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Photochemistry of (Benzophenonylmethyl)-tri-*n*-butylammonium Triphenylbutylborate: Inter- and Intra-Ion-Pair Electron Transfer Photoreduction

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Among critical inventions in photopolymerization science, several stand out for the long-term effects of the technology which resulted from them. The photodimerization of poly(vinyl cinnamates), for example, first reported by Minsk and coworkers at Eastman Kodak, led to the first negative photoresists;[2] the studies by Plamback on the photopolymerization of polyolacrylates as initiated by benzoin ethers at DuPont led to diverse applications in proofing and throughout the printing and coatings industries;[3] while the development of stereolithography by Hull led to what has quickly become the rapid prototyping revolution.[4] Carbocyanine alkyltriphenylborate salts have proven effective visible light sensitive photoinitiators[5−9] rapidly polymerizing polyolacrylate monomer systems.

Schuster and co-workers[10,11] have studied the photophysics of reactions of carbocyanine alkyltriphenylborate salts and have shown that electron transfer from the borate is to the singlet state of the cyanine cation. Since the lifetime of the cyanine singlet is short (picoseconds), said electron transfer is observed only in nonpolar solvents where the process can occur in the tight ion pair.[12] We have recently reported that photoreduction of fluorone dyes by triphenylbutylborate salts is useful for the initiation of free radical polymerization[13] and that intermolecular electron transfer from the borate anion to the triplet state of the dye leads to the formation of butyl radicals which initiate polymerization. Since it is apparent that borate anions are especially beneficial and have many important applications in free radical polymerizations initiated by ketones of which the fluorones are but a single example, we have undertaken a more extensive study of reduction reactions in which trialkylarylborates are the electron donors. In view of our previous interest in intramolecular energy transfer from benzophenone triplets to easily dissociated functions such as peresters,[14] as part of this work we have studied benzophenone ammonium salts where complexation of an electron donor at the para position to the electron-accepting benzophenone might permit an intramolecular electron transfer to the triplet state of the ketone.

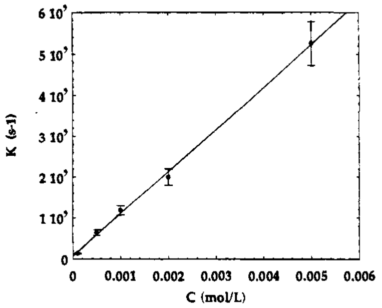
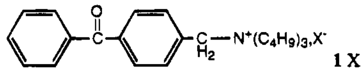


Figure 1. Concentration dependence of the triplet decay rate of (**1**) in MeCN.



1 X = Φ_3BBu; **2** X = Br; **3** X = BF_4

In this communication we report a new system involving the triplet state of an aromatic ketone (**1**) in which electron transfer can be either intramolecular or intermolecular depending on solvent polarity. (Benzophenonylmethyl)-tri-*n*-butylammonium triphenylbutylborate (**1**) was synthesized from (benzophenonylmethyl)-tri-*n*-butylammonium bromide (**2**) and lithium triphenylbutylborate in water. 4-(Bromomethyl)benzophenone, when treated with tributylamine in ether/chlroroform, gave **2** while **3** was obtained by metathesis with BF_4^-. All compounds were characterized by NMR and GC−MS. Purity was confirmed by elemental analysis and HPLC.

The photophysical properties of **1**−**3** are determined by the benzophenone (BP) chromophore as can be seen from their absorption and emission spectra. The absorption spectra of **1**−**3** above 300 nm are virtually identical and similar to BP absorption spectra. The n-π^* transition (λ_{max} = 340 nm) is red shifted by ~5 nm, but the absorption coefficient is also similar (ϵ ~200 $L\cdot mol^{-1}\cdot cm^{-1}$). The phosphorescence spectra [77 K in MeOH/EtOH (1:1)] are shifted 4 nm to the red relative to BP.

The photoreduction of benzophenone by electron donors such as amines has been studied extensively,[15] and early flash photolysis experiments confirmed the following mechanistic scheme.[16,17] Electron transfer from the amine to BP^{*3} forms $BP^{\bullet-}$ 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.[18,19]

Time-resolved transient spectroscopy and steady-state photolysis were used to investigate the interaction mechanism in **1**. Triplet decay rates were measured in MeCN and benzene using nanosecond laser flash photolysis.[20,21] While the quenching process in MeCN is found to be bimolecular from its concentration dependence (Figurel), we detected no triplet in benzene. Under the same conditions, where no electron transfer

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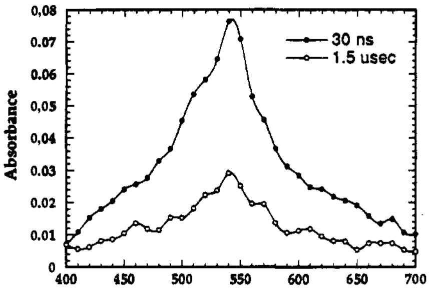


Figure 2. Triplet transient absorption spectra of (**3**), < 10^{-4} mol/L in benzene, recorded at 30 ns and 1.5 μs after the pulse.

Table 1. Triplet Absorption Maximum and Lifetimes

$BPCH_2N^+(C_4H_9)_3\ X^-$	solvent	concn (mol/L)[a,b]	λ_{max} (nm)	triplet lifetime (±10%)
1: $X = BuB(Ph)_3$	PhH	$<10^{-4}$		<10 ns
2; $X = Br$	PhH	$<10^{-4}$	540 ± 5	60 ns
3: $X = BF_4$	PhH	$<10^{-4}$	540 ± 5	1.5 μs

[a] Saturated solutions in benzene. [b] Deaerated by bubbling with argon.

is expected, the transient absorption of the triplet from **3** was detected in both solvents (Figure 2). This triplet absorbs similarly to that of BP^{*3} with $\lambda_{max} = 530$ nm in MeCN and 540 nm in benzene.[18,19] With bromide as the counteranion (**2**), the triplet lifetime was 60 ns (Table 1). These observations indicate that the triplet quenching in this system is an electron transfer process from the borate anion or bromide anion to BP^{*3} in the (benzophenonylmethyl)-tri-*n*-butyl ammonium cation. In the polar solvent MeCN ($\epsilon = 36$), **1** probably exists in the form of free ions and the electron transfer is an intermolecular process. When the concentration is increased, the triplet decay rate increases as a result of the intermolecular electron transfer quenching. The quenching rate constant obtained from the slope in Figure 1 is $1 \times 10^{10}\ M^{-1}\ s^{-1}$, indicating a diffusion-controlled process. Another indication for the intermolecular process in MeCN is that a mixture of compound **3**, where no electron transfer occurs, with tetrabutylammonium triphenylbutylborate gave the same quenching rate constant. On the other hand, in the nonpolar solvent benzene ($\epsilon = 2.3$) where we presume that **1** exists as a tight ion pair, electron transfer is an intramolecular process and too fast to measure on the nanosecond time scale.

In an attempt to measure the intramolecular electron transfer in neat benzene a picosecond flash experiment was conducted.[22,23] We were able to detect the immediate formation of a transient having $\lambda_{max} = 540$ nm, which we ascribe to the triplet absorption spectrum of the benzophenone moiety. However, the parent compound has poor solubility in benzene, which limited the absorbance of 355 nm, the excitation wavelength. This produced absorbance signals of poor signal-to-noise ratio which precluded measurement of a precise lifetime. The 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 which led to the lifetime of the triplet in this solvent mixture of 1,2 ns (Figure 3). It seems from these results that the triplet decay rate increases as the polarity of the solvent decreases. This, in turn, may reflect changes in the electron transfer rate constant.

By photolysis of BP or MeBP in the presence of tetrabutylammonium triphenylbutylborate salt, we were able to detect the transient absorption spectra of the radical anions $BP^{\bullet-}$ or $MeBP^{\bullet-}$ with maxima around 720 nm.[18] However, we were unable to detect any absorption in the spectral range for the expected analog radical (**4**) (Scheme 1) even in the polar solvent MeCN. In borate salts, it is known that back electron transfer is not significant since the boranyl radical, as it is produced, dissociates rapidly and irreversibly to give the alkyl radical and triphenylborane.[10,11] The failure to observe **4** indicates that its lifetime is less than 10 ns and it dissociates or rearranges during the laser pulse.

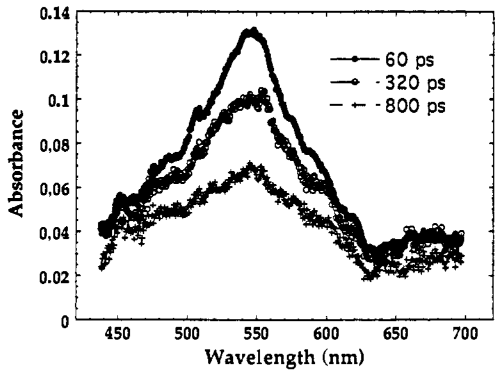
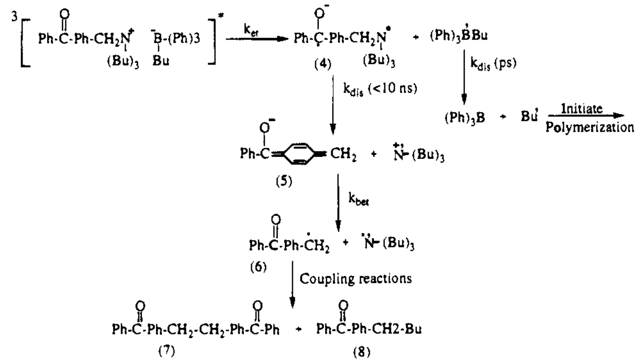


Figure 3. Triplet transient absorption spectra of (**1**), 5×10^{-3} mol/L in benzene (1% MeCN) recorded at 60, 320 and 800 ps after the pulse.

Scheme 1



Irradiation of **1** in MeCN gives *p,p'*-dibenzoylbibenzyl (**7**) as the principal isolated product. This implicates the $BPCH_2^\bullet$ radical, an intermediate most likely formed by the dissociation of **4** along with the $Bu_3N^{\bullet+}$ radical cation, in the reaction pathway. In support of this we observed an absorption peak with a long lifetime around 320 nm in the transient absorption spectra. We assign this absorption to the $BPCH_2^\bullet$ radical in agreement with the reported absorption of related benzyl radicals.[24]

On the basis of the above observations we propose the mechanism described in Scheme 1. Electron transfer from borate anion to BP^{*3} gives **4** and boranyl radicals, both of which dissociate rapidly. Radical **4** dissociates to give **5** and the amino cation radical followed by second electron transfer (k_{bet}) to give tributylamine and $BPCH_2^\bullet$ radical (**6**). The free energy estimated from the reported redox potentials of the amino cation radical and related benzyl radicals[25] shows that the electron transfer reaction from the ketone anion (**5**) to the amino cation radical would be very exothermic ($\Delta G \approx -2$ V). The $BPCH_2^\bullet$ is stable and couples either with a similar radical or to the butyl radical. Both products were separated and identified.

In summary, since the electron transfer in **1** is to the long-lived triplet excited state, the relative contributions of intermolecular or intramolecular processes could be shown to depend on the polarity of the solvent. Free radicals can be obtained by the unique elimination of a tri-*n*-butylammonium radical cation from **4** producting *p*-benzoylbenzyl in polar and nonpolar environments.

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