Photoinduced Inter- and Intra-Ion-Pair Electron Transfer Reactions in *N*-(*p*-Benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-butylammonium Triphenyl-*n*-butylborate and -Gallate Salts

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The photoreduction of *N*-(*p*-benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-butylammonium triphenyl-*n*-butylborate (**1**) and gallate (**2**) was studied using nano- and picosecond laser flash photolysis. An electron transfer reaction from the borate or the gallate counteranion to the excited triplet state of the benzophenone moiety (BP*³) was demonstrated. This reaction leads to the formation of benzophenone radical anion (**6**) and the boranyl radical, the latter of which dissociates rapidly to form butyl radical. The electron transfer rate was found to depend on the polarity of the solvent. In neat benzene, the short lifetime of the triplet obtained (300 ± 150 ps) indicates an intramolecular process and that the compounds exist as tight ion pairs. The addition of 1% MeCN increases the triplet lifetime up to 1.2 ns. The formation of a solvent-separated ion pair was suggested in this solvent mixture. However, in the polar solvent MeCN, **1** and **2** exist partially as free ions as determined by their dissociation constants. A diffusion-controlled intermolecular electron transfer process was shown in this solvent. The *p*-benzoylbenzyl radical (BPCH₂), most likely formed by the C–N cleavage bond in the radical anion (**6**), was identified as an intermedate in the reaction pathway. After the initial electron transfer reaction transfer reaction transfer reaction transfer reaction transfer reaction of **1**, 10⁻² M in MeCN, is 0.5 ± 0.05. Triplet quenching as well as coupling of the radical anion (**6**) with the butyl radical deriving from decomposition of the borate was suggested to compete with the C–N cleavage reaction.

Introduction

Photoinduced electron transfer reactions represent an important route to free radicals among whose uses is the initiation of vinyl polymerization.² It is apparent that borate anions are especially beneficial electron transfer donors, and these have many important applications in free-radical polymerizations initiated by different electron acceptor sensitizers. The oneelectron photooxidation of triarylalkylborates forms a boranyl radical which lives for a very short time and cleaves rapidly yielding triarylborane and an alkyl radical, the latter initiating polymerization. Schuster and his co-workers^{3,4} have studied the photochemistry and photophysics of carbocyanine alkyltriphenylborate salts and shown that electron transfer occurs from the borate to the singlet state of the cyanine cation. Since the lifetime of the cyanine singlet is short (picoseconds), the said electron transfer is observed only in nonpolar solvents where the process can occur in the tight ion pair.⁵ Electron transfer photooxidation of borates may also occur with uncharged acceptors.^{6,7} We have recently reported that photoreduction of fluorone dyes by triphenylbutylborate salts is an intermolecular electron transfer reaction from the borate anion to the triplet state of the dye that leads to the formation of butyl radicals which initiate polymerization.7

Rate constants for electron transfer are related to the free energy of the reactions (ΔG_{et}) according to classical Marcus theory.⁸ An important prediction of Marcus theory is the existence of the "inverted region". The electron transfer rate will increase with decreasing free energy of the reaction up to a maximum and then decrease as ΔG_{et} becomes more exoergic. Considerable attention has been made to testing the Marcus theory approach. Rehm and Weller were first to point out a discrepancy between the theory and experiment.⁹ For the intermolecular cases studied, electron transfer rates reached a plateau value in the highly exothermic region and inverted behavior is not seen down to a value of $\Delta G_{\rm et} \sim 2.5$ eV. The intra-ion-pair electron transfer rates from borates to an exited cationic acceptor are anticipated to be high and above the diffusion rate limit. This makes these systems attractive for investigation of electron transfer theories. The electron transfer rates obtained for series of cyanine-tetraarylborates in benzene were insensitive to the significant changes in the hard sphere radius of the borate anion suggesting the formation of penetrated ion pairs.¹⁰ In an attempt to obtain accurate and thermodynamically meaningful values for the oxidation potentials of tetraarylborates, Schuster and co workers developed a kinetic method¹¹ and found that the application of the Rehm-Weller relationship leads to an overestimation of the oxidation potentials when compared with those obtained from the classical Marcus relationship.

In a recent communication¹² we have outlined preliminary experiments dealing with the photoinduced electron transfer reaction of N-(p-benzoylbenzyl)-N,N,N-tri-n-butylammonium triphenyl-n-butylborate (1), in which the borate counteranion is complexed to the para position of the benzophenone moiety. Electron transfer from the triphenylbutylborate counteranion to the excited triplet state of the benzophenone moiety (BP*3) was demonstrated. The photoreduction of benzophenone by electron donors such as amines has been studied extensively,¹³ and early flash photolysis experiments confirmed the following mechanistic scheme.^{14,15} Electron transfer from the amine to BP*3 forms the radical anion BP^{•-} and the amino radical cation as a contact ion pair (CIP). Subsequent reactions of the CIP can be solvation to form a solvent-separated ion pair (SSIP), proton transfer to form neutral radicals, or back electron transfer. The extent of each depends on the rates of proton transfer and back electron transfer in each solvent.^{16,17}

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SCHEME 1: Synthesis of Salts 1–4. (a) Tributylamine, ether/chloroform, room temperature. (b) Lithium salt of triphenylbutyl borate, H₂O, room temperature. (c) Lithium salt of triphenylbutylgallate, THF. (d) HBF₄, 48 wt %.



Since electron transfer in (1) is to the long-lived triplet excited state of the benzophenone moiety, the relative contributions of the intermolecular or intramolecular processes are found to depend on the polarity of the solvent. In neat benzene, the process is very fast as indicated by a measured triplet lifetime of 300 ± 150 ps which suggests an intramolecular process and that the compound exists as a tight ion pair. However, in acetonitrile the compound exists partially as free ions with their amount relative to the tight pair depending on dissociation constant and concentration. Accordingly both inter- and intramolecular electron transfer processes were shown in this case.

The present work represents further mechanistic studies of the benzophenone—borate (1) and the extension of these studies to the benzophenone—gallate system (2). The unique elimination of a tri-*n*-butylammonium radical cation from the radical anion formed after the initial electron transfer step (see Scheme 2) produces *p*-benzoylbenzyl radical and free amine. This was further investigated by comparing the photochemistry to the case where the borate counteranion was complexed to the meta position of the benzophenone (5). In the latter case, since free amine was also obtained, an elimination step forming an amino radical cation and the anion of the ketone is not a necessary step in the reaction mechanism, and the elimination of the free amine occurs directly as a result of intramolecular electron transfer in the radical anion.

Results

1. Synthesis. The synthesis of the compounds 1-4 is described in Scheme 1. 4-Bromomethylbenzophenone, when treated with tributylamine in ether/chloroform gave *N*-(*p*-benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-butylammonium bromide (3). *N*-(*p*-benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-butylammonium triphenyl-*n*-butylborate (1) and the gallate analog salt (2) were synthesized from 3 and the lithium salts of triphenylbutylborate or -gallate, respectively, in water, while 4 was obtained by treating 3 with fluoroboric acid in water.

N-(*m*-benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-ethylammonium triphenyl*n*-butylborate (**5**) was prepared in similar way to (**1**) except that 3-bromomethylbenzophenone and triethylamine were used in step (a). Details of the synthesis are given in the Experimental Section.



Figure 1. Ground state absorption spectra of 10^{-3} M of 1 in MeCN.



2. Absorption and Emission Spectra. The photophysical properties of all compounds (1-5) are determined by the benzophenone (BP) chromophore as can be seen from their absorption and emission spectra. Their absorption spectra above 300 nm are virtually identical and similar to that of benzophenone (Figure 1). The $n-\pi^*$ transitions are slightly red-shifted by (~5 nm) relative to benzophenone but the absorption coefficients are similar ($\epsilon \sim 150 \text{ Lmol}^{-1} \text{ cm}^{-1}$).

Excitation of 10^{-3} M solutions of (1-5) at 335 nm in acetonitrile (MeCN) and at room temperature results in very weak fluorescence. This is not surprising knowing that intersystem crossing in benzophenone is very fast (<10 ps) and triplet quantum yield formation is ~1. The fluorescence in the bromide case (3) is ~3 times less intense when compared to 1 at the above conditions. This can be related to the difference in the dissociation constants of the two salts as will be discussed later. The bromide salt under these conditions is less dissociated and exists mostly as a tight ion pair while the borate salt exists more as separated ions. Therefore, quenching of the singlet state either by electron transfer or by enhanced intersystem crossing will be more efficient in the bromide case.

The phosphorescence spectra obtained at 77 K in methanol/ ethanol (1:1) matrix for the compounds 1-4 were identical but shifted 4 nm to the red relative to BP. The phosphorescence quantum yields were about the same.

3. Transient Spectra and Triplet Decay Kinetics. A. Nanosecond Laser Flash Photolysis. Nanosecond time-resolved transient absorption spectroscopy with excitation at 355 nm using the third harmonics of a Q-switched Nd:YAG laser was used to investigate the interaction mechanism. The triplet decay rates and transient absorption spectra of 1 and 4 were measured in acetonitrile (MeCN), benzene, and methanol (MeOH). In 4 when no electron transfer is expected from the ⁻BF₄ counteranion to the excited triplet state of BP, the triplet transient absorption spectrum was obtained in the three solvents. The transient absorption spectrum of 10⁻³ M solution of 4 obtained in benzene (1% MeCN by volume),¹⁸ 0.12 and 4.2 µs after the pulse is shown in Figure 2a. The two absorptions at 330 and 540 nm decay with the same rate and we assign them to the triplet absorption of the benzophenone moiety in agreement with literature.^{16,17,19} Within this time scale no triplet was detected for 1 and 2 under the same conditions as can be seen for 1 in Figure 2b, indicating a very fast quenching of the triplet. The peak at 320 nm is assigned to the *p*-benzoylbenzyl radical (BPCH₂•) as will be discussed later (see Scheme 2). However, the transient absorption spectra of $1 (10^{-3} \text{ M})$ in the polar solvent



Figure 2. Transient absorption spectra recorded at two delay times after the laser pulse of (a) 10^{-3} M of **4** in benzene (1% MeCN), (b) 10^{-3} M of **1** in benzene (1% MeCN), and (c) 10^{-3} M of **1**, in MeCN.

MeCN as given in Figure 2c shows that the triplet is forming immediately after the pulse at 330 and 540 nm, but in contrast to the case of 4 the two absorptions do not decay at the same rate. While the peak at 530–540 nm decayed almost completely after $\sim 1 \ \mu s$, the peak at 330 nm does not decay, suggesting that by quenching the triplet a new transient is forming at this wavelength with longer lifetime. As mentioned above, this is the BPCH₂• radical formed in the reaction pathway (Scheme 2).

The transient absorption spectra obtained by photolysis of a mixture (1:1) of 2×10^{-3} M of 4-methylbenzophenone (MeBP) and tetrabutylammonium triphenyl-n-butylborate in MeCN are shown in Figure 3. As the triplet at 530 nm decays, a transient absorbing around 720 nm forms. We assign this transient to the radical anion MeBP.- which is in agreement with the literature reported values for BP with amines.¹⁶ For comparison, we were unable to detect any absorption in that spectral range for the expected analog radical anion from 1 or 2. Alcohols are known to stabilize BP radical anions through hydrogen bonding.^{14,16} The transient absorption spectra obtained for 1, 10^{-3} M in MeOH, at different time intervals, are shown in Figure 4a. As the triplet absorption at 540 nm decays, two new transients absorbing at 550 and 620-630 nm form. It has previously been shown that BP*- absorption in MeOH is blue shifted to ~615 nm compared to its absorption in MeCN (~720 nm), as a result of hydrogen bonding.^{14,16} Accordingly, we assign the absorption at 620-630 nm in Figure 4a to the radical anion (6) formed after the initial electron transfer step (Scheme 2). Under the same conditions, 4 gives the transient absorption



Figure 3. Transient absorption spectra recorded at three delay times after the laser pulse of 2×10^{-3} M (1:1) mixture of 4-methylbenzophenone and tetrabutylammoniuom triphenyl-*n*-butylborate in MeCN.



Figure 4. Transient absorption spectra recorded at three delay times of (a) 10^{-3} M of 1 and (b) 10^{-3} M of 4 in MeOH.

spectra shown in Figure 4b, where only the transient absorbing at 550 nm is formed after the triplet decay. In this case no electron transfer is expected. The only possible quenching reaction of the excited triplet state of the BP moiety would be by hydrogen abstraction which leads to the formation of the related ketyl radical. On the basis of these experiments and comparing to the BP ketyl radical absorption reported in the literature, we assign the absorption obtained at 550 nm as the analog ketyl radical of 1 or 4.

We show the triplet decay rate obtained for 10^{-3} M solution of **4** in MeCN as a function of concentrations of tetrabutylammonium triphenyl-*n*-butylborate and -gallate, respectively in Figures 5 and 6. The triplet decay rate increases as a result of the intermolecular electron transfer quenching with an increase in concentration. A similar concentration dependence was obtained when the triplet decay rate was measured for **1** and **2** at different concentrations. It is clear from these results that the quenching process in this solvent is bimolecular which means that the ions exist mostly as a separated ions. The quenching rate constants obtained by linear fitting of the data in Figure 5 and 6 are 8.88×10^9 and 1.47×10^9 M⁻¹ s⁻¹ for **1** and **2**, respectively. The quenching rate constant is ~6 times faster in the borate case relative to the gallate case.



Figure 5. Concentration dependence of the triplet decay rate of the benzophenone moiety in 1 in MeCN. Inset depicts the nonlinear concentration dependence.



Figure 6. Concentration dependence of the triplet decay rate of the benzophenone moiety in 2 in MeCN. Inset depicts the nonlinear concentration dependence.

B. Picosecond Laser Flash Photolysis. Failure to observe the triplet transient from 1 in benzene and the radical anion (6)in MeCN and benzene in the nanosecond experiment may indicate that their lifetimes are less than the instrument response time ca 10 ns. The triplet of 2 is quenched very rapidly in benzene, probably as a result of very fast electron transfer in this solvent. A picosecond flash experiment was used to measure the rate of electron transfer in 1 in neat benzene, though we were able to detect an immediate formation of a transient having $\lambda_{\text{max}} = 540$ nm which we ascribe to the triplet absorption spectrum of the benzophenone moiety. Since the parent compound has poor solubility in benzene, the absorbance at 355 nm, the excitation wavelength, was limited. This produced absorbance signals of poor signal-to-noise ratio which precluded measurement of a precise lifetime, but our best estimate was 300 ± 150 ps. The addition of 1% (by volume) of MeCN to benzene caused the solubility to increase such that it was possible to obtain good kinetic data under these conditions. This led to a measurement of the lifetime of the triplet in this solvent mixture of 1.2 ns (Figure 7). However, under these conditions we still could detect no radical anion.

4. Production Analysis and Quantum Yields. Irradiation of 10^{-2} M of **1** in MeCN and MeOH gives mainly p,p'-(benzoyl)bibenzyl (9) (Scheme 2). Compounds 9 and 10, as well as tributylamine, were isolated and identified from the reaction mixture (see Experimental Section). This implicates the BPCH₂• radical (8), an intermediate most likely formed by the dissociation of the radical anion (6) along with the tributylammonium radical cation, in the reaction pathway (see Scheme 2). In support of this we also observed an absorption peak formed with long lifetime around 320 nm in the transient absorption spectra as can be seen in Figure 2b, and c. We assign



Figure 7. Transient absorption spectra of 1, 5×10^{-3} M in benzene (1% MeCN) recorded at 60, 320, and 800 ps after the pulse.

TABLE 1: Quantum Yields for the Photolysis Reaction ofAerated and Degassed 10^{-2} M Solutions of (1) in MeCN

compound	degassed (±10%)	aerated (±10%)
1	0.50	0.52
(BPCH ₂) ₂ (9)	0.14	0.065
BPCH ₂ Bu (10)	0.12	0.057

this absorption to the BPCH₂• radical (8) in agreement with the reported absorption of related benzyl radicals.²⁰

The quantum yields of disappearance of **1** in MeCN were measured using an actinometric method based on the known benzophenone—benzhydrol reaction.²¹ Though the original measures were reported for benzene we had to use MeCN due to the low solubility of the parent compound in benzene. Results were corrected according to the differences in the absorption coefficients of the compound in the two solvents and are summarized in Table 1.

Two main observations result from the data reported in Table 1. First, the quantum yield for the disappearance of 1 is only 0.5 and is independent in the presence of oxygen. Second, the quantum yield of formation of products 9 and 10 is oxygen dependent. On the other hand, photolysis of 4 under the same conditions, but for longer time (20 min compared to 1 min photolysis with 1 gives quantum yield of 0.003 for the final product (10) in the degassed sample. Thus there is almost no reaction in this case.

Discussion

The triplet decay rates in 1 and 2 in MeCN are found to be bimolecular from their concentration dependence (Figures 5 and 6). In the polar solvent MeCN ($\epsilon = 36$), 1 or 2 probably exist in the form of free ions (depending on their equilibrium constants) and the quenching process would thus be intermolecular. The observation that almost no triplet quenching or radical formation occurs in 4 allows us to assume that the triplet quenching observed in 1 and 2 is due to an electron transfer process. Accordingly, the rate constants for the intermolecular electron transfer would be 8.88×10^9 and 1.47×10^9 M⁻¹ s⁻¹ for 1 and 2, respectively, obtained by linear fitting of the data in Figures 5 and 6. On the other hand, in the nonpolar solvent benzene ($\epsilon = 2.3$) it may be that the compounds exist as tight ion pairs, in which case the electron transfer process would be intramolecular and probably the triplet decay is complete on a subnanosecond time scale as shown in Figure 2. In the picosecond experiment, the triplet absorption of **1** in benzene was observed with approximately 300 ps lifetime. This supports the contention that intramolecular decay is occurring. No bimolecular reaction would be possible at such short time and at 1×10^{-4} M, the concentration used in this experiment. The

SCHEME 2



addition of 1 vol % MeCN to benzene increases the lifetime of the triplet to 1.2 ns, again consistent with the process being intramolecular. It seems that the triplet decay rate increases as the polarity of the solvent decreases. The literature contains a number of reports dealing with the nature of radical ion pair systems obtained by photoinduced electron transfer reactions in various solvents.²² In general, in less polar solvents the formation of a contact ion pair (CIP) was confirmed while increasing the polarity of the solvent leads to the formation of solvent-separated ion pair (SSIP). In a similar way, we could assume that the addition of 1% MeCN to benzene results in changing the structure of 1 or 2 from a tight ion pair form to the solvent-separated ion pair form. This, in turn, may reflect the increase in the triplet decay rate as given above.

The bimolecular triplet quenching rate constants in 1 and 2 in MeCN, as reported above, were obtained by linear fitting of the data in Figures 5 and 6. However, a closer look at the data shows that the concentration dependence of the triplet decay rates is not linear as shown in the insets in Figures 5 and 6. This can be explained in terms of an equilibrium between dissociated ions and the tight ion pair in these systems. The data in Figures 5 and 6 were obtained by adding increasing amounts of triphenylbutylborate or -gallate counteranions to a fixed concentration of **4**. As the concentration of the borate or the gallate counteranion increases, the concentration of the *N*-(*p*benzoylbenzyl)-*N*,*N*,-tri-*n*-butylammonium cation will decrease and the tight ion pair will form depending on the equilibrium constant (eq 1).



In the nanosecond experiment, one can follow the quenching rate of the triplet of the benzophenone moiety in the separated form only since that process is bimolecular. The quenching rate is too fast in the tight ion pair and canot be seen. In fact, we have observed that the initial absorption immediately after the laser pulse in the transient triplet decay experiments decreases as the concentration of the counteranion increases. This indicates that the concentration of the benzophenone moiety is decreasing under these conditions as well. This implies that the actual concentration of the borate or the gallate anions should be smaller than the initially added concentration as was plotted in Figures 5 or 6, and the data points should be shifted to lower concentrations accordingly. At very low concentrations of the borate or the gallate counteranions, we could assume that the concentration of the tight ion pair is very small. Therefore, if we take the slope of the straight line between the two lowest concentrations data points in Figures 5 and 6, the triplet quenching rate constants will be 1.73×10^{10} and 3.29×10^{9} M^{-1} s⁻¹, respectively, and the electron transfer rates would be diffusion controlled.

The proposed mechanism for the photoreduction of the borate compound (1) is given in Scheme 2. The same mechanism pertains for the gallate case (2). Electron transfer from the borate anion to the excited benzophenone moiety BP*3 gives the radical anion (6) and the boranyl radical both of which dissociate rapidly. The estimated lifetime for the triphenylbutylboranyl radical is 250 fs¹¹ and it dissociates to give triphenylborane and the butyl radical. Such a short lifetime implies irreversible dissociation and back electron transfer to the radical anion to form 1 or 2 would be virtually nonexistent reaction. On the other hand, we were unable to detect the radical anion (6) in benzene even in the picosecond experiment. However, in MeOH where hydrogen-bonding stabilization occurs, it was possible to detect its transient absorption around 620 nm on the nanosecond time scale (Figure 4). Benzophenone is known to be H-bonded to alcohols in the ground state and one should expect that the radical anion to be H-bonded as its forms. A possible explanation for the H-bonding effect given by Fessenden et al.16 was based on the fact that the lowest excited triplet state $(n-\pi^*)$ of benzophenone has a lower dipole moment than the ground state.²³ Excitation will shift the electron density away from the oxygen atom and this could disrupt the H-bonding. As the triplet state is quenched by electron transfer to form the radical anion the H-bonding will again be formed, and this results in the blue shift in its absorption.

The observation of the tributylamine along with the coupling products (9) and (10) in the reaction mixture suggested that the radical anion (6) reacts rapidly to give the *p*-benzoylbenzyl radical BPCH₂• (8) and the amine. The formation of the radical (8) was confirmed by its transient absorption spectra at 320 nm



(Figure 2). In fact, the elimination of the amine from **6** can occur either by intramolecular electron transfer followed by immediate cleavage of the carbon-nitrogen bond or through the formation of the ketone anion (**7**) and the amino radical cation as shown in Scheme 2. At this point, we have no spectroscopic evidence for the formation of either the amino radical cation or the ketone anion. The free energy estimated from the reported redox potentials of the amino cation radical and related benzyl radicals²⁴ predicts that the electron transfer reaction from ketone anion to the amino cation radical would be very exothermic ($\Delta G \approx -2$ V) which means that they live for a very short time and are not detectable under the present experimental conditions. The *p*-benzoylbenzyl radical (BPCH₂•) is stable and couples either with a radical like itself or with the butyl radical.

In an attempt to further investigate the driving force for this elimination process, 5, in which complexation of the borate counteranion is meta to the benzoyl group, was synthesized. The elimination of the amino radical cation and the formation of the ketone anion (7) in the para-substituted compound should be facilitated by aromatic conjugation. This would be impossible in the meta-substituted compound and elimination would lead to the formation of very unstable intermediate. Therefore, the dissociation of the radical anion to form the meta analog anion of 7 and the amino radical cation would be unlikely. The results obtained for 5, however, were similar to those obtained for 1, thus indicating the substitution pattern has no effect on the outcome. Triethylamine was formed along with the expected coupling products. This result indicates that the dissociation step of the radical anion to form the ketone anion and the amino radical cation is not necessary, though it still might be operative with the para compound (1).

The quantum yield for disappearance of $1 (10^{-2} \text{ M in MeCN})$ measured in the steady state experiment is 0.5 ($\pm 10\%$). The actinometric method used is based on the assumption that the triplet quantum yield is unity in BP. Since the phosphorescence spectra obtained for compounds (1-4) were comparable to that of BP one would assume that the triplet quantum yields in these compounds are also similar. At the concentration (10^{-2} M) used in this experiment, as we have discussed before, the borate salt would be partially in its tight pair form and the electron transfer reaction would be partially intramolecular and very fast. The back electron transfer is expected to be minor as result of the rapid dissociation of the boranyl radical. Under these conditions one would expect a higher quantum yield for the disappearance of 1. For the cyanine triphenylalkylborate, the dissociation constant obtained from conductivity measurements is 3.2×10^{-2} M in MeCN.⁴ Assuming a similar dissociation constant for 1, the degree of dissociation at 10^{-2} M concentration would be 0.8. Therefore, bimolecular quenching such as triplet-ground state quenching may be responsible for lowering the quantum yield if the rate is comparable to the electron transfer rate in this solvent.

In the actual experiment wherein the quantum yields were measured, the change in the concentration of borate (1) after photolysis was estimated from the decrease in its peak area obtained by HPLC analysis. Unfortunately, under our detection conditions we were unable to distinguish the different borate salts. Accordingly, one possible explanation of the low measured quantum yield is that there is another reaction in which the radical anion (6) re-forms 1 or another borate salt which competes with the elimination reaction that releases the amine. If this is the case the amount of borate (1) which reacts during the photolysis experiment would be larger than what is obtained from the HPLC measurement and accordingly the quantum yield would be higher.

In Scheme 3 we describe the coupling reaction between the butyl radical (formed by the dissociation of the boranyl radical) with the radical anion as a possible reaction. Similar coupling reactions have been reported in the literature.²⁵

As shown in the scheme the coupling reaction would lead to the formation of a zwitterionic intermediate. From this intermediate no elimination reaction is possible, but it can react with Ph_3B in the presence or absence of water to give, in both cases, a borate salt. Under our experimental conditions we could not isolate and confirm the formation of these borate salts.

The observation that the same quantum yield is obtained for the disappearance of **1** in the presence or the absence of oxygen indicates that quenching of the triplet by oxygen could not compete with the electron transfer reaction. In fact, under our experimental conditions, we observe no effect of oxygen on the triplet decay of borate (1) at concentrations higher than 10^{-3} M. At lower concentrations, where the borate salt exists more as separated ions, the effect of oxygen becomes more significant. The presence of oxygen significantly impacts on the formation of the coupling products 9 and 10 as shown in Table 1. We observed this effect in the flash experiment where the presence of oxygen quenches the long lifetime part of the decay curve. This implies that oxygen reacts with the *p*-benzoylbenzyl radical (8) in competition with the coupling reactions. This result is not unanticipated since the oxidation of radicals by oxygen is well-known. Thus, we did not investigate the products under these conditions further.

Conclusions

In this paper we report a new photoinitiator system developed to initially involve the triplet state of an aromatic ketone (benzophenone) complexed to borate or gallate anions. Electron transfer from the borate or the gallate counteranions to the benzophenone moiety leads to the formation of a radical, an amine and a Lewis acid—the original triphenylboron or -gallium derivative. Since the electron transfer is to the long-lived triplet excited state, the relative contributions of intermolecular or intramolecular processes were shown to depend on the polarity of the solvent. In the nonpolar solvent (benzene) the electron transfer process is intramolecular and the electron transfer rate constant is very fast far behind the diffusion rate. In the polar solvent (MeCN) the electron transfer rate constant is diffusion controlled.

Picosecond and nanosecond laser flash photolysis, as well as steady state experiments, product analysis, and quantum yields measurements, were used to study the interaction mechanism. In these systems the elimination of tertiary amine through a C–N bond cleavage in the radical anion formed by the electron transfer reaction was shown. This unique elimination has already shown a potential use in photoimaging applications.²⁶

Experimental Section

General. Absorption spectra were recorded with a Hewlett Packard 8452A diode array UV-vis spectrophotometer. Fluorescence and phosphorescence spectra were measured using SPEX Fluorolog spectrophotometer. High performance liquid chromatography (HPLC) was used for photoproduct analysis. A HP 1050 Series instrument equipped with a diode-array detector (DAD) was used. A good separation between borate or gallate salts and their photoproducts was obtained using a reverse phase (HP LiChrosorb RP, 10 μ m, 200 × 4.6 mm) column. Acetonitrile was used as eluent at 0.5 mL/min flow rate and 40 °C column temperature. All solvents used are HPLC grade obtained from Aldrich Chemical Co.

Flash Photolysis. Nanosecond laser flash photolysis were carried out using the apparatus described previously.^{7,27} The third harmonics (355 nm) of a Q-switched Nd:YAG laser (Surelite I), giving approximately 80-90 mJ/pulse and a pulse width of 8 ns, was used for excitation. Only a small part of the pulse energy was used when measuring the transient decay kinetics to eliminate other decay processes such as T-T annihilation. Sample solutions were contained in 1 cm quartz cuvettes and were deaerated by continuous purging with argon during the experiment in the cases where oxygen had to be removed.

The third harmonic (355 nm) of a Nd:YAG active/passive mode-locked oscillator amplified through a double-pass Nd: YAG amplifier was used for excitation in the picosecond experiment. Pulse widths were ca. 30 ps with ~75 mJ/pulse at 1064 nm. The basic features of the pump–continuum probe coupled with a diode array spectrography system are as described earlier.²⁸ Multiple wavelength and single wavelength²⁹ were used to obtain the kinetic waveforms. The sample solutions were ~10⁻⁴ M in neat benzene or 5×10^{-3} M in benzene (1% MeCN) and were flowed through a 1 cm quartz cuvette.

Steady State Photolysis and Quantum Yields. Photolysis were carried out in a Rayonet model photochemical reactor fitted with filter-coated mercury lamps (300–400 nm) with output maximum at 365 nm. The photoproducts were separated using silica gel column chromatography with hexane–ethyl acetate (9:1) and characterized by NMR, HPLC, and mass spectroscopy. The main products **9** and **10** were synthesized independently³⁰ and these samples were used for comparison.

The actinometer solution (2 mL) containing benzophenone and benzhydrol, 0.1 M each, in benzene was degassed with three freeze-pump-thaw cycles. The sample was irradiated for 20 min and the amount of the reacting benzophenone was determined from the change in its absorption at 344 nm. Using the calibrated $\phi_{act} = 0.68$ from ref 21, the light intensity was calculated to be 3.45×10^{18} photons/min. Under the same conditions, 10^{-2} M solution of borate (1) was irradiated for 1 min only to avoid secondary reactions. The concentration of products formed and the disappearance of **1** were determined using HPLC method calibrated with the synthesized standard compounds.

Synthesis. Melting point determinations (uncorrected) were made using a Thomas Hoover capillary melting point apparatus. Elemental analysis was performed by Atlantic Microlab, Inc. Proton NMR spectra were recorded on 200 and 400 NMR spectrometers. NMR spectrum resonance positions are reported relative to the tetramethylsilane standard on the δ scale in parts per million (ppm). ¹¹B NMR were recorded on Varian Unity+400 (128 MHz) with B(OMe)₃ as the external standard. Unless otherwise mentioned, starting reagents and solvents were obtained from Aldrich Chemical Co. and used as received.

N-(*p*-Benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-butylammonium Bromide (3). 4-Bromomethylbenzophenone³¹ (10.0 g; 36.34 mmol) was dissolved in ether-chloroform (2:1) mixture at room temperature. Tributylamine (8.76 g; 47.26 mmol) was added and the solution stirred at room temperature for 24 h during which a precipitate was formed. The precipitate was filtered and recrystallized from ethanol-ethyl acetate (1:10) mixture; 11.70 g (70% yield) of white crystals was obtained: mp 160–161 °C. ¹H NMR (acetone, δ): 7.90 (m, 4 H), 7.68 (m, 1 H), 7.58 (m, 4 H), 5.11 (s, 2 H), 3.50 (m, 6 H), 2.06 (m, 6 H), 1.43 (m, 6 H), 1.00 (t, *J* = 7 Hz, 9 H). Anal. Calcd for C₂₆H₃₉-BrNO: C, 67.86; H, 8.26; Br, 17.37. Found: C, 67.79; H, 8.28; Br, 17.43.

*N-(p-Benzoylbenzyl)-N,N,N-tri-n-butylammonium Tetra***fluoroborate (4).** *N-(p-Benzoylbenzyl)-N,N,N-tri-n-butylam*monium bromide (3) (0.21 g; 0.45 mmol) was dissolved in 10 mL of water at 50–55 °C. Undissolved dusty materials were filtered out (if any present). Fluoroboric acid (0.5 mL 48 wt %) in water was added at 50 °C dropwise with stirring. A precipitate was formed immediately. Water (10 mL) was added and stirred for 30 min. Product was filtered and washed with water; 0.16 g (80% yield) of white solid was obtained: mp 78– 79 °C. Anal. Calcd for C₂₆H₃₉BF₄NO: C, 66.86; H, 8.14; Br, 0.0. Found: C, 66.93; H, 8.19; Br, 0.0.

N-(p-Benzoylbenzyl)-N,N,N-tri-n-butylammonium Triphenyl-*n*-butylborate (1). Lithium triphenyl-*n*-butylborate³² 0.80 g (2.61 mmol) was dissolved in 9 mL of water and undissolved particles, if any were filtered out. N-(p-Benzoylbenzyl)-N,N,N-tri-n-butylammonium bromide (1.22 g; 2.65 mmol) in 25 mL water-methanol (5:1) was added to the borate solution dropwise with stirring at room temperature. A white solid was formed immediately and stirring was continued for another 1 h after the addition of 25 mL of water. The white solid was filtered and dried overnight. After recrystallization from ethylacetate/ethanol, 1.20 g (68%) of white crystals were obtained: mp 133–133.5 °C. ¹H NMR (acetone, δ): 7.92 (m, 2 H), 7.80 (m, 4 H), 7.68 (m, 1 H), 7.59 (m, 2 H), 4.73 (s, 2 H, $N-CH_2$ -ph), 3.36 (m, 6 H, $N-CH_2-CH_2$), 1.95 (m, 6 H, $N-CH_2-CH_2$, 1.45 (m, 6 H, $N-C_2H_4-CH_2$), 1.23 (m, 2 H, $B-CH_2$), 1.02 (m, 13 H, N-CH₃ and $B-CH_2-C_2H_4$), 0.77 (t, 3 H, B-CH₃). ¹¹B NMR (DMSO): d -29.41. Anal. Calcd for C₄₈H₆₂BNO: C, 84.87; H, 9.13; N, 2.06. Found: C, 84.93; H, 9.21; N, 2.00.

N-(p-Benzoylbenzyl)-N,N,N-tri-n-butylammonium Triphenyl-*n*-butylgallate (2). Triphenylgallium³³ (1.88 g; 6.25 mmol) was dissolved in 16 mL of dry benzene under a nitrogen atmosphere, and 2.5 mL (2.5 M) of butyllithium was added into it at room temperature. A white precipitate was formed immediately and stirring was continued for 2 h under nitrogen. Dry hexane (15 m) was added and stirred for another 1 h. The precipitate was filtered and dried under vacuum. Lithium salt of triphenyl-*n*-butylgallate (1.50 g; 66% yield) was obtained as white powder, mp >250 °C; 0.56 g (1.45 mmol) of the lithium salt of triphenyl-n-butylgallate and 0.56 g (1.21 mmol) of 3 were dissolved in anhydrous THF. The solution was stirred overnight under nitrogen at room temperature. The solution was concentrated by evaporating solvent under vacuum, and the product was precipitated by adding water. After drying under vacuum, 0.42 g (46%) white solid was obtained. Anal. Calcd for C_{48} -H₆₂GaNO: C, 78.09; H, 8.40; N, 1.90. Found: C, 77.43; H, 8.21; N, 1.89.

N-(m-Benzoylbenzyl)-N,N,N-tri-n-ethylammonium Triphenyl-n-butylborate (5). The compound was synthesized as (1) in overall yield of 12% after recrystallization. mp 107-108 °C (from acetone). ¹H NMR (DMSO- d_6 , 200 MHz) d 7.78 (m, 7 H), 7.61 (m, 2 H), 7.19 (br s, 6 H), 6.89 (t, J = 7 Hz, 6 H), 6.73 (t, J = 7 Hz, 3 H), 4.57 (s, 2 H), 3.19 (q, J = 7 Hz, 6 H), 1.29 (t, J = 7 Hz, 9 H), 1.18 (m, 2 H), 0.85 (m, 4 H), 0.75 (t, J = 7.4 Hz, 3 H). ¹¹B NMR (DMSO, 128 MHz) δ -28.77. Anal. Calcd for C42H50BNO: C, 84.69; H, 8.46; N, 2.31. Found: C, 84.71; H, 8.42; N, 2.31.

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