Photochemical Reduction of Transition Metal Substituted Heteropoly Anions in Nonpolar Solutions

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Photochromism of $[SiW_{11}O_{39}Ni(X)]^{6-}$ as a tetraheptylammonium salt in various solvents under broadband UV light is observed in the presence of alcohols. The reaction proceeds faster with benzyl alcohol than with ethanol. Benzaldehyde is identified as the oxidized product of benzyl alcohol. Photochemistry is a reliable means to produce stable reduced transition metal substituted heteropoly tungstates in nonpolar media, where they hold promise as multielectron reduction catalysts. Preliminary reactivity toward CO_2 reduction is demonstrated.

Introduction

Heteropoly tungstate anions[1] are promising candidates for electrocatalysis because of their high stability in multiple redox states, tunable redox potentials, and capacity for reversible multiple electron transfer.[2] These anions resemble the local atomic structures of bulk metal oxides, to which they are often compared. For example, $[SiW_{12}O_{40}]^{4-}$ has a Keggin structure with a central Si(IV) atom and an octahedral arrangement of six oxides surrounds each tungsten(VI) atom, which can reversibly accept electrons without disrupting the structure.[3] Removing a tungsten-oxide pair leaves a square-pyramidal vacancy for the stable "lacunary" structure of $[SiW_{11}O_{39}]^{8-}$.[4] Various transition metal ions coordinate within this vacancy with one solvent molecule completing the octahedral ligand arrangement, yielding transition metal substituted heteropoly tungstates (TMS HPTs) such as $[SiW_{11}O_{39}Ni(H_2O)]^{6-}$.[2,5] Anson and Toth demonstrated the multielectron reduction of nitrite to ammonia catalyzed by $[SiW_{11}O_{39}Fe(H_2O)]^{6-}$ and other TMS−HPTs in aqueous solution.[6] Such reactivity exploits inner-sphere electron transfer by direct coordination of the substrate molecule and intermediates, which must displace the H_2O solvent ligand on the substituted transition metal to form the proposed species $[SiW_{11}O_{39}Fe(HNO_2)]^{6-}$ and $[SiW_{11}O_{39}Fe(NO)]^{6-}$. Pope showed that TMS HPTs dissolve in nonpolar solvents with tetraheptylammonium (tha$^+$) counterions ion paired such as (tha)$_6$-$[SiW_{11}O_{39}Ni(H_2O)]$.[7] These salts readily dehydrate in anhydrous conditions leaving the transition metal five-coordinated, e.g. (tha)$_6[SiW_{11}O_{39}Ni(\_)]$, and therefore become highly reactive.[7] Our group demonstrated that weak ligands such as CO_2 bind to the exposed site on several TMS HPTs in toluene or dichloromethane solutions forming species such as (tha)$_6[SiW_{11}O_{39}Ni(CO_2)]$ with an η^1 Ni−C bond.[8] Hydrogen bonding from a small amount of H_2O or alcohol stabilizes the CO_2 complex.

In principle, TMS HPTs could be electrocatalysts for the multielectron reduction of carbon dioxide and similar substrates because of this direct bonding. This requires the catalyst to be reduced in noncoordinating solvents, as in reaction 1.

$$(tha)_6[SiW_{11}O_{39}Ni(\_)] + 2H^+ + 2e^- \rightleftharpoons$$
$$(tha)_6[H_2SiW_{11}O_{39}Ni(\_)] \quad (1)$$
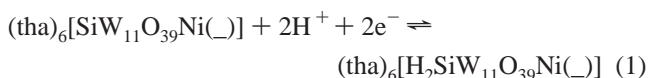
However, electrochemical reduction of the tetraheptylammonium salts of polytungstates in nonpolar solvents such as dichloromethane is difficult, as the large organic counterions insulate the anions from the electrode surface, preventing them from accepting electrons. The reduced catalyst also reductively dechlorinates the solvent.[9] Therefore, another method is needed to reduce the catalyst in nonpolar solvents. This paper describes the *photochemical* reduction of anhydrous (tha)$_6[SiW_{11}O_{39}Ni(\_)]$ under conditions amenable to CO_2 fixation.

Heteropoly tungstates develop a characteristic visible light absorption when reduced, and the reduction products are thus called "heteropoly blues." The electrochromism and photochromism of heteropoly tungstates is well studied in solid and aqueous forms.[10] Photochemical reduction involves oxidizing an adjacent molecule in a process similar to titanium dioxide photocatalysis,[11,12] and molecular oxygen is typically used to regenerate the catalyst for continued photocatalytic oxidation.[11] Yamase presented photochemical mechanisms for several types of polyoxometalates in various states by ESR techniques,[13] including details of the alkoxyl radical intermediates proposed here as generated by vanadium[14] polyoxometalates. Observations of the photoredox reactions of molybdenum polyoxometalates provide additional insight for the primary fundamental steps in question.[15]

Almost all of the published reports concentrate on unsubstituted polytungstates and polymolybdates, and few focus on TMS HPTs as photocatalysts. In one of these reports, the photocatalytic oxidation rates for typical organic substrates using $[SiW_{11}O_{39}Mn^{II}(H_2O)]^{6-}$ and $[SiW_{11}O_{39}Cu^{II}(H_2O)]^{6-}$ in oxygenated aqueous solution diminishes by about an order of magnitude with respect to unsubstituted $[SiW_{12}O_{40}]^{4-}$.[16] In another report, the substituent's coordination site covalently links the photocatalyst via an amine to a silica substrate as $[SiW_{11}O_{39}Ni(NH_2R)]^{6-}$,[17] where R represents the organic link between the amine and the silica. This allows catalyst recovery and may adsorb organic molecules near the catalyst,[18] but blocks direct access to the coordination site.

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Photoreactivity characteristic of light-induced charge separation with alcohol substrates occurs only when preceded by effective precomplexation of the substrate and the catalyst.[12,19] Unsubstituted polyoxometalates directly complex with strong ligands such as alcohols. Weak ligands such as CO_2[8] require both charge and substrate localization.[6] Photocatalytic CO_2 reduction using aqueous TiO_2 suspensions[20] suffers from low efficiency presumably due to minimal preassociation and a tendency for single electron localization on TiO_2 surfaces.[21] The $[PW_{10}O_{40}Ti_2]^{7-}$ photocatalyst circumvents the multielectron kinetic barrier with protonation-dependent electron localization at the titanium substitution.[22] However, the transition metal substitutions in this case are hexacoordinated with oxides, and therefore do not provide a covalent binding site for the CO_2 substrate. Direct coordination of the substrate on the transition metal substitution as $(tba)_5[PW_{11}O_{39}Cu(R_2S)]$, where tba^+ represents the tetrabutylammonium ion, likely explains the highly active photo oxidation of thioethers in deoxygenated acetonitrile solution despite no observable activity of $(tba)_3$-$[PW_{12}O_{40}]$ under these conditions.[23] The reduced catalysts produced in this study can also be formed electrochemically in acetonitrile and other polar organic solvents,[24] and therefore did not receive much attention.[23]

We exploit the well-known photoreduction of polyoxometalates by alcohols to produce the reduced species, $(tha)_6[H_2-SiW_{11}O_{39}Ni(\_)]$, which cannot be directly produced electrochemically in nonaqueous solvents. The residual alcohol provides the hydrogen bonding necessary to bind CO_2 at the open coordination site. This system shows capacity for rapid multielectron photoassisted reduction catalysis of CO_2.

Experimental Section

Toluene and hexane were dried by refluxing with sodium and then distilling and storing over activated sieves. Chloroform was similarly treated using calcium hydride as the drying agent. Ethanol was dried by storage over activated sieves. Benzyl alcohol was used as received from Acros Organics. All solvents and solutions were handled under an argon atmosphere.

Cyclic voltammetry was recorded with a EG&G Princeton Applied Research potentiostat/Galvanostat model 273A. A 20 mM solution of $K_6[SiW_{11}O_{39}Ni(H_2O)]$ was prepared in 1 M pH 4.5 lithium acetate buffer. A glassy carbon working electrode ($\sim$5 mm^2) was measured against a Ag/AgCl (saturated KCl) electrode with a platinum auxiliary at a 30 mV/s scan rate. The potential scale was calibrated using $PW_{12}O_{40}^{3-}$ in 0.1 M H_2-SO_4 solution.

$K_6[SiW_{11}O_{39}Ni(H_2O)]$ was synthesized in aqueous solution and purified by recrystallization.[5] The anion was phase transferred from water to toluene using tetraheptylammonium bromide.[7] The toluene layer containing $(tha)_6[SiW_{11}O_{39}Ni(H_2O)]$ was separated and dried under vacuum at 70 °C. The tarry solid, $(tha)_6[SiW_{11}O_{39}Ni(\_)]$, was then dissolved in the appropriate anhydrous solvent to 60 mM. All spectra were measured at this concentration. About 4 mL of this stock was transferred under argon to a Schlenk flask with a 1 cm quartz cuvette sidearm. The sample was irradiated in the cuvette with magnetic stirring. UV/vis spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer with the same cuvette.

The beam from a 1 kW Oriel Xe lamp passed a dichroic mirror and a 10 cm jacketed water filter to remove the IR portion of the radiation. A quartz lens focused the subsequent beam onto the sample.
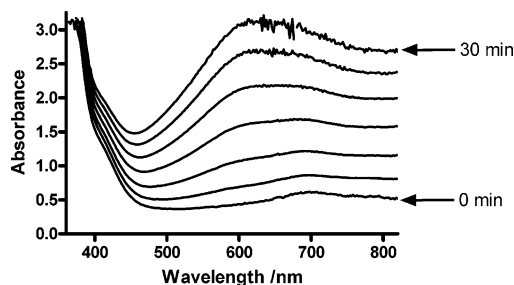
Figure 1. Developing visible absorbance of $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ in benzyl alcohol with UV irradiation. The bottom spectrum is prior to irradiation. The other spectra, in ascending order, correspond to times of 5, 10, 15, 20, 25, and 30 min, respectively. The emerging broad band centered at 610 nm indicates reduced $(tha)_6[H_2SiW_{11}O_{39}Ni(ROH)]$. A similar progression is seen with ethanol as the solvent.
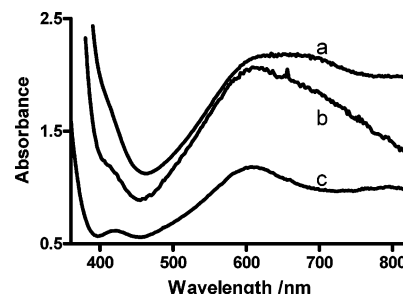
Figure 2. Photochemically reduced $(tha)_6[H_2SiW_{11}O_{39}Ni(ROH)]$ in benzyl alcohol (a) and in ethanol (b). Comparable absorbances at 610 nm indicate a similar amount of reduced catalyst. Electrochemically reduced aqueous $[H_2SiW_{11}O_{39}Ni(H_2O)]^{6-}$ (c).

IR spectra were obtained using a Nicolet 6700 FTIR in transmission mode with 500 scans at 8 cm^{-1} resolution. The sample was loaded in a sealed liquid IR cell consisting of NaCl plates with a 0.015 mm spacer. The cell was loaded by syringe in a glovebox under a purified argon atmosphere.

Results

The catalyst appeared pale yellow in toluene solution as $(tha)_6$-$[SiW_{11}O_{39}Ni(\_)]$, and slightly green in alcohol solution as $(tha)_6$-$[SiW_{11}O_{39}Ni(ROH)]$. The blue color characteristic of reduced heteropoly tungstates was therefore easily distinguished. Blue wisps appeared within seconds on the irradiated face of the cuvette containing anoxic $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ dissolved in alcohol. The whole solution turned blue within several seconds at full lamp power. Figure 1 shows the emergence of a broad peak from 500 to 800 nm indicative of reduced $(tha)_6$-$[H_2SiW_{11}O_{39}Ni(ROH)]$. The photoreduction of $(tha)_6[SiW_{11}O_{39}-Ni(X)]$, where X is either an open coordination site or occupied by alcohol, required the presence of either ethanol or benzyl alcohol as an electron donor. The reaction proceeded in neat alcohol solution with a coordinated alcohol, and with either alcohol diluted in toluene as the predominantly coordinatively unsaturated species. The reaction proceeded in hexane solution with benzyl alcohol, but only transiently with ethanol. The blue color instantly bleached with exposure to oxygen in any medium. Photochromism did not occur in chloroform solutions with either alcohol present, and a residue precipitated on the irradiated face, presumably due to reductive dechlorination of the chloroform,[9] which releases HCl and causes acid hydrolysis of the heteropoly tungstate.

Figure 2 shows the absorption spectra of $(tha)_6[SiW_{11}O_{39}-Ni(ROH)]$ following partial photoreduction in the presence of
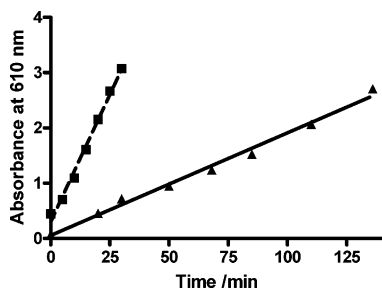
Figure 3. Emergence of the absorbance at 610 nm as a function of time in benzyl alcohol (dashed line) and ethanol (solid line). The linear progression indicates effective zero-order kinetics in both cases. The reaction proceeds about seven times faster in benzyl alcohol, which is more easily oxidized than ethanol.
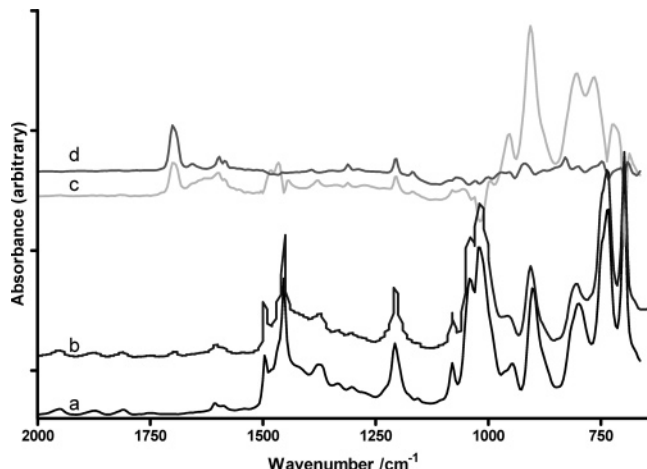

Figure 4. Transmission FT-IR spectra of $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ in neat benzyl alcohol before (a) and after 2 days of irradiation (b), as well as the subtraction of spectra a and b (c). Spectrum *d* is the subtraction of $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ with benzaldehyde spiked subtracted from $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ in neat benzyl alcohol. Notice the carbonyl that appears at 1705 cm^{-1}.

benzyl alcohol (a) and ethanol (b), respectively. Note that the spectra closely match the spectrum of $[H_2SiW_{11}O_{39}Ni(H_2O)]^{6-}$ produced by conventional electrolysis in aqueous buffer (c). A plot of the absorbance at 610 nm is shown in Figure 3 in ethanol and in benzyl alcohol vs irradiation time. Both plots are linear, and the slope in benzyl alcohol is approximately seven times larger than the slope in ethanol. The difference in rates qualitatively reflects the oxidation potentials of the two alcohols.

Figure 4 shows the IR spectra of $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ in neat benzyl alcohol before and after irradiation. The difference between these spectra matches the spectrum of benzaldehyde, the expected product of benzyl alcohol oxidation.[25] Benzoic acid did not match as well as benzaldehyde, particularly in the carbonyl region. From the observed carbonyl intensity, we estimate that the exhaustively irradiated solution contains approximately 16 mM benzaldehyde. The changes between 1000 and 600 cm^{-1} after irradiation are observed with either reductant, and are likely due to changes in the environment near the $(tha)_6$-$[SiW_{11}O_{39}Ni(ROH)]$ upon reduction.

The reduction occurred in ethanol with $(tha)_6[SiW_{11}O_{39}Ni-(ROH)]$ concentrations between 20 and 240 mM. Concentrating the photoreduced samples under vacuum bleached the blue color, and no products were observed following concentration. Headspace IR in a 10 cm path length cell revealed only a trace increase in CO_2, presumably due to traces of O_2 completely oxidizing the alcohol.[11] Product identifications using NMR (^{1}H and ^{13}C) spectra were inconclusive, possibly due to signal
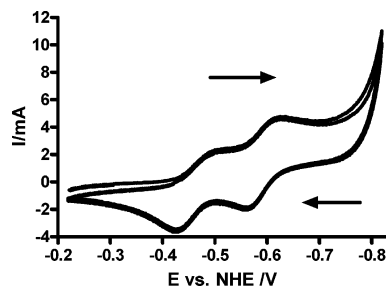

Figure 5. Cyclic voltammogram of 20 mM $SiW_{11}O_{39}Ni^{6-}$ in aqueous lithium acetate buffer at pH 4.5.

broadening by the paramagnetic Ni atom. The reduced heteropoly crashed out of ethanol solution as tiny blue droplets when water was added. The blue residue redissolved in nonaqueous media, but the blue color bleached, possibly because of the concentration effects previously mentioned or by inadvertent exposure to oxygen. Traces of benzaldehyde and acetaldehyde were identified by GC analysis of the distillate after the reaction with benzyl alcohol and ethanol, respectively. A metastable solid residue, likely an acetal oligomer, appeared during extended irradiation in either neat alcohol solution.

CO_2 bubbled through a solution of $(tha)_6[H_2SiW_{11}O_{39}Ni(\_)]$ in dry toluene bleached the blue color in approximately 10 min, as the UV/vis spectrum returned to that observed for $(tha)_6$-$[SiW_{11}O_{39}Ni(\_)]$ or $(tha)_6[SiW_{11}O_{39}Ni(CO_2)]$, which are difficult to distinguish.[8] In contrast, CO_2 bubbled through a solution of the potassium salt of $[H_2SiW_{11}O_{39}Ni(H_2O)]^{6-}$ in 50:50 ethanol: water produced no reaction for up to $1^1/_2$ h.
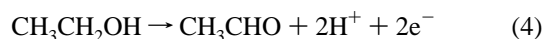
Discussion

Positive product identification verifies the redox process shown in reaction 2.

$$(tha)_6[SiW_{11}O_{39}Ni(X)] + C_6H_5CH_2OH \xrightarrow{UV}$$
$$(tha)_6[H_2SiW_{11}O_{39}Ni(X)]^{6-} + C_6H_5CHO \quad (2)$$
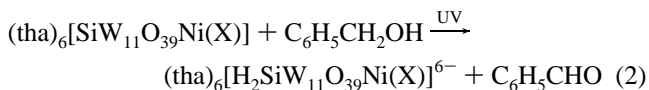
The reduced form of the heteropoly complex, $(tha)_6[H_2SiW_{11}$-$O_{39}Ni(X)]$, is identified in the UV/vis spectra following photoreduction, and the benzaldehyde product is clearly identified using in situ IR spectroscopy. Photo oxidation of benzyl alcohol to benzaldehyde was reported using unsubstituted Wells−Dawson heteropoly tungstates and molybdates with air under real or simulated solar irradiation over the course of weeks or days.[25] The reaction shown here occurred within seconds. The reaction proceeds faster with benzyl alcohol than with ethanol because benzyl alcohol is more easily oxidized (reactions 3 and 4).

$$C_6H_5CH_2OH \rightarrow C_6H_5CHO + 2H^+ + 2e^- \quad (3)$$

$$E^0_{red,aqueous} = -0.558 \text{ V}^{27}$$

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \quad (4)$$

$$E^0_{red,aqueous} = -0.197 \text{ V}^{26}$$

These potentials may increase by about 0.1 V in pure organic media.[26] This effect and that of the unknown environment near the $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$, which may be described as a reverse micelle, are ignored for the sake of discussion.
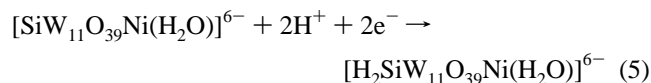
The reduction of $[SiW_{11}O_{39}Ni(H_2O)]^{6-}$ in aqueous solution as determined by cyclic voltammetry (Figure 5) proceeds

Photochemical Reduction

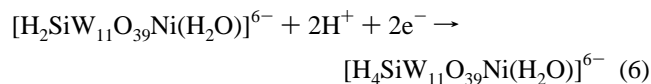*J. Phys. Chem. B, Vol. 110, No. 21, 2006* **10579**
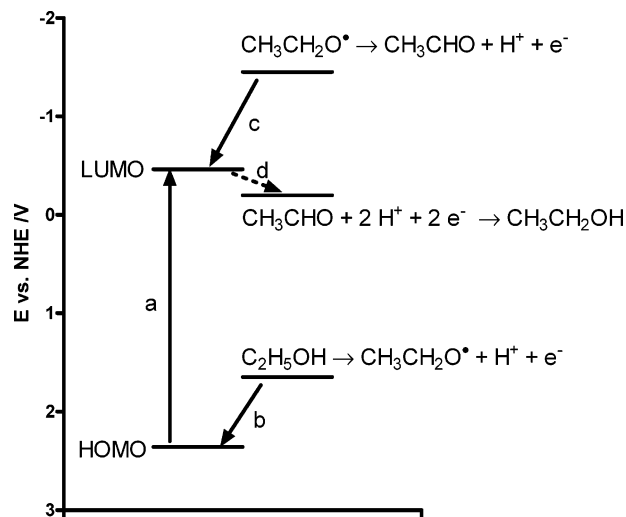
Figure 6. Proposed photochemical energy diagram. Absorption of a photon causes excitation (a). Ethanol oxidizes to fill the hole (b), generating the ethoxyl radical. The ethoxyl radical donates an electron to the LUMO (c), forming the 2-electron reduced heteropoly and acetaldehyde. The reduced heteropoly may slowly reduce the aldehyde (d).

according to reactions 5 and 6.

$$[SiW_{11}O_{39}Ni(H_2O)]^{6-} + 2H^+ + 2e^- \rightarrow$$
$$[H_2SiW_{11}O_{39}Ni(H_2O)]^{6-} \quad (5)$$

$$E^{1/2}_{red,aqueous} = -0.461 \text{ V}$$

$$[H_2SiW_{11}O_{39}Ni(H_2O)]^{6-} + 2H^+ + 2e^- \rightarrow$$
$$[H_4SiW_{11}O_{39}Ni(H_2O)]^{6-} \quad (6)$$

$$E^{1/2}_{red,aqueous} = -0.591 \text{ V}$$

Both quasi-reversible redox couples were coulometrically confirmed as two electron reductions. These potentials should become increasingly negative in solvents of lower Lewis acidity.[28]

The first 2-electron reduction potential suggests a slightly favorable reaction with benzyl alcohol, and unfavorable with ethanol, but neither reaction proceeds in the dark. Note that the bond that forms between the Ni and the O of the alcohol in water-free environments, which is likely necessary for the photoinitiated electron transfer, is not shown here. Our difficulty isolating reaction products, particularly acetaldehyde, suggests that the aldehydes either remain in close association with the catalyst or quantitatively form metastable aldol adducts.

Supported by detailed observations,[13-15] the mechanism can be broken down into three steps: photoexcitation followed by two one-electron events. First, the $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ absorbs a photon, promoting an electron from the HOMO to the LUMO (Figure 6a). Using the potential from reaction 4 as the position of the LUMO, and a HOMO−LUMO gap of 2.82 eV as determined by the onset of UV absorption, the hole in the HOMO is calculated at a potential of +2.36V. The hole extracts an electron from the bound ethanol, with a corresponding proton transfer (Figure 6b), causing reaction 7.

$$CH_3CH_2OH \rightarrow CH_3CH_2O^\bullet + H^+ + e^- \quad (7)$$
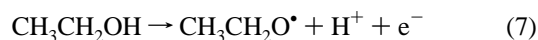
$$E^0_{red,aqueous} = +1.65 \text{ V}^{29}$$

Ignoring radical rearrangement, the ethoxyl radical donates an electron directly to the LUMO of $(tha)_6[H_2SiW_{11}O_{39}Ni(X)]$ (Figure 6c) and further oxidizes according to reaction 8, while donating the second electron to the $SiW_{11}Ni$.

$$CH_3CH_2O^\bullet \rightarrow CH_3CHO + H^+ + e^- \quad (8)$$
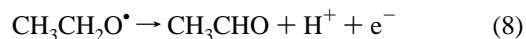
$$E^0_{red,aqueous} = -1.45 \text{ V}^{30}$$

Disproportionation of two one electron reduced catalysts is less likely than this mechanism because of the restricted electron transfer across the tetraheptylammonium envelope. Therefore, the emergence of 2-electron oxidized products suggests the 2-electron reduced TMS HPT. The final products, as well as the intermediates, are subject to back reactions (Figure 6d). The back reaction occurs most quickly in hexane because of the high reduction potential of the reduced catalyst in this environment.[28]

A plot of the absorbance at 610 nm vs time of irradiation (Figure 3) is linear, revealing an apparent zero order reaction. This shows that the reactants are not significantly depleted, and there is no concentration dependent back reaction within the initial stages of the reaction investigated. However, the reaction did reverse when the solution was concentrated after the reaction and the reaction did not proceed when the concentration of $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ was higher than 240 mM. It is possible that the reduced $(tha)_6[H_2SiW_{11}O_{39}Ni(\_)]$ is only stable at low concentration or low ionic strength. Alternatively, the $(tha)_6[H_2SiW_{11}O_{39}Ni(\_)]$ could decompose[22] under these conditions according to reaction 9, as observed with other photochemically reduced polyoxometalates.[13]

$$(tha)_6[H_2SiW_{11}O_{39}Ni(X)]^{6-} \rightarrow$$
$$(tha)_6[SiW_{11}O_{39}Ni(X)]^{6-} + H_2 \quad (9)$$
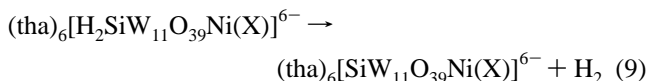
The sensitivity of the reduced $(tha)_6[H_2SiW_{11}O_{39}Ni(\_)]$ to CO_2 in dry toluene is preliminary evidence for CO_2 reduction, and product analyses are currently underway. The insensitivity of the reduced $[H_2SiW_{11}O_{39}Ni(H_2O)]^{6-}$ to CO_2 in water confirms the role of the coordination site in the CO_2 reduction mechanism. The rapid appearance of the blue species and subsequent bleaching with CO_2 suggest relatively fast reaction rates, which may increase with system optimization.

Conclusions

This paper shows that $(tha)_6[SiW_{11}O_{39}Ni(ROH)]$ is photochemically reduced in nonpolar solvents by alcohols. The photochemically produced $(tha)_6[H_2SiW_{11}O_{39}Ni(\_)]$ is sensitive to CO_2, suggesting CO_2 reduction. Other transition metal substituted heteropoly tungstates will likely behave similarly, and some may serve as reduction photocatalysts for other stubborn substrates.

References and Notes

(1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: New York, 1983.
(2) Sadakane, A.; Steckhan, E. *Chem. Rev.* **1998**, *98*, 219−237.
(3) Teze, A.; Herve, G. *Inorg. Synth.* **1990**, *27*, 93−94.
(4) Teze, A.; Herve, G. *Inorg. Synth.* **1990**, *27*, 85−87.

(5) Weakley, T. J. R.; Malik, S. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935−2944.

(6) Toth, J. E.; Anson, F. C. *J. Am. Chem. Soc.* **1989**, *111*, 2444−2451.

(7) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737−2738.

(8) Szczepankiewicz, S. H.; Ippolito, C. M.; Santora, B. P.; Van de Ven, T. J.; Ippolito, G. A.; Frankowiak, L.; Wiatrowski, F.; Power, T.; Kozik, M. *Inorg. Chem.* **1998**, *37*, 4344−4352.

(9) Sattari, D.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, *8*, 634−635.

(10) Yamase, T. *Chem. Rev.* **1998**, *98*, 307−325.

(11) Hisikia, A.; Mylonas, A.; Papaconstantinou, E. *Chem. Soc. Rev.* **2001**, *30*, 62−69.

(12) Kim, S.; Park, H.; Choi, W. *J. Phys. Chem. B* **2004**, *108*, 6402−6411.

(13) Yamase, T. *Catal. Survey Asia* **2003**, *7*, 203-217.

(14) Yamase, T.; Ohtaka, K. *J. Chem. Soc., Dalton Trans.* **1994**, 2599−2608.

(15) Yamase, T.; Yano, Y.; Ishikawa, E. *Langmuir* **2005**, *21*, 7823−7832.

(16) Mylonas, A.; Hisikia, A.; Papaconstantinou, E.*J. Mol. Catal.* **1996**, *114*, 191−200.

(17) Guo, Y.; Hu, C.; Jiang, C.; Yang, Y.; Jiang, S.; Li, X.; Wang, E. *J.* Catal. **2003**, *217*, 141−151.

(18) Ozer, R. R.; Ferry J. L. *J. Phys. Chem. B* **2002**, *106*, 4336−4342.

(19) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347−6354.

(20) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature (London)* **1979**, *277*, 637−638.

(21) Szczepankiewicz S. H.; Colussi A. J.; Hoffmann M. R. *J. Phys. Chem.* B, **2000**, *104*, 9842−9850.

(22) Yamase, T.; Sugeta, M. *Inorg. Chim. Acta* **1990**, *172*, 131−134.

(23) Chambers, R. C.; Hill, C. L. *Inorg. Chem.* **1991**, *30*, 2776−2781.

(24) For Example: Zhang, J.; Bond, A. M.; Richardt, P. J. S.; Wedd, A. G. *Inorg. Chem.* **2004**, *43*, 8263−8271. and references therein.

(25) Ruther, T.; Bond, A. M.; Jackson, W. R. *Green Chem.* **2003**, *5*, 364−366.

(26) Coulson, D. M.; Crowell W. R. *J. Am. Chem. Soc.* **1952**, *74*, 1290−1294.

(27) Pratt, C.; Cornely, K. Oxidative Phosphorylation. In *Essential Biochemistry*; John Wiley & Sons: New York, 2004; p 373.

(28) Keita, B.; Bouaziz, D.; Nadjo, L. *J. Electrochem. Soc.* **1988**, *135*, 87−91.

(29) Koppenol, W. H. *FEBS Lett.* **1990**, *264*, 165−167.

(30) The potential is calculated by assuming that the sum of reactions 6 and 7 equals reaction 3.