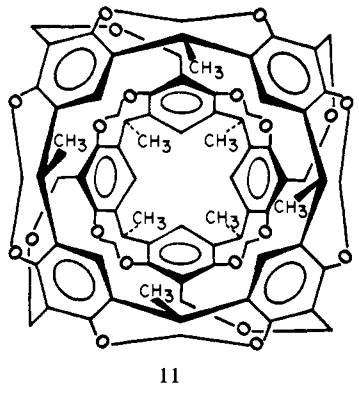
the *eeee* conformation of **10b** (C_{2v} symmetry). The marked upfield shift of the methine signal from δ 5.67 to 3.92 as the temperature is lowered correlates with the methine protons moving into the shielding cone of the naphthalene rings as the latter occupy the *e* positions. (3) Although all protons shift between 30 and −50 °C, above 30 and −50 °C their signals do not change. The spectra above 30 °C show no detectable (<5%) C_{2v} conformer, and that below −50 °C shows no detectable (<2%) C_{4v} conformer. Thus the conversion of the *aaaa* to the *eeee* conformer is favored by >3 kcal mol^{-1} as the temperature is lowered. Molecular models provide a definitive prediction that **10a** is less strained than **10b**. Although **10a** and **10b** possess molecular surfaces of equal magnitude, in solution, the more *extended surfaces* of **10b** must contact and orient more solvent molecules than the more *confined surfaces* of **10a**. These contacts are expected to be enthalpy stabilizing but entropy destabilizing for both systems.[13] In the conversion **10b** → **10a**, some collected and oriented solvent molecules are liberated. At low enough temperatures, **10b** is the more stable conformer in solution because its more favorable enthalpy of solvation overrides the sum of the unfavorable *TS* of solvation and the greater strain energy of this conformer. As the temperature increases, the unfavorable *TS* cancels more of the favorable enthalpy until the free energy of solvation no longer overrides the greater strain energy of **10b**. Above this temperature, **10a** dominated in the equilibrating mixture, since its stability in solution does not depend as much as that of **10b** on its free energy of solvation. To our knowledge, **10** is quite unique in providing conformations that present so widely differing opportunities for solvation.

Of the four cavitands, **7** and **10** crystallize only with, and **8** and **9** only without, solvent of crystallization. Molecular models of **7** and **10** are unable to fill their rigid cavities intermolecularly. These compounds crystallize only as solvates. Models of **8** and **9** are able to fill their cavities intermolecularly. These compounds do not form solvates. This correlation strongly suggests that solvent parts fill the cavities of **7** and **10** since voids are rarely encountered in crystal lattices. In spite of many attempts, crystals of **7** and **10** suitable for structure determination have not yet been grown.

This investigation has demonstrated that cavitands with large internal surfaces can be designed and readily prepared. When their molecular models cannot fit together intermolecularly to fill their enforced cavities, they crystallize only as solvates. One of the four cavitands contains mobile flaps whose conformations are governed by a balance between strain and solvation effects. Cycle **9** is the key intermediate in a projected synthesis of closed surface cavitand **11**, whose molecular model is unstrained and whose cavity is large enough to imprison models of compounds as large as C_6H_6, $(CH_2)_4O$, and $(CH_3CH_2)_2O$ or seven molecules of H_2O.



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Supplementary Material Available: Experimental procedures for compounds **6**, **7**, **8**, **9**, and **10** (3 pages). Ordering information is given on any current masthead page.

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Transients Generated upon Photolysis of Colloidal TiO_2 in Acetonitrile Containing Organic Redox Couples

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Increasing recognition of the importance of photoinduced electron-transfer reactions in synthetically useful transformations has led to an intense investigation of various methods for sensitization of redox reactions of organic substrates. One such method sure to enjoy future prominence involves the use of semiconductor powders as photocatalysts responsive in the visible and ultraviolet regions. Despite several recent reports outlining efficient photoinduced redox reactions of organic substrates, little firm evidence is available regarding the mechanisms of such reactions, particularly in nonaqueous solvents. This deficiency has prompted us to investigate the identity of transients formed upon irradiating colloidal TiO_2 particles in nonaqueous solvents in the presence of organic redox systems, a medium which simultaneously incorporates the heterogeneity of the powder-catalyzed reactions and the possibility for spectroscopic analysis of mechanistically relevant transients. Although semiconductor band theory predicts that photocatalyzed oxidations or reductions could occur with donors or acceptors whose redox potentials lie within the range between the valence and conduction bands of the metal oxide, little evidence for organic radical ion intermediates generated in this way from neutral precursors has yet been reported. We describe here transient spectra that affirm the occurrence of semiconductor-mediated electron transfer and demonstrate the involvement of radical ions, the first such data reported for organic redox couples in nonaqueous solvents.

Acetonitrile suspensions of colloidal TiO_2 were prepared by controlled hydrolysis[1] of titanium tetraisopropoxide, a route parallel to that reported by Graetzel[2] in aqueous solution. A preparation was considered successful if it exhibited the following properties: optical transparency, high absorbance near 350–360 nm, ability to photocatalyze the oxidative cleavage of 1,1-diphenylethylene,[3] and resistance to significant precipitation for at least 24 h. Although the required water could be provided from several sources (wet trifluoroethanol, glacial acetic acid, concentrated hydrochloric or perchloric acids), the latter two reagents were found to give the best results consistently.

In a typical experiment, such a colloidal suspension was made 0.01 M in *trans*-stilbene or 1×10^{-4} M in methyl viologen. The resulting mixture was excited with a laser pulse (third harmonic of a Q-switched Nd:YAG laser (355 nm)), and the formation of transient spectra was monitored by using a previously described apparatus.[4] The time-resolved transient spectra obtained in the presence of stilbene (Figure 1) corresponded closely to those reported for the *trans*-stilbene radical cation.[5,6] Although the broad absorption between 550 and 700 nm is not yet explained, a second band at 695 nm has been reported for the stilbene radical cation in viscous media.[6]

The shape and intensity of this spectrum are unaffected by dissolved oxygen, since identical results are obtained while bubbling oxygen or nitrogen through the solution. A rough estimate for

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[1] Hardee, K. L.; Bard, A. J. *J. Electrochem. Soc.* **1975**, *122*, 739. In our adaptation of Bard's procedure, 20 mL of the solvent mixture was treated with 0.5 mL of a 10:1 mixture of isopropyl alcohol:titanium isopropoxide. The latter was added as repeated injections with a 10-μL syringe while the solution was continuously stirred.

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

[4] Rodgers, M. A. J.; Foyt, D. C.; Zimek, Z. A. *Radiat. Res.* **1978**, *75*, 296. Lindig, B. A.; Rodgers, M. A. J. *J. Phys. Chem.* **1979**, *83*, 1683.

[5] Rodgers, M. A. J. *Trans. Faraday Soc.* **1971**, *67*, 1029.

[6] Torikai, A.; Kato, H.; Kuri, Z.-I. *J. Polymn. Sci., Polymn. Chem.* **1976**, *14*, 1065.

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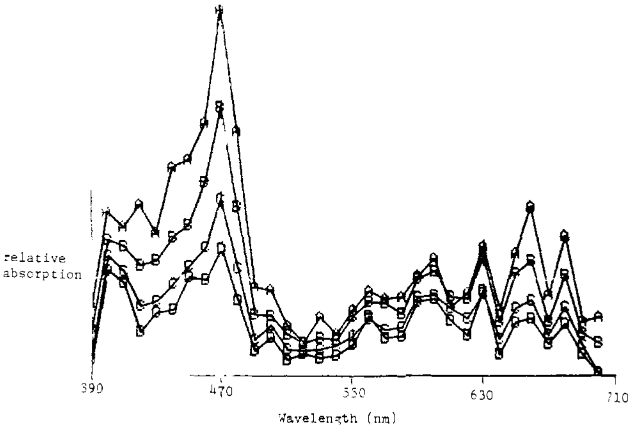

Figure 1. Transient production of the *trans*-stilbene radical cation sensitized by colloidal TiO_2 (λ excitation = 355 nm, 0.01 M *trans*-stilbene in colloidal TiO_2 suspended in 0.1 M perchloric acid in acetonitrile). Times after flash (μs): A, 13; B, 52; C, 95; D, 126.

the quantum yield of radical cation formation (relative to that reported for the triplet yield of benzophenone[7]) is 0.005.[8] The yield of the stilbene radical cation did not appear to be affected by the addition of methyl viologen as might have been expected if the stilbene oxidation efficiency were limited by competition with electron-hole recombination. Possible contributory factors to the low yield include the presence of isopropanol from our colloid preparation and/or the presence of adsorbed oxygen at the particle surface, which may lead to rapid chemical reactions that consume the cation radical.

Although no evidence for the formation of the stilbene radical anion (λ_{max} 490 nm[9]) could be obtained, reduction could be observed upon analogous excitation of colloidal TiO_2 in the presence of methyl viologen (Figure 2). Here the transient produced agrees well with that reported for the singly reduced radical cation.[10] One significant difference in the formation of this reduction product and the oxidation product from *trans*-stilbene is that not all of the production of the methyl viologen cation radical is prompt. With 10^{-4} M solutions, about half of the transient absorption attributable to the one-electron reduction occurs with the laser flash, with the remainder developing over a period of 15–20 μs. Since methyl viologen dication absorbs weakly at 355 nm, the prompt fluorescence may be due entirely to direct excitation, the slower formation being derived from TiO_2 sensitization. The time scale for such slower electron transfer corresponds, perhaps coincidentally, to that observed in laser coulostatic flash experiments for redox systems at the surface of TiO_2 single crystals in aqueous[11] and nonaqueous[12] electrolytes.

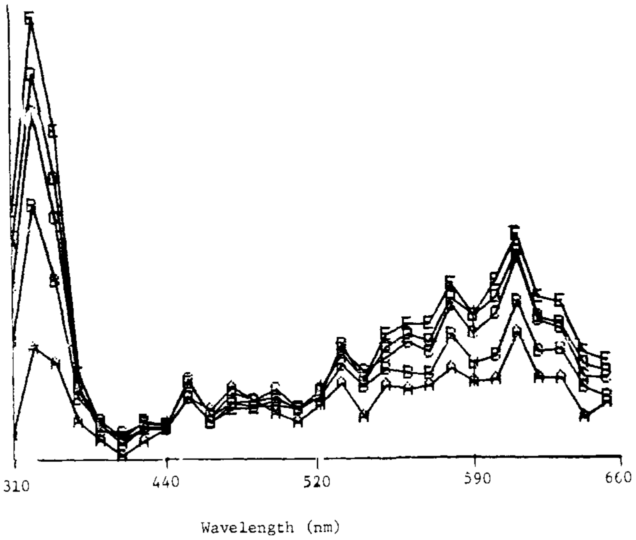

Figure 2. Growth of the absorption spectrum of methyl viologen^{+}·sensitized by colloidal TiO_2 (λ excitation = 355 mm, 1 × 10^{-j} M methyl viologen^{2+} in colloidal TiO_2 suspended in 0.1 M perchloric acid in acetonitrile). Times after flash (μs): A, 0.4; B, 1; C, 2.2; D, 4.4; E, 10.

Although previous work has demonstrated the formation of oxidized and reduced species at metal oxide powders[13] or colloids[14] in aqueous suspensions (where hydroxy radical is throught to be a major oxidant[15]), these results represent direct observations of organic radical ions in nonaqueous solvents at colloidal TiO_2 and provide important mechanistic insight into the general problem of organic transformations occurring upon photocatalysis at heterogeneous surfaces.[3,16,17]

Acknowledgment. Generous support of this research by the U.S. Department of Energy, Fundamental Interactions Branch, is acknowledged. M.A.F. is grateful for support as an Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher–Scholar. This work was conducted at the Center for Fast Kinetics Research, a facility funded by the National Institutes of Health and by the University of Texas at Austin.

Registry No. TiO_2, 13463-67-7; acetonitrile, 75-05-8; *trans*-stilbene, 103-30-0; methyl viologen, 1910-42-5; *trans*-stilbene radical cation, 59532-48-8; oxygen, 7782-44-7; methyl viologen radical cation, 25239-55-8.

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(7) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970.

(8) This value is corrected for fractional TiO_2 absorption of the incident pulse. Whether this low value is caused by rapid chemical reaction of the photoinduced radical ion pair or by low concentrations of radicals derived from small quantities of water or isopropyl alcohol is at present unknown.

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(10) For example, see: Kalyanasundaram, K.; Dung, D. *J. Phys. Chem.* **1980**, *84*, 2551.

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Carbon–Carbon Bond Formation via the Reaction of Trialkylallylstannanes with Organic Halides

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In connection with ongoing synthetic studies in our laboratories, we required a method for the replacement of halogen by an allyl moiety in substrates such as bromolactone **1** (Table I). Very few methods compatible with such substrates are known, since conversion of **1** to an organometallic derivative, or reaction of such substrates with organometallic derivatives, is frustrated by an obviously facile reductive elimination possibility. Palladium-catalyzed processes have been employed for this type of conversion but are in general limited to substrates without aliphatic β hydrogens.[2] We have found the reaction of allyltri-*n*-butylstannane with halides or other precursors to carbon-centered radicals to

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(1) Fellow of the Alfred P. Sloan Foundation, 1981–1983.

(2) For recent reviews of palladium-catalyzed C–C bond forming reactions, note: Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

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