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# Electron transfer followed by double fragmentation reactions: mechanism of photogeneration of tertiary amines and radicals from tetraorganyl borates[1]

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## Abstract

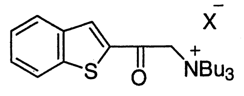
The double fragmentation reactions of *N*,*N*,*N*-tributyl-*N*-acetobenzo[b]thiophene ammonium borates have been investigated. The primary step in the cleavage reactions is electron transfer from the borate anion to the excited acceptor. This generates radical pairs that decompose by rapid carbon–nitrogen and carbon–boron bond fragmentation. Transient spectra and photoproducts are consistent with this bond cleavage. Tertiary amines are formed as a result of reductive carbon–nitrogen bond scission. The boranyl radicals formed undergo oxidative carbon–boron bond cleavage to generate alkyl or phenyl radicals, depending on the structure of the borate. Both cleavage processes are irreversible, and their rates easily exceed the rate of the back electron transfer reaction. The net quantum yields for photodecomposition are also high. Detailed mechanistic studies were carried out. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Double fragmentation reactions; Photogeneration; Tetraorganyl borates

## 1. Introduction

Photoinduced electron transfer may lead to radical pairs capable of undergoing rapid bond cleavage [1–10]. The efficiency of such reactions in ion radicals is often limited by low quantum yields that result from rapid back electron transfer, especially when singlet state quenching is involved. Triplet acceptors result in spin-forbidden back electron transfer, thus increasing the efficiency significantly [11–13]. Another approach to encourage high quantum efficiency of the bond cleavage reaction is to use a system where the donor and the acceptor undergo simultaneous rapid fragmentation that also competes with back electron transfer [14,15].

We have been interested in the development of reactions induced by electron transfer [16–18], particularly for tetraorganyl borates complexed to light absorbing acceptors [19–28], also capable of rapid fragmentation. We describe herein a system (Chart 1) designed with tetraorganyl borates that examines fragmentations of the photogenerated radical ions that convert them to radicals. We will demonstrate a possible mechanism by which photoactivation of triphenylbutyl borate (**1a**) and tetraphenyl borate (**1b**) results in bond cleavage and produces reactive amines and radicals in a single step. The non-oxidizable tetrafluoroborate (**1c**) is used as a model compound.



**1**

**a**. X = $Ph_3BBu$
**b**. X = $Ph_4B$
**c**. X = $BF_4$

## 2. Results

### 2.1. Photophysical properties

The absorption spectrum of **1b** in acetonitrile ($1.03 \times 10^{-5}$ M) shows a broad band at 310 nm ($\log \varepsilon = 4.30$) that is independent of the structure of the anion. This absorption maximum is red shifted (14 nm) without change of shape compared to that of a model, 2-acetylbenzo[b]thiophene, in acetonitrile (Fig. 1). This suggests that substantial interaction exists between nitrogen cation and boron anion in acetonitrile solvent. The spectrum of 2-acetylbenzo[b]thiophene is unaffected by the addition of sodium tetraphenyl or triphenylbutyl borate excluding the possibility of a ground state charge-transfer (CT) complex between the borate and the acceptor molecule.

The fluorescence emission of **1c** (non-reactive counter ion $BF_4^-$) has a peak maximum at 437 nm in acetonitrile on

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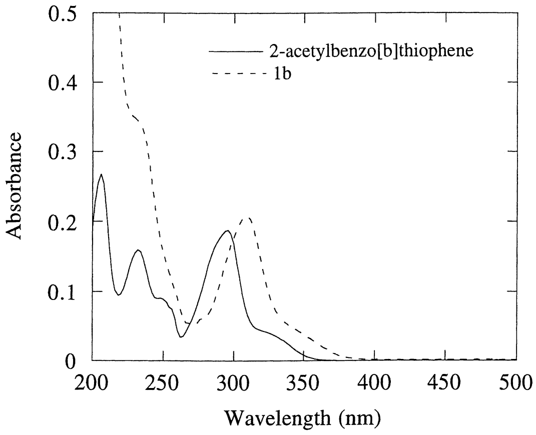


Fig. 1. Absorption spectra of **1b** and 2-acetylbenzo[b]thiophene in acetonitrile.

excitation at 355 nm ($\Phi_f = 0.088 \pm 0.01$). The quantum efficiency of fluorescence is independent of the excitation wavelength throughout the absorption band consistent with the existence of only one conformation for **1c** in solution. No fluorescence quenching was observed upon the addition of borate donors such as $Ph_4B^- Bu_4N^+$ or $Ph_3BuB^- Bu_4N^+$. The position of the fluorescence excitation spectra (monitoring at 437 nm) was red shifted in benzene.

Fig. 2 shows the phosphorescence spectrum of **1c** (excitation $\lambda$, 355 nm) in EPA at 77°K. This spectrum, and the corresponding long wavelength excitation spectrum (monitored at 530 nm), was found to be identical irrespective of the excitation wavelength demonstrating the existence of only one species. The lifetime of phosphorescence was found to be 38.6 ms and the emission decayed with first order kinetics ($k_p = 25.9\ s^{-1}$). The energy of the lowest triplet state ($E_T$) was estimated from this phosphorescence peak to be 53.8 kcal mol$^{-1}$. (($\Phi_p$) for **1c** was determined to be $3.4 \times 10^{-3}$ in EPA at 77°K relative to benzophenone ($\Phi_p = 0.84$)) [29]. The quantum yield for triplet formation ($\Phi_T$) was estimated to be 0.29 from Eq. (1):

$$\Phi_T = \Phi_P[k_T + (1/\tau_P)]/(1/\tau_P) \quad (1)$$

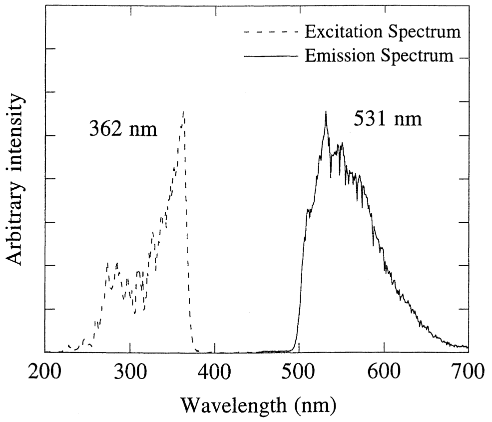


Fig. 2. Phosphorescence and excitation spectra of **1c** in EPA.

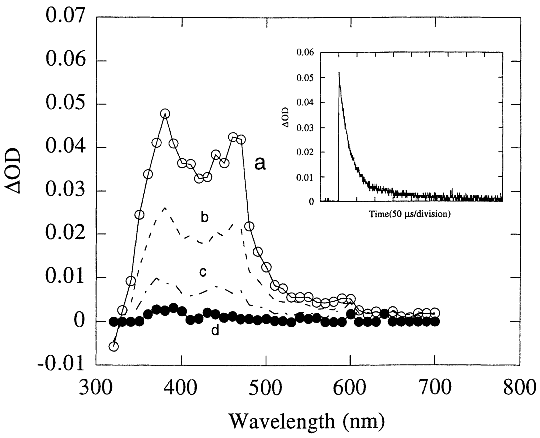


Fig. 3. Transient spectra of **1c** in acetonitrile recorded at (a) 3.0 µs, (b) 24 µs, (c) 69 µs, (d) 200 µs after irradiation. Insert: time profile at 380 nm.

where $k_T$ and $\tau_P$ denote the rate constant for deactivation of the triplet ($k_T = 2.15 \times 10^3\ s^{-1}$ for **1c** in EPA at 77°K) and the lifetime of phosphorescence, respectively.

### 2.2. Triplet–triplet absorption spectra

Laser flash photolysis of **1c** at 355 nm in oxygen free acetonitrile ($3 \times 10^{-4}$ M) gave the transient spectra shown in Fig. 3. There were two maxima at 380 and 460 nm, both of which decay exponentially with a lifetime of 46.5 µs. These absorptions have been assigned to the triplet state based on bimolecular quenching behavior with molecular oxygen and with borate anions. This triplet spectrum was compared with that of the independently generated triplet transition from 2-acetobenzo[b]thiophene and with that of the oxygen analog benzo[b]furan ($\lambda_{max} = 420$ nm; $\tau$=44 µs) [30]. The absence of second order components in the kinetic profiles exclude any contribution from triplet–triplet annihilation [31].

### 2.3. Quenching rate constants

Quenching rate constants, $k_q$, for various borates were measured by monitoring the decay of the triplet absorption of **1c** at 380 nm. The concentration of **1c** was fixed ($3 \times 10^{-4}$ M) while the concentrations of added borates were varied over a range that reduced the lifetime of the triplet. The $k_q$ values were calculated from a linear fit of $k_{obs}$ versus concentration employing the Stern–Volmer (SV) relation:

$$k_{obs} = 1/\tau_T + k_q[Q] \quad (2)$$

$\tau_T$ is the lifetime of the triplet state in the absence of quencher, $Q$. We may presume from the linear SV plot, Fig. 4, that quenching is of the dynamic type. The resulting rate constants, together with the $\Delta G^0$ values, are listed in Table 1. Since the quenching constants for the borates are in the range $10^8$–$10^9\ M^{-1}\ s^{-1}$, electron transfer from the borate anions to the triplet state of **1c** is the mechanism for triplet quenching.

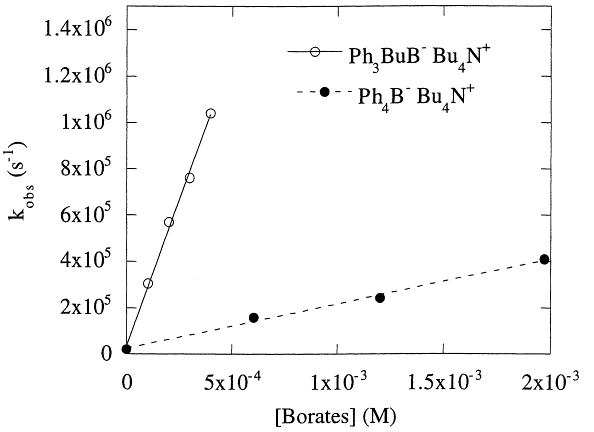


Fig. 4. Stern–Volmer plots of **1c** with triphenylbutyl and tetraphenyl borates.

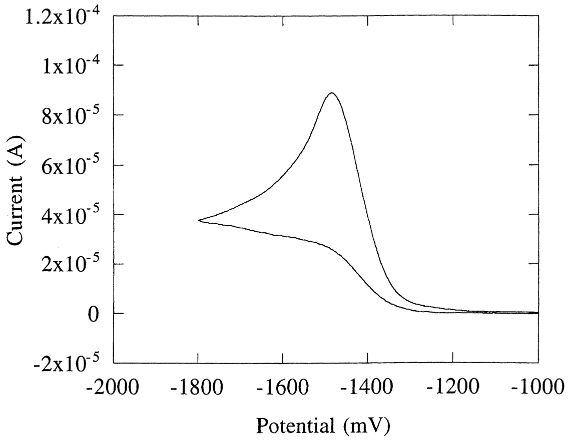


Fig. 5. Cyclic voltammogram of **1c** in acetonitrile.

Table 1
Free energy changes ($\Delta G_{et}$) for electron transfer, quenching constants ($k_q$) and quantum yield for disappearance ($\Phi_d$) of **1a** and **1b**

| Compound | $\Delta G_{ete}$ (eV) | $k_q$ ($M^{-1}$ $s^{-1}$) | $\Phi_T$[a] | $\Phi_d$[b] |
|---|---|---|---|---|
| **1a** | −0.48 | $2.53 \times 10^9$ | 0.29 | 0.89 |
| **1b** | −0.28 | $1.92 \times 10^8$ | 0.26 | 0.56 |

[a] From triplet state quenching experiments.
[b] From steady-state experiments.

### 2.4. Thermodynamics of electron transfer

The quenching constant is often nearly diffusion-controlled when $\Delta G_{et} < -10$ kcal mol$^{-1}$ [32]. $\Delta G_{et}$ can be estimated by Rehm–Weller equation [33]:

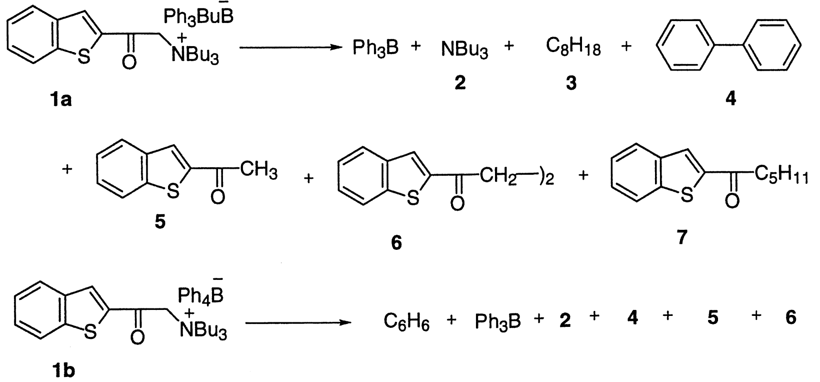
$$\Delta G_{et} = E_{ox} - E_{red} - E_{0-0} + C \tag{3}$$

where the symbols have their usual meanings. In highly polar solvents such as acetonitrile, the coulombic term $C$ is negligible [34]. Cyclic voltammetry experiments showed the observed waves gave an irreversible reduction of the acceptor **1c** due to a fragmentation reaction, and only the peak potential could be obtained (Fig. 5). The average peak potential was ca. −1.15 V versus SCE. The oxidation potentials of $Ph_4B^-$ $Bu_4N^+$ and $Ph_3BuB^-$ $Bu_4N^+$ are known to be 0.90 and 0.70 V versus SCE, respectively [35]. $\Delta G_{et}$ is estimated (Table 1) and suggests that photoinduced electron transfer from the borate anion to the excited triplet state of the acceptor is thermodynamically favorable, and the rate for electron transfer should be very fast unless the Marcus reorganization energy is substantial [36].

### 2.5. Products studies and quantum yields for disappearance

Direct irradiation of **1c** in degassed acetonitrile solution at 350 nm produces no observable changes in $^1$H NMR spectra and no photoproducts were detected by HPLC analysis even after prolonged (1 h) photolysis. A similar irradiation in the presence of the polymerizable monomer, methyl methacrylate, produced no detectable polymerization. In contrast, under the same conditions, the borates **1a** and **1b** give both substantial polymerization and identifiable photoproducts (Scheme 1) [37].

When irradiated at 350 nm in acetonitrile **1a** and **1b** produce a yellow color. In typical $^1$H NMR experiments,



Scheme 1. Photolysis products of **1a–b** in acetonitrile at 350 nm.

Table 2
Product studies for the photolysis of **1a** and **1b** in acetonitrile for 1 h

| Compounds[a] | Products (% yields) | | | |
|---|---|---|---|---|
| | **3**[b] | **5** | **6** | **7** |
| **1a** | 7 | 5 | 34 | 10 |
| **1b** | – | 9 | 39 | – |

[a] 100% conversion determined by TLC.
[b] Calculated by GC.

irradiation for 30 min leads to the disappearance of the methylene peaks around 4.70 ppm and the appearance of a new peak around 3.40 ppm due to the formation of the corresponding amine by C–N bond cleavage. Irradiation to less than 20% conversion resulted in similar product distributions. Thus, the net reaction is the extremely clean conversion of **1a** and **1b** to reactive amines in quantitative yield as outlined in Scheme 1. When photolysis reactions were performed on a preparative scale, the yields of isolated products represent only the lower limits shown in Table 2.

While the photoreactions appear general, the quantum yields show a strong dependence on the structure of the donor. When the reaction is monitored via appearance of *t*-butyl amine in the $^1$H NMR ($CD_3CN$), the reaction of **1a** proceeds faster than that of **1b**. The quantum yields of disappearance ($\Phi_d$) of **1a** and **1b** were determined by irradiation in acetonitrile at 366 nm using acridine dimerization as the actinometer ($\Phi_d = 0.032$) [38]. We also calculate the $\Phi_d$ from quenching data using Eq. (4) to verify that the values obtained by the two different methods are consistent.

$$\Phi_d = \Phi_T\{k_q[\text{borate}]/(k_T + k_q[\text{borate}])\} \quad (4)$$

$\Phi_T$ is the quantum yield for triplet formation and $k_T$ the rate constant for deactivation of the triplet. The quantum yields, $\Phi_d$, at low conversion are summarized in Table 1.

### 2.6. Transient absorption spectra of intermediates

Fig. 6 shows the nanosecond transient absorption spectrum of **1b** in degassed acetonitrile recorded 0.6 µs after laser excitation ($\lambda = 355$ nm) at room temperature. Absorption bands were observed at 380 and 440 nm. These are in good agreement with triplet absorption, and both bands decay in an exponential manner. The 440 nm band decays almost completely 60 µs after the laser pulse, while the 380 nm band persists at a low intensity on the microsecond time scale. The inset shows the decay of the 380 nm band, and that it consists of two components. The faster component decays following a first order kinetic law, while the slower component is best fitted with second order kinetics ($k/\varepsilon = 3.75 \times 10^5\ \text{s}^{-1}$ cm). The transient absorption spectra measured from **1a** under similar conditions (not shown) exactly resemble that of the spectra of **1b**. This strongly indicates the same reactive intermediates are formed in both the cases.

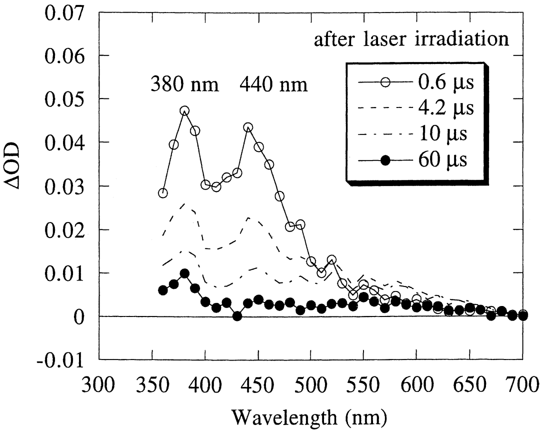
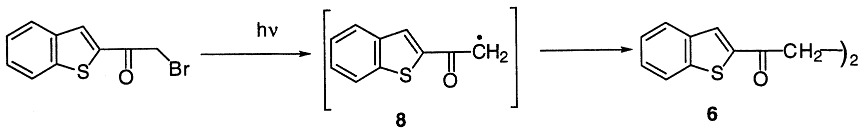


Fig. 6. Transient spectra of **1b** in acetonitrile.

In order to identify the reactive intermediates, 2-bromoacetyl benzo[b]thiophene was studied as a model compound under similar conditions. A transient spectrum was observed with a band at 380 nm after the laser pulse. The decay behavior of this transient again suggests two components, one of which is best fitted with second order kinetics ($k/\varepsilon = 3.33 \times 10^5\ \text{s}^{-1}$ cm). The only possible reactive intermediate resulting following photolysis of 2-bromoacetyl benzo[b]thiophene is the 2-acetylbenzo[b]thiophenyl radical **8** (Scheme 2). The behavior and the position of the absorption maxima near 380 nm is consistent with the transient obtained from **1a** or **1b**. Furthermore, the triplet state of **1c** when quenched by $Ph_4B^-$ $Bu_4N^+$ or $Ph_3BuB^-$ $Bu_4N^+$ is accompanied by an absorption at 380 nm. We thus assign the reactive intermediate at 380 nm from photolysis of **1a** or **1b** and from the mixture (**1c** and borate anion) to be 2-acetylbenzo[b]thiophenyl radical **8**. The faster component observed at 380 nm is assigned to the decay of **1b** triplet (Fig. 7). The short lifetime transient compares with the triplet lifetime of the acetyl benzo[b]thiophene chromophore in a solution containing $1 \times 10^{-3}$ M $Ph_4B^-$ anion. The decay profile shows residual absorption probably due to the stable coupling product formed from the radicals.



Scheme 2. Photolysis mechanism for 2-bromoacetylbenzo[b]thiophene.

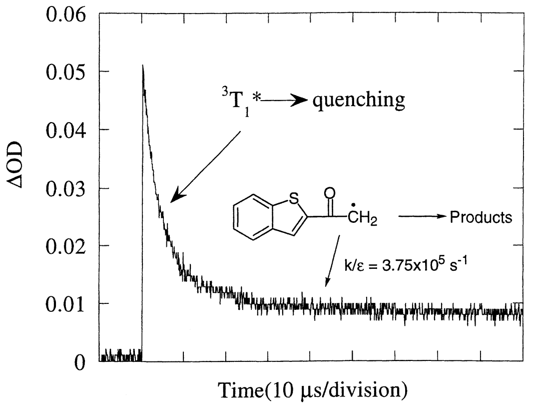


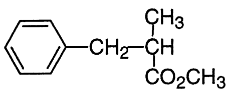
Fig. 7. Kinetic profile of transient absorption of **1b** in acetonitrile at 380 nm.

## 3. Discussion

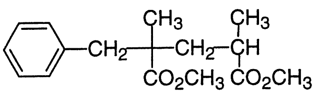
Each photoreaction is initiated by excitation of the electron acceptor in acetonitrile solvent, since none of the donor anions absorb beyond 300 nm. The quenching of acceptor triplets by borate anions involves an energetically favorable electron transfer. The observation that the radicals of both the acceptor and the donor are unstable (that is they are not formed in a reaction that is electrochemically reversible) and give fragmentation products from the photolysis supports an electron transfer mechanism for both oxidative and reductive photofragmentation.

The rate constants, $k_q$, for quenching of the triplet state of **1c** by borate anions are large (close to diffusion controlled), and as expected, dependent on the oxidation potentials of the donors. If the proposed photoinduced intramolecular electron transfer occurs in **1a** and **1b** upon excitation at 355 nm, and that one would expect to detect the acceptor-boranyl radical pair in the transient absorption spectra. This was not observed under our conditions, however, the absorption at 380 nm due to acetylbenzo[b]thiophene radical **8** was observed. Photolysis of both **1a** and **1b** in acetonitrile gave products **5** and **6** clearly proving that radical **8** is the common intermediate. The minor product **5** is formed by hydrogen abstraction from acetonitrile while **6** is a dimeric product formed from radical **8**.

GC analysis of the reaction mixture of **1a** shows product **7** and *n*-octane **3**. Formation of **7** occurs from a cross-coupling reaction of **8** and with an *n*-butyl radical; **3** is the result of dimerization of free *n*-butyl radicals. Careful analysis of the photoproducts formed from **1b** revealed the formation of benzene in less than 8% yield (detected by GC–MS), while no indication of benzene was found for **1a**. Benzene is probably produced by hydrogen abstraction of the phenyl radical from acetonitrile [39,40]. We also detect the adduct of phenyl radical with methyl methacrylate. When equal molar amounts of **1b** and freshly distilled methyl methacrylate were irradiated in distilled acetonitrile, the products, **9** and **10**, are produced in low yields. These results indicate not only the existence of phenyl radical but also that it can initiate radical polymerization with acrylate monomers [37].



**9**

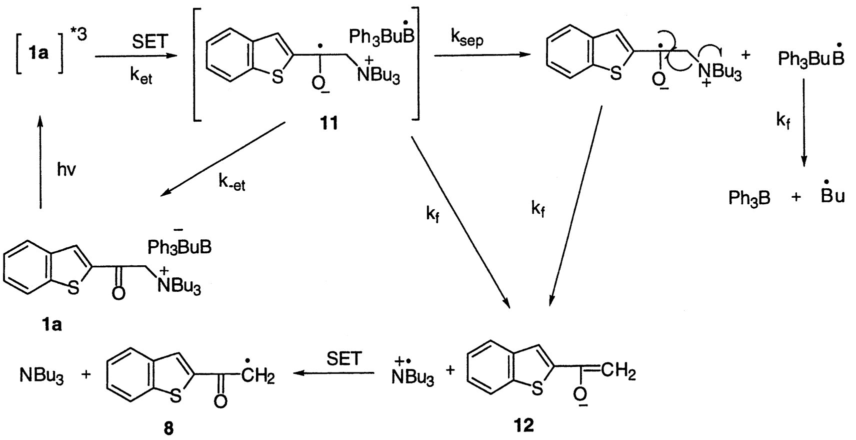


**10**

The results allow proposal of a mechanism for the photogeneration of amines and alkyl or aryl radicals (Scheme 3). Radical pair **11** is formed after electron transfer from borate anion to the excited acetobenzo[b]thiophene. The carbon-centered radical fragments at the carbon–nitrogen bond to a more stable anion **12**. The overall driving force for this is the conversion of highly energetic radical anion to a stabilized **12** and the nitrogen cation radical. Therefore, this reaction is exothermic and the fragmentation step is irreversible. This type of homolytic dissociation of the carbon–nitrogen bond is not surprising because of the low electronegativity difference between the carbon and nitrogen atom (nitrogen is the closest of the first row elements to carbon) [41,42]. In fact, similar C–N bond cleavage reactions followed by elimination of tertiary amine have been reported for other systems [16–18]. Heterolytic C–N bond cleavage in present system is ruled out, since it does not lead to formation of the radical **8**.

Borate salts, especially cyanine borates, exist as a solvent separated ion pair in polar solvents [27] though this is not the case for **1a** and **1b** in acetonitrile. Our spectroscopic observation reveals that **la** and **1b** in acetonitrile have interaction between the ion-pairs. The interaction is not expected if the ion-pairs are solvent separated. Hence, the quenching process is, in principle, close to being intramolecular in acetonitrile. The initial step is an electron transfer from the borate anion to the triplet state of the acceptor to form a radical pair **11**. This radical pair can disappear either by back electron transfer, $k_{-\mathrm{et}}$, to regenerate the reactants or by diffusion followed by rapid fragmentation of carbon–nitrogen bond to radical **8** and tertiary amine. Therefore, the quantum efficiencies would be determined by the competition among the three processes in the initially formed radical pair **11**. They are back electron transfer ($k_{-\mathrm{et}}$), radical pair separation ($k_{\mathrm{sep}}$) and bond fragmentation ($k_{\mathrm{f}}$) Scheme 3.

If $k_{\mathrm{f}}$ is comparable to or larger than $k_{-\mathrm{et}}$ and $k_{\mathrm{sep}}$, high quantum efficiencies for disappearance (Scheme 3) are expected [9,43]. In the present case, the quantum efficiencies, are expected to be high for the following reasons: (a) high redox energies of the reactants decrease $k_{-\mathrm{et}}$ [44], (b) triplet state electron transfer where $k_{-\mathrm{et}}$ is spin forbidden process [45,46], (c) polar media facilitate ion-radical pair separation [47,48]. Table 3 shows that the quantum yields of disappearance are very high, although the agreement with the corresponding values obtained from the quenching rate constants is not good. However, this provides strong support for the efficiency of amine generation as a result of carbon–nitrogen bond cleavage. In this respect, steric effects likely play an important role due to the bulkiness of the tributyl group on nitrogen. This bulky group forces the carbon–



Scheme 3. Proposed mechanism for photocleavage reaction.

nitrogen bond to approach a perpendicular plane with respect to the acceptor; and this enables an effective hyperconjugative interaction of the carbon–nitrogen bond with the excited $\pi$-system of the acceptor making for an effective dissociation [42].

The initially formed radical pair **11** has a very short lifetime. Since the boranyl radical lifetimes are known to be 45 ps and 250 fs, respectively, [48] other reactions including $k_{-\mathrm{et}}$ or $k_{\mathrm{sep}}$ cannot compete. In the case of $Ph_4B$ radical, $k_{-\mathrm{et}}$ might compete with $k_f$. However, the lifetime of radical anion has proven to be subpico second [2]. With the short lifetime of **11**, the probability of other reactions that might compete with fragmentation decreases. This lends further support to the idea that bond fragmentation probably occurs directly from radical pair **11** before separation of the radical ions.

The quantum yield $\Phi_d$ for **1a** is higher than for **1b**. This implies that the $Ph_4B$ radical has a slower rate constant for decomposition. The quantum yields of decomposition for **1a** and **1b** are consistent with the oxidation potentials of the donor, since the triplet energy of electron transfer and the reduction potential for both cases are equal. These results are in agreement with quenching rates of electron transfer.

## 4. Experimental

*N*,*N*,*N*-tributyl-*N*-acetobenzo[b]thiophene ammonium borates **1a–c** were prepared by *N*,*N*,*N*-tributyl-*N*-acetobenzo[b]thiophene ammonium bromide with sodium or lithium borate according to an earlier reported procedure [49] and were recrystallized before use. Unless mentioned, all other compounds were obtained from Aldrich and recrystallized prior to use.

$^1H$ NMR spectra were taken on Gemini GEM-200 (200 MHz) spectrometer. Absorption spectra were recorded using a Hewlett Packard 8452A diode array UV–Vis spectrophotometer. Fluorescence and phosphorescence spectra were measured using a SPEX Fluorolog 2 spectrophotometer. Phosphorescence experiments were performed at 77°K in EPA (ether : isopentane : ethanol = 5 : 5 : 2) under argon with excitation at 355 nm. The source was a Xe lamp pulse passed through the monochrometer. The quantum yields of fluorescence and phosphorescence were determined relative to 9,10-diphenylanthracene [50,51] and benzophenone [31], respectively. GC–MS was performed on a Hewlett-Packard 5988 mass spectrophotometer 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.

All electrochemical experiments were conducted on a BAS-100 potentiostat with a BAS PA-1 preamplifer. Ag/$AgNO_3$M tetrabutylammonium perchlorate in acetonitrile was used as the reference electrode. The working electrode and counter electrode were platinum and a platinum wire, respectively. The rate of the scan was adjusted to 200 mV per second in all experiments.

Nanosecond laser flash photolysis experiments employed a kinetic spectrophotometric detection system, which has been previously described [52]. The excitation source was the third harmonic from a Q-switched Nd:YAG laser (355 nm; 60 mJ pulse$^{-1}$; 8 ns pulse). However, only a small fraction of pulse energy was used in order to eliminate unnecessary control kinetic spectrophotometer.

### 4.1. Product isolation and identification

All products were separated by chromatography on silica gel with hexanes : ethyl acetate (9 : 1) as eluent and identified by comparison with authentic samples or characterized by spectral means.

A typical preparative-scale reaction was carried out as follows. Compound **1a** or **1b** (0.75 g) was dissolved in 5 ml

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[2] We were unable to see the growth of formation of radical anion 11 using picosecond flash photolysis. Therefore, we think that the bond-breaking process leading to the formation of 11 is coupled to the primary electron transfer process and occurs on the subpicosecond time scale.

of dry acetonitrile in a Pyrex test tube containing a magnetic bar. The solution was deoxygenated with argon. The solution was irradiated at 300–400 nm for 1 h in a Rayonet reactor. The resulting solution was added to 50 ml of water. The aqueous solution was extracted twice with 20 ml portions of methylene chloride, and the combined organic layer dried over magnesium sulfate. After evaporation of the solvent, the yellow oils were chromatographed on silica gel with hexanes and ethyl acetate as eluent. Compound **6**: $^1$H NMR ($CDCl_3$: 7.96 (m, 1H), 7.88 (m, 2H), 7.46 (m, 2H), 3.12 (s, 4H). Compound **9**: $^1$H NMR (200 MHz, $CDCl_3$, $\delta$ (ppm)): 7.93 (m, 1H), 7.86 (m, 2H), 7.45 (m, 2H), 2.58 (m, 2H), 1.61 (m, 2H), 1.27 (m, 4H), 0.87 (t, $J = 7.2$ Hz, 3H); MS, *m/z* (% relative intensity): 232 ($M^+$), 217, 203, 190, 175, 161, 147 (100%), 128, 115, 43.

### 4.2. *Reaction of* **1b** *with methyl methacrylate*

The interaction of phenyl radicals with methyl methacrylate was investigated by examining the photodecomposition of **1b** in methyl methacrylate in the presence of anhydrous acetonitrile. The general procedure is as follows: 0.50 g (0.73 mol) of **1b** was dissolved in 2 ml of anhydrous acetonitrile and added to freshly distilled 0.075 g (0.75 mmol) methyl methacrylate. The resultant solution was degassed by the freeze-thaw technique, sealed under vacuum and placed in a Rayonet reactor. The mixture was irradiated at 300–400 nm for 1 h. The products were analyzed by GC–MS. Compound **9**: MS, *m/z* (% relative intensity): 178 ($M^+$), 118, 91 (100%), 65, 51. Compound **10**: MS, *m/z* (% relative intensity): 278 ($M^+$), 218, 187, 131, 91 (100%), 59, 41.

### 4.3. *Quantum yields determination*

In each experiment, 3.0 ml of sample solution in acetonitrile in a quartz cell (1.0 × 1.0 × 3.5 cm) was deoxygenated by purging with argon for 10 min, sealed and irradiated with 200 W mercury lamp at 366 nm using 360 ± 50 nm band glass filter. Acridine dimerization in air saturated methanol ($3 \times 10^{-4}$ M, $\Phi_d = 0.032$, $l_{ex} = 360$ nm) was used as the actinometer [38]. The photodissociation of the sample was monitored by UV–Vis absorption spectroscopy. The change of concentration versus irradiation time is expressed as follows:

$$-\frac{dc}{dt} = \frac{10^3 \Phi_d I_0}{d} \times [1 - \exp(-2.303A)]$$

where $I_0$, $d$, $\Phi_d$ and $A$ denote the intensity of excitation light, path length of cell, quantum yield of the reaction and absorbance at the excitation wavelength, respectively. The above equation can be rewritten as

$$\ln[\exp(2.303A) - 1] = -2.303 \times 10^3 \Phi_d e I_0 t + \ln[\exp(2.303A_0) - 1]$$

$\Phi_d$ and $I_0$ can be calculated from the plot of $\ln[\exp(2.303A_0) - 1]$ versus irradiation time. Quantum yields are the averages of three measurements.

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## References

[1] A. Albini, A. Sulpizio, in: Fox, M.A., Chanon, M. (Eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988, Part C, p. 88.
[2] F.D. Saeva, Top. Curr. Chem. 156 (1990) 59.
[3] J.K. Kochi, Acta Chem. Scand. 44 (1990) 409.
[4] J.W. Leon, D.G. Whitten, J. Am. Chem. Soc. 115 (1993) 8038.
[5] B.R. Arnold, J.C. Scaiano, W.G. McGimpsey, J. Am. Chem. Soc. 114 (1992) 9978.
[6] F.D. Saeva, D.J. Breslin, H.R. Luss, J. Am. Chem. Soc. 113 (1991) 5333.
[7] D. Tanner, J.J. Chen, L. Chen, C.J. Luelo, Am. Chem. Soc. 113 (1991) 8074.
[8] M. Ohashi, S. Otani, S. Kyushin, Chem. Lett. (1991) 631.
[9] P. Maslak, J. Kula, J.E. Chateauneuf, J. Am. Chem. Soc. 113 (1991) 2304.
[10] C.P. Andrieux, A.L. Goranda, J.-M. Saveant, J. Am. Chem. Soc. 114 (1992) 6892.
[11] G.II Jones, W.A. Haney, X.T. Phan, J. Am. Chem. Soc. 110 (1988) 1922.
[12] H.D. Roth, R.S. Hutton, J. Phys. Org. Chem. 3 (1990) 110.
[13] P.P. Levin, P.F. Pluzhnikov, V.A. Kuzmin, Chem. Phys. 137 (1989) 331.
[14] L. Chen, M.S. Farahat, H. Gan, S. Farid, D.G. Whitten, J. Am. Chem. Soc. 117 (1995) 6398.
[15] P. Maslak, W.H. Chapman, J. Org. Chem. 55 (1990) 6334.
[16] S. Hassoon, A. Sarker, M.A.J. Rodgers, D.C. Neckers, J. Am. Chem. Soc. 117 (1995) 11369.
[17] S. Hassoon, A. Sarker, A.Y. Polykarpov, M.A.J. Rodgers, D.C. Neckers, J. Phys. Chem. 100 (1996) 12386.
[18] A.M. Sarker, Y. Kaneko, A.V. Nikolaitchik, D.C. Neckers, J. Phys. Chem. 102 (1998) 5375.
[19] A.M. Sarker, Y. Kaneko, D.C. Neckers, J. Photochem. Photobiol. A 117 (1998) 67.
[20] A.M. Sarker, A. Lungu, A. Mejiritski, Y. Kaneko, D.C. Neckers, J. Chem. Soc., Perkin Trans. 2 (1998) 2315.
[21] A.M. Sarker, A. Lungu, D.C. Neckers, Macromolecules 29 (1996) 8047.
[22] A.M. Sarker, A.Y. Polykarpov, D.C. Neckers, A.M. deRaaff, J. Polym. Sci., Polym. Chem. 34 (1996) 2817.
[23] R. Popielarz, A.M. Sarker, D.C. Neckers, Macromolecules 31 (1998) 951.
[24] A.M. Sarker, A. Mejirtski, B.R. Wheaton, D.C. Neckers, Macromolecules 30 (1997) 2268.
[25] A. Mejirtski, A.M. Sarker, B.R. Wheaton, D.C. Neckers, Chem. Mater. 9 (1997) 1488.
[26] A. Mejirtski, A.Y. Polykarpov, A.M. Sarker, D.C. Neckers, Chem. Mater. 8 (1996) 1360.
[27] S. Chatterjee, P.D. Davis, P. Gottschalk, M. Kurz, B. Sauerwein, X. Yang, G.B. Schuster, J. Am. Chem. Soc. 112 (1990) 6329.
[28] S. Chatterjee, P. Gottschalk, P.D. Davis, G.B. Schuster, J. Am. Chem. Soc. 110 (1988) 2326.
[29] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry. 2nd ed., Marcel Decker, New York, 1993.

[30] Y. Kaneko, A.M. Sarker, D.C. Neckers, Chem. Mater. 1998, in press.
[31] R.S. Becker, G. Favaro, G. Poggi, A. Romani, J. Phys. Chem. 99 (1995) 1410.
[32] A. Weller, Pure Appl. Chem. 54 (1982) 1885.
[33] D. Rehm, A. Weller, Isr. J. Chem. 8 (1970) 259.
[34] T. Ganguly, D.K. Sharma, S. Gauthier, D. Gravel, G. Durocher, J. Phys. Chem. 96 (1992) 3757.
[35] G.B. Schuster, Pure Appl. Chem. 62 (1990) 1565.
[36] R.A. Marcus, Annu. Rev. Phys. Chem. 15 (1964) 155.
[37] S. Hu, A.M. Sarker, Y. Kaneko, D.C. Neckers, Macromolecules 31 (1998) 6476.
[38] K. Niizuma, M. Koizumi, Bull. Chem. Soc. Japan 36 (1963) 1629.
[39] J.P. Lorand, J. Am. Chem. Soc. 96 (1974) 2867.
[40] R.G. Kryger, J.P. Lorand, N.R. Stevens, N.R. Herron, J. Am. Chem. Soc. 99 (1977) 7589.
[41] J. Michl, V. Bonacic-Koutecky, 1990. Electronic Aspects of Organic Photochemistry, Wiley, New York, 1990, p. 138, 292 and 374.
[42] J. Michl, Acc. Chem. Res. 23 (1990) 127.
[43] S. Sankararaman, J.K. Kochi, J. Chem. Soc., Chem. Commun. (1989) 1800.
[44] I.R. Gould, D. Ege, J.E. Moser, S. Farid, J. Am. Chem. Soc. 112 (1990) 4290.
[45] X. Ci, R.S. da Silva, D.E. Nicodem, D.G. Whitten, J. Am. Chem. Soc. 111 (1989) 1337.
[46] E. Haselbach, E. Vauthey, P. Suppan, Tetrahedron 44 (1988) 7335.
[47] H. Gan, U. Leinhos, I.R. Gould, D.G. Whitten, J. Phys. Chem. 99 (1995) 3566.
[48] S.T. Murphy, C. Zou, J.B. Miers, R. Balloew, D. Dlott, G.B. Schuster, J. Phys. Chem. 97 (1993) 13152.
[49] A.M. Sarker, Y. Kaneko, D.C. Neckers, J. Org. Chem., submitted for publication.
[50] S. Hamai, F. Hirayama, J. Phys. Chem. 87 (1983) 83.
[51] S.R. Meech, D. Phillips, J. Photochem. 23 (1983) 193.
[52] W.E. Ford, M.A.J. Rodgers, J. Phys. Chem. 98 (1994) 3822.