6476 *Macromolecules* **1998,** *31,* 6476−6480

Reactivities of Chromophore-Containing Methyl Tri-*n*-butylammonium Organoborate Salts as Free Radical Photoinitiators: Dependence on the Chromophore and Borate Counterion[1]

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Received April 20, 1998; Revised Manuscript Received July 15, 1998

ABSTRACT: Several UV absorbing chromophores have been incorporated in ammonium triphenylbutyl- and tetraphenylborates as light-harvesting groups, and the reactivity of the resulting salts as unimolecular free radical initiators has been studied. The results are compared with kinetic and thermodynamic data calculated for the primary photochemical step leading to generation of the initiating species. The dependence of the initiation reactivities on the structure of both the chromophore and the borate counteranion is discussed.

Introduction

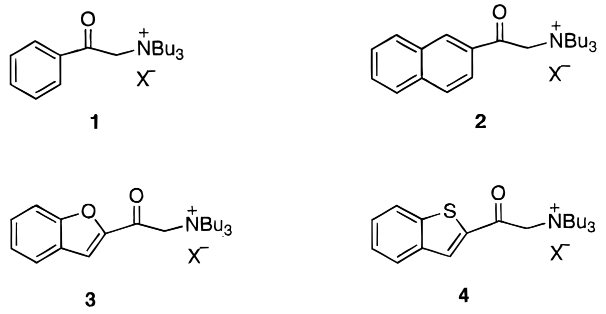
Cyanine triarylalkyl borates are well recognized as radical photoinitiators,[2−8] and other dyes have also been paired with triarylalkyl borates to form initiating systems.[9−14] We have recently reported that mid-UV-absorbing chromophores containing borate salts can be used to create a number of novel photochemical processes.[15,16]

The mechanism of radical chain initiation by the triarylalkyl borate salts involves a photoinduced electron transfer process from borate anion to the excited state of the chromophore. This is thought to produce a triarylalkylboranyl radical that rapidly fragments at the C−B bond giving triarylboron and an alkyl radical. However, recently, tetraarylborate salts, in particular, tetraphenylborate salts containing different chromophores, have also been found to be effective in initiating acrylate polymerization.[17,18] Since tetraarylborates are more stable and more easily synthesized/purified than the corresponding triarylalkylborates, the tetraaryl compounds are attractive for particular applications. The mechanisms of radical chain initiation are quite different for tetraaryl as opposed to triarylalkylborate systems. We suspect an α-amino alkyl radical formed in a secondary process as the initiating species when chromophore ammonium tetraarylborate compounds are used as initiators.[19]

To probe the reactivity of UV-absorbing ammonium organoborate salts, and the dependence of the photopolymerization rate on both the chromophore and the borate anion, we have studied the relative initiation efficiencies of a series of compounds containing different chromophores. Reaction kinetics were obtained by following the polymerization using fluorescence probe methodology,[20] and the relative efficiencies of the initiators calculated in representative monomers using a protocol previously described.[21] The results of these initiation efficiency measurements were compared with kinetic and thermodynamic data as calculated for the electron-transfer process.

Many traditional spectroscopic methods have been employed to study the kinetics of polymerization reactions. The most common of these are real time infrared (RTIR) spectroscopy,[22] Fourier transform IR spectroscopy,[23] and nuclear magnetic resonance (NMR) spectroscopy.[24] We have developed a rapid scan fluorimeter[25] for monitoring polymerization reactions and recently established a method that uses this instrument to measure reactivity of various photoinitiators.[20] The technique is based on changes in the fluorescence emission spectra of a probe molecule associated with the polymerization reaction. Molecules whose fluorescence emissions are sensitive to such changes can be used to monitor the degree of polymerization, and are often termed fluorescence probes. Various probe molecules have been developed for this purpose in earlier studies from this group.[26−28] The fluorescence spectra of these molecules all exhibit pronounced blue shifts when the resins they reside in are polymerized. A typical charge-transfer probe,[25,26] 5-dimethylaminonaphthalene-1-sulfonyl-*n*-butylamide (DASB), was employed in this study.

Chart 1

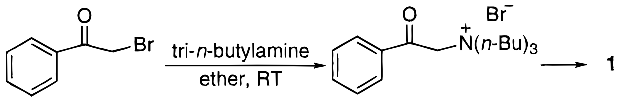


a: $X = Ph_3BBu$; b: $X = Ph_4B$; c: $X = BF_4$

The reactivities of four borates initiator systems (Chart 1) in a typical monomeric environment, triethylene glycol diacrylate (TEGDA), were studied. Each group contained the same light-absorbing chromophore with either tetraphenyl borate or triphenylbutyl borate as the counteranion. Compounds with tetrafluoroborate anion (non oxidizable) were also studied as controls to obtain kinetic and thermodynamic data pertaining to the electron transfer process. The reactivities of the initiators have been shown to be strongly dependent on the characteristics of both the chromophore and the counterion.

S0024-9297(98)00616-0 CCC: $15.00

Scheme 1



Experimental Section

Triethylene glycol diacrylate (TEGDA) was purchased from Sartomer and used as received. Kinetic measurements were carried out on a CM-1000 cure monitor at Spectra Group Ltd., Inc. Solutions of each initiator in TEGDA containing 0.05 wt % of DASB were prepared. The concentration of the initiators in each of the solution was maintained constant at 8.0×10^{-3} M. A precisely 0.1 mm thick layer of each of solution was prepared by squeezing a drop of the mixture between two glass slides separated by the appropriate spacers. A small spot on this thin layer was cured with the excitation beam of the CM-1000, and the polymerization process simultaneously monitored from the change of the fluorescence spectrum of the incorporated probe, which in turn was indicated by the ratio of the fluorescence intensity at two wavelengths on each side of the emission maximum. The excitation of both the initiator and the probe was accomplished by the monochromic excitation beam of CM-1000 set at 350 nm. All kinetic measurements were obtained under steady-state irradiation conditions, and the relative reactivity of the initiators was calculated as described earlier.[20]

UV–visible spectra were obtained using an HP 8452 diode array spectrophotometer. NMR spectra were taken with a Varian Gemini 200 NMR spectrometer using the solvent indicated. Chemical shifts are in ppm with TMS as the internal standard. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm i.d. × 0.25 mm film thickness DB-5 ms column (J & B Scientific), interfaced to an HP 2623A data processor. Thin-layer chromatography was performed with Whatman silica gel coating TLC plates. Elemental analyses were obtained from Atlantic Microlab Inc. Phosphorescence spectra were recorded using a SPEX Fluorolog 2 spectrophotometer. Phosphorescence experiments were carried out at 77 K in EPA (ether:isopentane:ethanol = 5:5:2) under argon with a 3.0 ms Xe lamp pulse passed through a 350 nm monochromator as the light source. The quantum yields of phosphorescence were determined relative to that of benzophenone.[29] All electrochemical experiments were conducted on a BAS-100 potentiostat with a BAS PA-1 preamplifier. A solution of $Ag/AgNO_3$ containing 0.1 M tetrabutylammonium perchlorate in acetonitrile was used as the reference electrode. The working electrode and the counter electrode were platinum and a platinum wire, respectively. The rate of the scan was adjusted to 200 mW/s in all the experiments.

Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers[30] using the third harmonic of a Q-switched Nd:YAG laser as the excitation source. The sample solution in a quartz cuvette was purged with argon for five minutes before, and during the experiment. The samples were excited with 355 nm pulses (pulse width ca. 7 ns).

The syntheses of compounds **2**, **3**, and **4** have been described.[31] Compound **1** was synthesized according to the procedure outlined in Scheme 1.

***N*-Phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium Bromide.** Tri-*n*-butylamine (15.40 g, 83.02 mmol) was added to a solution of 2-bromoacetophenone (6.61 g, 33.21 mmol) in ether, and the resulting mixture was stirred at room temperature overnight. The white precipitate formed was filtered and washed repeatedly with ether. Recrystallization from ethyl acetate affords the title compound as white crystals in 72% yield: mp 186–187 °C (ethyl acetate); ^1H NMR (CD_3CN) δ 8.12 (m, 2H), 7.73 (m, 1H), 7.58 (m, 2H), 5.22 (s, 2H), 3.60 (m, 6H), 1.67 (m, 6H), 1.37 (m, 6H), 0.94 (m, 9H); ^{13}C NMR (CD_3CN) δ 192.28 (C=O), 135.76, 129.83, 129.41, 118.24, 62.10, 61.11, 24.77, 20.26, 13.71. Anal. Calcd for $C_{20}H_{34}BrNO$: C, 62.53; H, 8.85; N, 3.64; Br, 20.80. Found C, 62.75; H, 8.81; N, 3.64; Br, 20.86.

***N*-Phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium Triphenylbutylborate (1a).** An aqueous solution of lithium triphenylbutyl borate (0.90 g, 2.94 mmol) obtained by treating 1.6 M solution of butyllithium in hexanes with triphenylboron in benzene at 10 °C was added slowly to a stirred aqueous solution of *N*-phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium bromide (1.0 g, 2.60 mmol). Slightly more than a stoichiometric amount of lithium triphenylbutylborate was used to ensure complete conversion of *N*-phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium bromide. A white solid gradually precipitated as the mixture was stirred for an additional 30 min. The solid was filtered, washed with water, and then air-dried. After recrystallization from ethyl acetate, **1a** was obtained as white crystals in 58% yield: mp 118–119 °C; ^1H NMR (CD_3CN) δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.74 (m, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.27 (m, *ortho* to B, 6H), 6.96 (m, *meta* to B, 6H), 6.80 (t, $J = 7.4$ Hz, *para* to B, 3H), 4.75 (s, 2H), 1.64 (m, 8H), 1.34 (m, 8H), 0.94 (m, 9H), 0.78 (t, $J = 7.4$ Hz, 3H). Anal. Calcd for $C_{42}H_{58}BNO$: C, 83.62; H, 9.61; N, 2.32. Found: C, 83.50; H, 9.66; N, 2.31.

***N*-Phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium Tetraphenylborate (1b).** To a stirred solution of *N*-phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium bromide (2.60 g, 6.77 mmol) in water was added an equimolar amount of aqueous solution of sodium tetraphenylborate (2.32 g, 6.78 mmol). A thick white precipitate formed immediately. After being stirred at room temperature for an additional 30 min, the mixture was diluted with water and filtered. The precipitate was recrystallized from ethyl acetate, and **1b** was obtained as white needles in 80% yield: mp 151–152 °C (ethyl acetate); ^1H NMR (CD_3CN) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.74 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.4$ Hz, 2H), 7.28 (m, 8H, *ortho* to B), 7.00 (t, $J = 7.4$ Hz, 8H, *meta* to B), 6.84 (t, $J = 7.4$ Hz, 4H, *para* to B), 4.76 (s, 2H), 3.51 (m, 6H), 1.67 (m, 6H), 1.36 (m, 6H), 0.94 (t, $J = 7.4$ Hz, 9H). Anal. Calcd for $C_{44}H_{54}BNO$: C, 84.79; H, 8.66; N, 2.25. Found: C, 84.92; H, 8.71; N, 2.24.

***N*-Phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium Tetrafluoroborate (1c).** *N*-Phenacyl-*N*,*N*,*N*-tri-*n*-butylammonium bromide (1.0 g, 2.60 mmol) was dissolved in water and any insoluble materials were filtered out. To this vigorously stirred solution was added drop by drop an excess amount of aqueous solution of fluoroboric acid (48 wt %) at room temperature. A white precipitate formed immediately and the solution was further diluted with water and stirred for 30 min. The white precipitate was filtered and washed with water, and **1c** was obtained in 77% yield: mp 88–89 °C. Anal. Calcd for $C_{20}H_{34}BF_4NO$: C, 61.43; H, 8.70; Br, 0.0. Found: C, 61.47; H, 8.70; Br, 0.0.

Results and Discussion

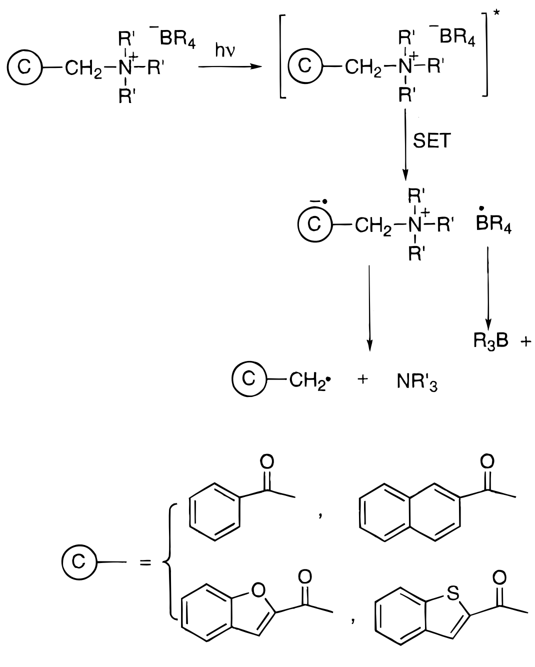
1. General Mechanism. Upon oxidation, tetraorganyl borate anions that have at least one alkyl group have been shown to produce free radicals that can be utilized for initiating polymerization reactions, eq 1. A

$$R_4B^- - 1e^- \rightarrow R_3B + R^\bullet \qquad (1)$$

general mechanism for the intramolecular single electron-transfer induced oxidation of tetraorganyl borate is displayed in Scheme 2.[14] When irradiated, the light-absorbing chromophore is promoted to its excited state, which is subsequently reduced by the intramolecularly situated borate anions. The resulting chromophore radical anion further fragments into a substituted alkyl radical and a free amine while the borate radical decomposes as above. When triphenylbutylborate is employed as the counterion, $R^\bullet$ is a butyl radical.[12] When tetraphenylborate is employed as the counterion, initiation derives from a secondary reaction between the free amine produced and the excited state of the remaining product chromophores.[14]

2. Relative Initiator Reactivity. The relative reactivities of compounds **1a**–**4a** and **1b**–**4b** were

Scheme 2



measured by recording the initiated polymerization reaction profiles in TEGDA under steady-state conditions. A representative example is shown in Figure 1 for reactions in which compounds **1a** and **1b** were used as the initiators.

Profiles are expressed in terms of intensity ratios at two wavelengths as detected from the incorporated fluorescence probe plotted against reaction time. After an induction period, polymerization starts, and this results in a shift in the fluorescence spectrum and an increase in the ratio.[32] The reaction slows as the reactive monomer is depleted.

The efficiency of the polymerization is deduced from several parameters in the kinetic profile. The most obvious of these is the length of the induction time—the time required for the reacting radicals derived from the photoinitiator to consume inhibitors present in the monomer system. For example, under the same reaction conditions, the induction period for polymerization initiated by **1a** was approximately two-thirds that of the reaction initiated by **1b**. Since the concentration of inhibitors present in the monomer system is the same in both cases, the shorter induction period for **1a** vs **1b** evidences that more initiating radicals or more reactive radicals are produced in the photoreaction of **1a** than from **1b** and that **1a** is a more efficient initiator than **1b**.

A more quantitative indication of initiator efficiency is the initial rate of polymerization. This can be derived from the slope of the polymerization profiles at their inflection points where the polymerization reaction is occurring at maximum rate.[33] The relative efficiencies of initiation for different initiators with reference to a standard compound can be calculated from eq 2,[21] where

$$\Phi_{rel} = (R_p/R_{pref})^2 \times (1 - 10^{-A_{ref}})/(1 - 10^{-A}) \quad (2)$$

R_p, and R_{pref} are the rates of polymerization measured using a photoinitiator of interest and the reference initiator and A and A_{ref} are the absorbances of the initiators in the polymerization samples.

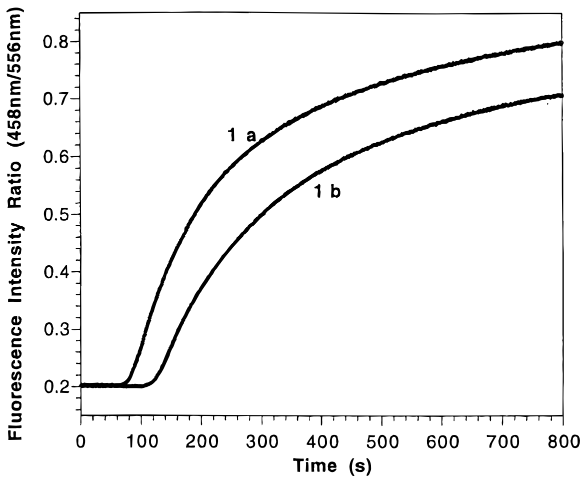


Figure 1. Polymerization kinetic profiles of TEGDA monomer initiated by 8.0×10^{-3} M photoinitiators **1a** and **1b**.

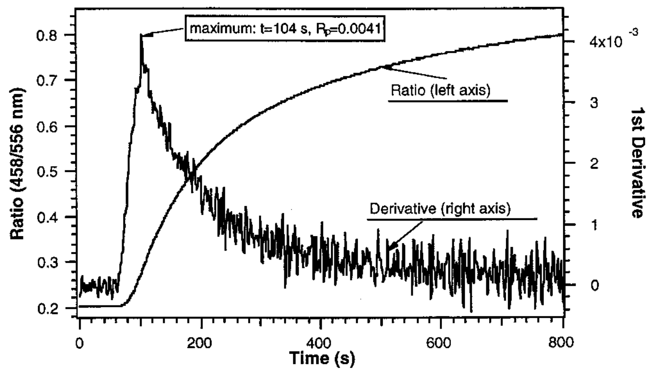


Figure 2. Differentiation of the kinetic profile of a polymerization reaction initiated by **1a**. The rate of polymerization is obtained from the maximum value of the derivative curve.

Table 1. Relative Initiation Efficiencies of Compounds 1a–4a and 1b–4b as Photoinitiators for the Polymerization of TEGDA

compounds	Φ_{rel}	compounds	Φ_{rel}
1a	1 (ref)	**1b**	0.41
2a	0.84	**2b**	0.21
3a	3.78	**3b**	1.28
4a	1.39	**4b**	0.46

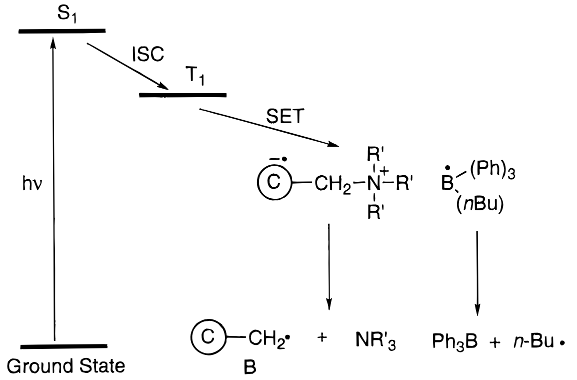
The rate of polymerization as initiated by **1a** was obtained by differentiating the polymerization profile (Figure 2). The maximum in the derivative plot (right axis) is reached at the inflection point of the kinetic profile (left axis).

The absorbance of the initiator at 350 nm in the polymerization sample is calculated from the UV absorption spectrum of this initiator recorded in neat monomer and was maintained between 0.08 and 0.2 depending on the chromophore. The low absorbances maintain the uniformity of the light intensity throughout the polymerizing sample and ensure steady-state reaction conditions.

The relative initiation efficiencies calculated using compound **1a** as the reference (i.e., its efficiency was taken as 1) are displayed in Table 1.

Overall, compounds (**1a**–**4a**) containing triphenylbutylborate are better initiators than the corresponding compounds containing tetraphenyl borate (**1b**–**4b**).[16] Tetraphenylborate salts are reduced almost as rapidly as triphenylbutylborates salts, but the formed tetraphenylboranyl radical does not eliminate phenyl radical

Scheme 3



efficiently. It prefers, instead, to regain the electron borrowed by the acceptor (undergo back electron transfer). In the specific instances reported here, the reduced acceptor undergoes irreversible elimination more rapidly than back electron transfer occurs. In other words, it puts the borrowed electron to use before the tetraboranyl radical can regain it. As a result, compounds containing tetraphenyl borate (**1b**−**4b**) can initiate polymerization in modest to good efficiencies in agreement with an earlier report.[18]

When the reactivities of compounds containing the same borate counterion are compared, these are found dependent on the chromophore employed. Compounds containing the benzofuranyl carbonyl chromophore (**3**) are most efficient, followed by compounds containing the benzothienyl carbonyl chromophore (**4**). Compounds containing the naphthyl carbonyl group (**2**) react with the least efficiency.

3. Dependence on Chromophore. For the sake of simplicity, we will compare only compounds **1a**−**4a** from which the same reacting radical (*n*-butyl radical) was produced after irradiation.[34] The relative efficiency of initiation therefore reflects the relative quantity of *n*-butyl radical released from the borates when the same number of photons is absorbed by the initiators. In this sense, the relative initiator efficiency is a measurement of relative yields of initiating radical under the polymerizing conditions.

The yield of butyl radical should be related to the factors governing the photochemical and photophysical processes leading its formation. A general picture of these processes is outlined in Scheme 3 for compounds **1a**−**4a**.

When irradiated, **1a**−**4a** are promoted to their singlet excited state (S_1). Intersystem crossing (ISC) to triplet states (T_1) occurs before intramolecular single electron transfer (SET),[35] Scheme 3. The yield of T_1 obviously influences the final yield of butyl radical. The intersystem crossing of the chromophore **1** is expected to be rapid and the quantum yield of triplet formation close to that of benzophenone.[36] The triplet characteristics of the chromophores involved in compounds **2**−**4** were investigated by studying the steady-state phosphorescence spectra and time-resolved laser flash photolysis of borates **2c**−**4c** with the nonreducing gegenion BF_4^- in acetonitrile, Table 2. Quantum yields for triplet formation (Φ_T) were calculated according to eq 3, where

$$\Phi_T = \Phi_p\{[k_T + (1/\tau_p)]/(1/\tau_p)\} \quad (3)$$

Φ_p is the quantum yield of phosphorescence, k_T is the rate constant of triplet deactivation in EPA at 77 K, and τ_p is the lifetime of phosphorescence.

Table 2. Triplet Parameters Obtained by Studying Compounds 2c−4c

	2c	**3c**	**4c**
$\lambda_{max,p}$ (nm)[a]	488, 525	490, 525	531
E_T (kcal/mol)[a]	58.6	58.2	53.8
τ_p (ms)[a]	1040	60.2	38.6
Φ_p[a]	5.5×10^{-4}	4.0×10^{-3}	3.4×10^{-3}
Φ_T[a]	0.82	0.54	0.29
$\lambda_{max,T\to T}$ (nm)[b]	430	420	380, 460
τ_T (μs)[b]	42.9	44.0	46.5

[a] From phosphorescence measurements. [b] From laser flash photolysis.

Table 3. Reduction Potentials and Excited Triplet Energies of the Light-Absorbing Chromophores 1c−4c

compounds	E_{red} (V vs SCE)	E^T (kcal/mol)
1c	−1.62	72.8
2c	−1.27	58.6
3c	−1.32	58.2
4c	−1.15	53.8

Table 4. ΔG_{et} Associated with a Single Electron Transfer 1a−4a

	1a	**2a**	**3a**	**4a**
ΔG_{et} (ev)	−0.84	−0.57	−0.51	−0.48

The quantum yields of triplet (Φ_T) formation are quite different and vary among these four chromophores. This is likely due to the differing degrees of delocalization of the excited electron of the carbonyl group over the adjacent aromatic ring in the singlet excited states of these chromophores. Triplet lifetimes are, however, similar as measured by transient spectroscopy, suggesting that delocalization in the triplet states are more similar among these chromophores.

The free energy change (ΔG_{et}) associated with a single electron transfer from the borate anion to the excited-state chromophore is calculated using eq 4,[37] where E^T

$$\Delta G_{et} = E_{ox}\,(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - E^T - Ze^2/\epsilon a \quad (4)$$

is the triplet energy of the light-absorbing chromophore derived from the phosphoresce spectra measured for compounds **1c**−**4c**, where such an electron-transfer process was known to not occur.[14]

E_{red} is the reduction potentials of the chromophore measured for compounds **1**−**4c** against the SCE electrode in acetonitrile (Table 3),

$Ze^2/\epsilon a$ is the Coulombic energy, the free energy gained by bring the radical ions formed to an encounter distance *a* in a solvent of dielectric constant *e*, and E_{ox} is the oxidation potentials of the borate anions.[9]

The highly negative ΔG_{et} values, Table 4, reveal that the electron transfer processes from the borate counterions to the excited state of the chromophores are thermodynamically favorable.

The kinetics of electron transfer from the borate counterion to the excited-state chromophore were measured by quenching the excited state of **1c**−**4c** with added triphenylbutyl borate ammonium salt. Rate constants for quenching were obtained by measuring the triplet lifetimes of **1c**−**4c** at different borate concentrations, Table 5. More rapid quenching of the benzofuranyl and benzothienyl carbonyl chromophores in compounds **3c** and **4c** was observed as compared to **2c**.

Table 5. Quenching Rate Constants of the Triplet Excited State of 1c−4c with Triphenylbutylborates in Acetonitrile Solution

compounds	k_q (M^{-1} s^{-1})
1c	
2c	1.28×10^8
3c	1.23×10^9
4c	2.53×10^9

The yield of the SET process could not be measured directly since the efficiency of the electron-transfer process in yielding products depends on both the rates of the forward electron transfer and the back electron transfer (if it exists).

As revealed in this study, the kinetic or the thermodynamic data associated with the electron-transfer process show no apparent relationship to the reactivities of these compounds as photoinitiators. This is because the kinetic or thermodynamic data for the SET process do not indicate the efficiency of the SET step, not to mention the efficiency of radical formation, which depends on the overall efficiencies of several processes.

On the other hand, the relative reactivity data obtained in this study reveal the overall efficiency of all of the processes leading to the formation of the *n*-butyl radical. For compounds **1a**−**4a**, the efficiency for the formation of *n*-butyl radical depends on the combination effects of Φ_T as well as the efficiency of the SET process. Therefore, reactivity data truly reflect the overall efficiency of the compounds as photoinitiators. It is believed that directly measuring initiation reactivities of these chromophore-containing borate salts will benefit the design and selection of better materials and improve performance in this series.

4. Conclusions. In summary, we have measured, directly, the initiation reactivities of several chromophore-containing borate salt photoinitiators. Reactivity depends on both the borate counterion and the characteristics of the light-absorbing chromophore. For compounds possessing the same chromophore, enhanced initiation efficiency was achieved with a triphenylbutylborate as the counterion over those with a tetraphenylborate counterion. For compounds containing the same borate counterion, initiation reactivities differ with different chromophores. This difference in reactivity reflects the overall efficiency of all the photophysical and photochemical processes of the chromophore prior to the formation of the initiating radical. These processes include the following: (1) the rate of ISC to triplet state, the efficiency of which depends on how much of the excitation energy is lost by fluorescence, internal conversion to ground state, and/or other routes; (2) competition between back electron transfer, where the efficiency of net electron transfer is often not revealed from kinetic and thermodynamic calculations obtained for the SET only; (3) other side reactions not leading to an initiating radical, such as the coupling reaction between the chromophore substituted alkyl radical (**B** in Scheme 3) and the *n*-butyl radical. Data obtained for any of these processes independently do not reveal the reactivity of a specific compound as photoinitiator. In this study, comprehensive reactivity data were obtained under polymerization conditions by monitoring the polymerization reaction using fluorescence probes.

Acknowledgment. Financial support from the National Science Foundation (NSF DMR-9526755) and Spectra Group Limited, Inc. is gratefully acknowledged. Valuable discussions with Drs. George S. Hammond and Bernd Strehmel are also acknowledged. Shengkui Hu thanks the McMaster Endowment for a Fellowship.

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MA980616X