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Use of Organic Molecules as Mechanistic Probes for Semiconductor-Mediated Photoelectrochemical Oxidations: Bromide Oxidation

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Cyclohexene has been used as an organic probe for mechanism in the semiconductor-photocatalyzed oxidation of bromide in acetonitrile. Products derived from bromine addition and from cyclohexenyl radical mediated autoxidation were isolated. These results implicate a mechanism in which the photoexcited semiconductor effects a one-electron oxidation of adsorbed bromide, producing surface-bound bromine atoms. These potentially could abstract hydrogen from cyclohexene to initiate autoxidation or could migrate along the semiconductor surface, producing bromine (Br_2), which migrates into solution where it is rapidly trapped in conventional electrophilic addition.

Initiation of organic oxidations by photoexcitation of semiconductor powders[1] offers a potential route for simultaneously achieving high reactivity (by virtue of photoinduced electron exchange at the semiconductor liquid interface) and high selectivity (by selective substrate adsorption or flux-controlled current densities).[2] The importance of such reactions could be extended even further if appropriate mediated reactions, photoelectrochemically initiated by electron or hole capture at the surface of the excited semiconductors, could be found.

We report here our investigation of such a system: the oxidation of bromide on TiO_2 powders in oxygenated acetonitrile containing cyclohexene. We find that photoelectrocatalysis is useful not only for the introduction of heteroatoms into hydrocarbons but also as a mechanistic probe to determine details of the primary redox reaction and to delineate the utility of mediated organic photoelectrosynthesis.

Scheme I. Proposed Mechanisms for Semiconductor-Mediated Bromide Oxidation

$$Br^- + h^+ \rightarrow Br\cdot)_{ads} \xrightarrow{Br^-} Br_2^-\cdot \rightleftharpoons \frac{1}{2}Br_2 + Br^- \qquad (A)$$

$$Br^- + h^+ \rightarrow Br\cdot)_{ads} \rightleftharpoons Br_2)_{ads} \qquad (B)$$

$$\text{-}MO^- + h^+ \rightarrow M\text{-}O\cdot \xrightarrow{Br^-} M\text{-}O\text{-}Br^-\cdot \rightarrow M\cdot + OBr^- \qquad (C)$$

The photoelectrochemical oxidation of bromide, for example, has been reported in water using colloidal or powdered forms of TiO_2 as the photoactive semiconductor surface. Three mechanisms, summarized in Scheme I, have been proposed for this reaction. First, bromide capture of the photogenerated hole on irradiated TiO_2 colloids has been proposed[3,4] to form the bromine atom. This species than reacts rapidly with bromide to produce the anion radical $Br_2^-\cdot$. Two of such anion radicals disproportionate to give bromine and to regenerate two bromide ions. A second possible route[5] describes halogen production on doped TiO_2 powders (with or without platinization) as the reaction of two bromide ions with two photogenerated holes to give the adsorbed dihalogen (Br_2) directly. Finally, a third reaction path[6,7] involves the neutralization of adsorbed oxide ions by the photogenerated hole to produce an activated oxygen species which in turn converts adsorbed bromide to hypohalite. The desorption of the hypohalite deactivates the ion, with the final products showing critical pH dependence.

Cyclohexene[1] is known to react rapidly with each of the critical intermediates formed in these mechanisms (Scheme II). If parallel reactivity could be observed with adsorbed bromine, bromine atom, and hypobromite as is observed in free solutions of these species, product analysis of the organic olefinic trap could identify the operative mechanism. We also hoped to test the relative importance of these three routes to determine whether halide oxidation

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[1] Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314.

[2] For a succinct review of the principles of photoelectrochemistry, see: Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 139.

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[5] Reichman, B.; Byvik, C. E. *J. Phys. Chem.* **1981**, *85*, 2255.

[6] Herrmann, J. M.; Pichat, P. *J. Chem. Soc., Faraday Trans. 1*, **1980**, *76*, 1138.

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Scheme II. Cyclohexene Trapping of Bromide Oxidation Products

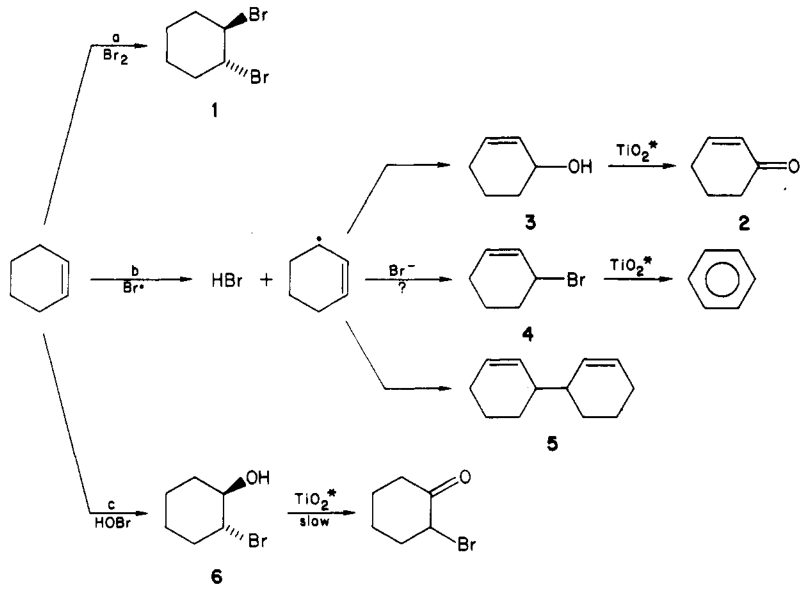


Table I. Product Distribution from TiO_2-Mediated[a] Bromide Oxidation Products Trapped by Cyclohexene

	chemical yield (±7%)[b,c]			
% conversn	1	2	3	6
5	60	16	16	
23	50	13	10	tr[c]
36	50	13	3	2
68	42	14	3	2

[a] Aerated suspensions of 100–500 mg of TiO_2 in anhydrous CH_3CN containing ~0.1 M $MePPh_3^+Br^-$ and ~0.1 M cyclohexene, irradiated with $320 < \lambda < 400$ nm at ~45 °C. [b] Based on cyclohexene consumed. [c] Trace quantities (≤5%) of cyclohexene oxide, [2 + 2] dimer of cyclohexene with cyclohexenone, and bicyclohexenenyl. Neither benzene nor 3-bromocyclohexene could be detected.

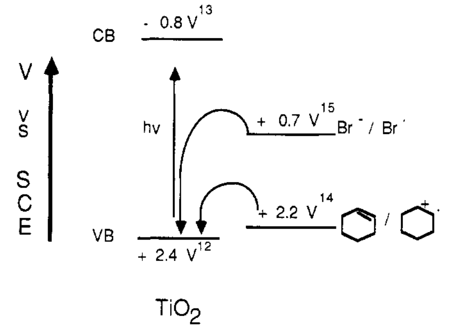
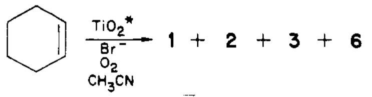


Figure 1. Band positions and redox potentials for relevant redox transformations in the TiO_2-Mediated bromide oxidation trapping experiments.

might be used for specific mediated olefin functionalization.

Results and Discussion

Aliquots of TiO_2 powder suspended in a 0.1 M aerated acetonitrile solution made approximmtely 0.1 M in **1** and in tetrabutylammonium or methyltriphenylphosphonium bromide and contained within Pyrex test tubes were exposed to long wavelength ultraviolet irradiation ($\lambda > 350$ nm) in a Rayonet photochemical reactor. We assumed minimal surface charge on TiO_2 immersed in this neutral organic medium. The several products isolated from the reaction mixture are shown in eq 1. Traces of secondary



(1)

oxidation and photolysis products[8] could also be detected. The distribution of products observed at varying extents of cyclohexene trapping are summarized in Table I. Dibromide remains a major product as the reaction proceeds, although the fraction of oxygenation product depends on the extent of cyclohexene disappearance. Control experiments establish that O_2, TiO_2, and irradiation were all required for product formation. No thermal formation of trapping products could be observed in this system even at 75 °C. Platinization did not significantly alter either the rate of trapping or the organic product distribution. Low quantum yields (<0.05) of oxidation were observed, and overnight irradiation was generally required to produce isolable quantities of product.

Several of the potential products (expected from Scheme II) are labile under the reaction conditions. Independent studies of authentic samples reveal the following: **2** is weakly photoactive under the irradiation conditions; **3** is photocatalytically converted by irradiated TiO_2 to **2**; as an aerated acetonitrile solution, **4** is transformed by excited TiO_2 into benzene, with small amounts of **2**, **6**, and phenol also being formed; and the halohydrin **6** is inefficiently oxidized to 2-bromocyclohexanone.

That the fraction of cyclohexenol **3** produced decreases with increasing conversion implies that it is destroyed in a secondary oxidative route more efficiently than it is formed from cyclohexene, as would be expected from the product reactivity studies. Although the direct oxidation of cyclohexene to **2** and **3** has been reported,[9] it proceeds at least five times more slowly than does the bromide-mediated reaction. This kinetic ordering can be predicted from the relative locations of the oxidation potentials of Br^- and **1**, respectively, within the band gap and near the valence band of TiO_2 (Figure 1). The direct oxidation of cyclohexene by efficient capture of a photogenerated oxidant (hole) will be slower and more reversible than that of bromide and therefore probably occurs by indirect chain

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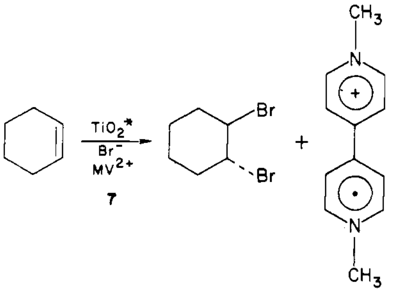
[8] These include small quantities of 2-hydroxycyclohexanone and mixtures of photodimers of **2** and the crossed photodimer of **1** and **2**.

[9] Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 6757.

autooxidation initiated perhaps by inefficient photogeneration of hydroperoxy radical by O_2 reduction and subsequent protonation by metal oxide surface hydroxyls or by strongly adsorbed water. The resulting alcohol **3** is itself oxidizable, generating cyclohexenone **2** by subsequent photocatalyzed oxidation.

Of mechanistic significance is the nearly complete absence of **4**, **6**, and benzene. Since the latter product would have accumulated had significant quantities of **4** been formed, its absence argues against the effectiveness of the TiO_2 surface to mediate allylic bromination or halohydrin formation. Since only trace quantities of bicyclohexenyl can be found, we infer that the cyclohexenyl radical is effectively scavenged by oxygen.

The mediated bromide oxidation requires a coupled reduction, a role filled under our conditions by oxygen. To establish oxygen's role as the reductant, we sought comparison with an alternate reducing agent. Methyl viologen (**7**) is known to accept an electron from TiO_2[10] and can potentially act as a reduction partner for the bromide oxidation. Upon irradiation in a parallel experiment in which 0.1 M methyl viologen replaced oxygen and in which suspension agitation was accomplished by a stream of dry nitrogen, the formation of the intensely blue monocation **8**, the reduction product of methyl viologen could be observed (eq 2). This product acts as an internal light filter, significantly slowing the overall rate of photoreaction. In the absence of adsorbed oxygen,[11] however, nearly no dibromide **2** could be observed. Thus, cyclohexene apparently does not compete successfully with the photogenerated methyl viologen monocation for the photogenerated bromine. An irreversible reduction partner is thus required for the success of the photooxidation.



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(2)

Only *trans*-dibromide **2** (no cis isomer) is formed in the presence of oxygen. Since sequential transfer of surface bound bromine atoms to the olefinic double bond would have been expected to lead to *cis*-dibromide, no evidence for chemical reactivity from surface-bound bromine atoms could be found.

Conclusions

These results clearly show that organic products derived from routes a and b, but not c, of Scheme II can be detected. Whether the cyclohexenyl radical derived products (**2**, **3**, and **5**) implicate chemical reactivity of surface-bound bromine atom or whether they are derived from radical chain processes emanating from oxygen reduction is unclear, although no evidence of radical addition to the cyclohexene double bond could be obtained. The isolation of substantial quantities of *trans*-dibromide **1** implies that at least significant quantities of photogenerated bromine atoms become detached from the surface as bromine molecules and can be trapped in normal electrophilic addition sequences, although our work does not unambiguously demonstrate whether this desorption occurs as $Br\cdot$, $Br_2^-\cdot$, or Br_2.

That oxygenation represents a major reaction route implies that the cyclohexenyl radical can participate in chain-carried autoxidation, producing cyclohexenol and its further oxidation product cyclohexenone. Interception of the cyclohexenyl radical by oxygen (either dissolved, absorbed, or from a surface-lattice position) blocks bromination to allylic bromide and interferes with radical dimerization to bicyclohexenyl **5**.

We conclude, as Graetzel saw on colloidal TiO_2, that the initial Br^- oxidation produces bromine atoms which are converted near the photocatalyst surface to bromine, a species which migrates into solution where it can react in conventional fashion.

Experimental Section

Materials. Acetonitrile (MCB, reagent) was distilled under nitrogen from calcium hydride and stored over 3A molecular sieves (Aldrich). Titanium dioxide (TiO_2, MCB, technical grade powder) was dried overnight at 110 °C and stored in a vacuum desiccator containing calcium chloride. Tetrabutylammonium bromide from Columbia Organic was used without purification. Gases (O_2, N_2, and Ar) were dried by passage through a drying tube (6 cm × 30 cm) of activated molecular sieve. Cyclohexene (Aldrich) was distilled before use and was shown to be greater than 99% pure by gas liquid chromatography.

Apparatus. Irradiations were carried out in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co.) equipped with 350-nm lamps and a cooling fan. Gas chromatography–mass spectroscopic analyses were performed on a Finnigan Model 4023 automated GC/MS equipped with an INCOS data system and a capillary column (SGE, BP1). Routine gas chromatography was performed with a Varian Model 1400 equipped with a capillary column and FID connected to a Hewlett-Packard 3390A reporting integrator.

Procedure. Standard solutions of bromide, olefin, and biphenyl were employed. The titania was weighed and placed in a 25 mm × 200 mm Pyrex test tube to which was added the appropriate volume of standard solution to give a total volume of 20 mL. The test tube was sealed with a wired septum and suspended in the Rayonet over a magnetic stirrer. Gases were bubbled through the solution for 10–15 min, then the exit needle removed, and the inlet needle raised out of the solution, leaving the system under a positive pressure. The septum was wrapped with aluminum foil and then the magnetic stirrer, cooling fan, and illumination turned on. The temperature was monitored by a thermometer suspended near the reaction vessel. After illumination, the reaction mixture was vacuum filtered by using a fine glass frit funnel. The filtrate was sampled for gas chromatographic analysis with biphenyl as an internal standard.

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Registry No. TiO_2, 13463-67-7; cyclohexene, 110-83-8; tetrabutylammonium bromide, 1643-19-2; methyltriphenylphosphonium bromide, 1779-49-3.

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(11) Exclusion of absorbed oxygen and water from the TiO_2 powder surface is accomplished by overnight heating in a vacuum muffle furnace.

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