bianthrones fall in different kinetic zones, one in which the catalytic rate is governed by the forward electron-transfer reaction between quinone anion radicals and bianthrone and the other in which the catalytic rate is governed by the conformational change with electron transfer as a preequilibrium. The results provide additional evidence of the importance of conformational change in certain redox reactions and the efficacy of homogeneous redox catalysis in the study of such systems.

Acknowledgment. We thank Professor J. M. Savêant for tabulated theoretical data from ref 4e. This research was supported by the National Science Foundation (Grant CHE81-11421).

Registry No. 1, 434-85-5; **1** (radical anion), 70793-05-4; **2**, 24541-19-3; **2** (radical anion), 79982-16-4; duroquinone, 527-17-3; 2-chloro-9,10-anthraquinone, 131-09-9; 2-methyl-1,4-naphthoquinone, 58-27-5; 2,6-dimethoxy-1,4-benzoquinone, 530-55-2; 2,5-di-*tert*-butyl-1,4-benzoquinone, 2460-77-7; duroquinone radical anion, 3572-98-3; 2-chloro-9,10-anthroquinone radical anion, 58272-39-2; 2-methyl-1,4-naphthoquinone radical anion, 34524-96-4; 2,6-dimethoxy-1,4-benzoquinone radical anion, 26547-64-8; 2,5-di-*tert*-butyl-1,4-benzoquinone radical anion, 3599-40-4.

Intramolecular Electron Transfer and Dehalogenation of Nitroaromatic Anion Radicals[1]

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Abstract: A series of nitroaromatic compounds, containing Cl, Br, or tosyl groups at various positions, were synthesized and studied by pulse radiolysis in aqueous alcohol solutions. One-electron reduction of the compounds produces the anion radicals which then undergo an intramolecular electron transfer and eliminate X^- (Cl^-, Br^-, or TsO^-). The rates of X^- elimination vary over six orders of magnitude and are affected by the C–X bond dissociation energies, the size and nature of the group bridging the X with the π system, and the relative positions of these groups. Intramolecular electron transfer through space is also demonstrated.

Introduction

One-electron reduction of aromatic compounds, which contain a halogen and an electron-affinic substituent, has been shown to produce initially an anion radical and subsequently to dehalogenate,[5-14] e.g.

$$\mathrm{XCH_2ArS} \xrightarrow{e^-} \mathrm{XCH_2Ar\dot{S}^-} \rightarrow \mathrm{X^-} + \mathrm{\dot{C}H_2ArS} \qquad (1)$$

The dehalogenation has been viewed as an intramolecular electron transfer reaction, where the added electron is initially at the π system of the substituent (S = NO_2, CN, COR, etc.) and the aromatic ring and is later transferred to the C–X σ bond to form X^- and a carbon-centered radical. The lack of significant overlap between the π system and the σ bond causes the delay in the electron transfer. The transition state must have considerable overlap of the π system with the partially broken σ bond. The rates of these processes have been found to vary over many orders of magnitude (from $<1\ s^{-1}$ to $>10^7\ s^{-1}$) and are also dependent on the nature of X and S and their relative positions on the molecule, i.e., the C–X bond strength, the electron affinity of S, and the charge density distribution in the anion radical.[10-13]

In the present study we have synthesized a number of halogen-substituted nitroaromatic compounds in order to examine in greater detail the effect of the C–X bond strength on the rate of dehalogenation and the importance of direct electron transfer from S^- to a vincinal halogen through space rather than through the aromatic π system.

Method

One-electron reduction and dehalogenation were monitored by kinetic spectrophotometric pulse radiolysis. The substrate was dissolved in *i*-PrOH or *t*-BuOH and then diluted with water. The solution was deoxygenated by bubbling with pure nitrogen or N_2O and then irradiated with 10-ns 8-MeV electron pulses from an ARCO LP-7 linear accelerator. Each pulse produces 3–4 μM total radical concentration. One-electron reduction is achieved by reaction of the substrate with either e_{aq}^- or $(CH_3)_2\dot{C}OH$. The details of these reduction processes under the various experimental conditions employed have been discussed previously.[10-13] The computer-controlled pulse radiolysis apparatus, which allows determination of transient spectra at various times after the pulse and kinetic measurements of the spectral changes, has also been described earlier.[15] This technique allows us to follow the formation and decay of the nitro anion radical, i.e., to directly determine absolute rate constants for the two steps in reaction 1.

Results and Discussion

α-Substitution on *p*-Nitrobenzyl Halides. The rates of dehalogenation of the anion radicals of *p*-nitrobenzyl chloride and bromide were determined to be $4 \times 10^3\ s^{-1}$ and $1.7 \times 10^5\ s^{-1}$, respectively.[10] α-Substitution is expected to decrease the benzylic

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(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2323 from the Notre Dame Radiation Laboratory.

(2) St. Mary's College.

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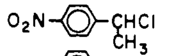
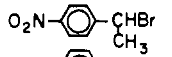
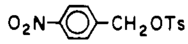
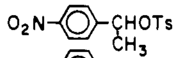
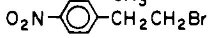
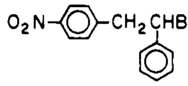
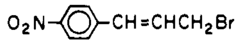
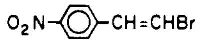
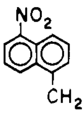
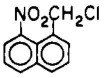
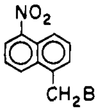
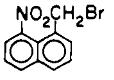
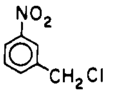
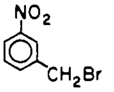
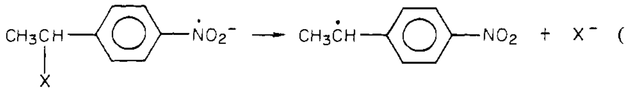
Table I. Rates of Dehalogenation of Nitroaromatic Anion Radicals and Absorption Maxima for the Radicals before and after Dehalogenation

compound	k, s^{-1}	λ_{max}, nm anion radical	 radical after dehalogenation
	4×10^3	310	350
	9.7×10^4	315	360
	1.7×10^5	320	350
	3.5×10^6	320	360
	2.9×10^4	322	360
	$\sim 1 \times 10^2$	305	
	8×10^4	300	360
	$\sim 2 \times 10^{-1}$	300	
	3×10^1	307	370
	1×10^5	345	395
	≤4	350	
	$\sim 1 \times 10^1$	390	
	$\sim 4 \times 10^2$	285 392	
	5.8×10^2	~290 395	
	2.4×10^3	290 395	375
	<5	290	
	6×10^1	290	

C–X bond dissociation energy[16] by stabilizing the resulting benzyl radical, and thus to increase the rate of dehalogenation. The results indeed show that methyl substitution increases the rates by a factor of ~20 for both the chloro and the bromo derivative (Table I).


(2)

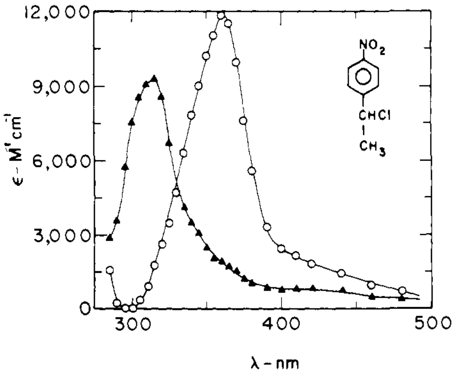


Figure 1. Transient absorption spectra observed in the pulse radiolysis of p-$O_2NC_6H_4CHClCH_3$. The solution contained 2.6×10^{-4} M substrate and 0.5 M t-BuOH at pH 7 and was deoxygenated by bubbling with N_2. The spectrum of the anion radical (▲) was observed 1 μs after the pulse and the spectrum of the benzyl radical (○) 30 μs later. Extinction coefficients were calculated assuming a yield of radicals equal to $G_{e_{aq}^-} = 2.8$ and using thiocyanate dosimetry.

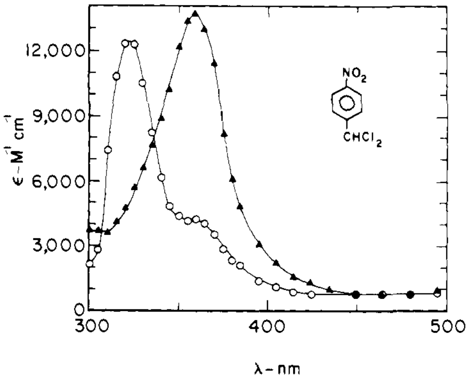


Figure 2. Transient absorption spectra observed with p-$O_2NC_6H_4CHCl_2$. Solution containing 9×10^{-4} M substrate and 3 M i-PrOH at pH 7 was saturated with N_2O. Spectra recorded 5 μs (○) and 100 μs (▲) after the pulse. Extinction coefficient were calculated assuming $G = 6$.

The transient spectra recorded with the chloro derivative are presented in Figure 1. In general they resemble those reported for p-nitrobenzyl chloride.[10] The anion radical p-$CH_3CHClC_6H_4\dot{N}O_2^-$ observed 1 μs after the pulse exhibits λ_{max} 315 nm with ϵ_{max} 9500 M^{-1} cm^{-1}. The $CH_3\dot{C}HC_6H_4NO_2$ radical observed 30 μs later exhibits λ_{max} 360 nm with ϵ_{max} 12 000 M^{-1} cm^{-1}. The rate constant for reaction 2 is determined by monitoring the decay of absorption at 300–320 nm and the buildup of absorption at 350–380 nm. In both cases $k = (9.7 \pm 1.0) \times 10^4$ s^{-1} is obtained and is independent of substrate concentration (8×10^{-5} M to 3×10^{-4} M) as expected for an intramolecular process.

Similar spectra were observed with p-$CH_3CHBrC_6H_4NO_2$. The rates of decay at 320 nm and buildup at 360 nm are much faster than those obtained with the chloro analogue and give $k_2 = 3.5 \times 10^6$ s^{-1}.

α-Substitution with Cl also increases the rate of dehalogenation. The spectra observed with p-$NO_2C_6H_4CHCl_2$ are given in Figure 2. The anion radical p-$Cl_2CHC_6H_4\dot{N}O_2^-$ exhibits λ_{max} 322 nm with ϵ_{max} 12 500 M^{-1} cm^{-1}. The product radical $Cl\dot{C}HC_6H_4NO_2$ has λ_{max} 360 nm with ϵ_{max} 13 700 M^{-1} cm^{-1}. The rate of dehalogenation as derived from both the decay at 310–325 nm and buildup at 350-365 nm is $(2.9 \pm 0.5) \times 10^4$ s^{-1}, i.e., faster than the corresponding rate for the monochloro derivative by a factor of 7. This enhancement factor by α-Cl substitution is smaller than the factor of 20 observed for enhancement of dechlorination by α-CH_3 substitution, probably indicating a slight difference in the C–Cl bond dissociation energy. For comparison we have also synthesized the analogous compound with α-phenyl substitution, i.e., p-$NO_2C_6H_4CHClC_6H_5$, but unfortunately its rapid hydrolysis in water prevented the pulse radiolysis measurement.

p-Nitrobenzyl Tosylate. In comparison with p-nitrobenzyl chloride, where $k = 4 \times 10^3$ s^{-1}, the p-toluenesulfonate derivative

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[16] Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516, 1537.

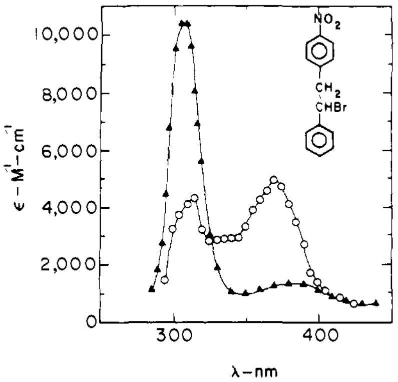

Figure 3. Transient absorption spectra observed with p-$O_2NC_6H_4CH_2CHBrC_6H_5$. Solution containing 2×10^{-4} M substrate and 3 M i-PrOH at pH 7 was bubbled with N_2O. Spectra were recorded 0.1 ms (▲) and 100 ms (○) after the pulse. Extinction coefficients were calculated assuming $G = 6$.

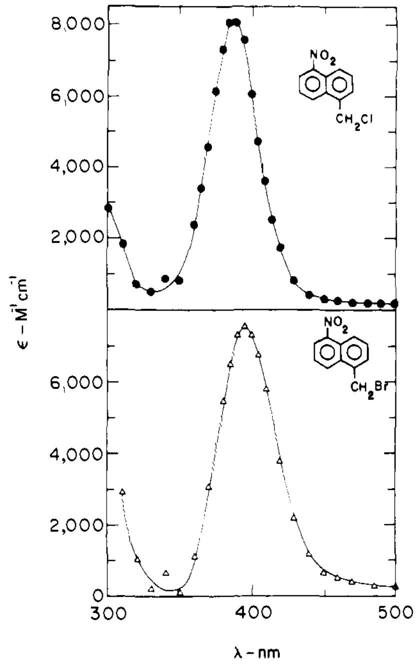

Figure 4. Transient absorption spectra observed with 1-halomethyl-5-nitronaphthalenes. Solutions containing 1×10^{-4} M substrate and 3 M i-PrOH at pH 7 were bubbled with N_2O. The spectra were recorded 50 μs after the pulse. Extinction coefficients were calculated assuming $G = 6$. A similar spectrum was obtained for the bromo derivative with N_2 bubbled aqueous t-BuOH solution 5 μs after the pulse (taking $G = 2.8$).

p-$NO_2C_6H_4CH_2OTs$ gives a longer-lived anion radical (λ_{max} 305 nm, ϵ_{max} 8000 M^{-1} cm^{-1}) which decays with a rate only $\sim 1 \times 10^2$ s^{-1}; i.e., reductive elimination of the tosylate is much slower than that of chloride (by a factor of $\sim$40). On the other hand, methyl substitution at the α-position increases the rate of tosylate elimination to 3×10^4 s^{-1} (Table I); i.e., it becomes similar to the rate of chloride release from the analogous anion radical (p-$NO_2C_6H_4CHClCH_3$)$^{-}\cdot$.

Substitution of α-H by CH_3 is thus found to increase the rate of Cl^- and Br^- release by a factor of $\sim$20 but the rate of TsO^- release by a factor of $\sim$800. The reason for this difference may lie in steric interaction. In both series of compounds, however, the rate of anion release is in the order TsO < Cl < Br. This order found for the anion radicals is different from that (Cl < Br < TsO) generally found in solvolytic displacement reactions of the parent compounds.[17] The reason for this difference is unclear.

Substitution on p-Nitrophenylethyl Bromide. Dehalogenation from a position β to the phenyl ring is much slower than that from the α; e.g., the anion radical of p-$NO_2C_6H_4CH_2CH_2Br$ debrominates with a rate[11] of only $\sim$0.2 s^{-1}, while that of p-$NO_2C_6H_4CH_2Br$ eliminates Br^- six orders of magnitude more rapidly,[10] $k = 1.7 \times 10^5$ s^{-1}. This large difference is caused partially by variations in the distance of the Br from the sites of high negative charge density and partially by differences in the C–Br bond strengths. In order to distinguish between the two effects, we have prepared a β-phenyl-substituted analogue, i.e., p-$NO_2C_6H_4CH_2CHBrC_6H_5$. In this case the distance of the Br from the negative charge is as in p-$NO_2C_6H_4CH_2CH_2Br$ but the C–Br bond strength (the stability of the resulting radical) is similar to that of p-$NO_2C_6H_4CH_2Br$. The spectra of the anion radical and of the resulting benzyl type radical from p-$NO_2C_6H_4CH_2CHBrC_6H_5$ are shown in Figure 3. The kinetics of decay at 300–320 nm and of buildup at 350–390 nm give $k = 30$ s^{-1} for the Br^- release. This value is four orders of magnitude lower than that observed for p-$NO_2C_6H_4CH_2Br$ and two orders of magnitude higher than that for p-$NO_2C_6H_4CH_2CH_2Br$. Therefore, we can assign the former difference ($\times 10^{-4}$) to the effect of the distance (an additional CH_2) and the latter difference ($\times 10^2$) to the effect of bond strength (i.e., radical stabilization of benzyl vs. alkyl).

p-Nitrophenylvinyl and -allyl Bromide. A double bond separating the Br from the p-nitrophenyl group should allow partial transmittance of the negative charge from the ring to the bromine. In fact, the anion radical of p-$NO_2C_6H_4CH{=}CHCH_2Br$ was found to undergo debromination with a rate of $\sim 1 \times 10^5$ s^{-1} (Table I), five orders of magnitude higher than that of p-$NO_2C_6H_4CH_2CH_2Br$. This rate is only slightly lower than that observed with p-$NO_2C_6H_4CH_2Br$. The small difference is probably the result of a slightly higher C–Br bond dissociation energy (57.2 kcal/mol for allyl bromide as compared with 54.7 kcal/mol for benzyl bromide)[16] or of a difference in negative charge distribution. (The charge on the carbon bound to the CH_2X group determines the effectiveness of this group in channeling the electron to the X.[10] The relative charge can be estimated from the ESR hyperfine constants: 3.9 G for p-H in $C_6H_5\dot{N}O_2^-$ vs. 2.45 G for the β-CH_2 in $CH_2{=}CHC_6H_4\dot{N}O_2^-$.[18])

The anion radical of p-$NO_2C_6H_4CH{=}CHBr$ decays very slowly; its rate of debromination is ≤ 4 s^{-1} (Table I). The situation here is comparable to that in p-bromonitrobenzene, where, despite the ready availability of the negative charge, debromination is very slow because of the high C–Br bond strength (76.4 kcal/mol for vinyl, 79.2 kcal/mol for phenyl, vs. 54.7 kcal/mol for benzyl)[16] or the lower stabilization of the vinyl or phenyl σ radicals as compared with benzyl.

Nitronaphthalenes. Four derivatives of 1-nitronaphthalene containing either CH_2Cl or CH_2Br at either position 5 or position 8 were synthesized in order to examine the importance of intramolecular electron transfer "through space" as compared with that through the aromatic π system. The results obtained with these compounds are shown in Figures 4 and 5 and in Table I. The anion radicals exhibit absorption maxima around 290 and 390 nm in all cases. Those derived from the 5-isomers (Figure 4) have ϵ_{max} $\sim$8000 M^{-1} cm^{-1}, similar to values obtained for other nitroaromatic anion radicals. On the other hand, those derived from the 8-isomers (Figure 5) exhibit considerably lower extinction coefficients, only $\sim$2500 M^{-1} cm^{-1}. This difference may be attributed to steric interaction between the substituents at positions 1 and 8 which prevents alignment of the $\dot{N}O_2^-$ group in the plane of the naphthalene rings and thus decreases conjugation between them. This effect, which was demonstrated previously[19] by ESR parameters of ortho-substituted nitrobenzene anion radicals, may cause the observed decrease in extinction coefficients.

The rates of dehalogenation were monitored by following the decay at 390 nm. Only in the case of 1-bromomethyl-8-nitro-

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(17) Streitwieser, A. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962.

(18) Berndt, A. In "Magnetic Properties of Free Radicals"; Fischer, H.; Hellwege, K. H., Ed.; Landolt-Börnstein New Series, Vol. 9, Part d1, Chapter 14, Springer-Verlag: Berlin, 1980.

(19) Neta, P.; Meisel, D. *J. Phys. Chem.* **1976**, *80*, 519, and reference therein.

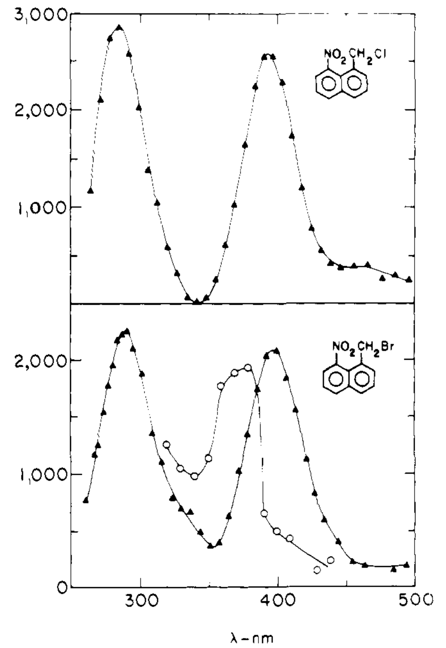

Figure 5. Transient absorption spectra observed with 1-halomethyl-8-nitronaphthalenes. Conditions as in Figure 4: (○) recorded 1.5 ms after the pulse. Similar spectra of the anion radicals were also obtained with *t*-BuOH instead of *i*-PrOH.

naphthalene was the dehalogenation sufficiently rapid to allow observation of the spectrum of the resultant benzyl type radical (Figure 5, bottom). The rates are summarized in Table I. Debromination is again found to be faster than dechlorination by about an order of magnitude, and in both sets dehalogenation at position 8 is faster than that at position 5.

The ESR hyperfine constants for the anion radical of 1-nitronaphthalene are 1.6 G for the proton at position 5 and 0.75 G for that at position 8, respectively higher and lower than the value of 1.1 G for the *m*-H in nitrobenzene anion radical.[18,20] The rate of dehalogenation of the CH_2X group at position 5 is found to be somewhat higher than that of the *m*-nitrobenzyl halides, as expected. On the other hand, dehalogenation from position 8 is an order of magnitude faster than that from position 5, despite the lower spin density. Since it has been established that the spin density on a particular carbon is a major factor is determining its effectiveness as a channel for the electron,[10] the present finding clearly indicates that dehalogenation from position 8 takes place predominantly by an electron transfer from the $\dot{N}O_2^-$ group directly to the halogen, not via the naphthalene π system.

Summary and Conclusion

Nitrobenzyl halides and tosylate undergo one-electron reduction to form the anion radicals, which then transfer an electron intramolecularly and release the halide or tosylate ion. The rates of anion release are in the order TsO < Cl < Br (different from the order in solvolysis). α-Substitution with CH_3 or Cl increases the rate by decreasing the C–X bond dissociation energy through stabilization of the resultant radical.

When the halogen is further removed from the ring by one additional carbon atom the rates of dehalogenation drop by several orders of magnitude. Most of this effect is ascribable to the distance, but part of it results from the difference in bond strength between aliphatic and benzylic positions. Halogen bound via an allyl group dehalogenates practically as rapidly as that in a benzylic position, while that via a vinyl group does not.

Rates of dehalogenation of various halomethylnitronaphthalenes demonstrate that when the two substituents are at positions 1 and 8 the intramolecular electron transfer takes place predominantly through space and not via the aromatic π system.

Experimental Section

Where possible, commercially available materials were used in this study. The syntheses of compounds not commercially available are described below. (*p*-Nitrophenyl)dichloromethane[21] and 1-bromo-2-(*p*-nitrophenyl)ethene[22] were synthesized by literature procedures. Other compounds were made as outlined below. In all cases the infrared, NMR, and mass (GC/MS) spectra were consistent with the assigned structures. No attempts were made to maximize product yields.

1-Halo-1-(*p*-nitrophenyl)ethane. 1-(*p*-nitrophenyl)ethanol (prepared by $NaBH_4$ reduction of *p*-nitroacetophenone),[23] upon treatment with refluxing thionyl chloride, was converted to the chloride, obtained as a yellow oil after vacuum distillation.[23] Likewise, the bromide was obtained upon treatment of the alcohol with PBr_3 at 60–70 °C for 6 h with subsequent vacuum distillation of the product (mp 36–37 °C).[24]

1-Tosyl-1-(*p*-nitrophenyl)ethane. 1-(*p*-nitrophenyl)ethanol (1.0 g) was treated with 2.3 g of *p*-toluenesulfonyl chloride (2 equiv) in 20 mL of pyridine at 0 °C. After the reaction mixture was allowed to stand in the cold for 48 h, it was poured into ice water. The product was removed by filtration and recrystallized from 2-propanol (mp 73–76 °C).

1-Phenyl-1-bromo-2-(*p*-nitrophenyl)ethane. Benzyltriphenylphosphonium bromide[25] (3.35 g, 0.01 mol) was dissolved in 65 mL of toluene. To this solution, stirred under a nitrogen atmosphere, was added 0.01 mol of butyllithium (5.12 mL of 1.55 M solution in hexane). The resulting red-orange mixture was refluxed for 1 h after which 1.2 g (0.01 mol) of *p*-nitrobenzaldehyde was added. After 2.5 h of reflux the mixture was cooled and filtered, and the yellow filtrate was washed with water. After drying over magnesium sulfate, the solvent was removed under vacuum to give 0.5 g of *p*-nitrostilbene (mp 158 °C). The stilbene was dissolved in a minimal amount of glacial acetic acid and HBr was bubbled through the solution for 2 h. After evaporation to dryness, the residue was recrystallized from alcohol to give 0.45 g of the bromide (mp 104 °C). Anal. Calcd: C, 54.9; H, 3.95; N, 4.57; Br, 26.1. Found: C, 55.29; H, 4.00; N, 4.53; Br, 26.77.

1-(*p*-Nitrophenyl)-3-bromopropene-1. Cinnamyl alcohol, formed by the borane–THF reduction of *trans*-cinnamic acid, was treated with phosphorus tribromide to give the corresponding allylic bromide.[26]

5-Nitro- and 8-Nitro-1-halomethylnaphthalene. A mixture of 5-nitro- and 8-nitronaphthoic acid was made by the method of Eckstrand.[27] Upon fractional crystallization from ethanol, a substantial quantity of the 5-nitro isomer could be obtained in pure form. The residue, however, consisted of a mixture of the two isomers which could not be satisfactorily separated by crystallization techniques.

It was discovered that the 5-nitro isomer could be reduced to the corresponding alcohol using borane/THF while the 8-nitroanaphthoic acid reacted very slowly under these conditions. Thus 20 mL (0.02 mol) of BH_3–THF (Aldrich) was added slowly to a THF solution of the 5-nitronaphthoic acid (2 g, 0.009 mol). The resulting mixture was kept under nitrogen overnight. Upon quenching the reaction in water, extracting with ether, and back extracting of the organic phase with $NaHCO_3$, the 5-nitro-1-hydroxymethylnaphthalene was obtained in good yield (0.9 g, 0.0045 mol). When the above procedure was performed on the mixture of 5-nitro and 8-nitro acids using excess reducing agent, the residual unreacted 8-nitronaphthoic acid was found in the $NaHCO_3$ extract and could be isolated by neutralization. In essence this provided an efficient method of purification for the 8-nitro-1-naphthoic acid.

The 8-nitronaphthoic acid, when treated with one equivalent of BH_3–THF for 36 h at room temperature, was partially reduced to the alcohol (mp 71–72 °C). It was convenient to simply recycle the recovered acid several times until sufficient alcohol was obtained for conversion to the halide.

Both 5-nitro and 8-nitro-1-hydroxymethylnaphthalene could be converted to the corresponding halides (chloride or bromide) by treatment with thionyl chloride or bromide in chloroform. Thus, to 0.2 g (0.001

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[20] Actually, it would be more precise to compare the hyperfine constants for 5-methyl- and 8-methyl-1-nitronaphthalene anion radicals, but these are not known. The 5-methyl group is expected to have little effect on the spin density. However, steric hindrance in the 8-methyl derivative twists the $\dot{N}O_2^-$ group out o the plane of the rings and thus lowers the spin densities on the ring carbons. Therefore, while the value of 1.6 G for position 5 is a reasonable estimate, the value of 0.75 G for position 8 is probably an overestimate.

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mol) of 5-nitro-1-hydroxymethylnaphthalene in 20 mL of dry chloroform was added 0.06 mL (0.001 mol) of $SOCl_2$ over a 30-min period with vigorous stirring. After stirring for an additional hour, the chloroform was removed by distillation. The residue, upon distillation under reduced pressure, gave the expected 5-nitro-1-chloromethylnaphthalene (mp 97 °C). The other halides were similarly prepared: 8-nitro-1-chloromethylnaphthalene,[28] 5-nitro-1-bromomethylnaphthalene (mp 98 °C), 8-nitro-1-bromomethylnaphthalene (mp 98 °C).

Registry No. *p*-$NO_2C_6H_4CH_2Cl$, 100-14-1; *p*-$NO_2C_6H_4CH(CH_3)Cl$, 19935-75-2; *p*-$NO_2C_6H_4CH_2Br$, 100-11-8; *p*-$NO_2C_6H_4CH(CH_3)Br$, 19935-81-0; *p*-$NO_2C_6H_4CHCl_2$, 619-78-3; *p*-$NO_2C_6H_4CH_2OTs$, 4450-68-4; *p*-$NO_2C_6H_4CH(CH_3)OTs$, 82925-36-8; *p*-$NO_2C_6H_4CH_2CH_2Br$, 5339-26-4; *p*-$NO_2C_6H_4CH_2CH(Ph)Br$, 83966-28-3; *p*-$NO_2C_6H_4CH{=}CHCH_2Br$, 75059-04-0; *p*-$NO_2C_6H_4CH{=}CHBr$, 13161-29-0; *m*-$NO_2C_6H_4CH_2Cl$, 619-23-8; *m*-$NO_2C_6H_4CH_2Br$, 3958-57-4; $(CH_3)_2\dot{C}OH$, 5131-95-3; *p*-$NO_2C_6H_4CH_2Cl$ radical anion, 34509-98-3; *p*-$NO_2C_6H_4CH(CH_3)Cl$ radical anion, 83966-31-8; *p*-$NO_2C_6H_4CH_2Br$ radical anion, 34512-14-6; *p*-$NO_2C_6H_4CH(CH_3)Br$ radical anion, 84024-96-4; *p*-$NO_2C_6H_4CHCl_2$ radical anion, 83966-32-9; *p*-$NO_2C_6H_4CH_2OTs$ radical anion, 83966-33-0; *p*-$NO_2C_6H_4CH(CH_3)OTs$ radical anion, 83966-34-1; *p*-$NO_2C_6H_4CH_2CH_2Br$ radical anion, 77145-96-1; *p*-$NO_2C_6H_4CH_2CH(Ph)Br$ radical anion, 83966-35-2; *p*-$NO_2C_6H_4CH{=}CHCH_2Br$ radical anion, 84024-97-5; *p*-$NO_2C_6H_4CH{=}CHBr$ radical anion, 84024-98-6; *m*-$NO_2C_6H_4CH_2Cl$ radical anion, 74261-77-1; *m*-$NO_2C_6H_4CH_2Br$ radical anion, 74261-79-3; *p*-$NO_2C_6H_4CH_2\cdot$, 19019-93-3; *p*-$NO_2C_6H_4\dot{C}H(CH_3)\cdot$, 83966-40-9; *p*-$NO_2C_6H_4CHCl\cdot$, 83966-41-0; *p*-$NO_2C_6H_4CH_2\dot{C}HPh$, 83966-42-1; *p*-$NO_2C_6H_4CH{=}CHCH_2\cdot$, 83966-43-2; 1-(chloromethyl)-5-nitronaphthalene, 6625-54-3; 1-(chloromethyl)-8-nitronaphthalene, 19190-51-3; 1-(bromomethyl)-5-nitronaphthalene, 83966-29-4; 1-(bromomethyl)-8-nitronaphthalene, 83966-30-7; 1-(chloromethyl)-5-nitronaphthalene radical anion, 83966-36-3; 1-(chloromethyl)-8-nitronaphthalene radical anion, 83966-37-4; 1-(bromomethyl)-5-nitronaphthalene radical anion, 83966-38-5; 1-(bromomethyl)-8-nitronaphthalene radical anion, 83966-39-6; 8-nitronaphthanen-1-ylmethyl radical, 83966-44-3.

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Heterojunction Silicon/Indium Tin Oxide Photoelectrodes: Development of Stable Systems in Aqueous Electrolytes and Their Applicability to Solar Energy Conversion and Storage

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Abstract: An approach to circumvent the problem of poor photoelectrochemical (PEC) stability of Si in aqueous electrolytes is the use of heterojunction photoelectrodes comprising the Si/SiO_x/indium tin oxide (ITO) structure. As in a Schottky barrier electrode system, the maximum photovoltage attainable with these electrodes is limited by the barrier height at the Si/ITO heterojunction. Both n- and p-Si substrates have been studied. In regenerative PEC systems designed for the conversion of solar energy to electricity, the efficacy of charge transfer at the ITO/electrolyte interface is shown to be a crucial factor. Of the redox electrolytes tested (S^{2-}/S_x^{2-}, I_3^-/I^-, $[Fe(CN)_6]^{3-/4-}$ and $Fe^{2+/3+}$ EDTA), the $[Fe(CN)_6]^{3-/4-}$ couple was by far the most efficient in terms of charge transfer across the ITO/electrolyte interface. Optical-to-electrical conversion efficiencies (η) of 1.57% and 5.7% (~AM 1 illumination) were attained for PEC cells based on n- and p-Si substrates, respectively. Detailed tests have revealed long-term stability in $[Fe(CN)_6]^{3-/4-}$ electrolytes once the ITO film thickness (≥50 Å) and solution pH (~12–14) were optimized. n-Si/ITO electrodes were used for the photooxidation of Cl^- from concentrated LiCl and NaCl electrolytes to illustrate the chemical inertness and stability of these electrodes. Catalytic modification of the ITO surface with RuO_2 was found to be necessary to sustain Cl_2 production. Values of η up to 2.7% were recorded with this PEC system at 100 mW/cm^2. Finally, the applicability of Si/ITO heterojunction electrodes for the photoassisted splitting of water was demonstrated. Preliminary experiments have revealed a 40% reduction in the threshold voltage required for water photolysis. Catalytic modification of the ITO surface was again a prerequisite for efficient performance of these electrodes. Pt and RuO_2 electrocatalysts were used for p- and n-Si substrates, respectively. Experiments with ITO thin-film electrodes on inert Ti substrates show that the observed behavior of Si/ITO electrodes may be rationalized on the basis of electrocatalytic activity of the ITO/electrolyte interface biased by the ITO/Si heterojunction. Kinetics at this interface are a key factor and in the extreme case (e.g., regenerative systems based on the I^-/I_3^- redox couple) may nullify any voltage gained by illumination at the Si/ITO heterojunction.

A key problem with photoelectrochemical (PEC) devices for conversion and storage of solar energy is electrode stability.[1] Recent work has focused, therefore, on the strategy of depositing an inert layer (e.g., metal, polymer) on the semiconductor surface to inhibit electrolyte attack.[2-4] We describe here the performance and characterization of an alternative photoelectrode structure that facilitates the use of narrow band-gap semiconductor substrates in aqueous media. The model substrate that we have chosen to illustrate our approach is Si—mainly because of the advanced degree of technology that exists on this material. Figure 1 is a schematic of the electrode structure that we have employed, which comprises n- or p-Si substrates on which are deposited successive layers of SiO_2 and indium tin oxide (ITO) by suitable means. As will be discussed below, we have also investigated catalytic

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