

## Photochemistry of organoborates: intra-ion pair electron transfer to cyanines

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**Abstract** Cyanine borate  $\{R(Ph)_3B^-\}$ ; R = alkyl} salts dissolved in non-polar solvents exist predominantly as ion pairs. Irradiation of the ion pair with visible light absorbed by the cyanine leads to formation of a locally excited singlet state of the dye. The singlet excited cyanine in the ion pair is capable of oxidizing the borate anion to the boranyl radical  $\{R(Ph)_3B\cdot\}$ . The rate constant for this electron transfer reactions ( $k_{et}$ ) depends on the free energy change ( $\Delta G_{et}$ ). This latter value was estimated for a series of borates and the relationship between  $k_{et}$  and  $\Delta G_{et}$  appears to give a maximum value consistent with the quadratic law predicted from Marcus theory. The boranyl radical undergoes carbon-boron bond cleavage to generate a free alkyl radical. The rate of bond cleavage depends directly on the stability of the alkyl radical formed. When stabilized alkyl radicals are formed, carbon-boron bond cleavage is faster than the back electron transfer reaction that regenerates the cyanine borate ion pair. Carbon-boron bond cleavage of the boranyl radical in the systems examined is irreversible and the bond dissociation energy of the parent hydrocarbon is a good predictor of the yield of radicals. The free alkyl radicals formed by the irradiation - electron transfer - bond cleavage sequence may be used in meaningful chemical processes such as the initiation of polymerization.

### INTRODUCTION

The photochemical reactions of organoborate salts have not been extensively explored. We report herein that photoinitiated one-electron oxidation of alkyltriphenylborate salts generates a boranyl radical. The details of this reaction were explored with 1,4-dicyanonaphthalene as sensitizer and when the borates are part of an ion pair with a cyanine dye.<sup>1</sup>

**Preparation and oxidation potentials of alkyltriphenylborates  $M^+[R(Ph)_3B]^-$**  The preparation of alkyltriphenylborates proceeds smoothly from the reaction of an alkyllithium (or Grignard reagent) and triphenylborane<sup>2</sup> These borates are easily isolated as their crystalline tetramethylammonium salts. They are stable in air and protic solvents and are soluble in acetonitrile.

An issue of primary concern is the oxidation potential of the alkyltriphenylborates. Cyclic voltammetry gives irreversible oxidation waves for each of the borates examined with peak potentials that vary systematically with the structure of the borate. Those borates bearing alkyl groups capable of forming "stabilized" radicals (i.e., benzyl and 2-naphthylmethyl) have peak potentials lower than borates that can generate only "unstabilized" radicals (i.e., cyclopropyl and phenyl).

Since electrochemical methods are unsuitable for measurement of thermodynamically meaningful oxidation potentials of the borates, we turned to a kinetic method for the determination of these values. Rehm and Weller<sup>3</sup> conclude from examination of numerous cases that the rate constant for electron transfer quenching ( $k_{et}$ ) between an electronically excited acceptor and an electron donor in acetonitrile solution obeys the formulae shown below. In these equations  $\Delta G_{et}$  is directly related to the thermodynamic oxidation potential of the donor, and  $\Delta G_{et}^*$ , is defined in second equation ( $\Delta G_{et}(0)$ , the activation energy when  $\Delta G_{et} = 0$  is assigned a constant value of 2.4 kcal/mole in acetonitrile solution). Thus, by application of the Weller equation to the electron transfer quenching of excited electron acceptors with known reduction potentials and singlet energies, thermodynamically meaningful oxidation potentials for electron donors may be calculated.

$$k_{\text{et}} = \frac{2 \times 10^{10}}{1 + 0.25 \left[ \exp\left(\frac{\Delta G_{\text{et}}^*}{RT}\right) + \exp\left(\frac{\Delta G_{\text{et}}}{RT}\right) \right]}$$

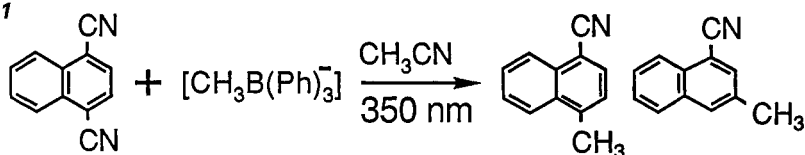
$$\Delta G_{\text{et}}^* = \left[ \left(\frac{\Delta G_{\text{et}}}{2}\right)^2 + (\Delta G_{\text{et}}^*(0))^2 \right]^{1/2} + \frac{\Delta G_{\text{et}}}{2}$$

We examined the fluorescence quenching for a series of polycyclic aromatic hydrocarbons by the borates to gain a measure of the borate oxidation potentials. The reaction was monitored by time resolved absorption spectroscopy. These experiments show that the electron transfer from the borate forms the aromatic hydrocarbon radical anion and, when combined with the results of fluorescence quenching experiments, confirms that it is the singlet excited state of aromatic hydrocarbon which accepts the electron. Substitution of the values of  $k_{\text{et}}$  obtained in experiments with the borates as electron donors into eqs. 1 and 2 gives the "kinetically" determined oxidation potentials. As expected for a case where a chemical reaction follows electron transfer, the kinetically determined oxidation potentials ( $E_{\text{ox}}^k$ ) for the borates are more positive than are the peak potential values determined by cyclic voltammetry ( $E_{\text{ox}}^P$ ).

**Dicyanonaphthalene sensitized reaction of alkyltriphenylborates** The fluorescence of 1,4-dicyanonaphthalene (DCN) is quenched by benzyltriphenylborate at the diffusion controlled limit ( $1.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  in  $\text{CH}_3\text{CN}$ ). This is not an unexpected finding since  $\Delta G_{\text{et}}$  for electron transfer from this borate to DCN excited singlet state is exothermic by more than 10 kcal/mol. The generation of DCN radical anion in this process was confirmed by measurement of its characteristic absorption spectrum using laser flash photolysis techniques.

Irradiation of DCN at 350 nm in a deoxygenated acetonitrile solution containing methyltriphenylborate gives 3-methyl-1-cyanonaphthalene and 4-methyl-1-cyanonaphthalene (ratio 3-methyl : 4-methyl = 1 : 1.6) in essentially quantitative yield. This experiment is summarized in Scheme 1. Similarly, photolysis of DCN in acetonitrile solution containing benzyltriphenylborate gives a 95% yield of the 3-, and 4-benzyl-1-cyanonaphthalenes. In this case, a low yield of toluene is also observed.

Scheme 1



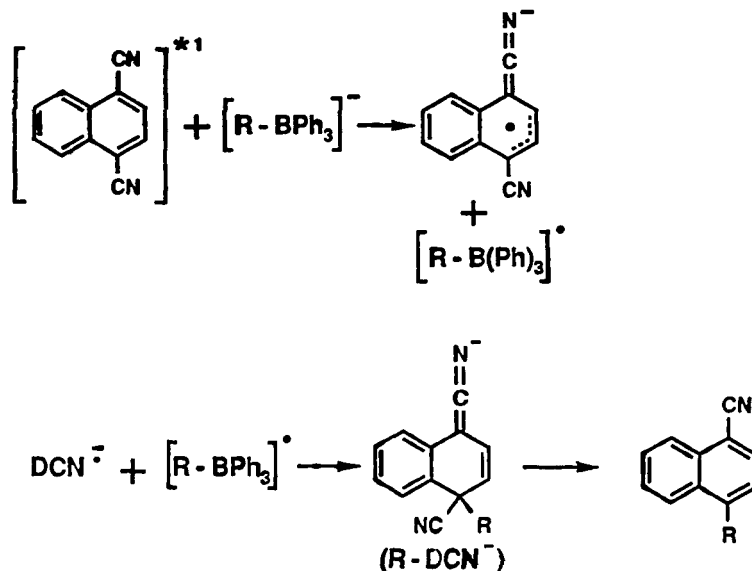
Yield: 95% at 78% conversion

Ratio:  $\frac{\text{3-methyl}}{\text{4-methyl}} = 0.6$  In dry,  $\text{O}_2$ -free  $\text{CH}_3\text{CN}$

These experimental findings lead to postulation of the mechanistic hypothesis shown in Scheme 2 (only formation of the 4-substituted isomer is shown, an analogous path leads to the generation of the 3-alkyl substituted isomer). Irradiation creates the excited singlet state of DCN which is quenched by electron transfer to generate the dicyanonaphthalene radical anion and the alkyltriphenylboranyl radical. Next a reaction between the boranyl radical and the reduced dicyanonaphthalene generates the alkylated DCN anion depicted as R-DCN $^-$  on Scheme 2. Finally, loss of a cyanide anion generates the observed products.

Formation of the alkylated cyanonaphthalenes could proceed by a direct displacement of triphenylborane from the boranyl radical by the dicyanonaphthalene radical anion (one-step  $\text{S}_{\text{N}}2$ -like reaction) or by initial homolytic cleavage of the alkyl carbon-boron bond of the boranyl radical to generate a free alkyl radical ( $\text{R}\cdot$ ) followed by its combination with dicyanonaphthalene radical anion (two step  $\text{S}_{\text{N}}1$ -like reaction). These two possibilities are shown in Scheme 3. These cases may be distinguished by employing the cyclization of the hexenyl radical as an indicator of the formation of free radicals in solution.

Scheme 2

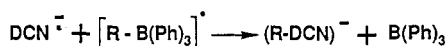


Irradiation of dicyanonaphthalene in the presence of 5-hexenyltriphenylborate gives four isomeric products. These were identified as 3- and 4-(5-hexenyl)-1-cyanonaphthalene and 3- and 4-(cyclopentylmethyl)-1-cyanonaphthalene, Scheme 4 (where only the 4-alkyl substituted isomers are shown). When this same system is irradiated with a nitrogen laser (instead of a lamp), the ratio of unrearranged to rearranged products decrease. On the basis of the known unimolecular rate constant for the cyclization of the hexenyl radical,<sup>4</sup> these observations support carbon-boron bond cleavage to form free alkyl radicals and the operation of the  $S_N1$ -like mechanism outlined in Scheme 3.

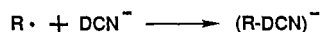
In summary, these experiments show that alkyltriphenylborates are readily prepared, stable, relatively easily oxidized compounds. Single electron oxidation of the borate generates a boranyl radical which cleaves to give triphenylborane and a free alkyl radical.

Scheme 3

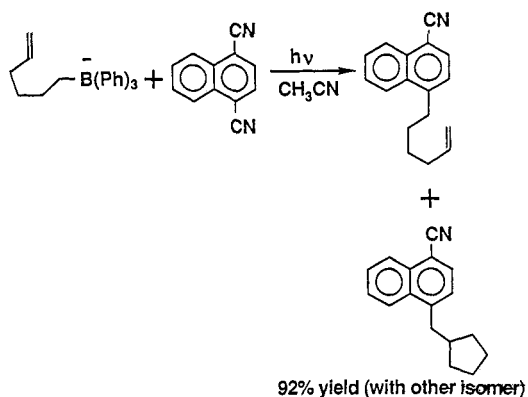
1) Displacement of  $B(Ph)_3$  (one step):



2) Carbon-Boron bond cleavage (two steps):



Scheme 4



**Cyanine dyes: photochemistry and photophysics** Cyanine dyes are intensely colored cationic compounds of immense practical importance because of their use in color photography and as saturable absorbers for mode-locked lasers. As a consequence, the photochemistry and photophysics of these dyes have been studied extensively.

Cyanine dyes are most commonly prepared as their halide salts. Electronic excitation of an unaggregated cyanine dye in solution leads to formation of its excited singlet state. The lifetime and properties of the singlet state depend on the details of structure and on the medium in which the dye is dissolved. For typical cyanine dyes dissolved in relatively non-viscous solvents, the excited state lifetime of the dye generally is less than one nanosecond. The most important pathway for deactivation of the excited singlet state under these circumstances is rotation about a formal carbon-carbon double bond to form a ground state isomer. This photoisomerization of cyanines has been examined

in great detail from both the experimental<sup>5</sup> and theoretical<sup>6</sup> viewpoint. In viscous solvents, where photoisomerization is inhibited, cyanines often fluoresce efficiently, but most cyanine dyes fluoresce weakly in fluid solutions. The photophysical reactions of cyanine dyes in solution are summarized in Scheme 5.

The structure of *N,N'*-dimethyldimethylindocarbocyanine ( $\text{Cy}^+\text{X}^-$ ) has been studied in the solid state by means of X-ray crystallography. As its iodide<sup>7</sup> or perchlorate salt<sup>8</sup> it adopts an extended "all-trans" geometry. Analysis of the temperature dependence of the  $^1\text{H}$  NMR spectrum shows that  $\text{Cy}^+\text{BF}_4^-$  dissolved in methanol solution also adopts the all-trans planar geometry.<sup>9</sup>

At room temperature in benzene solution,  $\text{Cy}^+\text{PF}_6^-$  fluoresces with modest efficiency:  $\Phi_{\text{fl}} = 0.047 \pm 0.01$ . The fluorescence efficiency is independent of excitation wavelength throughout the visible absorption band. The time dependence of the fluorescent emission from benzene solutions of  $\text{Cy}^+\text{PF}_6^-$  at room temperature shows a single kinetically first-order decay with a lifetime of  $260 \pm 10$  ps. The absorption and fluorescence data reveal a 0-0 absorption band for  $\text{Cy}^+\text{PF}_6^-$  in benzene at 564 nm which corresponds to a singlet energy ( $\Delta E^{*1}$ ) of 50.7 kcal/mol.

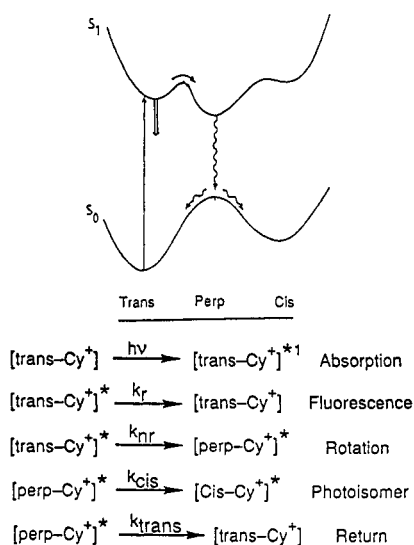
The electrochemical behavior of the cyanine dyes has been studied extensively.<sup>10</sup> In acetonitrile solution with tetrabutylammonium tetrafluoroborate as the supporting electrolyte,  $[\text{Cy}]^+$  shows a reversible reduction wave at -1.00 V vs SCE. The reduction generates the cyanine radical,  $[\text{Cy}]^\cdot$ . Related radicals formed by the one electron reduction of other cyanine dyes have been observed by ESR and optical absorption spectroscopy.<sup>11</sup>  $[\text{Cy}]^\cdot$  has an apparent absorption maximum at ca. 427 nm.

Laser flash photolysis of  $\text{Cy}^+\text{PF}_6^-$  reveals formation of several transient intermediates. An absorption spectrum recorded 60 ps after excitation of  $\text{Cy}^+\text{PF}_6^-$  in benzene solution shows bleaching of the absorption bands characteristic of the dye. Most of the absorption intensity of  $[\text{Cy}]^+$  grows back into the spectrum with a lifetime of  $250 \pm 10$  ps according to a first order rate law. An absorption spectrum recorded 5 000 ps after the excitation of  $\text{Cy}^+\text{PF}_6^-$  reveals a new absorption feature with an apparent maximum at 580 nm that is assigned to the mono-cis photoisomer of the dye. Related experiments conducted on a longer time scale show that the mono-cis photoisomer eventually returns to  $[\text{Cy}]^+$ . The time-resolved spectroscopic behavior of  $\text{Cy}^+\text{PF}_6^-$  is analogous to that previously observed for other cyanine dyes.<sup>5</sup>

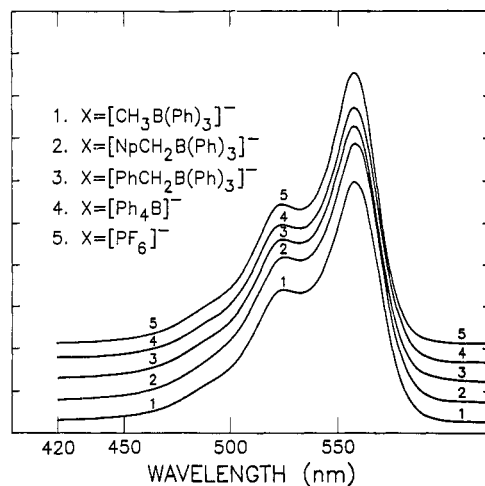
**Cyanine borates** Cyanine borate salts are prepared by metathesis of the appropriate tetramethylammonium borate and the indocarbocyanine chloride in acetonitrile-water solution. The electronic absorption spectra of representative examples of the cyanine borates in benzene solution are shown in Scheme 6 along with that of  $\text{Cy}^+\text{PF}_6^-$  for comparison. Of importance is the observation that these spectra are independent of the structure of the anion. Thus, excitation of  $\text{Cy}^+[\text{R}-\text{B}(\text{Ph}_3)]^-$  with visible light generates a locally excited state of  $[\text{Cy}]^+$  which has the same radiative rate constant as does  $\text{Cy}^+\text{PF}_6^-$ .

Scheme 5

## Fluorescence of Cyanines:



Scheme 6



Salts dissolved in organic solvents exist as a mixture of freely solvated ions and ion pairs. Since the state of association plays an important role in controlling the photochemistry of the cyanine borates, we examined their behavior in a range of organic solvents. The conductance of solutions containing incompletely dissociated electrolytes has been extensively investigated.<sup>12</sup> Determination of the extrapolated molar conductance at infinite dilution ( $\Lambda_0$ ) provides a useful experimental means for estimation of the dissociation constant ( $K_{eq}$ ) for these electrolytes, Scheme 7.

We measured the conductivity of solutions of  $Cy^+PF_6^-$  in a series of solvents with different dielectric constants. The Fuoss equation,<sup>13</sup> relates the value of  $K_D$  to the dielectric constant of the solvent and the center-to-center distance at contact of the ions in the ion pair. A plot of the conductivity-data-derived dissociation constants for  $Cy^+PF_6^-$  according to the Fuoss equation gives values of  $K_{eq}$  which may be extrapolated to benzene solution.

These experiments show that the cyanine borates in benzene solution exist essentially exclusively as tight-ion pairs over the concentration range used in the study of their photochemistry. In solvents with higher dielectric constants than benzene, such as ethyl acetate, the proportion of the cyanine dye associated as ion pairs changes significantly over the concentration range of interest. Tight ion pair formation has important consequences in both the kinetics and thermodynamics of the reactions of electronically excited cyanine borates.

### Free energy and rate constant for electron transfer in cyanine borate ion pairs

With knowledge of the oxidation potentials of the borates, the reduction potential of the cyanine dye and its singlet energy, and the equilibrium constants for association of the cyanine borate into ion pairs, it is possible to calculate the driving force for electron transfer from the borate to the excited state of the cyanine.

Calculation of the free energy change for a photoinitiated electron transfer process begins with the estimation or measurement of the terms in eq 1:  $E_{ox}$  and  $E_{red}$  are the oxidation and reduction potentials of the borate and cyanine;  $\Delta E^{*1}$  is the energy of the cyanine singlet state; and  $W_r$  and  $W_p$  are work terms associated with bringing the reactants from infinity to the encounter distance and separating the products from the encounter to infinity, respectively.

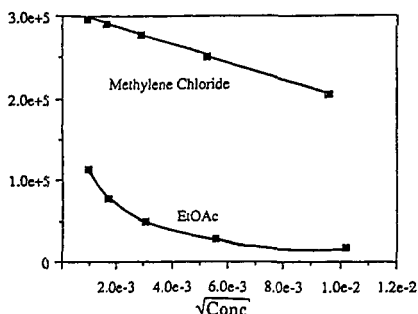
$$\Delta G_{et} = E_{ox} - E_{red} - \Delta E^{*1} - (W_p - W_r) \quad (1)$$

The potentials for reduction of  $[Cy]^+$  and oxidation of the borates were obtained from experiments carried out in acetonitrile solution. But the photochemical experiments on the cyanine borates were performed in benzene solution where formation of the required ion pairs is complete. Thus calculation of  $\Delta G_{et}$  requires inclusion of the effect of the solvent change on the electrochemical potentials.

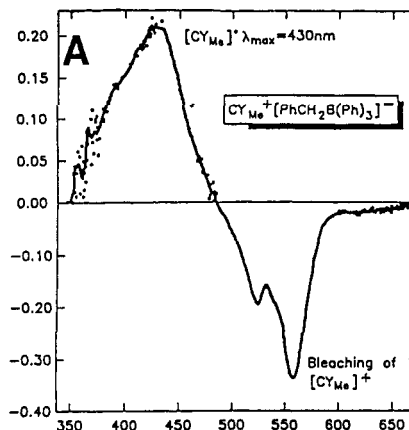
The usual procedure for incorporation of solvent effects on electrochemical potentials is by consideration of the difference in the solvation energies of the ions according to the Born equation. The change in solvent from acetonitrile to benzene has an enormous effect on the values of the electrochemical potentials of the cyanine and the borates. This is a matter of some concern since the approximations required for application of the Born equation to the cyanine borates are crude. However, the same assumptions are required in the calculation of  $W_r$ . This value is similarly large but enters eq 1 with a sign opposite that of the solvent change. On this basis it is reasonable to expect that the errors introduced by the approximations of the Born equation will approximately cancel.

Scheme 7

Molecular Conductivity =  $\Lambda = \Lambda^\infty - S \gamma^{1/2} C^{1/2}$   
 Association Constant =  $K_{eq} = (1 - \gamma) / C \gamma^2$



Scheme 8



The value of  $W_r$  may be calculated from the estimates of  $K_{eq}$ . This approach gives  $W_r \approx 0.96$  eV in benzene solution. Since intra-ion pair electron transfer in the cyanine borates generates neutral products, we set  $W_p \approx 0$ . Incorporation of these values into eq 1 gives reasonable estimates for  $\Delta G_{et}$  of the singlet excited cyanine borate ion pairs. These values are listed in Table 1.

The fluorescence efficiencies of the  $[Cy]^+$  salts in benzene solution depend on the identity of the borate anion and provides a direct measure of the rate constant for electron transfer reactions ( $k_{et}$ ) from the borate to the excited singlet state of the cyanine. We determined the relative fluorescence efficiencies  $[\Phi(PF_6^-)/\Phi(RB^-)]$  of dilute solutions of cyanines in benzene where the salts exist exclusively as ion pairs. In general, as the "stability" of the radical formed from carbon-boron bond cleavage increases (i.e., phenyl versus benzyl) the magnitude of  $k_{et}$  increases. The values of  $k_{et}$  are listed in Table 1.

**Photolysis of cyanine borates: products** Etter and co-workers<sup>14</sup> irradiated cyanine borates in the solid state. They suggested that alkyl radicals are intermediates in this reaction. We put the generation of radicals from the irradiation of cyanine borates on a quantitative basis by studying the photolysis of  $Cy^+[Ph(CH_2)_3B(Ph)_3]^-$  in ethyl acetate solutions containing tri-n-butylstannane. Irradiation under these conditions generates n-propylbenzene, presumably by hydrogen atom transfer from the stannane to the photogenerated 3-phenylpropyl radical. The quantum yield for radical formation in this process was estimated to be 0.14 by extrapolation to infinite stannane concentration.

Irradiation of a benzene solution of  $Cy^+[PhCH_2B(Ph)_3]^-$  with an 18 ps long light pulse at 532 nm instantaneously gives the transient spectrum shown in Scheme 8. Inspection of this spectrum shows bleaching of the absorptions of the cyanine dye and a new feature with a maximum absorbance at 430 nm assigned to  $[Cy]^\cdot$ . There are no meaningful changes in this transient absorption spectrum for times up to 10,000 ps after the excitation pulse. In particular, none of the photoisomer seen in the irradiation of the  $Cy^+PF_6^-$  salt is evident in these spectra. Related spectral changes are observed following the pulsed irradiation of the other cyanine borates. These results shown that the relative quantum efficiencies for the formation of  $[Cy]^\cdot$  depends on the structure of the borate.

#### **Cyanine (naphthyl)methyltriphenylborate: carbon-boron bond cleavage and formation of boranyl radicals**

One-electron oxidation of an alkyltriphenylborate generates a boranyl radical. Cleavage of the carbon-boron bond in the boranyl radical generates triphenylborane and an alkyl radical. In principle this reaction could be reversible. We examined the properties of the (2-naphthyl)methyltriphenylboranyl radical in an attempt to measure the equilibrium constant for this reaction.

Pulsed irradiation of a  $N_2$ -purged benzene solution of 2-(bromomethyl)naphthalene gives a transient absorption spectrum with apparent maximum absorbance at 385 nm assigned to the (2-naphthyl)methyl radical. If  $[NpCH_2]^\cdot$  reacts with triphenylborane to form the boranyl radical, then addition of triphenylborane to the solution will increase the rate of decay of  $[NpCH_2]^\cdot$ . Pulsed irradiation of 2-(bromomethyl)naphthalene in a  $N_2$ -purged solution containing triphenylborane shows an increase in lifetime of  $[NpCH_2]^\cdot$  due to the scavenging of residual  $O_2$  by the triphenylborane, Scheme 9. There is no detectable reaction of  $[NpCH_2]^\cdot$  with triphenylborane.

Pulsed irradiation of a benzene solution of  $Cy^+[NpCH_2B(Ph)_3]^-$  (532 nm, 18 ps) instantaneously gives a transient absorption spectrum showing bleaching of the absorptions of  $[Cy]^+$ , the appearance of  $[Cy]^\cdot$ , and a shoulder on the high energy side of the  $[Cy]^\cdot$  absorption assigned to  $[NpCH_2]^\cdot$ . This experiment shows that the naphthylmethyl radical is formed instantaneously on the time scale.

Calculation from the experimental limits to the rate constants for carbon-boron bond cleavage and formation in the (naphthylmethyl)triphenylboranyl radical permits estimation of the equilibrium constant ( $K_{BC}$ ) for the reaction of triphenylborane with naphthylmethyl radical. In benzene solution at room temperature,  $K_{BC} > 2 \times 10^4$  M. Thus formation of the naphthylmethyl radical following oxidation of  $[NpCH_2B(Ph)_3]^-$  is very fast and essentially irreversible.

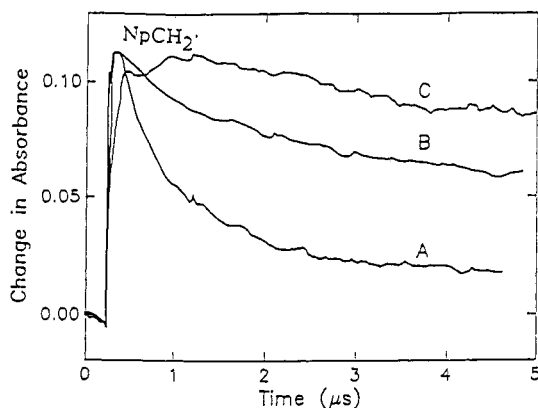
**A mechanism for intra-ion pair electron transfer of cyanine borates** The experimental findings reported above support postulation of the reaction mechanism shown in Scheme 10. The cyanine and borate exist as an ion pair in benzene solution. This self-association is a prerequisite for the photo-initiated reaction since the lifetime of the excited singlet state of the cyanine is too short to allow an efficient diffusive encounter at experimentally achievable concentrations of the borate. Irradiation of the ion pair with visible light generates the excited singlet state of the cyanine which can undergo three possible reactions: fluorescence, rotation to a photoisomer, or electron transfer to form the cyanine and boranyl radicals. Once formed, the cyanine-boranyl radical pair may undergo back electron transfer to regenerate the ion pair, or undergo

Table 1.

Borate	$E_{ox}^p$ V vs. SCE	$E_{ox}^k$ V vs. SCE	$k_{nr}$ ( $s^{-1}$ )
$[PhC\equiv CB(Ph)_3]^-$	0.95	1.51	$1.6 \times 10^9$
$[Ph_4B]^-$	0.90	1.45	$4 \times 10^{10}$
$[H_2C=CH-B(Ph)_3]^-$	0.84	1.45	$4.8 \times 10^{10}$
$[cyclo-C_3H_5-B(Ph)_3]^-$	0.83	1.43	$8.9 \times 10^{10}$
$[CH_3B(Ph)_3]^-$	0.81	1.39	$1.1 \times 10^{11}$
$[n-BuB(Ph)_3]^-$	0.70	1.21	$2.4 \times 10^{11}$
$[PhCH=CHB(Ph)_3]^-^a$	0.63	1.16	$1.2 \times 10^{11}$
$[PhCH_2B(Ph)_3]^-$	0.39	1.09	$3.3 \times 10^{11}$
$[m-TolCH_2B(Ph)_3]^-$	0.36	1.10	
$[NpCH_2B(Ph)_3]^-$	0.28	1.07	$3.9 \times 10^{11}$
$[n-BuB(Ar)_3]^-^b$	0.60	1.11	$2.4 \times 10^{11}$

cleavage of a carbon-boron bond to form an alkyl radical  $[R\cdot]$  and triphenylborane. The radicals formed might couple to form an alkylated cyanine  $[Cy-R]$ , or their diffusion from the initial solvent cage will give free radicals. The observation of significant sensitivity of reaction rates and free radical yields to the structure of the borate-bound alkyl group is a consequence of competition within the photo-initiated electron transfer, bond-cleavage, cage-escape reaction sequence. Analysis of the structural dependence of the rates and efficiencies reveals important details about intra-ion-pair electron transfer reactions and the chemistry of boranyl radicals.

Scheme 9



- [A] Irradiation of  $NpCH_2Br$  in Benzene ( $N_2$ -purged).  
 [B] Irradiation of  $NpCH_2Br$  and  $BPh_3$  (0.0013 M) in Benzene ( $N_2$ -purged).  
 [C] Irradiation of  $NpCH_2Br$  and  $BPh_3$  (0.021 M) in Benzene ( $N_2$ -purged).

Rate constants for electron transfer in the cyanine borate ion pairs may be related to the free energy of the reaction through the classical Marcus equation, eq where  $\lambda$  is the reorganization energy.<sup>15</sup> A plot of the data for the intra-ion-pair electron transfer in the cyanine borates according to this approach is shown in Scheme 11.

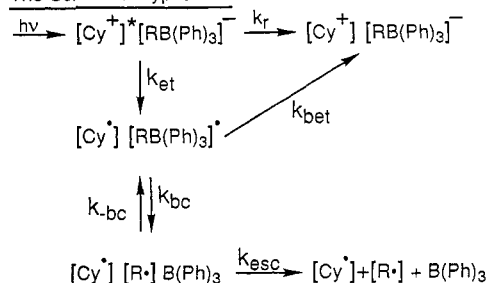
$$\Delta G_{et}^{\ddagger} = \lambda/4 (1 + \Delta G_{et}/\lambda)^2 \quad (2)$$

Although the range of free energies for the electron transfer reactions covered by the data shown in Scheme 11 is narrow and restricted to values near zero, it is possible to reach some tentative conclusions about the functional dependence of  $k_{et}$  on  $\Delta G_{et}$ . Two factors are recognized as contributing to  $\lambda$ ; the solvent reorganization term ( $\lambda_s$ ), and differences in vibrational frequencies between the reduced and oxidized form of the reagents ( $\lambda_v$ ). The value of  $\lambda_s$  for a non-polar solvent such as benzene is readily calculated to be nearly zero. Thus the reorganization energy revealed by our measurements may be associated primarily with  $\lambda_v$ . Analysis of the data shown in Scheme 11 according to the Marcus equation shows that  $\lambda_v$  is ca. 0.4 eV. Of course the precise value of  $\lambda$  is dependent on the assumptions made in the calculation of  $\Delta G_{et}$ . These findings are consistent with our postulate of an electron transfer reaction to generate the cyanine radical and alkyl-triphenylboranyl radical pair as intermediates in the photoinitiated reactions of these salts, however confirmation of the functional dependence of the rates awaits results from a wider range of values for  $\Delta G_{et}$ .

**Scheme 10**

Overview: Electron Transfer in Electronically Excited Cyanine Borate Ion Pairs

The Scheme: Hypothesis



According to the mechanism proposed in Scheme 10, the radical pair formed by electron transfer from the borate to the excited cyanine may undergo back electron transfer to regenerate the initial ion pair or it may undergo carbon-boron bond cleavage to form triphenylborane and the alkyl radical in a solvent cage with  $[\text{Cy}]^\cdot$ . In principle, the efficiency of formation of free radicals in this process might be controlled by a decrease in the equilibrium constant for carbon-boron bond cleavage in the series of borates, or it could be due to an increase in the rate constant for back electron transfer ( $k_{\text{bet}}$ ). The findings suggest that the first explanation is more reasonable.

According to the Marcus equation, the rate constant for back electron transfer should be determined by the free energy for this reaction,  $\Delta G_{\text{bet}}$ . For all cases examined, back electron transfer is very exothermic and its exothermicity decreases through the series from  $[\text{Ph}_4\text{B}]^-$  to  $[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$ . Since  $\lambda_s$  is negligible, it is reasonable to expect that the back electron transfer falls in the Marcus inverted region. If so, and if the efficiency of radical formation were controlled primarily by  $k_{\text{bet}}$ , then  $[\text{Ph}_4\text{B}]^-$  should give more radicals than does  $[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$ , opposite to the experimental findings. Nevertheless, the prediction that the rate of the back electron transfer reaction is retarded by inverted region behavior may play an important role in radical formation. If the back electron transfer rates were not somehow slowed, carbon-boron bond cleavage of the boranyl radical might not ever be competitive.<sup>16</sup>

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**Scheme 11**