

# Photochemistry of Carbocyanine Alkyltriphenylborate Salts: Intra-Ion-Pair Electron Transfer and the Chemistry of Boranyl Radicals

Subhanakar Chatterjee,<sup>†</sup> Paul D. Davis,<sup>‡</sup> Peter Gottschalk,<sup>‡</sup> Michael E. Kurz,<sup>§</sup> Björn Sauerwein,<sup>†</sup> Xiqiang Yang,<sup>†</sup> and Gary B. Schuster<sup>\*,†</sup>

Contribution from the Department of Chemistry, University of Illinois, Roger Adams Laboratory, Urbana, Illinois 61801-3731, Mead Imaging Incorporated, 3385 Newmark Drive, Miamisburg, Ohio 45342, and Department of Chemistry, Illinois State University, Normal, Illinois 61761. Received February 22, 1990

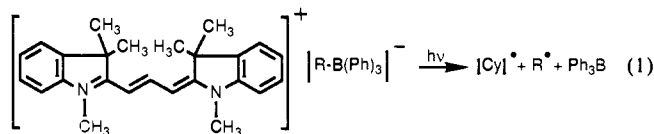
**Abstract:** Cyanine borate  $[R(Ph)_3B^-]$  salts dissolved in nonpolar solvents exist predominantly as ion pairs. Irradiation of the ion pair with visible light absorbed by the cyanine leads to formation of a locally excited singlet state of the dye. The singlet excited cyanine in the ion pair is 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.

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.<sup>1</sup> As a consequence, the photochemistry and photophysics of the cyanines have been studied extensively and much has been learned.

Cyanine dyes are most commonly prepared as their halide or perchlorate salts  $(Cy^+X^-)$ ,  $X^- = Cl^-, Br^-, I^-, ClO_4^-$ , etc.). When these salts are dissolved in water, or other polar, hydrogen-bonding solvents, aggregates form that have special optical and chemical properties.<sup>2</sup> In contrast, dilute solutions of these salts in less polar, non-hydrogen bonding solvents generally do not give evidence for aggregation. Electronic excitation of an unaggregated cyanine dye with visible light leads to formation of its excited singlet state  $[Cy^+(S_1)]$ . The lifetime and properties of  $Cy^+(S_1)$  depend on the details of structure and on the medium in which the dye is dissolved. For typical cyanine dyes dissolved in relatively nonviscous solvents, the excited-state lifetime of the cyanine generally is less than one nanosecond. The most important pathway for deactivation of  $Cy^+(S_1)$  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>3</sup> and theoretical<sup>4</sup> viewpoint. In viscous solvents, where photoisomerization is inhibited, cyanines often fluoresce efficiently, but most cyanine dyes fluoresce weakly in fluid solutions. The excited singlet states of simply substituted cyanine dyes do not intersystem cross to their triplet states with measurable yields. The short singlet lifetime and the lack of triplet-state formation prohibits the use of cyanine dyes as photosensitizers in the conventional sense. However, aggregated cyanines adsorbed on silver halide grains are certainly useful sensitizers in color photography.<sup>2</sup>

Borates are well-known trivalent, tetracoordinate, anionic compounds of boron.<sup>5</sup> We recently discovered that photoinitiated one-electron oxidation of alkyltriphenylborates  $[R-B(Ph)_3]^-$  starts a reaction sequence which ultimately leads to the formation of free alkyl radicals.<sup>6</sup> On the basis of the earlier work of Davies and co-workers,<sup>7</sup> we postulated that one-electron oxidation of the borate gives a boranyl radical  $[R-B(Ph)_3]^{\cdot-}$  which subsequently fragments to form triphenylborane and the alkyl radical.

Herein we report investigation of the photochemistry of borate salts of dimethylindocarbocyanine  $[(Cy^+)R-B(Ph)_3]^-$  dissolved in nonpolar solvents.<sup>8</sup> Under these conditions, irradiation of the cyanine dye with visible light results in efficient sensitization of the borate and the generation of free alkyl radicals, eq 1. This



reaction is useful for the initiation of photopolymerization of vinyl monomers with visible light. Our study of the mechanism of the cyanine borate photoreaction by time-resolved spectroscopy and

(1) Dienes, A.; Shank, C. V.; Trozzolo, A. M. In *Creation and Detection of Excited States*; Ware, W. R., Ed.; Dekker: New York, 1974; Vol. 2, Chapter 4. West, W.; Gilman, P. B. In *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; Macmillan: New York, 1977; p 277.

(2) West, W.; Pearce, S. *J. Phys. Chem.* **1965**, *69*, 1894. Kasha, M.; Rawls, H. *J. Photogr. Sci.* **1973**, *21*, 11. West, W.; Gilman, P. B., Jr. In *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; Macmillan: New York, 1977; Chapter 10.

(3) McCartin, P. J. *J. Phys. Chem.* **1965**, *47*, 2980. Chibisov, A. K. *J. Photochem.* **1976/77**, *6*, 199. Kuzmin, V. A.; Darmanyan, A. P. *Chem. Phys. Lett.* **1978**, *54*, 159. Akesson, E.; Sundstrom, V.; Gillbro, T. *Chem. Phys. Lett.* **1985**, *121*, 513. Dietz, R.; Rentsch, S. K. *Chem. Phys.* **1985**, *96*, 145. Akesson, E.; Sundstrom, V.; Gillbro, T. *Chem. Phys.* **1986**, *106*, 269. Laermer, F.; Elsaesser, T.; Kaiser, W. *Chem. Phys. Lett.* **1989**, *156*, 381. Berndt, K.; Durr, H.; Feller, K.-H. *Z. Phys. Chem. (Leipzig)* **1987**, *268*, 250.

(4) Rulliere, C. *Chem. Phys. Lett.* **1976**, *43*, 303. Mialocq, J. C. *Chem. Phys.* **1982**, *73*, 107. Lounnot, D.-J.; Brunero, P.; Foussier, J.-P.; Faure, J. *J. Chim. Phys.* **1982**, *79*, 343. Smedartchina, Z.; Dietz, F. *J. Photochem.* **1985**, *30*, 13. Momicchioli, F.; Baraldi, I.; Berthier, G. *Chem. Phys.* **1988**, *123*, 103.

(5) Brown, H. C. *Hydroboration*; W. A. Benjamin: New York, 1962.

(6) Lan, J. Y.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 4261. Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 6710.

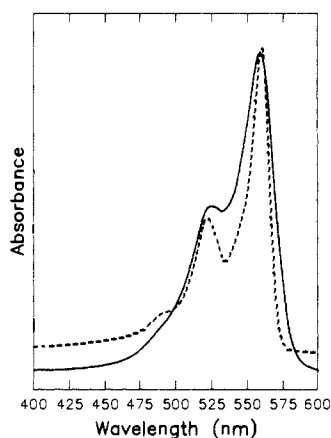
(7) Davies, A. G.; Roberts, B. P. *J. Organomet. Chem.* **1969**, *19*, P17. Davies, A. G.; Griller, D.; Roberts, B. P.; Tudor, R. *J. Chem. Soc., Chem. Commun.* **1970**, 640. Davies, A. G.; Hook, S. C. W.; Roberts, B. P. *J. Organomet. Chem.* **1970**, *22*, C37. Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc. (B)* **1971**, 1823. Davies, A. G.; Roberts, B. P. *J. Chem. Soc. (B)* **1971**, 1830. Bancroft, E. E.; Blount, H. N.; Janzen, E. G. *J. Am. Chem. Soc.* **1979**, *101*, 3692.

(8) Some of these results have been reported in preliminary form: Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326.

<sup>†</sup> University of Illinois.

<sup>‡</sup> Mead Imaging Incorporated.

<sup>§</sup> Illinois State University.



**Figure 1.** Absorption spectra of *N,N'*-dimethyldimethylindocarbocyanine hexafluorophosphate at room temperature in benzene solution (solid line) and at 77 K in glassy 2-methyltetrahydrofuran solution.

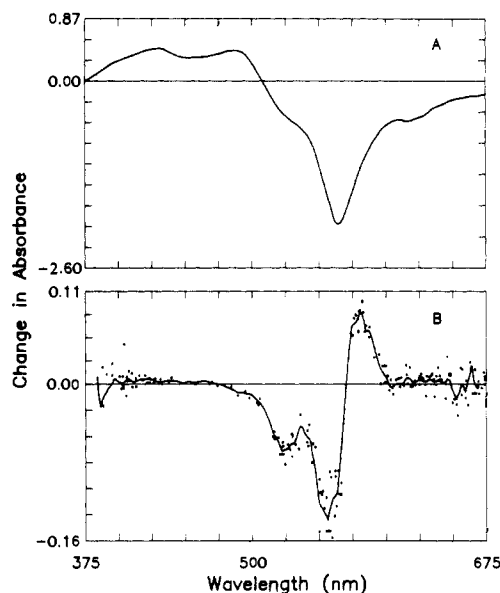
by conventional chemical analysis reveals an intra-ion-pair charge recombination electron-transfer reaction rendered irreversible by the rapid cleavage of the alkyl carbon-boron bond of the boranyl radical. We explored the relationship between the structure of the borate and the rate constant for electron transfer from the borate to the excited indocarbocyanine and how the structure of the borate affects the stability of the boranyl radical. These experiments support postulation of the reaction mechanism shown in Scheme 1.

## Results

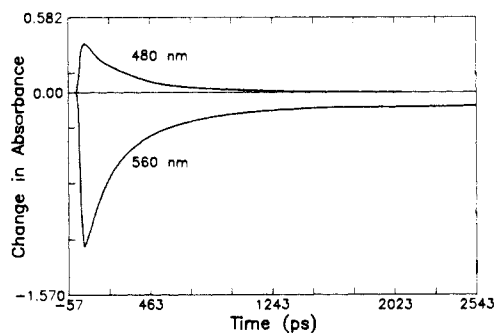
**(1) *N,N'*-Dimethyldimethylindocarbocyanine Hexafluorophosphate ( $Cy^+PF_6^-$ ). Structure and Physical Properties.** The structures of the cyanine dyes have been studied extensively in the solid state by means of X-ray crystallography. In particular, analysis of dimethylindocarbocyanine either as its iodide<sup>9</sup> or perchlorate salt<sup>10</sup> reveals an extended "all-trans" (*EEEE*) geometry. Similarly, analysis of the temperature dependence of the <sup>1</sup>H NMR spectra of cyanine dyes<sup>11</sup> showed that  $Cy^+BF_4^-$  dissolved in methanol solution adopts the all-trans planar geometry.<sup>12</sup> These findings are supported by analysis of the electronic absorption spectrum of the dye.<sup>13</sup> Figure 1 shows the absorption spectra of  $Cy^+PF_6^-$  dissolved in benzene at room temperature and in a frozen solution of 2-methyltetrahydrofuran at 77 K. Apart from a modest sharpening characteristic of reduced thermal motion in the frozen solution, there are no changes in band shape or position in the low-temperature spectrum that would indicate participation by more than one conformation of the dye in the spectra recorded at room temperature.

At room temperature in benzene solution,  $Cy^+PF_6^-$  fluoresces with modest efficiency:  $\Phi_f = 0.047 \pm 0.01$ . The quantum efficiency for fluorescence is independent of excitation wavelength throughout the visible absorption band. This finding, too, is consistent with the existence of only one conformation for this cyanine dye in solution. The time dependence of the fluorescent emission from benzene solutions of  $Cy^+PF_6^-$  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  $Cy^+PF_6^-$  in benzene at 564 nm which corresponds to a singlet energy ( $E^*$ ) of 50.7 kcal/mol.

The electrochemical behavior of the cyanine dyes has been studied extensively.<sup>14</sup> In acetonitrile solution with tetrabutyl-



**Figure 2.** Absorption spectra recorded following laser flash photolysis of *N,N'*-dimethyldimethylindocarbocyanine hexafluorophosphate in benzene solution. Spectrum A was recorded 60 ps after the laser pulse, spectrum B was recorded 5000 ps after the laser pulse.



**Figure 3.** Time dependence of the absorption recovery (560 nm) and decay of the  $S_1 \rightarrow S_n$  (480 nm) for *N,N'*-dimethyldimethylindocarbocyanine hexafluorophosphate in benzene solution following an 18-ps excitation pulse at 532 nm.

ammonium tetrafluoroborate as the supporting electrolyte,  $[Cy]^+$  shows a reversible reduction wave at  $-1.00$  V vs SCE. The reduction generates the cyanine radical,  $[Cy]^*$ . Related radicals formed by the one-electron reduction of other cyanine dyes have been observed by ESR and optical absorption spectroscopy.<sup>15</sup> We generated  $[Cy]^*$  by controlled potential electrolysis of  $[Cy]^+$  at a semitransparent gold electrode in anhydrous acetonitrile solution.<sup>16</sup> As the reduction proceeds, the absorptions due to  $[Cy]^+$  decrease and a new feature assigned to the cyanine radical with an apparent absorption maximum at ca. 427 nm grows into the spectrum.

Laser flash photolysis of  $Cy^+PF_6^-$  reveals formation of several transient intermediates. Figure 2a shows an absorption spectrum recorded 60 ps after excitation of  $Cy^+PF_6^-$  in benzene solution (532 nm, 18 ps, 250  $\mu$ J). Immediate consumption of  $[Cy]^+$  is evident in this spectrum from the bleaching of the absorption bands characteristic of the dye. Most of the absorption intensity of  $[Cy]^+$  grows back into the spectrum with a lifetime of  $250 \pm 10$  ps according to a first-order rate law, Figure 3. A new absorption feature with apparent maxima at 430 and 480 nm is evidence in the spectrum recorded 60 ps after excitation of the dye. Both of these bands appear instantaneously and then decay completely

(9) Nakatsa, K.; Yoshioka, H.; Nishigaki, S. *Kwansei Gakuin Univ. Annu. Stud.* **1980**, *29*, 213.

(10) Allmann, R.; Waskowska, A.; Olejnik, S. *Cryst. Struct. Commun.* **1982**, *11*, 1077.

(11) Henrichs, P. M. *J. Chem. Soc., Perkin 2* **1976**, 542. Henrichs, P. M.; Gross, S. *J. Am. Chem. Soc.* **1976**, *98*, 7169.

(12) Allmann, R.; Anis, H.-J.; Benn, R.; Grahn, W.; Olejnek, S.; Waskowska, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 876.

(13) West, W.; Pearce, S.; Grum, F. *J. Phys. Chem.* **1967**, *71*, 1316. Cooper, W.; Lovell, S. P.; West, W. *Photogr. Sci. Eng.* **1970**, *14*, 184.

(14) Lehnard, J. *J. Imaging Sci.* **1986**, *30*, 27.

(15) Siegel, J.; Friedrich, M.; Kuhn, V.; V. Grossmann, J.; Fassler, D. *J. Inf. Rec. Mater.* **1986**, *14*, 215.

(16) This experiment was performed on the *N,N'*-di-*n*-butylindocarbocyanine hexafluorophosphate.

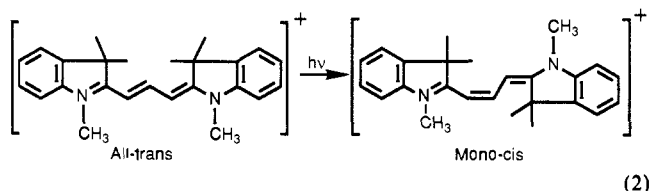
**Table I.** Oxidation Potentials of Tetrabutylammonium Borates, Relative Fluorescence Efficiencies of Cyanine Borates, Nonradiative Rate Constants for Singlet Excited Cyanine Borates, Efficiency of Cyanine Radical Formation, and Bond Dissociation Energies of the Boron-Bound Alkyl Groups

borate	$E_{ox}^p$ V vs SCE <sup>c</sup>	$E_{ox}^k$ V vs SCE <sup>d</sup>	$\Phi(PF_6^-)/$ $\Phi(RB^-)^e$	$k_{nr},$ $s^{-1}$	$\Phi_{cy},^f$	BDE, <sup>h</sup> kcal/ mol
[PhC≡CB(Ph) <sub>3</sub> ] <sup>-</sup>	0.95	1.51	1.4 <sup>f</sup>	$5.6 \times 10^9$ <sup>f</sup>		
[Ph <sub>4</sub> B] <sup>-</sup>	0.90	1.45	11	$-4.4 \times 10^{10}$	0.067	110
[H <sub>2</sub> C=CH-B-(Ph) <sub>3</sub> ] <sup>-</sup>	0.84	1.45	12	$5.2 \times 10^{10}$	0.18	108
[cyclo-C <sub>3</sub> H <sub>5</sub> -B-(Ph) <sub>3</sub> ] <sup>-</sup>	0.83	1.43	24	$9.3 \times 10^{10}$	0.21	106
[CH <sub>3</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	0.81	1.39	27	$1.1 \times 10^{11}$	0.50	105
[ <i>n</i> -BuB(Ph) <sub>3</sub> ] <sup>-</sup>	0.70	1.21	60	$2.4 \times 10^{11}$	0.73	98
[PhCH=CHB-(Ph) <sub>3</sub> ] <sup>-a</sup>	0.63	1.16	32	$1.2 \times 10^{11}$	0.14	
[PhCH <sub>2</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	0.39	1.09	82	$3.3 \times 10^{11}$	1.00	88
[ <i>m</i> -TolCH <sub>2</sub> B-(Ph) <sub>3</sub> ] <sup>-</sup>	0.36	1.10				
[NpCH <sub>2</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	0.28	1.07	100	$3.9 \times 10^{11}$	0.95	85
[ <i>n</i> -BuB(Ar) <sub>3</sub> ] <sup>-b</sup>	0.60	1.11	60	$2.4 \times 10^{11}$	0.87	98

<sup>a</sup>PhCH=CH<sup>-</sup> stands for a *trans*-styryl group; Np stands for a naphthalene group. <sup>b</sup>Ar = 4-*tert*-butylphenyl. <sup>c</sup>Peak of the oxidation wave observed in the cyclic voltammogram. <sup>d</sup>Oxidation potential determined kinetically by the method of Rehm and Weller (see text). <sup>e</sup> $\Phi(PF_6^-)$  is the quantum yield for fluorescence of the cyanine hexafluorophosphate.  $\Phi(RB^-)$  is the quantum yield for fluorescence of the cyanine borate. <sup>f</sup>There are small changes in the absorption spectrum of this cyanine borate, so the radiative rate constant for the dye may be changed somewhat. <sup>g</sup> $\Phi_{cy}$  is the quantum efficiency for formation of cyanine radical measured by its absorbance at 430 nm relative to that for [PhCH<sub>2</sub>B(Ph)<sub>3</sub>]<sup>-</sup>. <sup>h</sup>BDE is the bond dissociation energy of the carbon-hydrogen bond for the hydrocarbon corresponding to the alkyl group of the borate.

following a first-order rate law with a lifetime of  $252 \pm 10$  ps. Figure 2b shows an absorption spectrum recorded 5000 ps after the excitation of  $Cy^+PF_6^-$ . The small residual bleaching of the dye revealed in Figure 3 is apparent in this spectrum as is a new absorption feature with an apparent maximum at 580 nm. Related experiments conducted on a longer time scale show that the absorption band at 580 nm decays after several microseconds and that all of the original absorption intensity of  $[Cy]^+$  returns on this time scale.<sup>8</sup>

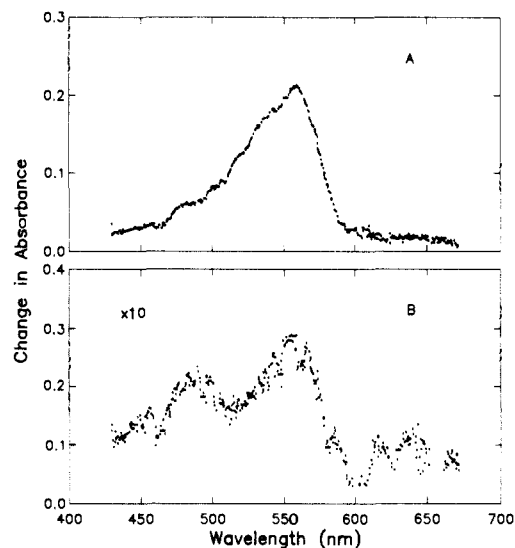
The time-resolved spectroscopic behavior of  $Cy^+PF_6^-$  is analogous to that previously observed for other cyanine dyes. Excitation of the dye generates  $Cy^+(S_1)$ . The bands at 430 and 480 nm are assigned to absorption by this excited singlet state  $\{Cy^+(S_1) \rightarrow Cy^+(S_n)\}$  since both bands decay with the same rate constant as the dye absorption recovers, and this rate constant is the same as that measured for decay of  $Cy^+(S_1)$  by time-resolved fluorescence spectroscopy. Similar  $S_1 \rightarrow S_n$  absorption features have been reported recently for a pyrimidocarbocyanine dye.<sup>17</sup> The absorption band with apparent maximum at 580 nm is assigned to the photoisomer formed by rotation about one of the central bonds of  $Cy^+(S_1)$ , eq 2. Similar photoisomerization has



been observed in a wide range of cyanine dyes and has been extensively studied.<sup>3,4,18</sup> The mono-cis photoisomer regenerates  $[Cy]^+$  by a thermal process over a period of several microseconds.

(17) Penzkofer, A.; Ossig, F. *Chem. Phys. Lett.* **1989**, *154*, 111.

(18) Müller, A.; Pflüger, E. *Chem. Phys. Lett.* **1968**, *2*, 155. Knudtson, J. T.; Eyring, E. M. *J. Phys. Chem.* **1974**, *23*, 2355. Dietz, F.; Rentsch, S. K. *Chem. Phys.* **1985**, *96*, 145. Fassler, D.; Feller, K.-H. *J. Mol. Struct.* **1988**, *173*, 377. Feller, K.-H.; Gadonas, R.; Krasauskas, V. *Z. Phys. Chem. (Leipzig)* **1989**, *270*, 421. Tredwell, C. J.; Keary, C. M. *Chem. Phys.* **1979**, *43*, 307. Mialocq, J. C.; Goujon, P.; Arvis, M. *J. Chim. Phys.* **1979**, *76*, 1067. Jaraudias, J. *J. Photochem.* **1980**, *13*, 35.



**Figure 4.** Absorption spectra recorded following excitation of chrysenes in acetonitrile solution. Spectrum A was recorded 0.5  $\mu$ s after laser excitation of a solution containing no borate, it shows the triplet-triplet absorption of chrysenes. Spectrum B was recorded 5  $\mu$ s after excitation of a chrysenes solution containing 0.016 M tetramethylammonium *n*-butyltris(4-*tert*-butylphenyl)borate; it shows both residual triplet-triplet absorption of the chrysenes and the absorption of the chrysenes radical anion formed from the electron-transfer reaction of excited singlet chrysenes with the borate.

As has been previously noted for related cyanine dyes, there is no evidence for formation of triplet cyanine  $[Cy^+(T_0)]$  in the direct irradiation of  $Cy^+PF_6^-$ .<sup>19</sup>

(2) **Alkyltriphenylborates. Chemical and Physical Properties.** Alkyltriphenylborates<sup>20</sup> as their tetramethylammonium salts are readily prepared by the reaction of an alkylmetal (generally lithium or magnesium) with triphenylborane.<sup>21</sup> Exchange of the metal cation with tetramethylammonium chloride gives the ammonium salts of the borates as stable, colorless solids. The panoply of alkyl triphenylborates examined in this work is listed in Table I.

An issue of primary concern for analysis of the photochemistry of the cyanine borate salts is the oxidation potential of the alkyltriphenylborates. Cyclic voltammetry under standard conditions or at very high sweep rates with ultra-microelectrodes gives irreversible oxidation waves for each of the borates examined. The peak potentials observed in these experiments are listed in Table I; they 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 those borates that can generate only "unstabilized" radicals (i.e., cyclopropyl and phenyl).

Since electrochemical methods proved 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>22</sup> concluded 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 formula shown in eq 3. In this equation  $\Delta G_{et}$  is directly related to the ther-

$$k_{et} = 2 \times 10^{10} / \{1 + 0.25[\exp(\Delta G_{et}^*/RT) + \exp(\Delta G_{et}/RT)]\} \quad (3)$$

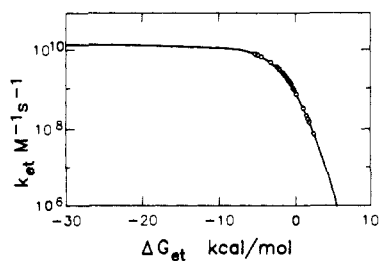
modynamic oxidation potential of the donor, and  $\Delta G_{et}^*$ , defined

(19) Sauerwein, B.; Schuster, G. B. *J. Phys. Chem.*, submitted for publication.

(20) Most of the borates examined are indeed alkyl substituted. However some, such as tetraphenylborate, do not have an alkyl substituent. We refer generically to the entire set as alkylborates for the sake of simplicity.

(21) Negishi, E.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 6837.

(22) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.



**Figure 5.** Rehm-Weller plot for determination of the oxidation potentials of the borates by kinetic means. The solid line is the rate dependence of  $\Delta G_{et}$  predicted from eqs 3 and 4. The open circles are the results from fitting the observed fluorescence quenching rate constants. The values of  $E_{ox}^k$  listed in Table I are calculated from  $\Delta G_{et}$  and the known reduction potentials and singlet energies of the fluorescers.

in eq 4, is the geometric mean of  $\Delta G_{et}$  and  $\Delta G_{et}(0)$  (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 eqs 3 and 4 to

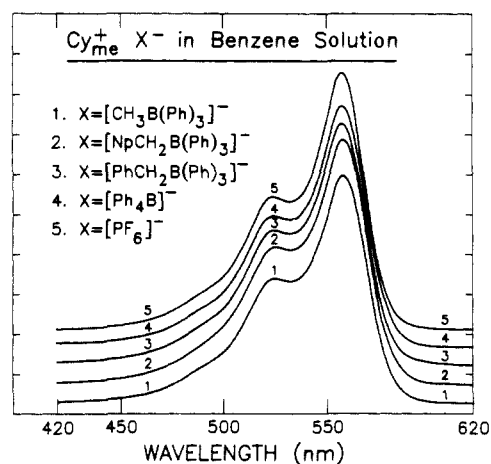
$$\Delta G_{et}^* = [(\Delta G_{et}/2)^2 + (\Delta G_{et}^*(0))^2]^{1/2} + \Delta G_{et}/2 \quad (4)$$

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.

We examined the fluorescence quenching for a series of polycyclic aromatic hydrocarbons to gain a measure of the borate oxidation potentials. To insure that the studied quenching process is indeed electron transfer, the reaction was monitored by time-resolved absorption spectroscopy. Figure 4a shows the transient absorption spectrum recorded 0.5  $\mu$ s after excitation of chrysene (344 nm, 10 mJ, 20 ns) in a nitrogen-saturated acetonitrile solution. The feature at 565 nm is assigned to chrysene triplet-triplet absorption.<sup>23</sup> Figure 4b shows the transient absorption spectrum recorded 5  $\mu$ s after excitation of chrysene in an acetonitrile solution containing 0.016 M tetramethylammonium *n*-butyltris(4-*tert*-butylphenyl)borate. The new feature with maximum absorbance at 485 nm is assigned to the chrysene radical anion by comparison with the spectrum of this species generated by radiolysis.<sup>24</sup> Inspection of the spectra in Figure 4 reveals that the amount of chrysene triplet formed is reduced when the borate is present in the solution. Kinetic analysis of these data by the Stern-Volmer method gives  $k_{et}(\tau) = 92 \pm 10 \text{ M}^{-1}$ . These experiments show that the electron transfer from the borate to form the chrysene radical anion occurs and, when combined with the results of fluorescence quenching experiments described below, confirms that it is the singlet excited state of chrysene which accepts the electron.

The rate constant for the electron-transfer quenching of singlet chrysene by tetramethylammonium *n*-butyltris(4-*tert*-butylphenyl)borate in acetonitrile solution was determined from the quenching of its fluorescence and by measuring its singlet lifetime over a range of borate concentrations. Both methods give the same result:  $k_{et} = (1.93 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{et}(\tau) = 97 \pm 2 \text{ M}^{-1}$ . Related experiments were carried out for a range of fluorescers and the ensemble of borates listed in Table I. The values for  $k_{et}$  obtained in this manner are presented in the form of a Rehm-Weller plot in Figure 5. Substitution of  $k_{et}$  for the borates into eqs 3 and 4 gives the oxidation potentials listed in Table I. As expected for a case where a very fast chemical reaction follows electron transfer, the kinetically determined oxidation potentials ( $E_{ox}^k$ ) for the borates are more positive than are the peak potential values determined by cyclic voltammetry ( $E_{ox}^p$ ).

**(3) Cyanine Borates. Preparation, Absorption, and Ion-Pairing in Solution.** The cyanine borate salts were prepared by metathesis of the appropriate tetramethylammonium borate and the indo-cyanine chloride in acetonitrile-water solution. The cyanine borate generally was separated as a solid formed during the slow



**Figure 6.** The absorption spectra of equal concentrations of  $[\text{Cy}]^+\text{PF}_6^-$  and several cyanine borates in benzene solution at room temperature.

evaporation of the solvent and then was purified by recrystallization. The samples used in this work were homogeneous by thin-layer chromatography and gave satisfactory elemental analyses.

The electronic absorption spectra of representative examples of the cyanine borates in benzene solution are shown in Figure 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; the oscillator strength of the transition and the energy of  $\text{Cy}^+(S_1)$  are unaffected by changing the counter ion from  $\text{PF}_6^-$  to these borates. The findings show that excitation of  $\text{Cy}^+[\text{R}-\text{B}(\text{Ph}_3)]^-$  with visible light generates a locally excited state of  $[\text{Cy}]^+$  which will have the same radiative rate constant ( $k_f$ ) as does  $\text{Cy}^+\text{PF}_6^-$ . The absorption spectra of the phenylethynyl borate is shifted slightly (ca. 3 nm) from that of the cyanine hexafluorophosphate. This may indicate a ground-state interaction for this case.

Salts dissolved in organic solvents exist as a mixture of freely solvated ions, ion pairs, and higher aggregates whose relative proportion depends on concentration and the details of structure. 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>25</sup> Interpretation of the specific functional relationship between the concentration of the electrolyte and the molar conductance ( $\Lambda$ ) is complex. Nonetheless, determination of the extrapolated molar conductance at infinite dilution ( $\Lambda_0$ ) provides a useful experimental means for estimation of the dissociation constant ( $K_D$ ) for these electrolytes. According to eqs 5 and 6, where  $S$  is the coefficient

$$\Lambda = \gamma[\Lambda_0 - S(\gamma C)^{1/2}] \quad (5)$$

$$K_D = (C\gamma^2)/(1 - \gamma) \quad (6)$$

from the Fuoss-Onsager theory,<sup>26</sup>  $C$  is the concentration of dissolved salt, and  $\gamma$  is the fraction of the dissolved salt that is dissociated,  $K_D$  can be roughly estimated by measuring  $\Lambda$  at various electrolyte concentrations in nonpolar solvents with the additional assumption of unit activity coefficients for the ions and the ion pair.

We measured the conductivity of solutions of  $\text{Cy}^+\text{PF}_6^-$  in a series of solvents with different dielectric constants; typical results are shown graphically in Figure 7 and the derived values of  $K_D$  are listed in Table II. For relatively polar solvents these measurements show a linear relationship between  $\Lambda$  and the square root of the

(25) Barthel, J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 260. Smedley, S. I. *The Interpretation of Ionic Conductivity in Liquids*; Plenum Press: New York, 1980; Chapter 2.

(26) Fuoss, R. M.; Onsager, L.; Skinner, J. F. *J. Phys. Chem.* **1965**, *69*, 2581.

(23) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(24) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988, p 77.

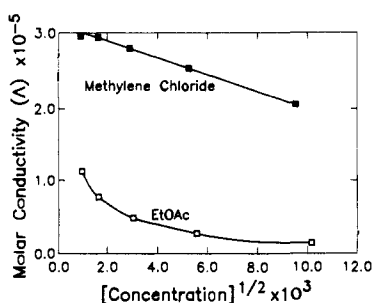


Figure 7. The concentration dependence of the molar conductivity of  $[\text{Cy}]^+\text{PF}_6^-$  measured in methylene chloride and in ethyl acetate solution at room temperature.

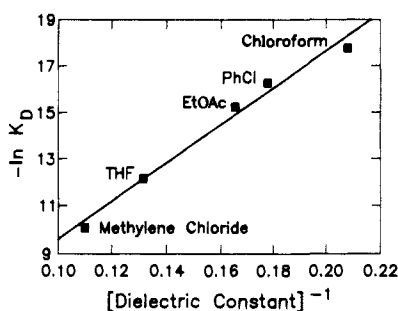


Figure 8. Fuoss plot of the natural log of the dissociation constant for  $[\text{Cy}]^+\text{PF}_6^-$  obtained from the conductivity measurements against the reciprocal of the solvent dielectric constant.

Table II. Equilibrium Constant and Ion Pair Stabilization for Cyanine Hexafluorophosphate in Solvents of Various Dielectric Constant

solvent	dielectric: $\epsilon$	$K_D$ , M	ion pair stabilization, eV <sup>a</sup>
$\text{CH}_3\text{CN}$	36	$3.2 \times 10^{-2}$	0.05
$\text{CH}_2\text{Cl}_2$	9.0	$4.3 \times 10^{-5}$	0.26
THF	7.6	$5.0 \times 10^{-6}$	0.32
$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	6.0	$2.6 \times 10^{-7}$	0.39
$\text{C}_6\text{H}_5\text{Cl}$	5.6	$8.8 \times 10^{-8}$	0.42
$\text{CHCl}_3$	4.8	$1.9 \times 10^{-8}$	0.46
benzene	2.3	$9 \times 10^{-17}$	0.96
dioxane	2.1	$5 \times 10^{-18}$	1.0

salt concentration. In less polar solvents, the relationship is nonlinear. In these cases  $K_D$  was estimated at the lowest  $\text{Cy}^+\text{PF}_6^-$  concentration by correcting the  $A_0$  value obtained with more polar solvents for the change in viscosity according to the Walden product.<sup>27</sup>

The Fuoss equation,<sup>28</sup> eq 7, relates the value of  $K_D$  to the dielectric constant of the solvent ( $\epsilon$ ) and the center-to-center distance at contact of the ions in the ion pair ( $a$ ); the other symbols in the equation have their conventional meanings. Figure 8 shows

$$K_D = [3000/4\pi Na^3] \exp[-e^2/(a\epsilon k_B T)] \quad (7)$$

a plot of the conductivity-data-derived dissociation constants for  $\text{Cy}^+\text{PF}_6^-$  according to the eq 7. The value of  $K_D$  extrapolated to benzene solution, where dissociation is too weak to measure by conductivity in our apparatus, is listed in Table II.

Several observations substantiate the estimate of  $K_D$  in benzene solution for  $\text{Cy}^+\text{PF}_6^-$ . First, Fuoss and Kraus<sup>29</sup> measured  $K_D$  directly for tetraisoamylammonium picrate in benzene solution and found a value of ca.  $10^{-17}$  M. This dissociation constant is within a factor of 10 of our estimate for the cyanine salt. Second, the slope of the line shown in Figure 8 provides an estimate for

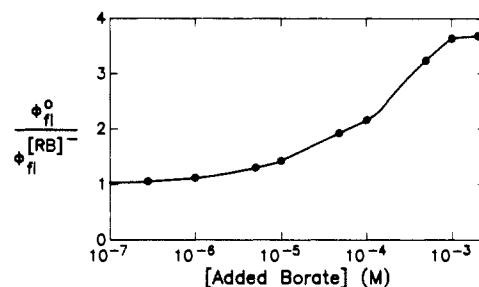


Figure 9. The dependence of the fluorescence intensity from *N,N*-dimethyldimethylindocarbocyanine in ethyl acetate solutions containing increasing amounts of tetramethylammonium *n*-butyltris(4-*tert*-butylphenyl)borate.

the center-to-center distance of  $[\text{Cy}]^+$  and  $\text{PF}_6^-$  in the ion pair of  $7 \pm 2$  Å. This value is within experimental error of that obtained by means of X-ray crystallography.<sup>9</sup> Finally, we determined  $K_D$  in ethyl acetate solution indirectly by quenching the fluorescence of  $\text{Cy}^+\text{PF}_6^-$  with added tetramethylammonium *n*-butyltris(4-*tert*-butylphenyl)borate (see below). The value of  $K_D$  obtained by this method is consistent with that calculated from the conductimetric measurements.

These experiments show that the cyanine borates in benzene solution exist, essentially, exclusively as tight-ion pairs over the concentration range described herein during 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.

(4) **Photolysis of Cyanine Borates. Generation of Free Alkyl Radicals.** Etter and co-workers<sup>30</sup> found that irradiation of cyanine borates in the solid state leads to transfer of an alkyl group from the borate to the cyanine with concomitant bleaching of the cyanine dye. They suggested that alkyl radicals are intermediates in this reaction. We irradiated an oxygen-free benzene solution of  $\text{Cy}^+[\text{n-BuB}(\text{Ph})_3]^-$  at 532 nm with a mode-locked laser. Analysis of this reaction mixture by gas chromatography shows *n*-octane among the products. Since octane formation can only occur from the coupling of free *n*-butyl radicals, this finding shows conclusively that irradiation of  $\text{Cy}^+[\text{R-B}(\text{Ph})_3]^-$  can generate free alkyl radicals.

The generation of radicals from the irradiation of cyanine borates was put on a more quantitative basis by studying the photolysis of  $\text{Cy}^+[\text{Ph}(\text{CH}_2)_3\text{B}(\text{Ph})_3]^-$  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. Additional evidence for free-radical formation from the irradiation of cyanine borates comes from the observation that their irradiation in butyl acrylate solutions with visible light leads to polymerization of the acrylate.

(5) **Cyanine Borates. Fluorescence Spectroscopy.** The fluorescence efficiencies of the  $[\text{Cy}]^+$  salts in benzene solution depend on the identity of the borate anion and provide a direct measure of the rate constant for the nonradiative reactions ( $k_{nr}$ ) of the excited cyanine that are dependent on the borate. Analysis of the fluorescence efficiency data according to eq 8, where  $\tau(\text{PF}_6^-)$

$$k_{nr} = \tau(\text{PF}_6^-)^{-1} [\Phi(\text{PF}_6^-) / \Phi(\text{RB}^-) - 1] \quad (8)$$

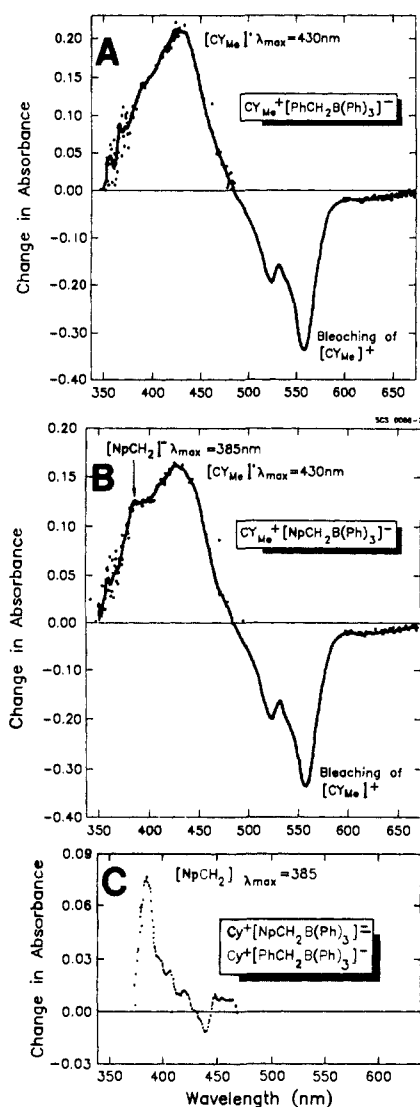
is the lifetime of  $\text{Cy}^+\text{PF}_6^-$  and  $\Phi(\text{RB}^-)$  and  $\Phi(\text{PF}_6^-)$  are the fluorescence quantum yields for the borate and  $\text{PF}_6^-$  salts, respectively, gives the rate constant for reaction of  $\text{Cy}^+(\text{S}_1)$  with its borate counter ion.

(27) Walden, P. Z. *Physik. Chem.* **1906**, *55*, 207. Walden, P.; Busch, G. *Z. Physik. Chem.* **1929**, *140*, 89.

(28) Fuoss, R. M. *J. Solution Chem.* **1986**, *15*, 231.

(29) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 3614.

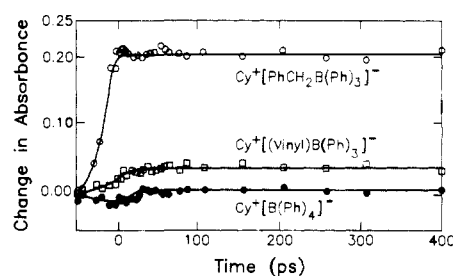
(30) Etter, M. C.; Holmes, B. N.; Kress, R. B.; Filipovich, G. *Isr. J. Chem.* **1985**, *25*, 264.



**Figure 10.** (A) Absorption spectrum recorded immediately after excitation of  $[\text{Cy}]^+[\text{PhCH}_2\text{B}(\text{Ph})_3]^-$  in benzene solution with an 18-ps laser pulse. The spectrum shows formation of  $[\text{Cy}]^*$  ( $\lambda_{\text{max}} = 430 \text{ nm}$ ) and the bleaching of the dye absorption. (B) Absorption spectrum recorded immediately after excitation of  $[\text{Cy}]^+[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$  in benzene solution with an 18-ps laser pulse. In addition to the features characteristic of  $[\text{Cy}]^*$  and bleaching of the dye, a new feature with absorption at 385 nm is apparent. (C) The difference spectrum obtained by subtracting spectrum 10A from spectrum 10B shows the peak at 385 nm characteristic of the 2-methylnaphthyl radical.

We have determined the relative fluorescence efficiencies  $[\Phi(\text{PF}_6^-)/\Phi(\text{RB}^-)]$  of dilute solutions (to avoid complications from self-absorption) of cyanines in benzene where the salts exist exclusively as ion pairs. The relative fluorescence efficiencies and the derived values of  $k_{\text{nr}}$  are listed in Table I. It is apparent from inspection of these data that  $k_{\text{nr}}$  is strongly dependent on the nature of the alkyl group bound to the boron atom of the borate. In general, as the "stability" of the radical formed from carbon-boron bond cleavage increases (i.e., phenyl versus benzyl) the magnitude of  $k_{\text{nr}}$  increases.

The fluorescence efficiency of cyanine borate<sup>16</sup> in ethyl acetate solution is dependent on the concentration of added tetra-*n*-butylammonium borate. Figure 9 shows the relative fluorescence efficiency of  $[\text{Cy}]^+$  in ethyl acetate as the concentration of tetramethylammonium *n*-butyltris(4-*tert*-butylphenyl)borate is increased from  $5 \times 10^{-7}$  to  $3 \times 10^{-3} \text{ M}$ . At low concentrations of added borate, the fluorescence efficiency of the cyanine is essentially the same as that of  $\text{Cy}^+\text{PF}_6^-$ . As the concentration of the added borate increases, the fluorescence efficiency of the cyanine decreases. However, the lifetime of the cyanine that does fluorescence is unaffected by the increase in the borate concen-

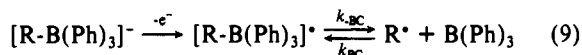


**Figure 11.** The absorption of  $[\text{Cy}]^*$  monitored at 430 nm following excitation of a benzene solution of the indicated cyanine borate with an 18-ps laser pulse. The time dependence of the absorption for the benzyl case shows that radical formation is faster than decay of  $[\text{Cy}]^+(\text{S}_1)$ . For the vinylborate, back electron transfer and cleavage of the carbon-boron bond have competitive rates. For the tetraphenylborate, back electron transfer is much faster than bond cleavage and almost no cyanine radical is observed.

tration. These findings show that over the borate concentration range studied in these experiments, the fraction of the cyanine borate present as ion pairs in ethyl acetate changes significantly. Only the unassociated cyanine cations fluoresce, there is no (or very little) fluorescence from the cyanine borate ion pair.

**(6) Cyanine Borates. Laser Flash Photolysis.** Irradiation of a benzene solution of  $\text{Cy}^+[\text{PhCH}_2\text{B}(\text{Ph})_3]^-$  with an 18-ps long light pulse at 532 nm instantaneously<sup>31</sup> gives the transient spectrum shown in Figure 10a. 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  $[\text{Cy}]^*$ . There are no meaningful changes in this transient absorption spectrum for times up to 10000 ps after the excitation pulse. In particular, none of the photoisomer seen in the irradiation of the  $\text{Cy}^+\text{PF}_6^-$  salt is evident in these spectra. Related spectral changes are observed following the pulsed irradiation of the other cyanine borates. For example, laser flash photolysis of the vinyltriphenylborate salt shows instantaneous bleaching of the cyanine absorptions with simultaneous formation of  $[\text{Cy}]^*$ . However, when compared under identical experimental conditions, it is apparent that the changes in absorptions for the vinylborate case are significantly smaller than those for the benzyl borate. Even more striking are the results from irradiation of the tetraphenylborate salt. In this case there is hardly any formation of  $[\text{Cy}]^*$  and the  $\text{Cy}^+(\text{S}_1)$  formed during the excitation has nearly completely returned to  $[\text{Cy}]^+$  by the end of the pulse. These results are shown graphically on Figure 11, and the relative quantum efficiencies for the formation of  $[\text{Cy}]^*$  are collected in Table I.

**(7) Cyanine (Naphthylmethyl)triphenylborate. The Rates of Carbon-Boron Bond Cleavage and Formation of Boranyl Radicals.** One-electron oxidation of an alkyltriphenylborate generates a boranyl radical. Carbon-boron bond cleavage of the boranyl radical to generate triphenylborane and an alkyl radical may, in principle, be reversible, eq 9 where  $k_{\text{BC}}$  and  $k_{\text{BC}}$  are the rate



constants for formation and cleavage of the bond, respectively. We examined the properties of the (2-naphthylmethyl)triphenylboranyl radical in an attempt to measure  $k_{\text{BC}}$  and  $k_{\text{BC}}$ .

Pulsed irradiation of a  $\text{N}_2$ -purged benzene solution of 2-(bromomethyl)naphthalene (337 nm, 13 ns, 7 mJ) gives the transient absorption spectrum shown in Figure 12. The feature with apparent maximum absorbance at 385 nm is assigned to the (2-naphthyl)methyl radical ( $[\text{NpCH}_2]^*$ ).<sup>32</sup> Under these experimental conditions, the absorption of  $[\text{NpCH}_2]^*$  decays over a period of ca. 20  $\mu\text{s}$  according to a complex kinetic law. If  $[\text{NpCH}_2]^*$  reacts with triphenylborane to form the boranyl radical, then addition of the borane to the solution will increase the rate

(31) In these experiments, time = 0 is defined to be when the probe and pump beams have their maximum temporal overlap; the spectrum shown was recorded 15 ps later.

(32) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177.

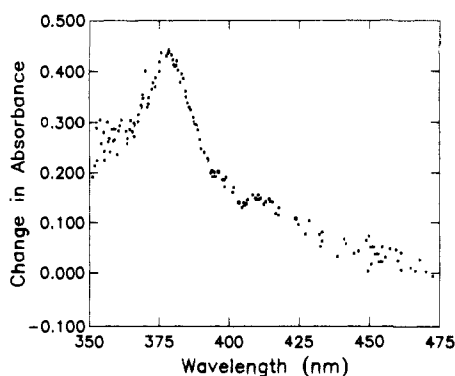
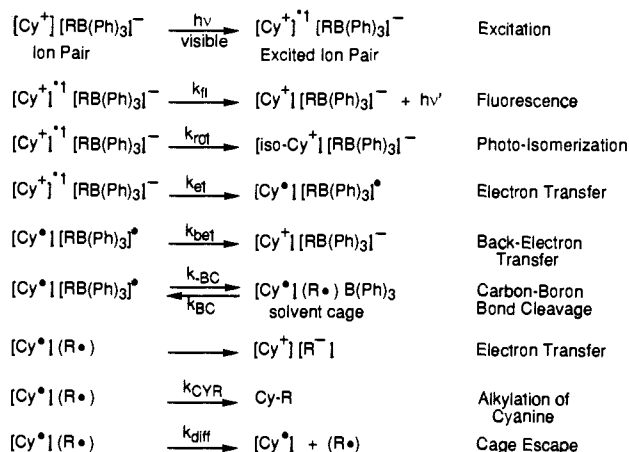


Figure 12. Absorption spectrum recorded 20  $\mu$ s after excitation of 2-(bromomethyl)naphthalene in benzene solution. The peak with apparent maximum at ca. 385 nm is assigned to the 2-methylnaphthyl radical.

### Scheme I



of decay of  $[\text{NpCH}_2]^*$  and a value for  $k_{BC}$  may be obtained from the data. In fact, pulsed irradiation of 2-(bromomethyl)naphthalene in a  $\text{N}_2$ -purged solution containing 0.021 M triphenylborane gives  $[\text{NpCH}_2]^*$ , but its half-life for decay is found to have increased to more than 100  $\mu$ s by the presence of the borane—not decreased as was expected. The increase in lifetime of  $[\text{NpCH}_2]^*$  is a consequence of the consumption of the residual  $\text{O}_2$  by the triphenylborane. There is no detectable reaction of  $[\text{NpCH}_2]^*$  with triphenylborane under the conditions we explored. This observation permits calculation of an upper limit for  $k_{BC}$  in this case of  $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

Pulsed irradiation of a benzene solution of  $\text{Cy}^+[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$  (532 nm, 18 ps, 250  $\mu$ J) instantaneously<sup>31</sup> gives the transient absorption spectrum shown in Figure 10b. Inspection of this spectrum shows bleaching of the absorptions of  $[\text{Cy}]^+$ , the appearance of  $[\text{Cy}]^*$ , and a new absorption feature which appears as a shoulder on the high energy side of the  $[\text{Cy}]^*$  absorption. The new feature in the spectrum shown in 10b can be readily assigned to the absorption of  $[\text{NpCH}_2]^*$  by subtracting the transient spectrum from the pulsed irradiation of  $\text{Cy}^+[\text{PhCH}_2\text{B}(\text{Ph})_3]^-$  (Figure 10a) recorded under identical conditions. This process gives the transient difference spectrum shown in Figure 10c. The difference spectrum clearly reveals that the naphthylmethyl radical is formed instantaneously on the time scale of this experiment. This finding permits estimation of a lower limit for the magnitude of  $k_{BC}$  in this case of  $1 \times 10^{11} \text{ s}^{-1}$ .

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 shown in eq 9. In benzene solution at room temperature,  $K_{BC} > 2 \times 10^4 \text{ M}$ . Thus formation of the naphthylmethyl radical following oxidation of  $[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$  is very fast and essentially irreversible.

### (8) Effect of Solvent Viscosity on the Yield of Cyanine Radical.

Carbon-boron bond cleavage after electron transfer from a borate to the excited cyanine dye generates an alkyl radical, the cyanine radical, and triphenylborane within the same solvent cage. Coupling of the alkyl radical with the cyanine radical has been observed when this reaction is carried out in the solid state.<sup>30</sup> We sought evidence for the occurrence of this reaction in fluid solution.

If combination of the alkyl and cyanine radicals in the solvent cage occurred, the absorption of  $[\text{Cy}]^*$  would decay without concomitant recovery of the bleaching of the cyanine dye. In benzene solution, there is neither decay nor recovery of the absorptions of  $[\text{Cy}]^*$  or  $[\text{Cy}]^+$ , respectively. We sought to increase the cage lifetime, and hence the probability of radical coupling, by increasing the solvent viscosity. But irradiation of  $\text{Cy}^+[\text{MeB}(\text{Ph})_3]^-$  in tetralin or *p*-cymene solution (3.6 and 5.2 times the viscosity of benzene, respectively)<sup>33</sup> similarly showed no significant decay or bleaching recovery. Thus, even in the viscous solvents examined, escape of the methyl and cyanine radicals is faster than their in-cage combination.

### Discussion

The experimental findings reported above support postulation of the reaction mechanism shown in Scheme I. The cyanine and borate exist as an ion pair in benzene solution. This self-association is a prerequisite for the photoinitiated reaction since the lifetime of the excited singlet state of the cyanine is too short to allow an efficient diffusible encounter at experimentally achievable concentrations of the borate.<sup>34</sup> 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 cleavage of a carbon-boron bond to form an alkyl radical  $[\text{R}\cdot]$  and triphenylborane. The  $[\text{Cy}^*][\text{R}\cdot]$  radical pair formed in the latter process might undergo electron transfer to form  $[\text{Cy}^+]$  and an alkyl anion  $[\text{R}^-]$ , or the radicals might couple to form an alkylated cyanine  $[\text{Cy-R}]$ , 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 photoinitiated 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.

(1) **Intra-Ion-Pair Electron Transfer. Estimation of the Free Energy ( $\Delta G_{et}$ ).** Calculation of the free energy for a photoinitiated electron transfer process begins with the estimation or measurement of the terms in eq 10.  $E_{ox}$  and  $E_{red}$  are the oxidation and

$$\Delta G_{et} = E_{ox} - E_{red} - E^* - (W_p - W_r) \quad (10)$$

reduction potentials of the electron donor and acceptor;  $E^*$  is the energy of the excited 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.<sup>35</sup>

The electrochemical reduction of  $[\text{Cy}]^+$  in acetonitrile solution is reversible and the potential obtained has a well-defined thermodynamic meaning. No such meaning may be associated with the irreversible peak potentials of the borates measured by cyclic voltammetry. However, the estimates for the oxidation potentials of the borates obtained by the kinetic method of Rehm and Weller may give thermodynamically meaningful values. A key assumption of the Rehm-Weller method<sup>22</sup> is that  $\Delta G_{et}(0)$  has a constant value independent of the structure of the donor and acceptor. This proposal appears to be valid for a wide range of outer-sphere electron transfer reactions carried out in polar sol-

(33) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

(34) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1294. Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669.

**Table III.** Oxidation and Reduction Potential Data and Rate Constants for Electron Transfer for Cyanine Borates in Acetonitrile and Benzene Solution

borate	$(E_{ox} - E_{red})_{MeCN}$ , eV	$(E_{ox} - E_{red})_{PhH}$ , eV	$\Delta G_{et}$ , eV	$k_{et}$ , S <sup>-1</sup>
[PhC≡CB(Ph) <sub>3</sub> ] <sup>-</sup>	2.51	1.41	0.30	~(5 × 10 <sup>9</sup> )
[Ph <sub>4</sub> B] <sup>-</sup>	2.45	1.35	0.24	4 × 10 <sup>10</sup>
[H <sub>2</sub> C=CHB(Ph) <sub>3</sub> ] <sup>-</sup>	2.45	1.35	0.24	4.8 × 10 <sup>10</sup>
[cyclo-C <sub>3</sub> H <sub>5</sub> -B(Ph) <sub>3</sub> ] <sup>-</sup>	2.43	1.33	0.22	8.9 × 10 <sup>10</sup>
[CH <sub>3</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	2.39	1.29	0.18	1.1 × 10 <sup>11</sup>
[ <i>n</i> -BuB(Ph) <sub>3</sub> ] <sup>-</sup>	2.21	1.11	-0.01	2.4 × 10 <sup>11</sup>
[PhCH=CHB(Ph) <sub>3</sub> ] <sup>-</sup>	2.16	1.06	-0.05	1.2 × 10 <sup>11</sup>
[PhCH <sub>2</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	2.09	0.99	-0.13	3.3 × 10 <sup>11</sup>
[ <i>m</i> -tolCH <sub>2</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	2.10	1.00	-0.11	
[NpCH <sub>2</sub> B(Ph) <sub>3</sub> ] <sup>-</sup>	2.07	0.97	-0.14	3.9 × 10 <sup>11</sup>
[ <i>n</i> -BuB(Ar) <sub>3</sub> ] <sup>-</sup>	2.11	1.01	-0.10	3.0 × 10 <sup>11</sup>

$$^* \Delta G_{bet} = -E^{*1} - \Delta G_{et} = -(E_{ox} - E_{red})_{CH_3CN}$$

vents.<sup>35</sup> We assume that this approach is valid for the oxidation of the borates and therefore treat  $E_{ox}^k$  as if they were true thermodynamic oxidation potentials.

The potentials for reduction of [Cy]<sup>+</sup> 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 eq 11 (the Born

$$(E_{ox} - E_{red})_{PhH} = (E_{ox} - E_{red})_{MeCN} - e^2/2 [1/r_- + 1/r_+] [1/\epsilon_{(PhH)} - 1/\epsilon_{(MeCN)}] \quad (11)$$

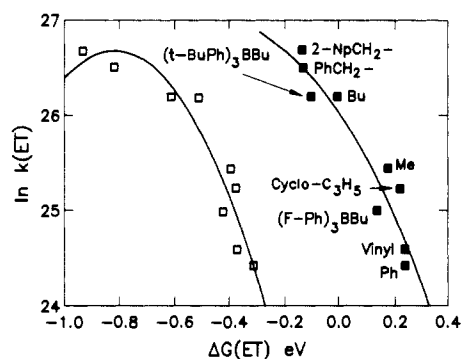
equation) where  $r_-$  and  $r_+$  are the radii of the spherical cation and anion, respectively and  $\epsilon_{(PhH)}$  and  $\epsilon_{(MeCN)}$  are the dielectric constants of benzene and acetonitrile, and  $e$  is the electronic charge.<sup>34,35</sup>

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; these are summarized in Table III. This is a matter of some concern since the cyanine is certainly not spherical, and other approximations required for application of the Born equation to the cyanine borates are similarly crude. Fortunately, however, the same assumptions are required in the calculation of  $W_r$  (below), this value is similarly large but enters eq 10 with a sign opposite that of the solvent change.

There has been considerable discussion in the literature concerning the appropriate procedure for estimation of  $W_r$  and  $W_p$ .<sup>35,36</sup> When either the reactants or products of the electron transfer reaction are a pair of oppositely charged ions, the Coulombic attraction force has a significant impact on the estimate of  $\Delta G_{et}$ ; particularly so when the solvent dielectric constant is small. The effect of Coulombic stabilization of the cyanine borate ion pair may be calculated from eq 12 where the terms have the same

$$W_r = e^2/2 [1/r_- + 1/r_+] [1/\epsilon_{(PhH)}] \quad (12)$$

meaning as in eq 11. Comparison of eqs 11 and 12 shows that they differ only in that  $1/\epsilon_{(MeCN)}$  is subtracted from  $1/\epsilon_{(PhH)}$  in the former but not the latter equation. Since the dielectric constant of benzene is so much smaller than that of acetonitrile (2.28 and 36.2 d, respectively), there is only a small difference between the estimate of the effect of solvent change by the Born equation and the value of the Coulomb energy. Thus the errors introduced into



**Figure 13.** The dependence of the rate constant for electron transfer on the free energy of transfer of an electron from the indicated borate to the excited singlet state of the cyanine dye. The open symbols are calculation of  $\Delta G_{et}$  from the peak potentials of the cyclic voltammograms, the filled symbols calculated for the same borates but from the kinetically determined oxidation potentials.

the calculation of  $\Delta G_{et}$  by the approximations inherent in this approach should cancel.

The value of  $W_r$  may be calculated from eq 12 or from the estimates of  $K_D$  extrapolated from the conductivity data by means of the Fuoss equation. Both approaches give the same result:  $W_r \approx 0.96$  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 10 gives the estimates for  $\Delta G_{et}$  of the singlet excited cyanine borate ion pairs listed in Table III.

**(2) Intra-Ion-Pair Electron Transfer. Measurement of the Rate Constant.** Examination of the fluorescence of the cyanine borate salts shows that there is a rapid reaction between the excited dye and the borate ( $k_{nr}$ ). The results of the laser spectroscopy experiments show that this reaction is an electron transfer which can have two limiting outcomes. For borates capable of generating stabilized alkyl radicals (i.e., benzyl), nearly all of the excited cyanine dye is converted to [Cy]<sup>\*</sup> by the electron transfer ( $k_{et}$ ) reaction which is completed during the 18-ps laser pulse. For borates incapable of generating a stabilized radical (i.e., phenyl), there is very little formation of [Cy]<sup>\*</sup>. In these cases electron transfer occurs, but back electron transfer ( $k_{bet}$ ) is much faster than competing processes ( $k_{BC}$ , and cage escape of the radical pairs) and there is no net reaction. For the borates with structures between these two extremes, electron transfer is followed by competition between bond cleavage and back electron transfer. With this model for the reaction mechanism, the nonradiative reaction rate constants ( $k_{nr}$ ) obtained from the fluorescence quenching experiment can be assigned to intra-ion-pair electron transfer from the borate to the excited cyanine ( $k_{et}$ ). These values are tabulated in Table III.

Rate constants for electron transfer may be related to the free energy of the reaction through the classical Marcus equation, eq 13, where  $\lambda$  is the reorganization energy.<sup>37</sup> A plot of the data for the intra-ion-pair electron transfer in the cyanine borates according to this approach is shown in Figure 13.

$$\Delta G_{et}^* = \lambda/4(1 + \Delta G_{et}/\lambda)^2 \quad (13)$$

Comparison of the rate constant dependence on the oxidation potentials of the borates determined electrochemically with those measured kinetically shows that the two curves are displaced along the  $\Delta G_{et}$  axis but that they have approximately the same shape. Since we feel that the kinetically determined values are closer to the thermodynamically meaningful potentials, the latter curve will be used in the analysis of the electron transfer reaction.

Although the range of free energies for the electron transfer reactions covered by the data shown in Figure 13 is narrow and restricted to values near zero, it is possible to reach some tentative conclusions about the functional dependence of  $k_{et}$  on  $\Delta G_{et}$ . The

(35) Chibisov, A. K. *Russ. Chem. Rev.* **1981**, *50*, 615. Weller, A. Z. *Physik. Chem. Neue Folge* **1982**, *133*, 93. Kuzmin, M. G.; Soboleva, I. V. *Prog. React. Kinet.* **1986**, *14*, 157. Kosower, E. M. *Ann. Rev. Phys. Chem.* **1986**, *37*, 127. Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. Suppan, P. *Chimia* **1988**, *42*, 320.

(36) Schmidt, J. A.; Liu, J.-Y.; Bolton, J. R.; Archer, M. D.; Gadzekpo, V. P. Y. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1027. Heitele, H.; Finckh, P.; Weeren, S.; Pöllinger, F.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1989**, *93*, 5173.

(37) Marcus, R. A. *J. Phys. Chem.* **1956**, *24*, 966. Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.



rate constants obtained are far greater than those commonly observed for intermolecular electron-transfer reactions since ion pairing eliminates the limitation imposed by diffusion. In this circumstance Marcus theory predicts that the electron-transfer rates will be controlled by  $\lambda$ , a Franck–Condon-like reorganizational parameter. 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 ( $\lambda_r$ ). The value of  $\lambda_s$  for a nonpolar solvent such as benzene is readily calculated to be nearly zero.<sup>35</sup> Thus the reorganization energy revealed by our measurements may be associated primarily with  $\lambda_r$ . Analysis of the data shown in Figure 13 according to the Marcus equation (correlation coefficient = 0.95) shows that  $\lambda_r$  is ca. 0.4 eV. Of course the precise value of  $\lambda$  is dependent on the assumptions made in the calculation of  $\Delta G_{et}$ . We note, however, that the internal reorganization energy revealed in these experiments is similar to the value recently reported by Farid and Gould in related charge recombination reactions.<sup>38</sup> These findings are consistent with our postulates of an electron-transfer reaction to generate the cyanine radical and alkyltriphenylboranyl 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  $\Delta G_{et}$ .

**(3) Chemistry of the Cyanine–Boranyl Radical Pair. Bond Cleavage and Back Electron Transfer.** According to the mechanism proposed in Scheme I, 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  $[\text{Cy}]^*$ . It is clear from our spectroscopic studies that the efficiency of  $[\text{Cy}]^*$  formation depends on the alkyl group bound to boron. For  $\text{Cy}^+[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$ , radical formation is very efficient, but for  $\text{Cy}^+[\text{Ph}_4\text{B}]^-$  hardly any  $[\text{Cy}]^*$  is formed; the other examples studied fall in between these extremes. In principle, this effect might be caused by a decrease in the equilibrium constant for carbon–boron bond cleavage ( $K_{BC}$ ) in the series as the “stability” of the alkyl radical formed decreases, or it could be due to an increase in the rate constant for back electron transfer ( $k_{bet}$ ) in this series. Our findings suggest that the first explanation is more reasonable.

According to the Marcus equation,<sup>37</sup> the rate constant for back electron transfer should be determined by the free energy for this reaction,  $\Delta G_{bet}$ . Values of  $\Delta G_{bet}$  may be calculated from the cyanine reduction potential and the borate oxidation potentials according to eq 14; these are listed in Table III. It is clear for

$$\Delta G_{bet} = -[E_{ox} - E_{red}]_{\text{MeCN}} \quad (14)$$

all cases examined that back electron transfer is a very exothermic process and that its exothermicity decreases through the series from  $[\text{Ph}_4\text{B}]^-$  to  $[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$ . Moreover, the possible errors in the calculation of the borate oxidation potentials would tend to make the back electron transfer even more exothermic than the values listed. Since these reactions are run in benzene solution where  $\lambda_s$  is negligible, it is reasonable to expect that these back electron transfers fall in the Marcus inverted region where  $k_{bet}$  decreases with increasing reaction exothermicity. Inverted region behavior has been observed in related back electron transfer reactions by Farid and Gould. If this is so, and if the efficiency of radical formation were controlled primarily by  $k_{bet}$ , then, contrary to our findings,  $[\text{Ph}_4\text{B}]^-$  should give more radicals than does  $[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$ . On this basis we suggest that the radical yield is controlled primarily by  $K_{BC}$ . 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>39</sup>

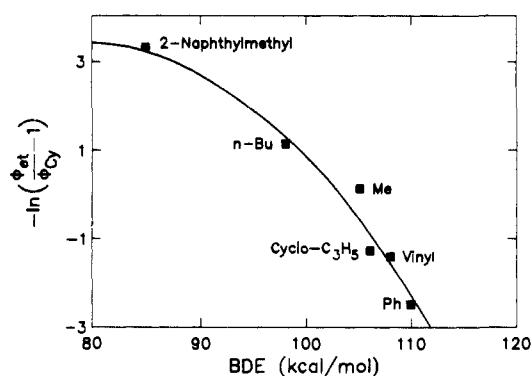


Figure 14. A correlation between the efficiency of radical formation from irradiation of cyanine borate ion pairs with the bond dissociation energy of the alkyl radical that is formed.

We are able to obtain a lower limit for  $k_{BC}$  for  $\text{Cy}^+[\text{NpCH}_2\text{B}(\text{Ph})_3]^-$ ; laser spectroscopy shows that  $[\text{NpCH}_2]^*$  is formed in less than 18 ps after excitation of the cyanine borate ion pair. In this case, the efficiency of radical formation is at its maximum value and we conclude that  $k_{BC} \gg k_{bet}$ . When a less-stable radical (i.e., phenyl) would result from carbon–boron bond cleavage, hardly any  $[\text{Cy}]^*$  is formed; which suggests that here  $k_{BC} \ll k_{bet}$ . These observations may be put on a more quantitative basis by comparing the radical yield with the carbon–hydrogen bond dissociation energy (BDE, Table I) for the hydrocarbon parent of the radical according to eq 15 where  $\Phi_{Cy}$ , and  $\Phi_{et}$  are the experimentally determined radical formation and electron-transfer efficiencies, and  $\alpha$  is the correlation parameter for a presumed linear free-energy relationship between  $k_{BC}$  and BDE. A plot of the data according to eq 15, Figure 14, is nonlinear

$$\ln \left( \frac{\Phi_{et}}{\Phi_{Cy}} - 1 \right) = \ln(k_{bet}/A) - \alpha(\text{BDE})/RT \quad (15)$$

since both  $k_{bet}$  and BDE depend on the structure of the boron-bound alkyl group, but the trend is unmistakable—a decrease in BDE leads to an increase in  $\Phi_{Cy}$ .

**(4) The Cyanine Radical–Alkyl Radical Pair: Electron Transfer, Coupling, and Cage Escape.** The final stage in the reaction sequence proposed in Scheme I is the competition between (1) cage escape to give free radicals with combination of  $\text{R}^*$  and  $[\text{Cy}]^*$  to form an alkylated cyanine and (2) electron transfer from  $[\text{Cy}]^*$  to  $\text{R}^*$  to regenerate the cyanine dye and form an alkyl anion. The latter process is thermodynamically impossible for the cases studied. Even the benzyl radical<sup>40</sup> is too difficult for the cyanine radical to reduce. Also, we have shown experimentally that coupling of  $\text{R}^*$  and  $[\text{Cy}]^*$  is slower than cage escape even in *p*-cymene solution. Thus, it appears that every alkyl radical formed from carbon–boron bond cleavage, for the cases studied, leads to generation of a free radical. High efficiency in this step insures the practical utility of the cyanine borates as photoinitiators of polymerization.

## Conclusions

Cyanine borate salts dissolved in nonpolar solvents such as benzene exist exclusively as ion pairs. Irradiation of the ion pair leads to formation of a locally excited singlet state of the cyanine. The rate constant for electron transfer from the borate to the excited cyanine in the ion pair ( $k_{et}$ ) depends on  $\Delta G_{et}$ . 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 rate of carbon–boron bond cleavage in the boranyl radical 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

(38) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991. Gould, I. R.; Moser, J. E.; Ege, D.; Moody, R.; Armitage, G.; Farid, S. *J. Imaging Sci.* **1989**, *33*, 44.

(39) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 6575.

(40) Sim, B. A.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 754.

the cyanine borate ion pair. This may be due to inhibition of the latter reaction by its large exothermicity in accord with predictions from Marcus theory. Carbon-boron bond cleavage of the boranyl radical in the systems examined is irreversible and leads to cage-escape and the formation of free alkyl and cyanine radicals. In this regard, 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.

### Experimental Section

**General.** Absorption spectra of solutions at room temperature were recorded with a Perkin-Elmer model 552 UV-vis spectrometer in quartz cuvettes with pathlengths ranging from 0.1 to 5.0 cm. Absorption spectra recorded at 77 K were measured with the sample contained in a 0.1-cm pathlength log-stemmed cuvette immersed in a cylindrical Dewar flask filled with liquid nitrogen. Fluorescence spectra of optically dilute solutions of the cyanine salts were recorded on a Farrand Mark I spectrofluorimeter. Quantum yields for the fluorescence of the cyanine borates in benzene solution ( $\Phi_{RB}$ ) were determined on freshly prepared samples by comparison with the fluorescence of Rhodamine B in ethyl alcohol solution ( $\Phi = 0.5$ ). The cyanine borates concentration was generally  $1 \times 10^{-7}$  M ( $OD_{530} \approx 0.01$  for a 1-cm path) to avoid problems caused by reabsorption of emitted light. The fluorescence lifetimes of the cyanine hexafluorophosphate in benzene solution at  $20 \pm 0.5^\circ$  C were measured with excitation at 532 nm by the phase-modulation method. The conductivity of cyanine hexafluorophosphate solutions was determined by means of a Dionex conductivity detector. Typically at least five dye concentrations were measured over the range from  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  M for each solvent investigated. The solution under measurement was flowed through the cell. The conductance of the solvent blank were subtracted for each concentration before analysis of the data. The oxidation potentials of the borates were determined by cyclic voltammetry as their tetramethylammonium salts in acetonitrile solution (ca.  $1 \times 10^{-3}$  M) containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. A glassy carbon working electrode, polished with diamond paste between each run, and a Pt counter electrode were used. The sweep rate was 250 mV/s. Elemental analysis were performed by the Micro-analytical Laboratory of the University of Illinois.

**Picosecond Transient Absorption Spectrometer.** The pump-probe method was used for picosecond spectroscopy. A single pulse (18 ps, 1066 nm) was extracted from a mode-locked Nd YAG laser (Quantel, type 501-C). The fundamental wavelength of 1064 nm was partly frequency up-converted with a KDP type II crystal to give green (532 nm) light. The latter is freed from residual IR by means of a dichroic reflector and a filter and is then guided to the sample in a fixed optical path where its energy is 250  $\mu$ J in ca. 3 mm<sup>2</sup>.

The residual IR (40 mJ) is delayed by using a motorized delay stage; quadruple reflection gives delays of up to 10 ns. The IR beam was focussed into a 10-cm path length cell filled with 70% D<sub>2</sub>O in H<sub>2</sub>O to generate picosecond continuum.<sup>41</sup> After removal of residual IR light, the white light was focussed onto an optical flat for homogenization and depolarization and a cubic beam splitter to form two beams. One beam probed the area that has been previously excited by the (532 nm) pump light; the other serves as the reference beam probing an unexcited sample area. Detection of the two spectra is accomplished with a dual diode array Reticon (Princeton Instruments). Data readout and manipulation is performed with an IBM XT compatible computer which also controls the instrumental setup (delay line position, data averaging etc.).

Difference absorption spectra are calculated according to

$$\Delta OD = (IX_0 - BX_0)(IN - BN) / (IX - BX)(IN_0 - BN_0)$$

**Table IV.** Spectroscopic and Electrochemical Data Used in the Determination of the Kinetic Oxidation Potentials by the Method of Rehm and Weller

	chrysene	pyrene	DMA <sup>c</sup>	naphthalene
$E_{s1}^a$ , eV	3.435	3.34	3.114	3.986
$-E_{red}^b$ (SCE), V	2.295	2.04	1.976	2.544
$\tau_r^c$ , ns	43.4	403	16.2	99.8
$E_{red}^*$ (SCE), V	1.140	1.30	1.138	1.442

<sup>a</sup> Singlet energy of the excited state of the fluorescer. <sup>b</sup> Reduction potential for the ground state of the fluorescer. <sup>c</sup> Lifetime of the fluorescer in nitrogen-saturated acetonitrile solution. <sup>d</sup> Reduction potential of the excited singlet state of the fluorescer. <sup>e</sup> DMA is 9,10-dimethylanthracene.

where IX is the measured intensity with excitation and beams on, IN is the intensity with only probe light, BX denotes the background from the pump beam, and BN is the background with no beams hitting the sample. The subscript o refers to the spectrum of the unexcited sample (reference beam). This method of calculation achieves corrections for variations in probe beam intensity, fluorescence, and scattered pump light. The sample was flowed through a 2-mm quartz cuvette, each portion was excited only once.

**Synthesis of the Cyanine Borates.** Typically, ca. 50 mg of cyanine chloride dissolved in 10 mL of acetonitrile was mixed with a solution containing 1 equiv of the tetramethylammonium borate dissolved in ca. 10 mL of acetonitrile. A 4–5-mL portion of water was added to the mixture, and the solvent volume was reduced in the dark under a stream of N<sub>2</sub> gas. The cyanine borate generally precipitates as the mixture becomes more concentrated and richer in water. The solid cyanine borate was collected by filtration and recrystallized from an acetonitrile-water (4:1) until it was homogeneous by thin-layer chromatography and gave a satisfactory elemental analysis (C, H, N).

**Oxidation Potentials of Alkyltriphenylborates Determined by the Kinetic Method.** The fluorescence intensity from nitrogen-saturated acetonitrile solutions of the aromatic hydrocarbons used as electron acceptors, Table IV, was monitored at varying borate concentrations. The excitation wavelength was chosen so that the light was absorbed only by the fluorescer. Concentrations of the fluorescer were adjusted so that the absorbance at the irradiating wavelength is ca. 0.08. Rate constants for electron transfer were determined from the slope of the linear Stern-Volmer plots and the lifetime of the fluorescer measured in nitrogen-saturated acetonitrile solution in the absence of the borate. The data are presented in Figure 5 and Table IV.

**Quantum Yield of Free Radical Formation from Irradiation of Cy<sup>+</sup>-[PhCH<sub>2</sub>B(Ph)<sub>3</sub>].** Optically dense, nitrogen-saturated ethyl acetate solutions of the cyanine borate (ca.  $5 \times 10^{-4}$  M) containing varying amounts of tri-*n*-butylstannane (0–0.15 M) were irradiated in closed, Pyrex test tubes through a yellow filter ( $\lambda > 480$  nm) in a Rayonet photoreactor equipped with RPR 550 lamps. Essentially all of the incident light was absorbed by the cyanine throughout the irradiation period. Control experiments indicated negligible reaction of the dye with the stannane in the dark. After the irradiation was complete (ca. 2 min), the tubes were opened, and the yield of propylbenzene was determined by capillary gas chromatography. Plots of the reciprocal of the propylbenzene yield against reciprocal stannane concentration were linear. The quantum yield of free radical formation was calculated by comparing the propylbenzene yield at extrapolated infinite stannane concentration with the light dose obtained from actinometry with K[Cr(NH<sub>3</sub>)(SCN)<sub>3</sub>].

**Acknowledgment.** This work was supported in part by a grant from the National Science Foundation and in part by a Grant from Mead Imaging Corporation. Professor Larry Faulkner, Mr. M. Kropp, Ms. A. Strezo, and Mr. M. Bruns of the Chemistry Department of the University of Illinois helped with the electrochemistry experiments.

(41) Alfano, R. R.; Shapiro, S. L. *Phys. Rev. Lett.* **1970**, *24*, 584.