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Valence Isomerization of Quadricyclene Mediated by Illuminated Semiconductor Powders

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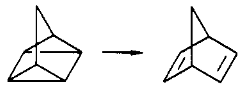
Quadricyclene undergoes valence isomerization to norbornadiene in the presence of photoexcited n-type semiconductor powders. For samples irradiated under comparable conditions of time and intensity, the yield of the diene product varies with (i) the semiconductor in the order CdS > TiO_2 ≥ ZnO and (ii) the solvent in the order dichloromethane > acetonitrile > tetrahydrofuran. The presence of oxygen in a sample diminishes the product yield, whereas both methylviologen dication and diphenylamine enhance the yield. The quantum efficiency of norbornadiene production appears to be rather low ($\sim 10^{-2}$ for CdS) in these heterogeneous systems. These observations are interpreted in terms of the redox chemistry that results upon interaction of the photogenerated electron-hole pairs in the semiconductor with the surrounding organic medium.

Introduction

Rearrangement of the highly strained hydrocarbon, quadricyclene (Q) to its more stable valence isomer, norbornadiene (NBD) (eq 1) proceeds at a negligibly slow rate at 25 °C because of a substantial symmetry-related kinetic barrier.[1,2] The barrier height drops appreciably, however, in the corresponding cation radical, $Q^{\bullet+}$, and the latter species undergoes rapid and essentially irreversible isomerization to $NBD^{\bullet+}$ (eq 2).[1,3] Consequently, single-electron oxidation of Q to $Q^{\bullet+}$ represents an attractive strategy for promoting the valence isomerization of this robust molecule. Several routes to the structurally labile cation radical have been reported, including (1) photochemical oxidation of Q by an electronically excited photosensitizer,[4] (2) electrochemical oxidation of Q at a metallic electrode,[5] and (3) chemical oxidation of Q by a photochemically generated ground-state oxidant.[6] In each case, the generation of $Q^{\bullet+}$ resulted in the production of NBD and, in some systems, quantum yields or electrocatalytic factors[7] considerably above unity were measured. This latter observation is diagnostic of the operation of a redox chain sequence consisting of eq 2 and the thermodynamically favorable oxidation of Q by $NBD^{\bullet+}$ (eq 3).[8]



Q NBD (1)

$$Q^{\bullet+} \longrightarrow NBD^{\bullet+} \tag{2}$$

$$NBD^{\bullet+} + Q \longrightarrow NBD + Q^{\bullet+} \tag{3}$$

A potentially attractive route to $Q^{\bullet+}$ that has yet to be explored involves oxidation of the parent hydrocarbon at the surface of an illuminated n-type semiconductor. The thermodynamic requirement that the photogenerated holes in the valence band of the semiconductor lie at a potential sufficiently positive to oxidize Q is satisfied by a number of oxide and non-oxide materials (Table I). An inexpensive and experimentally straightforward technique for conducting this type of heterogeneous oxidation step utilizes the semiconductor as a powder suspended in the organic reaction medium.[9] The efficiency of light absorption can be quite high in such a system and interfacial reactions are facilitated by the large surface area-to-volume ratio of the semiconductor particles.

Table I. Conduction Band and Valence Band Positions of Semiconductors in Acetonitrile

semiconductor	conduction band potential, V vs. SCE[a]	valence band potential, V vs. SCE[a]
CdS	−0.85	1.6
TiO_2	−0.8	2.3
ZnO	−0.76	2.4

[a] Values taken from: Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 7427. Kohl, P. A.; Bard, A. J. *Ibid.* **1977**, *99*, 7531.

Prompted by the preceding considerations, we investigated the use of irradiated n-type semiconductor powders as catalysts for the isomerization of Q to NBD. Our results and their significance in terms of the elementary processes occurring within the semiconductor and at the semiconductor–liquid interface are reported here.

Experimental Section

(a) Reagents. Quadricyclene was prepared and purified by the procedure of Smith.[10] Methylviologen dichloride (Aldrich) was converted to the hexafluorophosphate salt by dissolution in water followed by precipitation with excess ammonium hexafluorophosphate. Following recrystallization from hot acetonitrile, the solid was dried over P_4O_{10} in an evacuated desiccator for 24 h. Diphenylamine (Aldrich) was recrystallized from hot methanol, while tetrabutylammonium perchlorate (Fisher) was recrystallized from hot dichloromethane; both reagents were then dried over P_4O_{10} in vacuo for 24 h. Solvents were of at least reagent grade quality and were used as received.

Titanium dioxide (Aldrich) of 99.999% purity was obtained as small chunks, which were ground to a powder in a mortar and pestle and then dried at 170 °C for 24 h. Zinc oxide powder (Fisher) of 99.8% purity was also dried at 170 °C for 24 h. Cadmium sulfide powder (Aldrich) of 99.999% purity was used as received from the supplier. Under an electron microscope, the

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[1] (a) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chem. Acta* **1979**, *62*, 583. (b) Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110.

[2] For a discussion of a photochemical energy storage cycle based upon the NBD-Q interconversion, see: Hautala, R. R.; King, R. B.; Kutal, C. In *Solar Energy: Chemical Conversion and Storage*; Hautala, R. R., King, R. B., Kutal, C., Eds.; Humana: Clifton, NJ, 1979; p 333.

[3] Roth, H. D.; Manion Schilling, M. L.; Jones, G., II. *J. Am. Chem. Soc.* **1981**, *103*, 1246.

[4] (a) Jones, G., II; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805. (b) Borsub, N.; Kutal, C. *J. Am. Chem. Soc.* **1984**, *106*, 4826.

[5] Yasufuku, K.; Takahashi, K.; Kutal, C. *Tetrahedron Lett.* **1984**, *25*, 4893.

[6] Kutal, C.; Kelley, C. K.; Ferraudi, G., submitted for publication.

[7] Electrocatalytic factor is defined as (mol of NBD formed)/(faraday of electricity consumed).[5]

[8] The $E_{1/2}^{ox}$ values for NBD and Q in CH_3CN are 1.56 and 0.91 V (vs. SCE), respectively. Gassman, P.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

[9] For excellent reviews of the physical principles and chemical applications of irradiated semiconductor powders, see: (a) Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 139. (b) Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314. (c) Kalyanasundaram, K. In *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic: New York, 1983; Chapter 7.

[10] Smith, C. D. *Org. Synth.* **1971**, *51*, 133.

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Table II. Conversion of Q to NBD in the Presence of Illuminated Semiconductor Powders

run	system[a]	N_2-purging	% yield[b]
a	$Q/CdS/CH_2Cl_2$	yes	1.8
b	$Q/CdS/CH_2Cl_2$	no	0.8
c	$Q/CdS/CH_3CN$	yes	1.2
d	$Q/CdS/CH_3CN$	no	0.6
e	Q/CdS/THF	yes	0.7
f	$Q/TiO_2/CH_3CN$	yes	0.1
g	$Q/ZnO/CH_3CN$	yes	0.0
h	$Q/CdS/CH_3CN/TBAP$[c]	yes	0.9
i	$Q/-/CH_3CN$	yes	0.0

[a] Conditions: [Q] = 0.067 M; 20 mg of semiconductor powder in 3 mL of solvent; irradiation time of 3 h at ≥350 nm. [b] Calculated according to eq 4. [c] [TBAP] = 0.02 M.

CdS appeared as irregularly shaped particles whose morphology suggested a high degree of crystallinity. Most of the particles possessed lateral dimensions of 1–2 μm.

(b) Equipment and Procedures. Electronic absorption spectra were recorded on a Cary 15 spectrophotometer. Electron micrographs of semiconductor powders were taken with a Phillips 505 scanning electron microscope. Photolyses were performed with a 200-W high-pressure mercury-arc lamp, whose output was passed through a Corning 0-52 glass filter to remove light of wavelengths below 350 nm. In some experiments, an interference filter was used to isolate the 366-nm Hg line. Light intensity at this specific wavelength was determined by ferrioxalate actinometry.[11] Irradiated and dark control samples were analyzed by gas chromatography on a Varian 2700 chromatograph equipped with a flame ionization detector and containing a 12 ft × $^1/_8$ in. stainless steel column packed with 5% OV-101 on Chromosorb G-HP (80–100 mesh). The operating temperatures of the instrument were as follows: injector, 130 °C; column, 90 °C; detector, 250 °C. A 20 mL/min flow rate of nitrogen carrier gas was employed.

In a typical photochemical experiment, 3 mL of a quadricyclene solution, 20 mg of a semiconductor powder, and 6 μL of nonane (as an internal standard for gas chromatographic analysis) were added to a 1 cm (diameter) × 10 cm cylindrical Pyrex tube, which could be capped with a rubber septum. The sample was deoxygenated by bubbling with a stream of nitrogen gas for 20 min and then irradiated with stirring in a thermostated cell holder maintained at 25 °C. Stirring was sufficiently vigorous to ensure that a suspension of the semiconductor powder was exposed to the incident light beam. Following photolysis, the sample was centrifuged to collect the solid material at the bottom of the tube and aliquots of the supernatant liquid were analyzed by absorption spectroscopy and/or gas chromatography. Percentage yields of product were calculated according to eq 4.

$$\%\ \text{yield} = \frac{\text{mol of NBD produced during photolysis}}{\text{mol of Q present before photolysis}} \times 100 \quad (4)$$

Results

Table II summarizes the results of exploratory experiments in which various semiconductor powders suspended in stirred solutions of Q were irradiated at ≥350 nm for 3 h. Isomerization of Q to NBD occurs under these conditions with percentage yields that depend upon the semiconductor employed. Low but easily measurable amounts of NBD are produced in CdS suspensions (runs a, c, e), whereas only traces of the diene result in samples containing TiO_2 (run f) and ZnO (run g). For CdS, the % yield drops in the presence of oxygen (runs b, d) and upon switching the solvent from dichloromethane to acetonitrile to tetrahydrofuran (THF) (runs a, c, e). Addition of the inert electrolyte tetrabutylammonium perchlorate (TBAP), on the other hand, causes little change (compare runs c and h). Control experiments established that NBD is not generated in the dark or in the absence of the semiconductor powder (run i).

Table III. Conversion of Q to NBD in the Presence of Illuminated Semiconductor Powders and Methylviologen Dication

run	system[a]	N_2-purging	% yield[b]
a	$Q/CdS/CH_3CN/MV^{2+}$	yes	10.5
b	$Q/CdS/CH_3CN/MV^{2+}$	no	2.0
c	$Q/TiO_2/CH_3CN/MV^{2+}$	yes	6.0
d	$Q/TiO_2/CH_3CN/MV^{2+}$	no	4.3
e	$Q/ZnO/CH_3CN/MV^{2+}$	yes	0.6
f	$Q/-/CH_3CN/MV^{2+}$	yes	0.0

[a] See footnote *a* of Table II; $[MV^{2+}]$ = 0.007 M. [b] Calculated according to eq 4.

Table IV. Conversion of Q to NBD in the Presence of Illuminated Semiconductor Powders and Diphenylamine

run	system[a]	N_2-purging	% yield[b]
a	$Q/CdS/CH_3CN$	yes	1.2
b	$Q/CdS/CH_3CN/DPA$	yes	1.6
c	$Q/CdS/CH_3CN/DPA/TBAP$	yes	2.2
d	$Q/CdS/CH_3CN/DPA/TBAP$	no	1.4
e	$Q/CdS/CH_2Cl_2/DPA/TBAP$	yes	3.5
f	Q/CdS/THF/DPA/TBAP	yes	0.6

[a] See footnote *a* of Table II; [DPA] = 0.04 M; [TBAP] = 0.02 M. [b] Calculated according to eq 4.

Table V. Relative Rates of NBD Production in Illuminated $Q/CdS/CH_3CN/MV^{2+}$ Suspensions

run[a]	[Q], M	irradn time, h	R_N[b]
a	0.067	3	1.0
b	0.20	3	1.5
c	0.33	3	2.1
d	0.20	0.5	1.0
e	0.20	1	1.3
f	0.20	2	1.9
g	0.20	3	2.4

[a] Conditions: 20 mg of CdS powder in 3 mL CH_3CN; $[MV^{2+}]$ = 0.007 M. [b] Relative rate of NBD production.[12] Note that different light intensities were used in experiments a–c vs. d–g, so that only comparisons of R_N values within the two sets of data are valid.

Table III records the effects of added methylviologen dication (MV^{2+}) on the % yield of NBD in irradiated $Q/semiconductor/CH_3CN$ suspensions. The presence of this electron acceptor causes a significant increase in yield for each of the semiconductor powders investigated (compare runs a, c, e in Table III with runs c, f, g in Table II). Once again, oxygen decreases the yield and the effect is more pronounced for CdS (runs a, b) than for TiO_2 (runs c, d). Light scattering from the suspended semiconductor particles precludes an accurate determination of the quantum yield of NBD production in these systems. Nevertheless, we attempted to estimate the magnitude of this important quantity for a $Q/CdS/MV^{2+}/CH_3CN$ suspension irradiated at 366 nm. Under the assumption that all of the incident photons were absorbed by the semiconductor, a quantum yield of 0.01 was obtained. To the extent that scattering reduced the amount of light actually absorbed, this value represents a lower limit to the true quantum yield.

The data compiled in Table IV reveal that the addition of the electron donor, diphenylamine (DPA), to a $Q/CdS/CH_3CN$ suspension causes a modest increase in the % yield of NBD (runs a, b), whereas an even higher yield results when both DPA and electrolyte, TBAP, are present in the system (run c). Two trends noted earlier reappear in the present data. Thus, oxygen depresses the NBD yield (run d) as does changing the solvent from CH_2Cl_2 to CH_3CN to THF (run c, e, f).

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(11) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956** *235*, 518.

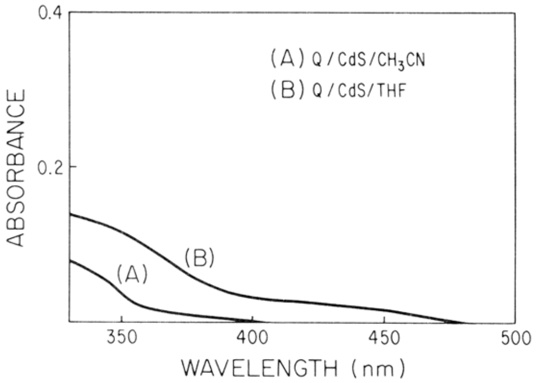

Figure 1. Electronic absorption spectra of solutions from irradiated suspensions of (A) $Q/CdS/CH_3CN$ and (B) Q/CdS/THF. Conditions: [Q] = 0.067 M; 20 mg of semiconductor powder in 3 mL of solvent; 3-h irradiation time. Spectrum of solution from an irradiated $Q/TiO_2/CH_3CN$ suspension is coincident with the base line.

Data summarized in Table V demonstrate that the relative rate of NBD production (R_N)[12] in illuminated $Q/CdS/MV^{2+}/CH_3CN$ suspensions depends upon both the initial concentration of Q and the total time of irradiation. More concentrated Q samples generally yield larger R_N values (runs a–c), although attempts to fit the results to standard rate expressions proved unsuccessful.[13] At constant Q concentration, the rate drops steadily with increasing time of irradiation (runs d–g).[14]

Side products were not evident in the gas chromatograms of photolyzed samples. In one long-term photolysis experiment, 26.5% of the Q initially present in a $Q/CdS/MV^{+2}/CH_3CN$ suspension isomerized to NBD while the total hydrocarbon (Q + NBD) concentration decreased by 1.8%. This respectable mass balance (>92%) indicates that the Q to NBD conversion can proceed with high chemical specificity (at least in this particular system).

Spectral studies, on the other hand, did reveal the accumulation of one or more absorbing product(s) during the course of photolysis. Figure 1 depicts the electronic absorption spectra of the solutions that result from irradiating Q/semiconductor/solvent suspensions for 3 h and then removing the semiconductor powders by centrifugation. A new, weak absorption tailing out to longer wavelengths appears in the spectra of the two samples that contain CdS, whereas a similar feature is absent in the spectrum of the solution derived from the TiO_2 suspension. A more complicated situation arises in systems containing both Q and MV^{2+} since, as illustrated in Figure 2, these two components form a ground-state complex (eq 5), whose absorption extends out beyond 400 nm.[15] At the con-

$$Q + MV^{2+} \rightleftarrows Q\text{–}MV^{2+} \qquad (5)$$

centrations most commonly employed in the photochemical experiments (Table III), 2% of the added MV^{2+} exists in complexed form. Most importantly, we find that direct photoexcitation of this complex does not result in the production of NBD (Table III, run f). Pronounced increases in absorbance in the visible region do occur, however, upon irradiating $Q/\text{semiconductor}/CH_3CN$ suspensions containing MV^{2+} (Figure 2).

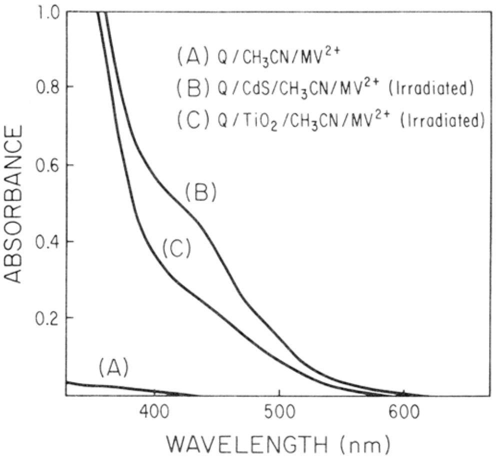

Figure 2. Electronic absorption spectra of (A) complex formed between Q and MV^{2+} in CH_3CN; (B) solution from an irradiated $Q/CdS/CH_3CN/MV^{2+}$ suspension; (C) solution from an irradiated $Q/TiO_2/CH_3CN/MV^{2+}$ suspension. Conditions: [Q] = 0.067 M; $[MV^{2+}]$ = 0.007 M; 20 mg of semiconductor powder in 3 mL of CH_3CN; 3-h irradiation time.

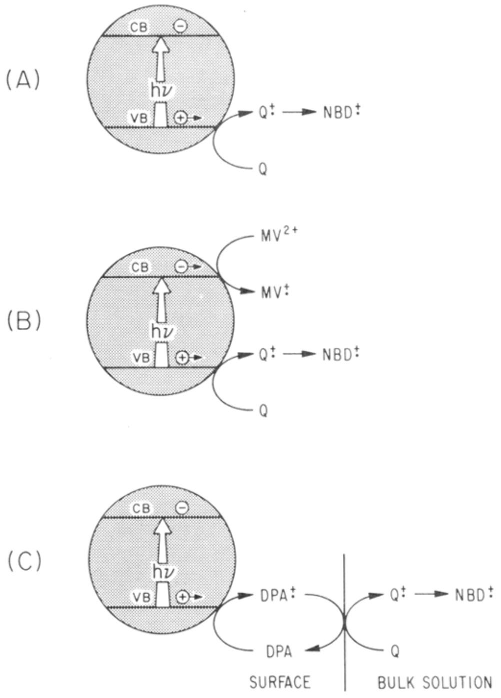

Figure 3. (A) Schematic representation of the radical cation mechanism for isomerization of Q to NBD at an illuminated semiconductor particle: VB = valence band, CB = conduction band. (B) Same as A except with added methylviologen dication. (C) Same as A except with added diphenylamine. The ultimate fate of $NBD^{\bullet+}$ is to accept an electron from the semiconductor, Q, or an impurity in the solvent.

Following irradiation of a $Q/CdS/MV^{2+}/CH_3CN$ suspension for 2.5 h, the semiconductor powder was removed and the remaining solution photolyzed for an additional 2.5 h. Compared to the yield of NBD during the initial exposure period (8.5%), the subsequent photolysis afforded a negligible amount (0.2%) of product.

Discussion

Excitation of an n-type semiconductor with a photon of energy greater than the band gap results in the creation

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[12] The amount of NBD formed during the indicated photolysis period is considered to be proportional to the rate of NBD production.

[13] (a) For example, the R_N vs. [Q] data in Table V (runs a–c) do not obey a simple first-order expression or the rate law derived for a unimolecular surface reaction.[13b] (b) Laidler, K. J *Chemical Kinetics*; McGraw-Hill: New York, 1965; Chapter 6.

[14] Since the Q concentration remains essentially constant (changes < 4%) during these photolyses, the steady drop in R_N cannot be attributed to consumption of the reactant.

[15] (a) Analysis of complex formation by the method of Cilento and Sanioto[15b] yields values of 0.3 M^{-1} for the formation constant and 1.1 × 10^2 M^{-1} cm^{-1} for the extinction coefficient of the complex at 350 nm. (b) Cilento, G.; Sanioto, D. L. *Z. Phys. Chem.* **1963**, *223*, 333.

of an electron-hole (e^-–h^+) pair.[9] Migration of the hole to the surface generates an oxidizing site whose redox potential is defined by the energy of the valence band. The information provided in Table I reveals that the photogenerated holes in each of the semiconductor powders examined in this study are capable of accepting an electron from Q. Consequently, these powders are potentially attractive as catalysts for the photoinduced conversion of Q to NBD via a pathway involving the corresponding cation radicals (Figure 3A).

Despite the favorable energetics noted above, the production of NBD occurs with low efficiency in simple Q/semiconductor systems exposed to band-gap irradiation (Table II). A number of factors could be responsible for this poor performance. One possibility is rapid recombination of e^-–h^+ pairs within the semiconductor particle. This process, which has been reported to occur within a few tenths of a nanosecond in colloidal CdS[16] and 1–30 ns in colloidal TiO_2,[17] depletes the supply of oxidizing sites available to Q at the semiconductor surface. Another unproductive process is reverse electron transfer from the semiconductor to $Q^{\bullet+}$. To accommodate the low product yields, this back-transfer must occur more rapidly than the rearrangement of $Q^{\bullet+}$ to $NBD^{\bullet+}$.[18] A final possibility is the rapid fouling of the semiconductor surface by a Q-derived polymeric material. Precedent for this type of surface deactivation, which effectively blocks the oxidation of additional Q molecules, has been reported in a study[5] of the electrochemical oxidation of Q at a Pt electrode. Each of these factors can now be considered in more detail.

Scavenging of conduction-band electrons by a reducible substrate should prolong the lifetime of the corresponding holes in the valence band by delaying e^-–h^+ recombination.[16] Oxygen ($E_{1/2}^{red} = -0.82$ V vs. SCE, in CH_3CN)[19], for example, has frequently been observed to enhance the photocatalytic effect of h^+ in n-type semiconductor powders by trapping e^- as superoxide ion (eq 6).[20] In all of

$$e^- + O_2 \rightarrow O_2^- \qquad (6)$$

the systems investigated here, however, oxygen exerted a negative influence on the NBD yield (see Tables II–IV). Rapid reverse electron transfer from O_2^- to $Q^{\bullet+}$ on the semiconductor surface would account for this behavior, although other possible causes cannot be excluded.[21] More encouraging results were obtained in systems containing the methylviologen dication ($E_{1/2}^{red} = -0.45$ V vs. SCE, in CH_3CN).[22] This species readily accepts an electron from the conduction bands of illuminated TiO_2 and CdS.[16] Moreover, adsorption of MV^{2+} onto the surface of CdS depletes the number of surface states which can act as recombination centers for e^- and h^+.[16] Both of these factors should tend to lengthen the lifetimes of photogenerated holes in the valence band and thereby enhance the probability of Q oxidation at the semiconductor surface (Figure 3B). In agreement with this expectation, we find that the addition of MV^{2+} to Q/semiconductor suspensions causes a marked improvement in the yield of NBD (compare runs c and f in Table II with runs a and c in Table III). Even under these relatively favorable circumstances, however, the quantum efficiency of NBD production has an estimated value of only a few percent.

The possibility that oxidation of Q on the semiconductor surface results in the formation of a polymeric coating that impedes further h^+–Q reaction was addressed in a series of experiments involving added diphenylamine. Since this amine ($E_{1/2}^{ox} = 0.83$ V vs. SCE)[23] is oxidized more easily than Q, we had hoped that it would function as a redox mediator[24] between holes at the surface and Q molecules in the bulk solution (Figure 3C). In addition to ameliorating the problem of surface inactivation, the strategy of generating $Q^{\bullet+}$ (and $NBD^{\bullet+}$) at a site remote from the semiconductor should facilitate the establishment of a redox chain (eq 2 and 3) and the attendant highly efficient conversion of Q to NBD. No compelling evidence for this type of catalytic behavior was obtained, however, as the addition of DPA enhances the NBD yield by a factor of only two. This disappointing result probably reflects the high reactivity of $DPA^{\bullet+}$ cation radical and its consumption via pathways not involving the oxidation of Q.[25]

Comparisons between product yields obtained with the different semiconductor powders used in this study must be treated with caution, since the surface areas of these materials are unknown. Nevertheless, it is interesting to note that the order in which the yields vary, CdS > TiO_2 ≥ ZnO (see Tables II and III), exhibits an inverse correlation with the reported band gaps of the semiconductors (Table I). Presumably, this relationship reflects the fact that a semiconductor with a smaller band gap can aborb a greater fraction of the incident light.

Solvent influences the production of NBD in irradiated Q/CdS (Table II) and Q/CdS/DPA/TBAP (Table IV) suspensions with the yields decreasing in the order CH_2Cl_2 > CH_3CN > THF. Interestingly, the same solvet dependence was reported by de Mayo et al.[26] in their detailed study of the photoinduced dimerization of phenyl vinyl ether in the presence of various semiconductor powders. While no correlation could be found between the yield of dimer and either the polarity or dielectric constant of the solvent, it was noted that solvents of moderate polarity generally afforded the best results. This behavior was attributed to processes occurring on the semiconductor surface, and we adopt a similar explanation for our findings. Thus, a solvent of high polarity can successfully compete for adsorption sites on the semiconductor, thereby lowering the effective surface concentration of Q. On the other hand, the inability of a low polarity solvent to dis-

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(16) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977.

(17) Rothenberger, G.; Moser, J.; Grätzel, M.; Serpone, N.; Sharma, D. K. *J. Am. Chem. Soc.* **1985**, *107*, 8054.

(18) For an example where reverse electron transfer competes successfully with rearrangement of a cation radical, see: Fox, M. A.; Chen, C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 6757.

(19) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970; p 505.

(20) (a) Okada, K.; Hisamitsu, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1980**, 941. (b) Barber, R. A.; de Mayo, P.; Okada, K. *Ibid.* **1982**, 1073. (c) Fox, M. A.; Chen. M.-J. *J. Am. Chem. Soc.* **1983**, *105*, 4497.

(21) (a) Al-Ekabi, H.; de Mayo, P. *J. Phys. Chem.***1985**, *89*, 5815. (b) Other possible causes are: (i) oxygen competes with the organic substrate for active sites on the semiconductor surface; (ii) electron donation to the photogenerated hole by chemisorbed oxygen competes with oxidation of the substrate. Al-Ekabi, H.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1231.

(22) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

(23) Dvorak, V.; Nemec, I.; Zyka, J. *Microchem. J.* **1967**, *12*, 99.

(24) While the oxidation of Q by $DPA^{\bullet+}$ is slightly endoergic and thus the equilibrium $Q + DPA^{\bullet+} \rightleftarrows Q^{\bullet+} + DPA$ lies to the left, the rapid, irreversible conversion of $Q^{\bullet+}$ to $NBD^{\bullet+}$ competes effectively with reverse electron transfer from $Q^{\bullet+}$ to DPA and thereby tends to drive the overall isomerization process toward completion. For a full discussion of redox mediators, see: Shono, T. *Electroorganic Chemistry as a New Tool in Organic Synthesis*; Springer-Verlag: Berlin, 1984; p 114.

(25) (a) Formation of *N,N′*-diphenylbenzidine via coupling of two $DPA^{\bullet+}$ cation radicals has been reported.[25b] Since this intermolecular process is blocked by substituents in the para position of the phenyl ring, a compound such as tri-*p*-tolylamine ($E_{1/2}^{ox} = 0.75$ V vs. SCE, in CH_3CN[25C]) may be a more promising candidate for a redox mediator. (b) Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087. (c) Reference 19 p 278.

(26) Draper, A. M.; Ilyas, M.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1984**, *106*, 6222.

place active species (e.g., cation radicals) or products from the surface also can result in low conversions.

At least two factors complicate the kinetics of NBD production in illuminated Q/CdS/MV^{2+}/CH_3CN suspensions (Table III). The first is competitive and unproductive absorption by a ground state Q–MV^{2+} complex (Figure 2) whose concentration tracks that of Q (eq 5). Consequently, as the initial Q concentration is increased, a correspondingly larger fraction of the incident radiation is absorbed by the complex. The second factor also involves competitive absorption but, in this case, by one of more photochemically derived species (Figure 2) whose concentration increases as a function of irradiation time. Although these species have not been identified,[27] they appear to play no role in the formation of NBD. Their main effect is to decrease the fraction of light absorbed by the semiconductor particles as photolysis proceeds and thereby cause a steady decline in the rate of NBD production (Table V).

Concluding Remarks

Our main findings can be summarized as follows. (1) Quadricyclene rearranges to its more stable isomer, norbornadiene, in the presence of irradiated n-type semiconductor powders. (2) The key step in the mechanism of this process involves the oxidation of Q to its structurally labile cation radical by photogenerated holes that migrate to the semiconductor surface (Figure 3A). (3) The percentage yield of NBD depends upon the semiconductor in an order, CdS > TiO_2 ≥ ZnO, which is inverse to that of the band gaps. (4) Addition of the methylviologen dication increases the product yield by capturing photoexcited electrons in the conduction band and thus prolonging the lifetime of the corresponding holes in the valence band (Figure 3B). (5) Addition of the hole relay, diphenylamine, causes a modest increase in the product yield (Figure 3C) but does not appear to facilitate the operation of a catalytic redox chain cycle (eq 2 and 3) in the bulk solution. (6) Solvent effects upon the NBD yield can be attributed to surface phenomena. (7) Although attempts to manipulate the kinetics of electron transfer led to some improvements in system performance (points 4 and 5), the quantum efficiency of NBD production is disappointingly low.

Finally, it should be noted that the present study provides one of the few reported examples of an organic valence isomerization process mediated by an illuminated semiconductor.[28,29]

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Registry No. TiO_2, 13463-67-7; ZnO, 1314-13-2; CdS, 1306-23-6; Ph_2NH, 122-39-4; quadricyclene, 278-06-8; norbornadiene, 121-46-0; methylviologen dication, 64890-16-0.

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[27] The spectral results are not consistent with a significant steady-state concentration of methylviologen cation radical, $MV^{\bullet+}$. See: Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

[28] For another, very recent, example, see: Al-Ekabi, H.; de Mayo, P. *J. Phys. Chem.* **1986**, *90*, 4075.

[29] (a) The editor kindly called to our attention a very recent paper by Draper and de Mayo[29b] concerning the Q to NBD isomerization in the presence of irradiated CdS and ZnO. The observations of these workers agree in essential detail with those reported here and lend additional support to the intermediacy of photogenerated cation radicals in the mechanism of isomerization. (b) Draper, A. M.; de Mayo, P. *Tetrahedron Lett.* **1986**, *27*, 6157.

Partial Loss of Deuterium Label in Wilkinson's Catalyst Promoted Decarbonylations of Deuterioaldehydes

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Decarbonylations of *trans*-2-phenylcyclopropanedeuteriocarboxaldehyde and cycloheptanedeuteriocarboxaldehyde with Wilkinson's catalyst give phenylcyclopropane and cycloheptane with partial loss of deuterium label. Loss of deuterium label is not a consequence of orthometalation of deuteriotris(triphenylphosphine)rhodium(I), a plausible reactive intermediate, for the loss is observed even when $RhCl(P(C_6D_5)_3)_3$ is used to effect the decarbonylation. Decarbonylations of *trans*-2-phenylcyclopropanecarboxaldehyde with Wilkinson's catalyst in benzene containing *O*-deuterioethanol afford d_0 and d_1 phenylcyclopropane and d_0 and d_1 aldehyde; neither hydrocarbon product nor recovered aldehyde is deuterium labeled when 1,1-dideuterioethanol is present in the decarbonylation reaction mixture. The hydroxyl hydrogen of ethanol associated with $RhCl(P(C_6H_5)_3)_3$ as normally synthesized, however, is not the hydrogen source: ethanol is not detected by ^1H NMR in solutions of the catalyst, loss of deuterium label occurs even when $RhCl(PPh_3)_3$ is prepared free of possible contamination by ethanol from $[ClRh(C_2H_4)_2]_2$, and it is seen as well with an alternative ethanol-free decarbonylation catalyst, $ClRh(dppp)_2$. The hydrogen source is water retained in commercial Wilkinson's catalyst. Decarbonylations of deuterioaldehyde in the presence of excess D_2O give d_1 product with high preservation of label.

The facile decarbonylation of aldehydes[2,3] effected by Wilkinson's catalyst, tris(triphenylphosphine)rhodium(I) chloride,[4] now enjoys an established position in organic synthesis, for it is widely applicable and highly stereose-

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