tribution of reduced complexes (CoL_n^+ (n = 0–3)) initially produced is kinetically determined, equilibration of Co(I) and L does occur via a sequence of outer-sphere electron-transfer processes culminating in net binding of L (the equilibrium $CoL_n^+ + CoL_{n+1}^{2+} \rightleftharpoons CoL_n^{2+} + CoL_{n+1}^+$ lies to the right). The high rate constants found for these equilibrations require outer-sphere self-exchange rates greater than 10^8 M^{-1} s^{-1} for the $CoL_n^{2+/+}$ couples ($n > 0$), indicating very similar structures for CoL^{2+} and CoL^+ and for CoL_2^{2+} and CoL_2^+, as has been previously noted for CoL_3^{2+} and CoL_3^+. The stepwise binding constants for Co^+ and L are large 10^6–10^{12} M^{-1}), and the $CoL_n^{2+/+}$ reduction potentials vary from <–1.6 V (n = 0) to –0.95 V (bpy (n = 3)). The magnitudes of the stability constants of the cobalt(I) complexes and of the self-exchange rates of the Co(I)–Co(II) couples suggest the importance of Co(I) πd to $L\pi^*$ back-bonding in the CoL_2^+ and CoL_3^+ series.

Acknowledgment. This work was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH0016 with the U.S. Department of Energy supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank D. Comstock for his assistance with some of the experiments.

Registry No. $Co(bpy)^{2+}$, 15878-93-0; $Co(bpy)_2^{2+}$, 15878-94-1; $Co(bpy)_3^{2+}$, 15878-95-2; $Co(dmb)^{2+}$, 93503-94-7; $Co(dmb)_2^{2+}$, 93503-95-8; $Co(dmb)_3^{2+}$, 47837-98-9; $Co(bpy)^+$, 93503-96-9; $Co(bpy)_3^+$, 47780-35-8; $Co(bpy)_2^+$, 23852-07-5; $Co(dmb)^+$, 93503-97-0; $Co(dmb)_2^+$, 93503-98-1; $Co(dmb)_3^+$, 47837-97-8; $Co(bpy)R^{2+}$, 93503-99-2; $Co(bpy)_2R^{2+}$, 93530-03-1; $Co(bpy)_3R^{2+}$, 93504-00-8; $Co(dmb)R^{2+}$, 93504-01-9; $Co(dmb)_2R^{2+}$, 93504-02-0; $Co(dmb)_3R^{2+}$, 93504-03-1; $Co(bpy)CO_2^+$, 93504-04-2; $Co(bpy)_2CO_2^+$, 93504-05-3; $Co(bpy)_3CO_2^+$, 93504-06-4; $Co(dmb)CO_2^+$, 93504-07-5; $Co(dmb)_2CO_2^+$, 93504-08-6; $Co(dmb)_3CO_2^+$, 93504-09-7; R·, 5131-95-3; CO_2^-·, 14485-07-5; OH, 3352-57-6.

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Photocatalytic Generation of Hydrogen by 1:12 Heteropolytungstates with Concomitant Oxidation of Organic Compounds

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Received June 21, 1984

1:12 heteropolytungstates with the Keggin structures $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $FeW_{12}O_{40}^{5-}$ and $H_2W_{12}O_{40}^{6-}$ undergo multielectron photoreduction in the presence of a great variety of organic reagents in near-visible and UV light. Photoaddition of electrons drives the redox potential to more negative values sufficient to reduce, from a thermodynamic point of view, hydrogen ions in the presence of a Pt catalyst. It turns out that hydrogen is produced in the presence and absence of Pt. Photoreduction proceeds to the extent that the rate of photoreduction matches the back-reoxidation by H^+. The reduction step at which this takes place depends on the tungstate used. Thus, for instance, with PW_{12}^{3-} this happens at a higher reduction step than $H_2W_{12}^{6-}$, which is reduced at more negative reduction potentials. When Pt catalyst is present, the reduction potential at which the steady-state H_2 evolution is obtained is less negative. Average rate constants, from all four tungstates, of H_2 evolution at the steady state were (5.6 ± 3.1) × 10^{-4} and (2.6 ± 1.8) × 10^{-4} s^{-1} with and without Pt, respectively. The efficiency of H_2 production is of the order of one molecule of hydrogen per 100 photons absorbed. The low yield represents the low efficiency of photoproduction of higher reduction products. For $PW_{12}O_{40}^{3-}$ the quantum yields of photoaddition of the first and second electron are ca. 0.15 and 0.01, respectively.

Introduction

Heteropolycompounds (HPC) of molybdenum and tungsten are known to undergo multielectron reduction in distinct reduction steps by chemical and electrochemical means.[2] The reduction is reversible in the sense that reduced HPC can be reoxidized without decomposition. Reduction has been subsequently obtained by radiolysis through a variety of short-lived organic radicals,[3] whereas recently the multielectron photoreduction of these compounds in the presence of a variety of organic reagents has been demonstrated.[4]

It has been pointed out that reduced HPC could, from a thermodynamic point of view, reduce H^+.[5] While this work was in progress, hydrogen was produced from photoreduced $SiW_{12}O_{40}^{4-}$,[6] whereas the feasibility of hydrogen production by the chemically reduced form of this compound has been demonstrated by Russian workers,[7] who recently extended their work to photochemistry.

Table I. UV Spectral Data for Oxidized 1:12 Tungstates and Half-Wave Potentials for the First Two 1-Electron Reductions[2a]

anion	λ,[a] nm	$E_{1/2}$,[b] V	pH dependence
PW_{12}^{3-}	265.0	–0.023	none
		–0.266	none
SiW_{12}^{4-}	262.0	–0.187	none
		–0.445	none
FeW_{12}^{6-}	264.0	–0.349	none
		–0.577	below pH 4.0
$H_2W_{12}^{6-}$	257.5	–0.581	below pH 4.9
		–0.730	below pH 5.4

[a] In 1 M sulfuric acid. [b] In 1 M sulfate at 25 °C.

This paper describes and compares the photochemical production of hydrogen by a series of 1:12 tungstates in which there is a progressive variation of charge and reduction potential.

Experimental Section

The 1:12 tungstates, namely $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $FeW_{12}O_{40}^{5-}$, and $H_2W_{12}O_{40}^{6-}$, designated for simplicity as PW_{12}^{3-}, SiW_{12}^{4-}, FeW_{12}^{5-}, and

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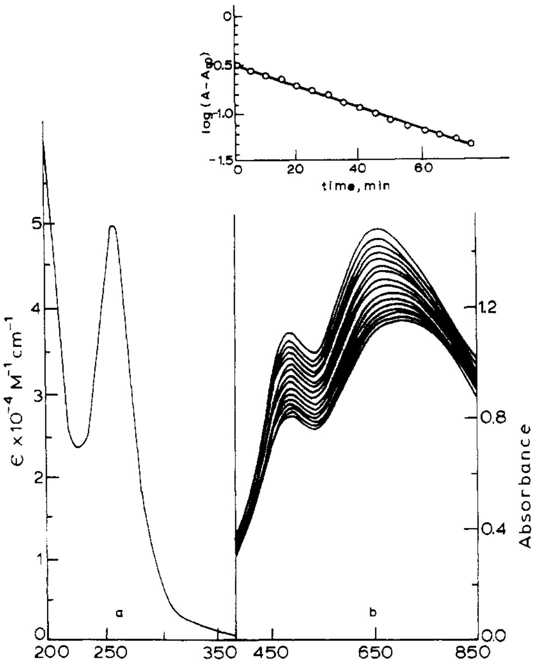

Figure 1. Typical absorption spectra and kinetic runs of HPC. Spectra: (a) nonreduced PW_{12}^{3-} showing the oxygen to metal CTB that are responsible for the photosensitivity; (b) photoreduced PW_{12}^{3-} showing gradual reoxidation, by H^+, after illumination had been shut off. Maximum absorbance corresponds to addition of ~1.4 electrons. Conditions: $[PW_{12}^{3-}] = 5 \times 10^{-4}$ M; [isopropyl alcohol] = 1.0 M; [Pt catalyst] = ~5 × 10^{-6} M in 0.1 M $HClO_4$. Inset: kinetics of absorbance change corresponding to reoxidation of reduced PW_{12}^{3-} with concomitant evolution of hydrogen.

$H_2W_{12}^{6-}$, respectively, were prepared according to well-established methods.[2a] Spectral and electrochemical potentials were in accordance with the well-known literature data, presented in Table I at the suggestion of one reviewer. All chemicals were of analytical grade.

Aqueous solutions of HPC in the presence of organic compounds were deaerated with Ar, scrubbed with V^{2+}, and photolyzed with a high-pressure Hg arc and a 150-W Xe lamp using filters or a monochromator. The progress of photoreduction was followed by the characteristic spectra of reduced HPC. Actinometry was monitored during photolysis with a selenium photocell calibrated with iron(III) oxalate. The liberated hydrogen was collected over the solution, withdrawn with a syringe, and analyzed with a Perkin-Elmer gas chromatograph using N_2 as carrier gas, and a 1-mm i.d. × 4-m length column packed with a 50–60 mesh molecular sieve.

Colloidal Pt was made, in situ, from K_2PtCl_4, by reduction with the photochemically reduced tungstates, which took place before evolution of hydrogen. It was also made by boiling H_2PtCl_6 with sodium citrate.[6] The data reported below were obtained with Pt reduced with sodium citrate.

It should be noted that the efficiency of the Pt catalyst dropped to about 50% after ~20 h of photolysis.

Results and Discussion

It has been reported that 1:12 tungstates are photosensitive at near-visible and UV light in the presence of a great variety of organic additives.[4,5] Excitation is accompanied by multielectron reduction of HPC, producing the so-called heteropoly blues (HPB), and oxidation of the organic species. Consecutive photoreduction drives the redox potentials toward more negative values, which, as is known, are oxidized back to the original nonreduced species by atmospheric oxygen. This is used in the photocatalytic oxidation of organic compounds.[4b] If, however, oxygen is excluded, the redox potentials are negative enough[2] to cause, from a thermodynamic point of view, reduction of H^+.[5] This may be accomplished in the presence of a Pt catalyst to overcome the high reduction potential necessary for the reduction of atomic hydrogen [$H^+ + e^- \rightarrow H$; $E°_7 = -2.2$ V] and produce instead molecular hydrogen [$2H^+ + 2e^- \rightarrow H_2$; $E°_7 = -0.41$ V and $E_0 = 0.0$ V, where E_7 and E_0 are potentials at pH 7 and 0, respectively].[9]

Table II. Maximum Number of Electrons Added Photochemically in the Presence of Isopropyl Alcohol (1.0 M) in 0.1 M $HClO_4$[a]

	max no. of added electrons			max no. of added electrons	
compd	without Pt[b]	with Pt[b]	compd	without Pt[b]	with Pt[b]
PW_{12}^{3-}	2.2	1.3	FeW_{12}^{5-}	1.4	0.3
SiW_{12}^{4-}	1.7	0.9	$H_2W_{12}^{6-}$	1.2	0.2

[a] Conditions: [HPC] = 5 × 10^{-4} M; photolysis with Xe 150-W lamp without filter (deaeration with Ar). [b] Values within 20%; concentration of Pt catalyst ~5 × 10^{-6} M.

Table III. Average Rates of Hydrogen Evolution and HPB Reoxidation of All Photochemically Reduced Tungstates[a]

	rate, 10^{-10} mol s^{-1}		
condition	H_2 evolution[b]	reoxidn of HPC[c]	rate const of reoxidn of HPC,[d] 10^{-4} s^{-1}
with Pt[e]	4.4 ± 1.8	4.2 ± 1.8	5.6 ± 3.1
without Pt	3.6 ± 1.6	2.2 ± 1.0	2.6 ± 1.8

[a] Conditions: [HPC] = 5 × 10^{-4} M; [isopropyl alcohol] = 1.0 M in 0.1 M $HClO_4$; photolysis with a Xe 150-W lamp without filter (deaerated with Ar). [b] Obtained by dividing the total H_2 produced, at the steady state, by the time. [c] Calculated, at the steady state, from the initial ~5% of reoxidation, after the lamp had been shut off. [d] Calculated from pseudo-first-order rate plots with A_∞ obtained from best linear fit. A_∞ is not easy to define as there is, depending on the HPC, a mixture of reduced tungstates in solution, each one having as A_∞ its lower, by one electron, oxidation step. [e] Concentration of Pt catalyst ~5 × 10^{-6} M.

It turns out that reduced HPC are capable of H_2 evolution with and without a Pt catalyst. Whereas they are not useful as sensitizers, they absorb very little in the visible region, they seem to be useful as electron carriers (relays). Photoreduction proceeds to the extent that the rate of photoreduction matches the back-reoxidation by H^+. The reduction step at which this takes place depends on the HPC used. Thus, for instance, with PW_{12}^{3-} this happens at a higher reduction step than with $H_2W_{12}^{6-}$, which is reduced at more negative reduction potentials. When Pt catalyst is present, the reduction potential at which the steady-state H_2 evolution is obtained is less negative. However, it should be noted that after ~100 h of photolysis, i.e. ~30 cycles, the effectiveness of the Pt catalyst was practically nullified.

Figure 1 shows typical absorption spectra and kinetics of reoxidation by H^+ of HPC. With, for instance, CH_3OH and 1:12 tungstates given generally as W_{12}^{n-}, the hydrogen evolution is obtained by the reactions (1)–(4), which are in essence dehydration

$$W_{12}^{n-} + CH_3OH \xrightarrow{h\nu} W_{12}^{(n+1)-} + \dot{C}H_2OH + H^+ \quad (1)$$

$$W_{12}^{(n+1)-} + CH_3OH \xrightarrow{h\nu} W_{12}^{(n+2)-} + \dot{C}H_2OH + H^+ \quad (2)$$

$$W_{12}^{(n+1)-} + \dot{C}H_2OH \rightarrow W_{12}^{(n+2)-} + CH_2O + H^+ \quad (3)$$

$$W_{12}^{(n+2)-} + H^+ \rightarrow W_{12}^{(n+1)-} + {}^1/_2H_2 \quad (4)$$

of methanol (eq 5). However, the hydrogen produced does not

$$CH_3OH \rightarrow CH_2O + H_2 \quad (5)$$

come from the alcohol, as the two processes, i.e. photolysis and hydrogen production, could take place independent of each other.[4b,7] Reactions 1 and 2 represent the photochemical reduction of W_{12}^{n-}, which is followed by radical reduction (reaction 3). The $\dot{C}H_2OH$ radical, as well as other hydroxyalkyl radicals, are known to be powerful reducing reagents, able to reduce HPC.[3] The reaction mechanism presented here is similar to the photocatalytic oxidation of organic compounds by HPC,[4b] except that reoxidation

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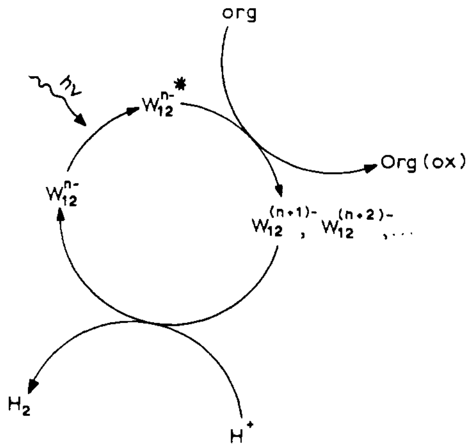

Figure 2. Schematic diagram of H_2 evolution by 1:12 tungstates. "Org" is an organic reagent that undergoes irreversible oxidation. Hydrogen is produced with and without the Pt catalyst.

of reduced tungstates takes place by H^+.

Another possible mechanism would be the formation of an alkoxide. However, tungstate ions in HPC are already coordinated to six oxygen atoms, and another oxygen on a seventh coordination site is unlikely.[10]

Table II shows the maximum number of electrons obtained with and without a Pt catalyst, whereas (Table III shows the average rates of hydrogen evolution and HPC reoxidation for all four photochemically reduced tungstates. It should be noted that the extent of reduction and, subsequently, the rate of hydrogen evolution are a function of the intensity of incident light. Extent of reduction is the point at which a steady state is obtained; i.e., the rate of photoreduction of HPC (reactions 1–3) is matched by the rate of reoxidation by H^+ (reaction 4).[11]

Apparently HPC also serve as heterogeneous catalysts, in the absence of metallic Pt, but are not as effective. The cycle for H_2 evolution is depicted in Figure 2. The rate of H_2 production is limited by the low quantum yield of HPB production. The quantum yield for the first reduction step (addition of one electron) is of the order of ~0.15, with alcohols, glycols, and glycol acids presenting generally higher quantum yields than carboxylic acids. The quantum yield drops to about ~0.01 for the second reduction step of PW_{12}^{3-}.[12] This is in accordance with the ease of hydrogen abstraction from organic compounds.[13]

Reoxidation of HPBs by H^+ seems to be 100% efficient. The rate of reoxidation of HPB (reaction 4) was followed by the change in absorbance of the HPB bands at ~750 nm, after the photolysis lamp was shut off (Table III; Figure 1). This was done by carefully excluding oxygen, first by deaeration and second by repeating cycles of photoreduction and back-reoxidation in which the leftover oxygen was consumed. The total production of hydrogen, measured by gas chromatography, verified reaction 4. About 1 mL of hydrogen was generally produced from 10 mL of HPC (5×10^{-4} M) and isopropyl alcohol (1 M) in 0.1 M $HClO_4$, after 24 h of photolysis with a 150-W Xe lamp. This amounts to an efficiency of the order of one molecule of hydrogen per 100 photons absorbed. The low yield represents the low efficiency of photoreduction of higher reduction products as mentioned before.

Comparing this to other systems, one notes that here one substance, the HPC, functions as sensitizer, relay, and catalyst, as opposed to three components, namely $Ru(bpy)_3^{2+}$, MV^{2+}, and the platinum catalyst used in the best known system so far. A serious disadvantage, though, is the low absorptivity of HPC in the visible area. However, with appropriate sensitizers, these compounds might be useful as relays and photocatalysts. Work, on these matters, is in progress.

Acknowledgment. We thank M. Z. Hoffman and N. Rakintzis for useful discussions and comments. Financial support from NATO is gratefully acknowledged.

Registry No. $PW_{12}O_{40}^{3-}$, 12534-77-9; $SiW_{12}O_{40}^{4-}$, 12363-31-4; $FeW_{12}O_{40}^{5-}$, 12181-27-0; $H_2W_{12}O_{40}^{6-}$, 12207-61-3; CH_3OH, 67-56-1; Pt, 7440-06-4; H_2, 1333-74-0; isopropyl alcohol, 67-63-0.

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(10) See for instance: Charman, H. B. *J. Chem. Soc. B* **1967**, 629 and references therein.

(11) The calculations of the maximum number of electrons, obtained at the steady-state condition, was made simply from the absorbance and the known molar absorptivities of the reduced species. For instance, if the absorbance indicated that the there was a mixture of 1- and 2-electron-reduced products, then if C_1 and C_2 were the corresponding percent concentrations and ϵ_1 and ϵ_2 the molar absorptivities, $C_1\epsilon_1 + C_2\epsilon_2 = 100A/C_t$ and $C_1(1e) + C_2(2e) = 100\ Y_e$, where Y_e is the total number of electrons added to the HPC and C_t is the concentration of HPC.

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(13) See for instance: Swallow, A. J. *Prog. React. Kinet.* **1978**, *9*, 195.

Notes

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Kinetics of Stepwise Aquation of the *trans*-Dicyanotetraamminechromium(III) Cation

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Received February 15, 1984

In transition-metal chemistry, cyanide stands out among the acido ligands because of several features of kinetic interest: (i) the exceptional stability of the coordinate bond; (ii) the large trans effect; (iii) the high basicity that enables extensive proton uptake by the coordinate group.[1] As part of a continuing study of the ground-state[2] and excited-state reactivity[3–5] of Cr(III) cyano ammines, we report here on the aquation kinetics of *trans*-$Cr(NH_3)_4(CN)_2^+$ and *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$. The purpose was to characterize the role of protonation, with regard to both its equilibrium and kinetic aspects, made particularly significant by the trans arrangement of the CN^- ligands.

Besides our previous account on $Cr(NH_3)_5(CN)^{2+}$,[2] other kinetic studies of CN^- aquation in Cr(III) systems have been reported for some members of the $Cr(H_2O)_{6-n}(CN)_n^{3-n}$ series.[6–9]

Experimental Section

trans-$[Cr(NH_3)_4(CN)_2](ClO_4)$ was prepared by a reported procedure.[10] *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ was obtained in situ by acid

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(1) For recent reviews on cyano complexes see: (a) Griffith, W. P. *Coord. Chem. Rev.* **1975**, *17*, 177. (b) Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: London, 1976.

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