Photoinduced Electron-Transfer Reactions: Highly Efficient Cleavage of C−N Bonds and Photogeneration of Tertiary Amines[1]

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The photocleavage of tertiary amine from tetraphenylborates complexed, via ammonium ions, to various chromophore electron acceptors has been studied by laser-flash photolysis. Electron transfer from the borate anions to acceptor excited states is determined to be the primary photochemical step leading to homolytic C−N bond scission and concomitant formation of the corresponding tertiary amine. This pathway was established by direct observation of *p*-benzoylbenzyl (**7a**), *p*-acetylbenzyl (**7b**), *β*-naphthylmethyl (**7c**), and 7-methoxycoumarin-4-methyl (**7d**) after laser-flash photolysis from *N*-(4-benzoyl)benzyl-*N*,*N*,*N*-tributylammonium tetraphenylborate (**1a**), *N*-(4-acetyl)benzyl-*N*,*N*,*N*-trimethylammonium tetraphenylborate (**1b**) *N*,*N*,*N*-tributyl-*N*-(2-methylnaphthalene)ammonium tetraphenylborate (**1c**), and *N*,*N*,*N*-tributyl-*N*-(4-methyl-7-methoxycoumarin)ammonium tetraphenylborate (**1d**), respectively. The presence of radicals (**7a**−**7d**) was also suggested by the reaction products. Comparison of the rate constants for quenching of the triplet states from excited (**1a**, **1b**) and singlet states from (**1c**, **1d**) reveals the efficiency of C−N bond cleavage. Quenching constants in the range of 10^9-10^{12} M^{-1} s^{-1} were observed. Differences are accounted for in terms of variations in the electron-accepting excited states and structural characteristics of the chromophore acceptors.

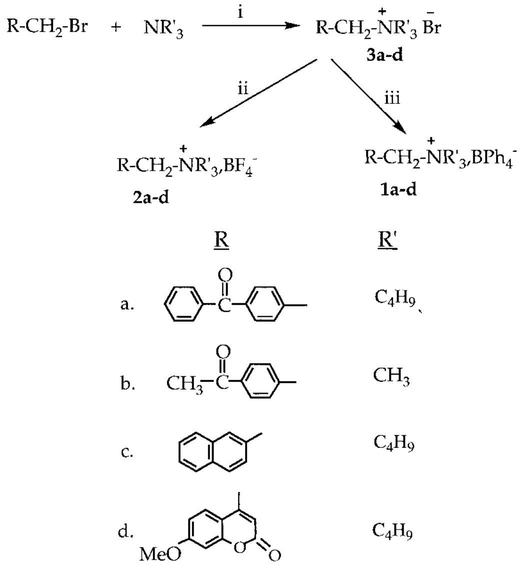
Introduction

One method of generating radical ions involves deposition of light energy into acceptor or donor molecules, thus converting them into potent redox reagents capable of undergoing electron transfer with ground-state substrates.[2] Radical ions may undergo unimolecular fragmentation reactions to radicals and ions.[3,4] Rapid bond-cleavage reactions that take place after electron transfer represent an excellent route for the photogeneration of a variety of reactive intermediates.[5] If the system is self-destructive such that the concomitant/subsequent bond-cleavage reaction is rapid, energy-wasting back electron transfer processes between the initially formed redox pair can, in principle, be avoided.

Though extensive studies have been reported on the fragmentation of C−C bonds in photogenerated radical ions,[6] C−N bond scission from photogenerated reactive intermediates is less common.[7] Photolabile amine precursors are, however, reported to be useful as photocleavable amino acid precursors in biological systems.[8] Certain photoreactive[9] carbamates[10] are known to generate both primary and secondary amines. Since tertiary amines are better catalysts than primary and secondary amines,[11] particularly in acyl transfer reactions where the formation of undesirable amide-related products need be avoided,[12] we pursued systems that dissociate by C−N cleavage to produce tertiary amines and have recently shown them to be a useful component in imaging thin polymer films.[13]

The experimental system selected was based on previous work and involved tetraphenylborate as the electron donor. Different chromophores (Scheme 1) served as the electron acceptors. A simple unimolecular C−N bond scission in the formed radical ions served as a model for tertiary amine formation while providing an internal probe of photoelectron-transfer dynamics.[14]

SCHEME 1: Synthesis of Amine Precursors



(i) ether, room temperature, overnight; (ii) HBF_4 48 wt% in H_2O; (iii) $NaBPh_4$, H_2O, rt.

Synthesis and Steady-State Spectroscopy

Precursors of *N*-(4-benzoyl)benzyl-*N*,*N*,*N*-tributylammonium tetraphenylborate (**1a**), *N*-(4-acetyl)benzyl-*N*,*N*,*N*-trimethylammonium tetraphenylborate (**1b**), *N*,*N*,*N*-tributyl-*N*-(2-methylnaphthalene)ammonium tetraphenylborate (**1c**), and *N*,*N*,*N*-tributyl-*N*-(4-methyl-7-methoxycoumarin)ammonium tetraphenylborate (**1d**) were synthesized according to the procedures shown in Scheme 1. Bromomethyl precursors were converted to ammonium bromide salts **3a**−**d** by reaction with tertiary amines in 78−86% yield. The reactions were performed in

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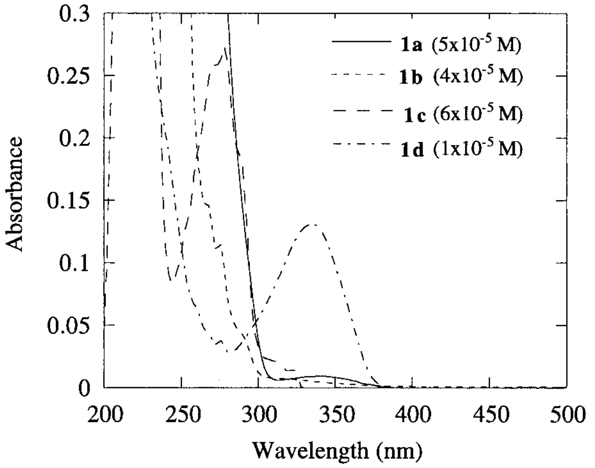


Figure 1. Absorption spectra of **1a**−**1d** in acetonitrile.

TABLE 1: Product Studies for the Photolysis of 1a−1d in Acetonitrile (2.5 × 10^{-2} M) for 1 h

		products (% yield)[b]	
compd	conversion (%)[a]	5	6
1a	95	38	16
1b	70	40	15
1c	12	34	11
1d	98	43	9

[a] Determined by ^{1}H NMR analysis, cf. text. [b] Calculated on basis of conversion.

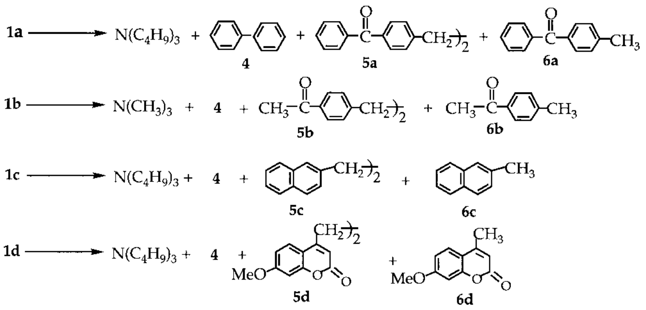
solvents from which the resulting ammonium bromide precipitated under strictly anhydrous conditions. Borate complexes **1a**−**d** were obtained by reaction of the ammonium bromide with the sodium salt of tetraphenylborate in water. The borates were stable for months at room temperature.

The steady-state absorption spectra of **1a**,**b** and **1d** in acetonitrile had n−π* transitions centered at 335−340 nm though the molar absorption coefficients differed (Figure 1). The spectra of **1a**,**b** and **1d** in nonpolar solvents were similar in shape to those in acetonitrile, however, were significantly shifted to the red, suggesting the lower excited singlet state was an n−π* state. The molar extinction coefficient for **1d** was 13 000 M^{-1} cm^{-1} (334 nm) in acetonitrile indicating that the π−π* transition overlapped with the n−π* transition in this region.[15] The spectrum of **1c** evidenced only π−π* transitions with a substantial tail at longer wavelengths. All spectra were independent of anion structure and essentially identical to those of the chromophores in the absence of complexing agent in the same solvent. Thus, there was no indication of charge-transfer complex formation.

Photolysis Products

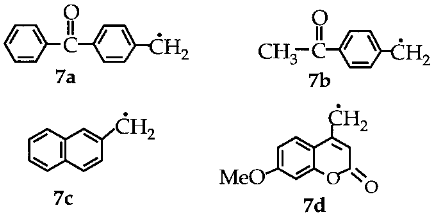
Nondegassed solutions (acetonitrile) were irradiated in a Rayonet photoreactor (λ_{max} = 350 nm). The efficiency of C−N bond cleavage in **1a** and **1d** proved to be high, and 95% and 98% conversions, respectively, were obtained after just 1 h. Because of the low absorption of **1b**,**c** around 350 nm, **1b** showed moderate conversion (70%) while **1c** gave only 12% conversion (Table 1). Conversion to tertiary amine was determined by ^{1}H NMR from the disappearance of the methylene peaks around 4.40 ppm (for **1a**) and the appearance of a new peak at 2.43 ppm due to the formation of amine. To assess if any products resulted from secondary photoprocesses, **1a** was irradiated to less than 20% conversion, and product distributions were found to be identical under these conditions. Likewise, no amine was formed in control experiments carried out under similar reaction conditions (vide infra) with **2a**−**2d** when the nonreducing gegenion BF_4^- was present. Excited-state electron transfer from tetraphenylborate to chromophore acceptor was thus responsible for photocleavage of the C−N bond.

SCHEME 2: Photolysis Products of 1a−d in CH_3CN at 350 nm



The products formed from irradiation of **1a**−**d** in acetonitrile were identified by comparing HPLC retention times with authentic samples, as well as from MS fragmentation patterns (Scheme 2). Since trends in the formation of products were similar in all cases, the mechanism of photocleavage of the ammonium borates appeared to be a general process. When reactions were performed on a preparative scale, the yields of isolated products represent only lower limits but product distributions were similar in both small-scale and large-scale reactions. The respective tertiary amines were produced in virtually quantitative yields from **1a**−**1d** as determined by ^{1}H NMR spectroscopy. Major radical-coupling products were formed by **7a**−**7d** (Chart 1), while products **6a**−**6d** derived by hydrogen abstraction were minor (Table 1). At room temperature, photodimer **5d** was quite insoluble in acetonitrile and precipitated during the photolysis. This product was identified by high-resolution mass spectrometry and elemental analysis.

CHART 1



Quenching Experiments

The primary process of C−N bond cleavage was further studied by quenching experiments using, as the electron donor, tetrabutylammonium tetraphenylborate ($Ph_4B^-Bu_4N^+$) which successfully quenched the triplet states of **2a**,**b** and the singlet states of **2c**,**d** in acetonitrile at room temperature. In the case of triplet-state quenching, addition of $Ph_4B^-Bu_4N^+$ resulted in a change in the form of the transient decay profile, while singlet-state quenching resulted in a change of emission intensity (excited at 320 nm for **2c** and 355 nm for **2d**). In all cases, linear Stern−Volmer plots were observed (Figure 2). Rate constants for quenching were determined by measuring the effects of the additive on the lifetimes of the triplet or singlet states and are shown in Table 2. The quenching rate is not affected by the substitutents on the quaternary nitrogen atom.

On the basis of the oxidation potentials of tetraphenylborate,[5a] the reduction potentials of **2a**−**d**, and the energy of their excited

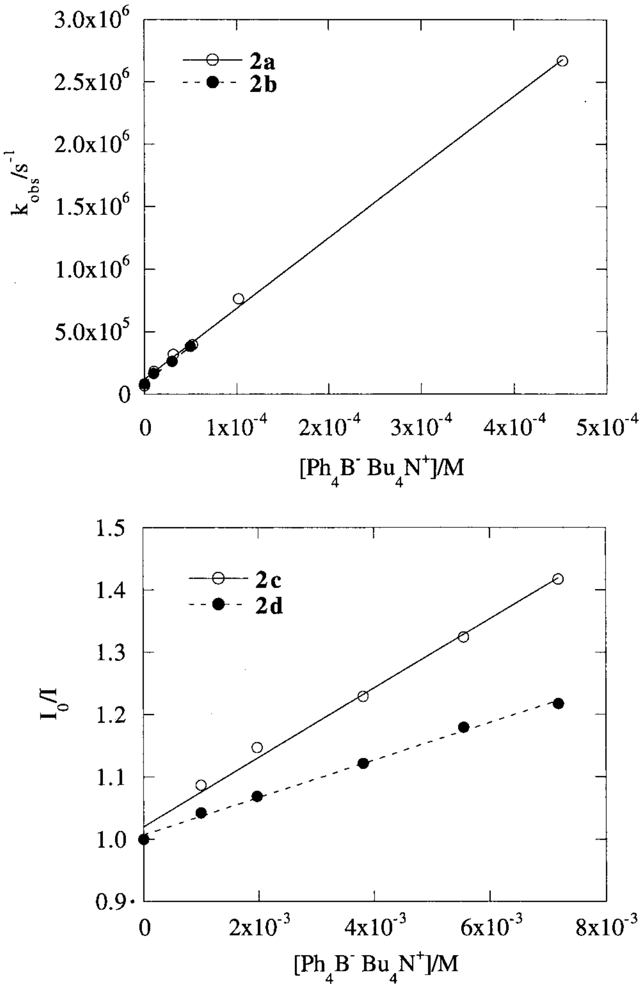


Figure 2. Triplet-state quenching of **2a**,**b** and singlet-state quenching of **2c**,**d** by tetrabutylammonium tetraphenylborate in acetonitrile.

TABLE 2: Reduction Potentials (E_{red}), Free Energy Changes ($\Delta G°$) for Electron Transfer, and Quenching Rate Constants (k_q) for the Excited States of 2a−2d with Tetrabutylammonium Tetraphenylborate in Acetonitrile

compds	E_{red} (V) vs SCE	$E_{\mathrm{s,t}}$ (eV)	$\Delta G°$ (eV)	k_q (M^{-1} s^{-1})
2a	−1.49	3.01(t)[a]	−0.62	5.65×10^9
2b	−1.62	3.16(t)[b]	−0.64	5.76×10^9
2c	−2.10	3.88(s)[c]	−0.88	6.25×10^9 [e]
2d	−1.30	3.63(s)[d]	−1.43	5.94×10^{12} [f]

[a] Reference 34. [b] Reference 35. [c] Reference 36. [d] Reference 37. [e] $I_0/I = 1 + k_q\tau_s\ [Ph_4B^-]$; $\tau_s = 8.9$ ns for 1-cyanonaphthalene.[37] [f] $I_0/I = 1 + k_q\tau_s\ [Ph_4B^-]$; $\tau_s = 5.1$ ps ($\Phi_f = 0.022$ for **2d**); $\tau_f = 0.23$ ns for 4-methyl-7-methoxycoumarin in methanol.[38]

states, the free energy change ($\Delta G°$)[16] associated with electron transfer can be estimated (Table 2). Electrochemical measurements were carried out in acetonitrile using cyclic voltammetry with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. In all cases, wave characteristics indicated irreversible one-electron reduction at peak voltages (Table 2). This was taken as evidence for rapid bond cleavage reaction (on the time scale of the electrochemical experiments) of all reduced chromophore tertiary ammonium cations.

Quantum Yields

Quantum yields for the photodecomposition of borates **1a**−**d** in CH_3CN (5×10^{-3} M) were determined at 366 nm in a quartz cell having a path length of 10 cm. The quantum yields of photodecomposition Φ_d of **1a**, **1b**, **1c**, and **1d** in CH_3CN were 0.49, 0.42, 0.20, and 0.07, respectively. In CH_3CN, the ammonium borates were in ionic equilibrium; thus, diffusion of the ions was required for electron-transfer reaction. Participation of longer lived triplet states in **1a** and **1b** accounted for higher values of Φ_d, while the shorter lifetimes of the singlet state of both **1c** and **1d** decreased the value of Φ_d in acetonitrile. Photodecomposition of borate **1d** in PhH (3×10^{-4} M) was found to proceed with $\Phi_d = 0.20$. In nonpolar solvents such as PhH, borate **1d** existed as a tight ion pair, thus eliminating the diffusion-controlled step.

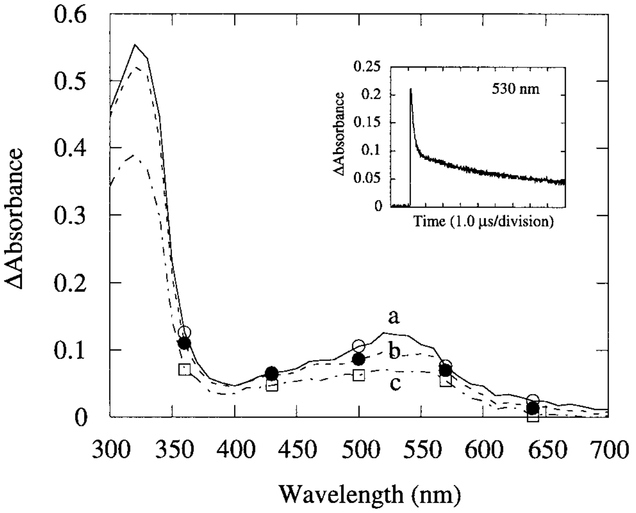


Figure 3. Transient absorption spectra obtained by laser photolysis (355 nm) of **1a** in acetonitrile (1×10^{-3} M): (a) 300, (b) 590, and (c) 3200 ns. Insert: time profile at 530 nm.

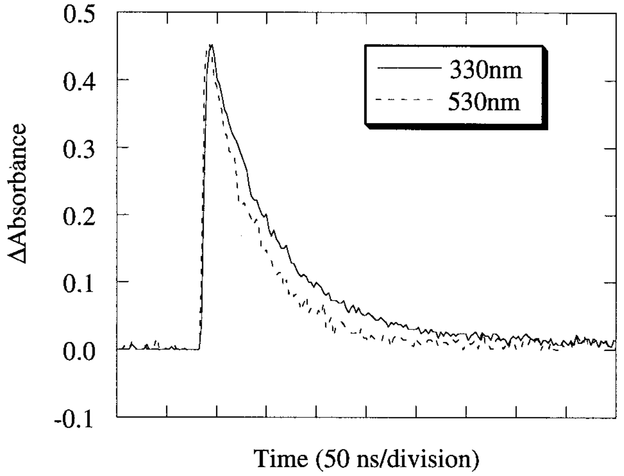


Figure 4. Time profile of transient absorption (normalized) of **1a** in acetonitrile in the presence of oxygen (20-min bubbling).

Laser-Flash Photolysis

Laser-flash photolysis of **1a** in degassed acetonitrile (1×10^{-3} M) at 355 nm (7 ns, 70 mJ) lead to a transient with absorption maxima at 335 and 530 nm (Figure 3). Transient absorption decay at 530 nm consisted of two components. The lifetime of the faster component was 200 ns on the basis of a first-order kinetic law. The decay of the slower component was consistent with a second-order rate law ($k/\epsilon = 1.17 \times 10^6$ cm s^{-1}). Both absorption bands (335 and 530 nm) were quenched by oxygen; however, the time profiles were not the same (Figure 4), indicating that the absorptions occurred from two different species. Under similar conditions, a solution of **2a** displayed a

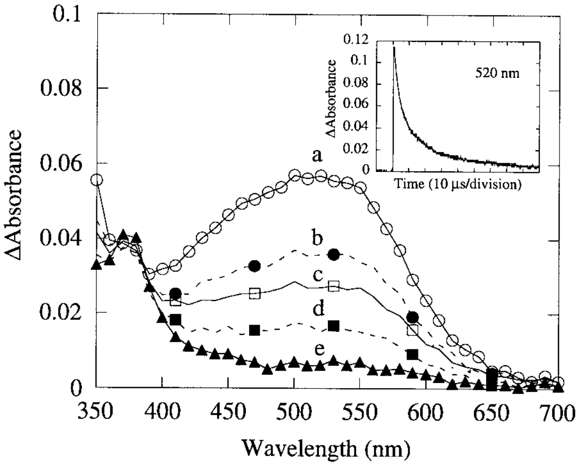


Figure 5. Transient absorption spectra recorded by 355-nm laser-flash photolysis of **2a** in acetonitrile (1×10^{-2} M): (a) 6, (b) 12, (c) 18, (d) 30, and (e) 75 μs. Insert: time profile at 520 nm.

triplet−triplet absorption with maxima at 320 and 550 nm ($\tau = 13.2$ μs).[17] The decay of both suggested a one-component system, and the behavior toward oxygen was also similar. 4-Methylbenzophenone, whose triplet absorption spectra was very similar to that of **2a**, behaves in an analogous fashion. The triplet state of **2a** was found to be quenched by $\mathrm{Ph_4B^-Bu_4N^+}$ (1×10^{-3} M, acetonitrile, $k_q = 5.65 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$) with concomitant observation of absorptions at 335 and 530 nm. The 530-nm band showed similar behavior to that of **1a**, indicating the presence of similar species.

4-(Bromomethyl)benzophenone was studied as a model compound under similar flash photolysis conditions. A transient spectrum was observed with bands at 335 and 530 nm. The 530-nm band decayed with second-order kinetics ($k/\epsilon = 2.49 \times 10^8$ cm $\mathrm{s^{-1}}$) that differed from those observed for the 335-nm absorption. The only possible radical product that resulted following laser-flash photolysis of 4-(bromomethyl)benzophenone was *p*-benzoylbenzyl radical, **7a**. This assignment was in complete agreement with the results of photolysis product studies of **1a** wherein a coupled product **5a** from the *p*-benzoylbenzyl radical **7a** was isolated. We thus assigned the reactive intermediate observed at 530 nm upon laser-flash photolysis of **1a** and the mixture (**2a** and $\mathrm{Ph_4B^-Bu_4N^+}$) to be the *p*-benzoylbenzyl radical **7a**. The absorption at 335 nm was from residual absorption due to a stable coupling product of the radicals.

The time-resolved transient spectrum for **1b** (1×10^{-2} M, acetonitrile) showed (Figure 5) two absorption bands at 380 and 520 nm, respectively. Decay of the 520-nm absorption was fitted by second-order kinetics ($k/\epsilon = 1.75 \times 10^6$ cm $\mathrm{s^{-1}}$). Laser-flash photolysis of **2b** in acetonitrile gave only one absorption at 360 nm assigned to the triplet state.[18] This triplet state was quenched by $\mathrm{Ph_4B^-Bu_4N^+}$ with a rate constant $k_q = 5.76 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ and was accompanied by the appearance of a new absorption at 520 nm. The decay behavior was practically identical to that of **1b** (520-nm band); therefore, we concluded we were observing the *p*-acetylbenzyl radical **7b**. This assignment was consistent with the results of product studies which show that the product **5b** derived from radical **7b** was the major product.

Figure 6 shows the transient absorption of **1c** (1×10^{-2} M, acetonitrile) with a maximum at 380 nm decaying in a bimolecular reaction ($k/\epsilon = 1.07 \times 10^8$ cm $\mathrm{s^{-1}}$). Triplet absorption was observed at 420 nm for 2-methylnaphthalene under identical conditions. Therefore, the band at 380 nm was assigned to the 2-naphthylmethyl radical **7c**.[19] This assignment was confirmed from an independently generated spectrum of the radical obtained from the photolysis of 2-(bromomethyl)-naphthalene.

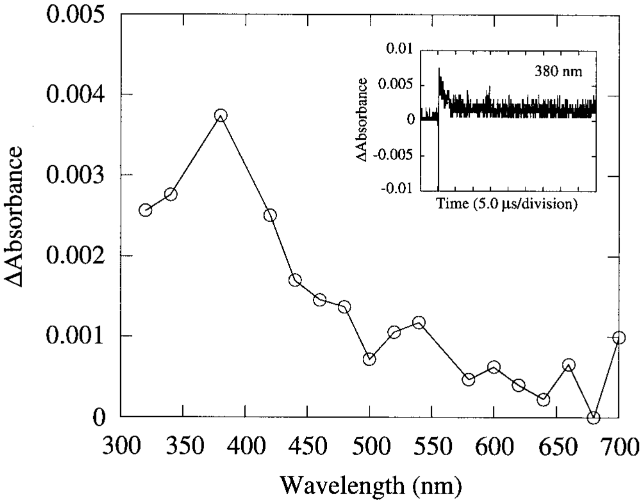


Figure 6. Transient absorption spectra of **1c** in acetonitrile (1×10^{-2} M) at 2.5-μs delay times after the laser pulse. Insert: time profile at 380 nm.

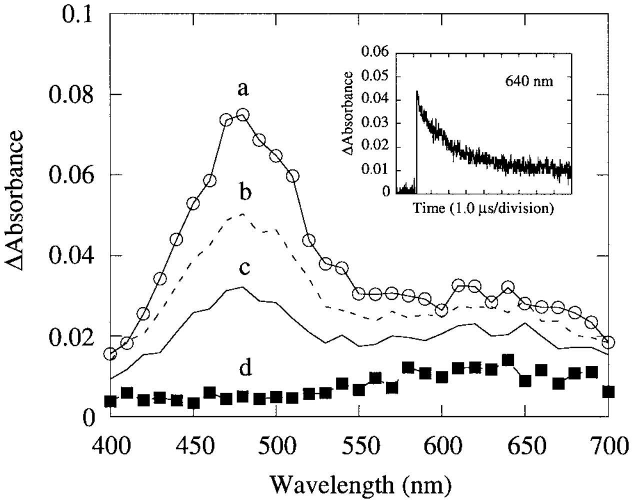


Figure 7. Transient absorption spectra of **1d** in acetonitrile (1×10^{-4} M): (a) 0.59, (b) 1.2, (c) 1.8, and (d) 5.6 μs. Insert: time profile at 640 nm.

Laser-flash photolysis of **1d** in acetonitrile (5×10^{-4} M) gave the transient absorption spectra shown in Figure 7. Following the excitation laser pulse, transient absorption bands at 480 and 600−700 nm were observed. The 480-nm band had an exponential decay with a lifetime of 1.5 μs. The broad absorption band 600−700 nm decayed with second-order kinetics ($k/\epsilon = 1.3 \times 10^7$ cm $\mathrm{s^{-1}}$). Both transient species were quenched by the addition of oxygen. The short-lived species absorbing at 480 nm was assigned to the triplet state of **1d** by comparing with literature data.[18] Further confirmation of this assignment was achieved from independent generation of transient spectra by photolysis of 4-methyl-7-methoxycoumarin in benzene ($\tau = 1.2$ μs, max = 470 nm). Similar results were obtained with **2d** (1×10^{-4} M) under identical experimental conditions where no oxidizable group was present. The absorption at 480 nm was unaffected by the addition of $\mathrm{Ph_4B^-Bu_4N^+}$ (acetonitrile, 2×10^{-3} M). However, a new broad absorption at 600−700 nm appeared upon photolysis of **2d** with decay behavior similar to that observed for **1d** at approximately

640 nm. This broad absorption at 600−700 nm was assigned to the radical **7d** by comparison to spectra generated from 4-bromomethyl-7-methoxycoumarin under similar experimental conditions.

Picosecond transient absorption studies of **1d** in benzene (3×10^{-4} M) showed the presence of broad 600−700 nm absorption forming immediately after a 30-ps laser-excitation pulse. The presence of radical **7d** in the reaction system on this time scale indicated a fast rate of C−N bond cleavage in the reduced 7-methoxycoumarin tertiary ammonium cation.

Discussion

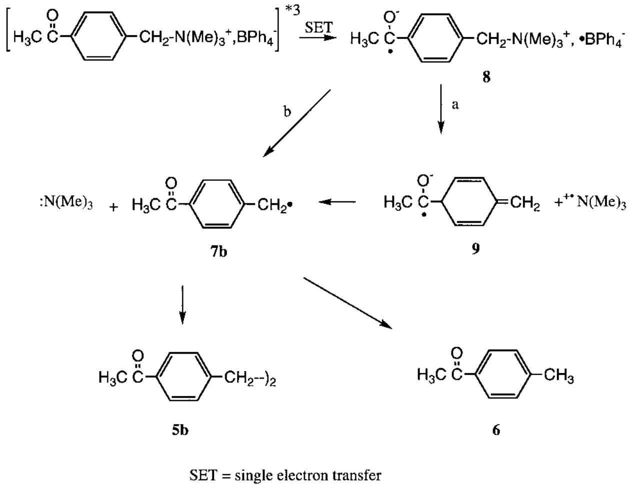
The rate constants for bimolecular quenching of the excited states of **2a**−**d** by $Ph_4B^-Bu_4N^+$ are given in Table 2 along with reduction potentials and excited-state energies. Rate constants (k_q) for the quenching of each of the excited states were high and approached diffusion-controlled limits. Though the reduction potential of **2a** was lower than that of **2b**, the triplet-state energy of **2b** was higher than that of **2a**, thus compensating for the reactivity toward bimolecular quenching and providing a nearly constant driving force for forward electron transfer. Despite its high reduction potential, the reactivity of the excited singlet state of **2c** was higher than that for either **2a** or **2b**. This can be accounted for in terms of the higher excited-state energy of the singlet state of **2c** compared to the triplet energy of both **2a** and **2b**. The quenching of **2d** exceeded diffusion-limited rates due to its low reduction potential as well as its large excited-state energy. In each case, $\Delta G°$, the driving force for electron transfer, was negative indicating a highly exothermic process. Despite the similar reactivities of the triplet and singlet excited states of the respective compounds (Table 2), it seems noteworthy that the efficiency of amine formation (conversion percent) of **1c** was significantly lower as a result of competitive deactivation of the singlet state.[20] However, the conversion (percent) and yield of products in the case of **1d** were much higher, indicating that structural characteristics are also important.

Spectroscopic evidence suggests that electron transfer takes place from the donor ($Ph_4B^-Bu_4N^+$) to the excited triplet or singlet states depending on the acceptor. As a result, C−N bond cleavage occurs homolytically in the corresponding reduced tertiary ammonium cations, and the radicals **7a**−**d** are formed. This bond-cleavage pattern was confirmed by direct observation of radicals **7a**−**7d** by laser-flash photolysis, and each radical was identified by comparison with identical radicals as produced by independent, known routes. All transient absorption spectra have the common decay characteristics of bimolecular reactions.

Additional support for formation of radicals **7a**−**7d** comes from the isolated photolysis products (Scheme 2). Photolysis of **1a**−**1d** in acetonitrile at 350 nm in the presence of oxygen resulted in the formation of **5a**−**d** and **6a**−**6d** as the major and minor products, respectively. In the absence of oxygen, a similar distribution of products results though yields are higher. The minor products, in all cases, were formed via hydrogen abstraction from CH_3CN, a poor but known hydrogen donor.[21] This was confirmed using CD_3CN in the photolysis, and observing a molecular ion peak indicated that deuterium had been incorporated in **6a**−**6d**. That radical coupling products are the major products indicates relatively long lifetimes for **7a**−**7d**.

Heterolytic C−N bond scission was ruled out because of the absence of products that could be attributed to ionic intermediates.[22] Thus, the acetamide would be an expected product in acetonitrile. The source of biphenyl in the product mixture was not clear. Trapping experiments employing TEMPO (2,2,6,6-tetramethyl-l-piperidinyloxy) failed to detect phenyl radical, though in the absence of oxygen the yield of biphenyl was significantly lower. It seems reasonable to conclude that biphenyl[23] is formed as a result of the intramolecular coupling of two phenyls from tetraphenylborate, a result consistent with other experiments.[24]

SCHEME 3: Proposed Mechanism for Photocleavage Reaction



A representative mechanism proposed for the photocleavage of **1a**−**1d** is represented with **1b** in Scheme 3. According to Scheme 3, radical **7b** is formed from the triplet radical pair **8** generated after the electron transfer via pathways a and b. We were unable to detect transient absorbance corresponding to the triplet radical pair **8** formed on the picosecond time scale, nor could we detect transient **9** as suggested in pathway a for **7b** using picosecond flash photolysis. The bond-breaking process leading to the formation of radicals in each case is coupled to the primary electron-transfer process and occurs on the sub-picosecond time scale. Back electron transfer to the tetraphenylboranyl radical ($\tau = 45$ ps) would likely be impossible on this time scale because of the rapid C−N bond cleavage.[25,26] Since back electron transfer to regenerate starting material is also spin-forbidden in triplet radical pairs, and the triplet radical pair must undergo intersystem crossing to the singlet state, which subsequently collapses forming ground state, it is not surprising that the product yields reveal that back electron transfer is minor for the triplet reactions (**1a**,**b**) where the efficiency of the amine formation approaches unity.

Back electron transfer may be significant for the photoreaction of **1c**, in which the singlet radical pair was formed.[27] This assumption is consistent with low quantum yield for the disappearance of **1c**, which is smaller than the others. The overall efficiency of photoreduction, therefore, is low. Another explanation for the lower efficiency of amine generation is the low molar extinction coefficient at 350 nm for **1c**. It shows only a tail absorption beyond 325 nm.

Structural features in **1d** and its efficient photocleavage invite additional comments. Although electron transfer occurred in the excited singlet state in **1d**, the yield of products and rate of conversion to amine suggested a relatively minor role for back electron transfer and the importance of nuclear vibrational motion in electron-transfer processes. Compound **1d** having an electron-donating methoxy group in the 7-position and an electron-withdrawing substituent in the 4-position provided positional push−pull substituents and was the main reason for ultrafast electron transfer. The drastic change in reaction rate as a function of the push−pull substituents on the coumarin has been previously observed[28] wherein amino and trifluoromethyl substituents were at 7- and 4-position, respectively. Enhanced reactivity was rationalized in terms of the static and dynamic roles of the rotational motion of the amino group. A similar effect of the amino group on the rate of electron transfer is often discussed in the studies of twisted intramolecular charge transfer (TICT), such as in the case of *N*,*N*-dimethylaminobenzonitrile.[29]

In the present system, rotational motion of the 7-methoxy group plays an important role. Change in the vibrational character of the methoxy group by substitution may cause a change in the electron-transfer rate. A change in electron-transfer dynamics from changing the vibrational parameters has been explained in terms of the extended Sumi−Marcus model.[30] However, we considered that the presence of nonreversible electron transfer was due to both electronic effects as well as vibrational motion. The presence of an electron-withdrawing substituent in the 4-position and an electron-donating substituent in the 7-position of coumarin allowed for a large value of the electron-transfer rate constant. This ultrafast reaction took place from a nonreversible state successfully competing with back electron transfer.

Conclusion

We have presented a new sequence of reactions involving excited-state electron transfer followed by C−N bond cleavage which successfully competes with back electron transfer. The reactions fulfill the requirements of high efficiency in the generation of reactive tertiary amines. Release of amine from borate-complex precursors is a rapid process, assuming the rate constant for decay of the excited states, $10^9-10^{12} M^{-1} s^{-1}$. These desirable criteria for the new generation of phototriggers provide a promising future for their application to polymer curing, imaging, and other applications.

Experimental Section

General. Melting-point determinations were carried out on a Thomas capillary melting point apparatus; all temperatures were uncorrected. Elemental analysis was performed by Atlantic Microlab, Inc., Georgia. ^{1}H NMR spectra and ^{13}C NMR spectra were taken on Gemini GEM-200 (200 MHz) and Gemini GEM-200 (50 MHz) spectrometer, respectively. UV−vis and emission spectra were recorded on a Hewlett-Packard 8452 diode array spectrophotometer and SPEX Fluorolog spectrophotometer, respectively. GC-MS was performed on a Hewlett-Packard 5988 mass spectrometer coupled to a HP 5880A GC, interfaced to a HP 2623A data processor. GC measurements were carried out on a Hewlett-Packard (HP) 5890 gas chromatograph.

Nanosecond-flash-photolysis studies were performed using a kinetic spectrophotometric detection system previously described.[31] The excitation pulse (7-ns duration, 355 nm) of light was the third harmonic of a Q-switched Nd:YAG laser. Typical excitation pulse amplitudes were a few millijoules per pulse. Transients produced were followed temporally and spectrally by a computer-controlled kinetic spectrophotometer. Picosecond transient absorption measurements were performed on a setup described by Logunov and Rodgers.[32]

Reduction potentials were measured on a BAS-100 potentiostat equipped with BAS PA-1 preamplifer. The reference electrode was a Ag/AgNO$_3$ in tetrabutylammonium perchlorate solution (0.1 M in acetonitrile). The working electrode was a platinum wire.

General Procedure for Synthesis of Ammonium Bromide Salts (3a−3c). Tertiary amine was added in excess with stirring at room temperature to a solution of the respective bromomethyl compound in chloroform−ether (1:2). A white precipitate formed within 12 h (in some cases, almost immediately) and was separated by filtration and dried. After recrystallization from a suitable solvent, white crystals were obtained (70−80% yield).

*N-(4-Benzoyl)benzyl-N,N,N-tributylammonium Bromide (**3a**).* Mp 160−161 °C (ethyl acetate/acetone). ^{1}H NMR (acetone): δ 7.90 (m, 4H), 7.68 (m, 1H), 7.58 (m, 4H), 5.11 (s, 2H), 3.50 (m, 6H), 2.06 (m, 6H), 1.43 (m, 6H), 1.00 (t, J = 7 Hz, 9H). ^{13}C (CD$_3$OD): δ 199.18, 142.61, 139.99, 136.11, 135.73, 134.91, 133.38, 132.91, 131.54, 64.40, 61.50, 27.02, 22.54, 15.86. Anal. Calcd for $C_{26}H_{38}BrNO$: C, 67.86; H, 8.26; Br, 17.37. Found: C, 67.79; H, 8.28; Br, 17.43.

*N-(4-Acetyl)benzyl-N,N,N-trimethylammonium Bromide (**3b**).* Mp 196−196.5 °C (acetone/methanol). ^{1}H NMR (CD$_3$CN): δ 8.13 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 4.68 (s, 2H), 3.18 (s, 9H), 2.66 (s, 3H). ^{13}C NMR (CD$_3$OD): δ 201.44, 141.89, 136.38, 135.71, 131.87, 71.33, 55.29, 28.86. Anal. Calcd for $C_{12}H_{18}BrNO$: C, 52.98; H, 6.62; N, 5.15; Br, 29.38. Found: C, 52.90; H, 6.60; N, 5.16; Br, 29.42.

*N,N,N-Tributyl-N-(2-methylnaphthalene)ammonium Bromide (**3c**).* Mp 120−121 °C (ethyl acetate/ethanol). ^{1}H NMR (CD$_3$CN): δ 8.00 (m, 4H), 7.72 (m, 3H), 4.63 (s, 2H), 3.15 (m, 6H) 1.82 (m, 6H), 1.36 (m, 6H), 1.00 (t, J = 7.4 Hz, 9H). ^{13}C NMR (CD$_3$OD): δ 134.31, 130.25, 129.43, 129.38, 129.01, 128.85, 128.32, 126.12, 63.30, 59.41, 25.13, 20.74, 14.00. Anal. Calcd for $C_{23}H_{36}NBr$: C, 68.01; H, 8.86; Br, 19.60. Found: C, 68.07; H, 8.87; Br, 19.64.

*N,N,N-Tributyl-N-(4-methyl-7-methoxycoumarin)ammonium Bromide (**3d**).* 4-(Bromomethyl)-7-methoxycoumarin (1.0 g, 3.72 mmol) was suspended in methanol (20 mL), and tributylamine (2.75 g, 14.88 mmol) was added to it. The mixture was refluxed overnight during which time the reaction mixture became clear. The solution was concentrated by evaporating the solvent. After adding hexanes (30 mL), it was kept at 0 °C overnight. The solid was filtered and recrystallized from ethyl acetate−ethanol. **3d** as white crystals (1.05 g) was obtained (75% yield); mp 157−158 °C. ^{1}H NMR (CD$_3$CN): δ 8.21 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.92 (d, J = 2.5 Hz, 1H), 6.58 (s, 1H), 4.87 (s, 2H), 3.89 (s, 3H), 3.42 (m, 6H), 1.75 (m, 6H), 1.29 (m, 6H), 0.91 (t, J = 7.2 Hz, 9H). Anal. Calcd for $C_{23}H_{36}BrNO_3$: C, 60.82; H, 7.93; N, 3.08; Br, 17.60. Found: C, 60.25; H, 8.00; N, 2.99; Br, 17.22.

General Procedure for Synthesis of Tetraphenylborate Complexes (1a−1d). The ammonium bromide salt was dissolved in a minimum of water, and undissolved dust materials, if present, were filtered. An equivalent amount of the sodium tetraphenylborate in water was added dropwise at room temperature with stirring. A thick white precipitate formed immediately. This was diluted by the addition of water and filtered. After recrystallization, white needles of the tetraphenylborate complex (75%−85% yields) were obtained.

*N-(4-Benzoyl)benzyl-N,N,N-tributylammonium Tetraphenylborate (**1a**).* Mp 197−198 °C (ethanol/acetone). ^{1}H NMR (acetone, δ): 7.83 (m, 4H), 7.68 (m, 1H), 7.54 (m, 4H), 7.26 (m, 8H, ortho to B), 6.99 (t, J = 7.4 Hz, 8H, meta to B), 6.83 (t, J = 7.4 Hz, 4H, para to B), 4.39 (s, 2H), 3.05 (m, 6H), 1.75 (m, 6H), 1.37 (m, 6H), 0.99 (t, J = 7.4 Hz, 9H). Anal. Calcd for $C_{50}H_{58}BNO$: C, 85.87; H, 8.29; N, 2.00. Found: C, 85.87; H, 8.41; N, 2.08.

*N-(4-Acetyl)benzyl-N,N,N-trimethylammonium Tetraphenylborate (**1b**).* Mp 205−206 °C (ethanol/acetonitrile). ^{1}H NMR

(CD_3CN): δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.28 (m, 8H), 7.00 (t, $J = 7.0$ Hz, 8H), 6.85 (t, $J = 7.0$ Hz, 4H), 4.34 (s, 2H), 2.93 (s, 9H), 2.60 (s, 3H). Anal. Calcd for $C_{36}H_{38}BNO$: C, 84.58; H, 7.43; N, 2.74. Found: C, 84.62; H, 7.41; N, 2.78.

*N,N,N-Tributyl-N-(2-methylnaphthalene)ammonium Tetraphenylborate (**1c**).* Mp 174−175 °C (ethanol). ^1H NMR (CD_3CN): δ 8.00 (m, 4H), 7.63 (m, 2H), 7.50 (m, 1H), 7.26 (m, 8H, ortho to B), 6.99 (t, $J = 7.0$ Hz, 8H, meta to B), 6.83 (t, $J = 7.2$ Hz, 4H, para to B), 4.46 (s, 2H), 3.06 (m, 6H), 1.79 (m, 6H), 1.37 (m, 6H), 1.00 (t, $J = 7.0$ Hz, 9H). Anal. Calcd for $C_{47}H_{56}BN$: C, 87.48; H, 8.68, N, 2.17. Found: C, 87.40; H, 8.72; N, 2.18.

*N,N,N-Tributyl-N-(4-methyl-7-methoxycoumarin)ammonium Tetraphenylborate (**1d**).* Mp 149−150 °C (ethanol). ^1H NMR (CD_3CN): δ 7.71 (d, $J = 9.8$ Hz, 1H), 7.26 (m, 8H), 6.98 (m, 10H), 6.83 (m, 4H), 6.19 (s, 1H), 4.42 (s, 2H), 3.90 (s, 3H), 3.21 (m, 6H), 1.17 (m, 6H), 1.26 (m, 6H), 0.93 (t, $J = 7.0$ Hz, 9H). Anal. Calcd for $C_{47}H_{56}BNO_3$: C, 81.42; H, 8.08; N, 2.02. Found: C, 81.28; H, 8.07; N, 2.05.

*N,N,N-Tributyl-N-(4-methyl-7-methoxycoumarin)ammonium Tetrafluoroborate (**2d**).* Bromide **3d** (0.30 g, 0.66 mmol) was dissolved in water (20 mL) and undissolved dust materials were filtered, if present. Aqueous fluoroboric acid (1.0 mL, 48 wt %) was added dropwise with stirring. A white precipitate was formed immediately. Water (50 mL) was added, and the solution was stirred for 15 min. The product (0.15 g, 50% yield) was filtered and washed with water; mp 160−162 °C. Anal. Calcd for $C_{23}H_{36}BF_4NO_3$: C, 59.91; H, 7.81; N, 3.04; F, 16.48. Found: C, 60.03; H, 7.83; N, 3.06; F, 16.45.

*N-(4-Benzoyl)benzyl-N,N,N-tributylammonium Tetrafluoroborate (**2a**).* Prepared as above (80% yield); mp 78−79 °C. Anal. Calcd for $C_{26}H_{38}BF_4NO$: C, 66.86; H, 8.14; Br, 0.0. Found: C, 66.93; H, 8.19; Br, 0.0.

*N-(4-Acetyl)benzyl-N,N,N-trimethylammonium Tetrafluoroborate (**2b**).* Prepared as **2d** (83% yield); mp 152−53 °C. Anal. Calcd for $C_{12}H_{18}BF_4NO$: C, 51.67; H, 6.45; N, 5.02; F, 27.25. Found: C, 51.72; H, 6.42; N, 5.08; F, 27.20.

*N,N,N-Tributyl-N-(2-methylnaphthalene)ammonium Tetrafluoroborate (**2c**).* Prepared as **2d** (62% yield); mp 147−48 °C. Anal. Calcd for $C_{23}H_{36}BF_4N$: C, 66.88; H, 8.72; N, 3.39; F, 18.40. Found: C, 66.93; H, 8.70; N, 3.41; F, 18.37.

4^1-(Bromomethyl)acetophenone. 4^1-Methylacetophenone (3.0 g, 22.35 mmol), *N*-bromosuccinimide (4.38 g 24.60 mmol), and AIBN (30 mg) in carbon tetrachloride (50 mL) was refluxed overnight. After the reaction mixture was cooled, succinimide was filtered. The solvent was evaporated and recrystallized from hexanes. The white crystals (2.68 g, 57% yield) were obtained: mp 34−35 °C. ^1H NMR ($CDCl_3$) δ: 7.90 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 4.48 (s, 2H), 2.57 (s, 3H). ^{13}C NMR ($CDCL_3$) δ: 199.40, 144.79, 138.84, 131.25, 128.86, 34.20, 28.69. Anal. Calcd for C_9H_9BrO: C, 50.73; H, 4.23; Br, 37.50. Found: C, 50.62; H, 4.22; Br, 37.57.

General Procedure for Photolysis. Preparative-scale photolysis was carried out in a Rayonet photochemical reactor fitted with filter-coated mercury lamps (300−400 nm) with output maximum at 350 nm. Samples for irradiation were placed in a ca. 15-mm internal diameter Pyrex tube immersed in a water-cooled bath during the course of reaction. The mixture of photoproducts was subjected to careful silica gel chromatography with hexanes−ethyl acetate (8:1) as eluent. All photoproducts were isolated and fully characterized by a combination of NMR, GC−MS analysis, elemental analysis, and TLC with comparison to authentic samples. New compounds were synthesized independently.

General Procedure for Determination of Quantum Yield of Photodecomposition of the Borates. A solution of a borate in CH_3CN or benzene (35 mL) was placed in a quartz cell (10-cm path length), degassed with bubbling N_2 for 30 min, and sealed. The concentration of borates **1a**, **1b**, **1c**, and **1d** was 5×10^{-3} M in CH_3CN and 3×10^{-4} M for **1d** in benzene. Irradiation was carried out using 366-nm light from a 200-W Hg lamp isolated from the spectrum with two-color glass filters (cutoff at 340 nm and at 400 nm) that was passed through a 10-cm water filter and focused into the sample. The irradiation time varied from 30 s for **1d** in PhH to 15 min for **1d** in CH_3CN. The maximum degree of photodecomposition was 25% for **1a** in CH_3CN. The intensity of 366-nm light was determined using anthracene dimerization reaction in O_2 free benzene (1.05×10^{-2} M, 25 °C, quantum yield of anthracene disappearance is 0.0706).[33] The concentration of the remaining borates was determined by HPLC.

HPLC Analysis of the Borates. Typically, 1 M aqueous HCl (3 drops) was added to the borate solution (25 μL), which was then diluted to 5 mL with MeOH. This pretreated sample was analyzed on a Hewlett-Packard 1050 HPLC equipped with Nucleosil AB C18 column (15.0 cm × 4.6 mm, Altech) and a UV absorbance detector set of 370 nm. The eluent was MeOH.

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