77 K (in spite of the long triplet lifetime of 2) tends to support the former pathway.

The marked difference between the photochemical reactivity of the naphthocyclopropanes (12, 16) and naphthocyclobutane (2) cannot be explained on the basis of thermochemical arguments, since the strain release upon C–C bond cleavage is comparable for all three compounds. However, a simple explanation may be sought in the much bigger $\sigma\sigma^*$ excitation energy of cyclobutane compared with cyclopropane.[44] The higher propensity of cyclopropane toward conjugative interaction is born out in the relevant compounds by a shift of the ^1L_a ($\pi\pi^*$) absorption band: from acenaphthene to naphthocyclopropane (2) the red shift amounts to only 300 cm^{-1}, whereas in the naphthocyclopropane (12) the ^1L_a band is shifted by 1500 cm^{-1}.[45] A natural orbital correlation diagram[46] reveals an intended correlation of a nonbonding biradical π orbital with a σ^* orbital; thus, it is not surprising that the activation barrier for fission of the peri σ bond in the lowest $\pi\pi^*$ excited state (^1L_b) is higher for 2 than for 12 or 16.

Conclusions

Each of several different products can be obtained in high yield from the azo compound 1 by choosing the appropriate conditions for the formation and the subsequent reactions of the biradical intermediate 1,4-perinaphthadiyl (b). The combined results of low-temperature spectroscopy, flash photolysis, and product analyses are rationalized in terms of Scheme II in which both the singlet and the triplet state of b appear as true, kinetically distinct intermediates. The reactions of b are mainly controlled by three variables: (i) the method of initiating the reaction—pyrolysis, direct photolysis, or sensitization of 1—which determines the multiplicity of b when it is initially formed; (ii) the temperature,

which influences the relative efficiency of three competing decay channels from ^{1}b—low temperatures favoring the nonactivated ISC to ^{3}b; (iii) the partial pressure of oxygen, which traps ^{3}b and catalyzes ISC from ^{1}b.

The seemingly minor difference in structure between the tetramethylene-bridged naphthoquinodimethane b and the trimethylene-bridged derivatives c and d has a very profound influence on the reactivity. The singlet state of d was found to be too short-lived to react with oxygen or to undergo ISC even at low temperature.[8] This work has provided evidence that the singlet biradical ^{1}b has a lifetime on the order of 1 ns at room temperature, sufficient for intermolecular reactions and spontaneous ISC to ^{3}b to compete with ring closure to naphthocyclobutane (2). Further work is aimed toward a direct detection of ^{1}b. The factors responsible for the stabilization of ^{1}b are open to question.

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Acid-Catalyzed Nucleophilic Aromatic Photosubstitution. A Reconsideration of Protonation in Excited States of Nitrobenzenes[†]

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Abstract: 3-Bromonitrobenzene is photosubstituted inefficiently but cleanly by chloride ion to give 3-chloronitrobenzene. The photosubstitution is catalyzed by hydronium ion; the limiting quantum yield of 0.021 at infinite [H$^+$] and 3.0 M [Cl$^-$] is only 2-fold higher than the quantum yield (0.011) of the uncatalyzed photosubstitution at 3.0 M [Cl$^-$]. The limiting quantum yield at infinite chloride ion concentration with no added acid is also 0.021. That 2-propanol does not intervene on the photosubstitution pathway to cause photoreduction indicates that radical intermediates are not involved, and the absence of deuterium incorporation on the aromatic ring accompanying photosubstitution indicates that the catalysis does not involve formation of a dihydrobenzene intermediate. The reaction appears to be an example of the so-called S$_N$2 ^{3}Ar* mechanism and the catalysis to be a manifestation of protonation of the $^3\pi,\pi^*$ state, which is the higher energy triplet state in 3-bromonitrobenzene.

Elucidating the mechanisms of nucleophilic aromatic photosubstitution reactions continues to occupy the attention of photochemists.[1-14] A mechanistic classification scheme put forward by Havinga and co-workers[2,15] for these reactions rationalizes the

preference for substitution meta to a nitro group in a π,π^* triplet nitrophenyl ether. A recent supplement to this scheme attributes

[†] Dedicated to the memory of Douglas Phelps Susens.
[‡] Deceased April 17, 1987.

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nucleophilic photosubstitution para to the nitro group in Smiles photorearrangement to a change of mechanism.[1,16] The alternative mechanism involves electron transfer and radical coupling as the route to the σ complex and may account for the change from meta to para displacement on 1,2-dimethoxy-4-nitrobenzene[11a] when the nucleophile is changed from difficultly oxidizable nucleophiles such as hydroxide, ammonia, or methylamine to better electron donors such as dimethylamine or morpholine.

Our interest in catalysis of photoreactions[17] led us to search for an acid-catalyzed aromatic photosubstitution. We expected that, should an example be found, it would provide an additional mechanistic characterization of these reactions. We report herein a quantitative description of a novel example of acid-catalyzed photosubstitution, namely, photosubstitution on 3-bromonitrobenzene by chloride ion giving 3-chloronitrobenzene.

Experimental Section

Chemicals were of the highest grades commercially available. 3-Bromo- and 3-chloronitrobenzenes were recrystallized and were homogeneous by capillary GC analysis. Solvents (HPLC or spectrograde) were from Aldrich. GC/MS analyses were carried out with a Hewlett-Packard 5992B instrument, and quantitative GC analyses were carried out with a Hewlett-Packard 5880A instrument. Both instruments were equipped with 25 m × 0.2 mm (i.d.) cross-linked methyl silicone capillary columns. NMR spectra were obtained with an IBM NR300 spectrometer. 3-Bromonitrosobenzene was synthesized by an adaptation of a published procedure.[18]

Preparative irradiations were carried out at ~20 °C with an immersion reactor equipped with a Pyrex filter and a Hanau TQ 150-W mercury lamp or a Hanovia 450-W mercury lamp. Preparative reactions concerned with deuterium incorporation were carried out in Pyrex glassware at ~40 °C with a Rayonet RPR-208 reactor equipped with 300- or 350-nm lamps. Quantum yield measurements were carried out at 313 nm with a merry-go-round apparatus illuminated by a Hanovia 450-W mercury lamp surrounded by a Pyrex vessel containing 0.002 M K$_2$CrO$_4$ in 5% aqueous K$_2$CO$_3$. Sample solutions of 3–5 mL (20% CH$_3$CN–80% water, v/v) of 1.00 × 10^{-3} M 3-bromonitrobenzene were contained in Ace Glass Inc. O-ring-sealed Pyrex tubes;[19] samples absorbed >98% of the light entering the tubes, and conversions were kept below 10%. 3-Bromonitrobenzene at 2.5 × 10^{-3} M, especially at high salt concentration, is near or over the limit of solubility; the data for Figure 1 were obtained at this concentration. Reaction solutions were prepared from stock solutions of 12 M hydrochloric acid (assayed by titration), 12 M aqueous lithium chloride (Fisher, prepared gravimetrically), and 1.00 × 10^{-2} M 3-bromonitrobenzene in spectrograde acetonitrile. Chromatographic analyses were carried out on extracted products obtained by shaking the contents of the tubes vigorously with 0.5 mL of
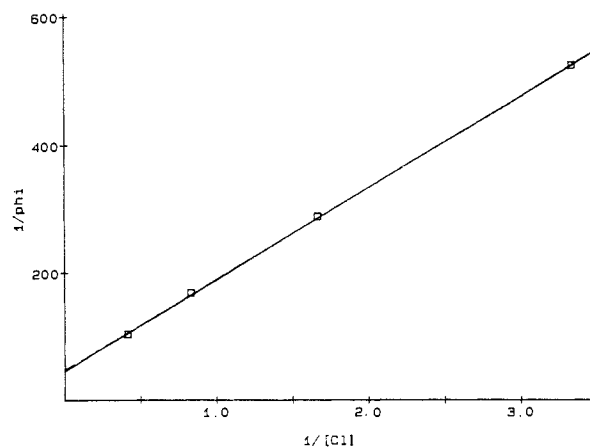

Figure 1. Dependence of quantum yield of 3-chloronitrobenzene on chloride ion concentration.
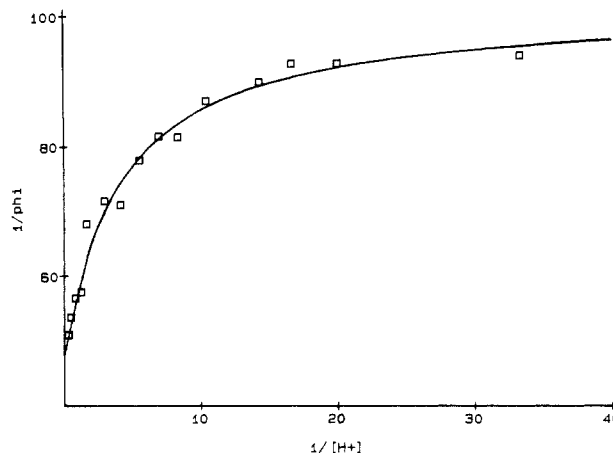

Figure 2. Dependence of quantum yield of 3-chloronitrobenzene on hydrogen ion concentration at 3.0 M chloride ion.

cyclohexane or ether containing tetradecane (1.19 × 10^{-3} M) as an integration standard. That cyclohexane, ether, CHCl$_3$, and CH$_2$Cl$_2$ as extractants all gave identical recoveries of chloro- and bromonitrobenzenes from the same aqueous solution indicates that the recoveries were quantitative. Quantitation of the extracted compounds was done by comparing peak area ratios with those of extracts from calibration samples. The actinometer for the early measurements was photohydrolysis of 3-nitroanisole;[20] later measurements, that agreed with the earlier ones, are based on the azoxybenzene actinometer.[21] Quantum yield measurements for different runs were reproducible to ±10%, and duplicate samples in a single run were reproducible to ±5%. Each data point in Figures 1 and 2 represents an average of two measurements. Series of experiments analogous to those of Figure 2 were carried out at total electrolyte concentrations ([HCl] + [LiCl]) of 1.8 and 6.0 M, as well as at 3.0 M. The results at 1.8 and 6.0 M are not complete, but they show the same behavior as that in Figure 2, including an intercept near Φ^{-1} = 50. At 6 M electrolyte concentration, solubility is a frequent problem.

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 3-bromonitrobenzene (2.5 × 10^{-3} M) in acetic acid–water (1:4, v/v) or acetonitrile–water (1:4, v/v) containing lithium chloride (1–6 M) was monitored by gas chromatography/mass spectroscopy of the products extracted into dichloromethane. At conversions of less than 20% of starting material, the only volatile product (≥90%) was 3-chloronitrobenzene, which was confirmed by comparison of its retention time and mass

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spectrum with those of an authentic sample. Authentic samples of the ortho, meta, and para isomers of chloro- and bromonitrobenzenes were separable under our GC conditions, and neither the ortho nor para isomers, nor nitrobenzene, could be observed. At conversions of over 95% in a Rayonet reactor with 300-nm lamps, only 3-chloronitrobenzene was observable by GC for acetonitrile–water (1:4, v/v) solutions containing 3 M HCl or 3 M LiCl.

The dependence of the 3-chloronitrobenzene quantum yield on the concentration of lithium chloride in acetonitrile–water is shown in Figure 1. The dependence is clearly first order, and the intercept of the least-squares regression line represents a limiting quantum yield of 0.021.

The dependence of the quantum yield on the hydrogen ion concentration at constant 3.0 M chloride ion is shown by Figure 2. Hydrogen ion concentration was varied, while chloride ion was maintained at 3.0 M by using mixtures of HCl and LiCl. The plot shows that the photosubstitution is catalyzed by hydronium ion to the first order at concentrations greater than $\sim$0.1 M and that uncatalyzed photosubstitution occurs at low hydrogen ion concentration. The curve shown was fit to the data points by convergent iteration with a function of the form shown in eq 1,

$$f(x) = A[1 + [B/[C + (D/x)]]] \tag{1}$$

where x is $[H^+]^{-1}$; the form of eq 1 was dictated by our kinetic treatment (see eq 8 in Discussion). The peculiar fact should be noted that the dynamic range of the catalysis is small in this case. The value of the quantum yield for the uncatalyzed photosubstitution at 3 M [Cl$^-$] is 0.011, which increases only about a factor of 2 (to 0.021) at the extrapolated intercept corresponding to infinite [H$^+$] for the catalyzed reaction.

From previous work on HCl-catalyzed photoreduction of nitrobenzene,[22,23] we know that 2-propanol at 0.1 M is capable of efficiently trapping an intermediate by hydrogen atom donation and diverting the reaction to photoreduction if the reaction is initiated by electron transfer from chloride ion. When we used 2-propanol as a probe of the photosubstitution on 3-bromonitrobenzene, we found no evidence for a radical reaction. Thus, irradiation of 3-bromonitrobenzene in 3.0 M LiCl or 2.9 M LiCl–0.1 M HCl in acetonitrile–water containing 0.13 M 2-propanol gave 3-chloronitrobenzene as the only volatile product. A specific search by GC for the expected volatile photoreduction products, 3-bromonitrosobenzene and chlorinated 3-bromoanilines, with retention time information provided by authentic samples, revealed that no more than traces were formed. We conclude that 2-propanol does not intervene in this photosubstitution process.
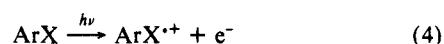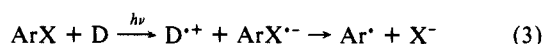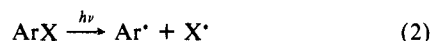
The mechanism of catalysis by protons for this case is unique because acid catalyses previously established for nitrobenzenes in hydrochloric acid involved protonation of a geminate radical pair[22] or proton-induced tautomerization of a Meisenheimer adduct.[23] We wished to learn whether the new catalytic reaction involved protonation of the ring. Samples (50 mL) of 3-bromonitrobenzene (51.1 mg, 5.06 × 10^{-3} M) in acetonitrile–deuterium oxide (1:4, v/v) were irradiated at 350 nm for 108 h in the Rayonet reactor in Pyrex glassware. Sample A contained 3 M DCl; sample B contained 3 M LiCl; and sample C contained 3 M D$_2$SO$_4$. The irradiation time was sufficient to cause complete conversion of starting material to 3-chloronitrobenzene in samples A and B; no photochemistry (other than possible deuterium incorporation) was expected in C. Following irradiation, the solutions were extracted with 3 volumes of ether, the extracts were concentrated, and the halogenated nitro compounds were isolated by preparative gas chromatography. (The principal impurity seemed to be solvent-derived tar.) The isolated halonitrobenzenes were analyzed by proton NMR at 300 MHz. The spectrum of the material from sample C showed four distinct proton signals that were identical in position and area with those of 3-bromonitrobenzene. Similarly,

the peak positions and areas for the materials isolated from samples A and B were identical with those of 3-chloronitrobenzene. We conclude that deuterium was not appreciably incorporated in any of these nitrobenzene derivatives.

The samples were also injected into the gas chromatograph–mass spectrometer, and average ion intensity data from approximately 20 mass spectra were obtained in two runs for the single chromatogram peak in each run. The intensities in the same spectrum of the M + 1 and M + 3 peaks relative to those of M and M + 2, respectively, were those expected from normal abundances, implying that no deuterium was incorporated. Comparison of mass spectra of samples A–C with those of undeuteriated authentic samples (all peak intensities normalized to M = 100%), showed that the ratios of M + 1 intensities and of M + 3 intensities were unity (±5%). Clearly, incorporation of deuterium accompanying photosubstitution under either acid-catalyzed or uncatalyzed conditions is negligible.
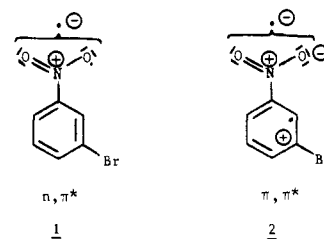
Discussion

Three well-documented primary processes exist for photodisplacement of halides from aromatic rings, as shown in eq 2–4.[24]

$$\text{ArX} \xrightarrow{h\nu} \text{Ar}^{\cdot} + \text{X}^{\cdot} \tag{2}$$

$$\text{ArX} + \text{D} \xrightarrow{h\nu} \text{D}^{\cdot+} + \text{ArX}^{\cdot-} \rightarrow \text{Ar}^{\cdot} + \text{X}^- \tag{3}$$

$$\text{ArX} \xrightarrow{h\nu} \text{ArX}^{\cdot+} + \text{e}^- \tag{4}$$

We see no evidence whatsoever for photolability of 3-bromonitrobenzene on extended irradiation in aqueous acetonitrile containing 3 M sulfuric acid. Moreover, photosubstitution by chloride ion occurs cleanly in the presence of 0.13 M 2-propanol, an efficient hydrogen atom donor. If any of the primary processes of eq 2–4 occurred for 3-bromonitrobenzene, one would expect to find at least some disappearance of starting material or formation of nitrobenzene or coupling products in the above experiments. Indeed, the reaction reported here has the earmarks of the so-called S$_N$2 ^{3}Ar* mechanism.[2,24]

The description of nitrobenzene excited states is not straightforward, because most nitrobenzenes neither fluoresce nor phosphoresce. From a variety of evidence, a picture has emerged on which a consensus exists.[25-27] For nitrobenzene and its derivatives bearing weakly interacting substituents such as bromine, the excited singlet crosses ($\simeq 10^{-12}$ s, $\Phi_{ISC} \simeq 0.7$) to a short-lived triplet ($\tau \simeq 10^{-9}$ s) of n,π* configuration (ca. 60 kcal mol^{-1}). The π,π* triplet of nitrobenzene lies a few kilocalories above the n,π* triplet, and the two states are populated according to the Boltzmann distribution. The π,π* state can become the lower triplet, especially in polar solvents, if moderately strong donor substituents are present on the ring. The situation in regard to effects of substituents on relative energies and populations of states appears to parallel closely the well-documented behavior of aromatic ketones.[28] Modified valence bond representations of the n,π* and π,π* states are shown by structures 1 and 2, respectively.

n,π* π,π*

1   2

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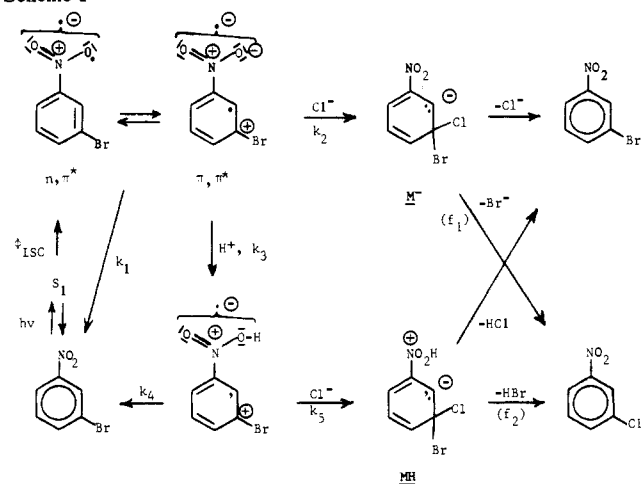
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Scheme I

Scheme II

We propose that the observed meta photosubstitution proceeds from the π,π^* triplet state. This assignment is consistent with the strong relationship already established between meta-to-nitro orientation of nucleophilic photosubstitution in nitrophenyl ethers and the π,π^* state.[2,14] Structure **2** reveals that nucleophilic ring attack at the position bearing the cation-stabilizing substituent is a reasonable expectation for this excited state whose electron hole is located on the ring.

We propose the overall mechanism shown in Scheme I. The quantum yield expression according to this scheme is given by eq 5, where χ represents the fraction of triplets in the reactive

$$\Phi = \Phi_{ISC}\chi\left[\frac{f_1 k_2[Cl^-] + k_3[H^+]\left(\dfrac{f_2 k_5[Cl^-]}{k_4 + k_5[Cl^-]}\right)}{k_1 + k_2[Cl^-] + k_3[H^+]}\right] \quad (5)$$

state and f_1 and f_2 represent the fractions of σ complexes M^- and MH that eliminate bromide ion or hydrogen bromide to form product. Under conditions where $[H^+]$ is very low, the expression is approximated by eq 6. Inversion of eq 6 yields a convenient

$$\Phi = \Phi_{ISC}\chi\left(\frac{f_1 k_2[Cl^-]}{k_1 + k_2[Cl^-]}\right) \quad (6)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}\chi f_1}\left(1 + \frac{k_1}{k_2[Cl^-]}\right) \quad (7)$$

working expression, eq 7. According to eq 7, the intercept of Figure 1 at a value of 47 represents $1/(\Phi_{ISC}\chi f_1)$. If Φ_{ISC} is 0.7 and f_1 is 0.5, as would be expected for unselective elimination of similar leaving groups from a highly energetic σ complex such as M^-, χ is 0.060. This conclusion that only 6% of the triplets is available for reaction at an infinite concentration of chloride ion is consistent with our contention that reaction originates from a sparsely populated upper triplet state. The rate of interconversion of such triplets is not known; data reported by Hautala and Mayer[29] permit the estimate that a 13-kcal gap is crossed from $^3n,\pi^*$ (C=O) to $^3\pi,\pi^*$ (NO$_2$) to $^3n,\pi^*$ (NO$_2$) in p-nitrophenyl ketones with a rate constant of 10^{11}–10^{12} s^{-1}. The slope to intercept ratio (3.3) represents k_1/k_2. If k_1 is $\geq 10^9$ s^{-1}, then k_2 is $\geq 3 \times 10^8$ M^{-1} s^{-1}. This may be compared with the reported rate constant of 6.4×10^8 M^{-1} s^{-1} for nucleophilic attack by hydroxide ion on the π,π^* triplet state of 3-nitroanisole in 26% CH$_3$CN–H$_2$O[14] and of 1×10^8 M^{-1} s^{-1} for hydroxide ion attack on $^3\pi,\pi^*$ 1-fluoro-3-nitronaphthalene.[30]

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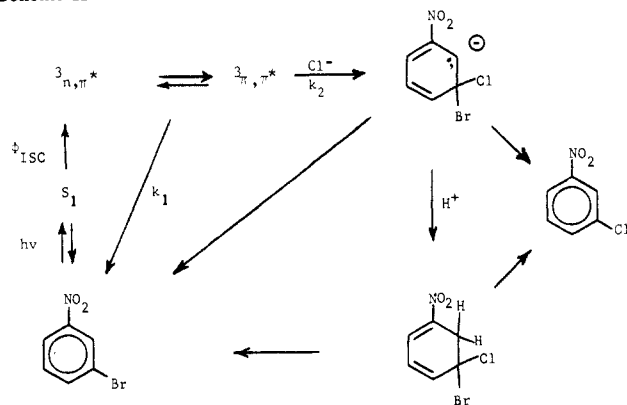
When the chloride ion concentration is constant and hydrogen ion concentration varies, the terms involving $[Cl^-]$ in eq 5 are constant, and eq 5 may be simplified to eq 8, where $\alpha = k_2[Cl^-]$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}\chi f_1\beta}\left(1 + \frac{\beta k_1 + \beta\alpha - \alpha}{\alpha + \beta k_3[H^+]}\right) \quad (8)$$

and $\beta = k_5[Cl^-]/(k_4 + k_5[Cl^-])$. Equation 8 assumes that the fractions of M^- and MH that form product are the same, namely, f_1. This equation predicts that a plot of Φ^{-1} vs $[H^+]^{-1}$ could show two regimes depending on circumstances. If $\alpha \gg \beta k_3[H^+]$, the plot will be invariant with $[H^+]$ changes, according to eq 9. In

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}\chi f_1}\frac{k_1 + \alpha}{\alpha} \quad (9)$$

the regime where $\alpha \ll \beta k_3[H^+]$, eq 8 may be simplified to eq 10, which predicts a linear relationship between Φ^{-1} and $[H^+]^{-1}$. Figure 2 indeed shows the two regimes of behavior predictable from eq 8.

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}\chi f_1\beta}\left[1 + \frac{k_1 + \alpha - (\alpha/\beta)}{k_3[H^+]}\right] \quad (10)$$

Additional rate constants are obtainable from the kinetic data of Figure 2. The convergent fit of the function shown in eq 1 to the data points in Figure 2, expressed according to their equivalents in eq 8, are shown in eq 11–13. The errors shown are the standard

$$A = 47.6 \pm 2.00 = 1/(\Phi_{ISC}\chi f_1\beta) \quad (11)$$

$$B = (1.02 \pm 0.07) \times 10^9 = \beta(k_1 + \alpha) - \alpha \quad (12)$$

$$D = (3.7 \pm 0.7) \times 10^9 = \beta k_3 \quad (13)$$

deviations; parameter C of eq 1 (which is $k_2[Cl^-]$) was set at 9.0 $\times 10^8$, from the minimum value of k_2, and $[Cl^-] = 3.0$ M. From the fact that the intercepts of Figure 1 (see eq 7) and Figure 2 (see eq 8 or 10) are identical, one concludes that β in eq 11 is unity. This implies that virtually all the excited states captured by a proton in k_3 also react successfully with 3 M chloride ion to make MH. The result that $\beta = 1.0$ can also be obtained from eq 12 by inserting the values (see above) of k_2 (in α) and k_1 and solving for β. If β is 1.0, then k_3 in eq 13 is equal to 4×10^9 M^{-1} s^{-1}, which corresponds to protonation of the π,π^* triplet by H$_3$O$^+$ at slightly below the rate constant for diffusion.

An alternative mechanism for acid catalysis is shown in Scheme II. We have derived quantum yield expressions for this scheme that agree with the behavior shown in Figures 1 and 2. This mechanism requires that deuterium would be incorporated at ring positions ortho and para to the nitro group for the photoreaction in D$_2$O containing 3 M DCl. That deuterium incorporation was not detectable in the isolated product by mass spectrometry nor by 300-MHz ^{1}H NMR caused us to dismiss this possibility. The mechanism has the additional problem that it must account for the 100% quantum yield enhancement by the acid catalyst at 3

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M [Cl⁻]. It is not clear why, if the first σ complex is virtually unselective in expelling Br⁻ vs Cl⁻, the protonated σ complex should be totally selective in expelling HBr rather than HCl, as would be required by Figure 2.

Precedent for our conclusion that the first-formed σ complex, M⁻, eliminates halogen too quickly for protonation to occur may be found in a report of Koch and co-workers.[31] They find that anion 3 exclusively eliminates chloride ion in ethanol rather than
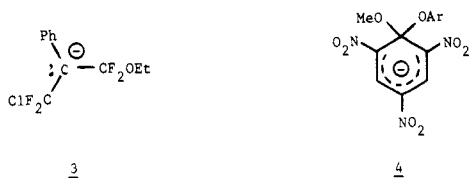

undergoing protonation at a rate near diffusion control. Indeed, we expect M⁻ to eliminate halogen unselectively on a time scale approaching the frequency of a molecular vibration, ca. 10^{-12} s. In support of this contention, elimination of leaving groups from nitro-stabilized Meisenheimer complexes has been shown to be strongly dependent on leaving group ability, as measured by the pK_a of the conjugate acid of the leaving group. A Brønsted plot for expulsion of phenoxide derivatives from 2,4,6-trinitroanisole adducts 4 is linear, with a slope of −0.70.[32] Phenoxide expulsion is faster than methoxide expulsion by a factor of 10^6.[33] Moreover, removal of one o-nitro group accelerates the expulsion of phenoxide by about (4 × 10^4)-fold,[34] to a rate constant estimated at 8 × 10^7 s⁻¹. If one removes all three conjugating nitro groups and changes the leaving group from a conjugate acid pK_a of 10 (phenoxide) to one of −5 or −7 (for Cl⁻ or Br⁻), one concludes that M⁻ would survive for not more than a few picoseconds.

We have reported[22,23] that chloride ion in water is capable of initiating chemistry with triplet nitrobenzene derivatives by an electron-transfer process. This process involves the n,π^* excited state; the radical intermediates involved can instigate efficient photoreduction, catalyzed by HCl, if 2-propanol is present at 0.1–0.2 M. When 3-bromonitrobenzene is irradiated in 2.9 M LiCl and 0.1 M HCl with 0.13 M 2-propanol present, photosubstitution giving 3-chloronitrobenzene proceeds normally but photoreduction does not occur. We regard this experiment as unequivocal evidence against a photosubstitution mechanism initiated by the electron-transfer process described earlier. This result is not unexpected since electron transfer provides a logical entree to photosubstitution para (or ortho), but not meta, to the nitro group,[1] since the odd electron in the nitrobenzene anion radical or its conjugate acid is delocalized to the ortho and para carbons, but not significantly to the meta one. Moreover, the result is consistent with our contention that the meta photosubstitution occurs from the π,π^* state rather than the n,π^* state. That the ^{3}n,π^* state does not generate appreciable HCl-catalyzed photoreduction under these conditions implies that the rate of its electron-transfer interaction with chloride ion at 3 M is slow relative to decay or that another step in the reaction[22] is unusually inefficient in this case.

At first glance it seems surprising that protonation of the $^3\pi,\pi^*$ state of 3-bromonitrobenzene should occur at a hydrogen ion concentration (0.25 M in 20% acetonitrile–water containing 3 M electrolyte is the midpoint of the dynamic effect in Figure 2)

comparable to that observed for protonation of the presumed triplet exciplex of nitrobenzene and chloride ion (0.05 M is the midpoint of the effect in 50% 2-propanol–water containing 6 M electrolyte).[22] On closer inspection, however, these proton acceptors may be quite similar. The modified valence bond representation of the π,π^* state (2) can be approximated closely by the valence bond structure (5). Corresponding valence bond representations of the exciplex are shown by 6 and 7. The electronic arrangement shown on the nitro group in 5 is identical with that for the nitro group in 6 and 7.
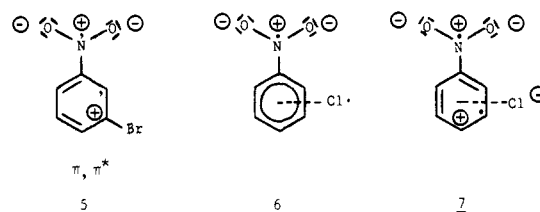
Attributing catalysis to protonation of the $^3\pi,\pi^*$ state rationalizes an otherwise puzzling result, namely, that the limiting quantum yield (0.021) at infinite [Cl⁻] is the same as the limiting quantum yield at infinite [H⁺] and 3.0 M [Cl⁻]. If the catalyst *intervened* on the reaction pathway *after* the primary process, causing some intermediate to form product efficiently rather than inefficiently, catalysis would be likely to cause the low uncatalyzed quantum yield (0.01 at 3.0 M [Cl⁻]) to increase by a factor much larger than the observed 2-fold. If, as we propose, hydrogen ion and chloride ion attack the same excited state, one that is present in a fixed, small amount because it is the upper state of two close-lying triplets, indeed the limiting quantum yields should be identical—barring differing efficiencies from the point of attack onward. That the extrapolated limiting quantum yields at infinite [H⁺] or infinite [Cl⁻] are much less than the estimated intersystem-crossing quantum yield of 0.7 indicates that the rate of populating the upper π,π^* state from the n,π^* state is not exceedingly fast. It must be comparable to or somewhat slower than the rate of decay.

Protonation of nitrobenzene derivatives in the triplet state in strongly acidic solutions has recently been proposed by others,[7,35] though they have not distinguished between the n,π^* and π,π^* states. That we are here proposing protonation of the π,π^* excited state ought not be construed as a change of our conclusion[22,23] that protonation of the n,π^* excited state is not likely. The n,π^* state still seems to us a poorer prospect for protonation than the ground state because the one-electron loss mainly from the non-bonding oxygen orbital (the protonation site) on excitation is less than compensated by the electron density contributed to that site by the half-occupied π^* orbital. In support of this conclusion, MNDO calculations on the ground state and first excited state (the n,π^* state) of nitrobenzene[36] reveal that the calculated ground-state dipole moment of 5.67 D (negative pole at the nitro group) is greatly reduced, to 0.885 D, on excitation.

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