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Photoelectrocatalytic Reduction of 4-Chlorobiphenyl Using Anion Radicals and Visible Light

Shyam S. Shukla and James F. Rusling*

Department of Chemistry (U-60), University of Connecticut, Storrs, Connecticut 06268

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Excitation of electrochemically generated anion radicals of anthracene and 9,10-diphenylanthracene with visible light (>470 nm) gave greater than 10-fold increases in the rates of reductive dechlorination of 4-chlorobiphenyl. Peak shapes and potentials of cyclic voltammograms of the hydrocarbon catalysts alone with the light on indicated an increase in the rate of mass transport to the glassy carbon electrode caused by convective thermal gradients. However, less than 4% of the light-assisted increase in electrocatalytic rate constant could be explained by a localized increase in temperature of the reaction layer near the electrode. Good agreement of current-potential data from illuminated electrodes with a model for a two-electron electrocatalytic dark reaction allowed computation of a conditional rate constant by nonlinear regression analysis of the voltammetric data, even in the presence of an exponentially increasing background current. Kinetic results suggested the establishment of a fast, light-assisted reduction pathway, featuring either a photoexcited anion radical of the catalyst or an electron ejected from the excited anion radical acting as a powerful reducing agent.

Photoexcitation of molecules and ions can produce species with greater reducing and oxidizing power than those molecules and ions in their ground states.[1] For example, photoexcited quinones have been used both in solution[2] and attached to an electrode[3] to oxidize aliphatic alcohols. Hydroquinone produced in the reactions was cycled back to quinone at an anode held at a potential much smaller than required for direct oxidation of the alcohol. The alcohol cannot be oxidized by the ground-state quinone, and the additional energy required is supplied by ultraviolet light. Also, oxidative cyclodimerization of 1,1-diphenylethylene has been effected by photoexcitation (>400 nm) of electrochemically generated phenothiazine cation radical.[4] A wide variety of organometallic complexes have been photoexcited and regenerated electrochemically to catalyze redox reactions.[1b]

Radical ions of compounds with more than one aromatic ring have advantages as light harvesters in photoredox reactions, since they can be generated electrochemically, are often relatively stable in organic solvents, and generally can be excited by light in the visible region. Moreover, flash photolysis experiments have shown that visible light can cause ejection of electrons from polyaromatic hydrocarbon anion radicals and that these electrons, either solvated or as ion pairs, are powerful reducing agents.[1c,d] For example, electrons photoejected from pyrene radical anion were used for rapid production of biphenylide anion radical by capture of the ejected electron by biphenyl.[5] Visible-laser-light excitation of pyrene radical anions produced at mercury cathodes in *N*,*N*-dimethylformamide (DMF) has been used for electrocatalytic reduction of chlorobenzene.[6] No reduction of chlorobenzene was observed under the same conditions with the light off. A considerable increase in reduction current was observed by cyclic voltammetry, and a variety of possible mechanisms were suggested as its cause.

Reductive dechlorination of chlorobiphenyls (PCB's) in DMF yields biphenyl as the ultimate product. These dechlorinations are catalyzed at mercury and glassy carbon electrodes by reversible organic redox couples in reactions where electrochemically generated anion radicals transfer electrons to the PCB's.[7] Since the anion radicals previously used have absorption bands in the visible region,[1c] excitation of these ions with visible light was expected to enhance the observed reaction rate with chlorobiphenyls and open the possibility of using solar energy to aid in decomposing PCB's. In order to test the feasibility of light as a driving force in electrocatalytic dechlorination of chlorobiphenyls, and to gain insight into the factors governing the increased voltammetric currents in such photoelectrocatalytic processes, we have studied the reduction of 4-chlorobiphenyl with photoexcited polyaromatic hydrocarbon anion radicals generated at glassy carbon electrodes. Herein we report the results of our investigations and an interpretation of the electrochemical results in terms of what is presently known of photophysics and photochemistry of aromatic hydrocarbon anion radicals.

Experimental Section

Chemicals and electrode materials were obtained and prepared as in previous work.[7] *N*,*N*-Dimethylformamide (DMF) was purified and dried as previously described and contained less than 0.03 mM water.[7c] Tetrabutylammonium iodide (TBAI, 0.1 M) in DMF was used as the supporting electrolyte. Electrocatalyst concentrations were between 0.1 and 0.5 mM, and a 37-40-fold excess of substrate was used. All solutions were purged with purified nitrogen for at least 5 min before use.

Three-electrode cells with a Ag/AgI reference electrode, a Pt-wire counterelectrode, and a glassy carbon working electrode (0.08 cm^2) were used. The cylindrical cell had a flat quartz window in its wall to admit light. The glassy carbon electrode was constructed as described previously,[8a] but with its glass shaft bent at a 90° angle so that the planar electrode surface faced the quartz window. The light source was a 1000-W high-pressure xenon-arc lamp (Model LX/1000-1, Kratos Schoeffel Instruments) operated at 880 W (40 A and 22 V) unless noted otherwise. Light from the lamp was focused via the built-in lens onto the entire electrode surface, after first passing through two flat glass bottles (4 cm each) containing water to minimize infrared radiation and an optical glass filter to remove wavelengths below 470 nm. The maximum power of the lamp passing through the filters was estimated[8b] at about 0.4 W per 50-nm band-pass, uncorrected for scattering.

Cyclic voltammetry (CV) and controlled-potential electrolyses were done with a laboratory-constructed ramp generator and potentiostat of conventional design. Positive feedback compensation of the cell's ohmic drop was used for all experiments. Glassy carbon electrodes were polished before each scan with 0.05-μm alumina on billiard cloth on a high-speed polisher for 3 min, then ultrasonically cleaned in distilled water for 2 min, dried, and washed with DMF. CV's were run with a 30-s wait at the switching potential to allow the cathodic current to decay to nearly zero.

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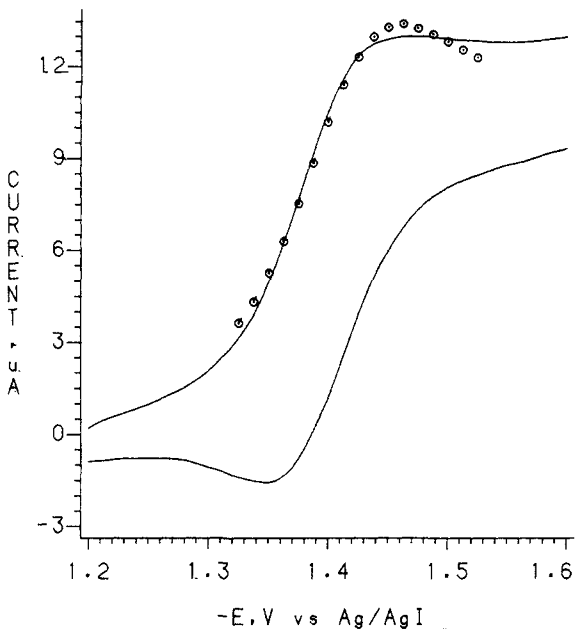

Figure 1. Cyclic voltammogram of 0.34 mM anthracene in TBAI/DMF at 0.04 V s^{-1} with the light on. Solid lines are experimental data. For comparison are shown circles computed from nonlinear regression analysis using reversible current functions.

Nicholson and Shain's reversible current function[9] was used for nonlinear regression analysis of cathodic voltammograms[10] of redox catalysts in the absence of substrate. Models for catalytic voltammograms similar to those previously described[7a-c] were used for nonlinear regression and computation of rate constants. For all regression analyses, absolute errors in the currents were assumed to be randomly distributed, and final values of parameters were independent of their initial estimates. Standard errors of regression parameters were computed by pointwise variance analysis.[7a]

Controlled-potential electrolysis (CPE) was done in a three-electrode cell similar to that described above, but with the electrode rotated at 1800 rpm. A 3-5-mL volume of solution was used. The glassy carbon working electrode had a straight shaft and was illuminated through the cell bottom. The working electrode potential was held at a value on the rising portion of the catalytic current-potential curve. Nitrogen was passed through the solution during the electrolysis. Electrolyzed solutions were analyzed by high-pressure-liquid chromatography using pure chlorobiphenyl and biphenyl as standards, by the method described previously.[7d]

Results

We first studied cyclic voltammograms of the catalyst redox couples in the absence of substrate, with the light on and off. Anthracene, 9,10-diphenylanthracene (9,10-DPA), pyrene, dimethyl terephthalate (DMT), and 4-chlorobiphenyl absorb light of wavelengths below 400 nm.[11] Anion radicals of pyrene, anthracene, 9,10-DPA, and DMT have absorbance maxima above 470 nm.[1c,d,6,12-16] Removal of wavelengths below 470 nm provided a source which excited the polyaromatic anion radicals but not their parents or the chlorinated aromatic compounds. There are two possible influences of illumination on the voltammograms: a change in the nature and concentration of redox-active species near the electrode, and localized heating and associated convection in the vicinity of the electrode. With the light off, the catalysts showed typical characteristics[17] of reversible redox couples, with ratios of anodic to cathodic peak currents near one, and differences

TABLE I: Voltammetric Results for Reversible Redox Couples in the Absence of Substrate[a]

compd	light	i_a/i_c	$E_{p/2,c} - E_{p/2,a}$, mV
anthracene	off	0.81	50
	on	0.88	47
9,10-DPA	off	0.88	54
	on	0.80	51
DMT	off	0.60	48
	on	0.89	47
pyrene	off	0.71	51
	on	0.73	41

[a] Scan rate 0.04 V s^{-1}, source power 880 W, except pyrene, 300 W. i_a and i_c are the anodic and cathodic peak currents; $E_{p/2,a}$ and $E_{p/2,c}$, the anodic and cathodic half-peak potentials.

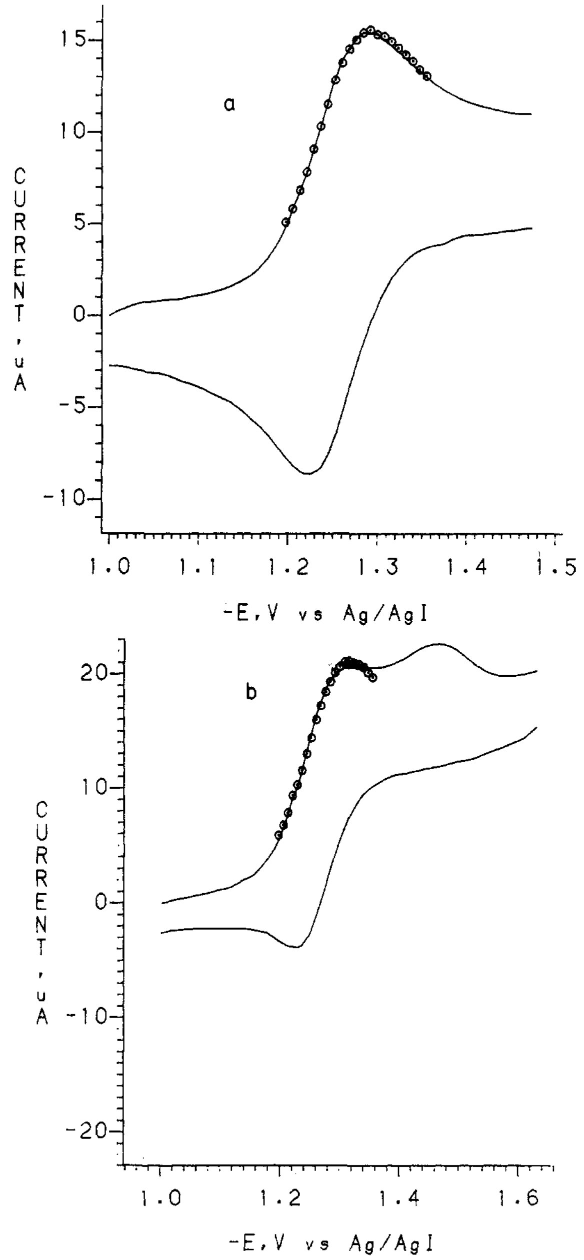

Figure 2. Cyclic voltammograms of 1.0 mM 9,10-DPA in TBAI/DMF at 0.04 V s^{-1} with (a) light off and (b) light on. Symbols as in Figure 1.

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of cathodic and anodic half-peak potentials close to the expected value of 54 mV at 25 °C. The second cathodic peak, corresponding to reduction of the anion radical to the dianion, was totally irreversible at both glassy carbon and mercury electrodes (scan rates to 1 V s^{-1}) for all compounds except DMT. The second peak for DMT had an anodic counterpart at glassy carbon electrodes with a peak potential 83 mV more positive than the cathodic dianion peak at 0.04 V s^{-1}, allowing estimation[18] of an apparent standard heterogeneous rate constant of 0.009 cm s^{-1}.

With the light on, cyclic voltammograms of the reversible redox couples became broader, approaching a sigmoid shape (Figure 1). Anodic to cathodic current ratios did not change appreciably, half-peak potential differences became slightly smaller (Table I), and peak currents increased by about 25% (Table II) when the light was on. Both 9,10-DPA (Figure 2) and pyrene showed small secondary peaks at potentials more negative than that of the primary cathodic peak. For pyrene, this peak was severely overlapped with the first reduction peak when the lamp was operated at 880 W, but the secondary peak shifted to more negative potentials as lamp power was decreased. Similar observations have been made for pyrene anion radical illuminated by laser light at mercury electrodes.[6b] No secondary peak under illumination was observed for anthracene or DMT.

Theoretical current functions for a reversible reduction gave better fits to the cathodic voltammograms (Figures 1 and 2) with the light off than with it on. Illumination makes the current–potential curve tend toward a sigmoid shape. In the fitting procedure used, n_{app} can be considered a peak shape parameter, becoming smaller as the peak gets broader.[10] A decrease in n_{app} is observed for each compound with the light on, providing a quantitative indication of peak broadening.

A current–potential curve controlled completely by convection, such as in rotating-disk voltammetry (RDV),[17] will have a sigmoid shape. When the equation describing reversible RDV[8a] was fit to the voltammetric data for the illuminated catalysts, standard deviations of the regressions were 20–30% larger than those in Table I. These results suggested that the convective effect, although significant, does not completely control mass transport.

No reduction peak for 4-chlorobiphenyl was observed at glassy carbon electrodes in the dark. In the presence of an excess of 4-chlorobiphenyl with the light off, cathodic peaks for anthracene and 9,10-DPA increase and become sigmoid shaped, and the anodic peak dissappears.[7] The reaction is a homogeneous redox electrocatalytic process[19] where the first step is reversible electron transfer to the catalyst (eq 1) and the rate-determining step (rds)

SCHEME I

$$A + e = A^{-}\cdot \qquad (1)$$

$$ArX + A^{-}\cdot \xrightarrow{k_1} ArX^{-}\cdot + A \qquad \text{rds} \qquad (2)$$

$$ArX^{-}\cdot \rightarrow Ar\cdot + X^{-} \qquad (3)$$

$$Ar\cdot + A^{-}\cdot \rightarrow A + Ar^{-} \qquad (4)$$

$$ArX^{-}\cdot + Ar\cdot \rightarrow ArX + Ar^{-} \qquad (5)$$

$$Ar^{-} + RH \rightarrow ArH + R^{-} \qquad (6)$$

$$Ar\cdot + SH \rightarrow ArH + S\cdot \qquad (7)$$

is homogeneous electron transfer from the anion radical to chlorobiphenyl, as shown in eq 2. Under the conditions used,[7] the process is pseudo-first order in catalyst and under pure kinetic control of the reaction in eq 2. The additional electron transfer and chemical steps (eq 3–7) lead to biphenyl as the product,[7] where RH is a proton donor and SH is the solvent or electrolyte. Scheme I is analogous to that found for the electrocatalytic reduction of halobenzenes and halopyridines.[20] With the light on in the

TABLE II: Results from Fitting Cathodic Peaks of Reversible Couples to Reversible Current Functions[a]

		$-E^{0\prime}$, mV vs. Ag/AgI			i_p, μA		
compd	light	measd	calcd	n_{app}	measd	calcd	rsd,[c] %
anthracene	off	1410	1417	0.93	11.73	11.91	1.49
9,10-DPA	off	1255	1257	0.87	12.95	13.13	1.23
DMT	off	1069	1070	1.02	17.32	17.34	0.65
pyrene[b]	off	1499	1504	0.89	25.31	26.09	3.7
anthracene	on	1408	1418	0.83	15.00	15.26	0.96
9,10-DPA	on	1269	1273	0.76	16.97	17.48	2.17
DMT	on	1082	1089	0.78	20.47	21.00	4.0
pyrene[b]	on	1511	1515	0.80	29.56	31.36	5.5

[a] Conditions same as in Table I. Standard errors in parameters estimated for rsd[c] = 1.5% were $E^0 \pm 5$ mV, $n_{app} \pm 0.06$, and $i_p \pm 1.5\%$. [b] Background current subtracted before regression analysis. [c] Standard deviation of the regression divided by $i_p \times 100\%$.

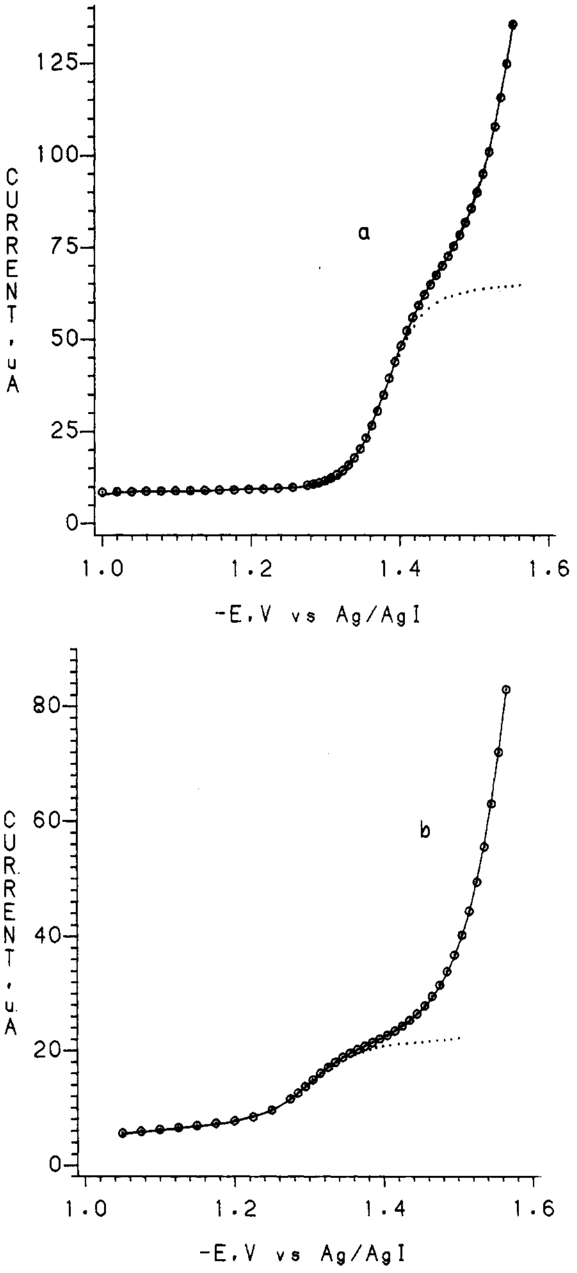

Figure 3. Cathodic voltammograms in TBAI/DMF for photoelectrocatalytic reduction of 4-chlorobiphenyl (40-fold excess) at 0.04 V s^{-1} with (a) 0.34 mM anthracene as catalyst and (b) 0.38 mM 9,10-DPA as catalyst. Solid lines are experimental data; circles computed from nonlinear regression analysis to eq 8; dots represent catalytic current deconvoluted by the regression analysis.

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TABLE III: Parameters and Their Standard Deviations for Nonlinear Regression Analysis to Eq 8 of Voltammograms for Light-Assisted Electrocatalytic Reductions

catalyst	N^a	log k^*_1, L mol^{-1} s^{-1}	F/RT, V^{-1}	$-E^{0\prime}$, mV vs. Ag/AgI	rsd, %
9,10-DPA	8^b	1.82 ± 0.62	35.7 ± 7.6	1283 ± 27	1.89
	9^c	1.78 ± 0.45	33.5 ± 6.7	1281 ± 21	1.89
anthracene	6^b	3.09 ± 0.59	41.4 ± 3.3	1374 ± 14	2.03
	6^c	3.09 ± 0.64	42.5 ± 4.3	1368 ± 22	2.25
9,10-DPA	6^d	$(1.99 \pm 0.20)^d$	44.5 ± 6.9	1320 ± 8	0.97
theory			38.92 (25 °C)	1315 (9,10-DPA) 1375 (anthracene)	

[a] Number of curves analyzed; scan rates 0.04–0.20 V s^{-1}. [b] Seven-parameter fits, 4-chlorobiphenyl in 40-fold excess over catalyst. [c] Five-parameter fits, same data as for *b*. [d] Dark reaction, seven-parameter fits, 40-fold excess of 4-bromobiphenyl. Standard errors of the regression parameters[7a] for analysis of a single current–potential curve estimated for rsd = 1.9% were log $k^*_1 \pm 0.06$, $F/RT \pm 3.6$ V^{-1}, $E^{0\prime} \pm 3$ mV.

chlorobiphenyl/catalyst systems, the limiting current of the sigmoid catalytic peak increases significantly over that in the dark. Nonlinear regression analysis of the catalytic voltammograms obtained with the light on gave good agreement (Figure 3) with the model based on Scheme I, and represented by

$$i = i_{1,c}/(1 + \theta) + i' \exp[S'(E' - E)] + m(E'' - E) + i'' \qquad (8)$$

Here, $i_{1,c}$ is the limiting catalytic current, $\theta = \exp[(F/RT)(E - E^0)]$, $S' = \alpha' F/RT$, where α' is the effective transfer coefficient for the exponential component of background current, E' is the potential at which background current i' flows, m is the slope of the linear portion of the background current, and i'' is the current at E'', with $E'' >> E^0$ and $E' < E^0$. The first term on the right-hand side of eq 8 represents the pure kinetic catalytic current, while the next two terms represent the exponential and linear portions of the background current. This model gave excellent agreement[7a] with data for electrocatalytic reduction of halogenated biphenyls in the dark at mercury electrodes, where the exponential term accounted for current from direct reduction of the substrate. In that work,[7a–c] the five parameters $i_{1,c}$, F/RT, E^0, S', and i' were used for nonlinear regressions, with current–potential data obtained by subtraction of the linearly extrapolated background from the catalytic current. This is equivalent to letting $m = i'' = 0$ in eq 8. From the data obtained with the light on, a "conditional" rate constant k^*_1 can be computed from $i_{1,c}$ (obtained by regression onto eq 8) from the expression[7a]

$$k^*_1 = (i_{1,c}/i_d)^2(7.778v/2c^*) \qquad (9)$$

where i_d is the peak current for the catalyst with the light on (without substrate), v is the scan rate, and c^* is the concentration of substrate.

In the present work, the background signal in the presence of substrate alone may include a contribution from surface reductions of glassy carbon[21] not likely to occur on mercury electrodes. To compensate for this possible problem, the additional parameters m and i'' were used to fit the same data to eq 8, but with currents measured from zero. Results of these five- and seven-parameter regression analyses for light-assisted reductions of 4-chlorobiphenyl with anthracene and 9,10-DPA showed little difference (Table III), suggesting that either method can be used to account for the background current in these systems. For either mode of computation, relative standard deviations of the regressions were on the order of 2% of $i_{1,c}$, agreement between calculated and measured currents was good (Figure 3), and rate constants and other parameters for the electrocatalytic reaction were almost identical. Mean computed values of F/RT and E^0 were within experimental error of each other for the five- and seven-parameter fits, and were close to their expected values (Table III). Comparison with results for the dark electrocatalytic reduction of bromobiphenyl with 9,10-DPA[7c] shows that the relative standard deviation is smaller for the dark reaction and that the precision in k_1 is better than that for the light-catalyzed reactions. Also, whereas a nearly random distribution of residuals vs. E was obtained in the absence of light, small systematic differences between computed and measured currents were found with the light on. The small decreases in precision of parameters and the small deviations from the model are probably caused by thermal and convective effects, and by irreproducibility in focussing the light on the electrode. Attempts to include terms in the model to account for convection yielded points of convergence that were not unique.

The general model[19] of which eq 8 is a special case predicts that the computed rate constant should be insensitive to changes in concentration of catalyst when a constant excess of substrate is maintained. This prediction holds within the standard deviation of the k^*_1 determinations for the light-catalyzed reductions as illustrated by values of log k^*_1 of 1.65, 1.86, and 1.84 obtained for 9,10-DPA and 4-chlorobiphenyl at 9,10-DPA concentrations of 0.19, 0.38, and 0.56 mM, respectively. Similar constancy of k^*_1 was found when anthracene was the catalyst at concentrations between 0.1 and 0.5 mM.

Light-assisted bulk electrolysis of chlorobiphenyl with 9,10-DPA as the catalyst was chosen to investigate product distribution, since the catalytic wave was at a potential far enough positive of the direct reduction to ensure that catalytic reduction was the predominant process. Analysis of electrolysis products by HPLC showed >99% yields of biphenyl, and no additional products were found.

As the subject of a previous study[6] at mercury electrodes, electrocatalytic reduction of chlorobenzene with photoexcited pyrene anion radicals and DMT dianions was briefly investigated for comparison with the chlorobiphenyl systems. Chlorobenzene could not be reduced directly at glassy carbon electrodes. No reaction between pyrene or DMT anions and chlorobenzene was observed in the dark. With the light on, electrocatalytic reduction waves were observed by cyclic voltammetry for the first cathodic peak of pyrene and the second cathodic peak of DMT. For the illuminated pyrene/chlorobenzene system at glassy carbon, five-parameter regression of the voltammetric data to eq 8 gave a relative standard deviation of 0.46% and a log k^*_1 of 4.1. For the DMT^{2-}/chlorobenzene system, the height of the dianion peak increased by about 70% with the light on, as opposed to a 18% increase in the first peak. These data allowed an estimate of k^*_1 of 10^2 L mol^{-1} s^{-1} for the reaction of DMT^{2-} with chlorobenzene. These results are qualitatively similar to those obtained at laser-illuminated mercury electrodes.[6]

Discussion

When no reducible substrate is present in solution, light from the xenon lamp of wavelengths above 470 nm has no observable influence on the redox chemistry of the catalyst couples investigated. Changes in one-electron cyclic voltammetric curve shapes when the light is on can be explained by localized heating caused by the lamp itself and by nonradiative decay from excited-state species. This results in thermal gradients in the solution and some convection, increasing the rate of mass transport of electroactive species to the electrode. Thus, voltammograms tend toward the sigmoid shapes observed in forced-convection experiments such as rotating-disk voltammetry.[17] The similarity of anodic to cathodic peak current ratios (Table I) suggests that approximately

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TABLE IV: Standard Potentials and Average Rate Constants for Light and Dark Electrocatalytic Reductions[a]

			$-E^{0\prime}$, V vs. SCE			
substrate	$-E^{0\prime}$, V vs. SCE	catalyst	$A/A^{-\cdot}$	$A/A^{-\cdot *}$	log k^*_1, L mol^{-1} s^{-1}	log k_1, L mol^{-1} s^{-1}
4-chlorobiphenyl	2.367	9,10-DPA	1.845	3.62	1.8	0.6
		anthracene	1.905	3.68	3.1	1.8
chlorobenzene	2.757	pyrene	2.039	4.52	4.1	<0.1
		DMT(2–)	(2.23)[b]		2	<0.1

[a] Standard potentials of substrates and $A/A^{-\cdot}$ from ref 7c. [b] For $A^{-\cdot}/A^{2-}$, estimated from the average potential of cathodic and anodic peaks on glassy carbon.

the same amount of anion radical is produced with the light on as with it off. The production of dianions of pyrene via eq 10 has

$$A^{-\cdot *} + A^{-\cdot} = A^{2-} + A \qquad (10)$$

been postulated as a possible cause of its photoelectrocatalytic activity,[6] where $A^{-\cdot *}$ is an unspecified photoexcited form of the anion radical, $A^{-\cdot}$. If equilibrium is in favor of the right-hand side of eq 10, the fate of A^{2-} could include back-donation of an electron to the electrode, which is thermodynamically favored at potentials of the first cathodic peak, and little change in the voltammetric response would result. If A^{2-} is formed at a rate less than diffusion controlled, it will be distributed in a reaction layer close to the electrode, and some of it would have to diffuse back to the electrode before back-donation could occur. However, fast chemical reactions destroy A^{2-} in our system, as evidenced by the absence of a peak for oxidation of A^{2-} in the dark for the hydrocarbon catalysts. Such reactions of A^{2-} in solution[22] should compete with back-donation of an electron, yielding a smaller anodic peak for $A^{-\cdot}$ with the light on. Within experimental error, no such decrease of the anodic peak current was observed (Table I) with the light on. Furthermore, disproportionation is not favored by the polar DMF (dielectric constant 36.7) and the bulky TBA^+ cations[1c,23–25] used in this work. For example, disproportionation equilibrium constants for the ground-state ion radicals are 2×10^{-14} for anthracene and 2×10^{-12} for 9,10-DPA.[22b] Although the nature of the excited species is not known, it should have a greater reducing power than $A^{-\cdot}$ which might drive the position of the equilibrium toward A^{2-}. Nevertheless, there is little experimental evidence to support a proposal that significant amounts of A^{2-} form in our systems.

With chlorobiphenyl or chlorobenzene present in the solution, the conditional photoelectrocatalytic rate constant k^*_1 was more than an order of magnitude greater than k_1 (light off) for each reaction studied (Table IV). One important contribution to k^*_1 could be local temperature effects in the reaction layer. Lund and Carlsson measured[6b] an increase in temperature of 12–13 °C at a mercury electrode in solutions of pyrene irradiated with a 7-W argon laser at 500 nm and found a cathodic peak current 2.8 times that in the dark. The power of our source at the glassy carbon electrode is less than 0.4 W per 50 nm band-pass (see Experimental Section), a total power input considerably less than that of the 7-W laser since UV and IR radiation is largely filtered. In agreement with this estimate, the maximum increase in cathodic current for any of our catalysts in the absence of substrate was only 30% (Table I). Assuming increases in current to be roughly proportional to local temperature near the electrode, and comparing our results to Lund's 180% increase in current for a 13 °C rise in temperature, we estimate a local temperature increase smaller than 3 °C. Estimating the free energy of activation of the dark reaction of anthracene anion radical with chlorobiphenyl from its rate constant at 25 °C by using the standard rate equation with a preexponential factor[26] of 3×10^{11} L mol^{-1} s^{-1} yields 55 kJ mol^{-1}. From this estimate, a local temperature of 71 °C would be required to explain the observed k^*_1. Similar conclusions followed from estimates on the other systems. Thus, considering a 5 °C rise in temperature as an upper limit, thermal effects can account for less than 4% of the difference between k^*_1 and k_1. (Note that convection and thermal effects on the current of the catalyst (i_d) are already accounted for in calculating k^*_1 by eq 9.)

Our conclusion about temperature effects is supported by the results for DMT. With that compound an 18% mass transport controlled increase in the first and second peaks was observed with the light on in the absence of substrate. With chlorobenzene present and the light on, the increase in the second peak for production of DMT^{2-} was three times that of the first. Thus, photoexcitation of DMT^{2-} results in a reduction of chlorobenzene with a k^*_1 of 10^2 L mol^{-1} s^{-1}, whereas no reaction at all is observed in the dark.

The principal conclusion to be drawn from the kinetic results obtained with anthracene and 9,10-DPA as catalysts is that a new reducing agent stronger than the anion radical is formed by excitation of a fraction of the catalyst anion radicals by visible light. This new reductant reacts with the substrate in a fast elementary step parallel to eq 2. The two most likely possibilities are (i) ejection of an electron from the excited anion radical (eq 11),

$$A^{-\cdot} + h\nu \rightarrow A^{-\cdot *} \rightarrow A + \text{e–(SH)} \qquad (11)$$

$$\text{e–(SH)} + ArX \rightarrow ArX^{-\cdot} \qquad (12)$$

$$A^{-\cdot *} + ArX \rightarrow A + ArX^{-\cdot} \qquad (13)$$

followed by reaction of the solvated or ion-paired electron with the chlorobiphenyl (eq 12)[27] or (ii) formation of a photoexcited anion radical with a long enough lifetime to react with the chlorobiphenyl (eq 13). Both alternative reduction paths (eq 12 and 13) are expected to be much faster[1a,c,d,5,27b] than the rate-determining step of the dark reaction (eq 2), and thus recycle additional amounts of the oxidized form of the catalyst (A) and increase the catalytic current over that from the dark reaction.

We discussed above the lack of evidence for dianion formation in the reversible redox reactions of the catalysts with the light on. Even if dianions do form without the substrate present, we do not expect generation of dianions of anthracene or 9,10-diphenylanthracene with chlorobiphenyl present in the photoelectrocatalytic systems. If a solvated or ion-paired electron is the reductant, it will be rapidly captured[5,27b] by the chlorobiphenyl, which is present in a large excess and will be more efficient at capturing an electron than the anion radical. Furthermore, 4-chlorobiphenyl[7c] has a standard potential ($E^{0\prime}$) in TBAI/DMF of −2.37 V vs. SCE, while the anion radicals of anthracene and 9,10-DPA have $E^{0\prime}$ values[22b] of −2.66 and −2.51 V vs. SCE, respectively, and reduction of chlorobiphenyl by a reductant is thermodynamically favored over that of the anion radicals.

The relative importance of the two pathways in eq 11–13 depends upon the lifetime of the reactive excited state and the efficiency of electron ejection, both of which are unknown for the

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[22] (a) Ultrahigh-purity DMF is required to observe any oxidation peak for anthracene or 9,10-DPA dianions on the cyclic voltammetric time scale. In DMF of the usual purity used for electrochemistry, the dianions are destroyed by very fast reactions.[22b] (b) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211–5217.

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[27] (a) Electrons in eq 11 and 12 are shown as solvated, but ion paired electrons could participate as well, although the capture of e–(SH) by the substrate is expected to be faster than from an ion–electron pair.[27b] TBA^+ ions are present in high concentration and a finite probability exists for formation of e–(TBA^+). (b) Fisher, M.; Ramme, G.; Claesson, S.; Swarc, M. *Proc. R. Soc. London, Ser. A* **1972**, *327*, 481–490.

anthracene and 9,10-DPA radical anions. For alternant hydrocarbon radical anions, the energy of the excited doublet (spin-allowed state) lies below that of the excited quartet state (spin forbidden).[14,28] Thus, population of the excited quartet by direct photoexcitation is probably small,[14] and, although the quartet should have a longer lifetime than the doublet state, it is not likely to be present in sufficient quantities to increase the observed reaction rate. Little is known about the lifetimes of excited doublets of alternant hydrocarbons, but lifetimes of doublet states of anthraquinone and dicyanoanthracene are on the order of 10–15 ns, and long enough to participate in reactions[29] with rates close to the diffusion-controlled limit.

It is possible that the photoelectrocatalytic reaction of pyrene with chlorobenzene is more complex than those described above. This is suggested by the secondary peak of unknown origin for pyrene alone, which overlaps with the primary peak under the conditions of present and previous[6b] experiments, and the much larger increase in observed rate constant with the light on. Although the product of this secondary reaction is unknown, it might well be another strong reducing agent. Furthermore, it is energetically possible for a pyrene dianion to participate in the photoelectrocatalytic reduction of chlorobenzene, since the standard potential of the latter is −2.76 V while that of $A^{-\cdot}/A^{2-}$ for pyrene is about −2.6 V vs. SCE.

The redox potential for the $A/A^{-\cdot *}$ couple, corresponding to the reaction

$$A + e + h\nu \rightarrow A^{-\cdot *} \tag{14}$$

can be approximated from[1b]

$$E^0(A/A^{-\cdot *}) = E^0(A/A^{-\cdot}) - E_{0-0} \tag{15}$$

where E_{0-0} is the one-electron potential corresponding to the zero spectroscopic energy of the excited state, estimated here from energies of the visible absorption bands[1c,12–16] of the catalyst anion radicals. The $E^0(A/A^{-\cdot *})$ values (Table IV) give a rough correlation with the difference between log k^*_1 and log k_1. The reducing strength of the photoexcited systems follows the apparent order pyrene >> anthracene > 9,10-DPA. However, this observation is difficult to interpret for a number of reasons. First, the measured k^*_1 has both a thermal and a light excited component. Second, standard potentials of the excited species are approximate and can be considered only as relative values, especially since the exact nature of the reactive species is in question. Thus, the actual free energies driving the light-catalyzed electron transfers and their relation to the energy required for diffusion-controlled rates in the polar DMF solvent is likewise uncertain.[30] One possibility is that the light-enhanced reactions are driven by free energies significantly more positive than that required for diffusion control. Alternatively, the true rates may be close to the diffusion limit, and variations in k^*_1 might be partly related to differences in the absorption coefficients of the catalyst anion radicals. For example, the large reducing power of the pyrene system could be partly attributed to a 6- to 8-fold greater absorption coefficient in the visible region compared to that of anthracene anion radical.[15] Finally, there is the previously discussed possibility that the pyrene system follows a more complex reaction pathway.

In summary, excitation of anion radicals of polycyclic aromatic hydrocarbons with visible light yields strong reducing agents which efficiently cleave chloride from chlorobiphenyl. Under the pseudo-first-order conditions used here, nonlinear regression analysis with a model similar to that for dark electrocatalytic dechlorination could be used to compute conditional rate constants from voltammograms obtained at illuminated electrodes. The reaction involves establishment of a rapid reduction pathway parallel to the dark reaction, but detailed elucidation of the mechanism awaits a more complete understanding of the photophysics of anion radicals of polycyclic aromatic hydrocarbons. Nevertheless, the use of visible light to increase the rate of halide cleavage suggests the possibility of using sunlight and electrocatalysis to destroy polyhalogenated biphenyls.

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Registry No. 9,10-DPA, 1499-10-1; DMT, 120-61-6; DMT^{2-}, 34471-11-9; $9,10\text{-}DPA^{-}$, 34505-64-1; C, 7440-44-0; 4-chlorobiphenyl, 2051-62-9; anthracene, 120-12-7; chlorobenzene, 108-90-7; pyrene, 129-00-0; anthracene anion radical, 34509-92-7; pyrene anion radical, 34512-41-9.

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