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Investigation of the Photocatalytic Activity of TiO_2-Polyoxometalate Systems

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The present study reports the investigation of polyoxometalate catalyzed electron transfer from the conduction band of photoexcited TiO_2 to molecular oxygen. The oxidation of 1,2-dichlorobenzene (DCB) was used as an index reaction for evaluating the photocatalyst systems $TiO_2-PW_{12}O_{40}{}^{3-}$, $TiO_2-SiW_{12}O_{40}$,$^{4-}$ and $TiO_2-W_{10}O_{32}{}^{4-}$ in oxygenated aqueous solution. Addition of these polyoxometalate (POM) anions to TiO_2 suspensions resulted in significant rate enhancement for DCB oxidation. Photodegradation kinetics exhibited [POM] dependence, experiencing different maximum ($k = 0.0318$ min^{-1}, 0.0108 min^{-1}, and 0.0066 min^{-1}) for each POM at different [POM] (0.1 mM $PW_{12}O_{40}{}^{3-}$, 0.07 mM $SiW_{12}O_{40}$,$^{4-}$ and 1 mM $W_{10}O_{32}$,$^{4-}$ respectively). The probability that the difference in the adsorption affinity of POMs on TiO_2 surface could account for the observed ranking of photodegradation rates was ruled out by adsorption isotherm experiments that revealed similar binding constants for each POM (467 M^{-1}, 459 M^{-1}, and 417 M^{-1} for $PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$, and $W_{10}O_{32}{}^{4-}$, respectively). DCB degradation over TiO_2 with O_2 or POM+O_2 systems can be modeled by the Langmuir−Hinshelwood (saturation kinetics) model. The concentration-independent rate constants (k_{L-H}) for TiO_2-O_2, $TiO_2-W_{10}O_{32}{}^{4-}$, $TiO_2-SiW_{12}O_{40}{}^{4-}$, and $TiO_2-PW_{12}O_{40}{}^{3-}$ were 0.0818, 0.152, 0.421, and 0.638 min^{-1}, respectively. An analysis of ΔG for electron transfer from the conduction band of TiO_2 to POMs in this study shows that the electron transfer takes place even when it is endothermic.

Introduction

Semiconductor photocatalysts have received a great deal of attention for their potential to utilize solar photons in chemical processes, including such diverse areas as photoelectrochemical electricity generation, CO_2 fixation, and the remediation of hazardous waste streams (*1*−*10*). The photoexcitation of these materials results in the promotion of a valence band electron to the conduction band of the semiconductor, creating strongly oxidizing sites (holes) and reducing sites (electrons) in the photocatalyst (*11*). These sites may react with materials adsorbed to the photocatalyst surface, or they may recombine without effecting a change in the immediate environment (*9, 12, 13*). Hole-electron recombination is a serious problem for the development of photocatalytically based technologies, and quantum yields for photocatalytic processes tend to be quite low (often less than 0.05).

However, there are strategies to reduce hole-electron recombination and increase photocatalyst efficiency. Typically, these involve the addition of sacrificial oxidants to scavenge conduction band electrons and enable holes to oxidize a targeted organic substrate. The least expensive of these is dioxygen; however, oxidants such as ozone, peroxydisulfate, periodate, bromate, chlorate, hydrogen peroxide, and others have all been successfully applied (*14*−*19*). It is also possible to remove conduction band electrons electrochemically, by depositing the photocatalyst on a conductive substrate and placing it at a sufficiently positive potential to harvest the photogenerated electrons (*20*−*22*). All of these techniques can boost photooxidation efficiency and have been thoroughly reviewed by other authors (*4, 6, 23, 24*).

Although added oxidants can have dramatic effects on photooxidation efficiency, it is difficult for any of them to compete on a cost-benefit basis with the potential of atmospheric dioxygen. Therefore, several investigators are taking the approach of developing surface modified photocatalysts that possess new, synthesized sites for catalyzing electron transfer from the conduction band to dioxygen (*25*−*33*). Typically, this is accomplished by the addition of transition metal islands to the photocatalyst particle. This addition can occur by dispersing metals in the semiconductor lattice by coprecipitation techniques or on the outside of the photocatalyst particle by photodeposition as metal islands (*27*). The effect of coprecipitation is difficult to predict; ions such as Fe^{3+} and Cu^{2+} at very low concentrations inhibit electron−hole recombination (*34*−*37*), while others including V^{2+} (*38*), Mo^{3+} (*39*), and Cr^{3+} (*38*) have been reported to facilitate the recombination of charge-carriers. Photodeposition of metal islands can be especially problematic because the island size can potentially grow large enough to “shade” the particle or block active sites.

Here, we report the investigation of TiO_2-polyoxometalate (POM) photocatalytic systems that utilize the anions $PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$, and $W_{10}O_{32}{}^{4-}$ as electron scavengers for photogenerated conduction band electrons. Yoon and co-workers recently reported enhanced photocatalytic reduction rates for methyl orange in a composite $TiO_2-PW_{12}O_{40}{}^{3-}$ system. In this paper, the authors interpreted their finding to be a result of joint photoexcitation of the TiO_2 and POM, with photoexcited POM serving as an electron-transfer catalyst to methyl orange (*40*). In contrast, our system utilizes POMs as ground-state oxidants to facilitate hole-electron separation.

The photocatalytic activity of all the systems in this study were measured by the photooxidation of the index chemical 1,2-dichlorobenzene (DCB) in aqueous solution. These POMs are known to be moderate ground-state oxidants with reduction potentials of $H_2NaPW_{12}O_{40}$ (−0.023 V vs SCE) (*41*), $H_4SiW_{12}O_{40}$ (−0.187 V vs SCE) (*41*), and $Na_4W_{10}O_{32}$ (−1.270 V vs SCE) (*42*). It has been demonstrated that the POMs in this study are structurally stable in their reduced state and are readily reoxidized by dioxygen or hydrogen peroxide (*41, 43*−*46*). In our work, we observe that these oxidants are more effective than dioxygen alone at removing conduction band electrons from TiO_2, even when POM reduction is energetically disfavored. The suggested sequence of reactions portrays the POM as an electron carrier between the photocatalyst particle and dioxygen (Scheme 1). This is analogous to the use of methyl viologen as an electron carrier, as reported by Willner and co-workers (*47*). The use of POMs in this study as electron carriers led to an apparent increase in DCB degradation rates of a factor of 8 relative to TiO_2 alone.

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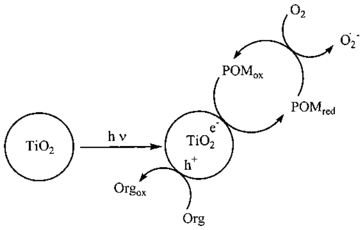
SCHEME 1. POM-Mediated Electron Transfer from Conduction Band of TiO_2 to the Molecular Oxygen



Experimental Section

Materials. TiO_2 (P-25; ca. 80% anatase, 20% rutile; average particle diameter is 30 nm with surface area 50 m^2/g) was kindly supplied by Degussa Co. Methyl *tert*-butyl ether (MTBE, GC^2 quality) was obtained from Burdrick and Jackson. $HNa_2PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (reagent grade) were obtained from Fluka. $Na_4W_{10}O_{32}$ was prepared by the method of Duncan et al. (*48*). 1,2-Dichlorobenzene (DCB, 99%), 2,3-dichlorophenol (99+%), 3,4-dichlorophenol (99+%), $HClO_4$ (99+%), and 4-bromoanisole (BA, 99%) were obtained from Aldrich Chemical Co. ASTM grade water (18 M Ω cm resistivity) was used for all experiments. Aqueous DCB solutions were prepared from a stock DCB-saturated aqueous solution. Analytical DCB stocks were prepared in GC^2 grade methanol. The internal standard for all quantitation was BA spiked into the extracting solvent. $W_{10}O_{32}^{4-}$ was confirmed by a comparison of the UV−vis absorption spectrum of product to that reported in the literature (*49, 50*). The UV−vis spectrum is provided in the Supporting Information.

Experimental Procedure

The reactor used in all experiments was an Ace Glass Schlenk reactor. The light source was a 100 W Hg arc lamp (Osram) filtered through a monochromator (Photon Technologies Incorporated) to select for output at 350 nm. The slits were set at 0.6 mm with a ±2.4 nm band-pass. Lamp output (12.6 $\times 10^{-6}$ einstein/min) was constant over the time frame of the experiments, as determined by ferrioxalate actinometry (*51*).

Aqueous TiO_2 suspensions were prepared (0.1 wt %) and adjusted to pH 1 with $HClO_4$ following POM addition. Experimental conditions were restricted to pHs < 3, because of the hydrolytic instability of the POMs in this study (*45*). The suspension was stirred for 15 min to ensure complete mixing. Aqueous DCB was added to achieve the desired substrate concentration. The reactor was allowed to equilibrate in the dark with stirring for 30 min prior to the beginning of illumination. The Hg arc lamp was always allowed to stabilize at least 15 min before use. Illuminations were carried out at 23 °C with constant stirring.

Samples (2 mL) were removed from the sample port with an adjustable spring-loaded syringe (Manostat). Samples were immediately placed in 20-mL EPA vials that had been precharged with 5 mL of chilled extraction solvent (MTBE with BA as an internal standard). To inhibit any further possible reaction, the samples were buffered to pH 7.0 with the addition of 0.2 mL of 1.0 M Na_2CO_3 and stored in the dark. DCB was immediately extracted from the aqueous phase by rapidly mixing samples on a vortex mixer for 30 s. The organic layer was removed and stored at 4 °C until analysis by GC-ITMS (gas chromatography with ion trap mass spectrometer) or GC-ECD (gas chromatography with electron capture detector).

For reduced POM measurements, the TiO_2−POM system was degassed under high-purity nitrogen for 2 h prior to illumination. Samples were taken by cannula (24 in., 14 gauge, Aldrich Chemical Co) and placed in sealed and degassed 10 mL EPA vials. The samples were centrifuged, and UV−vis absorbance was recorded by a Perkin-Elmer 283 spectrophotometer.

Adsorption isotherms were obtained by mixing 0.1 wt % Degussa TiO_2 in 20 mL EPA vials with varying concentrations of POMs at pH 1. The resulting suspensions were shaken for 24 h, centrifuged, and filtered through Micropore filter (2.5 mm). UV−vis absorbance spectra of the filtrate were recorded and used to quantify the extent of adsorption.

GC-ECD and GC-ITMS Conditions. GC-ECD Operating Conditions. GC-ECD analyses were done on a Hewlett-Packard 5890 GC equipped with a 7672A autoinjector, Chemstation integration package, and electron capture detector. Carrier gas was He, and N_2 was used as makeup. The carrier gas flow rate was 1.3 mL/min, and the method detection limit for DCB was 0.018 μM. The injector port was set for splitless operation at 250 °C. The autoinjector volume was set at 1 μL. The analytical column was a 30 m DB-5 with a 0.25-μm film thickness. The temperature program was as follows: 1 min at 80 °C, increase at a rate of 3 °C/min to 180 °C, isothermal at 180 °C for 1 min, increase at 20 °C /min to 250 °C, and isothermal for 7 min.

GC-ITMS Operating Conditions. GC-ITMS analyses were performed on a Varian 3800 GC equipped with a Varian 8200 autoinjector and Varian Saturn 2000 ITMS. The injector port was set for splitless operation at 250 °C. The autoinjector volume was set at 1 μL. The analytical column was a 30 m DB-5 with a 0.25-μm film thickness. Carrier gas (He) flow rate was 1.3 mL/min, and the method detection limit for DCB in the sample matrix was 0.41 μM. The temperature program was as follows: 1 min at 80 °C, increase at a rate of 3 °C/min to 180 °C, isothermal at 180 °C for 1 min, increase at 20 °C /min to 250 °C, and isothermal for 7 min. This method was applied to byproduct analysis also.

Result and Discussion

In this paper, we report a controlled exploration of the catalyzed electron-transfer process from the conduction band of TiO_2 to dioxygen in water. We employed three polyoxometalate anions, $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and $W_{10}O_{32}^{4-}$ as electron-transfer promoters. These anions were chosen because (a) their documented ability to undergo many successive electron transfers without chemical degradation (*45, 52−55*); (b) their small size and low absorbance at the wavelengths encountered in this study, which guaranteed that they would not affect light absorbing/scattering of the baseline TiO_2 suspension; (c) their similar structure (*56*), which suggested they would tend to sorb to TiO_2 surfaces with comparable binding constants; and (d) their widely differing reduction potentials (*41, 42*), which allowed us to probe their activity as a function of the ΔG for electron transfer.

The photooxidation of 1,2-dichlorobenzene (DCB) was used as the index reaction for evaluating the efficiency of the various photocatalytic systems. A baseline data set was established with a 0.1 wt % TiO_2 suspension at pH 1 ($HClO_4$), air-saturated, no added POMs. Under these conditions, the photocatalyzed oxidation of DCB proceeded rapidly (Figure 1), with the concurrent production of chlorophenolic byproducts in agreement with the observations of Ollis et al. (*57*) DCB was not observed to photodegrade directly in the absence of photocatalyst under our experimental conditions. Likewise, DCB alone with any of the polyoxometalates did not undergo any oxidation. Oxygen was required for rapid DCB oxidation in all experiments, even in the presence of POMs. Varying $[DCB]_o$ over TiO_2 revealed that DCB photodegradation could be modeled using the Langmuir−Hinshelwood approach (Figure 2) (*57−59*), with a correlation factor of 0.97, K_{L-H} of 84.6 M^{-1}, and k_{L-H} of 0.0818 min^{-1}

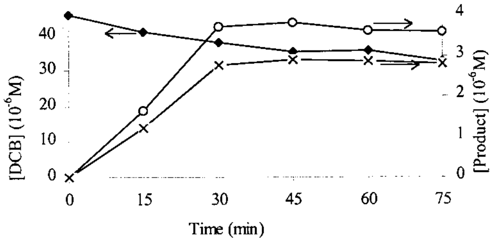


FIGURE 1. Index reaction of DCB degradation with 0.1 wt % TiO_2; ◆, DCB; × 3,4-dichlorophenol; ○, 2,3-dichlorophenol, all experiments at 350 nm, 23 °C, pH = 1, *I* = 12.6 × 10^{-6} eins/min.

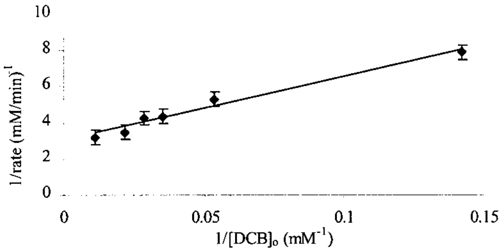


FIGURE 2. A plot of the experimental (rate constants)$^{-1}$ for DCB degradation vs ($[DCB]_o$)$^{-1}$ with TiO_2 (wt 0.1%) (R^2 = 0.97), all experiments at 350 nm, 23 °C, pH = 1, *I* = 12.6 × 10^{-6} eins/min.

$$\text{rate}_0^{-1} = (k_{L-H}\, K_{L-H}[DCB]_0)^{-1} + k_{L-H}^{-1}$$

where K_{L-H} is the association constant and k_{L-H} is the concentration-independent rate constant. Langmuir-Hinsheelwod type behavior has been regarded as an indication of a saturation kinetics (*57, 58*).

In the presence of oxygen, the addition of polyoxometalate anions to TiO_2 suspensions resulted in significant rate enhancement for DCB oxidation (Figure 3). The magnitude of the rate enhancement was "mapped out" over the range of [POM] from 0.04 to 2 mM at a constant $[DCB]_o$ of 40.0 μM. Over this range, we observed that *k* for DCB degradation experienced a different maximum value for each of the POMs studied (Figure 4a–c). The maximum *k* for DCB degradation occurred at 0.1 mM $PW_{12}O_{40}^{3-}$ (k = 0.0318 min^{-1}), at 0.07 mM $SiW_{12}O_{40}^{4-}$ (k = 0.0108 min^{-1}), and at 1 mM $W_{10}O_{32}^{4-}$ (k = 0.0066 min^{-1}). This can be contrasted against *k* (0.0041 min^{-1}) of TiO_2–O_2 at this DCB concentration. We also observed that [POM] concentrations above 2 mM resulted in significant *decreases* in *k* in our system. Speculatively, it can be assumed that this is due to (a) competition for surface sites between POMs and DCB and (b) rapid "short circuiting" of the photocatalyst by direct reoxidation of reduced POM by holes or some combination of the two.

The dependence of *k* on [POM] is in profile similar to what is observed in other studies where metal-island deposition was used as a strategy for enhancing oxidation rates (*25*). In those studies, the decrease in rate was often attributed to the occlusion of active sites on the photocatalyst surface. In this study, adsorption isotherms for POMs on TiO_2 were determined (Figure 5), to evaluate the possibility that excess POM addition may result in similarly "capped" surface sites. At pH 1, the TiO_2 surface is positively charged, while all the POMs in this study are negatively charged, which suggests that ion-exchange may facilitate surface-POM binding. In these experiments, the association constants (*K*) for $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and $W_{10}O_{32}^{4-}$ were determined as 467 M^{-1}, 459 M^{-1}, and 417 M^{-1}, respectively (Table 1) (*60*). These association constants are high compared to DCB's *K* of 84.6 on TiO_2, and the difference supports the hypothesis that the inhibitory effect of high [POM] is an artifact of competition for surface sites. It also explains the somewhat counterintuitive observation that in this case lower concentrations of electron scavengers are more effective than higher even at relatively high oxygen concentration (2 × 10^{-3} mol dm^{-3}) (*61*). This has clear importance for the eventual application of POMs for enhancing photocatalytic systems. For instance, the maximum *k* for DCB in the presence of $PW_{12}O_{40}^{3-}$ is obtained at a POM concentration of 0.1 mM. Given that *K* for $PW_{12}O_{40}^{3-}$ is 467 M^{-1}, this corresponds to only 30% surface coverage.

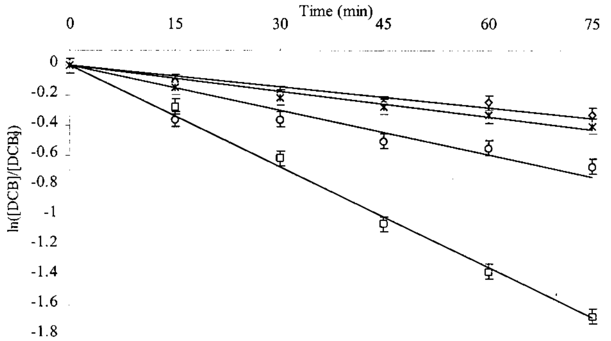


FIGURE 3. Pseudo-first-order degradation of DCB in the presence of TiO_2, TiO_2–$PW_{12}O_{40}^{3-}$, TiO_2–$SiW_{12}O_{40}^{4-}$, and TiO_2–$W_{10}O_{32}^{4-}$ systems. ◇, TiO_2 (wt 0.1%); *, TiO_2 (wt 0.1%)–$W_{10}O_{32}^{4-}$ (0.5 mM); ○, TiO_2 (wt 0.1%)–$SiW_{12}O_{40}^{4-}$ (0.5 mM); □, TiO_2 (wt 0.1%)–$PW_{12}O_{40}^{3-}$ (0.5 mM), all experiments at 350 nm, $[DCB]_o$ = 45.0 μM, 23 °C, pH = 1, *I* = 12.6 × 10^{-6} eins/min.

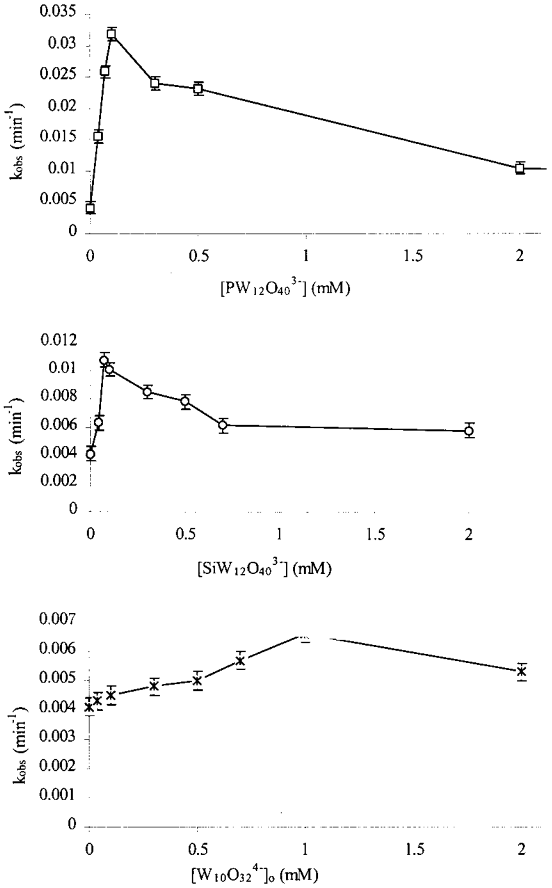


FIGURE 4. (a) Pseudo-first-order degradation rate constants of DCB with TiO_2–$PW_{12}O_{40}^{3-}$, all experiments at 350 nm, 23 °C, pH = 1, *I* = 12.6 × 10^{-6} eins/min. (b) Pseudo-first-order degradation rate constants of DCB with TiO_2–$SiW_{12}O_{40}^{4-}$, all experiments at 350 nm, 23 °C, pH = 1, *I* = 12.6 × 10^{-6} eins/min. (c) Pseudo-first-order degradation rate constants of DCB with TiO_2–$W_{10}O_{32}^{4-}$, all experiments at 350 nm, 23 °C, pH = 1, *I* = 12.6 × 10^{-6} eins/min.

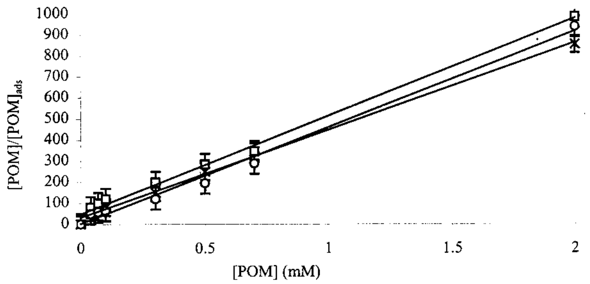


FIGURE 5. Adsorption isotherms of $TiO_2-PW_{12}O_{40}^{3-}$ (□), $TiO_2-SiW_{12}O_{40}^{4-}$ (○), and $TiO_2-W_{10}O_{32}^{4-}$ (*) system.

TABLE 1. Reduction Potentials, Calculated Free Energy Change for the Reduction of POMs by Conduction Band Electrons of TiO_2, Binding Constants of POM on TiO_2 Surface (Derived from Adsorption Isotherms), and Concentration Independent Degradation Rate Constants of DCB (Derived from Langmuir−Hinshelwood Plots)

	E (V vs NHE)	ΔG (kJ/mol)	K (M^{-1}) (TiO_2-POM)	k_{L-H} (min^{-1})
O_2	−0.125 (64)	13.1	84.6	0.0818
$Na_4W_{10}O_{32}$	−1.0288 (41)	81	417	0.152
$H_4SiW_{12}O_{40}$	0.0542 (41)	−23.5	459	0.421
$H_2NaPW_{12}O_{40}$	0.2182 (42)	−39.3	467	0.638

It should also be noted that the binding constants of contrasted POMs on TiO_2 are similar. This finding excludes the possibility that the observed difference on the photodegradation rate of DCB with three contrasting POMs over TiO_2 is not simply caused by the adsorption.

DCB oxidation continued to follow Langmuir−Hinshelwood kinetics even in the presence of POMs (Figure 6a−c). It is notable that k_{L-H} for DCB is found to be much higher in these experiments than in TiO_2-O_2 (Table 1). This could indicate a fundamental change in the TiO_2 surface with POM adsorption, which would be consistent with Serpone and co-worker's finding that anionic surfactants increase the oxidation rate of rhodamine B (*62*). In that work, it was proposed that surfactant adsorption facilitated rhodamine B's oxidation by neutralizing surface charges. It is also possible that DCB adsorption is exactly the same in the presence of POMs but that the more efficient scavenging of conduction band electrons by POMs results in a faster turnover of occupied sites. The concomitant reduction of polyoxometalates was qualitatively supported by the formation of a blue color in the suspensions during irradiation in the absence of oxygen (as verified by UV−vis absorption spectra, see Supporting Information).

The TiO_2−POM association constants are also useful for evaluating the role of adsorption as the dominant variable in predicting the effectiveness of POMs as electron scavengers. A comparison of the measured values shows that the POMs can be ranked as $PW_{12}O_{40}^{3-} \cong SiW_{12}O_{40}^{4-} > W_{10}O_{32}^{4-}$, which does not agree with the significant differences we observed in ranking the effectiveness of each POM by measuring their effect on k_{L-H} (Table 1).

Under our experimental conditions (pH 1), superoxide produced from the one electron reduction of molecular oxygen is readily protonated ($O_2^{\cdot-} + H^+ \rightarrow HOO^\cdot$ $pK_a = 4.88$) (*63, 64*). It is possible that $HOO^\cdot$ radicals produced from the reoxidation of reduced POMs could interfere with our observable directly reacting with 1,2-dichlorobenzene. However, the published bimolecular rate constants for reactions between $O_2^{\cdot-}$/ $HOO^\cdot$ and aromatic compounds are only on the order of 10^3-10^5 M^{-1} s^{-1} (*65, 66*), which is insignificant when compared to the rate of $HOO^\cdot$ dismutation.

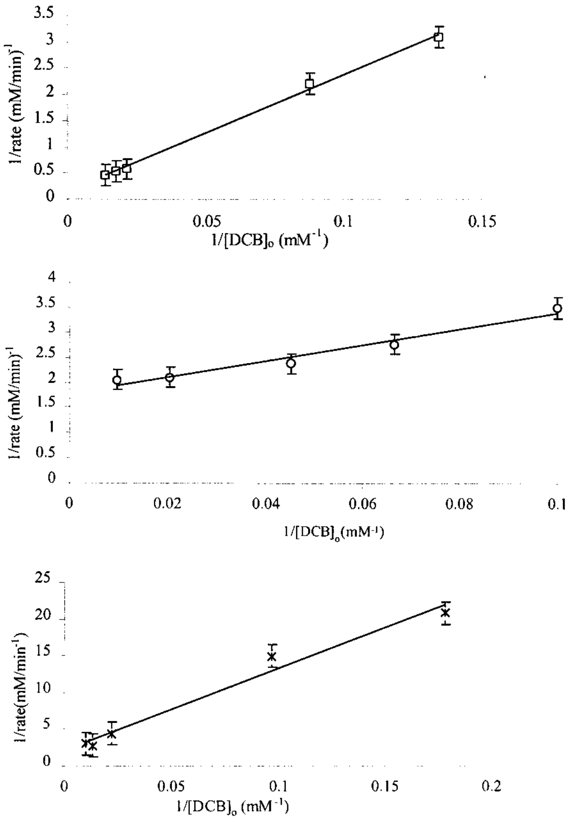


FIGURE 6. (a) A plot of the (observed degradation rate)$^{-1}$ of DCB vs ($[DCB]_o$)$^{-1}$with $TiO_2-PW_{12}O_{40}^{3-}$(0.1 mM) ($R^2 = 0.99$), all experiments at 350 nm, 23 °C, pH = 1, $I = 12.6 \times 10^{-6}$ eins/min. (b) A plot of the (observed degradation rate)$^{-1}$ of DCB vs ($[DCB]_o$)$^{-1}$with $TiO_2-SiW_{12}O_{40}^{4-}$(0.1 mM) ($R^2 = 0.97$), all experiments at 350 nm, 23 °C, pH = 1, $I = 12.6 \times 10^{-6}$ eins/min. (c) A plot of the (observed degradation rate)$^{-1}$ of DCB vs ($[DCB]_o$)$^{-1}$ with $TiO_2-Na_4W_{10}O_{32}$ (1.0 mM) ($R^2 = 0.98$), all experiments at 350 nm, 23 °C, pH = 1, $I = 12.6 \times 10^{-6}$ eins/min.

Previous investigations of electron transfer from TiO_2 have shown that ΔG for the one-electron reduction of the acceptor is a more useful predictor of the activity of added electron scavengers (*59, 67*). Using the one-electron $E°$ for dioxygen (*64*) and the POMs in this study, we determined the free energy change for the reduction of these species by TiO_2 according to the following

$$\Delta G = -F(E^o(\text{acceptor}) - E°(TiO_2)) \qquad (1)$$

where F is Faraday's constant, E^o(acceptor) is the standard reduction potential of the acceptor vs NHE, and $E^o(TiO_2)$ is the standard reduction potential of the conduction band electrons. The reduction potential for conduction band electrons was determined to have a value of −0.189 V vs NHE under our experimental conditions (pH 1) based on

$$E°(TiO_2) = -0.13 - 0.059\ (\text{pH}) \qquad (2)$$

The resulting ΔG values (Table 1) show that the reduction of $W_{10}O_{32}^{4-}$ by TiO_2 is actually more endothermic than the reduction of O_2 under our experimental conditions, even though $W_{10}O_{32}^{4-}$ is a more effective electron scavenger as indexed by k_{L-H}. The implication is that even POMs that are not spontaneously reduced may still serve as effective electron transfer promoters, opening the field to the consideration of materials that may be more resistant to hydrolytic decomposition at more environmentally relevant pHs. The reduction of other polyoxometalates in this study is more favored than the reduction of O_2 and is apparently kinetically favored also, with $PW_{12}O_{40}^{3-}$ the most effective electron scavenger. The coexistence of O_2 and POMs in the TiO_2 solution induces a competition between these two for the photogenerated conduction band electrons. The increased photodegradation rate of DCB in the presence of relatively POMs indicates that electron transfer to POMs is favored over that to O_2.

Acknowledgments

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Supporting Information Available

UV−vis absorbance of synthesized $Na_4W_{10}O_{32}$ and filtered $TiO_2-PW_{12}O_{32}^{3-}$(0.1 mM) in deoxygenated illuminated aqueous solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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