

corresponding PCD· in the radical pair.<sup>6,9</sup> Since the hyperfine coupling constant of the allylic hydrogens in the unsubstituted cyclohexadienyl radical has a large positive value (+47.7 G),<sup>10a</sup> we expect the corresponding PCD· coupling constant to be positive also. Applying the rules<sup>8</sup> for a "disproportionation reaction" between independently generated radicals as in eq 3 with a negative  $\Delta g$  and a positive hyperfine coupling, an emission line is predicted for the pentachloroacetone (pentachloroethane or chloroform) as we observe. The 3,5-hydrogens of the *biphenyl*, however, appear in enhanced absorption in the nmr spectrum. This cannot be compared with prediction as the absolute value of the hyperfine coupling constant in that position of the best available model, the cyclohexadienyl radical, is too small to presume that the sign of the highly substituted radicals is the same.<sup>10a</sup> The calculations of hyperfine coupling constants also require considerable approximations.<sup>10b</sup>

In toluene, xylene, mesitylene, and diphenylmethane direct abstraction of the benzylic protons by the pentachloroacetyl radical competes with phenyl addition to the aromatic ring. Such a chain-transfer process does not contribute to polarization;<sup>4</sup> it merely lessens the emission from the pentachloroacetone, formed by reaction 3. Indeed, the pentachloroacetone produced from a hexamethylbenzene substrate is not polarized since by far the major process there is not arylation but direct abstraction. We obtained additional experimental evidence that hydrogen is not polarized in a chain-transfer step, from the earlier studied BPO-cyclohexanone system.<sup>11</sup> We decomposed 5% solutions of BPO-*d*<sub>10</sub><sup>12</sup> or BPO-*f*<sub>10</sub><sup>12</sup> in cyclohexanone under conditions in which even a 1% solution of BPO-*h*<sub>10</sub> gave a large benzene emission signal. No polarization was observed in the abstraction products. Therefore, polarization was not induced when only a single radical was involved. The perchloro and the PCD· radical are both required in the polarizing step.

So far we have discussed the polarization of the protons on the cyclohexadienyl ring of the PCD·, as produced from the reaction of BPO-*d*<sub>10</sub> with hydrogen-containing aromatic compounds. When BPO-*h*<sub>10</sub> is decomposed in benzene-*d*<sub>6</sub>, the PCD· is deuterated in the radical-containing ring and polarized biphenyl is not expected. Nevertheless, an nmr emission spectrum corresponding to the ortho protons of biphenyl is observed<sup>13</sup> particularly in the absence of perchloro compounds. This polarization must be due to phenyl radicals which have escaped the initial polarizing cage and retained some polarization throughout the arylation reaction. In the same spectrum a large enhanced absorption nmr signal from phenyl benzoate is observed from the in-cage combination of benzoyloxy and phenyl radicals. Addition of only 5% perchloroalkane reduced the enhanced absorption to the much

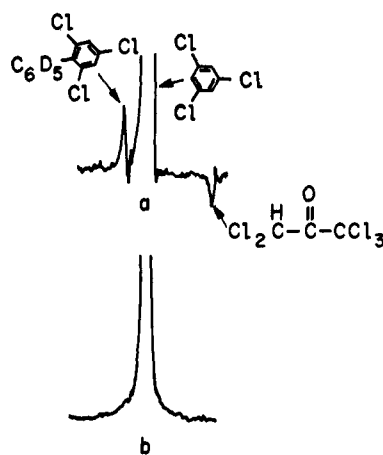
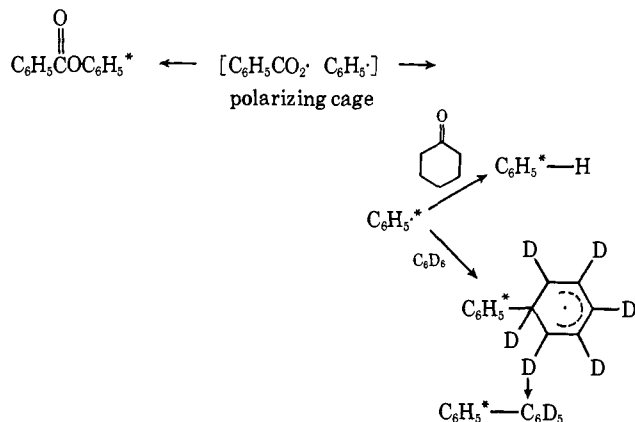


Figure 1. Nmr spectra of a BPO-*d*<sub>10</sub>-1,3,5-trichlorobenzene-hexachloroacetone solution (molar ratio, 0.1:1:1): (a) after 3 min at 127° in nmr probe; (b) after 10 min at 127° in nmr probe.

smaller peak usually observed for phenyl benzoate in aliphatic solvents.<sup>14</sup> We assume that this is due to solvent interference in the geminate recombination reaction.<sup>15</sup>



By using selectively substituted (Cl, D, or alkyl) reactants, we have been able to detect three kinds of protons of the PCD· intermediate by CIDNP. The role of the PCD· radical in the arylation reaction is thus demonstrated by a physical technique.

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## Quantum Yields of Silver Ion Reduction on Titanium Dioxide and Zinc Oxide Single Crystals

Sir:

Photochemical electron transfer reactions at the surfaces of solids in contact with metal ion solutions have been the subject of numerous investigations.<sup>1-4</sup>

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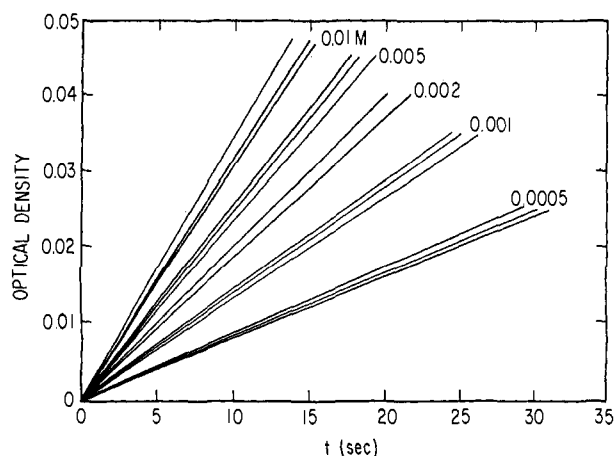


Figure 1. Silver deposition on  $\text{TiO}_2$  at different  $\text{AgNO}_3$  concentrations.

One reaction that has received considerable attention, partially because of its application in a photoimaging process,<sup>5</sup> is the reduction of silver ion by photoelectrons in metal oxide semiconductors. However, no quantum yield data nor *in situ* kinetic measurements have been reported for these charge-transfer reactions. Such measurements were difficult to make previously, because they were performed with oxide powders, which introduced considerable interpretative uncertainty due to light scattering in the powder systems. We have found that appropriately prepared single crystals of various semiconductors can be used for the photo-reduction of  $\text{Ag}^+$  from  $\text{AgNO}_3$  solution and have succeeded in measuring quantum yields and solution  $\text{Ag}^+$  concentration dependencies for crystals of  $\text{TiO}_2$  and  $\text{ZnO}$ . The use of single crystals offers the advantages of continuous product analysis during the reaction, effectively homogeneous surfaces, and theoretical modeling of the material properties of the substrate. We report here results for silver ion reduction. The accompanying oxidation process is not treated, but it is assumed to occur within the crystal substrate. Degradation of the crystal surface during irradiation is observed, and the transfer of electrons from oxide ions is consistent with the charge-transfer nature of the absorption transition.

Our experiments were performed in the cell compartment of a Cary Model 15 spectrophotometer. Single crystals of either  $\text{ZnO}$  ( $\pm C$  face) or  $\text{TiO}_2$  (rutile,  $C$  face) were lapped, chemically polished, and mounted in a standard rectangular 1-cm cell, so that the transmitted sample beam could be used as a measure of the amount of silver deposited. The cell was filled (completely immersing the crystal) with an aqueous solution of  $\text{AgNO}_3$  concentration between  $10^{-4}$  and 2.0  $M$ . Irradiation at a  $45^\circ$  angle to the front face of the cell was with a 100-W high-pressure mercury lamp filtered to select light predominantly in the 365-nm band, a region highly absorbed by the crystal but not by the solution. The relative intensity of the mercury lamp during each run was continuously monitored with a photomultiplier tube (1P28 RCA), which was calibrated

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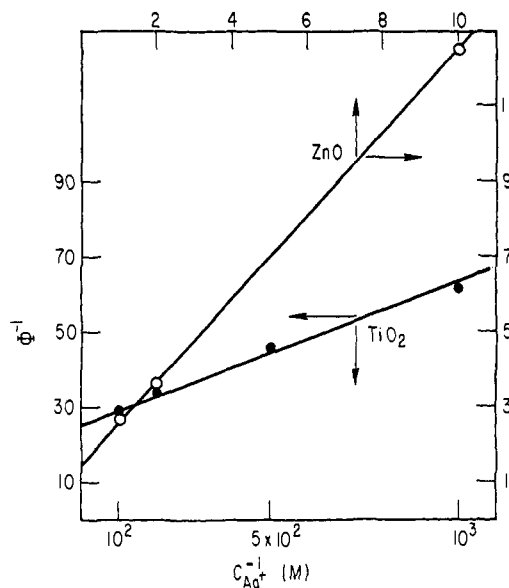


Figure 2. Typical Stern-Volmer plots for  $\text{Ag}^+$  reduction on  $\text{ZnO}$  and  $\text{TiO}_2$ .

periodically with ferrioxalate actinometry in the identical cell geometry.<sup>6</sup> Correction for reflectance loss from the crystal surface was made after independent reflectance measurements.

In a typical experiment, the wavelength selector of the Cary is set at 620 nm; the red light is not absorbed by the solution nor by a crystal containing no deposit. (An uv cutoff filter is placed before the Cary phototube to eliminate stray mercury light.) Upon commencement of uv irradiation, silver ions are reduced at the solid-solution interface, and metallic silver is deposited on the crystal surface. The amount of silver metal formation is measured continuously by recording the increase in the apparent optical density of the crystal-silver system. A very sensitive analytical procedure<sup>7</sup> was modified to determine the amount of silver corresponding to the apparent optical density. For a given deposition, the silver was dissolved off the crystal surface with  $\text{HNO}_3$  and then determined with an Orion 9416 specific ion electrode or by atomic absorption spectrophotometry with a Perkin-Elmer Model 303 spectrophotometer. For apparent optical densities of  $\leq 0.1$ , the quantity of silver/cm<sup>2</sup> of substrate surface is proportional to the optical density. Measurements were limited to very thin layers of silver ( $\Delta\text{OD} \leq 0.1$ ) to prevent significant attenuation of the uv light by the deposit during each measurement.

Typical kinetic data for a specific  $\text{TiO}_2$  crystal in solutions of different  $\text{AgNO}_3$  concentrations are shown in Figure 1. A dependence of quantum yield, calculated from the slopes in Figure 1 and the measured light intensities, on solution silver ion concentration is evident; these yields are independent of light intensity ( $10^{14}$  to  $2 \times 10^{16}$  photons/cm<sup>2</sup> sec) and dissolved oxygen. Figure 2 shows that for both  $\text{TiO}_2$  and  $\text{ZnO}$  the data obey a type of Stern-Volmer mechanism, as given by eq 1, where  $\Phi$  is the yield at silver concentration

$$\Phi = \Phi_{\text{lim}} C_{\text{Ag}^+} / (C_L + C_{\text{Ag}^+}) \quad (1)$$

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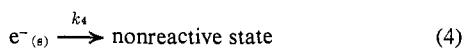
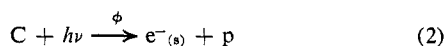
**Table I.** Kinetic Data for AgNO<sub>3</sub> on Metal Oxide Crystals

Material	$\Phi_{lim}$	$C_L, M$	$K, M^{-1}$ <sup>a</sup>
ZnO	0.3-0.6	0.2-0.6	3.5-0
TiO <sub>2</sub>	0.03-0.10	$1 \times 10^{-3}$ to $2 \times 10^{-2}$	970-0

<sup>a</sup> Calculated from eq 8; the largest value is obtained with the smallest  $\Phi_{lim}$  when  $\phi = 1$ .

$C_{Ag^+}$ ,  $\Phi_{lim}$  is the limiting yield at high  $C_{Ag^+}$ , and  $C_L$  is a constant. The parameters  $\Phi_{lim}$  and  $C_L$  vary considerably for different crystals, largely depending on surface preparation (Table I). However, the concentration dependence, eq 1, is applicable in every case.

The Stern-Volmer concentration dependence may be obtained from the following reaction scheme



In this scheme, it is visualized that excitation of crystal C produces surface electrons  $e^-(s)$  with an efficiency  $\phi$ ; these electrons then react with silver  $Ag^+(s)$  at the solid-liquid interface. Thus

$$\Phi = \phi k_3 N_{Ag^+} / (k_4 + k_3 N_{Ag^+}) \quad (5)$$

where  $N_{Ag^+}$  is the surface concentration of silver ions. Equation 5 is sufficient to describe our experimental results, if  $N_{Ag^+}$  is proportional to  $C_{Ag^+}$  and  $\Phi_{lim} = \phi < 1$ . This condition ( $\phi < 1$ ) requires a surface barrier to photoelectron transport. The effect of such a barrier and, hence, the value of  $\phi$  depend on substrate properties such as trapping and recombination of photogenerated charge carriers.

A more general derivation of eq 1 is obtained if discrete ion effects in the solution region at the interface are considered. A Langmuir adsorption isotherm with equilibrium constant  $K$  and  $N_s$  sites/cm<sup>2</sup> can be used to describe the relationship of concentration of adsorbed silver ions to the solution  $Ag^+$  concentration. This assumption and the use of eq 5 yield the Stern-Volmer dependence, eq 1, immediately with

$$\Phi_{lim} = \phi [1 - k_4 / (k_4 + k_3 N_s)] \quad (6)$$

and

$$C_L = k_4 / (k_4 + k_3 N_s) K \quad (7)$$

Moreover

$$K = (1/C_L)(1 - \Phi_{lim}/\phi) \quad (8)$$

Note that for this treatment it is not necessary to invoke the above-mentioned surface barrier to electron transport. The quantities  $C_L$  and  $\Phi_{lim}$  are experimentally determined (Table I). However, since  $\phi$  has not been measured, only a range of  $K$  values can be calculated for each material (note that  $\Phi_{lim} \leq \phi \leq 1$ ). These values of  $K$ , also listed in Table I, suggest that adsorption of  $Ag^+$  on ZnO may be considerably weaker than on TiO<sub>2</sub>.

The measured quantum yields for the reduction of  $Ag^+$  at the surface of TiO<sub>2</sub> and ZnO single crystals and the determination of  $Ag^+$  concentration dependencies have provided information regarding the material

properties of the two oxides. It may be anticipated that in the limiting region of high silver concentration the quantum yield should be determined by the substrate properties, e.g., eq 6. One such property is the concentration of electron trap levels (impurity sites, lattice vacancies, etc.) in the material. The presence of these traps in the bulk material could affect the value of  $\phi$ , while location on the surface could contribute to deactivation *via* reaction 4 (i.e., increases the value of  $k_4$ ). The near-unity value of  $\Phi_{lim}$  for ZnO implies that there is little or no effect on the surface reduction of  $Ag^+$  from either bulk or surface electron traps. However, the low limiting yields for TiO<sub>2</sub> could be the result of deactivation of photoelectrons by stable electron trap levels. It is not possible to specify whether these traps are in the bulk or at the surface, but their influence on the photoreactivity is consistent with literature reports in which large differences in electron trap distribution were observed after various surface treatments.<sup>8</sup> It may be concluded then that the differences in reactivity for the TiO<sub>2</sub> crystals that we examined resulted from differences in trap distribution induced during surface preparation.

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### Solution Photochemistry. VIII. Novel Rearrangements of Some Substituted Butadiene-Benzoquinone Diels-Alder Adducts<sup>1,2</sup>

Sir:

In a previous paper<sup>3</sup> we showed that  $n \rightarrow \pi^*$  excitation of the butadiene-*p*-benzoquinone Diels-Alder adduct **1** leads to formation of the novel tricyclic ene-diones **2** and **3** (Scheme I). As an extension of this work, we would like to report in the present communication that (a) photolysis of the 2,3-dimethylbutadiene-benzoquinone adduct **4** (*cf.* Scheme I) leads to products analogous to **2** and **3** (i.e., **5** and **6**) and in addition gives rise to the unusual tricyclic enone alcohol **7**, (b) the ratio in which these three products are formed is remarkably solvent dependent, (c) the structure of **7** provides corroborative evidence for the mechanism postulated previously,<sup>3</sup> (d) deuterium labeling studies are also in accord with this mechanism, (e) the photoproducts undergo novel thermal and photochemical interconversions, and (f) irradiation of the *trans,trans*-2,4-hexadiene-*p*-benzoquinone Diels-Alder adduct **8** does *not* give products analogous to **5**, **6**, or **7**, but yields instead the unique photoproduct **9**.

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