# Electron Transfer Photoreduction of 5,7-Diiodo-3-butoxy-6-fluorone with Tetrabutylammonium Triphenylbutylborate and *N,N*-Dimethyl-2,6-diisopropylaniline

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The photoreduction of 5,7-diiodo-3-butoxy-6-fluorone (DIBF) in the presence of the electron donors, tetrabutylammonium triphenylbutylborate (BORATE), and *N,N*-dimethyl-2,6-diisopropylaniline (DIDMA) was studied in acetonitrile solution. The transient phenomena examined using nanosecond laser flash photolysis confirm that the reduction is a one-electron transfer process from the electron donor to the excited triplet state of the dye. Triplet quenching rate constants were measured for BORATE and DIDMA as well as oxygen. The relative quenching rates for oxygen and DIDMA are ≈20:1. The electron transfer rates calculated are $6.7 \times 10^7$ and $1.2 \times 10^8$ $s^{-1}$ in the BORATE and DIDMA systems, respectively. The dye radical anion ($DIBF^{\bullet}$, $\lambda_{max} \approx 420$ nm) formed by the electron transfer reaction is the only product obtained in the BORATE case. However, with DIDMA the dye "neutral" radical ($DIBF^{\bullet}$, $\lambda_{max} \approx 360$ nm) was detected as the only product. $DIBF^{\bullet}$ formed after protonation of $DIBF^{\bullet-}$ by proton transfer from the amino cation radical. This implies that the proton transfer is too fast to measure on the nanosecond time scale. This is the first such observation in these systems. Singlet oxygen formed by oxygen quenching of the dye triplet was found to be quenched by the electron donors via an electron transfer process also. No quenching of DIBF triplet occurred in the presence of the electron acceptor (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI). The principal photobleached products detected by HPLC were reduced quinomethines in the DIDMA case and the ammonium salts of the reduced quinomethines in the BORATE case. Reoxygenation of these products regenerates the original dye in a reaction the rate of which depends on the polarity of the solution. However, the reoxygenation of the quinomethines is faster than that of their ammonium salts under the same conditions.

## Introduction

With few exceptions, most commercial applications of radiation cure use mercury resonance lamps as the light source and photoinitiators tuned to absorb at their principle radiation wavelengths in the UV, so a more specific name for the field is "UV curing." In the last few years, many fluorone dye derivatives have been developed by us for use as visible photoinitiators for polymerization.[2,3] Visible photoinitiators produce polymerization with visible light and have a number of advantages over UV counterparts. Visible sources require 110 V, produce no ozone, and have none of the dangers associated with ultraviolet wavelengths which the eye cannot detect. Further, visible light initiators are used at much lower concentrations than the UV ketonic systems which must be used in concentrations as high ≥1% by weight in the monomer for it to be polymerized in order to achieve the required performance characteristics. Visible systems can be designed to either bleach as they cause polymerization or not do so, depending on the application, thus adding flexibility in depth of cure impossible to attain with UV initiators. Pigmented and colored systems are also easier to polymerize. In virtually any instance, a visible absorption window can be found in a monomer formulation.

Photoreduction and photooxidation reactions of the fluorones can be used to initiate polymerization, in the presence of the appropriate coinitiator partner. Electron donors, such as tertiary amines, reduce fluorone excited states in a biomolecular electron transfer reaction. Electron transfer from the amine to the excited triplet state of the fluorone forms the dye anion radical and the amine cation radical. The latter rapidly releases a proton which transfers to the anion radical yielding a neutral dye and amino radicals, the latter of which initiates free radical polymerization.[4] Linden and Neckers have studied the oxidative bleaching of rose bengal onium salts[5] and have shown that the photobleaching of the dye occurs through an electron transfer from the excited singlet state to the strongly reducing gegenion. Subsequently, it was found that electron transfer is efficient from the excited triplet states of either ethyl eosin or ethyl erythrosin to diaryliodonium salts in acetonitrile solution as well.[6] The dual behavior of these dyes as electron donors and acceptors led to extensive investigation of ternary systems which include, in addition to the dyes themselves, reducing agents such as amines or borates and oxidizing agents such as aryliodonium salts. In the dye–amine–iodonium system, a free radical promoted cationic chain polymerization was demonstrated.[7,8]

Schuster and co-workers have studied intra-ion-pair electron transfer in the carbocyanine alkyltriphenylborate salts extensively.[9] They have shown that photoinitiated one-electron transfer from the alkyltriphenylborate anion to the cyanine cation in its singlet excited state leads to the formation of free alkyl radicals which can be used to initiate free radical polymerization processes. Recently, photopolymerization studies with six esters of decarboxylated rose bengal showed the triplets were reduced by an intermolecular electron transfer from triphenylalkylborate anion. This also led to the formation of a free alkyl radical which was capable of initiating polymerization.[10] A similar study with other initiators and several new borate salts is underway.[11]

Though a working mechanistic hypothesis for photoreduction of xanthene dyes by tertiary amines is basically accepted, little is known about the bleached photoreduced products. The bleaching behavior of rose bengal under chemical and photochemical reducing conditions has been previously reported.[12,13]

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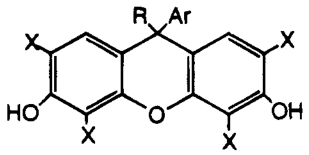
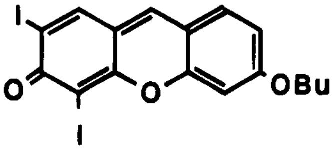
The reduction product, C-9 hydro (below), was the main bleached product obtained after photoreduction in the presence of triethanolamine.[13] Phillips and Read[14] reported that the photoreduction of decarboxylated eosin by tribenzylamine under anaerobic conditions produced a high yield of the cross-coupled product, where the amino radical coupled to the dye radical at the 9-position, in addition to the product with H at C-9.



R = H, $(PhCH_2)_2NCHPh$; X = Br, I

Xanthene dyes such as rose bengal and eosin have two negatively charged centers, are generally obtained as the disodium salts, and are not easily dissolved in most monomer mixtures. This led to the development of new fluorone derivatives having a neutral structure.[2,3] Of the many fluorone dyes developed, 5,7-diiodo-3-butoxy-6-fluorone (DIBF) has been found to have a number of practical advantages as a polymerization initiator. Therefore, we will concentrate on it only in this report.



DIBF

In this paper we report studies of the bleaching process in both the DIBF−diisopropyldimethylaniline (DIDMA) and DIBF−tetrabutylammonium triphenylbutylborate (BORATE) systems. Transient spectroscopic studies provide new important information on some of the photobleached products. For the first time we demonstrate the transient spectrum of the "neutral" dye radical obtained after proton transfer to the dye radical anion in the photoreduction of the dye−amine system. The identity of the photobleached products and their properties are important, especially from the point of view of applications in photopolymerization. It has also been observed that in the dye−amine system, one or more of the photoreduced products are unstable, being reoxidized to regenerate the dye. In terms of the color of the obtained photopolymer, this regenerates color in a photocoating. This recovery of color is much slower in the dye−borate system. In these studies we attempt to explain the recovery phenomena and the difference between the two systems. The effect of (4-octyloxyphenyl)phenyldiphenyliodonium hexafluoroantimonate (OPPI) on the transient spectra in both systems was also studied.

## Experimental Section

**Materials.** 5,7-Diiodo-3-butoxy-6-fluorone was synthesized by Tanabe et al.[3] Purity is higher than 95% as determined by HPLC. Tetrabutylammonium triphenylbutylborate was prepared by the addition of the alkyllithium to triphenylborane.[15] The resulting metal salt was metathesized with tetrabutylammonium chloride. The details of the preparation will be published later.[16] After recrystallization, it is found that the purity of the borate salt is higher than 99% (HPLC). DIDMA (>80%; HPLC) was obtained from Carbolabs Inc. and used without additional purification. We did not identify the components because the impurities separated well in the HPLC chromatogram and did not participate in the bleaching process. (4-Octyloxyphenyl)-phenyliodonium hexafluoroantimonate (OPPI) was synthesized by Bi[8] using known procedures. All the solvents used were HPLC grade, purchased from Aldrich Chemical Co.

**Flash Photolysis.** Laser flash photolysis experiments were performed using the apparatus described previously by Rodgers.[17] Laser irradiation at 470 nm was used from an optical parametric oscillator (OPO) pumped by a third harmonic (355 nm) of a nanosecond Q-switched Nd:YAG laser (Continuum Surelite I), giving approximately 6 mJ/pulse and a pulse width of 8 ns. The maximum energy was used for recording the transients spectra while only about 20% of the energy was used when measuring the transient decay kinetics. Transient species were monitored at 90° with respect to the laser beam by a computer-controlled absorption spectrometer which includes a 150 W xenon arc lamp, a Spex 1681 (0.22 m) monochromator, and a R928 photomultiplier. A LeCroy 9450 digital oscilloscope (400 MHz bandpass) was used to collect the signal and transfer it to a PC computer for averaging and analysis. Nonlinear regression analysis of the data was obtained using the Marquardt least-squares algorithm. The samples were contained in 1 $cm^2$ quartz cuvettes and were bubbled continuously with argon during the experiment in the cases where oxygen had to be removed. Prior to its bubbling through the sample, the argon gas was passed through an oxygen trap (Alltech Associates) which reduces the oxygen concentrations to less than 0.1 ppm.

**HPLC Analysis.** Solutions of DIBF and BORATE of DIBF and DIDMA (1:1) were prepared in acetonitrile containing 2% (by volume) chloroform. Chloroform was needed to increase the solubility of the DIBF to $5 \times 10^{-4}$ M/L. Freshly degassed samples were irradiated by a 100 mW laser beam at 488 nm from a Spectra-Physics Ar ion laser. The laser beam diameter was expanded to 1 cm to eliminate intensity effects. An irradiation time of 1 h was chosen for all experiments to give substantial bleaching, although the sample with DIDMA bleached completely very rapidly.

High-pressure liquid chromatography (HPLC) was used to detect the bleached products. A Hewlett-Packard 1050 Series instrument outfitted with diode-array detector (DAD) was used. A good separation between the different bleached and unbleached components was achieved using a reverse phase (HP LiChrosorb RP, 10 μm, 200 × 4.6 mm) column. Acetonitrile was used as eluent at 0.5 mL/min flow rate and 40 °C column temperature.

## Results

### 1. DIBF Triplet Formation and Quenching.

Most of the fluorone dyes intersystem cross rapidly to the triplet states and have low fluorescence quantum yields.[2a] DIBF is no exception. The formation of the triplets obtained within the width of the laser pulse used for the flash irradiation gives an intersystem crossing rate, $k_{isc}$, higher than $10^8$ $s^{-1}$. Therefore, and by analogy with the behavior of a similar system,[18] it is the dye in its triplet state which acts as an electron acceptor in the presence of electron donors.

Triplet lifetimes and quenching rate constants were measured for DIBF in deaerated and aerated solutions of acetonitrile and in the presence of DIDMA, BORATE, and OPPI. The results are reported in Table 1. A low dye concentration was taken to minimize the effect of self-quenching, and the laser energy was lowered enough to eliminate any triplet−triplet annihilation.[18,19] In order to compare with oxygen quenching, electron donor concentrations comparable to its concentration in aerated

**TABLE 1: DIBF**

| | $k_d$ (s$^{-1}$) = $k_1 + k_1$[Q] | $k_q$ (mol$^{-1}$ s$^{-1}$)·L) |
|---|---|---|
| 1. DIBF (argon) | $(6.91 \pm 0.30) \times 10^4$<br>$[\tau = (15 \pm 1)\ \mu s]$ | |
| 2. DIBF + air−$O_2$ | $(4.92 \pm 0.25) \times 10^6$<br>$[\tau = (200 \pm 10)$ ns] | $(2.55 \pm 0.15) \times 10^9$ |
| 3. DIBF + DIDMA (argon) | $(4.06 \pm 0.20) \times 10^5$<br>$[\tau = (2.5 \pm 0.13)\ \mu s]$ | $(1.21 \pm 0.08) \times 10^8$ |
| 4. DIBF + BORATE (argon) | $.97 \pm 0.16) \times 10^5$<br>$[\tau = (5 \pm 0.4)\ \mu s]$ | $(6.71 \pm 0.50) \times 10^7$ |
| 5. DIBF + OPPI (argon) | $(6.25 \pm 0.30) \times 10^4$<br>$[\tau = (16 \pm 1)\ \mu s]$ | ~0 |

[a] DIBF, $2 \times 10^{-5}$ M/L; $O_2$, $1.9 \times 10^{-3}$ M/L; DIDMA, $2.78 \times 10^{-3}$ M/L; BORATE, $1.9 \times 10^{-3}$ M/L; OPPI, $1.9 \times 10^{-3}$ M/L; solvent, MeCN.

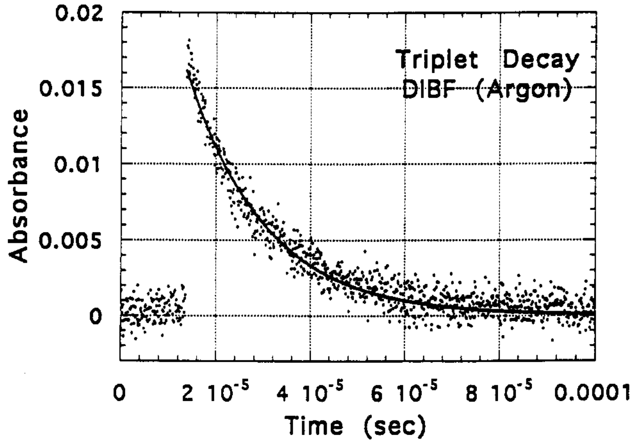


**Figure 1.** DIBF triplet absorption decay and its first-order fitting profile obtained from $2 \times 10^{-5}$ M deaerated solution in MeCN. ($\tau = 15\ \mu$s.)

acetonitrile[20] were used (Table 1). As expected, at these conditions of low laser energy and high concentration of quencher the triplet decay was a clean first-order process (Figure 1). The excitation wavelength was at the $\lambda_{max} = 470$ nm of the DIBF ground state absorption, and the triplet decay was monitored at 550 nm where the triplet transient absorption is at maximum and the ground state absorption is negligible. Interference from other species is also minimum at this wavelengths as we will see in the next section.

The results clearly show that quenching by oxygen is the primary first step and that the electron donor coinitiators have to be present at much higher concentration in order to compete well with oxygen quenching of the dye triplets. Under the above conditions, the triplet lifetime decreased from 15 $\mu$s in the deaerated sample to 200 ns in the aerated sample, ~75 times. The relative quenching constants for oxygen−DIDMA or oxygen−BORATE are about 20:1 and 38:1, respectively. DIDMA is a better quencher than BORATE by a factor of 2.

As was indicated in the Introduction, certain xanthenes are oxidized easily in the presence of strong oxidizing agents like the diaryliodonium salts. The photo-oxidation of ethyl eosin and ethyl erythrosin by diphenyliodonium salts are efficient, even favored, compared to photoreduction by *N,N*-dimethylamines.[6,7] In contrast, we found no quenching of DIBF triplets by the iodonium salt (OPPI) as can be seen from Table 1. Compared to eosin or rose bengal derivatives which are anionic, DIBF is a neutral molecule. The measured oxidation potentials for DIBF and eosin are 1.4 and 0.8 V (vs SCE), respectively. This might explain the poor electron donation properties of DIBF and that it is not quenched by the iodonium salt.

Aerated DIBF solutions are stable under photolysis conditions. Quenching of DIBF triplets by oxygen produces single oxygen as measured by its luminescence at 1270 nm. The quenching mechanism is mainly an energy transfer process.[21,22] Rate constants of singlet oxygen decay measured in the presence of DIDMA, BORATE, and OPPI are reported in Table 2. The results clearly show that singlet oxygen is quenched only by the electron donors and not by the electron acceptor. Electron transfer from borate anion to singlet oxygen was reported by Williams et al,[23] and it is likely that the quenching by DIDMA is an electron transfer process as well. The quenching rate of singlet oxygen by DIDMA is 2 times higher than that with the BORATE. These rates are in similar order to those in the case of DIBF triplet quenching

**TABLE 2: Singlet Oxygen Decay and Quenching[a]**

| | $k_d$ (s$^{-1}$) = $k_1 + k_q$[Q] | $k_1$ (mol$^{-1}$·s$^{-1}$·L) |
|---|---|---|
| 1. DIBF (air) | $(1.35 \pm 0.06) \times 10^4$<br>$[\tau = (73 \pm 4)\ \mu s]$ | |
| 2. DIBF (air) + DIDMA | $(2.45 \pm 0.1) \times 10^4$<br>$[\tau = (41 \pm 2)\ \mu s]$ | $(3.96 \pm 0.2) \times 10^4$ |
| 3. DIBF (air) + BORATE | $(1.71 \pm 0.08) \times 10^4$<br>$[\tau = (58 \pm 3)\ \mu s]$ | $(1.89 \pm 0.1) \times 10^4$ |
| 4. DIBF (air) + OPPI | $(1.39 \pm 0.06) \times 10^4$<br>$[\tau = (72 \pm 4)\ \mu s]$ | ~0 |

[a] DIBF, $2 \times 10^{-5}$ M/L; DIDMA, $2.78 \times 10^{-3}$ M/L; BORATE, $1.9 \times 10^{-3}$ M/L; OPPI, $1.9 \times 10^{-3}$ M/L; solvent, MeCN.

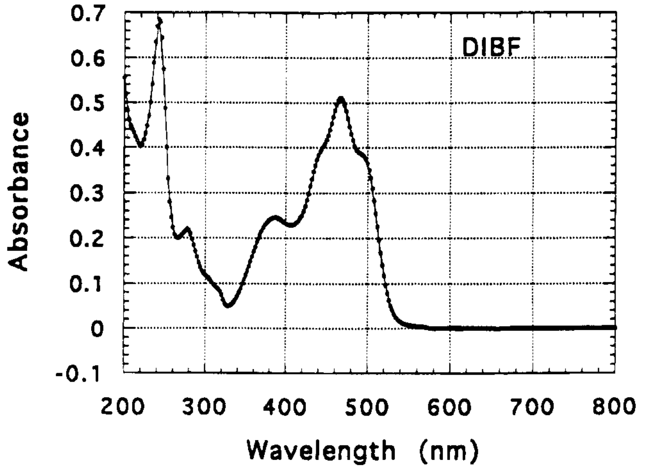


**Figure 2.** DIBF ground state absorption spectra obtained from $2 \times 10^{-5}$ M solution in MeCN.

**2. DIBF Radicals: Formation, Decay, and Absorption Spectra.** The absorption spectrum of DIBF ($2 \times 10^{-5}$ M/L) in acetonitrile is shown in Figure 2. Flash photolysis of the same solution (deaerated) gives the transient absorption spectrum (Figure 3) recorded at different times after the flash up to 80 $\mu$s. Immediate consumption of DIBF is evident in this spectrum from the bleaching of its ground state absorption bands. A new positive and broad absorption with features at 320 nm and from 520 to 800 nm is also evident in the spectrum. Since such absorptions are characteristic of triplet−triplet absorptions as reported for other xanthene dyes,[18,19,24−27] we assign this to the triplet. The decay of these absorptions is accompanied by the recovery of ground state absorption. That the triplets are the only products is indicated by the two sharp isobestic points at 340 and 520 nm. However, a careful inspection of the spectrum in Figure 3 shows that after almost complete decay of the triplets, there remains a small positive absorption centered at 420 nm. Absorptions near this wavelength were assigned in similar dyes to the dye radical anion.[18,19,27] Recently,[18] Klimtchuk et al. have shown that self-quenching of the dye triplet of a similar fluorone derivative (2,4,5,7-tetraiodo-3-

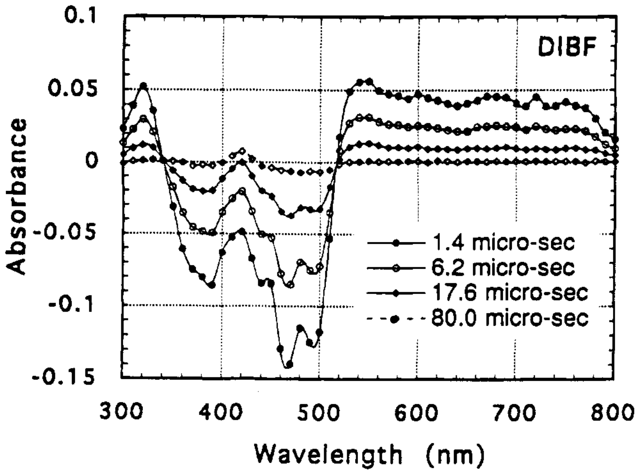


**Figure 3.** Transient absorption spectra recorded at different delay times obtained from DIBF ($2 \times 10^{-5}$ M) deaerated solution in MeCN.

hydroxy-6-fluorone (TIHF) was significant by an electron transfer process:

$$^{3}\text{dye}^{*} + \text{dye} \rightarrow \text{dye}^{\bullet+} + \text{dye}^{\bullet-} \tag{1}$$

$$^{3}\text{dye}^{*} + {}^{3}\text{dye}^{*} \rightarrow \text{dye}^{\bullet+} + \text{dye}^{\bullet-} \tag{2}$$

Although they were not able to detect the dye radical cation, the absorption of the dye radical anion clearly increased with the triplet decay. However, this was not the case with DIBF as can be seen from the transient spectra in Figure 3. The small amount of the radical anion detected can again be attributed to the poor electron donor properties of DIBF when compared to TIHF.

The transient absorption spectra after irradiation of DIBF in the presence of the electron donors, DIDMA and BORATE, and the electron acceptor, OPPI, recorded at different times after the flash, are shown in Figure 4. In the presence of BORATE, the radical anion ($\text{DIBF}^{\bullet-}$) absorbing at 420 nm (Figure 4a) grows as the only product formed from the DIBF triplet as indicated by the two clear isobestic points at 340 and 510 nm. On the other hand, when DIDMA is the electron donor, no radical anion is observed. Instead, a new product absorbing at 360 nm grows as the triplet decays (Figure 4b). We assign this spectrum to the neutral dye radical ($\text{DIBF}^{\bullet}$) obtained after protonation of the radical anion by proton transfer from the amine radical cation. The peak position is in excellent agreement with neutral dye radicals assigned for other dyes.[27] As mentioned, OPPI does not quench the DIBF triplet (Figure 4c), so no radicals are observed and the triplet decay accompanied by the recovery of the dye ground state is similar to the case of DIBF itself as shown in Figure 3.

The formation and the decay kinetics of the radical anion ($\text{DIBF}^{\bullet-}$) monitored at 420 nm are shown in Figure 5. Similar kinetics are obtained for the neutral radical ($\text{DIBF}^{\bullet}$) monitored at 360 nm. Double exponential analysis was used to fit the fast (formation) and the slow (decay) components. The measured formation rates of both radicals are identical within the experimental error (5−10%) to the DIBF triplet decay rates in each case as given in Table 3. With the knowledge that the quenching of the triplets by both DIDMA and BORATE is an electron transfer process, the quenching rates in each case become the electron transfer rate ($k_{\text{et}}$). In addition, the spectra in Figure 4 show that as the radicals decay, there is no significant recovery of the DIBF ground state. In other words, the radical decays producing the final bleached products. From the above we can conclude that back electron transfer is minor in both systems, although the quantum yields of radical formation need to be measured to confirm this conclusion.

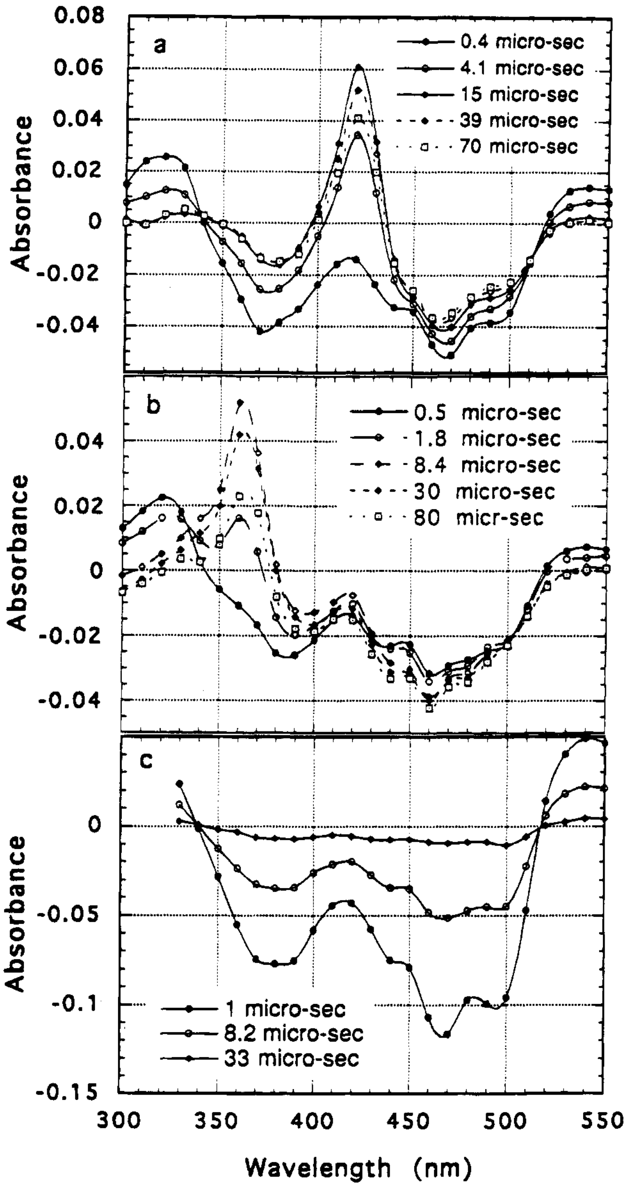


**Figure 4.** Transient absorption spectra recorded at different delay times of DIBF ($2 \times 10^{-5}$ M) in the presence of (a) BORATE ($1.9 \times 10^{-3}$ M), (b) DIDMA ($2.78 \times 10^{-3}$ M), and (c) OPPI ($1.9 \times 10^{-3}$ M) in MeCN.

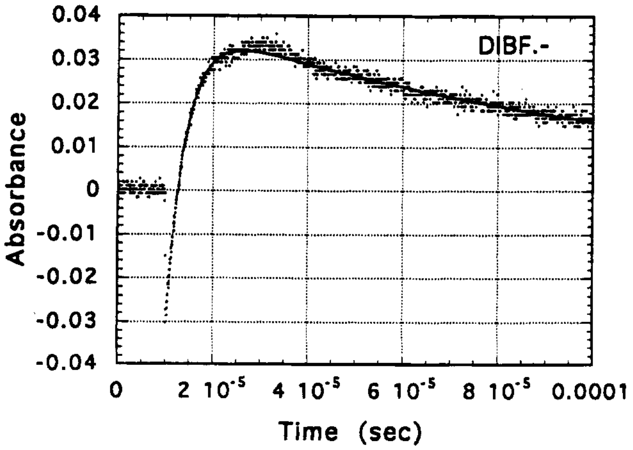


**Figure 5.** The radical anion ($\text{DIBF}^{\bullet-}$) formation and decay profiles detected at 420 nm from DIBF ($2 \times 10^{-5}$ M)−BORATE ($1.9 \times 10^{-3}$ M) solution in MeCN.

**TABLE 3: DIBF$^{\bullet-}$ and DIBF$^{\bullet}$ Radicals Formation and Decay Constants**[a]

| | $k_{\text{formation}}$ $10^{-5}$ (s$^{-1}$) | lifetime $\tau$ ($\mu$s) | $k_{\text{decay}}$[b] $10^{-4}$ (s$^{-1}$) | lifetime[b] $\tau$ ($\mu$s) |
|---|---|---|---|---|
| 1. DIBF$^{\bullet-}$ | 2.44 ± 0.20 | 4.11 ± 0.30 | 0.77 ± 0.07 | 130 ± 10 |
| (BORATE) | (1.97 ± 0.16 | 5.00 ± 4.00)[c] | | |
| 2. DIBF$^{\bullet}$ | 3.88 ± 0.20 | 2.50 ± 0.13 | 1.20 ± 0.10 | 83 ± 7 |
| (DIDMA) | (4.06 ± 0.20 | 2.50 ± 0.13)[c] | | |
| 5. DIBF$^{\bullet}$ | 4.30 ± 0.30 | 2.33 ± 0.15 | 2.10 ± 0.16 | 48 ± 4 |
| (DIDMA + OPPI) | (4.06 ± 0.20 | 2.50 ± 0.13)[c] | | |

[a] DIBF, $2 \times 10^{-5}$ M/L; DIDMA, $2.78 \times 10^{-3}$ M/L; BORATE, $1.9 \times 10^{-3}$ M/L; OPPI, $-1.9 \times 10^{-3}$ M/L; solvent, MeCN. [b] The decay of the radicals did not exactly fit first-order kinetics. However, the above decay rates and lifetimes are from first-order kinetics and are given for comparison only. [c] DIBF triplet decay and lifetime from Table 1.

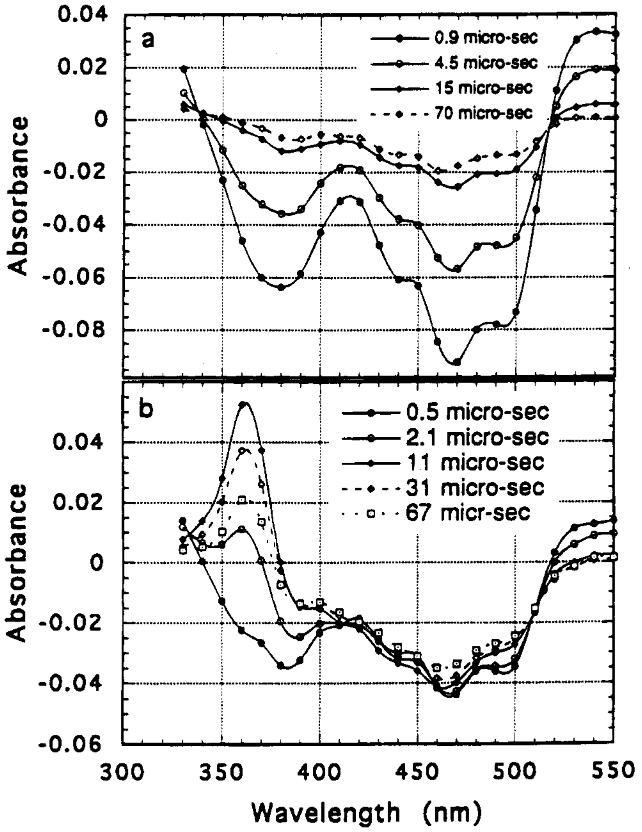
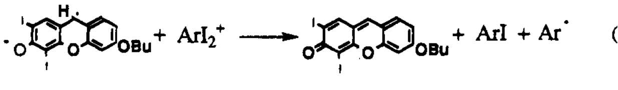


**Figure 6.** Transient absorption spectra recorded at different delay times of (a) DIBF–BORATE–OPPI and (b) DIBF–DIDMA–OPPI solutions in MeCN. (The concentration ratios are the same as the given in Figure 4.)

Irradiation of the tertiary systems, DIBF + BORATE + OPPI and DIBF + DIDMA + OPPI, under similar conditions gives the transient spectra shown in Figure 6. While the addition of OPPI quenches the radical anion (DIBF$^{\bullet-}$) completely, it has a smaller effect on the lifetime of the neutral radical on the same time scale. OPPI is a strong oxidizing agent, and it easily accepts electrons from the radical anion to regenerate the dye and release aryl radicals (eq 3). However, this electron transfer rate must be slow compared to the proton transfer rate or the neutral radical would not be obtained in the amine case.



(3)

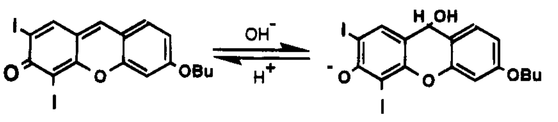
Regeneration of the dye can be seen clearly from the recovery of the ground state absorption in Figure 4a. However, dye recovery is not complete meaning a small amount of final bleached products was also obtained. If (3) is not very fast, one can expect such bleached products will be obtained. This will be discussed later.

**TABLE 4: DIBF ($5 \times 10^{-4}$ M/L) Solution in Acetonitrile (+2% (v/v) CHCl$_3$) and after Adding KOH Solid**[a]

| | rt (min) | peak area | |
|---|---|---|---|
| without KOH | 2.389 | 265 | anionic form |
| | 6.912 | 26604 | neutral form |
| with KOH, after 72 h | 2.495 | 822 | anionic form |
| | 6.856 | 24268 | neutral form |

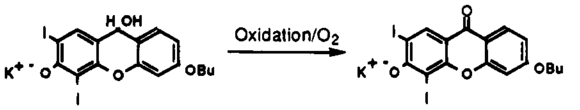
[a] The area of the peaks are relative for the same component (the same rt) only.

**3. Bleached Products.** The liquid chromatograms of DIBF were identical before and after steady state irradiation showing that DIBF is stable under the photolysis conditions. Detection by the DAD detector at 250 and 470 nm gives mainly one peak at retention time (rt) ≈ 7 min. The corresponding absorption spectrum taken at the maximum of the peak is identical to that of DIBF. Two small peaks at ~24 and ~7.6 min and two other minor peaks at ~10 and ~12 min appeared also which total less than 5%. The peak at rt = ~2.4 min was assigned as the "reduced" anionic form of DIBF since its concentration depends on the pH as shown in eq 4:



(4)

Although the solubility of solid KOH in the solvent (2% (v/v) CHCl$_3$ in acetonitrile) is small, adding a small amount to the DIBF solution results in an increase of the peak at rt = ~2.4 min with time. After 72 h its area increased approximately 3 times while the area of the DIBF peak at ~6.9 min decreased, Table 4. The corresponding absorption spectrum for the latter peak shows no absorption in the visible as expected. A new peak at ~4.8 min appears after 72 h also which, according to its absorption spectrum, is assigned to the xanthone derivative. The xanthone is obtained by oxidation of the reduced anionic form as



(5)

Solutions of DIBF, BORATE, and DIDMA in acetonitrile (+2% v/v CHCl$_3$) were stable and no change was detected in their chromatograms with time as were solutions of BORATE and DIDMA solutions under the photolysis conditions. The liquid chromatogram of BORATE shows one peak only (>99%) at rt ~2.8 min, the absorption spectrum of which is typical of the BORATE. No absorption occurs at wavelengths higher than 300 nm. The peak's rt was similar to that of the "reduced" anionic form of DIBF. This is expected since the BORATE has an anionic–cationic salt structure. Further exchanging the tetrabutylammonium cation of the borate salt for other alkylammonium cations has no effect on the rt. Thus, under our HPLC conditions any component with the anionic–cationic salt structure will elute with a rt around 2.5 min, depending on the concentration.

Liquid chromatograms of the solutions of DIBF with DIDMA and DIBF with BORATE before irradiation were identical to the combined separated chromatograms of each component in both cases. After irradiation, and in the DIBF–DIDMA system,

**TABLE 5: DIBF + DIDMA (1:1), $5 \times 10^{-4}$ M/L Solution in $CH_3CN$ (+2% $CHCl_3$) Before and After Irradiation and 72 h After Irradiation**[a]

| | rt (min) | peak area (mAU) | |
|---|---|---|---|
| before irad | 2.44 | 390 | anionic form |
| | 6.97 | 26590 | DIBF |
| | 7.60 | 2400 | DIDMA |
| after irrad | 2.53 | 930 | anionic form |
| | 7.06 | 1870 | DIBF |
| | 7.67 | 956 | DIDMA |
| | 8.83 | 430 | bleached 1 |
| | 10.49 | 5325 | bleached 2 |
| | 12.35 | 1308 | bleached 3 |
| 72 h after irrad | 2.59 | 1910 | anionic form |
| | 4.84 | 150 | xanthone derivative |
| | 6.89 | 3605 | DIBF |
| | 7.53 | 800 | DIDMA |
| | 8.44 | 380 | bleached 1 |
| | 9.99 | 4470 | bleached 2 |
| | 11.80 | 1300 | bleached 3 |

[a] The area of the peaks are relative for the same component (the "same" rt) only.

**TABLE 6: DIBF + BORATE (1:1), $5 \times 10^{-4}$ M/L Solution in $CH_3CN$(+2% $CHCl_3$) Before and After Irradiation**[a]

| | rt (min) | peak area (mAu) | |
|---|---|---|---|
| before irrad | 2.83 | 8110 | BORATE |
| | 6.98 | 25820 | DIBF |
| after irrad | 2.75 | 5540 | BORATE<br>bleached products |
| | 4.60 | (1860) | phenol |
| | 5.23 | 925 | $Ph_3B$ |
| | 5.74 | 1090 | Ph−Ph |
| | 6.97 | 20686 | DIBF |

[a] The peak areas compared were taken from the 250 nm chromatogram.

the sample is almost completely bleached and three new peaks appear at longer retention times (around 8.8, 10.5, and 12.4 min, respectively). There is also a significant decrease in the peaks of DIBF (7.06 min) and DIDMA (7.67 min) after irradiation, while the peak at 2.53 min (DIBF anionic form) increased. The peak areas are summarized in Table 5. If the irradiated sample was kept in the dark for 72 h, a new peak appeared at ~4.84 min which is proposed to be the xanthone form (eq 5). Moreover, we can see that as the DIBF peak is recovered, its anionic form increased and the bleached products decreased.

In the DIBF−BORATE system, bleaching is slower compared to that in the DIBF−DIDMA case. Only ~20% of DIBF is bleached in the same irradiation time, Table 6. Before irradiation, detection at four different wavelengths, 250 nm where only the BORATE absorbs, 318, 360, and 470 nm, shows that the BORATE and the DIBF peaks are those at rt = 2.83 and 6.98 min, respectively. After irradiation, it is clear that the peaks related to the BORATE (rt = 2.75 min) and DIBF (rt = 6.97 min) are decreased. However, it was observed that the peak (rt = 2.75 min) has more than one component in addition to the BORATE itself. Peaks were also detected at the same rt time in the higher wavelengths (318 and 360 nm) chromatograms. The new products have extended absorption to higher wavelengths as compared to the BORATE. Although we were not able to get good separation of these products under the present HPLC conditions, it was possible to see at least two other products (bleached products). There are also a few small peaks which came out at rt times between 4 and 6.5 min. The main three were identified as follows: phenol at rt = 4.6 min, triphenylborane at rt = 5.23 min, and biphenyl at rt = 5.74 min.

## Discussion

The flash photolysis results confirm that the photoreduction of DIBF in the presence of the electron donors, tertiary amine (DIDMA) or borate salts (BORATE), is a one-electron transfer process, Schemes 1 and 2. Electron transfer from the borate anion or the amine results in the DIBF radical anion ($DIBF^{\bullet -}$) initially and the boranyl radical pair in the first case and $DIBF^{\bullet -}$ and the amino radical cation pair in the second. The transient spectra in the BORATE case (Figure 4a) show that $DIBF^{\bullet -}$ is the only product obtained after quenching of the DIBF triplet. The formation of the radical anion was observed on the nanosecond time scale and at the same rate as the triplet decay rate. Thus, the cage escape to give free radicals ($k_d$, Scheme 1) in this system is very fast and occurs on a shorter time scale. Boranyl radical dissociation to give triphenylborane and alkyl radicals is known to be faster than the back electron transfer and depends on the stability of the alkyl radical formed, and the dissociation is irreversible.[9] In our system, where electron transfer process is intermolecular, one should expect that back electron transfer would be even less significant. In fact, the transient absorption and kinetic data obtained show this to be the case. The radical anion decay did not regenerate the dye as should be the case if back electron transfer occurs. Assuming that $k_{-\mathrm{et}} = 0$ (Scheme 1), and on the basis of the observation that the rate of radical formation is the same as the rate of triplet decay, we estimate the electron transfer rate in this system to be as the measured triplet quenching rate which is $6.71 \times 10^7$ $s^{-1}$ (Table 1). This result is in good agreement with the values obtained in the previous work[18] for dye−amine systems, but it is very low compared to the intramolecular electron transfer rate ($k_{\mathrm{et}} \approx 10^{11}$ $s^{-1}$) obtained for the cyanine−borate systems.[9]

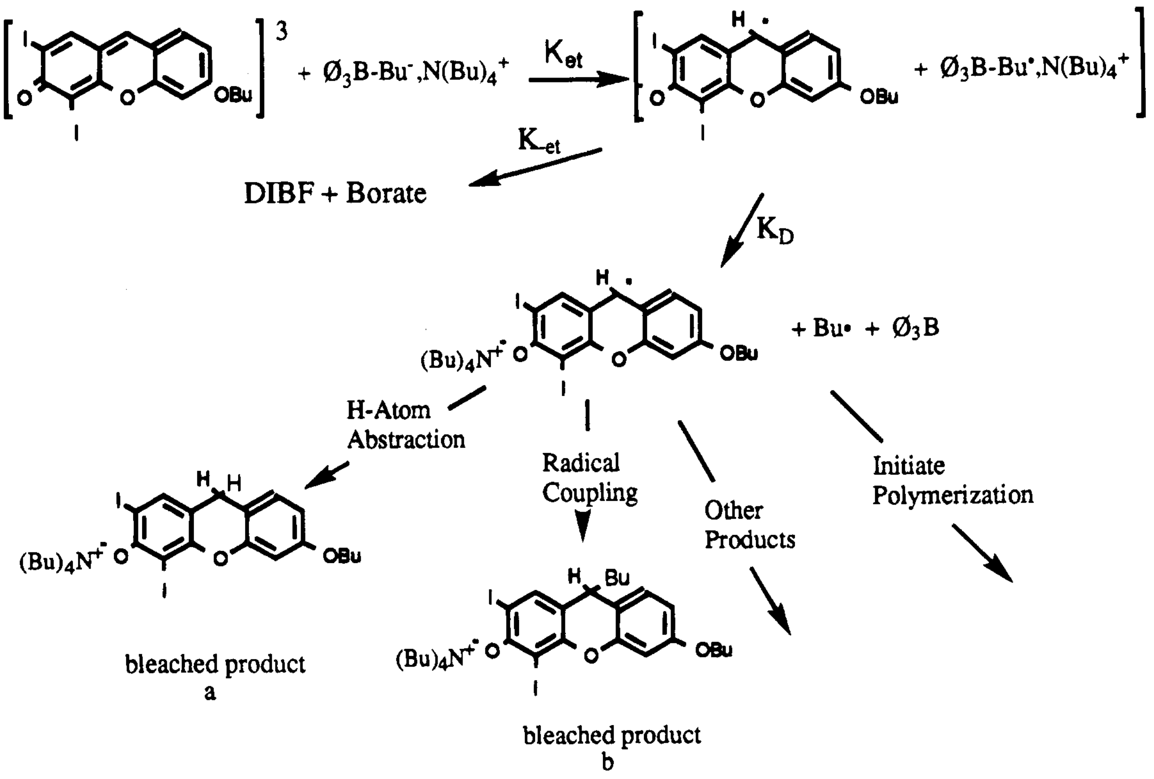
In the DIBF−DIDMA case, we were not able to detect the dye radical anion on the nanosecond time scale. Instead, the neutral dye radical ($DIBF^{\bullet}$) was obtained. Scheme 2 describes the proposed mechanism. After initial electron transfer from the amine nitrogen to the dye triplet, $DIBF^{\bullet -}$ and the amine cation radical pair are obtained. The dye radical anion has an oxygen radical centered at the 6 position, which promotes rapid proton transfer from the carbon α to the nitrogen of the amino cation radical,[28] giving the neutral dye radical and the amine radical. In the presence of monomer, it was found that the amine radical initiates polymerization. The protonation of the dye radical anion happens inside or outside the solvent cage as shown in the scheme. In either way it is too fast (large $k_{H+}$ and $K_d$) to measure on the nanosecond time scale. Also, in this case the radical formation rate was the same as the rate of dye triplet decay (Table 3) and the radical decay did not regenerate the dye. Therefore, and similar to the BORATE case, we estimate the electron transfer rate to be as the triplet quenching rate, $1.21 \times 10^8$ $s^{-1}$ (see Table 1). This rate is 1.8 times faster than in the BORATE case, and it is 5 times faster than in the similar system previously studied (TIHF−amine).[18]

The free energy change $\Delta G_{\mathrm{et}}$ for the electron transfer process calculated using the Rehm−Weller[29] equation (eq 6), where $E_{\mathrm{ox}}(D/D^{\bullet +})$ is the oxidation potential of the electron donor (DIDMA

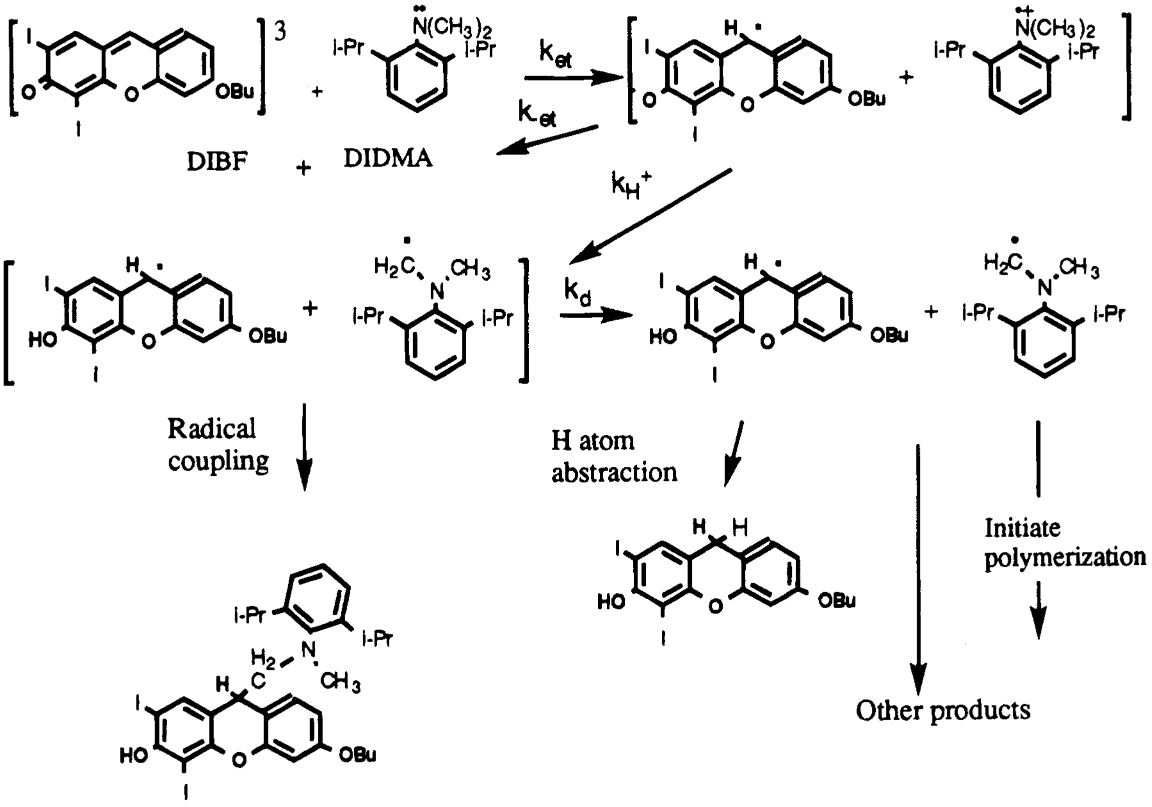
$$\Delta G_{\mathrm{et}} = E_{\mathrm{ox}}(D/D^{\bullet +}) - E_{\mathrm{red}}(A^{\bullet +}/A) - E^{\mathrm{T}}_{0-0} - Ze^2/\epsilon a \quad (6)$$

or BORATE), $E_{\mathrm{red}}(A^{\bullet +}/A)$ is the reduction potential of the electron acceptor (DIBF), and $E^{\mathrm{T}}_{0-0}$ is the triplet excitation energy, correlates well with the obtained electron transfer rates. $Ze^2/\epsilon a$ is the Coulombic energy, which is the free energy gained by bringing the two radical ions to an encounter distance $a$ in a solvent with dielectric constant $\epsilon$. The reduction potential of DIBF measured by square-wave voltammetry[30] in acetonitrile

**SCHEME 1: Proposed Mechanism in the Case of DIBF/BORATE**



**SCHEME 2: Proposed Mechanism in the Case of DIBF and DIDMA**

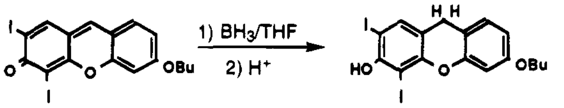


is −0.9 V (vs SCE). The triplet excitation energy is determined from the phosporescence spectrum to be 2.3 eV. The literature-reported oxidation potentials for similar borates[9] and amines[20] are ∼+0.7 and ∼+0.5 V, respectively. Assuming that the Coulombic energy is small, the calculated $\Delta G_{\mathrm{et}}$ values are −0.7 eV for the BORATE case and −0.9 eV for the DIDMA case, compared to −0.36 eV, the reported result for TIHF−amine from the previous work.[18]

The fate of the radical anion DIBF$^{\bullet-}$ formed from the BORATE (Scheme 1) and the neutral radical DIBF$^{\bullet}$ formed in the DIDMA case (Scheme 2) determines the final bleached products observed in both systems. This has a major effect on the final color of the formed solution. It was found that in the DIBF−DIDMA solution, after the solution was bleached by steady state irradiation, there is a relatively fast recovery of DIBF color (absorption). However, almost no recovery was found in the DIBF−BORATE solution. When OPPI was added to the solutions, color recovery was obtained in the BORATE case also.

Analysis of the bleached products supports the mechanisms proposed in Scheme 1 and 2. In the BORATE case, the ammonium counterion neutralizes the oxygen at the 6 position in the dye radical anion giving the radical as the ammonium salt. This radical abstracts a hydrogen atom from the solvent or couples to the butyl radical to give the reduced quinomethine ammonium salts a and b. Similarly, the neutral radical in the DIDMA case gives the quinomethines c and d.

After the irradiation of DIBF + DIDMA, three bleached products were obtained (Table 5). One product (bleached 1) was confirmed to be the dihydro reduced form c as proposed in Scheme 2. Dihydro derivative c could also be obtained by reducing DIBF chemically:



(7)

In Table 5, it can be seen that only the bleached products 1 and 2 decreased after 72 h while the concentration of DIBF recovered. If bleached product 1 is the dihydro derivative, bleached product 2 is likely the cross-coupled product d. Phillips and Read[14] reported that in the photoreduction of an eosin analog by tribenzylamine, 52% yield of the dihydro derivative and 39% yield of the cross-coupling product were obtained. In our case it seems that the cross-coupled bleached product is the principal product. However, and in agreement with Phillips and Read, we also observe that the cross-coupled product d is reoxidized re-forming the initiator.

After irradiation, the peak at rt ~ 2.5 min increased. Before irradiation, this peak was assigned as the "reduced" anionic form of DIBF (eq 1). After irradiation, this peak includes also the anionic forms of the reduced products c and d, whose amounts depend on the pH of the solution. We were not able to separate these anionic forms under the present HPLC conditions, but their existence was confirmed as follows: Adding KOH solid to a solution of the dihydro reduced product (prepared as in eq 7) increased significantly the peak at rt ~ 2.5.

Comparing the two cases, DIBF + DIDMA and DIBF + BORATE, shows, after irradiation, that in the case of the BORATE, no peaks were detected at higher rt. However, as the BORATE peak decreased, peaks with the same rt were observed with longer wavelength absorption. The UV−vis absorption spectra of the new peaks are similar to the absorption spectra of the anionic form of DIBF. This suggests that these forms have an ionic (salt) structure as proposed in Scheme 1.

The small amounts of phenol and biphenyl obtained after irradiation in the BORATE case (Table 6) are probably a result of the reaction of oxygen with triphenylborane,[23] since biphenyl and phenol are found in larger amounts in the mixture than is triphenylborane.

Reoxidation of the quinomethine-reduced products a, b, c, and d regenerates the original dye resulting in a colored solution. This reoxidation reaction depends on the polarity of the medium. In acetonitrile solution and in most of the photopolymer formulations, color recovery is fast when c and d are the reduced products but slow when a and b are the reduced products. This is reasonable since the reoxidation/deprotonation would be easier from the quinomethine c and d compared to the ammonium salts a and b under the same conditions.

## Conclusions

In this study we have shown that photoreduction of DIBF in the presence of electron donors is an electron transfer process from donor to the dye excited triplet state. However, in contrast to other similar dyes DIBF in its excited triplet state is found to be a very weak electron donor when no quenching occurs in the presence of strong oxidizing agents such as organic iodonium salts. From the transient kinetics and spectra and the analysis of the final bleached products, we are able to predict the pathway from the dye triplet through radical formation to final products. When BORATE is used as the electron donor, the dye radical anion ($DIBF^{\bullet -}$) is obtained as the only transient formed by quenching the dye triplet. However, when DIDMA is used, the neutral dye radical ($DIBF^{\bullet}$) is detected as the only product. $DIBF^{\bullet}$ obtained after protonation of $DIBF^{\bullet -}$ initially formed by the electron transfer is observed for the first time. Proton transfer from the amino cation radical is too fast to measure on the nanosecond time scale. Introducing OPPI to both systems oxidizes $DIBF^{\bullet -}$ efficiently re-forming DIBF but has little effect on $DIBF^{\bullet}$. The back electron transfer in both cases is not significant. Radical decay did not regenerate the original dye. The relative electron transfer rates ($k_{et}$) found for DIDMA and BORATE is $\approx$1.8 to 1. This correlates well with the calculated free energy $\Delta G_{et}$ in both systems.

Oxygen quenching of the dye triplet is $\approx$20 times faster than DIDMA quenching. This implies that a high concentration of electron donor is needed to compete with energy transfer to oxygen in photopolymerization formulations. The singlet oxygen produced was found to be quenched by the electron donors in an electron transfer process and would be more expected to facilitate polymerization than inhibit it.

Quinomethines and their ammonium salts were identified as the main bleached products in the DIDMA and the BORATE cases, respectively. These products can regenerate the original dye and color the solution (or the polymer) by reoxidation, depending on the polarity of the formulation. However, the reoxidation is more efficient in the case of the protonated quinomethines than it is with their ammonium salts.

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