Photocatalytic Reduction of Nitroorganics over Illuminated Titanium Dioxide: Electron Transfer between Excited-State TiO₂ and Nitroaromatics

John L. Ferry*

Department of Chemistry and Biochemistry, University of Texas at Austin, A5300, Austin, Texas 78712

William H. Glaze

Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill, 7400, Chapel Hill, North Carolina 27599

Received: October 2, 1997; In Final Form: December 31, 1997

The present study investigates the steady-state photocatalytic reduction of methyl viologen and a suite of monosubstituted nitrobenzenes. Reduction was carried out in deoxygenated, illuminated aqueous slurries of titanium dioxide (Degussa P25) in the presence of a sacrificial electron donor, 2-propanol. Langmuir—Hinshelwood plots were obtained for the reduction of each compound and found to be linear, with an average correlation of 0.98 and with a standard deviation on the correlations of 0.02. The concentration independent rates for nitroaromatic reduction obtained from these plots were normalized against the rate of methyl viologen reduction, and the ratio was used to solve for the rate constant of nitroaromatic reduction, assuming a bimolecular model. The assumptions behind this procedure were tested by the use of the Marcus expression. Using the reorganization energy for the reaction as the fitting variable, it was possible to fit the measured rates to the predicted rates with a reorganization energy of 138 kJ/mol.

Introduction

Although photocatalysts such as TiO_2 offer a means for the potential use of low-energy photons for the transformation of redox-active substrates, practical application of these materials is hindered by the lack of knowledge concerning the fundamental chemistry of electron-transfer processes at the photo-excited TiO_2 surface, especially with regard to kinetic models for these processes.

Suspensions of photocatalyst particles large enough so that no quantization of energy levels is encountered are generally opaque, and the few studies that have addressed the problem of measuring the electron-transfer kinetics of large photocatalyst particles have been forced to resort to techniques such as flash photolysis with diffuse reflectance transient absorbance measurements that are only applicable to substrates with very high extinction coefficients ($\epsilon \approx 10\ 000\ M^{-1}\ cm^{-1}$) and fluorescence quenching measurements.^{1–3} Although this technique is capable of elucidating the *decay* kinetics of reactive intermediates formed during the flash ($\geq 10^{-8}$ s time scale), it is only recently that practitioners have become able to observe the primary interfacial electron-transfer reactions happening in the picosecond regime.⁴ However, these works are limited to monitoring compounds with absorption spectra that fall into a specific "window", the region of the UV-visible spectrum where the substrate absorbs and TiO_2 does not. With the exception of textile dyes, there are few compounds of environmental relevance that can be observed using these techniques.

Photocatalytic reduction of organic compounds is encouraged by the addition of electron donors to the system. It has been shown that methyl viologen (MV^{2+}) is easily reduced by conduction band electrons in the presence of the electron donor poly(vinyl alcohol) (PVA).^{5,6} In this system, the corresponding α -hydroxy carbon-centered radical that results from the one-

SCHEME 1: Photocatalytic One-Electron Reduction of Nitrobenzene and Concommitant Oxidation of 2-Propanol



electron oxidation of PVA by valence band holes goes on to reduce the particle surface directly^{7,8} rather than react with MV^{2+} .

There are a number of organic compounds of environmental significance that are easily reduced photocatalytically, such as nitroaromatics and nitroaliphatics,^{9,10} haloalkenes,^{11,12} and haloalkanes.^{13,14} The reduction of nitrobenzene and monosubstituted nitrobenzenes has been shown to progress through the series $RNO_2 - RNO - RNHOH - RNH_2$,⁹ presumably through an anion radical intermediate between each stable product. In this series of reactions, the first step, the loss of RNO₂, is attributed to the one-electron reduction of the substrate by conduction band electrons and is illustrated in Scheme 1.

In this study, the ratio of the second-order rate constant for the photocatalytic one-electron reduction of methyl viologen by TiO₂ sols over the rate constant obtained for MV^{2+} reduction by Degussa P25 was measured. This ratio, in conjunction with the known value for the rate of photocatalytic MV^{2+} reduction, was used to determine the second-order rate constants for the one-electron reduction of nitroaromatics by large particles of TiO₂. This procedure enables the modeling of photocatalytic rates based on electrochemical properties of the substrate that are independent of such considerations as reactor configuration or light intensity.

Experimental Section

Illumination. The reactor assembly has been previously described.⁹ Illumination was carried out at 350 nm, using a Xe arc lamp (Osram) in conjunction with a monochromator (Photon Technologies Incorporated) to provide the necessary photons, with a bandwidth of 3 nm. Lamp output did not change over the duration of the experiments, as determined by ferrioxalate actinometry.

Materials. TiO₂ powder (Degussa P25, 30 nm diameter particles in aggregate form) was a gift from Dr. Mike Prairie at Sandia National Laboratories. Methyl viologen dichloride (MV²⁺, 98%), nitrobenzene (NB, 99+%), 4-nitrotoluene (4NT, 99%), 3-nitrotoluene (3NT, 99%), 4-nitrophenol (4NP, 99+%), 3-nitrophenol (3NP, 99+%), 4-nitrobenzonitrile (4NBN, 97%), 3-nitrobenzonitrile (3NBN, 98%), 4-(α , α , α -trifluoromethyl)nitrobenzene (4TFNT, 98%), $3-(\alpha,\alpha,\alpha-\text{trifluoromethyl})$ nitrobenzene (3TFNT, 99%), 4-chloronitrobenzene (4NCB, 99%), 3-chloronitrobenzene (3NCB, 98%), 4-aminotoluene (4AT, 99%), 3-aminotoluene (3AT, 99%), 4-aminobenzonitrile (4ABN, 98%), 3-aminobenzonitrile (3ABN, 98%), nitrosobenzene (NSB, 98%), aniline (AN, 99%), tribromomethane (99%), tetranitromethane (TNM, 99%), and LiClO₃ (99.5%) were from Aldrich Chemical Co. and used as supplied. Methanol (GC² grade), methyl-tert-butyl ether (MTBE, GC² quality), and 2-propanol (IsOH, GC² quality) were from Burdick and Jackson and used as supplied. Water was NIST grade supplied by a custom Dracor filtration system, arranged in the order: activated carbon, anion-exchange resin, cation-exchange resin, activated carbon, and macroreticular resin polisher.

Nitroaromatics. A TiO₂ suspension (0.1 wt % Degussa P25, 0.001 M LiClO₄) was degassed under vacuum (5 μ m Hg) for 1 h. The stock suspension was stored in a glovebox under nitrogen and used for several experiments. All other stock solutions were treated similarly.

Before assembling the reactor, 50 mL of the suspension was added to the test tube body, followed by sufficient IsOH to make a 0.20 M solution. Nitroorganic substrates were added from concentrated 2-propanolic stock solutions. The reactor was then sealed and moved out of the glovebox, and the solution was allowed to equilibrate with stirring under N_2 for 30 min before illumination.

Samples (2.5 mL) were removed from the top sample port using an adjustable 4 mL syringe (Manostat). Samples were immediately placed in 40 mL EPA vials (I-Chem) precharged with 2.5 mL of chilled extraction solvent (MTBE with CHBr₃ internal standard) and stored sealed at 4 °C until extraction. Extraction was carried out on a vortex mixer for 40 s. The organic layer was analyzed for remaining substrate by GC-ECD analysis.

GC-ECD Conditions (Hewlett-Packard 5890). The injector port was set for splitless operation at 240 °C. The autoinjector volume was set at 3 μ L. The analytical column was a 30 m DB-5 with a 0.25 μ m film thickness. The temperature program was as follows: isothermal for 4 min at 80 °C, ramp at 12 °C/

min to 230 °C, ramp at 50 °C/min to 280 °C, and hold at 280 °C for 1 min. Carrier gas was He (99.999%, Sunox), and the flow rate at 80 °C was 1 mL/min.

Analytical Standards. Standards were dissolved in MeOH (GC² grade) and spiked into an aqueous matrix that is a duplicate of the experimental conditions (2.5 mL of 0.2 M alcohol, 0.1 wt % TiO₂, 0.001 M LiClO₄). Standards were extracted in an identical manner to samples. Standards were prepared on the day of the experiment, so they aged in a similar way to samples before analysis. The concentration range of all calibration curves covers at least two logs of substrate removal, with a minimum of seven points.

Methyl Viologen Analysis. Reactor preparation and charging for methyl viologen reduction experiments were exactly the same as for nitroaromatic reduction. However, rather than a stock solution of nitroaromatic, a stock solution of aqueous MV^{2+} was used to charge the reactor with substrate. Direct analysis of $MV^{+\bullet}$ proved difficult due to its sensitivity to oxygen, so an indirect method using TNM was developed instead. The reaction between TNM and one-electron reducing agents to produce the nitroform anion (NTF) is well known and is utilized here to measure indirectly the concentration of $MV^{+\bullet}$.¹⁵ NTF is quite stable in air, and its concentration may be measured by its UV absorbance at 350 nm ($\epsilon_{NTF} = 13500 \text{ L mol}^{-1} \text{ cm}^{-1}$).¹⁵ The reaction/sampling sequence is illustrated in the following expression:

$$e_{cb}^{-} + MV^{2+} \rightarrow MV^{+\bullet} \xrightarrow{\text{cannula}} MV^{+\bullet} + TNM \rightarrow \text{nitroform} \xrightarrow{\text{filter}, UV - \text{vis}} (1)$$

Rather than remove the reduced MV²⁺ solution with a syringe, the samples were taken by forcing the reaction mixture through a cannula into an oxygen-free 2 mL volumetric flask, precharged with 200 μ L of methanolic TNM (2.00 mM). When the appropriate volume was obtained, the cannula tip was removed from the suspension and sampling ceased. The receiving flask was stored until the experiment was completed, then the contents were filtered through a 0.2 μ m nylon filter into a quartz cuvette for analysis in a UV–vis spectrophotometer.

Results and Discussion

Langmuir—**Hinshelwood Plots.** All of the substrates used in this study exhibited saturation kinetics at higher concentrations; that is, they exhibited a change from apparent first-order at low substrate concentration to zero-order at high concentration. This has been observed many times before^{11,12,16,17} and does not necessarily reflect an actual change in mechanism; rather it is assumed to be a result of surface saturation. The most common procedure (in photocatalytic studies) for extracting a concentration-independent rate constant from such data is through the use of Langmuir—Hinshelwood kinetics.^{16,17} This approach begins with the assumption that the substrate is at equilibrium with respect to partitioning between the surface and the solution phase. The extent of surface coverage, θ , is given by the expression:

$$\theta = K[S]/(1 + K[S])$$
(2)

where K = rate of adsorption/rate of desorption and [S] is the substrate. The experimentally observed rate is proportional to the extent of surface coverage, θ , according to the following:

$$rate = - d[S]/dt = k_{LH}\theta$$
(3)

TABLE 1: Langmuir-Hinshelwood Plot Data Summary

substrate	concentration range (µM)	$k_{ m LH} imes 10^{-8}$ (s ⁻¹)	$K \times 10^{4}$ (M ⁻¹)	r^2
NB	55.7-2.0	1.45	17.6	0.99
4TFNT	23.3 - 2.3	5.10	5.86	0.99
4NBN	51.0-3.5	4.57	6.41	0.96
4CNB	23.8 - 4.7	2.90	2.61	0.99
4NP	52.0 - 4.6	1.16	31.1	0.99
4NT	67.7 - 4.0	1.75	7.39	0.93
3TFNT	22.6 - 1.9	1.60	8.18	0.99
3NBN	47.3-4.8	1.66	20.3	0.96
3CNB	26.7 - 1.0	1.65	10.8	0.98
3NP	55.9-9.7	1.62	9.02	0.99
3NT	51.0 - 4.8	2.30	1.46	0.98
MV^{2+}	150.0 - 10.7	0.61	5.27	0.97

Substituting in the value for θ from in eq 2 yields the following expression:

$$rate = k_{LH} K[S] / (1 + K[S])$$
(4)

The inverse of eqn 4 is

$$\frac{1}{\text{rate}} = \frac{1}{k_{\text{LH}}K[S]} + \frac{1}{k_{\text{LH}}}$$
(5)

Photocatalytic reduction of nitroorganics has been shown to generate products that may compete with starting material for conduction band electrons. To avoid this complication, initial rates $(\ln([S]/[S]_o) \ge -1)$, where $[S]_o$ is the initial [S]) were used. Since the reactions were pseudo-first-order in S, indicating that the concentration of adsorbed S was significantly higher than the concentration of conduction band electrons, the initial rate (in units of s⁻¹) was expressed as

$$rate_{o} = k_{obs} \ln([S]/[S]_{o})$$
(6)

so that under initial conditions the final expression was

$$\frac{1}{k_{\rm obs}} = \frac{1}{k_{\rm LH}K} + \frac{[S]_{\rm o}}{k_{\rm LH}}$$
(7)

where k_{LH} is the concentration-independent rate constant for the reaction. Thus, for each substrate a plot of $[S]_0^{-1}$ vs $(k_{obs}[S]_0)^{-1}$ should yield a straight line with a slope of $(k_{LH}K)^{-1}$ and a *y*-intercept of k_{LH}^{-1} , with k_{LH} in s⁻¹ and *K* in M⁻¹. When the data from the substrates reduced in this study were plotted in this manner, approximately linear correlations were found for every one (R^2 values > 0.93). The concentration-independent rate k_{LH} , the equilibrium constant *K*, the concentration range on the Langmuir–Hinshelwood plot from which they were determined, and the correlation coefficient for the individual plot are reported for each substrate in Table 1. All of the Langmuir–Hinshelwood plots for this study are available in the Supporting Information.

Solving for the Intrinsic Rate. Obtaining the value of k_{LH} for methyl viologen reduction allowed the normalizing of the rest of the data against the known intrinsic rate of methyl viologen reduction, which is $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1.6}$ In any photocatalytic system, the intrinsic rate of reaction (k_{in}) for any compound can be solved for by the following equation:

$$k_{\rm in} = k_{\rm LH}$$
 (reactor coefficient) (8)

The *reactor coefficient* is a descriptor that entails all the things that make a reactor configuration unique, such as the steadystate concentrations of holes and electrons, photon dose per



Figure 1. Hammett σ -effects on the rate of nitrobenzene reduction, *para*-substituted nitrobenzenes (\bullet), *meta*-substituted nitrobenzenes (\bullet); *k* determined from eq 10.

 TABLE 2: Bimolecular Rates for Nitrobenzene Reduction

 As Determined by Eq 10

substrate	$k_{ m in} (imes 10^7) \ { m M}^{-1} { m s}^{-1}$	substrate	$k_{\rm in} (imes 10^7) \ { m M}^{-1} { m s}^{-1}$
NB	2.9	3TFNT	3.2
4TFNT	7.5	3NBN	3.3
4NBN	9.0	3CNB	3.3
4CNB	5.7	3NP	3.2
4NP	2.3	3NT	4.5
4NT	3.5		

particle, etc. We assumed that the reactor coefficient was the same for all of the experiments in this study, since all of those terms were held constant from experiment to experiment, varying only the substrate. Taking the ratio of k_{LH} for MV²⁺ over that of k_{LH} for another electron acceptor (such as RNO₂) yielded the equality:

$$\frac{k_{\rm in}^{\rm MV^{2+}}}{k_{\rm in}^{\rm RNO_2}} = \frac{k_{\rm LH}^{\rm MV^{2+}}}{k_{\rm LH}^{\rm RNO_2}} \tag{9}$$

This was rearranged to solve for $k_{in}^{RNO_2}$:

$$k_{\rm in}^{\rm RNO_2} = k_{\rm in}^{\rm MV^{2+}} \left(\frac{k_{\rm LH}^{\rm RNO_2}}{k_{\rm LH}^{\rm MV^{2+}}} \right)$$
(10)

with the core assumption being that RNO₂ and MV²⁺ interact with the TiO₂ surface in approximately the same manner. Grätzel and co-workers found that although polymeric viologens adsorb strongly to TiO₂, monomeric viologens do not, instead relying on outer- or hard sphere interactions to react.⁶ Henglein and co-workers observed that TNM did not adsorb strongly either.^{18,19} Although TNM was not obviously a good analogue for nitroaromatics, it does possess nitro-groups in plenty, and if nitro-groups caused adsorption it should adsorb. After the nitro-group is eliminated as a sorber, it seemed unlikely that any of the substrates chosen for this study had functionalities that allowed for ready sorption onto TiO₂ in water, with the possible exception of nitrophenol, although the possibility of π -complexation could not be ruled out. The solution of eq 10 for all the compounds tested is provided in Table 2. Table 2 reveals that although the rate constant displays a marked dependence on the identity of the ring substituent in the para position, there was essentially no change in rate for substituents in the meta position, which is graphically demonstrated in a Hammett σ -plot for the reduction rates, Figure 1.²⁰ Such an effect is consistent with a reduction mechanism where electron addition occurred from the conduction band of the excited particle to the π^* -orbital of the nitroaromatic; the presence of

SCHEME 2: Homogeneous Model for Hard Sphere Electron Transfer



SCHEME 3: Photocatalytic Model for Hard Sphere Electron Transfer, Assuming Photoexcitation after the Adsorption Step



a node in the *meta* position for this orbital blocked the substituent from affecting the ring, rendering all *meta*-substituted nitrobenzenes essentially equal to nitrobenzene in their reactivity.²⁰

Predicting the Intrinsic Rate. The intrinsic rate constants predicted by eq 10 for the para-substituted substrates were analyzed by using a slightly modified form of the Marcus equation. Typically, the Marcus approach to electron transfer involves the interaction of two hard spheres, one of which is an electron donor and one of which is an electron acceptor, Scheme 2.²¹ Upon collision, which occurs with rate constant of k_d , the two form a precursor complex. Although they often drift apart again, with a rate constant of k_{-d} (and an equilibrium constant K equal to k_d/k_{-d}), occasionally it will happen that the energy levels of the donor orbital and acceptor orbital will fluctuate to within $\pm RT$ of each other, allowing an electron transfer to occur. In situations where this step is irreversible, it will have a rate constant of k_{el} . The new complex is referred to as a successor complex, and the reaction is complete when it breaks apart into two new species. This was applied to photocatalytic systems by assuming the precursor complex was equivalent to substrate adsorbed to the particle surface prior to illumination, Scheme 3, and that the association constant Kobtained from the Langmuir-Hinshelwood expression was equivalent to the association constant of the precursor complex for the solution-phase case. Random photoexcitation of the semiconductor surface was considered analogous to the random thermal excitation experienced by the precursor complex. The alternative model, that photoexcitation preceded the formation of the precursor complex, was tested by attempting to react photoreduced TiO₂ in the dark with nitrobenzene under otherwise identical reaction conditions; no reduction of nitrobenzene

or oxidation of the reduced particulates were observed on the time scale of our experiments. Nitrobenzene was chosen as a representative substrate due to its central location on the Hammett σ -plot (Figure 1). The similarity of photoreduced TiO₂ and trapped conduction band electrons has been demonstrated previously by comparisons of the transient absorption spectrum of conduction band electrons with the absorption spectrum of photoreduced sols, which are identical.²¹

According to Marcus theory, the free energy of activation for the overall reaction, ΔG^{\ddagger} , is given by the following expression:

$$\Delta G^{\ddagger} = \frac{Z_1 Z_2 e^2 f}{D r_{12}} + \frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 \tag{11}$$

In this equation, the first term is the electrostatic term and is used to solve for change in free energy upon forming the precursor complex when Z_1 and Z_2 possess a charge. Z_1 and Z_2 are the charges on the donor and acceptor, *e* is the electronic charge, f is a measure of ionic strength effects, D is the dielectric constant of the solvent, and r_{12} is the collision distance for the donor and acceptor.²² In this study, one of the species is assumed to be the surface, activated by a photon postcomplexation, and the other was the substrate. Since the experimental pH was 4.85, very close to the point of zero charge for TiO₂, and there was no charge on the organic molecule (Z_2 is zero), the electrostatic term was neglected. The second term is the parabolic term, representing the free energy change associated with ΔE for the reaction and the impact product formation has on the surrounding solvent environment. When product is formed, the energy requirement involved in adjusting the solvent and product to their new configuration is λ (reorganization energy), and ΔG° is the value of ΔG° adjusted for the ionic strength effects of the medium, according to the following expression:

$$\Delta G^{\circ'} = \Delta G^{\circ} + (Z_1 - Z_2 - 1) \frac{e^2 f}{D r_{12}}$$
(12)

In this work, with a very low ionic strength and no charge on the electron acceptor, the second term is neglected and ΔG° is considered equivalent to $\Delta G^{\circ'}$. So, in the present study, a careful analysis of the reaction conditions suggests that the complex Marcus equation (eq 11) simplifies to

$$\Delta G^{\dagger} = \frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ}}{\lambda} \right)^2 \tag{13}$$

 ΔG^{\ddagger} was related to $k_{\rm el}$ through the Eyring equation:

$$k_{\rm el} = \chi Z e^{-\Delta G^{\ddagger/RT}} \tag{14}$$

In this expression, χ is the transmission coefficient and Z the universal frequency factor, which has a value of $6 \times 10^{11} \text{s}^{-1.22}$ The transmission coefficient is assumed to have a value of 1, which is equivalent to saying that all activated complexes yield reaction. When eqs 13 and 14 were combined, an expression was obtained that related k_{el} with ΔG° for the process and λ (the reorganization energy)

$$k_{\rm el} = \chi Z e^{-(\lambda/4RT)(1+(\Delta G^{\circ}/\lambda))^2}$$
(15)

that could be expressed as

Photocatalytic Reduction of Nitroorganics

$$\log \frac{k_{\rm el}}{Z} = -\frac{\lambda}{4RT} \left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 \tag{16}$$

The steady-state approximation for the donor-acceptor complex was used to solve for $k_{in}^{RNO_2}$, the rate constant obtained by normalizing k_{LH} for the nitrated organics against k_{LH} for MV²⁺, assuming the irreversible case

$$k_{\rm in}^{\rm RNO_2} = \frac{k_{\rm d}}{1 + \frac{k_{\rm d}k_{\rm -d}}{k_{\rm el}k_{\rm d}}}$$
(17)

where k_d is the bimolecular rate constant for the formation of the precursor complex and k_{-d} the rate constant for the back reaction. In this instance, since the particle has essentially no diffusion coefficient, k_d was assumed to have a value of 10^8 M^{-1} s⁻¹. Since the reaction was a surface reaction, the ratio of k_d/k_{-d} is equal to *K*, the association constant describing adsorption at equilibrium, yielding the following expression

$$k_{\rm in}^{\rm RNO_2} = \frac{k_{\rm d}}{1 + \frac{k_{\rm d}}{k_{\rm el}K}} \tag{18}$$

In this work, the values for *K* were derived from the Langmuir– Hinshelwood plots and are listed in Table 1. When eq 13 was substituted for the ΔG^{\ddagger} expression in eq 14 and the resulting equation substituted into eq 18 for $k_{\rm el}$, the final expression was (neglecting the ionic terms)

$$k_{\rm in}^{\rm RNO_2} = \frac{k_{\rm d}}{1 + \frac{k_{\rm d}}{KZ}} e^{[(\lambda/4)(1 + (\Delta G^{\circ}/\lambda))^2]/RT}$$
(19)

The oxidation potential for conduction band electrons at pH 4.85 was determined to be -0.416 V vs NHE,⁶ based on the known pH dependence of the position of the conduction band edge for TiO₂:

$$E_{\rm b}^{\circ} = -0.13 - 0.059 \,(\text{pH})$$
 (20)

The one-electron reduction potentials for all the *para*-substituted nitrobenzenes in this study were available from the pulse radiolysis literature.^{23,24} These values were used to calculate $\Delta G^{\circ'}$ for the reduction of the *para*-substituted nitrobenzenes by conduction band electrons, according to the following:

$$\Delta G^{\circ} = -F(E^{\circ'}(\text{ArNO}_2) - E^{\circ'}(\text{TiO}_2))$$
(21)

The resulting ΔG° values are presented in Table 3.

Equation 19 was used to solve for the value of $k_{in}^{RNO_2}$ for each of the *para*-substituted nitrobenzenes, with the reorganization energy λ used as the fitting variable. The minimal residual for the data set was obtained with $\lambda = 138$ kJ/mol. The literature value for the reorganization energy for the one-electron reduction of nitrobenzene is in close agreement at 125 kJ/mol.²⁵ The measured and calculated rates were plotted together in Figure 2 for illustrative purposes. The reorganization energy is probably so large due to the significant change in the structure of the substrate since it progresses from a neutral, moderately polar molecule to a charged anion radical, although this explanation is speculative.

Conclusions

The observation that the rate of reduction differed between substrates indicated that the rate of substrate reduction, rather



Figure 2. Marcus plot for *para*-substituted nitrobenzenes. Points represent measured rates; the line is the predicted rate based on eq 19, with λ of 138 kJ/mol.

 TABLE 3: Reduction Potentials and Calculated Free

 Energy Change for the Reduction of *para*-Substituted

 Nitrobenzenes by Conduction Band Electrons

substituent	E ^o ' (V vs NHE)	$\Delta G^{o'}$ (kJ/mol)
Н	-0.485	3.44
CF_3	-0.383	-3.23
CN	-0.322	-9.12
Cl	-0.428	1.10
OH	-0.492	7.35
CH_3	-0.465	4.74

than the rate of donor oxidation, was the rate-determining step in the system. The reduction kinetics for all substrates were found to obey Langmuir-Hinshelwood kinetics, a result consistent with the hypothesis that the reaction occurred solely on the surface but not proof of it. The observation that the reduction rates of para-substituted nitrobenzenes were sensitive to the identity of the substituent and the rates of *meta*-substituted nitrobenzene reduction were not is consistent with the hypothesis that the rate-controlling step of nitroaromatic reduction was a one-electron transfer of the π^* -orbital of the substrate. The ratio of reduction rates between each para-substituted nitrobenzene and methyl viologen could be used to estimate the rate constant for the initial electron transfer step: this was confirmed by modeling the reaction using the aqueous one-electron reduction potentials for the substrate to calculate a theoretical rate constant and comparing it to the rates derived from the data.

Acknowledgment. We express gratitude to the National Renewable Energy Laboratory and the UNC Department of Environmental Sciences and Engineering for supporting this work and Mr. Randall Goodman and Mr. Clifford Burgess for their considerable assistance in designing and maintaining the reactor.

Supporting Information Available: Langmuir–Hinshelwood plots for MV²⁺, NB, 4CNB, 3CNB, 4NP, 3NP, 4NBN, 3NBN, 4NT, and 3NT (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Fox, M. A.; Dulay, M. T. J. Photochem. Photobiol., A: Chem. 1996, 98, 91.

(2) Draper, R. B.; Fox, M. A. Langmuir 1990, 6, 1396.

(3) Kamat, P. J. Phys. Chem. 1989, 93, 859.

(4) Colombo, D. P.; Bowman, R. M. J. Phys. Chem. 1996, 100, 18445.

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

- (6) Moser, J.; Grätzel, M. J. Am. Chem. Soc. 1983, 105, 6547.
- (7) Bard, A. J. J. Phys. Chem. 1982, 86, 172.
- (8) Bard, A. J. Science 1980, 207, 139.
- (9) Ferry, J. L.; Glaze, W. H. Langmuir, in press.
- (10) Mahdavi, F.; Bruton, T. C.; Li, Y. J. Org. Chem. 1993, 58, 744.

(11) Glaze, W. H.; Kenneke, J. F.; Ferry, J. L. Environ. Sci. Technol. 1993, 27, 177.

(12) Kenneke, J. F.; Ferry, J. L.; Glaze, W. H. The TiO₂-Mediated Photocatalytic Degradation of Chloroalkenes in Water. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: New York, 1993.

(13) Bahneman, M. J.; Moenig, J.; Chapman, R. J. Phys. Chem. 1987, 91, 3782.

(14) Choi, W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1995**, *27*, 1646.
(15) Asmus, K. D.; Henglein, A.; Ebert, M.; Keene, J. P. *Ber. Bunsen–Ges. Phys. Chem.* **1964**, *68*, 657–663.

(16) Pruden, A. L.; Ollis, D. F. J. Catal. 1983, 82, 404.

(17) Ollis, D. F.; Hsiao, C.; Budiman, L.; Lee, C. L. J. Catal. 1984, 88, 89.

(18) , Bahneman, D. W.; Henglein, A.; Spahnel, L. Faraday Discuss. Chem. Soc. 1984, 78, 151.

(19) Henglein, A. Pure Appl. Chem. 1984, 56, 1215.

- (20) Lowry, T. L.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987.
- (21) Howe, R. F.; Grätzel, M. J. Phys. Chem. 1985, 89, 4495–4499.
 (22) Eberson, L. Electron Transfer Reactions in Organic Chemistry; Spinger-Verlag: New York, 1987.
- (23) Meisel, D.; Neta, P. J. Am. Chem. Soc. 1975, 97, 5188.
- (24) Jagannadham, V.; Steenken, S. J. J. Am. Chem. Soc. 1984, 106, 6542.
- (25) Nelsen, S. F.; Blackstock, S. C.; Haller, K. J. Tetrahedron 1986, 42, 6101.