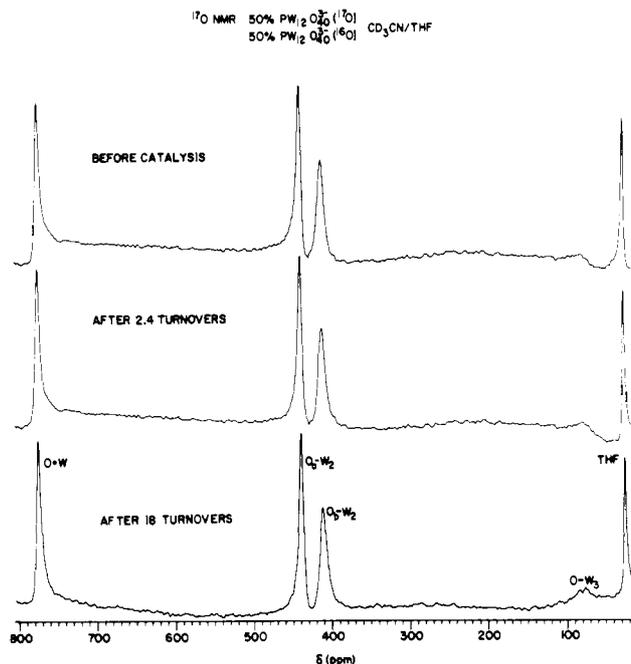


Figure 2. ^{17}O NMR experiment. Catalytic photochemical dehydrogenation of THF by 50.0% unlabeled $\alpha\text{-(Bu}_4\text{N)}_3\text{PW}_{12}\text{O}_{40}$, 50.0% ^{17}O -labeled $\alpha\text{-(Bu}_4\text{N)}_3\text{PW}_{12}\text{O}_{40}$. Before catalysis (top), after 2.4 turnovers (middle), and after 18 turnovers (bottom); one turnover = 1 equiv of H_2 produced per equivalent of complex present. Conditions: 24.4 mg each of ^{17}O -labeled (23 atom % ^{17}O) and unlabeled complex, 15 mg of $\text{Pt}(\text{O})$ precursor in 1.8 mL of THF and 1.6 mL of CD_3CN ; $\lambda > 290$ nm light. NMR parameters: 27.131 MHz = spectrometer frequency; 90 $^\circ$ pulse width = 34 μs ; resolution = 3.9 Hz per point; relaxation delay = 0; 25 000 acquisitions per spectrum. Chemical shifts are reported in ppm (positive to lower fields) and referenced to THF (+25.4 ppm relative to water).

of ^{17}O -labeled polyoxometalates do not change after catalytic photodehydrogenation of organic substrates. One exemplary experiment is illustrated in Figure 2. A 50:50 mixture of ^{17}O -labeled and unlabeled $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ gave no indication of changes in peak shape, chemical shifts, or relative peak intensities after 2.4 turnovers and after 18 turnovers with respect to photochemical hydrogen production from THF (Figure 2).

All the above evidence suggests strongly that no appreciable degree of polyoxometalate decomposition takes place during the redox and nonredox processes that are operable during the catalytic photodehydrogenation of organic substrates by these complexes. Unfortunately, however, none of the above evidence establishes that the intact polyoxometalates are the kinetically important species in these catalytic processes. All the above data constitutes necessary, but not sufficient, evidence that the complexes stay intact at all times. Indeed, there are many documented cases in the literature where the kinetically important species are present in far lower steady-state concentrations than the principal and structurally similar species.⁴³ One must be particularly careful when ruling out the possibility that there exist kinetically important species other than intact **1**, when it is clear that there are both kinetic and thermodynamic driving forces for the formation and reformation of the Keggin structure in solution. Various dou-

(37) O'Donnel, S. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1976**, 2290.

(38) Kazanskii, L. P.; Chuvaev, V. F.; Spitsyn, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2, 256.

(39) Lebedeva, L. I.; Vanchikova, E. V. *Zh. Neorg. Khim.* **1974**, 19, 3285.

(40) The literature values for the ^{183}W chemical shifts in $\text{PW}_{12}\text{O}_{40}^{3-}$ of -99.46 and -98.83 ⁴¹ in D_2O and -86.7 in 1:4 v/v $\text{CD}_3\text{CN}/\text{DMF}$ ⁴² already suggest that ^{183}W chemical shifts in polyoxotungstates may be quite sensitive to medium.

(41) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, 101, 267.

(42) Gansow, O. A.; Ho, R. K. C.; Klemperer, W. G. *J. Organomet. Chem.* **1980**, 187, C27.

(43) For a recent well-defined example see: Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, 102, 5952.

(35) Four literature values for the ^{31}P chemical shift of $\text{PW}_{12}\text{O}_{40}^{3-}$ are -14.9 ,³⁶ -14.96 ± 0.5 ,³⁷ -15.1 ,³⁸ and -17.7 ± 0.5 .³⁹

(36) Massart, R.; Constant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, 16, 2916.

Table III. Areas under Absorption Curves and Rates of Photoreduction (k_{obsd}) for **1** over Specified Low-Energy Spectral Ranges

solv and subst ^a	integrated absorption ^{b,c}			$k_{\text{obsd}}^{\text{b,d}}$ min ⁻¹		
	340–500	380–500	400–500	$\lambda > 340$	$\lambda > 380$	$\lambda > 400$
ethanol	12.35	0	0	0.31	0	0
THF	13.12	0	0	0.56	0	0
DMF	24.96	1.32	0	1.45	0.109	0
DMA	29.18	2.99	0.77	1.59	0.150	<10 ⁻³
NMP	35.27	4.66	1.36	2.19	0.520	0.08

^aSubstrate abbreviations in ref 32. ^bWavelengths in nanometers. ^cConcentrations of **1** were 3.35 mM. Integrated absorptions or areas under absorption curves determined as described in Experimental Section. ^dFirst-order rate constants for photochemical production of reduced **1**. Procedure for determining k_{obsd} described in Experimental Section. Values for k_{obsd} of 0 defined as no reduced complex detectable after 1-h irradiation time.

ble-labeling experiments will establish in principle not only that polyoxometalate molecules suffer no net decomposition but also display no skeletal isomerization, intermolecular oxygen atom exchange, or other structure altering processes during the catalytic photodehydrogenation of organic substrates. The viability and experimental difficulty of the actual double-labeling experiments will be the problem, however.

It is also difficult to establish unequivocally the nature of the excited states that lead to productive photochemistry. Unfortunately the type III polyoxometalates examined do not fluoresce or phosphoresce at ambient laboratory temperature; hence common techniques using emission such as selective fluorescence quenching cannot be used to address this problem. The absorption spectra and the qualitative photochemical action spectra for a number of polyoxometalates in different organic media have been examined. The absorption and action spectra closely trace each other. Also, however, examination of the absorption and photochemical action spectra of the complexes as a function of medium uncovered heretofore unobserved features of the electronic structure of polyoxometalates in the presence of organic compounds.

Nature of the Charge-Transfer Excited States of Polyoxometalates in Organic Media. Polyoxometalates in their most stable and oxidized forms are d⁰ complexes. The electronic structure of these complexes independent of solvent effects has been largely ignored to date. Polyoxometalate electronic structures have been ignored experimentally in part, as Pope has pointed out,² because the electronic spectra are quite featureless and uninformative. Polyoxometalate electronic structure in large part has been ignored theoretically because of its complexity. Klemperer and co-workers have calculated the electronic states of the hexametalates, M₆O₁₉ⁿ⁻, one of the simpler polyoxometalate structural families and found that a predictable complex manifold of charge-transfer excited states exists.⁴⁴ The three other groups that have investigated the photooxidation of alcohols by polyoxometalates have attributed the actual substrate oxidation process to oxygen-to-metal charge-transfer excited states of the complexes.^{18–20} Certainly these states appear to be involved in substrate oxidation, particularly in the case of decatungstate, but the photoredox phenomena is more complex than what has been suggested.

Quantitative examination of the absorption spectra of polyoxometalates in a variety of organic media has shown that the spectra are not only solvent dependent but also that different regions of the absorption envelope display different sensitivities to medium. The absorption spectra of **1**, an exemplary type III polyoxometalate at constant concentration in H₂O, and three different organic media are illustrated in Figure 3. In the high-energy region near the oxygen-to-metal CT band absorption maximum, there are moderate to small changes in the absorption spectra of **1** from solvent to solvent. The extinction coefficients at λ_{max} are similar in several organic solvents and approximately 30% higher than in H₂O while the λ_{max} values are nearly invariant from solvent to solvent ($\lambda_{\text{max}}^{\text{H}_2\text{O}} = 266$ nm, $\lambda_{\text{max}}^{\text{EtOH}} = \lambda_{\text{max}}^{\text{THF}} = \lambda_{\text{max}}^{\text{DMF}} = 268$ nm). In contrast, the low-energy portion of the absorption envelope, the absorption tail, is highly sensitive to medium. This effect is illustrated in Figure 4 where the absorption tails ($\lambda >$

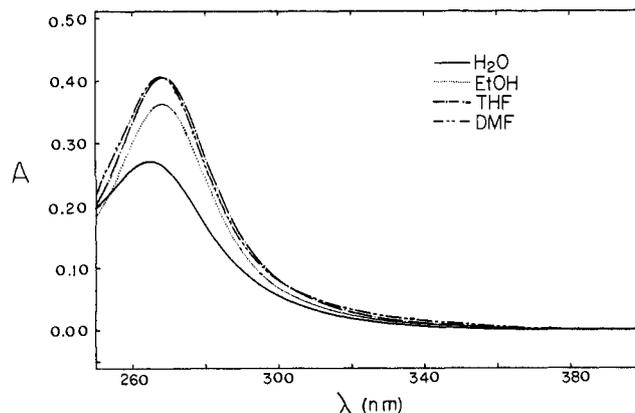


Figure 3. Electronic absorption spectra, $\lambda = 250$ – 400 nm, of α -H₃PW₁₂O₄₀·6H₂O, **1**, in water and three exemplary organic solvents, ethanol, tetrahydrofuran and *N,N*-dimethylformamide. All spectra were obtained by using 0.70 mM solutions and 0.1 mm path length cells.

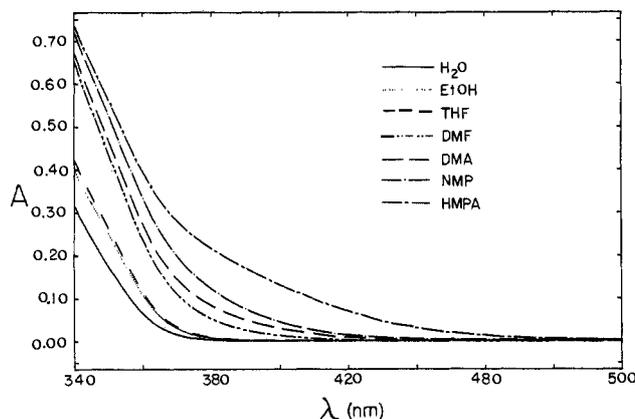


Figure 4. Electronic absorption spectra, $\lambda = 340$ – 500 nm, of **1** in several media. All spectra were obtained by using 3.37 mM solutions and 1.0 mm path length cells.

340 nm) for several solutions of **1** at constant concentration are compared. This heteropolytungstate complex is colorless in H₂O, pale yellow in DMF and DMA, and dark yellow in HMPA³² in accord with Figure 4. In no case is the absorption tail into the visible due to small amounts of photoreduced polyoxometalate. It is the low-energy region where most of the photoinduced redox chemistry is observed. The data in Table III and Figure 5 illustrate this point. The areas under the absorption curves or the integrated absorptions for **1** in the low-energy region correlate directly and linearly with the photoredox activity of the complex. Table III illustrates the correlation between the integrated absorptions for **1** and observed rate constants for production of reduced polyoxometalates from **1** over specified low-energy spectral ranges. Since the absorbance for **1** is zero in all solvents prepared here at $\lambda > 500$ nm, the wavelength ranges used in the photochemistry, >340 , >380 , and >400 nm, correspond to the wavelength ranges used to determine the areas under the absorption curves, 340–500, 380–500 and 400–500 nm, respectively (Table III). One exem-

(44) Klemperer, W. G., unpublished results.

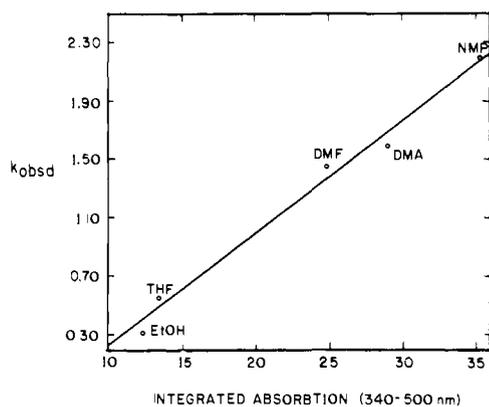


Figure 5. Plot of k_{obsd} ($\lambda > 340 \text{ nm}$) for the formation of reduced polyoxometalate vs. the integrated absorption (340–500 nm) of 3.35 mM solutions of **1** in the indicated organic substrates.

ply set of data in a low-energy spectral range is plotted in Figure 5, k_{obsd} , $\lambda > 340 \text{ nm}$, vs. the integrated absorption $\lambda = 340\text{--}500 \text{ nm}$. The plot is linear with a correlation coefficient of 0.992. The linear correlation between the absorption spectra and the photoredox chemistry of **1** as manifested in Table III and Figure 5 coupled with the evidence presented above that **1** suffers no decomposition during the photoredox catalysis suggests that charge-transfer excited states associated with the intact reactant polyoxometalate are probably the species that oxidize the organic substrate.

Sufficient experimental information is now available to construct a model for the charge-transfer electronic states and associated photochemistry of polyoxometalates in organic media. A model must accommodate all the experimental observations. To summarize, there are four facts that pertain to **1** in organic media: (1) qualitatively different solvent sensitivities in low- (tail) and high-energy regions of the ultraviolet–visible spectral range are observed; (2) there is a close correlation between the absorption and photochemical action spectra in the low-energy region; (3) solvent-dependent absorption is present in the low-energy region that is absent in the spectra of the solvent or the polyoxometalate alone; and (4) irradiation of these low-energy bands results in high quantum yields of polyoxometalate reduction and organic substrate oxidation. The above observations could be rationalized by attributing all electronic transitions and photoredox processes to intramolecular oxygen-to-metal charge-transfer excited states with different states predominating in the high- and low-energy spectral regions. However, based on recently investigated intermolecular intervalence charge-transfer phenomena in inorganic complexes,^{45–48} and substantial literature on the spectroscopy and photochemistry of intermolecular charge-transfer complexes between neutral molecules,⁴⁹ we feel that a different model for the electronic transitions is preferable for explaining the above observations. We propose that intramolecular oxygen-to-metal charge-transfer transitions predominate in the high-energy region of the ultraviolet–visible spectral range near the absorption maximum ($268 \pm 2 \text{ nm}$ for **1** in all media examined to date) and intermolecular charge-transfer transitions predominate in the low-energy region as illustrated in Figures 3 and 4, respectively. The latter inter-

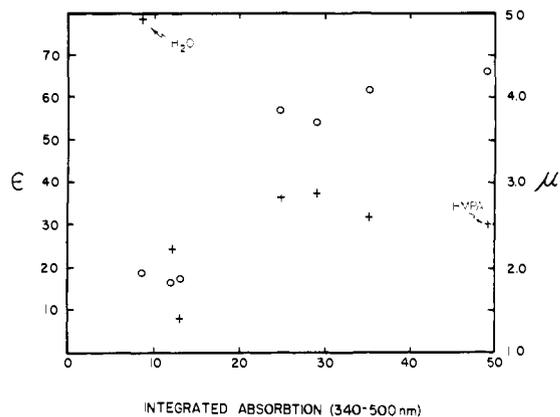


Figure 6. Plot of solvent dielectric constant, ϵ , (+) and dipole moment, μ , (O) as a function of the integrated absorption (340–500 nm) of **1** in different media (3.35 mM solutions). On the figure from left to right the solvents are H₂O, ETOH, THF, DMF, DMA, NMP, and HMPA.

molecular transitions are largely solvent-to-polyoxometalate charge transfer in origin and phenomenologically related to outer-sphere charge-transfer (OSCT) and intervalence intermolecular transitions in ion pairs.^{45–48} In the case of the polyoxometalates in organic media, however, the electronic/redox partners are not both ions as in the literature cases,^{45–48} but one partner is an ion, the other a neutral molecule. The organic substrate–polyoxometalate intermolecular charge-transfer transitions can be viewed as arising from a heretofore undocumented type of intermolecular electron donor–acceptor (EDA) complex. Molecular EDA complexes, particularly those between neutral organic molecules, have been thoroughly investigated.⁴⁹ The principal theoretical treatment for EDA complexes in general that remains popular today is the simple valence bond treatment of Mulliken.⁵⁰ In recent years, the applicability of electron donor–acceptor charge-transfer complexes to organometallic compounds has been demonstrated. Extensive research largely by Kochi and co-workers has definitively shown how widespread and important these intermolecular charge-transfer interactions are to the physical and chemical properties of many organometallic species.⁵¹

The solvent dependence of the shifts in the absorption tail, Figure 4, follows the solvent dependence of documented intermolecular charge-transfer transitions. If the absorption spectra of **1** in the various organic solvents (absorption at a particular wavelength on the featureless low-energy absorption tail or integrated absorption over a specified spectral range) is plotted against either the Kosower Z value⁵² or the Reichardt–Dimroth E_T value⁵³ of the solvent, good monotonic albeit not strictly linear correlations are obtained. Strict linearity would not be expected in such plots unless there was no component of intramolecular oxygen-to-metal charge-transfer character in those transitions, an unlikely situation. The Kosower Z value is a measure of solvent polarity based on the solvatochromism of 1-alkylpyridinium halides. The specific transitions examined in these systems are intermolecular charge-transfer transitions in ion pairs.⁵² Similarly, the Reichardt–Dimroth E_T values for solvent polarity are based on the solvent dependence of charge-transfer transitions in ionic organic species. In the latter case, however, highly soluble pyridinium phenolbetaines are used as the reference compounds and the charge-transfer transitions examined are intramolecular processes.^{53,54} The plot of the low-energy absorbance of **1** vs. the

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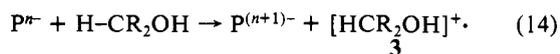
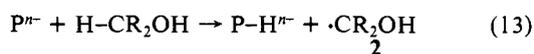
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dipole moment, μ , of the solvent shows some correlation, but the plot of absorbance vs. the dielectric constant, ϵ , the most common measure of solvent polarity, gives no discernible correlation whatsoever (Figure 6). The photochemistry observed for polyoxometalates in organic media is the same as that of organic EDA charge-transfer complexes inasmuch as irradiation of the intermolecular CT bands in both cases results in intermolecular redox chemistry with high quantum yields.

Comprehensive elucidation of all the molecular forces that produce the intermolecular organic substrate-to-polyoxometalate charge-transfer character of the complexes solvated in organic media will require much rigorous and detailed work. From the data available thus far, however, it is apparent that these interactions are partly dependent on hydrogen bonding and partly dependent on other intermolecular forces between substrate and complex. The electronic absorption spectra of the free acid forms of the polyoxometalates are very solvent dependent. It is these forms that are capable of the strongest hydrogen-bonding interactions. Likewise, the Kosower Z values and Reichardt-Dimroth E_T values reflect sensitivity to hydrogen-bonding effects. Quaternary ammonium forms of the polyoxometalates show electronic absorption spectra that are solvent dependent although they are less so than the corresponding free acid forms. Sensitivity of the electronic structure of polyoxometalates to medium also appears to increase qualitatively as the size of the polyoxometalate increases.

Mechanisms of Organic Substrate Oxidation and Light-to-Chemical Energy Conversion. The catalytic photochemical dehydrogenation of organic substrates by polyoxometalates is comprised of both photochemical and thermal processes as described above. Unfortunately, neither the mechanisms for the photochemical nor the thermal processes are well understood. With the previously discussed data in hand, we now address two key questions associated with this chemistry. What is the specific mechanism of organic substrate oxidation? What is the mechanism of trapping the energy in the incident ultraviolet and visible photons and converting the radiant energy to chemical energy?

The two most likely mechanisms for the key substrate oxidation step, and both have been proposed in conjunction with the literature studies of alcohol photooxidation by polyoxometalates,¹⁹⁻²² are radical hydrogen atom abstraction, eq 13, and electron transfer, eq 14. The product radical **2** or radical cation **3** both undergo

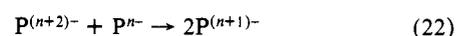
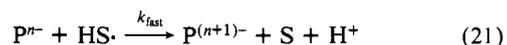
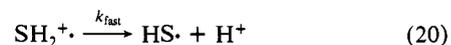
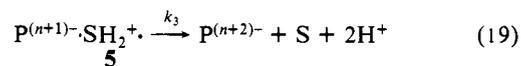
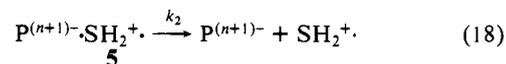
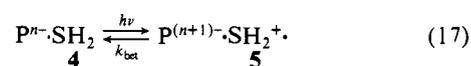
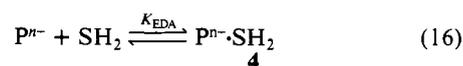
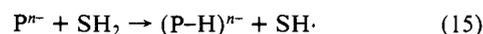


P^{n-} = polyoxometalate; R = H, alkyl, etc.

well-documented rapid subsequent reactions. From the studies on the catalytic photooxidation of alcohols by polyoxometalates, it is known that the rates of polyoxometalate photoreduction-organic substrate photooxidation are proportional to polyoxometalate and substrate concentration and are first order in photons.¹⁹⁻²² The reductions of oxidized polyoxometalate by alkyl radicals demonstrated by Papaconstantinou⁵⁵ and products that likely arise from freely diffusing radicals both implicate the intermediacy of radicals but none of the above data say much regarding the key substrate oxidation step. The single strongest piece of experimental evidence bearing on this step is the kinetic isotope effect, k_H/k_D , of 3.7 measured by Ward and co-workers for 2-propanol-2-*d* vs. 2-propanol-2-*H*.²⁰ Unfortunately, this isotope effect also does not rule out either hydrogen atom abstraction, eq 13, or electron transfer, eq 14. There are few if any values for the kinetic isotope effect k_H/k_D , for radical hydrogen atom abstraction where this process is solely rate determining during alcohol oxidation.⁵⁶ However, a kinetic isotope effect of $k_H/k_D = 16$ has been measured for the oxidation of benzaldehyde to benzoic acid by a metal complex under conditions where the

cleavage of a C-H bond is clearly rate determining.⁵⁷ There are few clear examples for homogeneous alcohol oxidation by initial electron transfer. Indeed, most rigorously studied alcohol oxidations by metal complexes proceed by inner-sphere processes.⁵⁸ As a consequence, no unequivocal value of k_H/k_D for an authentic case of alcohol oxidation by rate-determining electron transfer is available. Interestingly, a kinetic isotope effect of 2.2 in the oxidation of a ketone, cyclohexanone, by $Fe^{III}(phen)_3^{3+}$ was sufficiently low that authors used this as evidence that electron transfer occurs before proton loss in this reaction.⁵⁹ In summary, it is not yet clear from available evidence whether the photooxidation of alcohols by polyoxometalates proceeds by hydrogen atom abstraction or electron transfer and, as mentioned earlier, it is probably not likely that all the organic substrates photooxidized by polyoxometalates are necessarily oxidized by the same mechanism.

A general mechanism for the initial processes operable in the catalytic photodehydrogenation of organic substrates, SH_2 , by polyoxometalates that takes into account all the information now available on this photoredox chemistry is summarized in eq 15-22.



Substrate activation takes place in part by irradiation of the intermolecular charge-transfer bands of a polyoxometalate-substrate complex, **4** (eq 16 and 17), but probably also to some extent by a process most accurately characterized as hydrogen atom abstraction from substrate by an intramolecular oxygen-to-metal charge-transfer excited state of the polyoxometalate (eq 15). Electron-transfer oxidation of substrate by the polyoxometalate without formation of an EDA complex (eq 14) is unlikely for all but the most favorable oxidations. Included in the latter category are those few redox reactions between polyoxometalates and organic substrates that proceed thermally (e.g., $PMo_{12}O_{40}^{3-} + C_3H_7CHO$, Table I). The formation constant of the electron donor-acceptor charge-transfer complex between the reactants, K_{EDA} in eq 16, clearly depends on the structure and cations of the polyoxometalate, the organic substrate, and other medium effects. The ion pair complex, $P^{(n+1)-} \cdot SH_2^+$, **5**, formed upon photoinduced electron transfer has several possible fates. One of these, rapid thermal back reaction, or back electron transfer, k_{bet} , eq 17, will result in immediate loss of the chemical energy stored in the ion pair, **5**. At least two other processes will result in productive chemistry and the net utilization of the incident light energy. One productive process is diffusional separation of the ions in **5** followed by rapid irreversible decomposition of the substrate cation radical, SH_2^+ , eq 18 followed by eq 20 and 21. Similar processes involving the rapid and irreversible thermal decomposition of initial photoproducts to avoid back electron transfer has been a key mechanism for capturing light energy in other homogeneous systems. The second electron can also transfer

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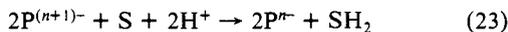
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prior to diffusion of the organic oxidation product, S, away from the reduced polyoxometalate (eq 19). This is one explanation as to why the photochemical steady state with particular complexes and organic substrates is such that each polyoxometalate molecule contains more than one electron. The disproportionation of the two-electron heteropoly blues and by inference other multielectron reduced polyoxometalates as well as eq 21 and 22 are well documented.^{2,21,60}

The net oxidation product, S, in the polyoxometalate-catalyzed photodehydrogenation of substrate SH₂, can be a chemically noninnocent species. The thermal reaction of S with the reduced polyoxometalate, e.g., eq 23, occurs rapidly in some cases, directly



affecting the net quantum yields for production of S and light-to-chemical energy conversion. A specific example when a reaction analogous to 23 markedly reduces the overall quantum yields is water oxidation, where H₂O₂, the oxidation product analogous to S, rapidly reoxidizes the reduced polyoxometalate.

The possible intermediacy of organic groups covalently bonded to the polyoxometalates during catalytic photodehydrogenation processes cannot be ruled out at this time. Acetal, ketal, and alkoxy complexes of polyoxometalates have been made,^{2,61-63} and

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very recently the structurally characterized tetramethoxypolyoxometalate, Na₄[Mo₈O₂₄(OCH₃)₄]·8MeOH,⁶² and the well-characterized dimethoxy complex Mo₂O₅(OCH₃)₂⁶³ were both shown to evolve formaldehyde upon irradiation with UV light. Formaldehyde evolution was coupled with Mo^{VI} reduction in both cases.

Acknowledgment. Support of this research by the National Science Foundation Grant CHE-8402994 is acknowledged. The use of the facilities at the University of South Carolina Regional NMR Center, funded by the National Science Foundation Grant CHE78-18723, is acknowledged. Much of the photochemical equipment was purchased by a grant from the Cottrell Research Corp. We thank Prof. Walter G. Klemperer for useful discussions.

Registry No. THF, 109-99-9; DMF, 68-12-2; NMP, 872-50-4; HMPA, 680-31-9; TMU, 632-22-4; DMA, 127-19-5; α-H₃PW₁₂O₄₀, 1343-93-7; K₇HNb₆O₁₉, 12025-96-6; K₈Ta₆O₁₉, 12142-54-0; (NH₄)₆-V₁₀O₂₈, 59858-44-5; α-H₃PMo₁₂O₄₀, 12026-57-2; α-(Bu₄N)₃PMo₁₂O₄₀, 53749-36-3; α-(Bu₄N)₃PW₁₂O₄₀, 53749-37-4; (Bu₄N)₂W₆O₁₉, 57241-87-9; α-(Bu₄N)₁₁H(P₂W₁₈O₆₂)₂, 68184-32-7; PhCHO, 100-52-7; i-C₃H₇-CHO, 78-84-2; CH₃CO₂H, 64-19-7; (CH₃)₂CO, 67-64-1; PhCN, 100-47-0; CH₃CH₂CN, 107-12-0; Me₂SO, 67-68-5; EtOH, 64-17-5; H₂O, 7732-18-5; Pt(0), 7440-06-4; H₄SiW₁₂O₄₀, 12027-38-2; Na₂WO₄, 13472-45-2; H₂¹⁷O, 13768-40-6; H₃P¹⁷O, 86119-84-8; n-Bu₄NBr, 1643-19-2; HC(O)NH₂, 75-12-7.

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New Mono-Dinitrogen Complexes of Molybdenum That Produce Ammonia and Hydrazine¹

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Contribution from the Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304. Received February 1, 1985

Abstract: A new, extensive series of mono-N₂ complexes of molybdenum is reported. The sodium amalgam reduction of MoCl₃(triphos), where triphos = PhP(CH₂CH₂PPh₂)₂, in tetrahydrofuran solution in the presence of 2L or L₂ and with a deficiency of N₂ led to the formation of Mo(N₂)(triphos)(L₂) (IA-F): IA, L₂ = 2 PPhMe₂; IB, L₂ = Me₂PCH₂PMe₂; IC, L₂ = 1,2-(Me₂As)₂C₆H₄; ID, L₂ = Ph₂PCH₂PPh₂; IE, L₂ = Ph₂PCH₂CH₂PPh₂; IF, L₂ = 1,1'-(Ph₂PC₆H₄)₂Fe, DPPFe. Complexes IC and IE were each a mixture of isomeric mono-N₂ complexes. Complex IF was isolated together with Mo(triphos)(η²-DPPFe)(η¹-DPPFe). Complexes IA-F all reacted with HBr in CH₂Cl₂ to afford ammonia, hydrazine, and N₂ (and some H₂) in varying yields. The highest yield of ammonia was obtained from IF, and the highest yield of hydrazine was obtained from IA (HCl/toluene at 70 °C).

Few of the more than 100 known mono-N₂ complexes of transition metals react to give more than a trace of ammonia and/or hydrazine.² This is in contrast to the behavior of (i) the bis-N₂ complexes of molybdenum and tungsten such as *cis*-W(N₂)₂(PMe₂Ph)₄ and *trans*-Mo(N₂)₂(triphos)(PPh₃), where triphos = PhP(CH₂CH₂PPh₂)₂, containing at least one monodentate ligand from which high yields of ammonia and occasionally hydrazine may be obtained,³⁻⁵ and (ii) the bridging-N₂ complexes

of titanium,⁶ zirconium,⁷ and tantalum⁸ from which high yields of hydrazine are obtained. We wish to report a new, extensive series of mono-N₂ complexes containing triphos that yield ammonia and hydrazine. These complexes contain five group 5 atoms bound to molybdenum. Only one such complex has been reported

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