(31) Fluorescence by attached molecules is sufficiently intense to be easily seen by the human eye in this flash experiment and can be easily seen on a fluorometer.
(32) Gerischer, H. In "Physical Chemistry", Eyring, H. Henderson, D., Jost, W., Eds.; Academic Press: New York, 1970; Vol. IXA, Chapter 5, and references cited therein.
(33) Kohl, P. A.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 7531-7539.
(34) Finklea, H. O.; Murray, R. W. *J. Phys. Chem.* **1979**, *83*, 353-358.
(35) Pasch, N. F.; Webber, S. E. *Chem. Phys.* **1976**, *16*, 361-365.
(36) We are grateful to Dr. M. A. J. Rodgers of the Center for Fast Kinetics Research at the University of Texas at Austin for assistance in the picosecond spectroscopy measurements.
(37) Bachmann, W. E.; Klotzel, M. G. *J. Org. Chem.* **1938**, *3*, 55-61.
(38) Berg, A. *Acta Chem. Scand.* **1949**, *3*, 655-659.

Chemically Modified Electrodes in Dye-Sensitized Photogalvanic Cells

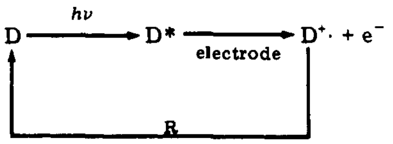
Marye Anne Fox,* Frédéric J. Nobs, and Tamara A. Voynick

Contribution from the Department of Chemistry, University of Texas at Austin, Austin, Texas 78712. *Received August 14, 1979*

Abstract: The photocurrents observed when arene-derivatized electrodes are used as anodes in an aqueous rhodamine B-hydroquinone photogalvanic cell are consistent with electron injection into the semiconductor from either an excited state or a reduced photoproduct. The attached molecules presumably function as energy or electron relays. The derivatized electrodes are more stable in long-term operation than is the parent tin oxide electrode.

Introduction

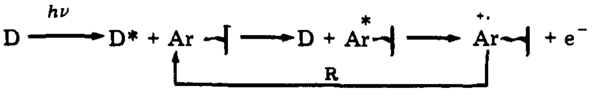
Current understanding[1-8] of the function of dye-sensitized semiconductor photoelectrochemical cells allows for two possible modes for the production of photocurrent. In the first, a dye molecule D is excited to a state from which electron transfer to the anode occurs readily (eq 1).[9] The oxidized dye is subsequently reduced by a reductant R to regenerate the dye. In the second, an excited dye molecule accepts an electron from the reducing agent. This reduced species injects an electron, giving rise to an oxidative photocurrent:[10,11]

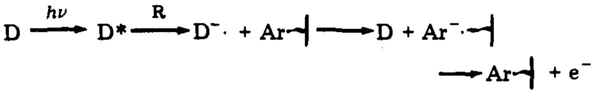

(1)

$$D \xrightarrow{h\nu} D^* \xrightarrow{R} D^-\cdot \xrightarrow[\text{electrode}]{} D + e^- \qquad (2)$$

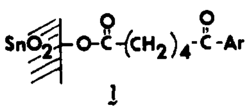
In either model, the efficiency of current production should depend significantly on several factors: (1) a long lifetime for the sensitizer excited state; (2) the chemical stability of the radical anion which functions as the electron source in the presence of supersensitizers; and/or (3) the disposition of the photo- or electroactive molecule at the semiconductor surface.

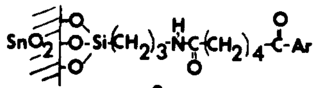
Our recent synthesis of several families of covalently modified tin oxide electrodes[12] makes available several modified surfaces in which the possibility of analogous surface-mediated energy or electron transfer can be tested. We hoped to examine whether a semiconductor electrode surface, modified by the near-monolayer attachment of an appropriate arene, could be converted to an excited state (eq 3) or a radical anion (eq 4) of the attached arene by energy or electron transfer from a dye sensitizer. The triplet energies and the reduction potentials of the dye and arene would be critical for operation of either mechanism.

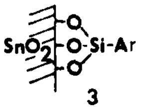

(3)


(4)

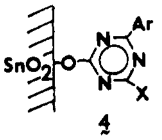
Since the production of photocurrent at a SnO_2 electrode in the presence of rhodamine B (RhB) with hydroquinone (HQ) as supersensitizer has been previously studied, we chose RhB as a sensitizer for our modified electrodes **1-4**.[12] The relevant triplet energies and the reduction potentials of these arenes are listed in Table I.

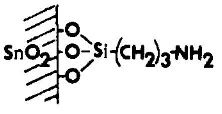

1


2


3

a: Ar = 1-naphthyl
b: Ar = 9-anthryl
c: Ar = 1-pyronyl
d: Ar = 1-hydroxyanthraquinone
e: Ar = 2-aminoanthraquinone


4


5

For efficient triplet energy transfer to an attached arene, the triplet of that arene must lie at lower energy than that of the sensitizing dye. Similarly, efficient electron transfer from a photoreduced radical anion of the dye can occur only if the reduction potential of the acceptor is less negative than that of the donor. Perusal of Table I demonstrates that anthracene and anthraquinone derivatives possess respectively a lower triplet energy and a less negative reduction potential than RhB. Neither naphthalene nor anthracene, both of which possess higher lying triplet states and less easily formed radical anions than RhB, should mediate photocurrent production by energy or electron transfer. Thus, triplet RhB may sensitize simple anthracene derivatives by energy transfer, while $RhB^-\cdot$ may transfer an electron exothermically to simple anthraquinone derivatives. If derivatization and attachment do not dramati-

0002-7863/80/1502-4036$01.00/0

Table I. Triplet Energies and Reduction Potentials of RhB and Some Arenes

	E_T, kcal/mol	ref	E_{pc}, eV vs. SCE	ref
RhB	43	13	−1.2	1
naphthalene	61	14	−2.5	18
anthracene	42	15	−2.0	18
pyrene	48	16	−2.1	19
anthraquinone	61	17	−0.9	20

cally alter the triplet energies or the reduction potential of molecules covalently bound to electrodes,[12] triplet sensitization by RhB of **3b** (but not of **3a**, **3c**, **4d**, or **4e**) should be conceivable. Similarly, exothermic electron transfer may proceed from $RhB^{-}\cdot$ to **4d** or **4e**.

Experimental Section

General Procedure for Photoelectrochemical Experiments. Photoelectrochemical measurements were conducted in a vacuum-tight three-compartment cell containing an optically flat Pyrex window. A Teflon support mounted about 1 mm from the inside wall of the irradiation window maintained a constant geometric spacing between the window and the semiconductor photoanode.[12] Ohmic contact to the semiconductor surface was made either by clamping an alligator clip or by attaching a copper wire with conductive silver paint reinforced by epoxy cement and silicone adhesive. The immersed, illuminated area of the semiconductor was 0.4 cm^2. A polished platinum wire, shielded from irradiation, was used as the counterelectrode. A +0.200-eV bias was applied with a PAR Model 173 potentiostat with a standard calomel electrode/agar bride reference electrode isolated from the solution by a fine porosity frit. Pretreatment and surface characterization of the semiconductor electrodes have been discussed elsewhere. The solutions were stirred with a magnetic stir bar during the long-term irradiations.

In the photoelectrochemical experiment, the semiconductor electrodes were irradiated with the focused light of an air-cooled 250-W high-pressure mercury arc on a optical bench. An IR filter (40 mm of water in a Pyrex cell) and a Corning 3-70 glass filter (λ >490 nm) were placed between the lamp and the semiconductor. A neutral density filter or a metal shutter could also be inserted for measurements of relative light intensity.

The pH of the aqueous rhodamine B solution containing 0.2 M Na_2SO_4 or KNO_3 as inert electrolyte was maintained with K_2HPO_4/NaOH or NaOAc/HOAc buffers. Stock solutions were employed for the series of experiments to ensure the absence of concentration or impurity effects. The solutions were deaerated by bubbling Ar, but the inert atmosphere had practically no influence on the photocurrents. The reported photocurrents were obtained as a difference between light and dark at +200 mV. For weak induced currents, the photocurrents were read from a galvanometer in series with the potentiostat. Cell temperature was maintained by efficient air cooling by a circulating fan or by immersion in a Pyrex-windowed constant-temperature bath. Significant data scatter was observed in such measurements, but the improvement of photocurrent generation at the modified electrodes is evident in Table II, which lists average values and variance obtained with four of each electrode type. The size of the photoinduced currents obtained if different sources of SnO_2-coated glass were employed varied by as much as 60%. The results reported here give comparisons for plates using the same SnO_2 source. When the derivatized electrodes were exposed to these conditions in the absence of dye, only extremely small (0.001-0.010 μA) photocurrents could be observed. The diminution of photocurrent after prolonged exposure to light is also listed in Table II.

Photoaction spectra were obtained as above except that the output of a 1000-W Hanovia xenon arc, having passed through a Bausch and Lomb double monochromator (slit width 10 mm), was used as the excitation source. The observed photocurrent was corrected for relative light intensity.

Results and Discussion

The photocurrents obtained at unmodified SnO_2 and at the chemically modified tin oxide electrodes are listed in Table II.

Table II. Rhodamine B Sensitized Photocurrents at Covalently Modified Electrodes[a]

electrode	initial, $\mu A/cm^2$	after 2 h irradiation, $\mu A/cm^2$	after washing[b] electrode, $\mu A/cm^2$
SnO_2	4.1 ± 0.6	1.5 ± 0.5	1.8 ± 0.5
1b	3.8 ± 0.4	2.0 ± 0.4	2.1 ± 0.4
2b	1.3 ± 0.2	1.0 ± 0.2	1.1 ± 0.2
3a	0.7 ± 0.3	0.6 ± 0.2	0.6 ± 0.2
3b	4.6 ± 0.4	3.9 ± 0.5	4.4 ± 0.4
3c	1.2 ± 0.4	0.7 ± 0.5	0.8 ± 0.5
4d	9.3 ± 0.5	8.5 ± 0.6	8.8 ± 0.5
4e	6.5 ± 0.7	6.0 ± 0.6	6.0 ± 0.6
5[c]	0.2 ± 0.1[c]	0.1 ± 0.2[c]	0.1 ± 0.2[c]
5	0.9 ± 0.2	0.7 ± 0.2	0.7 ± 0.2

[a] 1 × 10^{-4} M RhB, 3 × 10^{-3} M hydroquinone, 0.2 M KNO_3, distilled water, pH 4.5, λ >490 nm, polarization +0.200 eV vs SCE. The reported values represent (observed photocurrent − dark current) and are the average of photocurrents at three independently prepared electrodes. (Typical dark currents ranged from 0.05 to 0.15 $\mu A/cm^2$.) [b] Washing electrode: repeated (five times) rinse; 5 min soak-rinse in ethanol, dilute NaOH, and H_2O. [c] Initial solution silanation.

Effect of Chemical Modification. The effect of tin oxide coverage can be seen in comparing the initial currents observed (Table II) at unmodified SnO_2 with those obtained at **1b** (where ESCA analysis shows about 5–10% surface coverage),[12] at **3a** and **3c** (with 85% coverage) and at **5** (with nearly complete coverage). The similarity in the currents observed at SnO_2 and at **1b** can be attributed to the negligible insulating barrier established by the minor coverage at **1b**. When the surface coverage is more complete but where neither energy nor electron transfer relays can be established (**3a**, **3c**, and **5**) the current efficiency drops off. **5** prepared by gas-phase silanation shows a greater current density than **5** prepared by solution-phase silanation where significant polymerization has been observed. Thus, the formation of a thin insulating barrier reduces the observed current.

If the currents observed for gas-phase-prepared **5** are adopted as reference for the photocurrent behavior at the modified electrodes, then enhanced currents are obvious at **3b**, **4d**, and **4e**. Surface coverage by these arenes, then, improves the efficiency of photocurrent generation. The improvement in current density at **3b**, where energy-transfer sensitization is possible, is less significant than that observed at **4d** and **4e**, where an electron-transfer relay is conceivable.

In addition to these inferred modes of current enhancement, two other potential effects of covalent modification demand consideration: attached arene as supersensitizer or attached arene affecting dye aggregation. Photoenhancement from the first effect, in which attached anthraquinone acts as a reducing agent intimately involved in electron transfer from RhB*, is probably minor. At the positive bias applied during the photoelectrochemical measurements, anthraquinone will exist nearly completely in its oxidized form. Since its reduction potential lies at more negative potentials than that of *p*-benzoquinone,[12] electron transfer from solution-phase hydroquinone to generate reduced anthraquinone would be unlikely. In the absence of hydroquinone, very much smaller currents can be detected at SnO_2 or the modified electrodes. This is consistent with oxidative consumption of the sensitizing dye at the electrode surface. The second possibility is more difficult to exclude. The absorption spectrum of RhB adsorbed on **4d** is almost exactly the sum of **4d** alone + RhB adsorbed on SnO_2; i.e., no new absorption bands appear, no appreciable shifts of normal bonds are observed, and no dramatic difference in absorbance is detectable. If aggregation affected lifetimes more significantly than band position, however, aggregation may contribute, at least partially, to our enhanced photocurrents.

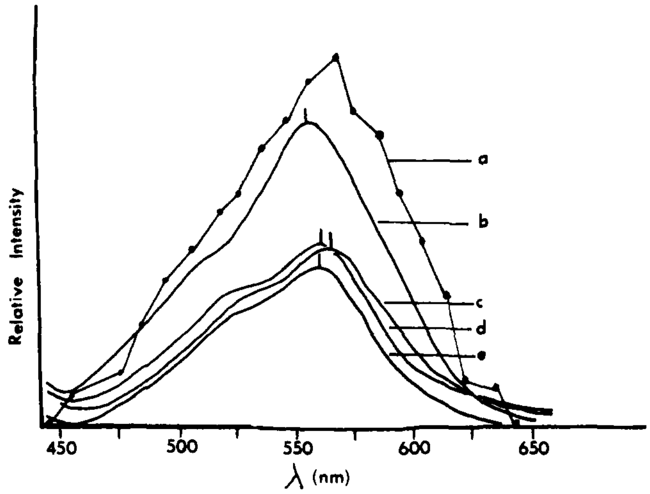


Figure 1. Absorption and action spectra for rhodamine B: modified electrodes. (a) Photoaction spectrum for **3b**–RhB–HO. (b) Absorption spectrum: 3×10^{-5} M RhB in H_2O. (c) Adsorption spectrum: RhB adsorbed onto SnO_2 (from 3×10^{3} M aqueous RhB). (d) Absorption spectrum: RhB adsorbed onto **15a** (from 3×10^{-3} M aqueous RhB). (e) Absorption spectrum: RhB adsorbed onto **3b** (from 3×10^{-3} M aqueous RhB).

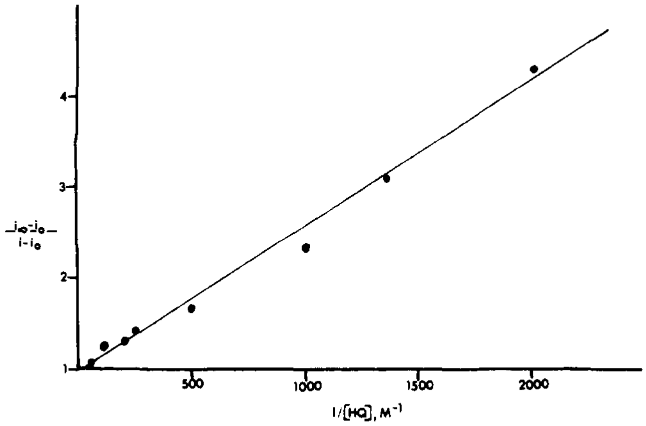


Figure 2. Stern–Volmer plot. Dependence of photocurrent on supersensitizer concentration at unmodified SnO_2.

However, if aggregation alone were responsible for our enhanced current, one might reasonably expect comparable enhancements at **3a**, **3b**, and **3c**. Since photocurrent at **3b** is more significant (Table II), we infer that some additional mode for current enhancement must be operative at **3b** and, by analogy, at **4d** and **4e**.

Photosensitization. That excitation of rhodamine B initiates the production of photocurrent can be established by comparing the photoaction spectrum at **3b** with the absorption spectrum of adsorbed RhB on SnO_2 or **3b** (Figure 1). Apparently adsorbed RhB is the principal light absorber, but the small shift in the photoaction spectrum toward shorter wavelengths is permissive of partial sensitization from solution-phase RhB. Although analogous action spectra are obtained at the other electrodes, electrodes **4d** and **4e** show slightly enhanced (+20%) absorption in the 450-500-nm region. This is consistent with partial sensitization by the arene itself, but the added adsorption is insufficient to explain the current enhancement observed at these electrodes.[21] Thus, even without solution-phase sensitizer, these modified electrodes could in principle serve to extend the range of photoresponse by the semiconductor and complement existing methodology[22-26] for attachment of dyes to semiconductor surfaces.

Lifetime of the Photoinjecting Transient(s). A simplified scheme in which either a dye excited state (eq 1 or 3) or radical anion (eq 2 or 4) injects electrons to a semiconductor in a photogalvanic cell leads to the following relationship between induced photocurrent and hydroquinone concentration:[26,27]

$$(i_\infty - i_0)/(i - i_0) = 1 + (k_q\tau[\mathrm{HQ}])^{-1}$$

where i_∞, i, and i_0 = photocurrents at infinite, intermediate, and zero supersensitizer concentrations, respectively, k_q = quenching constant for trapping by the supersensitizer, τ = the lifetime of the electroactive transient, and [HQ] = hydroquinone concentration. By observing the dependence of photocurrent on supersensitizer concentration, one can construct a Stern–Volmer plot ($(i_\infty - i_0)/(i - i_0)$ vs. 1/[HQ]) where the slope = $(k_q\tau)^{-1}$. Such a plot is linear for an unmodified SnO_2 surface (Figure 2). If diffusion-controlled capture of the electroactive species by hydroquinone is assumed ($k_q \sim 8 \times 10^9$ M^{-1} s^{-1}), a lifetime for the reactive transient of 80 ns is obtained, in reasonable agreement with that reported by Nasielski et al. for RhB-HQ at a bubbling gas SnO_2 electrode (70 ns).[8]

If the surface modification in our modified electrodes had no relay effect on electron transfer (i.e., if the electron injection proceeded exclusively by electron tunneling through the surface modification), such a plot should remain linear at our modified semiconductors. The slope, however, might be altered since both the rates of formation and decay of the active species and the rate of electron injection can be affected by the surface modification. The construction of such a plot for RhB/HQ at electrode **4d** (Figure 3) shows marked deviation from linearity. Such behavior is consistent with at least two species participating in the generation of photocurrent.

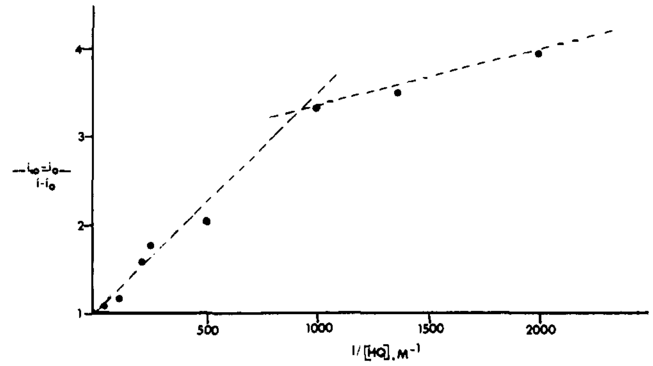


Figure 3. Stern–Volmer plot. Dependence of photocurrent on supersensitizer concentration at **4d**.

The crude lifetimes for these two photoactive species can be calculated from the Stern–Volmer plot (Figure 3) if diffusion-controlled interaction with hydroquinone is assumed. These (60 and 200 ns) differ both from the observed excited singlet or triplet lifetimes for RhB or for anthraquinone in solution and from the lifetime of the electroactive form of RhB at SnO_2. It seems probable, therefore, that the adsorption process does influence the lifetimes of excited states and/or radical anions. From the available data, we are unable to conclusively establish that the enhanced photocurrent arises from mediated energy transfer (eq 3) or electron transfer (eq 4). However, since an unmodified surface gives a linear Stern–Volmer plot, whatever the nature of the photoproduced transients, they must be derived from the covalently attached arene.

Quantum Efficiency. Conversion of these relative current densities to absolute quantum yields for electron photoinjection is difficult since light absorption at the surface of the electrode is not conveniently measurable. It has been shown that the low current densities observed at sensitized electrodes can be attributed to two factors: low absorbance of dye adsorbed as a monolayer at the electrode or within the diffusion distance of its excited-state lifetime (~3% of incident light at λ_{max}) and low quantum efficiency (<5%).[28,29] The reported quantum efficiency for RhB photooxidation through electron injection at ZnO is 0.01.[29] Since the energy level of RhB* lies well above the conduction band edge both in ZnO and SnO_2, comparable efficiency should be observed here. In any case, the net power conversion in these cells is significantly lower (10^{-3}–10^{-5}) than that observed in liquid photovoltaic cells.

Stability of the Modified Electrodes. Our modified electrodes, like SnO_2 itself, become less effective in producing dye-sensitized photocurrent after several hours of photogalvanic operation. The rate of power loss after covalent attachment is much lower than that for the unmodified surfaces, however, and this stabilization may represent the most significant improvement for photogalvanic cells which modified electrodes provide. While unmodified SnO_2 retains only about 1/3 of its original activity after 2 h, **4d** exhibits >90% of its initial efficiency after the same period. Analogous resistance to apparent chemical reaction with solution species has been reported at n-type silicon photogalvanic cells as well.[30] Whether covalent modification will improve photocurrent efficiency in anionic photogalvanic cells[31] is under current investigation in our group.

Soaking the partially degraded photoelectrodes in 0.1 M NaOH for 5 min restores only part of their initial reactivity in either the SnO_2 or modified electrodes. Apparently the strong adsorption of oxidation products cannot be reversed by this treatment. Longer cleaning periods (1 h, 0.1 M NaOH in an ultrasonic bath) invariably led to loss of the covalently attached molecules (as determined by cyclic voltammetry).

Conclusions

The above results demonstrate that covalent modification of electrode surfaces with molecules of appropriate reduction potentials and/or triplet energies can improve the efficiency of dye-sensitized semiconductor photogalvanic cells. The mechanism by which such cells function is consistent with Gerischer band theory, with electron ejection occurring from either a dye excited state or from the radical anion formed upon reducing the excited state with hydroquinone. The lifetimes of adsorbed species may differ significantly from those observed in solution. On a practical basis, covalent modification appears to greatly extend the operational lifetime of semiconductor electrodes in dye-sensitized photogalvanic operation. The possibility of manipulating photoredox properties of modified electrodes by covalent attachment of appropriate arenes is indeed viable.

Acknowledgment. Support of this research by the U.S. Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

References and Notes

(1) Gerischer, H.; Willig, F. *Fortschr. Chem. Forsch.* **1976**, *61*, 33–84, and references cited therein.
(2) Gerischer, H. *Top. Appl. Phys.* **1979**, *31*, 115–135.
(3) Memming, R. *Photochem. Photobiol.* **1972**, *16*, 325–333.
(4) Archer, M. D. *J. Appl. Electrochem.* **1975**, *5*, 17–38.
(5) Gerischer, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 263–274.
(6) Albery, W. J.; Archer, M. D. *Electrochim. Acta* **1976**, *21*, 1155–1163.
(7) Tributsch, H.; Calvin, M. *Photochem. Photobiol.* **1971**, *14*, 95–112.
(8) Nasielski, J.; Kirsch-De Mesmaeker, A.; Leempoel, P. *Electrochim. Acta* **1978**, *23*, 605–611. *Nouveau J. Chim.* **1978**, *2*, 497–502.
(9) Michel-Beyerle, E.; Gerischer, H.; Rebentrost, F.; Tributsch, H. *Electrochim. Acta* **1968**, *13*, 1509–1515.
(10) Melman, P.; O'Steen, D. S.; Prock, A.; Chance, R. R. *Chem. Phys.* **1977**, *22*, 71–77.
(11) Tributsch, H.; Gerischer, H. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 251–261.
(12) Fox, M. A.; Nobs, F. J.; Voynick, T. A., *J. Am. Chem. Soc.*, preceding paper in this issue.
(13) Chambers, R. W.; Kearns, D. R. *Photochem. Photobiol.* **1969**, *10*, 215–219.
(14) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 30.
(15) Gillispie, G. D.; Lim, E. C. *J. Chem. Phys.* **1976**, *65*, 2022–2023.
(16) Clar, E.; Zander, M. *Chem. Ber.* **1956**, *89*, 749–762.
(17) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537–4540.
(18) Freed, D. J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1971**, *93*, 2097–2103.
(20) Given, P. H.; Peover, M. E. *J. Chem. Soc.* **1960**, 385–393.
(21) Note that the relative photocurrent densities reported in Table II were obtained at wavelengths longer than 490 nm so that light absorption by attached arene should be minimal.
(22) Osa, T.; Fujihira, M. *Nature (London)* **1976**, *264*, 349–350.
(23) Fujihira, M.; Ohishi, N.; Osa, T. *Nature (London)* **1977**, *268*, 226–228.
(24) Fujihira, M.; Osa, T.; Hursh, D.; Kuwana, T. *J. Electroanal. Chem.* **1978**, *88*, 285–288.
(25) Hawn, D. D.; Armstrong, N. R. *J. Phys. Chem.* **1978**, *82*, 1288–1295.
(26) Shepard, V. R.; Armstrong, N. R. *J. Phys. Chem.* **1979**, *83*, 1268–1276.
(27) Kirsch-De Mesmaeker, A.; Kanicki, J.; Leempoel, P.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1978**, *87*, 849–856.
(28) Spitler, M.; Calvin, M. *J. Chem. Phys.* **1977**, *66*, 4294–4305.
(29) Spitler, M.; Calvin, M. *J. Chem. Phys.* **1977**, *67*, 5193–5200.
(30) Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1378–1385.
(31) Fox, M. A.; Kabir-ud-Din. *J. Phys. Chem.* **1979**, *83*, 1800–1801.