Photolysis of Substituted Benzenediazonium Salts: Spin-Selective Reactivity of Aryl Cations

Susan M. Gasper,† C. Devadoss, and Gary B. Schuster*,†

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

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Abstract: The photolysis of a series of substituted benzenediazonium salts was studied by low-temperature and time-resolved spectral methods and by analysis of products formed in alcohol solutions at room temperature. The spin multiplicity of the ground state aryl cations formed by nitrogen loss from the diazonium salt is known to depend on the nature of the substituent. The low-temperature spectroscopic experiments confirm a triplet ground state when the cation contains a *p*-amino group. These triplet cations are detected directly in fluid solution for the first time, and their lifetimes are estimated. Analysis of products reveals that these cations react predominantly from the initially formed singlet state rather than their triplet ground state.

Introduction

The photolysis and thermolysis of benzenediazonium salts have been studied extensively because of their wide range of industrial and biological applications. They find use in photolithography,[1] photoresist technology,[2] and photopolymerization.[3] Further, they are used as photoaffinity labeling reagents for proteins[4] and for acetylcholine binding sites.[5] The chemistry of benzenediazonium salts and the properties of aryl cations have been reviewed by Zollinger[6] and by Ambroz and Kemp.[7] It is well-known that diazonium salts undergo dissociative loss of molecular nitrogen, initiated thermally or photochemically (eq 1), and it is assumed that in the dissociation process the

$$ArN_2^+ \xrightarrow[\Delta]{h\nu} Ar^+ + N_2 \qquad (1)$$

primary product is an aryl cation. Aryl cations have been characterized as hyper-reactive[8] since they appear to lack selectivity in their reactions.

Aryl cations bearing powerful electron-donating groups (particularly *p*-amino) have been observed by optical and by ESR spectral methods at 77 K in frozen matrices. Kemp and co-workers[9–11] recorded ESR spectra of these aryl cations in polymer films and in glassy matrices at 77 K. This observation unambiguously supports assignment of their ground states as having triplet spin multiplicity. More recently, Ambroz and co-workers[12,13] reported the first measurement of the UV–vis absorption spectra of some aryl cations. Irradiation of benzenediazonium salts in LiCl or 37% H_2SO_4 glasses at 77 K gives triplet cations that are stable under these conditions. It should be noted here that irradiation of benzenediazonium salts in frozen alcohol glasses was found to encourage formation of radical species identified either as $Ar^•$ or $ArH^{•+}$.[13]

Despite the success of the low-temperature spectroscopic experiments, there have been only a few reports of attempts to detect aryl cations at room temperature in fluid solution by time-resolved spectroscopic methods. Bottcher and co-workers[14] were the first to carry out flash photolysis of various diazonium salts in aqueous solution. Initially, they reported detecting the aryl cations and assigned them lifetimes of several microseconds, but later experiments required them to reassign the detected species to aryl radicals.[15] Scaiano and Kim-Thuan[16] examined the light-induced decomposition of benzenediazonium salts by nanosecond laser flash photolysis, but their attempt to observe the aryl cation directly failed because of the very short lifetimes of these species. However, they devised a clever method to monitor the cations indirectly by observing the bleaching of potassium chromate solution by protons generated during photolysis of benzenediazonium salts in aqueous solution. By competitive quenching of the aryl cations with halides, they estimated an upper limit for the lifetime of aryl cations of a few hundred picoseconds.

The properties of aryl cations have also been probed by computational methods. Initially there was a spirited debate about the spin multiplicity of the phenyl cation ground state. Two likely electronic configurations were considered: $(\pi)^6(sp^2)^0$ and $(\pi)^5(sp^2)^1$ (Chart 1). The former must be a singlet state, but the latter can be either a singlet or triplet.

From studies of the hydrolysis of benzenediazonium salts, Taft[17] proposed that the phenyl cation is a triplet in its ground

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† Current address: School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332.

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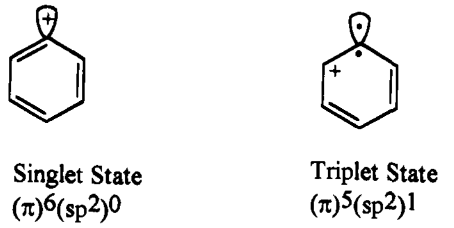
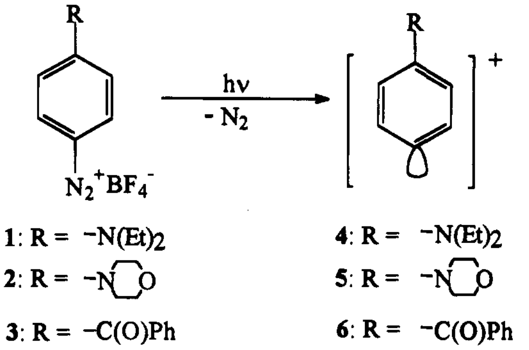
Chart 1. Electronic Configurations of the Phenyl Cation



state. This conclusion was challenged by Swain.[18] Pople and co-workers[19,20] applied *ab initio* molecular orbital methods to several aryl cations and concluded that the triplet will have lower energy than the singlet state only if it is substituted with an electron-donating group in the para position. This is a very important conclusion since modification of the substitution pattern of aryl cations will change the multiplicity of the ground state and presumably affect the chemical properties of the cation. This prediction has been verified by ESR spectroscopy,[11] but there are no reports known to us of attempts to correlate the reactivity of an aryl cation in solution with the predicted spin multiplicity of its ground state.

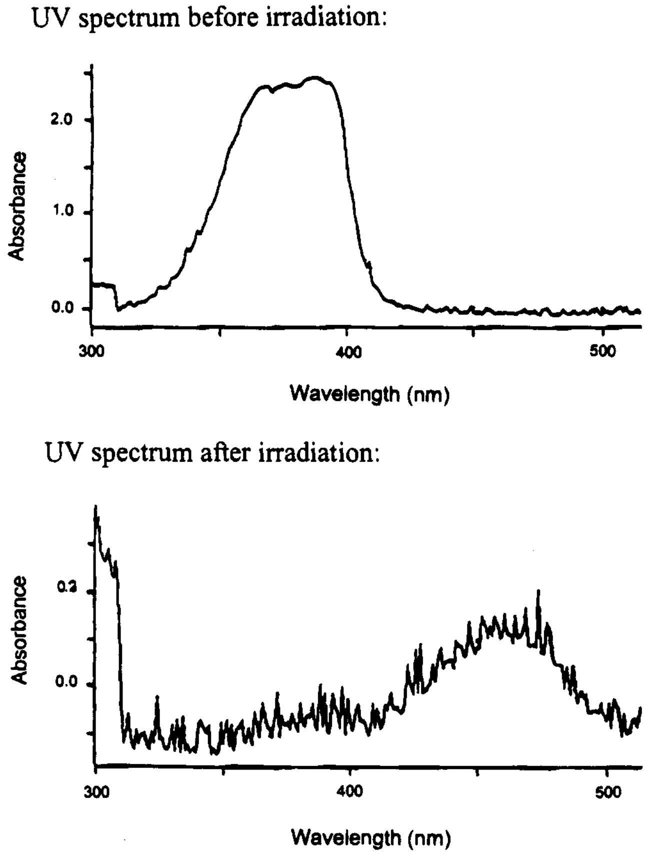
We report herein examination of the photolyses of 4-(diethylamino)benzenediazonium tetrafluoroborate (**1**), 4-morpholinobenzenediazonium tetrafluoroborate (**2**), and 4-benzoylbenzenediazonium tetrafluoroborate (**3**) by low-temperature absorption spectroscopy, time-resolved absorption spectroscopy, and analysis of reaction products. Aryl cations are detected directly in fluid solution for the first time. Although the corresponding aryl cations of **1** and **2** (**4** and **5**, respectively) both have triplet ground states, their direct irradiation in alcohol solvent gives, nearly exclusively, products of the singlet state reaction. Additionally, whereas the aryl cation formed from **3** (**6**) is expected to have a singlet ground state, product formation occurs from its triplet state.



Results

(1) Low-Temperature Absorption Spectroscopy. At room temperature, the absorption spectra of diazonium salts **1** and **2** both show strong bands with maxima at ca. 380 nm. In contrast, the absorption maximum of **3** occurs at ca. 245 nm, tailing to 360 nm. It should be noted that each of these three diazonium salts can be irradiated with the third harmonic of a Nd−YAG laser at 355 nm.

Shown in Figure 1 is the absorption spectrum of **2** dissolved in 37% H_2SO_4 recorded at 77 K (glass matrix). Irradiation of this sample at 350 nm for 10 min in a Rayonet photoreactor results in reduction of the intensity of the band at 380 nm and the concomitant appearance of a new band with maximum absorption at ca. 462 nm (Figure 1). Warming this irradiated solution to room temperature results in the disappearance of the 462 nm band. These results are similar to those reported by Ambroz and co-workers,[13] and on this basis, the 462 nm absorption is assigned to the triplet state of aryl cation **5**, formed by the loss of nitrogen from **2**. Similar results are obtained from irradiation of **1** under these conditions, except that the absorption maximum of the aryl cation occurs at ca. 442 nm. However, irradiation of benzoyl-substituted diazonium salt **3** does not lead to the appearance of a new absorption band. This observation is consistent with the theoretical prediction that aryl cation **6** will be a singlet in its ground state, since it lacks an electron-donating substituent. Consequently, it will be reactive under the conditions of this experiment.


UV spectrum before irradiation:

UV spectrum after irradiation:

Figure 1. (top) Absorption spectrum of **2** recorded in 37% H_2SO_4 at 77 K. (bottom) Same sample after irradiation for 10 min at 350 nm in a Rayonet reactor. Warming the sample to room temperature and recooling result in the regeneration of the absorption at 380 nm (mostly due to replenishment of the sample in the optical path) and disappearance of the band at 462 nm.

(2) Photolysis of Benzenediazonium Salts in Solution at Room Temperature. Examination of the photochemistry of diazonium salts **1**−**3** is restricted to polar solvents by solubility considerations. In simple alcohol solutions, such as methanol and ethanol, a spontaneous thermal reaction occurs that eventually results in the consumption of the diazonium salt. A similar process was observed by Becker and co-workers.[21] This reaction complicates product studies and spectroscopic measurements. However, we found that the thermal reaction occurs slowly, if at all, in 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) solution. The product studies and

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Chart 2. Photolysis Products

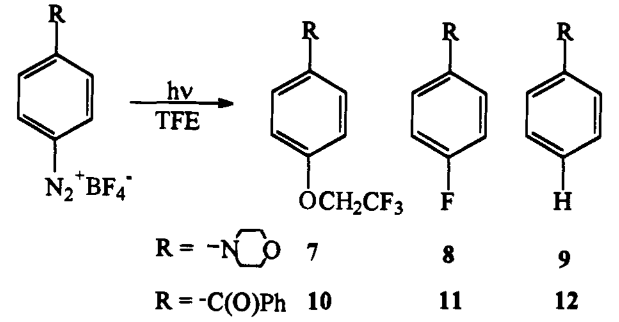

Table 1. Relative Product Yields for the Photolysis of **3** at 300 nm

solvent/atmosphere	ArH (**12**)	ArF (**11**)	$ArOCH_2CF_3$ (**10**)
TFE/air	18	26	56
TFE/N_2	96	2	2
HFP/air	negligible	30	70
HFP/N_2	57	15	28

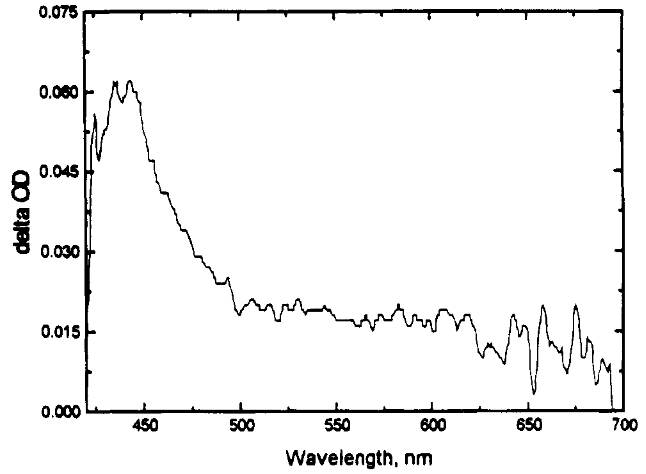

Figure 2. Time-resolved absorption spectrum recorded at 0 ps (see text) after irradiation of **1** in TFE solution with a 22 ps laser pulse at 355 nm.

time-resolved spectroscopic experiments reported below were carried out in these solvents.

Product formation can help in the assignment of the multiplicity of the reacting state of an aryl cation. Singlet cations possess an empty sp^2 orbital and thus are expected to react rapidly with alcohols to form ethers. Triplet cations, on the other hand, have an unpaired electron in a sp^2 orbital, and this "aryl radical" is expected to react with alcohols by hydrogen atom abstraction. Irradiation of **2** in nitrogen- or air-saturated TFE solution (2.00×10^{-3} M, 350 nm) gives three primary products (Chart 2); their relative yields were determined by GC: the trifluoroethyl ether (**7**) in >90% yield and *p*-fluoromorpholinobenzene (**8**) and morpholinobenzene (**9**) in a combined yield of <10%. Control experiments indicate that the aryl fluoride is not formed by a thermal Schiemann reaction, and since **8** is also formed in irradiations carried out in ethanol solution, the fluorine source must be the BF_4^- counterion. The quantum yield for the reaction (Φ_{-N_2}) is found to be 0.45. Similar results are obtained from the photolysis of **1**.

The direct irradiation of **3** in TFE solution (2.00×10^{-3} M, 300 nm) gives strikingly different product yields than those obtained from **1** and **2**, and the relative yields in this case depend on the concentration of oxygen in the solution. Irradiation of **3** in a N_2-purged solution gives benzophenone (**12**) in 96% yield, and trifluoroethyl ether **10** and the fluoride **11** are formed in 2% yield each. However, irradiation of **3** in air-saturated solution slows the rate of reaction measured by NMR spectroscopy ($\Phi_{-N_2} = 0.08$) and reduces the yield of **12** to 18% and the yields of **10** and **11** increase to 56% and 26%, respectively. When **3** is irradiated in an air-saturated HFP solution, the yield of ether increases to 70% and no benzophenone is detected among the products. These results are gathered in Table 1.

Interestingly, irradiations of **1** and **2** give ethers predominantly, and **3** (in N_2-purged solution) gives primarily the hydrogen-abstraction product **12**, which is a product indicative of the radical-like character of the reacting intermediate. These findings reveal that the products of photolysis of these diazonium salts, under these conditions, do not necessarily reflect the spin multiplicity of the aryl cation ground state.

Triplet sensitization of **2** was attempted in order to bypass its singlet excited state and to probe the chemistry of the triplet aryl cation **5**. The triplet state of *p*-methoxyacetophenone is quenched by **2**. Irradiation of a TFE solution containing **2** and the acetophenone at 313 nm (the *p*-methoxyacetophenone absorbs the light) gives different ratios of products than does direct irradiation. Triplet sensitization of **3** gives the same product ratios as does the direct irradiation. However, we have been unable to distinguish between electron transfer and energy transfer by the sensitizer.

(3) Transient Absorption Spectroscopy. Time-resolved spectroscopic examination of these diazonium salts was performed with a mode-locked Nd-YAG laser having a 22 ps pulse width (full width at half-maximum) at 355 nm. Figure 2 shows the transient absorption spectrum recorded at 0 ps (the pump and probe beams are exactly overlapped) after pulsed irradiation of **1** in TFE solution. The detected absorbance ($\lambda_{max} \approx 450$ nm) corresponds to the absorption assigned to the triplet of aryl cation **4** by low-temperature absorption and ESR experiments. It is important to note here that the change in absorbance recorded in this experiment is relatively small ($\Delta OD = 0.06$). This indicates either that the concentration of the detected transient is low or that it has a small extinction coefficient. The lifetime of **4** under the conditions of this experiment is too short to be resolved with the current apparatus. It decays within the laser pulse, leaving a weak, broad residual absorbance. Similar results are obtained in the flash photolysis of **2** ($\Delta OD_{460} = 0.06$).

Laser flash photolysis of diazonium salt **3** in TFE solution reveals important differences between it and **1** and **2**. Figure 3 shows transient absorption spectra recorded at −4 and 150 ps after irradiation of **3** with a 22 ps pulse. The spectrum shows relatively intense bands with peaks at ca. 425 and 615 nm. Both bands decay with similar time constants—when they are fitted to a monoexponential function, a decay time of 25 ps is found.

When the photolysis of **3** is carried out in the HFP solution, the transient absorption spectra obtained are similar to those seen in TFE but their decay behavior is different (Figure 4). The band with a maximum at 425 nm decays with complex kinetics, whereas the 615 nm band decays with an apparent lifetime of 26 ps. The decays are shown in Figure 4. This finding reveals that the two bands correspond (at least in part) to different species. Finally, it should be noted that the spectra show broad residual absorbances that do not decay out to 10 ns in both solvents. The complex kinetic behavior and residual absorption may indicate spectral overlap of the triplet state with another intermediate or reaction product.

The triplet−triplet absorption spectrum of *p*-nitrobenzophenone was recorded in TFE solution as a model to assist in identifying the transient species formed from irradiation of **3**.

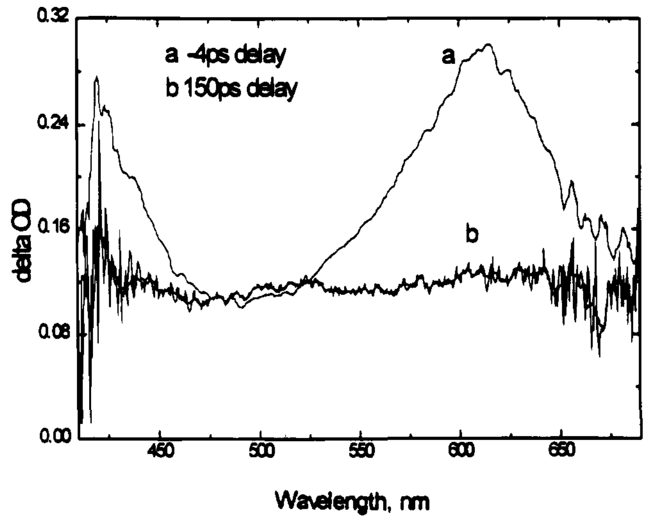

Figure 3. Time-resolved absorption spectra recorded after irradiation of **3** at 355 nm with a 22 ps laser pulse. The spectra are recorded at −4 and 150 ps.

Both nitro and diazonium groups are powerfully electron withdrawing; consequently they are expected to have similar effects on the spectra of benzophenone. This is confirmed experimentally for the ground-state absorption spectra, and we expect it to be true also for the triplet−triplet spectra. The triplet−triplet absorption spectrum of *p*-nitrobenzophenone (Figure 5) shows two bands with maxima at ca. 425 and 615 nm that are similar in shape and intensity ($\tau_{CH_3CN} = 150$ ps) to those observed for **3**. On this basis, we assign the transient absorbance detected in the flash photolysis of **3**, in part, to the triplet−triplet absorption of the diazonium salt.

Discussion

Our examination of the photolysis of benzenediazonium salts proceeded along three lines: low-temperature spectroscopy, time-resolved spectroscopy, and product analysis. Each set of experiments reveals a unique aspect of the properties of aryl cations, and from them, an understanding of the spin-selective chemical properties of these intermediates begins to emerge.

The low-temperature and time-resolved spectroscopic experiments are strictly consistent with previous experiments and theoretical predictions that assign triplet ground states to cations **4** and **5** and a singlet ground state to cation **6**. We are unable to detect **6** directly because of its high reactivity, so this conclusion is based upon negative evidence. However, the triplet ground states of both **4** and **5** are observed in the low-temperature and time-resolved experiments.

Direct irradiation of a benzenediazonium salt (ArN_2^+) leads to the formation of its excited singlet state ($^{1*}ArN_2^+$). As outlined in Chart 3 (nonproductive, energy-wasting steps are not shown), this excited state can lose N_2 as a singlet to form the singlet state of the aryl cation ($^1Ar^+$) or it can intersystem cross (ISC) to give its triplet state ($^{3*}ArN_2^+$). The triplet state of the diazonium salt can lose nitrogen to form the triplet aryl cation ($^3Ar^+$), or this state may be formed by ISC from $^1Ar^+$. The chemical and spectroscopic evidence indicates that benzenediazonium salt **3** follows a different path to aryl cation formation than do salts **1** and **2**.

Laser spectroscopy reveals the formation of the $^3Ar^+$ from irradiation of **1** and **2**. As far as we are able to determine, this is the first reported detection of an aryl cation in fluid solution. The lifetimes of triplet cations **4** and **5** in TFE or HFP solution are less than 15 ps and cannot be defined further with our present apparatus. As noted above, the absorbance measured for these cations is small, and this is probably indicative of its low concentration. This observation is consistent with the analysis of the products formed from steady-state irradiations of **1** and **2**.

The major products formed from the photolyses of **1** and **2** in TFE or HFP solution are their corresponding ethers. We associate these products with reactions of $^1Ar^+$. The evidence indicates that the mechanism for photolysis of diazonium salts **1** and **2** follows a path starting with loss of nitrogen from $^{1*}ArN_2^+$ to form $^1Ar^+$, which is faster than ISC from the excited diazonium salt. In turn, $^1Ar^+$ reacts with alcohol (ROH) to form the corresponding ether faster than ISC to its triplet ground state. This is consistent with the small absorbance changes observed in both the low-temperature and laser spectroscopy. The small amount of short-lived $^3Ar^+$ detected by laser spectroscopy is associated with either incomplete ISC of $^{1*}ArN_2^+$ to form $^{3*}ArN_2^+$ and its subsequent loss of nitrogen or ISC of $^1Ar^+$ to its ground state in competition with its reaction with ROH.

The mechanism for photolysis of diazonium salt **3** is more complex than it is for **1** and **2**. Since **3** may be viewed as a benzophenone derivative, it is expected that ISC of $^{1*}ArN_2^+$ will be accelerated.[22] The detection of $^{3*}ArN_2^+$ by laser spectroscopy supports this position. Loss of nitrogen from $^{3*}ArN_2^+$ gives $^3Ar^+$ initially. Since the triplet is not the ground state of this cation, it may undergo ISC to the singlet before it reacts, or it may react from its first-formed triplet state. The chemical evidence suggests that the predominant path followed depends on the reaction conditions.

In nitrogen-purged TFE solution, the major product formed from the photolysis of **3** is benzophenone, but in air-saturated solution, the trifluoroethyl ether dominates the product mixture. The effect of oxygen on the products could be attributed to its quenching of $^{3*}ArN_2^+$, but this seems unlikely. If oxygen effectively quenched $^{3*}ArN_2^+$, then the predominant product observed from photolysis in oxygen-containing solution would result from N_2 loss from $^{1*}ArN_2^+$ to form $^1Ar^+$ and its subsequent capture by ROH to give the ether. However, the lifetime of $^{3*}ArN_2^+$ is less than 100 ps, and the oxygen concentration in air-saturated solutions is too low to effectively quench a species with such a short lifetime.

An alternative explanation for the effect of oxygen on the photolysis of **3** is that it inhibits a radical chain reaction[23a] (see Chart 4) initiated by reaction of $^3Ar^+$ (or by $^{3*}ArN_2^+$ and subsequent nitrogen loss) with ROH. Hydrogen atom abstraction by $^3Ar^+$ from ROH, in competition with ISC, would give the arene radical cation ($ArH^{\bullet+}$) and the alcohol-derived radical ($CF_3CH^{\bullet}OH$). Electron transfer from the alcohol radical (followed by proton loss) within the encounter complex will generate ArH and the oxidized alcohol, but escape of $CF_3CH^{\bullet}$-OH could initiate a chain reaction by reducing ArN_2^+ to $ArN_2^{\bullet}$. Hydrogen abstraction by $ArN_2^{\bullet}$ (before or after loss of N_2) gives ArH and regenerates $CF_3CH^{\bullet}OH$ to continue the chain. A related mechanism might account for the formation of ArF from BF_4^-, since its yield increases in air-saturated solution.[23b]

The intervention of radical chain reactions would complicate the interpretation of the methoxyacetophenone-sensitized reaction of **2**. The triplet of the acetophenone is effectively quenched by ArN_2^+, and this could lead to $^{3*}ArN_2^+$ or $ArN_2^{\bullet}$

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(23) (a) A related effect of O_2 has been observed previously in photolysis of diazonium salts. Becker, H. G. O.; Israel, G. *J. Prakt. Chem.* **1979**, *321*, 579. (b) Formation of fluoride-containing products in the photolysis of diazonium salts has been suggested also to arise from reaction of the cation with BF_4^- in ion pairs.[23a]

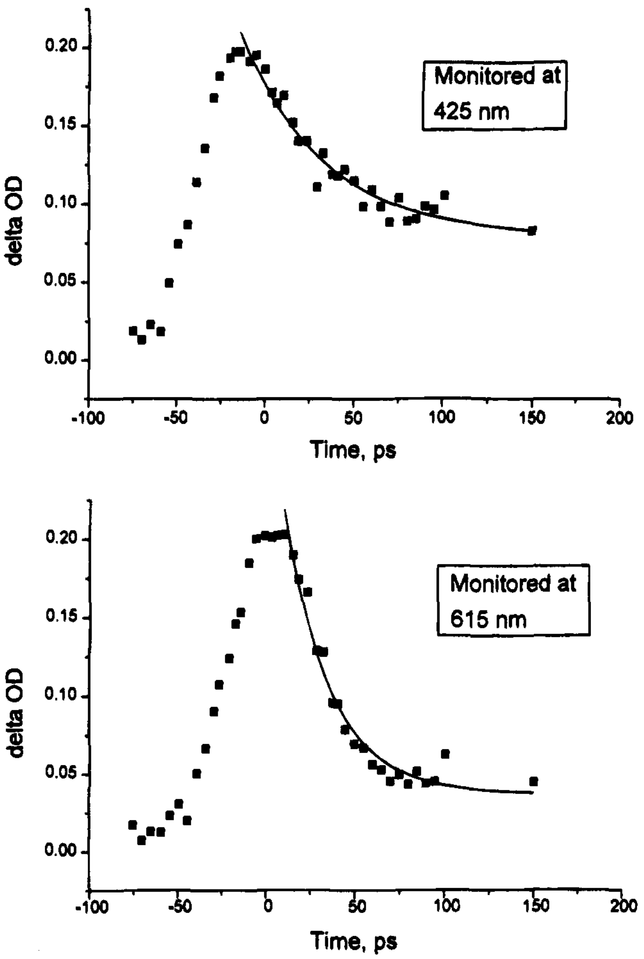

Figure 4. Kinetic analysis of the decay of the transient absorptions recorded after irradiation of **3** in a TFE solution at 355 nm with a 22 ps laser pulse: (top) monitored at 425 nm; (bottom) monitored at 615 nm. In both cases, the solid points are the experimental data and the line is the best fit to a single exponential decay.

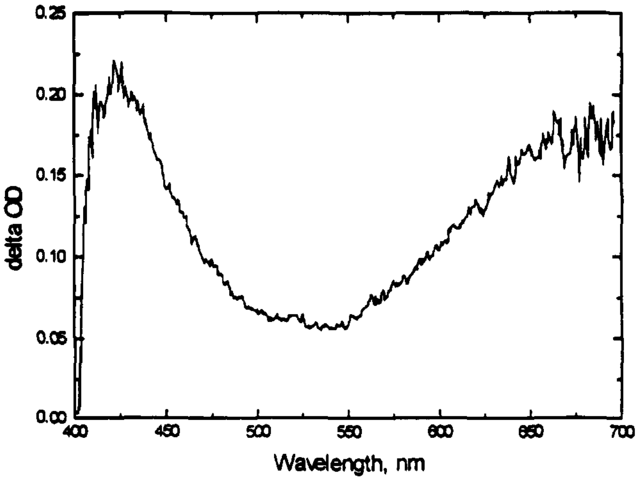

Figure 5. Absorption spectrum recorded 22 ps after irradiation of *p*-nitrobenzophenone in TFE solution at 355 nm with a 22 ps laser pulse.

Chart 3. Mechanism of Photolysis

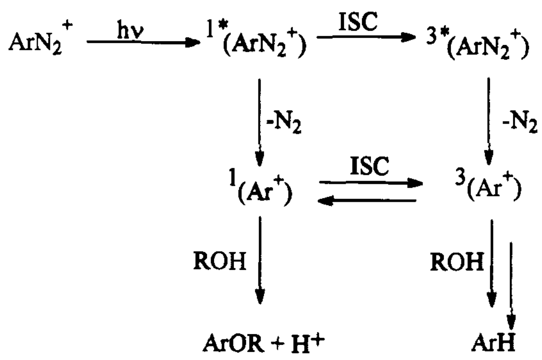

Chart 4. Chain Reaction Mechanism

Initiation

$^3Ar^+ \xrightarrow{CF_3CH_2OH} ArH^{+\bullet} + CF_3\dot{C}HOH$

$^{3*}ArN_2^+ \xrightarrow{TFE} ArHN_2^{+\bullet} \xrightarrow{-N_2} ArH^{+\bullet} + CF_3\dot{C}HOH$

Propagation

$CF_3\dot{C}HOH + ArN_2^+ \longrightarrow ArN_2^\bullet + CF_3CHO + H^+$

$ArN_2^\bullet + CF_3CH_2OH \xrightarrow{-N_2} ArH + CF_3\dot{C}HOH$

Termination

$CF_3\dot{C}HOH + ArH^{+\bullet} \longrightarrow ArH + CF_3CHO + H^+$

(by electron transfer). Electron transfer has been observed previously in the sensitization of diazonium ions.[24,25] Although the reduction potential of **2** is not known, it is electron-rich due to the presence of the morpholino group. Thus, it is possible that electron transfer is slowed down. Loss of nitrogen from $^{3*}ArN_2^+$ will give the triplet ground state of aryl cation **5** directly, and hydrogen abstraction by this species will lead eventually to the observed product (**9**). Alternatively, $^{3*}ArN_2^+$ itself could abstract a hydrogen atom before it loses nitrogen, and this path, too, would lead eventually to **9**. In either event, the methoxyacetophenone-sensitized experiment indicates that triplet intermediates are not formed in significant amount in the direct irradiation of **1** or **2**.

Finally, the formation of diazenyl radicals such as $ArN_2^\bullet$ may account for the residual absorption detected after decay of $^3Ar^+$ and $^{3*}ArN_2^+$ and the complex kinetics observed for $^{3*}ArN_2^+$. Support for this possibility comes from measurements by Becker and co-workers,[26] who find lifetimes of 20−3600 ns for $ArN_2^\bullet$.

Conclusion

The products formed in the photolysis of substituted benzenediazonium salts depend on the spin multiplicity of the reacting intermediates, which is not necessarily the multiplicity of the *ground* electronic state of the cation. The singlet state of the aryl cation is so reactive that under normal conditions it is nearly completely consumed before it can intersystem cross to the triplet, if that is the ground state. In fluid solution at room temperature, the lifetime of triplet aryl cations is less than 15 ps. These intermediates can also react irreversibly before intersystem crossing to a lower lying singlet state.

Experimental Section

General Procedure. UV−vis absorption spectra were recorded on a Cary 1E spectrophotometer. ^1H NMR spectra were taken on a General Electric QE-300 spectrometer. Pulse delays were set at 2 s to account for long relaxation of diazonium salts due to quadrupole moments. GC

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mass spectra were recorded on an HP-5890 gas chromatograph equipped with an HP 5970 Series mass selective detector. Solutions of diazonium salts for laser spectroscopy were prepared in either TFE or HFP to have absorbance at 355 nm between 1.5 and 2 in a 1 mm path length cell. The picosecond spectrometer is described elsewhere.[25] HFP and TFE were purchased from Aldrich Chemical Co. and were distilled before use. Photoproducts **7**, **9**, **11**, and **12** were purchased from Aldrich and recrystallized from ethanol. Elemental analyses were performed by the University of Illinois Microanalysis Laboratory.

Low-Temperature Photolysis. Solutions (1×10^{-4} M) of the diazonium salts were prepared in either 37% H_2SO_4 or absolute ethanol. Aliquots were placed in quartz ESR tubes and sealed. The tubes were submerged in a quartz Dewar filled with liquid nitrogen and were irradiated in the Rayonet photoreactor at the appropriate wavelength.

Steady State Photolysis. Solutions (2×10^{-3} M) of diazonium salts in the appropriate solvent were prepared in 1 cm path length quartz or pyrex cells. The cell was placed in a Rayonet photochemical reactor where it was purged with either air or nitrogen for at least 2 min. After purging, the solution was irradiated for 3 min with stirring by gas bubbles or a magnetic stir bar. For salts **1** and **2**, 350 nm lamps were used while 300 nm lamps were used for diazonium salt **3**. After irradiation, the solvent was evaporated under reduced pressure and the products were dissolved in a known amount of ether containing dicyclohexane as an internal standard. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph equipped with an OV-1 capillary column and a flame ionization detector. Product identity was confirmed by GCMS and comparison with authentic samples except for *p*-morpholinofluorobenzene. This product was identified only by GCMS.

Quantum Yield Measurements. Solutions of **2** in TFE were irradiated using the 313 nm line of a Hg–arc lamp, and the decrease in the absorbance at 380 nm was monitored by UV spectroscopy. The photon flux was measured using an azobenzene actinometer. A solution of **3** in TFE was irradiated in a Rayonet photoreactor at 300 nm and the solvent removed under reduced pressure. The resulting mixture was dissolved in CD_3CN containing a known amount of *p*-dioxane as an internal standard and the conversion of **3** measured by integration of the ^1H NMR (400 MHz) spectrum. The photon flux was measured using a potassium ferrioxalate actinometer.

***p*-Morpholinobenzenediazonium Tetrafluoroborate.** To a mixture of 6.2 mL of concentrated HCl and 6.2 mL of water in a 50 mL round bottom flask was added 4.45 g (0.025 mol) of *p*-morpholinoaniline. The brick red solution was cooled to 0 °C in an ice bath. With mechanical stirring, 1.8 g (0.026 mol) of $NaNO_2$ dissolved in the minimum amount of water was added dropwise over a period of 15 min. During the addition, dry ice was added periodically to keep the temperature near 0 °C. Upon complete addition of $NaNO_2$, 3.78 g of $NaBF_4$ (0.034 mol) dissolved in 12 mL of water was added and the resulting solution stirred at 0 °C for 45 min. During this time, a powdery yellow precipitate was formed. The precipitate was filtered and washed with cold aqueous 5% $NaBF_4$ solution and cold ether. The yellow solid was dissolved in acetone and filtered. Ether was added to precipitate the pure diazonium salt, which was then dried over $CaSO_4$ in a vacuum desiccator (53% yield). Decomposition temperature: 142 °C. UV (CF_3CH_2OH): λ_{max} 380 nm, ϵ_{max} 44 000 $M^{-1}\ cm^{-1}$. IR (KBr): $\nu = 2162.5\ cm^{-1}$. ^1H NMR (CD_3CN): δ 3.69 (t, 4H), 3.77 (t, 4H), 7.03 (d, 2H), 8.01 (d, 2H). Anal. Calcd for $C_{10}H_{12}N_3OBF_4$: C, 43.36; H, 4.36; N, 15.17. Found: C, 43.32; H, 4.35; N, 15.17.

***p*-Benzoylbenzenediazonium Tetrafluoroborate.** To a mixture of 1.86 mL of concentrated HCl and 1.86 mL of water in a 25 mL round bottom flask was added 1.48 g (7.5 mmol) of *p*-aminobenzophenone. The yellow slurry was cooled to 0 °C in an ice bath. With magnetic stirring, 0.52 g (7.5 mmol) of $NaNO_2$ dissolved in the minimum amount of water was added dropwise over a period of 7 min. Dry ice was added periodically to keep the temperature near 0 °C. Upon complete addition of the $NaNO_2$, 1.13 g (10 mmol) of $NaBF_4$ dissolved in 3 mL of water was added and the resulting solution stirred at 0 °C for 45 min. After this time, the precipitate formed and was removed by filtration and washed with cold aqueous 5% $NaBF_4$ solution and cold ether. A pink solid was isolated and, after three precipitations from acetone with ether, gave a white solid that was dried over $CaSO_4$ in a vacuum dessicator (20% yield). Decomposition temperature: 95 °C. UV (CF_3CH_2OH): λ_{max} 263 nm, ϵ_{max} 19 000 $M^{-1}\ cm^{-1}$. NMR (CD_3CN): δ 7.58 (t, 2H), 7.7–7.8 (d, t, 3H), 8.13 (d, 2H), 8.62 (d, 2H). Anal. Calcd for $C_{13}H_9N_2OBF_4$: C, 52.75; H, 3.06; N, 9.46. Found: C, 52.67; H, 3.07; N, 9.45.

(2,2,2-Trifluoroethoxy)-*p*-morpholinobenzene. A solution of 0.16 g (0.6 mmol) of *p*-morpholinobenzenediazonium tetrafluoroborate in 100 mL of TFE was irradiated with stirring at 350 nm in a Rayonet for 20 min. The solvent was removed by distillation and the residue washed with a saturated $NaHCO_3$ solution and extracted with ether. The ether layer was dried with $MgSO_4$, filtered, and concentrated by rotary evaporation to afford a brown film which was purified by column chromatography on silica gel using 20% ethyl acetate in petroleum ether as an eluent. The pure aryl ether was obtained as a white powder in 23% yield. Mp: 48 °C. ^1H NMR (CD_3CN): δ 3.01 (t, 4H), 3.74 (t, 4H), 4.45 (q, 2H), 6.90 (s, 4H). Anal. Calcd for $C_{12}H_{14}F_3NO_2$: C, 55.17; H, 5.40; F, 21.82; N, 5.36. Found: C, 55.15; H, 5.41; F, 21.67; N, 5.37.

(2,2,2-Trifluoroethoxy)-*p*-benzophenone. A solution of 0.34 g (1.1 mmol) of *p*-benzoylbenzenediazonium tetrafluoroborate in 100 mL of TFE was added to a 250 mL round bottom flask equipped with a condenser and magnetic stirrer. The solution was heated at reflux in the dark for 3 h. The solvent was removed by distillation and the residue washed with a saturated $NaHCO_3$ solution and extracted with ether. The ether layer was dried with $MgSO_4$, filtered, and concentrated by rotary evaporation to afford a brown oil. The aryl ether was purified by column chromatography on silica gel using 20% ethyl acetate in petroleum ether as an eluent. The pure aryl ether was obtained as a white powder in 40% yield. Mp: 65 °C. ^1H NMR (CD_3CN): δ 4.60 (q, 2H), 7.10 (d, 2H), 7.5–7.8 (t, t, d, d, 7H). Anal. Calcd for $C_{15}H_{11}F_3O_2$: C, 64.29; H, 3.96; F, 20.34. Found: C, 64.23; H, 3.91; F, 20.09.

(1,1,1,3,3,3-Hexafluoro-2-propoxy)-*p*-benzophenone. A solution of 0.64 g (2.0 mmol) of *p*-benzoylbenzenediazonium tetrafluoroborate in 15 mL of HFP was added to a 25 mL round bottom flask equipped with a condenser and magnetic stirrer. The solution was heated at reflux in the dark for 24 h. The solvent was removed under reduced pressure and the residue washed with a saturated $NaHCO_3$ solution and extracted with ether. The ether layer was dried with $MgSO_4$, filtered, and concentrated to afford a brown oil. The aryl ether was purified by column chromatography on silica gel using 95:5 hexane:ethyl acetate as an eluent. The pure aryl ether was obtained as a white powder in 35% yield. Mp: 44 °C. ^1H NMR (CD_3CN): δ 5.70 (septet, 1H), 7.26 (d, 2H), 7.53 (t, 2H), 7.63 (t, 1H), 7.82 (d, 2H), 7.84 (d, 2H). Anal. Calcd for $C_6H_{10}F_6O_2$: C, 55.18; H, 2.89. Found: C, 56.46; H, 2.88. HRMS: calcd for $C_{16}H_{10}F_6O_2$ 348.0585, found 348.0556.

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