Photoinduced electron transfer in ion pairs of cation-anion polymethine dyes

A. S. Tatikolov,[a]* L. A. Shvedova,[a] Kh. S. Dzhulibekov,[a] Zh. A. Krasnaya,[b] A. L. Sigan,[c] and V. A. Kuz'min[a]

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328
[c]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Photoinduced electron transfer in ion pairs of cation-anion polymethine dyes was studied by flash photolysis. The formation of radicals, which are the products of photoinduced transfer of an electron from an anion to a cation in the ion pairs, was observed during photoexcitation of a number of cation-anion dyes in nonpolar and some weakly polar solvents (in particular, in toluene and chloroform). Photoinduced electron transfer is also observed during triplet sensitization of ion pairs of the cation-anion dyes. The redox potentials of the cations and anions constituting the dyes were measured; the radical yields were compared with the free energies of photoinduced electron transfer. Photoinduced electron transfer in the systems under study was compared with similar process in cyanine-borate ion pairs.

Key words: cation-anion dyes, ion pairs; photoinduced electron transfer.

Cation-anion polymethine dyes belong to a new class of ionic dyes in which both a cation and an anion are dyes. Their photophysical and photochemical properties in polar solvents are identical with those of mixtures of the corresponding cationic and anionic dyes with simple counterions. However, in weakly polar and nonpolar solvents, where the dyes form ion pairs, these properties may change drastically. In particular, we established that a new short-wave intense band inactive in fluorescence excitation spectra appears in the absorption spectra of a number of cation-anion polymethine dyes as a result of the interaction between the cation and anion chromophores.[1,2] Other effects due to the proximity of a cation and an anion may also be manifested in ion pairs, *e.g.*, singlet-singlet energy transfer between the ions. In this process, photoexcitation of one of the ions gives rise not only to its own fluorescence but also to the fluorescence of a counterion. Furthermore, if the redox potentials of the ions are low in magnitude, electron transfer between the ions may be expected during the photoexcitation of ion pairs of such dyes, similar to that observed for cationic cyanine dyes with borate counterions having low oxidation potentials.[3]

In the present work, photoinduced electron transfer was studied for a number of cation-anion polymethine dyes, whose spectral and fluorescent properties have been investigated earlier.[1,2] The half-wave oxidation (for anions) and reduction (for cations) potentials of the corresponding simple anionic and cationic dyes were also measured to characterize the electron transfer process.

Experimental

Cation-anion dyes containing anions A_1—A_{14} and cations C_1—C_{10}, as well as the corresponding simple anionic and cationic dyes with cations K^+, $Me_2NH_2^+$, H^+ and anions I^-, ClO_4^-, p-$MeC_6H_4SO_2^-$, were studied. The dyes **1**—**22** were synthesized[4,5] at the N. D. Zelinsky Institute of Organic Chemistry of the RAS. Acetonitrile and chloroform of "pure" grade, as well as toluene of "pure for analysis" grade were used as solvents. Chloroform was passed through a column with Al_2O_3 in order to remove traces of acid.

Differential absorption spectra and decay kinetics of dye photoproducts were measured by flash photolysis using an apparatus with a flash energy of 50 J and duration (at the half height) of $5 \cdot 10^{-6}$ s. Photoexcitation of dye solutions (dye concentrations were $(1-5) \cdot 10^{-6}$ mol L^{-1}) was performed at a long-wave absorption band of the cation or the anion. Oxygen-free solutions of dyes were prepared by the freeze—pump—thaw method. Quantum yields of dye radicals were measured by using triplet states of methylene blue in ethanol (the triplet quantum yield is 0.52, see Ref. 6 ; $\lambda_{max}^{T-T} = 825$ nm, $\varepsilon_{max}^{T-T} = 1.65 \cdot 10^4$ L mol^{-1} cm^{-1}, see Ref. 7) or eosin in
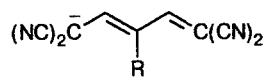
A_1—A_4

R = H (A_1), Me (A_2), CN (A_3), F (A_4)
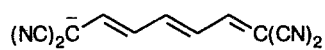
A_5
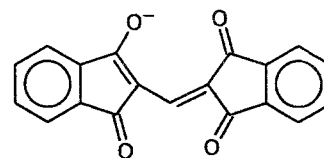
A_6
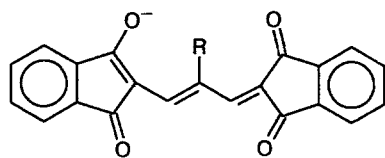
A_7—A_9

R = H (A_7), Me (A_8), F (A_9)
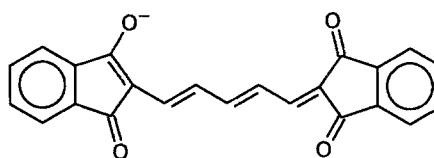
A_{10}
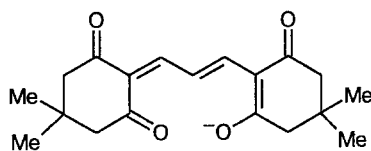
A_{11}
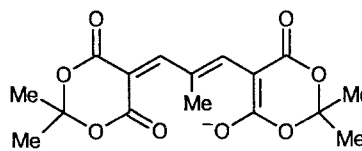
A_{12}
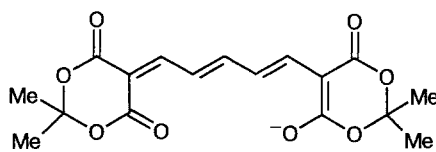
A_{13}
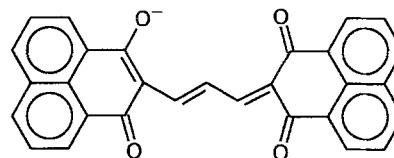
A_{14}
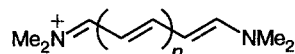
C_1 (n = 1)
C_2 (n = 2)
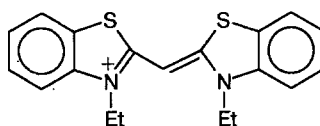
C_3
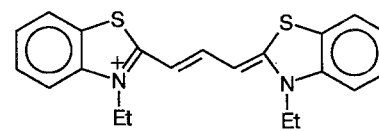
C_4
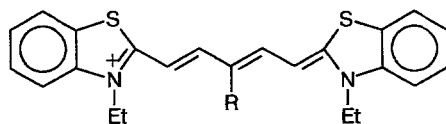
C_5, C_6

R = H (C_5), Me (C_6)
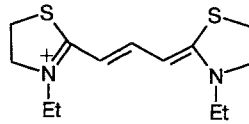
C_7
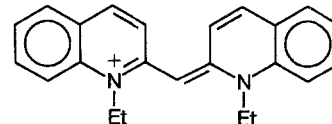
C_8
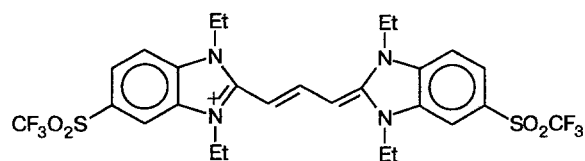
C_9
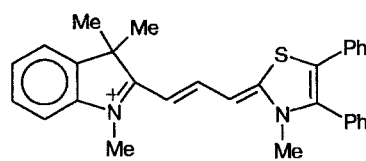
C_{10}

ethanol (the triplet quantum yield is 0.71, $\lambda_{max}^{T-T} = 580$ nm, $\varepsilon_{max}^{T-T} = 9.4 \cdot 10^3$ L mol^{-1} cm^{-1}, see Ref. 8) as standards. For identification of the photoproducts the dye radicals were obtained by reacting the dye triplet states (cations or anions) in acetonitrile with an electron donor or acceptor, respectively. 2,4,6-Trimethylphenol was used as the electron donor, anthraquinone as the electron acceptor. Because most of the dyes studied have low triplet quantum yields, their triplet states were obtained by triplet-triplet energy transfer from polycyclic hydrocarbons, anthracene ($E_T = 14700$ cm^{-1}), 1,2-benz-anthracene ($E_T = 16500$ cm^{-1}), 1,2-benzopyrene ($E_T = 18500$ cm^{-1}), 3,4,8,9-dibenzopyrene ($E_T = 12040$ cm^{-1}), 3,4,9,10-dibenzopyrene ($E_T = 14060$ cm^{-1}), and tetracene ($E_T = 10250$ cm^{-1}). The triplet energies of the dyes were estimated from triplet energies of the donors necessary to populate the dye triplet states.

Polarographic half-wave oxidation (E_{ox}) and reduction (E_{red}) potentials of the dyes were measured at the A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS, on an ECM-700 universal polarograph (at a platinum electrode). Acetonitrile was used as the solvent, tetraethylammonium perchlorate or tetrabutylammonium tetrafluoroborate was the supporting electrolyte. The speed of a potential change was 1 V s^{-1}. Acetonitrile was purified by refluxing sequentially over NaH, P_2O_5, and CaH_2, followed by rectification on a 1.5-meter column. In this work the potentials are given vs. a normal calomel electrode. Ferrocene ($E_{ox} = 0.40$ V)[9] was used as the standard in measuring oxidation potentials, while 1,1'-diethyl-2,2'-cyanine (C8; $E_{red} = -1.168$ V),[10] 3,3'-diethylthiamonomethincyanine (C3; $E_{red} = -1.485$ V),[10] and 3,3'-diethyl-10-methylthiadicarbocyanine (C6; $E_{red} = -0.969$ V)[11] were the standards for measuring reduction potentials. All measurements were made at 19±1 °C.

Results and Discussion

trans—cis-Isomerization is known to be one of the main photochemical processes that follows the photoexcitation of polymethine dyes.[12] In accordance with this, photoexcitation of most of the cation-anion dyes studied in polar as well as in nonpolar solvents also gives rise to the appearance of dye photoisomers (cations and/or anions).[13] However, the formation of additional photoproducts absorbing at shorter wavelengths than the initial dyes and decaying in the millisecond range is observed in some cases in weakly polar and nonpolar solvents (*e.g.*, in chloroform and toluene) in the absence of oxygen. From a comparison of the absorption spectra of these photoproducts with those of the radicals obtained from the dye triplet states under the influence of electron donors or acceptors, we draw the conclusion that the photoproducts are formed as a result of single-electron transfer between the anion (A$^-$) and the cation (C$^+$), which are converted into radicals of the anion and cation constituting the cation-anion dye (A· and C·, respectively). Figure 1 shows the absorption spectra of the photoproducts (except for photoisomers) formed during the photoexcitation of dye **17**, which contains cation C6 and anion A10, in chloroform (*1*) and, for comparison, the absorption spectra of radicals C· and A· (*2* and *3*) which appear during the quenching of the triplet states of the simple dyes (cation C6 and anion
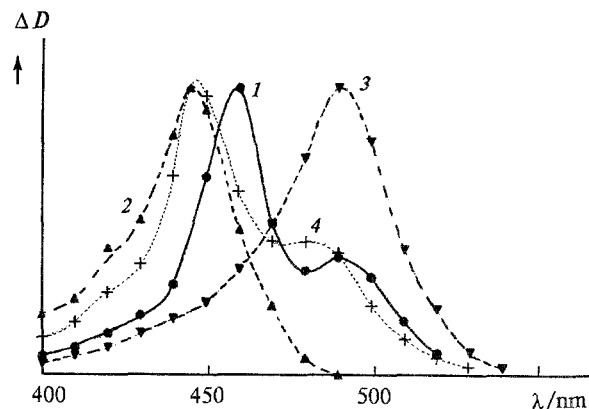

Fig. 1. Absorption spectra of the photoproducts (except for photoisomers) formed upon photoexcitation of dye **17** in chloroform (*1*) and the radicals appearing during quenching of the triplet states of cation C6 by an electron donor (*2*) and of anion A10 by an electron acceptor (*3*) in acetonitrile. The total absorption spectrum of radicals A· and C· formed during quenching of the triplet state of cation C6 by anion A10 in acetonitrile (*4*).

A10) in acetonitrile by an electron donor and acceptor, respectively. The total absorption spectrum of radicals A· and C· formed in quenching of the triplet state of cation C6 by anion A10 in acetonitrile (*4*) is also given. It can be seen from Fig. 1 that the absorption spectrum of the photoproducts of dye **17** in chloroform is similar to the total spectrum of radicals C· and A· (in chloroform the absorption spectrum of A· is shifted to a somewhat longer wavelength than in acetonitrile).

It should be noted that the direct photoexcitation of cation-anion dyes in polar solvents does not lead to the formation of radicals C· and A·. The time of radical formation is much shorter than the lifetime of the triplet state of the dyes ($5 \cdot 10^{-5}$—$2 \cdot 10^{-4}$ s under experimental conditions) and is limited by the duration of the exciting flash. Since the cation-anion dyes in weakly polar solvents are known to be in the form of ion pairs,[1] which are absent in polar solvents, it is possible to conclude that the radicals are formed in ion pairs as a result of photoinduced electron transfer involving an excited singlet state of the cation or anion according to the following scheme:

$$[C^+..A^-] + h\nu \rightarrow ([C^{+*}..A^-] \text{ or } [C^+..A^{-*}]) \rightarrow$$
$$\rightarrow [C^·..A^·] \rightarrow C^· + A^· , \qquad (1)$$
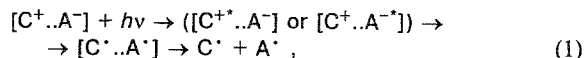
where [C$^+$..A$^-$] is an ion pair of the cation-anion dye. Ion pair formation brings the cation close enough to the anion so that electron transfer can occur between them. In polar solvents (*e.g.*, in acetonitrile or isopropanol), where the dyes exist as dissociated cations and anions, the realization of such an electron transfer would require very high concentrations of the dyes, which is practically not possible. Even in alcohols with a low dielectric constant, *e.g.*, in *tert*-pentanol ($\varepsilon = 5.8$; for chloroform $\varepsilon = 4.7$), the formation of A· and C· radicals is not

Table 1. Redox potentials (in acetonitrile, *vs.* normal calomel electrode) of the cations and anions constituting the cation-anion dyes

Cation	E_{red}/V	Anion	E_{ox}/V
C_1	−1.389	A_1	0.801
C_2	−1.148	A_2	0.702
C_3	−1.485[10]	A_3	1.210
C_4	−1.10[10]	A_4	0.809
C_5	−0.925	A_5	0.425
C_6	−0.969[11]	A_6	0.849
C_7	−1.342	A_7	0.539
C_8	−1.168[10]	A_8	0.460
C_9	−1.350	A_9	0.597
		A_{10}	0.318
		A_{11}	0.506
		A_{12}	0.689
		A_{13}	0.503
		A_{14}	0.616

observed, probably due to strong specific solvation of C^+ and A^- ions, which increases the distance between them in an ion pair and hinders the electron transfer.

The free energy of electron transfer is usually used to characterize the electron transfer process:[14,15]

$$\Delta G_{et} = E_{ox}(A^-/A^{\cdot}) - E_{red}(C^+/C^{\cdot}) - E_{00} + \Delta, \qquad (2)$$

where $E_{ox}(A^-/A^{\cdot})$ and $E_{red}(C^+/C^{\cdot})$ are the oxidation potential (in acetonitrile) of the anion and the reduction

potential of the cation, respectively, E_{00} is the energy of the electronic transition being excited, and Δ is a correction factor for the energy of the interaction between the ions in an ion pair and the solvation of the cation and the anion in the given solvent (in chloroform Δ is assumed to be equal to zero).[16] Table 1 shows the polarographic reduction potentials of the cationic dyes and the oxidation potentials of the anionic dyes that compose the cation-anion dyes studied. It can be seen from a comparison of the dyes of the same type, in particular, that for anions, elongation of the polymethine chain and the introduction of a methyl substituent in the *meso* position decreases E_{ox} (*cf.* anions A_1 and A_2; A_2 and A_5; A_6, A_7, and A_8) and the introduction of a CN group increases E_{ox} (*cf.* anions A_1 and A_3). In the case of cations the magnitude of E_{red} decreases when the length of the polymethine chain increases (*cf.* cations C_1 and C_2; C_3, C_4, and C_5).

Table 2 shows the results of the radical yield measurements in ion pairs of the cation-anion dyes in chloroform and toluene, as well as the spectral parameters (maxima of the absorption and fluorescence bands) used to estimate ΔG_{et}. It can be seen from the data of Table 2 that during direct photoexcitation the values of ΔG_{et} are negative for all dyes studied, therefore, the photoinduced transfer of an electron in the ion pairs of such dyes is energetically favorable. In accordance with this, direct photoexcitation in toluene, in which all these dyes form "tight" ion pairs, results in radicals according to reac-

Table 2. Spectral data, free energies of electron transfer (E_{00}) and radical yields (φ_R) from the excited singlet and triplet states of the cation-anion polymethine dyes

Dye	Anion	Cation	λ_{max}^{abs} [a] /nm	λ_{max}^{fl} [a] /nm	E_{00} [a] /cm⁻¹	ΔG_{et} [a] /eV	Radicals (φ_R) in CHCl₃	in toluene
1	A_1	C_4	450, 565	594	~21700 17300	−0.81 −0.26	— —	+ +
		T (C_4)			13750	0.18	—	+
2	A_1	C_7	420, 446	484	~21000[b]	−0.48	—	+
		T (A_1)			~16500	0.08	—	+
3	A_2	C_7	420, 448	483	~21000[b]	−0.58	—	+
		T (A_2)			~16500	−0.02	—	+
4	A_3	C_1	400, 414	450	~23300	−0.31	—	+
		T(A_3)			~16500	0.54	—	*c*
5	A_4	C_6	460, 662	495, 688	21000 14800	−0.85 −0.07	— —	+ +
		T (C_6)			~11000	0.41	—	+
6	A_5	C_4	567	592	17300	−0.64	—	+
		T (A_5 or C_4)			13750	−0.19	*c*	+
7	A_5	C_9	531	558	~18500	−0.54	—	+
		T (A_5)			~13000	0.15	*c*	+

Table 2 (*continued*)

Dye	Anion	Cation	λ_{max}^{abs} [a] /nm	λ_{max}^{fl} [a] /nm	E_{00} [a] /cm⁻¹	ΔG_{et} [a] /eV	Radicals (φ_R) in CHCl₃	in toluene
8	A₅	C₁₀	550	592	~17700	—	—	+
			T (A₅ or C₁₀)		~13000	—	c	+
9	A₇	C₃	425,	480,	22200,	−0.75	+	+
			571	610	17000	−0.10	+	+
			T (A₇)		~15200	0.13	+	+
10	A₇	C₄	524,		~16300[b]	−0.40	+	+
			565	585				
			T (C₄)		13750	−0.08	+	+
11[d]	A₇	C₅	560,	590,	17400,	−0.71	+	+(0.0054)
			660	680	14900	−0.40	+	+
			T (C₅)		~11000	0.09	+	+
12	A₇	C₇	446,	490,	21400	−0.79	+	+
			561	590	17400	−0.29	+	+
			T (A₇)		~15200	−0.02	+	+
13	A₇	C₈	462,		20500	−0.86	+	+
			570	585	17300	−0.46	+	+
			T (A₇)		~15200	−0.19	+	+
14	A₈	C₅	543,	590,	17700	−0.83	+	+
			657	692	14800	−0.46	+	+
			T (C₅)		~11000	−0.25	+	+
15[d]	A₈	C₆	554,	590,	17500	−0.76	+ (0.005)	+
			664	678	14900	−0.43	+ (0.0075)	+
			T (C₆)		~11000	0.06	+	+
16	A₉	C₆	574,	608,	16900	−0.55	+	+
			665	677	14900	−0.30	+	+
			T (C₆)		~11000	0.20	+	+
17[d]	A₁₀	C₆	600,		~13400[b]	−0.39	+ (0.0044)	+
			666	688				
			T (C₆)		~11000	−0.04	+ (0.11)	+
18	A₁₁	C₅	510,	540,	19100	−0.96	—	+
			660	684	14900	−0.43	—	+
			T (C₅)		~11000	0.06	c	+
19	A₁₂	C₅	480,		20400	−0.94	—	+
			680	694	14560	−0.21	—	+
			T (C₅)		~11000	0.24	c	+
20	A₁₃	C₁	417,	~470,	22600	−0.93	—	+
			570	589	17260	−0.27	—	+
			T (A₁₃)		~12300	0.35	c	+
21	A₁₃	C₆	564,	585,	17400	−0.70	—	+
			665	676	14900	−0.39	—	+
			T (C₆)		~11000	0.10	c	+
22	A₁₄	C₅	573,	597,	17100	−0.60	+	+
			660	684	14900	−0.32	+	+
			T (C₅)		~11000	0.17	+	c

[a] In chloroform. [b] The energy of the long-wavelength transition was estimated assuming symmetric splitting of the levels due to chromophore interaction in the ion pairs. [c] Not determined. [d] The dyes having the greatest radical yields.

tion (1). At the same time, in more polar chloroform radical formation is not observed for all dyes, but only for those in which the anion and the cation have terminal heterocycles with aromatic nuclei (*cf.* Table 2). This is probably due to the fact that, as has been shown earlier,[1] such dyes have lower dissociation constants in chloroform (form ion pairs better) than other dyes, and at the concentrations used in the experiment $((1—4) \cdot 10^{-6}$ mol $L^{-1})$ they form ion pairs at sufficiently high concentrations. Indeed, for dye 17, which has the lowest dissociation constant $(1.9 \cdot 10^{-7}$ mol $L^{-1})$,[1] the radical quantum yield is close to the highest one detected experimentally.

It can also be seen from Table 2 that for all dyes studied the radical quantum yields due to the direct photoexcitation of ion pairs are rather low, and are <0.01 both in chloroform and in toluene. At the same time, triplet-sensitized excitation (population of the triplet state of the cation or the anion in an ion pair using a triplet energy donor) may cause them to greatly increase (*e.g.*, to 0.11 for dye 17). This is evidence that the reverse transfer of an electron in the singlet radical pair $^1[C^{\cdot}..A^{\cdot}]$ formed from the excited singlet ion pair as a result of direct transfer of an electron plays an essential role:

$$^1[C^+..A^-]_0 + h\nu \longrightarrow {}^1[C^+..A^-]_1 \longrightarrow$$

$$\longrightarrow {}^1[C^{\cdot}..A^{\cdot}] \begin{cases} \longrightarrow C^{\cdot} + A^{\cdot} \\ \longrightarrow {}^1[C^+..A^-]_0 \end{cases} \quad (3)$$
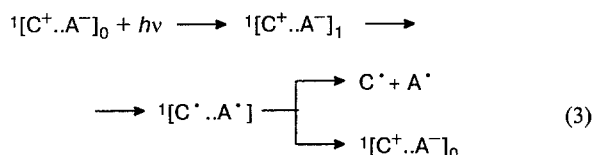
This reverse electron transfer competing with the escape of the radicals from a cage is probably the main reason for the low radical yields during the direct photoexcitation of the dye ion pairs. During triplet sensitization, a triplet ion pair $^3[C^+..A^-]$ with the excitation localized on an anion or a cation is formed, which then forms a triplet radical pair $^3[C^{\cdot}..A^{\cdot}]$ as a result of electron transfer. Within the latter radical pair reverse electron transfer to form the initial ion pair $^1[C^+..A^-]_0$ is impossible because of the spin exclusion, and only one channel of $^3[C^{\cdot}..A^{\cdot}]$ transformations, the escape of the radicals from a cage, is available. This gives rise to higher radical quantum yields from the triplet states.

It is to be noted that, unlike in direct photoexcitation, during triplet excitation ΔG_{et} is not always negative. In a number of cases it reaches rather high positive values (the maximum value of ΔG_{et} is 0.41 eV for dye 5, *cf.* Table 2). This points to the endothermicity of electron transfer for such dyes, which has to decrease the rate constant of electron transfer in the ion pairs. However, even for dye 5 in toluene the formation of radicals from the triplet ion pair is observed (*cf.* Table 2), which is probably explained by the relatively long lifetime of this ion pair (on the order of hundreds of microseconds, from the flash photolysis data), which increases the

probability of electron transfer even at the low rate constant.

Comparing the electron transfer processes following the direct photoexcitation of cyanine-borate ion pairs[3,17,18] and ion pairs of cation-anion dyes, one can conclude that the rate constants in the former case are apparently greater than in the latter one. For example, it has been shown[17] that for cation C_8 with a borate anion $(p\text{-Me}_3CC_6H_4)_3BBu^-$ (dye 23) in benzene, photoinduced electron transfer is so fast (the rate constant is $\sim 2 \cdot 10^{12}$ s^{-1}) that it completely suppresses the parallel process of cation photoisomerization. However, in the case of the cation-anion dyes, except for photoinduced electron transfer, photoisomerization of the cation and/or anion is regularly observed. This is probably due to the fact that for dye 23 ΔG_{et} is close to zero, which gives the maximum rate constant for the electron transfer.[17] Moreover, the cyanine-borate dyes probably form "tighter" ion pairs (penetrated ion pairs may even appear)[18] than the cation-anion ion pairs, which also promotes faster electron transfer.

The radical quantum yields in the cyanine-borate ion pairs are also greater than in the cation-anion dyes studied (*e.g.*, 0.6 for dye 23 in benzene).[17] This is due to the fast decomposition of the boranyl radicals that appear during the transfer of an electron from the cyanine-borate ion pairs to alkyl radicals and triarylborane, which excludes the reverse electron transfer in the radical pairs formed.[3]

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