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Kinetic Probes of the Mechanism of Polyoxometalate-Mediated Photocatalytic Oxidation of Chlorinated Organics

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The present study reports the development of kinetic probes to determine the possible role of hydroxyl radicals in the polyoxometalate-mediated photocatalytic oxidation of aqueous chlorinated organic compounds. Photocatalytic oxidation of the model chloroaromatic 1,2-dichlorobenzene (DCB) was carried out in oxygenated, illuminated solutions of three contrasting polyoxometalates (POMs), $\text{H}_2\text{NaPW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, or $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. The observed rate of DCB is pseudo-first-order in $[\text{DCB}]_0$ for all POMs over a concentration range of 2–20 μM , which was modeled by Langmuir–Hinshelwood-type kinetics. The effect of the HO^\bullet scavengers Br^- , 2-propanol, acetone, and acetone- d_6 on the rate of DCB oxidation was also evaluated in order to test the validity of the possible mechanisms that may account for the observed kinetic behavior. On the basis of their ability to reduce k_{exp} , the effectiveness of the scavengers is ranked as $i\text{-prOH} > \text{Br}^- > \text{acetone} = \text{acetone-}d_6$. This contrasts sharply with the ranking suggested by their intrinsic rate constants with HO^\bullet : $\text{Br}^- > i\text{-prOH} > \text{acetone} > \text{acetone-}d_6$. This discrepancy is explained by the hypothesis that interfacial electron transfer, rather than HO^\bullet -mediated oxidation, accounts for the loss of DCB.

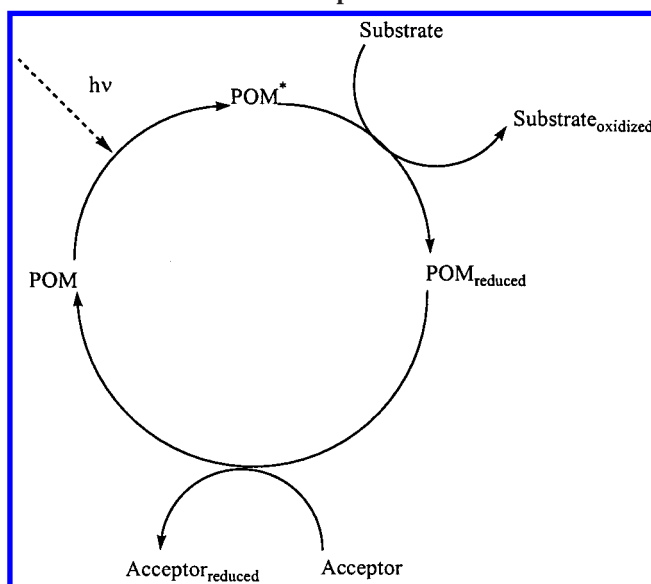
Introduction

The photocatalytic oxidation of organic matter is a cyclic process, typified by the application of a photoactive semiconducting material to facilitate the transfer of electrons from an organic substrate to (usually) an inorganic electron acceptor such as dioxygen.¹ The reoxidized form of the photocatalyst is then capable of engaging in another series of electron transfers that may continue until the organic donor is mineralized.^{2–6} In this work, the first step of the photocatalytic oxidation of aqueous 1,2-dichlorobenzene by solutions of three homogeneous photocatalysts, $\text{H}_2\text{NaPW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, was studied.

Excitation of the ligand-to-metal charge transfer band of photocatalytically active POMs ($\lambda_{\text{max}} \sim 250 \text{ nm}$) generates a strongly oxidizing excited state (POM^*), which for some POMs has been estimated to possess a reduction potential in excess of 2.5 V vs the NHE.⁷ POM^* can effect the oxidation of cosolutes directly via charge transfer⁸ or H-atom abstraction^{7,9–12} or indirectly through the intermediacy of solvent-derived radicals.^{2–4,13} The corresponding reduced polyoxometalates can be easily reoxidized to their original oxidation state by electron acceptors such as *tert*-butyl hydroperoxide or by dioxygen (Scheme 1).¹⁴ In this study, we employ a large stoichiometric excess of POM, so that we examine the kinetics of DCB oxidation by POM^* without interference from the POM reoxidation reaction.

The mechanism by which POMs photocatalytically oxidize organic compounds in aqueous solution is critical to their potential utility. Yamase et al.^{15–17} have presented spin-trapping evidence that HO^\bullet is generated in aqueous solutions of alkylammonium polymolybdates, $[\text{NH}_3\text{Pr}^i]_6[\text{Mo}_7\text{O}_{24}]$, and alkylammonium polytungstates, $[\text{NH}_3\text{Pr}^i]_5[\text{W}_6\text{O}_{20}(\text{OH})]$. In these works, the addition of the spin traps 2-methyl-2-nitrosopropane or *N*-benzylidene-*tert*-butylamine *N*-oxide to illuminated solutions of POMs in an electron paramagnetic resonance (EPR) cell

SCHEME 1: Photocatalytic Cycle of POM in the Presence of an Electron Acceptor and an Electron Donor



resulted in the evolution of an EPR spectrum similar to that obtained from the products of the reaction between these spin trapping reagents and HO^\bullet .^{15–17} These works are analogous to the spin-trap experiments done by Jaeger and Bard¹⁸ that demonstrated the presence of HO^\bullet and HOO^\bullet in suspensions of illuminated TiO_2 .¹⁸ Proposed oxidation via HO^\bullet was also supported by the observation that primary and secondary alcohols with weakly bound α -hydrogen atoms are effectively photooxidized by POMs, whereas *tert*-butyl alcohol was more difficult to oxidize.¹ Papaconstantinou and co-workers^{2–4,13} have also observed that the illumination of aqueous solutions of $\text{K}_4\text{W}_{10}\text{O}_{32}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the presence of phenol, *p*-cresol, chlorinated phenols, and hydrocarbons results in hydroxylation, a result consistent with a HO^\bullet -based mecha-

nism but not exclusive to it. Parallels can also be drawn between these studies and previous reports that inferred the presence of HO^\bullet in TiO_2 suspensions by virtue of byproduct analysis.^{19–21} However, other mechanisms can account for the formation of hydroxylated products. For instance, Fox and Dulay²² have presented evidence that direct hole-organic reactions may generate cation radicals, which may hydrate and generate hydroxylation products.

In organic solvents, POMs seem to oxidize substrates by direct photocatalytic electron transfer oxidations, rather than indirectly by radicals associated with oxidation of the supporting medium.^{23–27} Evidence has been presented by Hill and co-workers^{28–31} for the oxidation of several different aliphatic compounds, including 2-propanol, cyclohexanol, and cyclohexane, by direct electron/hydrogen-atom transfer. These results suggest a two-step mechanism, initiated by the transfer of an electron from a C–H bond of the substrate followed by rapid proton transfer. In this study, we report on the development of kinetic probes for resolving between the two possible mechanisms for the POM-mediated photocatalytic oxidation of aqueous aromatic compounds.

Experimental Section

Chemicals. Methyl *tert*-butyl ether (MTBE, GC² quality) was obtained from Burdick and Jackson; 2-propanol (*i*-prOH, GC² quality), acetone (GC² quality), and methanol (MeOH, GC² quality) were purchased from Fisher Scientific. Potassium bromide (KBr, 99+%) was obtained from Mallinckrodt. Acetone-*d*₆ (99.9%) was purchased from Cambridge Isotope Laboratories, Inc. $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (reagent-grade) were obtained from Fluka. 1,2-Dichlorobenzene (DCB, 99%), HClO_4 (99+%), and 4-bromoanisole (BA, 99%) were obtained from Aldrich Chemical Co. ASTM-grade water was used for all experiments.

Aqueous DCB solutions were prepared from a stock DCB-saturated aqueous solution. Analytical DCB stocks were prepared in GC²-grade methanol. The internal standard for all DCB quantitation was BA (99%) spiked into the extracting solvent.

Reactor. The reactor used in all experiments was an Ace Glass microphotochemical quartz reactor. The light source was a 100 W Hg arc lamp (Osram) filtered through a monochromator (Photon Technologies Inc.) to select for output at 254 nm. The slits were set at 0.6 mm with a ± 2.4 nm band-pass. Lamp output (12.5×10^{-6} einstein/min) was constant over the time frame of the experiments, as determined by ferrioxalate actinometry.³²

Experimental Procedure. Experiments were conducted in pH 1.0 solutions of 500 μM POM (pH adjusted with HClO_4 , OD > 2.5 au at 254 nm). Aqueous DCB was added to achieve the desired substrate concentration (2–20 μM). The reactor was allowed to equilibrate with stirring for 30 min prior to the beginning of illumination. The Hg arc lamp was always allowed to stabilize 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 pre-charged 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 gas chromatography with electron capture detection (GC-ECD) or ion-trap mass spectrometry (GC-ITMS).

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 50 °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 1 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. Carrier gas (He) flow rate was 1.3 mL/min and the method detection limit for DCB was 0.41 μM . 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 oven program was the same as for GC-ECD.

Results and Discussion

Photocatalytic Oxidation of Dichlorobenzene. The purpose of this study was to investigate the first step of the photocatalytic cycle and to probe the mechanism by which photocatalytic oxidation is initiated. Therefore, the ratio $[\text{POM}]/[\text{DCB}]_0$ was always ≥ 40 , to ensure that the POMs were not being used in a truly catalytic sense. This was done to minimize possible kinetic artifacts imposed by the differing reoxidation rates (by dioxygen) of the POMs in this study.³³ The more negative the ground-state reduction potential of the POM, the faster the reoxidation of the POM by O_2 .³⁴ The reoxidation rate can be ranked as $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (−0.187 V vs SCE) > $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$ (−0.023 V vs SCE) > $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.42 V vs SCE).^{7,35}

A high $[\text{POM}]/[\text{DCB}]_0$ ratio was maintained to prevent significant reduction of POM by the radicals generated from POM* and DCB.

Quantum yields were determined for the photocatalytic oxidation of DCB, with values of $\phi = 0.0080$ for $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\phi = 0.0063$ for $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$, and $\phi = 0.0051$ for $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Low quantum yields are a result of the low substrate-to-photocatalyst ratio, which was necessary to avoid kinetic artifacts from the reoxidation of reduced polyoxometalates.

Difference spectra of the UV absorbance of the POM–DCB solutions in this study did not reveal the appearance of any new absorption bands relative to DCB or POM solutions alone, suggesting that a possible POM–DCB complex did not represent a significant chromophore under our experimental conditions. This implies that the observable change in $[\text{DCB}]$ can be attributed solely to known POM photoprocesses.

DCB did not undergo significant photolysis in the absence of POM on the time scale of our experiments. Nor did we observe any significant reaction between DCB and POM in dark controls (control data provided as Supporting Information). The color of the three reaction solutions remained unchanged during the photolysis, indicating that no reduced POM was building up in the reactor. All three POMs demonstrated the capability to photocatalytically oxidize DCB in the aqueous phase (Figure 1).

Organic extracts were analyzed for possible oxidation products by GC-ITMS techniques. None were detected under our experimental conditions; it is probable that either they were too polar for analysis by this technique or their concentrations are below the detection limits of our analytical instruments. Keeping

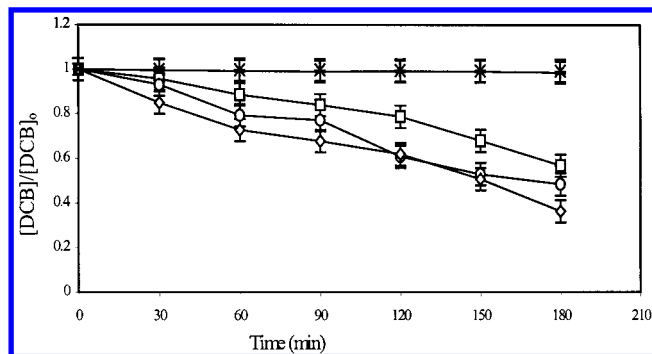


Figure 1. Photocatalytic degradation of DCB: $I = 12.5 \times 10^{-6}$ einstein/min, $[POM] = 0.50$ mM, $pH = 1.0$ (with $HClO_4$), $T = 23$ °C, $\lambda = 254$ nm. (a) \times , no POM ($[DCB]_0 = 3.33$ μM); (b) —, in the dark with $HNa_2PW_{12}O_{40}$ ($[DCB]_0 = 4.50$ μM); (c) \square , $H_4SiW_{12}O_{40}$ ($[DCB]_0 = 5.20$ μM); (d) \circ , $HNa_2PW_{12}O_{40}$ ($[DCB]_0 = 3.87$ μM); and (e) \diamond , $H_3PMo_{12}O_{40}$ ($[DCB]_0 = 3.63$ μM).

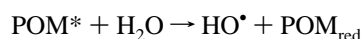
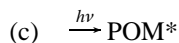
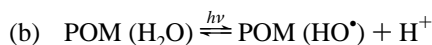
in mind that the $[DCB]_0$ is in the range of 2–20 μM , the possible products are too dilute to qualify by 1H NMR analysis. Since the GC-ITMS detection limits of the probable byproducts 2,3-dichlorophenol and 3,4-dichlorophenol are only 0.28 μM , if formed, their yield was only <1–10%.

Kinetic Implications on Mechanism. Experimental results could be adequately modeled by the Langmuir–Hinshelwood approach:

$$[POM]rate_0^{-1} = (kK[DCB]_0)^{-1} + k^{-1} \quad (1)$$

where K is the association constant and k is the observed rate constant for a given $[DCB]_0$. A plot of the initial rate vs the initial concentration yielded K values of 314, 264, and 132 M^{-1} for $H_4SiW_{12}O_{40}$, $HNa_2PW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$, respectively. These values are consistent with the K value of 118 M^{-1} found by Yamase and co-workers³⁶ in the study of DCB oxidation with paratungstate anion $W_7O_{24}^{6-}$ at pH 6–7 and the K value of 450 M^{-1} calculated by Einaga and Misono⁵ for the photocatalytic decomposition of 4-chlorophenol by $PW_{12}O_{40}^{3-}$ at pH 1.

However, it is known that the Langmuir–Hinshelwood approach does not provide restrictive mechanistic information. For instance, saturation kinetics could be observed for any of the following mechanisms:



Yet it must be acknowledged that the mechanisms given might not cover all the possibilities.

In this study, it was unlikely that DCB oxidation products would have a significant effect on k_{exp} , since the method of initial rates was used to obtain data. Therefore, given the ambiguity associated with the Langmuir–Hinshelwood approach, it was necessary to employ other kinetic probes to gain mechanistic insight into this system.

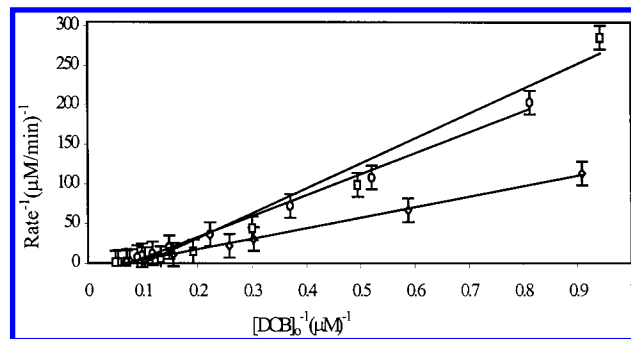


Figure 2. Plot of the experimental (rate constants)^{−1} for DCB degradation vs $([DCB]_0)^{-1}$; $I = 12.5 \times 10^{-6}$ einstein/min, $[POM] = 0.50$ mM, $pH = 1.0$ (with $HClO_4$), $T = 23$ °C, $\lambda = 254$ nm. (a) \square , $H_4SiW_{12}O_{40}$ ($r^2 = 0.97$); (b) \circ , $HNa_2PW_{12}O_{40}$ ($r^2 = 0.99$); and (c) \diamond , $H_3PMo_{12}O_{40}$ ($r^2 = 0.99$).

TABLE 1: Experimental, HO^\bullet Predicted, and Langmuir–Hinshelwood Rate Constants for DCB with Radical Scavengers Br^- and i -PrOH^a

scavenger	k_{LH} (min ^{−1})	k_{exp} (min ^{−1})	k_{pre-HO^\bullet} (min ^{−1})	$k_{exp}/k_{pre-HO^\bullet}$
$PW_{12}O_{40}^{3-}$				
1 μM KBr	0.00996	0.0088	0.00435	2.02
5 μM KBr	0.00981	0.0044	0.00129	3.42
1 μM i -prOH	0.00823	0.0074	0.00645	1.15
3 μM i -prOH	0.00882	0.0033	0.00515	0.64
$SiW_{12}O_{40}^{4-}$				
1 μM KBr	0.00118	0.0108	0.00564	1.92
5 μM KBr	0.0144	0.0057	0.00259	2.19
1 μM i -prOH	0.0177	0.0128	0.0160	0.80
3 μM i -prOH	0.00571	0.002	0.00302	0.66
$PMo_{12}O_{40}^{3-}$				
1 μM KBr	0.00414	0.0053	0.00113	4.71
5 μM KBr	0.00427	0.0034	0.000306	11.1
1 μM i -prOH	0.00504	0.0091	0.00257	3.54
3 μM i -prOH	0.00328	0.00570	0.00233	2.45

^a k_{LH} , rate constant derived from the Langmuir–Hinshelwood plot by Figure 2; k_{exp} , observed rate constants experimentally; k_{pre-HO^\bullet} , HO^\bullet predicted rate constant derived from eq 1; $k_{LH}/k_{pre-HO^\bullet}$, deviation of the observed rate constants from HO^\bullet predicted rate constant.

Effects of HO^\bullet Scavengers. The possible role of HO^\bullet in the aqueous oxidation of DCB was also tested by measuring how k_{exp} , the observed photocatalytic oxidation rate for DCB, was affected by the presence of radical scavengers.

In these experiments, DCB was photocatalytically oxidized in the presence of a series of added radical scavengers, i -prOH, Br^- , acetone, or acetone- d_6 . Under the hypothesis that free HO^\bullet was responsible for oxidizing DCB, the effects of the scavengers on k_{exp} should have been predictable based on their known bimolecular rate constants with HO^\bullet . The predicted value for k_{exp} in the presence of radical scavengers (k_{pre-HO^\bullet}) can be obtained from the following:

$$k_{pre-HO^\bullet} = \left(k_{LH} \frac{k_{HO+DCB}[DCB]}{k_{HO+DCB}[DCB] + k_{HO+scavenger}[scavenger]} \right) \quad (2)$$

k_{LH} is the rate constant predicted by the Langmuir–Hinshelwood plot (Figure 2). Observed degradation rates of DCB in the presence of these radical scavengers are tabulated in Table 1 along with the expected rate predicted by the Langmuir–Hinshelwood plot. By use of eq 2, a free HO^\bullet -based mechanism predicts the effectiveness of a given scavenger (equimolar) should be $Br^- > i$ -prOH > acetone > acetone- d_6 , based on their rate constants k for the reaction between HO^\bullet and these

TABLE 2: Experimental, HO• Predicted, and Langmuir–Hinshelwood Rate Constants for DCB with Radical Scavengers Acetone and Acetone-*d*₆

scavenger	k_{exp} (min ⁻¹)	$k_{\text{exp}}(\text{acet})/k_{\text{exp}}(\text{acet-}d_6)$
	PW ₁₂ O ₄₀ ³⁻	
1 μM acetone	0.0107	1.019
1 μM acetone- <i>d</i> ₆	0.0105	
	SiW ₁₂ O ₄₀ ⁴⁻	
1 μM acetone	0.0145	1.043
1 μM acetone- <i>d</i> ₆	0.0139	
	PMo ₁₂ O ₄₀ ³⁻	
1 μM acetone	0.00416	1.015
1 μM acetone- <i>d</i> ₆	0.0041	

scavengers (M⁻¹ s⁻¹): 1.1×10^{10} ,³⁷ 1.6×10^9 ,³⁸ 1.3×10^8 ,³⁹ and 2.5×10^7 ,⁴⁰ respectively. However, our data indicate that for all three POMs the ranking is *i*-prOH > Br⁻ > acetone = acetone-*d*₆.

It is possible to justify the ordering of Br⁻ and *i*-prOH in terms of a direct electron-transfer oxidation of DCB by POM but not by a model with free HO• as the oxidant. The electrostatic repulsion that occurs between two similarly charged species, negatively charged POM and bromide, could inhibit the probability of a reaction between these two species. This is analogous to surface-scavenger repulsion between cysteine and TiO₂ observed at pH < 3 by Ferry and Fox.⁴¹ The unexpected effectiveness of *i*-prOH as an oxidant scavenger can be explained by the previous observation of strong precomplexation of alcohols (including *i*-prOH) with the POMs in our study, as hypothesized by Fox et al.⁴² in an earlier work. The decrease in the photocatalytic activity of POM was observed by Einaga and Misono^{5,6} upon the addition of certain amount of ethanol, 2-propanol, and acetonitrile and was explained by the competitive complexation of these substrates with POM.

The effectiveness of *i*-prOH and Br⁻ may also be contrasted between POMs, with PMo₁₂O₄₀³⁻ more sensitive to the presence of scavengers than PW₁₂O₄₀³⁻, and it more so than SiW₁₂O₄₀⁴⁻. It is intriguing that this arrangement of POMs follows their ground-state E° ; it may be that E° of PMo₁₂O₄₀³⁻* is so high that it is less selective while the weakest ground-state oxidant exhibits greater selectivity in the presence of scavengers.

Kinetic Isotope Effect. One explanation for the observed ordering of scavengers could be that HO• is bound to the POM “surface” and that this association may have unexpected effects on the kinetics. However, the intrinsic rate constants of acetone ($k = 1.3 \times 10^8$ L mol⁻¹ s⁻¹)³⁹ and acetone-*d*₆ ($k = 2.5 \times 10^7$ L mol⁻¹ s⁻¹)⁴⁰ with HO• (aq) differ by more than a factor of 5. This large kinetic isotope effect indicates there is a considerable amount of bond breaking and new bond formation in the transition state during the HO•-mediated oxidation of acetone.⁴³ Acetone and acetone-*d*₆ were used as radical scavengers in POM-mediated photooxidation of DCB to determine whether the same isotopic dependence would be observed with POM*. Our data indicate no difference in the k_{exp} of DCB in the presence of acetone or acetone-*d*₆ (Table 2) for the three POMs within experimental error. It can be inferred from these data that surface-bound HO• does not play a significant role in the oxidation of acetone or acetone-*d*₆, leading us to conclude that charge transfer is a more plausible mechanism; these results also suggest HO• from other sources does not contribute significantly to this system.

A similar result could have been obtained if our scavengers served to quench POM* rather than intercept oxidative equivalents. However, if this was the case, we would have expected a greater difference between acetone and acetone-*d*₆, given the marked kinetic isotope effect often displayed in the quenching of excited molecules such as singlet oxygen (decay rates are 2.4×10^4 s⁻¹ and 1.0×10^3 s⁻¹ for acetone and acetone-*d*₆, respectively).⁴⁴ Nonetheless, it must be acknowledged that the possibility of this artifact remains.

Conclusion

The purpose of this study was to attempt to resolve between competing hypotheses for the mechanism of POM-mediated aqueous organic photooxidation by employing kinetic probes.

We feel that the failure of HO•-based kinetic models to predict the effect of added scavengers on k_{obs} and the lack of any significant kinetic isotope effects are strong indicators of an electron-transfer mechanism rather than a HO• mechanism. This may indicate that POM photocatalysis has a significant selectivity advantage over other aqueous photocatalytic systems that rely on HO• to effect organic oxidation.

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Supporting Information Available: Additional text describing radical side reactions and two figures showing dark control experiments and effect of Br⁻ on DCB photodegradation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Papaconstantinou, E. *J. Chem. Soc., Chem. Commun.* **1982**, 12.
- Mylonas, A.; Papaconstantinou, E. *J. Photochem. Photobiol. A: Chem.* **1996**, 94, 77.
- Mylonas, A.; Hiskia, A.; Papaconstantinou, E. *J. Mol. Catal. A: Chem.* **1996**, 114, 191.
- Mylonas, A.; Papaconstantinou, E. *J. Mol. Catal.* **1994**, 261.
- Einaga, H.; Misono, M. *Bull. Chem. Soc. Jpn.* **1997**, 70, 1551.
- Einaga, H.; Misono, M. *Bull. Chem. Soc. Jpn.* **1996**, 69, 3435.
- Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, 1.
- Yamase, T.; Usami, T. *J. Chem. Soc., Dalton. Trans.* **1988**, 183.
- Awad, M. K.; Anderson, A. B. *J. Am. Chem. Soc.* **1990**, 112, 1603.
- Jen, S.-F.; Anderson, A. B.; Hill, C. L. *J. Phys. Chem.* **1992**, 96, 5658.
- Akid, R.; Darwent, J. J. *J. Chem. Soc., Dalton. Trans.* **1985**, 395.
- Duncan, D. C.; Fox, M. A. *J. Phys. Chem.* **1998**, 102, 4559.
- Mylonas, A.; Papaconstantinou, E.; Roussis, V. *Polyhedron* **1996**, 3211.
- Balzani, V.; Bolletta, F.; Gondolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, 1.
- Yamase, T.; Sasaki, R.; Ikawa, T. *J. Chem. Soc., Dalton Trans.* **1981**, 628.
- Yamase, T.; Kruzomi, T. *J. Chem. Soc., Dalton Trans.* **1983**, 2205.
- Yamase, T. *Inorg. Chim. Acta* **1983**, 76, L25.
- Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* **1979**, 83, 3146.
- Matthews, R. W. *J. Chem. Soc., Faraday Trans.* **1984**, 80, 457.
- Anpo, M.; Shima, T.; Kubakawa, Y. *Chem. Lett.* **1995**, 1799.
- Harbour, J. R.; Tromp, J.; Hair, M. L. *Can. J. Chem.* **1985**, 63, 204.
- Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, 93, 341.
- Hill, C. L.; Brown, R. B. *J. Am. Chem. Soc.* **1986**, 108, 536.
- Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.
- Brown, R. B.; Renneke, R.; Hill, C. L. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1987**, 32, 205.
- Faraj, M.; Lin, C.-H.; Hill, C. L. *New J. Chem.* **1988**, 12, 745.
- Molinari, A.; Amadelli, R.; Carassiti, V.; Maldotti, A. *Eur. J. Inorg. Chem.* **2000**, 91.
- Chambers, R. C.; Hill, C. L. *Inorg. Chem.* **1991**, 30, 2776.
- Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1988**, 110, 5461.
- Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, 107, 5148.

- (31) Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. M.; Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 5471.
- (32) Demas, J. N.; Bowman, W. D.; Zalewski, E. F.; Velapoldi, R. A. *J. Phys. Chem.* **1981**, *85*, 2766.
- (33) Tanelian, C. *Coord. Chem. Rev.* **1998**, *178*, 1165.
- (34) Hiskia, A.; Papaconstantinou, E. *Inorg. Chem.* **1992**, *31*, 3.
- (35) Kozhevnikov, I. V. *Russ. Chem. Rev.* **1987**, *56*, 811.
- (36) Hu, C.; Yue, B.; Yamase, T. *Appl. Catal. A* **2000**, *194*, 99.
- (37) Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1972**, *76*, 2.
- (38) Motohashi, N.; Saito, Y. *Chem. Pharm. Bull.* **1993**, *41*, 2.
- (39) Wolfenden, B. S.; Wilson, R. L. *J. Chem. Soc., Perkin. Trans. 2* **1982**, 805.
- (40) Walling, C.; El-Taliawi, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 844.
- (41) Ferry, J. L.; Fox, M. A. *Langmuir* **1998**, *14*, 1725.
- (42) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 7.
- (43) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper Collins Publishers: New York, 1987.
- (44) Schmidt, R.; Afshari, E. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 788.