

HCl-Catalyzed Photoreduction of 4-Bromonitrobenzene as a Concomitant of Nucleophilic Aromatic Photosubstitution Involving Radical Intermediates

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Received August 17, 1987

Abstract: Irradiation of 4-bromonitrobenzene at 313 nm in aqueous solutions containing hydronium ion and relatively high concentrations of chloride ion cleanly but inefficiently forms 4-chloronitrobenzene. 2-Bromonitrobenzene is unreactive in photosubstitution by chloride ion. The photosubstitution is exclusively an acid-catalyzed reaction, and it is second order in chloride ion concentration. One chloride ion is consumed in the reaction, and the other functions as a catalyst. HCl-catalyzed photoreduction of 4-bromonitrobenzene is a major and highly efficient concomitant reaction when 2-propanol is present at 0.01 to 0.3 M; the major photoreduction products are 4-bromonitrosobenzene and 4-bromo-2-chloroaniline. The extrapolated limiting quantum yields (at infinite reagent concentration) are 0.5 for photosubstitution and 0.5-0.7 for photoreduction. The second-order dependence on chloride ion is found to require a quadratic expression rather than a simple squared term in the quantum yield expression. The parameters of the quadratic expression are found by a novel procedure based on iterative calculation to convergence to find the best fit to the plotted data points. The photosubstitution mechanism is proposed to involve electron transfer from chloride ion to the $^3n,\pi^*$ state forming an exciplex; acid catalysis is attributed to protonative capture of the exciplex.

Aromatic photosubstitution reactions continue to attract the attention of photochemists.¹⁻¹⁴ The recognition^{1,15,16} that differences of regiochemistry of nucleophilic photosubstitution manifest a deeper reality of mechanistic difference is an important milestone in this area. We have taken this view of these reactions for some time¹⁵ and have been looking for a reaction system involving catalysis as a probe with which to examine the hypothesis that para (to nitro) photosubstitution on a nitrobenzene derivative implies radical intermediates whereas meta photosubstitution implies heterolytic bond changes.

Our studies have concerned both the intramolecular photosubstitutions known as Smiles photorearrangements^{3,6} and intermolecular photosubstitutions.¹⁷ For the latter, we have recently focused on some hitherto unknown photosubstitutions, namely, displacements of bromide ion from 3- and 4-bromonitrobenzene by chloride ion, because they are simple reactions overall, are both acid catalyzed, and are susceptible to some mechanistic tests we

have developed in related systems.^{18,19} We have reported¹⁷ on the heterolytic acid-catalyzed photosubstitution of the meta compound, and we report here evidence for radical processes in acid-catalyzed displacement of bromide by chloride in 4-bromonitrobenzene.

Experimental Section

Chemicals were of the highest grades available commercially. 4-Bromo- and 4-chloronitrobenzene were recrystallized from ethanol-water and were homogeneous according to capillary GC analysis. Solvents (HPLC grade or spectrograde) were from Aldrich. Gas chromatography on a Hewlett-Packard 5880A instrument and gas chromatography-mass spectrometry on a Hewlett-Packard 5992A instrument were conducted with 25 m by 0.2 mm i.d. cross-linked methyl silicone capillary columns. Electronic spectra and absorbance measurements were obtained with a Beckman 5260 spectrophotometer. 4-Bromonitrosobenzene was synthesized by an adaptation of a literature procedure,²⁰ and 4-bromo-2-chloroaniline was from Aldrich.

Quantum yields were determined in 15 mm i.d. Pyrex test tubes or Ace Glass reaction tubes²¹ on 5.0-mL samples of 4-bromonitrobenzene (5.0×10^{-4} M) in acetonitrile-water (1:4, v:v) by use of a merry-go-round reactor illuminated by a Hanau TQ-150-W or a Hanovia 450-W mercury lamp. The lamp was cooled by tap water and surrounded by a filter solution of 0.002 M K_2CrO_4 in 5% aqueous K_2CO_3 to select 313-nm light. Samples absorbed >98% of the light entering the tubes, and conversions were always less than 20% and usually less than 10%. Quantitative monitoring of reaction progress was carried out by extracting the organic products into 0.5 or 1.0 mL of ether or cyclohexane containing tetradecane as an internal standard. Tests indicated that this method recovered the neutral organics quantitatively. Aniline derivative photoproducts were extracted after basifying the aqueous phase with NaOH. Early quantum yield measurements used an actinometer based on photohydrolysis of 3-nitroanisole,²² and later measurements, that agreed with the earlier ones, used the azoxybenzene actinometer.²³ Measured quantum yields were reproducible to $\pm 10\%$; reported data points on the plots each represent an average of 2-4 determinations. Dependence of quantum yield on chloride ion concentration was carried out at constant ionic strength by using mixtures of $LiBF_4$, $LiCl$, and 0.24 M HCl so that total electrolyte was 3.0 M. Dependence of quantum yield on hydrogen ion concentration was carried out with solutions containing HCl and $LiCl$

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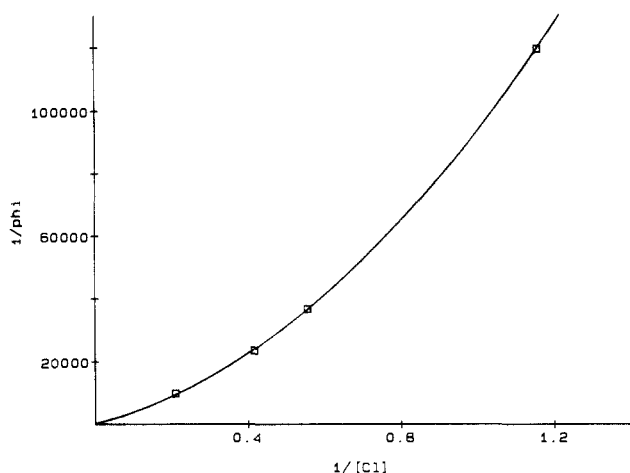


Figure 1. Dependence of 4-ClC₆H₄NO₂ quantum yield on concentration of chloride ion with no acid added.

so that total electrolyte concentration was 3.6 M.

Graphical data analysis was carried out with a DEC VAX 8600 computer and the RS/1 statistics software (BBN Software Products Corp.).

Results

Irradiation of 4-bromonitrobenzene (5.0×10^{-4} M) in acetic acid-water (1:4, v:v) containing LiCl (8.4 M) or a mixture of LiCl (7.8 M) and HCl (0.6 M) showed 4-chloronitrobenzene as the only volatile product (55–85%) at 20% conversion. This was verified by GC/MS analysis of an authentic sample. At 50–70% conversion, two unidentified products ($\leq 5\%$) from the HCl-containing solution could be observed. The three chloronitrobenzenes, the three bromonitrobenzenes, and nitrobenzene itself were all resolvable under our GC conditions, and all but the para isomers were shown to be absent at high conversions.

Irradiation of 2-bromonitrobenzene (2.5×10^{-3} M) in acetic acid-water (1:4, v:v) containing LiCl (7.8 M) and HCl (1.2 M) for 20 times the exposure needed to half-convert 4-bromonitrobenzene caused only minor loss ($\leq 10\%$) of starting material. The main products detected by GC/MS analysis were a trichloroaniline and a dichlorobromoaniline; these products indicate that the reaction occurring is mainly photoreduction-chlorination.¹⁹ Only a trace amount ($\leq 1\%$) of 2-chloronitrobenzene was produced. Two unidentified substances having retention times very close to that of 2-chloronitrobenzene were also observed in small amounts ($\leq 2\%$ yield). We conclude that the ortho isomer is unreactive in photosubstitution by chloride ion.

During our quantitative studies of 4-bromonitrobenzene, we found that the acetic acid cosolvent was an acid catalyst for the para photosubstitution, which caused us to change the solvent to CH₃CN-water (1:4, v:v). Photosubstitution was clean also in this solvent.

The dependence of the 4-chloronitrobenzene quantum yield on the chloride ion concentration when no acid is added is complex, as shown in Figure 1. Since the reaction solutions used for Figure 1 were not buffered and also did not contain constant electrolyte concentration, we present the results only for their qualitative aspects. The plot of Φ^{-1} versus $[\text{Cl}^-]^{-1}$ is nonlinear; a plot (not shown) of Φ^{-1} versus $[\text{Cl}^-]^{-2}$ is also not linear, though it is more nearly linear than the first-order plot. The curve connecting the data points of Figure 1 represents a fit by iterative convergence to the quadratic function shown in eq 1, where $x = [\text{Cl}^-]^{-1}$. The fit implies that there are two kinetically important steps involving

$$f(x) = A + Bx + Cx^2 \quad (1)$$

chloride ion on the reaction pathway, which is the photochemical equivalent of second-order dependence.

The dependence of the 4-chloronitrobenzene quantum yield on the hydronium ion concentration at constant 3.6 M $[\text{Cl}^-]$ is first order, as shown in Figure 2. We conclude that the photosubstitution is acid catalyzed. The extrapolated limiting quantum

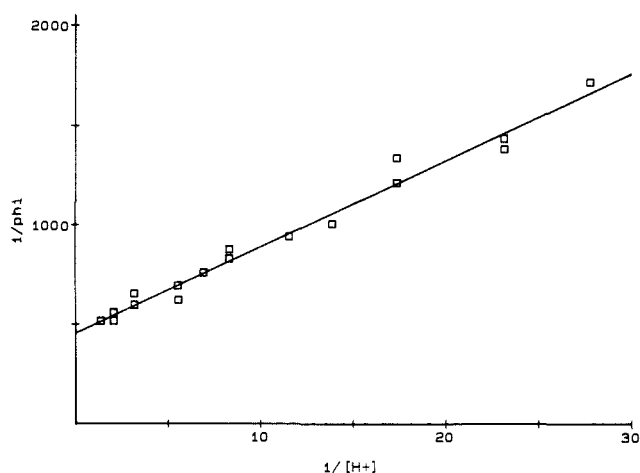


Figure 2. Dependence of 4-ClC₆H₄NO₂ quantum yield on concentration of hydrogen ion at constant $[\text{HCl}] + [\text{LiCl}] = 3.6$ M.

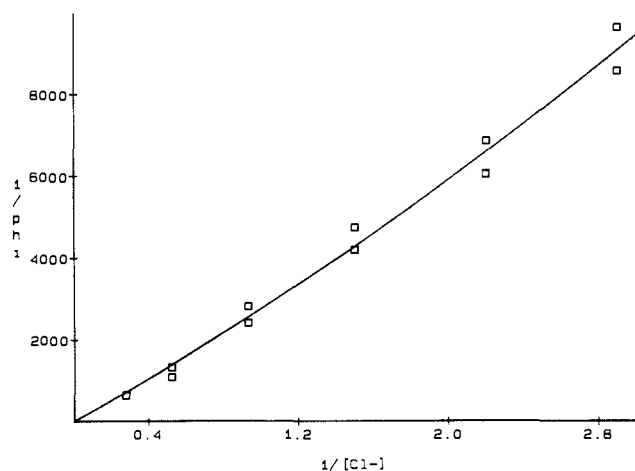


Figure 3. Dependence of 4-ClC₆H₄NO₂ quantum yield on concentration of chloride ion at 0.24 M $[\text{H}^+]$ and constant total electrolyte concentration ($[\text{HCl}] + [\text{LiCl}] + [\text{LiBF}_4] = 3.0$ M).

yield for 3.6-M $[\text{Cl}^-]$ at infinite $[\text{H}^+]$ is 0.0022. That the plot shows no sign of reaching a plateau at low hydrogen ion concentration implies that there is little, if any, photosubstitution that is not acid catalyzed.

With the acid dependence manifest, we redid the chloride ion dependence at constant 0.24 M $[\text{H}^+]$ and constant total electrolyte concentration of 3.0 M. The results are shown in Figure 3. These data are also fitted by a quadratic equation, the line on the plot having the formula of eq 2 where $x = [\text{Cl}^-]^{-1}$. Standard deviations

$$f(x) = 2.0 + 2551.5x + 199.7x^2 \quad (2)$$

of the *B* and *C* parameters are 2551.5 ± 235 and 199.7 ± 96 ; the parameter *A* was set at 2.0 before the fit (see discussion of Figure 2 and eq 1). The fit implies that the acid-catalyzed photosubstitution depends on chloride ion to the second order. Since one chloride ion is consumed stoichiometrically, the other is a catalyst of the photoreaction.

Our earlier work on nitrobenzene photoreactions^{18,19} led us to inquire whether HCl-catalyzed photoreduction of 4-bromonitrobenzene by 2-propanol would have an intermediate in common with the catalyzed photosubstitution. Indeed, products of nitro group photoreduction appeared when 4-bromonitrobenzene was irradiated in solutions containing LiCl (3.0 M), HCl (0.6 M), and 2-propanol (0.013–0.26 M). 4-Bromonitrosobenzene was detected by GC and identified by GC/MS by the coincidence of its mass spectrum and retention time with those of an authentic sample. Figure 4 shows the dependence of 4-bromonitrosobenzene appearance on the 2-propanol concentration. The plot indicates first-order dependence and a limiting quantum yield of 0.28. Also, we detected and identified 4-bromo-2-chloroaniline as a significant

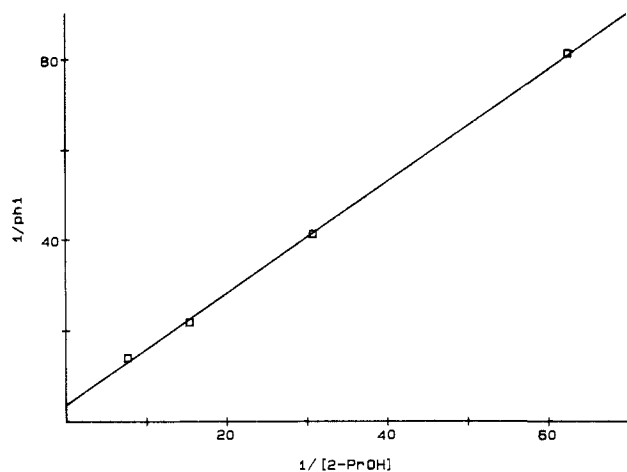


Figure 4. Dependence of 4-BrC₆H₄NO quantum yield on concentration of 2-propanol at constant [LiCl] = 3.0 M and [HCl] = 0.6 M.

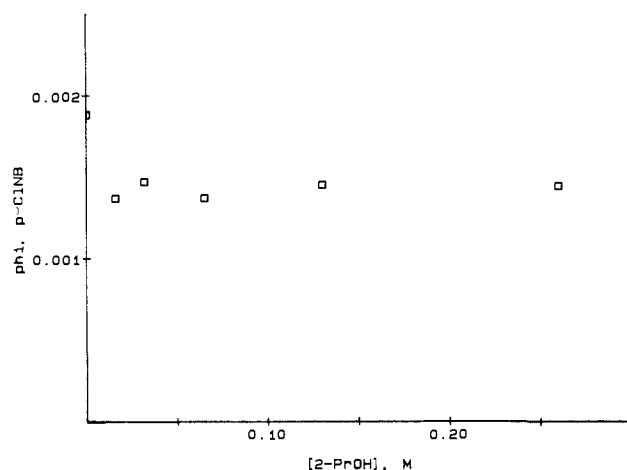


Figure 5. Dependence of 4-ClC₆H₄NO₂ quantum yield on concentration of 2-propanol at constant [LiCl] = 3.0 M and [HCl] = 0.6 M.

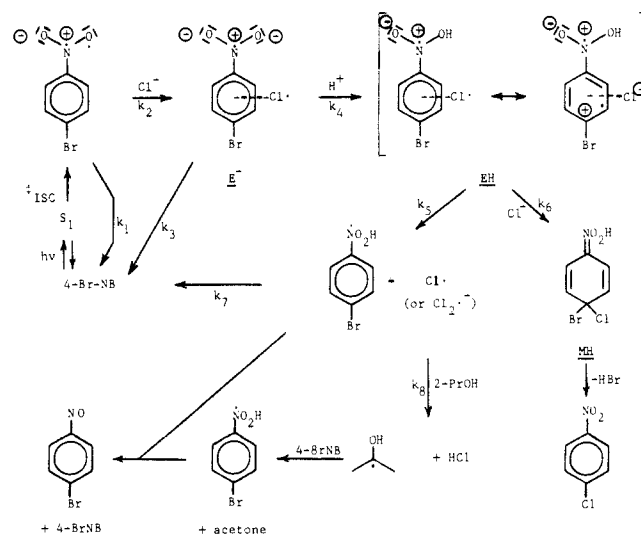
photoreduction product when the photolyzed solutions were basified and extracted. Several chlorinated anilines were also observed as minor products. The yields of these photoproducts varied with the extent of conversion. At 50% conversion, the percent yields were the following: 4-bromonitrosobenzene, 45 ± 10%; 4-bromo-2-chloroaniline, 50 ± 10%; other haloanilines, 5 ± 2%. At the 10–20% conversions used for the data of Figure 4, the percent yields were 65 ± 5%, 20 ± 5%, and <5%, respectively. Since 4-bromonitrosobenzene is reduced by two electrons from 4-bromonitrobenzene whereas 2-chloro-4-bromoaniline is reduced by four electrons, we estimate that the limiting quantum yield of nitroso product (0.28, from the intercept of Figure 4) actually represents about half of the limiting quantum yield of photoreduction, which would be 0.5–0.7.

We next inquired whether the photoreduction occurred at the expense of photosubstitution. Figure 5 shows that for 4-bromonitrobenzene in solutions of LiCl (3.0 M) and HCl (0.6 M), 0.017 M 2-propanol causes loss of about 25% of the photosubstitution product, but higher concentrations of the alcohol cause no further loss. The amount of photoreduction relative to photosubstitution is about 10:1 at 0.017 M 2-propanol, and it is about 60:1 at 0.26 M 2-propanol. Thus, the 2-propanol-dependent loss of photosubstitution product falls far short of accounting for the photoreduction products.

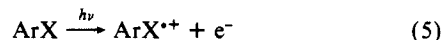
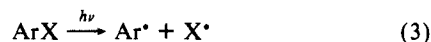
Discussion

Photodisplacement of halides from aromatic rings is a well-studied subject.²⁴ Three of the primary processes that have been

Scheme I



shown to lead to photosubstitution in other systems are shown in eq 3–5.²⁴ We dismiss all these as possibilities for our system



because none of them appear to lead to the observed chemistry. If 4-nitrophenyl radicals were produced as in eq 3 or 4, 2-propanol would convert them efficiently to nitrosobenzene,²⁵ which is not observed. In 0.86 M LiCl in acetonitrile–water, one would expect to see the coupling product, 4,4'-dinitrophenyl,²⁵ yet we see only 4-chloronitrobenzene in a quantum yield of 8.3×10^{-6} in such a medium (Figure 1). The anion radical of 4-bromonitrobenzene does not expel bromide ion appreciably (as in eq 4),²⁶ and the protonated radical ($\text{p}K_a \sim 3$) formed in acidic solution would be even less reactive in eq 4.²⁶ If solvated electrons were formed, as in eq 5, one expects that, in aqueous HCl, hydrogen atoms would result. These would react with ArNO₂ to make nitrocyclohexadienyl radicals that are not likely to form exclusively the observed chloro-substitution product.

Chlorine atoms in CCl₄ have been shown to substitute on 4-bromonitrobenzene to give 4-chloronitrobenzene,²⁷ but this product is a minor one. We see no evidence for the other products observed such as 4-bromochlorobenzene or 1,4-dichlorobenzene. Moreover, there is no means of generating chlorine atoms in our system (other than by photoreaction with the nitroaromatic; see below) since the medium is transparent to the 313-nm light.

Elucidating the photophysics of nitrobenzene derivatives is not straightforward because they generally show no fluorescence or phosphorescence. A general picture has evolved from several sources, however, on which a consensus exists.²⁸ Excitation of nitrobenzene and its derivatives bearing weakly interacting substituents populates a singlet state ($\tau \approx 10^{-12}$ s) that crosses ($\Phi_{\text{ISC}} \approx 0.7$) to a triplet ($E_T \approx 60$ kcal/mol, $\tau \approx 10^{-9}$ s) of n, π^* configuration. The π, π^* triplet of nitrobenzene lies a few kilocalories above the n, π^* triplet and can become the lower state, especially in polar solvents, if an electron donor substituent such as -OR is attached to the ring. It is likely that the observed photochemistry of 4-bromonitrobenzene occurs from a triplet n, π^* state.

We propose for this system the mechanism shown in Scheme I. Scheme I attributes acid catalysis to protonative capture of

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an exciplex, a process originally proposed by one of us^{29a} and since proposed for several other systems.^{18,29b-e} The quantum yield of photosubstitution (appearance of 4-chloronitrobenzene) is given for Scheme I by eq 6, which is inverted in eq 7 to form a convenient working expression. The quantum yield of photoreduction is given in inverted form by eq 8.³⁰

$$\Phi = \Phi_{\text{ISC}} \left(\frac{k_2[\text{Cl}^-]}{k_1 + k_2[\text{Cl}^-]} \right) \left(\frac{k_4[\text{H}^+]}{k_3 + k_4[\text{H}^+]} \right) \left(\frac{k_6[\text{Cl}^-]}{k_5 + k_6[\text{Cl}^-]} \right) \quad (6)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{ISC}}} \left(1 + \frac{k_1}{k_2[\text{Cl}^-]} \right) \left(1 + \frac{k_3}{k_4[\text{H}^+]} \right) \left(1 + \frac{k_5}{k_6[\text{Cl}^-]} \right) \quad (7)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{ISC}}} \left(1 + \frac{k_1}{k_2[\text{Cl}^-]} \right) \left(1 + \frac{k_3}{k_4[\text{H}^+]} \right) \times \left(1 + \frac{k_6[\text{Cl}^-]}{k_5} \right) \left(1 + \frac{k_7}{k_8[2\text{-PrOH}]} \right) \quad (8)$$

The protonated Meisenheimer adduct, MH^- , could be a source of some inefficiency, but we have no evidence on that question and have omitted partitioning of MH^- from eq 6 and 7. It is conceivable that MH^- could be totally unselective for elimination of HBr versus HCl, which would contribute a constant factor of 0.5 to eq 6, but we think it far more likely, since MH^- is fairly stable, that it is quite selective in eliminating HBr rather than HCl.

Equation 7 predicts the linear dependence of Φ^{-1} on $[\text{H}^+]^{-1}$ at constant $[\text{Cl}^-]$ that is shown by Figure 2. The slope of the correlation line (43.5) divided by the intercept (453) is the ratio k_3/k_4 , which is 0.096.

The data provide two independent means of evaluating the other two partitioning ratios in eq 7, k_1/k_2 and k_5/k_6 . The intercept of Figure 2 is defined by eq 9. The total quantum yield of

$$453 = \frac{1}{\Phi_{\text{ISC}}} \left(1 + \frac{k_1}{k_2[3.6]} \right) \left(1 + \frac{k_5}{k_6[3.6]} \right) \quad (9)$$

photoreduction at 3.6 M $[\text{Cl}^-]$, 0.6 M $[\text{H}^+]$, and infinite $[2\text{-PrOH}]$ will be represented by one-half of the observed intercept of 3.6 in Figure 4, since 4-bromonitrosobenzene represents about a half of the photoreduction equivalents. This intercept, according to eq 8, is shown in eq 10. Taking $\Phi_{\text{ISC}} = 0.7$ and k_1/k_2 and k_5/k_6 as single terms, eq 9 and 10 represent two equations and two unknowns. Solving them yields the result that $k_1/k_2 = 0.30$ and

$$1.8 = \frac{1}{\Phi_{\text{ISC}}} \left(1 + \frac{k_1}{k_2[3.6]} \right) \left(1 + \frac{0.096}{[0.60]} \right) \left(1 + \frac{k_6[3.6]}{k_5} \right) \quad (10)$$

$k_5/k_6 = 1050$. Because of the uncertainty in the limiting quantum yield of photoreduction, these numbers carry large errors, especially the value for k_1/k_2 .

A second approach is based on the quadratic fit to the data in Figure 3. The intercept of Figure 3 (see eq 7) can be calculated directly to be 2.0 from the values of Φ_{ISC} and k_3/k_4 at 0.24 M $[\text{H}^+]$. Thus, eq 7 under these conditions can be simplified to eq

11. The parameters of eq 1 and 2, expressed according to their equivalents in eq 11, are given in eq 12–14. The roots of si-

$$1/\Phi = 2.0[1 + (k_1/k_2)(1/[\text{Cl}^-])][1 + (k_5/k_6)(1/[\text{Cl}^-])] \quad (11)$$

$$A = 2.0 \quad (12)$$

$$B = 2551.5 = 2.0((k_1/k_2) + (k_5/k_6)) \quad (13)$$

$$C = 199.7 = 2.0(k_1/k_2)(k_5/k_6) \quad (14)$$

multaneous eq 13 and 14 are k_1/k_2 or k_5/k_6 equals 0.078 or 1276. It is gratifying to find reasonable agreement between these numbers and those estimated independently above. The above estimate indicates that k_1/k_2 is the smaller root and k_5/k_6 is the larger one.

This conclusion can also be reached by inspection of the reaction scheme (Scheme I) and the overall efficiencies. If at the k_1/k_2 stage the partitioning ratio were 1300, less than 0.3% of the excited states (at 3.6 M $[\text{Cl}^-]$) would proceed toward product. That would preclude the photoreduction quantum yield from attaining under any reaction conditions its limiting value of 0.5–0.7. If instead k_1/k_2 is 0.078 and k_5/k_6 is 1300, the traffic levels in the scheme correspond nicely to the highly inefficient photosubstitution and the highly efficient photoreduction.

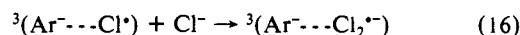
A telling test of the fitness of any new mechanism is whether its quantitative parameters give reasonable agreement with what would be expected from literature precedents. We examine this question below.

We have no independent knowledge of k_3 or k_4 , but if k_4 is diffusion controlled ($1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), then k_3 , the decay constant for the exciplex, is $1 \times 10^9 \text{ s}^{-1}$. That this is a reasonable rate constant for decay of this exciplex is shown by its similarity to that estimated³¹ for the decay in water of the chloride ion/9,10-anthraquinone-2-sulfonate triplet exciplex ($k_d \approx 2.5 \times 10^9 \text{ s}^{-1}$).

An excellent model for k_2 is the formation of the triplet exciplex from reaction of triplet n, π^* 9,10-anthraquinone-2-sulfonate (AQS) with chloride ion in water,³¹ which occurs with $k = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The AQS excited state has the same configuration as that of 4-bromonitrobenzene and virtually the same triplet energy (62³² versus 60 kcal/mol,²⁸ respectively), and the ground-state reduction potentials of the two molecules are virtually identical.³³ If k_2 is taken as $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, then k_1 is about $4 \times 10^7 \text{ s}^{-1}$, implying a triplet lifetime of about 25 ns.

That the energies of the $^3n, \pi^*$ and $^3\pi, \pi^*$ states of nitrobenzenes are inverted by electron donor substituents is shown by the triplet lifetimes of 0.8, 150, and 1020 ns for nitrobenzene in THF,²⁸ 3-nitrophenyl acetate in water,⁷ and 3-nitroanisole in 26% $\text{CH}_3\text{CN}-\text{H}_2\text{O}$,¹⁴ respectively. Using the well-documented photophysical behavior of aromatic ketones³⁴ as a guide, *m*-Br weakly lowers the π, π^* level, and *p*-Br lowers it slightly more, but not so strongly as does $-\text{OCH}_3$. The predicted lifetime of 25 ns seems reasonable on this basis.

The partitioning represented by k_5/k_6 is complicated by the possible role of chloride ion in forming the chlorine molecular anion radical, as shown in eq 15 and 16. Reaction 15 has a rate constant



of $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.^{35a} Thus at the chloride ion concentrations

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(30) Direct (noncatalyzed) photoreduction of nitrobenzenes by low concentrations of 2-propanol is inefficient (ref 28, 38, and 39) and may be ignored for the conditions reported here. For example, taking a rate constant for hydrogen abstraction from 2-PrOH of $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $[2\text{-PrOH}]$ of 0.13 M, Φ_{ISC} of 0.7, and τ_T of 25 ns, the direct photoreduction quantum yield is 0.0018, which is about 1–2% of the total photoreduction quantum yield (0.15) observed at 0.13 M 2-PrOH, 0.6 M HCl, and 3.0 M LiCl.

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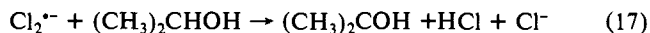
(35) (a) Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1979, NSRDS-NBS 65. (b) Hasegawa, K.; Neta, P. *J. Phys. Chem.* 1978, 82, 854–857.

used here, free chlorine atoms will be converted to Cl_2^- before any other bimolecular reactions can occur.

Time-resolved studies of the 9,10-anthraquinone-2-sulfonate/anion exciplexes³¹ indicate that chloride ion reacts with the chloride-containing exciplex to give the triple exciplex (eq 16) at approximately the rate of diffusion. Reactions of this type seem quite plausible in our system for the exciplex, E^- , and the protonated exciplex, EH . We omit them from Scheme I, however, because, under our conditions, we have no evidence for them. That implies either than the processes at the exciplex stage do not occur in our system or that they occur completely at all chloride ion concentrations used and are therefore kinetically invisible. The latter possibility seems to us the more likely.

If the decay constant k_3 in fact applied to E^- , a two-species exciplex, and k_5 and k_6 applied to EHCl^- , a triple exciplex ($p\text{-BrC}_6\text{H}_4\text{NO}_2\text{H} \cdots \text{Cl}^-$), this would rationalize why E^- apparently passes rapidly to ground-state molecules with intersystem crossing, whereas EHCl^- undergoes efficient EHCl^- dissociation to $p\text{-BrC}_6\text{H}_4\text{NO}_2\text{H}^+$ and Cl_2^- . Loeff, Treinen, and Linschitz³¹ have shown that, for the quinone system, the former exciplex retains a large spin-orbit coupling interaction that causes efficient ($\Phi \sim 1.0$) return to ground state.³⁶ Complexation of a second chloride ion in the triple exciplex reduces the spin-orbit coupling to a small value with the consequence that the exciplex dissociates efficiently ($\Phi \sim 1.0$). The conclusion that k_5 is a very facile reaction is consistent with our finding that nucleophilic attack by chloride ion on the protonated exciplex competes poorly with exciplex dissociation, i.e., $k_5/k_6 \approx 1300$.

The slope to intercept ratio (0.35) of Figure 4 represents the partitioning ratio k_7/k_8 in Scheme I. The rate constant for k_8 , shown in eq 17, has been reported^{35b} to be $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. This



implies that k_7 , reversion of $p\text{-BrC}_6\text{H}_4\text{NO}_2\text{H}^+$ and Cl_2^- to starting materials, occurs with a rate constant of $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Figure 5 suggests that 2-propanol can prevent formation of about 25% of the photosubstitution product. This is probably due to participation of $p\text{-BrC}_6\text{H}_4\text{NO}_2\text{H}^+$ and Cl_2^- in the reverse of k_5 .

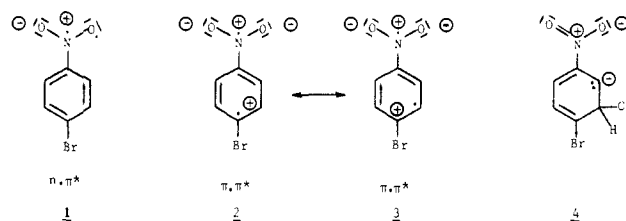
That 2-propanol at concentrations between 0.017 and 0.26 M has no effect on the quantum yield of photosubstitution is strong evidence that the exciplex itself does not react directly with the alcohol. The relatively massive quantum yield of photoreduction, therefore, depends upon an efficient dissociation of the exciplex. This result resolves a long-standing question in our research on electron hole transfer catalysis,^{15,18,19,37} namely, whether the hydrogen donor reacts directly with the hole of the exciplex or with that of a dissociated fragment.

We have proposed¹⁷ that acid-catalyzed photosubstitution on 3-bromonitrobenzene involves heterolytic attack by chloride ion on the upper, π, π^* triplet; the acid catalysis was attributed to protonation of the π, π^* triplet and subsequent heterolytic nucleophilic attack. We should consider the fitness of that mechanism for the para isomer.

The large limiting quantum yield of photoreduction (0.5–0.7) argues strongly for a well-populated triplet as the reactive state. The evidence that the n, π^* state is the lower triplet in nitrobenzenes lacking strong donor substituents, and the strong association of the n, π^* state with alcohol photoreduction^{38,39} and with chloride ion–electron transfer reactions¹⁹ make a strong case that reaction occurs from the n, π^* state. We have argued elsewhere^{17,18} that the $^3n, \pi^*$ state is not a reasonable prospect for protonation, and we continue firmly to hold this view.

Why should we not attribute para photosubstitution to a minor pathway from the π, π^* state that is independent of the HCl-catalyzed photoreduction? The valence bond approximations of the n, π^* and π, π^* excited states shown in 1, 2, and 3 give some

insight. Molecular orbital calculations on nitrobenzene π, π^* states⁴⁰ indicate that excitation causes electron density to be



removed most strongly from the carbon atoms meta to the nitro group. Thus 2 is a more important contributor than 3 for unsubstituted nitrobenzene, and that preference will be offset only slightly by the weak cation stabilizing effect of the para bromine. If chloride ion were to attack the π, π^* state, the electron distribution as well as the "energy gap law"⁴² predict that 4 should be the product. This adduct, having no reasonable leaving group other than chloride ion, would revert totally to starting material; this results in a minor quenching process.

With regard to experimental evidence, we adduce several arguments against a π, π^* photosubstitution process involving para attack. First, it provides no plausible reason why dependence on chloride ion should be second order. Second, the intercept of 2.0 for Figure 3 (limiting photosubstitution quantum yield of 0.5) produces partitioning terms for the radical pathway that agree with those estimated independently and with literature precedents, and a limiting quantum yield of 0.5 is too high for a minor process of a minor population state. Third, the meta isomer shows a large proportion of uncatalyzed photosubstitution¹⁷ that has the same ultimate quantum yield as the acid-catalyzed process; that the para isomer shows no indication of any non-acid-catalyzed reaction implies that it reacts by a different mechanism.

We dismiss on several grounds static or nearest neighbor solution effects⁴¹ involving Cl^- and triplet nitro aromatic as the explanation for the curvature of Figures 1 and 3. In order to see this effect, the probability of occurrence of the event (exciplex formation in this case) during an encounter lifetime must be high, and that seems unlikely for this case. Moreover, even at 3 M, the ratio of chloride ions to solvent is low (1:16); also, the ion is likely to be sheathed by solvent, unlike the case of a diene that can directly solvate its quencher.⁴¹ Finally if indeed at low $[\text{Cl}^-]$, we see ideal (dynamical) $1/[\text{Cl}^-]$ versus $1/\Phi$ behavior that deviates from ideality by becoming more efficient (per Cl^-) at higher $[\text{Cl}^-]$, Figures 1 and 3 curve the wrong way. Furthermore, the intercept extrapolated from the presumably well-behaved points at the upper right would be at negative $1/\Phi$, a result that defies rational explanation.

Whereas our main interest has been with the mechanistic details of photosubstitution, this study provides quantitative experimental evidence for two important features of photoreduction of aromatic nitro compounds that heretofore have been postulated.⁴² The evidence in Figure 4 that the efficiency is first order in the reductant concentration has not to our knowledge been demonstrated previously. Also, whereas the nitroso reduction product has been postulated as the first organic product, it has not previously been observed quantitatively, though Levy and Cohen⁴³ have observed qualitatively the nitroso product from 4-cyano-1-nitrobenzene.

The observation of 4-bromo-2-chloroaniline as a photoreduction product warrants comment. Nitrosobenzenes are easier to reduce than the corresponding nitrobenzenes. This occurs in part because the equilibrium for eq 18 favors the products.⁴⁴ Disproportion-



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(36) The expectation that E^- will revert efficiently to ground-state species argues against kinetic treatments based on reversible formation of the exciplex.

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ation of ArNOH^+ forms ArNO and 4-bromophenylhydroxylamine, which is reduced by four electrons from ArNO_2 . The chloride analogue of Bamberger rearrangement⁴⁵ of the latter would give the observed 4-bromo-2-chloroaniline that is in the same state of oxidation as the hydroxylamine. The conversion by HCl of nitrosobenzene to 2,4-dichloroaniline¹⁹ apparently does not occur under these weakly acidic conditions.

The recognition herein that second-order dependence on a reactant concentration for a photochemical reaction requires a quadratic expression and the treatment we have given it appear to be novel contributions. Indeed, whereas first-, second-, and third-order dependencies for ground-state reactions will appear as simple exponents of the concentration terms in the rate expression, for photochemical kinetics these dependencies appear in the Φ^{-1} expression in the form of binomial expansions, $(a + bx)^n$, where $x = [\text{reactant}]^{-1}$. This arises because each of the kinetically significant bimolecular partitionings along a photo-reaction pathway will appear in the inverted quantum yield expression in the following form, $a + (b/[\text{reactant}])$.

Summary

We have elsewhere¹⁷ presented evidence that photosubstitution of bromide ion by chloride ion in 3-bromonitrobenzene occurs by direct, heterolytic nucleophilic attack on the $^3\pi, \pi^*$ state. This reaction is first order in chloride ion, shows uncatalyzed reaction, and is catalyzed by acid, the catalysis being attributed to protonation of the π, π^* state. We conclude here that photosubstitution by chloride ion on 4-bromonitrobenzene involves electron transfer from chloride ion to the $^3n, \pi^*$ state as the primary process, the attachment of chloride at the para position occurring as an intermolecular reaction of an exciplex. This reaction is second order in chloride ion and is exclusively an acid-catalyzed process,

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the acid catalysis being attributed to protonative capture of the initial exciplex. The initial steps of this reaction can initiate efficient photoreduction by 2-propanol, whereas the heterolytic reaction occurs cleanly with no concomitant photoreduction in the presence of 2-propanol. Together these findings strongly support the postulate^{1,15,16} that meta-to-nitro regioselectivity in nucleophilic aromatic photosubstitution on nitrobenzene derivatives reflects heterolytic bond changes, whereas para-to-nitro regioselectivity reflects electron transfer and radical coupling as the route to the σ complex.

These results, taken together, are grounds for qualifying the recently claimed⁴⁶ ubiquity of single electron transfer (SET) processes in organic reactions. The cited theoretical study⁴⁶ "sets out to demonstrate that all so-called two-electron (or polar) pathways actually involve the shift of a single electron and are far more closely related to the established SET pathways than has been recognized till now." If SET from the attacking nucleophile occurred in the meta-to-nitro photosubstitutions,^{1-3,14,15,17} the regiochemistry would be controlled by the nitro aromatic radical, and bond formation would occur at the *ortho* or *para* carbons. This would make meta-to-nitro regioselectivity impossible, a conclusion at variance with the facts. We conclude that there is a real difference between the SET pathway and the heterolytic pathway in these photoreactions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also acknowledge support of the National Science Foundation (Grant CHE-8605343). NSF and the Research Corporation are thanked for grants to acquire the GC/MS instrument and NSF for a grant to acquire the UV-vis spectrophotometer. We thank Bonnie Kenney Mangold and Bruce Murch for preliminary experiments.

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Triene Photophysics and Photochemistry: Previtamin D₃

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Abstract: The origin of the wavelength dependent photochemical behavior of previtamin D₃ was investigated. The fluorescence spectrum and quantum yield of previtamin D₃ were determined at 302 and 307 nm, and both the intensity distribution and the fluorescence quantum yields were found to be independent of excitation energy. A large Stokes shift was observed which is consistent with an excited state torsional relaxation about the central double bond of the triene. The excited state displacement was reproduced by QCFF/PI calculations of the ground and excited states of a model compound. The excited state involved in the absorption and emission spectra is discussed.

Wavelength effects in solution photochemistry can arise from excited-state or ground-state properties.¹ This experimental variable has been studied in the photochemistry of polyenes, and it generally has been found that wavelength-dependent photochemistry arises from a variety of ground-state effects such as secondary reactions of the primary photoproduct,² independent excitation of conformational³⁻⁹ and structural isomers,¹⁰ and ex-

Table I. Quantum Yields of P₃ Conversion at Two Wavelengths

λ , nm	Pro ₃	L ₃	T ₃
253.7	0.014	0.040	0.41
302.5	0.02	0.09	0.29

citation of ground-state complexes.^{11,12} However, it has been suggested that wavelength dependencies may also result from the

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