

## 81. Transient Radicals Formed by Electron Transfer between Inorganic Ions and Excited Aromatic Molecules in Polar Solvents

by Marek Mac\* and Jakob Wirz

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

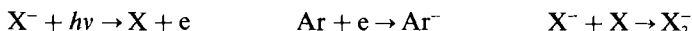
and Jan Najbar

Faculty of Chemistry, Jagiellonian University, Ingardena 3, PL-30-060 Krakow

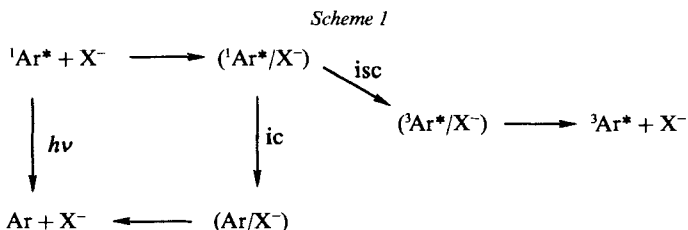
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Fluorescence quenching of aromatic molecules by inorganic anions has been the subject of many investigations, yet the nature of the quenching mechanism is not fully understood. The fluorescence-quenching rate constants correlate with electrochemical data, but the radicals expected to form upon transfer of an electron to the excited aromatic molecules have escaped observation. We report the first observation of radical-ion species formed by electron-transfer quenching with inorganic anions in acetonitrile. A decisive step leading to formation of separated radical ions is the trapping of the primary charge-transfer complex by a second inorganic ion.

**Introduction.** – It is commonly assumed that fluorescence quenching of aromatic molecules by inorganic anions is due to electron transfer. However, formation of the expected aromatic radical anions is usually not observed in transient absorption measurements. Such measurements were performed by *Watkins* [1] for a series aromatic molecules and halide anions as electron donors in MeCN. *Watkins* observed no anion radicals of the aromatic molecules (naphthalene, anthracene, pyrene, and phenanthrene), even when the concentration of the anions ( $I^-$ ,  $SCN^-$ ,  $Br^-$ , and  $NO_3^-$ ) was sufficient to quench the fluorescence almost completely. Under those conditions, the triplet state is formed with a quantum yield close to unity. For biphenyl and NaI, a small amount of anions of biphenyl was detected. These experiments were performed using a conventional flash-photolysis apparatus (150 J with a flash duration of 5  $\mu$ s). To avoid direct excitation of the quencher, appropriate glass or solution filters were inserted between the flash and the sample. Similar measurements without cut-off filters demonstrated the presence of anion radicals, produced by direct photoionization of the inorganic anions:



To explain the results obtained by exclusive excitation of the aromatic molecules, *Watkins* proposed the mechanism shown in *Scheme 1*.



Intersystem crossing (isc) of the encounter complexes ( $^1\text{Ar}^*/\text{X}^-$ ) was assumed to be much faster than internal conversion to the ground state, so that at high concentrations of quenchers  $\text{X}^-$  the triplet state of the aromatic molecules,  $^3\text{Ar}^*$ , is populated with a quantum yield of unity.

Similar results were obtained by *Shizuka et al.* [2] using an EtOH/H<sub>2</sub>O solvent mixture. Again, radicals were not detected. The absence of free radicals was interpreted by assuming that the dissociation of the ionic pair is much slower than the deactivation processes, isc, and back electron transfer. *Shizuka et al.* [2] observed that the fluorescence-quenching rate constants depend upon the free energy of the electron-transfer reaction that was calculated from electrochemical and spectral data. Similar observations have been reported for the quenching of the lowest excited singlet [3–6] and triplet [7–9] state of aromatic molecules by inorganic anions in polar solvents.

On the other hand, dihalide (or dithiocyanide) anion radicals were observed in the reactions of triplet ketones and quinones with inorganic anions in H<sub>2</sub>O [10], and of 5-nitro-2-furoic acid with inorganic anions in acetone and MeCN [7]. *Treinin* and coworkers [10] divided the investigated anions into two classes: *i*) I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, and SCN<sup>-</sup>, and *ii*) NO<sub>2</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, and N<sub>3</sub><sup>-</sup>. At low-to-moderate concentrations of the anions of class *i*, *Treinin* and coworkers [10] observed no or little radical formation, but, at anion concentrations much higher than required for complete quenching, these authors observed equimolar amounts of reduced ketones or quinones and dianion radicals, X<sub>2</sub><sup>-</sup>. Quenching of triplet ketones by anions from class *ii* led to the formation of radicals with a quantum yield equal to that of triplet quenching at all concentrations.

When aromatic donors such as anilines are used to quench excited aromatic acceptors such as 9,10-dicyanoanthracene or 2,6,9,10-tetracyanoanthracene, the resulting free radical ions have been observed in MeCN as a result of electron-transfer quenching [11] [12]. Moreover, the rate constants of back electron transfer depend on the free energy change of back electron transfer,  $\Delta_{\text{el}}G^\ominus$ , as predicted by *Marcus* theory [13]: the reaction rate constant decreases, when the free energy change of the reaction becomes larger than the solvent reorganization energy  $\Delta_{\text{el}}G^\ominus > -\lambda$  (*inverted Marcus region*) [11] [12].

The purpose of this paper is to elucidate the fate of charge-transfer radical pairs formed in fluorescence quenching of aromatic molecules by inorganic anions, and to explain the role of the solvent in the processes that take place after electron transfer in the encounter complexes.

**Results.** – We investigated the following systems in MeOH and MeCN by nanosecond transient absorption and steady-state fluorescence measurements: 1-cyanonaphthalene (1-CNN) with NaI, KSCN, and tetrabutylammonium bromide (TBABr) or NaBr; 9,10-dicyanoanthracene (9,10-DCA) with NaI, KSCN, and TBABr or NaBr; *p*-terphenyl with NaI, KSCN, and TBABr or NaBr; naphthalene and NaI; biphenyl with KSCN and LiBr; anthracene and NaI and LiBr; fluorene and KSCN.

The free energies of electron transfer were evaluated from electrochemical and spectral data according to *Eqn. 1* [2]

$$\Delta_{\text{el}}G^\ominus = E^{\text{ox}}(\text{X}^-) - E^{\text{red}}(\text{Ar}) - E_{\text{s}}(\text{Ar}), \quad (1)$$

where  $E^{\text{ox}}(\text{X}^-)$  and  $E^{\text{red}}(\text{Ar})$  are the appropriate half-wave potentials for oxidation of  $\text{X}^-$  and reduction of Ar in the ground state, respectively, and  $E_{\text{s}}(\text{Ar})$  is the singlet excitation

Table 1. Fluorescence-Quenching Rate Constants ( $K_{SV} = k_q \tau_{fl}^0$ ) of Aromatic Molecules by Inorganic Anions in MeCN. The electrochemical and spectral data for the calculation of  $\Delta_{et}G^\ominus$  were taken from [11] [16] [17].

Acceptor	Donor	$\Delta_{et}G^\ominus/eV$	$\tau_{fl}^0/ns$	$K_{SV}/M^{-1}$
9,10-DCA	$I^-$	-1.09	15.3 [11]	313.1
	$SCN^-$	-0.79		261.6
	$Br^-$	-0.59		216.5
1-CNN	$I^-$	-1.0	9.3 [14]	252.0
	$SCN^-$	-0.7		205.0
	$Br^-$	-0.5		100.0
<i>p</i> -Terphenyl	$I^-$	-0.76	1.0 [16]	36.2
	$SCN^-$	-0.46		15.2
Biphenyl	$SCN^-$	-0.42	13.0 [2]	181.0
	$Br^-$	-0.22		34.5
Anthracene	$I^-$	-0.48	5.0 [14]	90.0
	$SCN^-$	-0.18		23.0
Fluorene	$SCN^-$	-0.2	6.7 [2]	46.9

energy of the aromatic molecule. Table 1 shows the fluorescence-quenching data obtained for 9,10-DCA, 1-CNN, *p*-terphenyl, biphenyl, fluorene, and anthracene in the presence of the quenchers NaI, KSCN, and TBABr in MeCN. Figs. 1 and 2 show the dependence of the fluorescence-quenching rate constants on the free-energy change of electron transfer in MeCN and in MeOH, respectively. We observe that the fluorescence-quenching rate constants decrease with increasing free energy of electron transfer in both cases, thus, electron transfer is involved in the fluorescence-quenching mechanism.

The quantum yield of ion separation was estimated as follows. From fluorescence-quenching measurements, we obtained relative quantum yields of fluorescence,  $\Phi_{rel}^n = I_{[Q]}^n / I_{[Q]=0}^n$ , and from transient absorption measurements, we obtained relative triplet quantum yields,  $\Phi_{rel}^{tr} = A_{[Q]}^{t=0} / A_{[Q]=0}^{t=0}$ , where  $I$  are the integrated intensities of fluorescence and  $A$  are the initial absorbances of the triplet decays. The absolute quantum yields of triplet formation  $\Phi_{[Q]}^{tr}$  and of fluorescence  $\Phi_{[Q]}^n$  are equal to  $\Phi_{[Q]=0}^{tr} \cdot \Phi_{rel}^{tr}$  and  $\Phi_{[Q]=0}^n \cdot \Phi_{rel}^n$ .

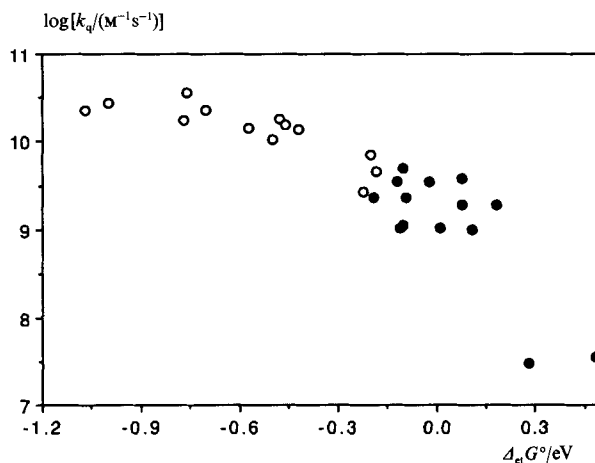


Fig. 1. Dependence of the logarithm of the fluorescence-quenching rate constants on  $\Delta_{et}G^\ominus$  in MeCN. Black circles: taken from Watkins [3], open circles: measured in this work.

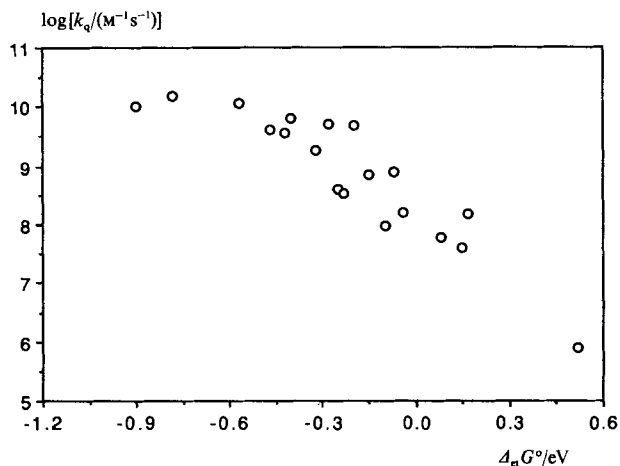


Fig. 2. Dependence of the logarithm of the fluorescence-quenching rate constants on  $\Delta_e G^0$  in MeOH

respectively. The known absolute quantum yields of intersystem crossing,  $\Phi_{[Q]=0}^{tr}$  [15–17], and of fluorescence,  $\Phi_{[Q]=0}^f$  [11] [16] [17], of the aromatic molecules add up to unity within experimental error. If we assume that the quantum yields of fluorescence, triplet-state formation, and ion separation in the presence of quenchers also add up to unity, the latter may be easily calculated from Eqn. 2.

$$\Phi_{sep} = 1 - \Phi_{[Q]}^{tr} - \Phi_{[Q]}^f \quad (2)$$

The concentration dependence of the fluorescence, triplet, and ion-separation quantum yields in MeCN is plotted in Fig. 3.

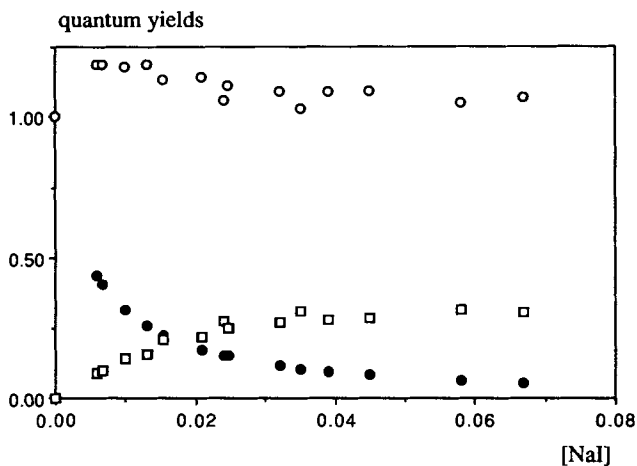


Fig. 3. Dependence of the relative quantum yields of triplet-state formation (open circles), of the relative quantum yields of fluorescence (black circles), and of the absolute ion-separation quantum yields (squares), as a function of quencher concentration for 1-CNN and NaI in MeCN. For details, see text. The relative quantum yields for  $[NaI] = 0$  are unity by definition.

We observed enhanced triplet-triplet absorption due to added quencher in every case. Moreover, in the presence of NaI in MeCN, we also observed a new transient absorption band located at  $\lambda_{\max} = 385$  nm and another band with  $\lambda_{\max} > 600$  nm for 9,10-DCA, 1-CNN, and *p*-terphenyl. The band around 385 nm may be attributed to  $I_2^-$  [18–20], while the band above 600 nm may be attributed to the corresponding aromatic anion radicals [21]. Figs. 4 and 5 show the transient absorption spectra of 1-CNN and 9,10-DCA in the presence of NaI in MeCN measured *ca.* 160 ns after excitation.

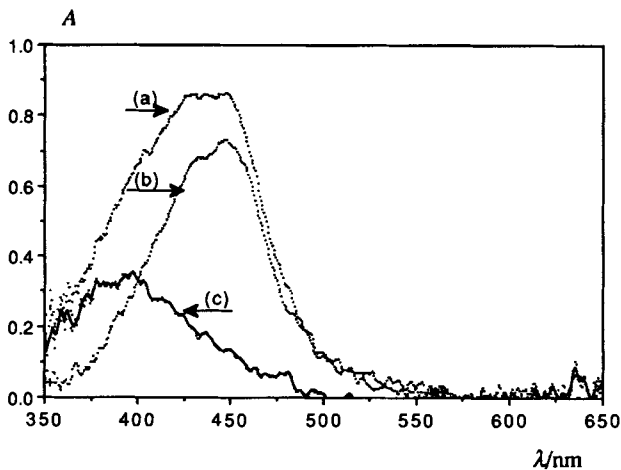


Fig. 4. Transient absorption spectra of a) 1-CNN and 0.03 M NaI; b) 1-CNN without quencher, and c) their difference spectrum in MeCN recorded *ca.* 160 ns after excitation at 308 nm

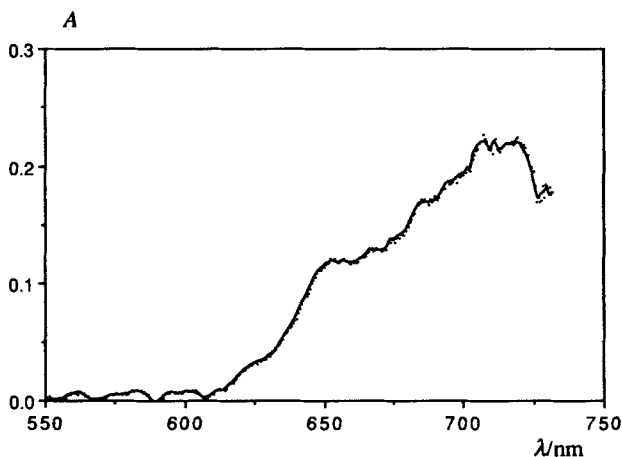


Fig. 5. Transient absorption spectrum of 9,10-DCA and 0.03 M NaI in MeCN recorded *ca.* 160 ns after excitation at 308 nm

Transient absorption spectra with  $Br^-$  and  $SCN^-$  as quenchers showed no significant absorptions that may be attributed to the corresponding anion radicals or  $X_2^-$  (365 nm for  $Br_2^-$  [19] [20] and 480 nm for  $(SCN)_2^-$  [7]). For  $Br^-$  and  $SCN^-$  as quenchers, we found that the quantum yield of triplet formation approaches unity at high quencher concentrations.

In MeOH, no absorptions due to the radical anions of the aromatic molecules were observed.

**Discussion.** – According to the *Marcus* theory [13], the dependence of the electron-transfer rate constants on the free energy of electron transfer has the form of *Eqn. 3*,

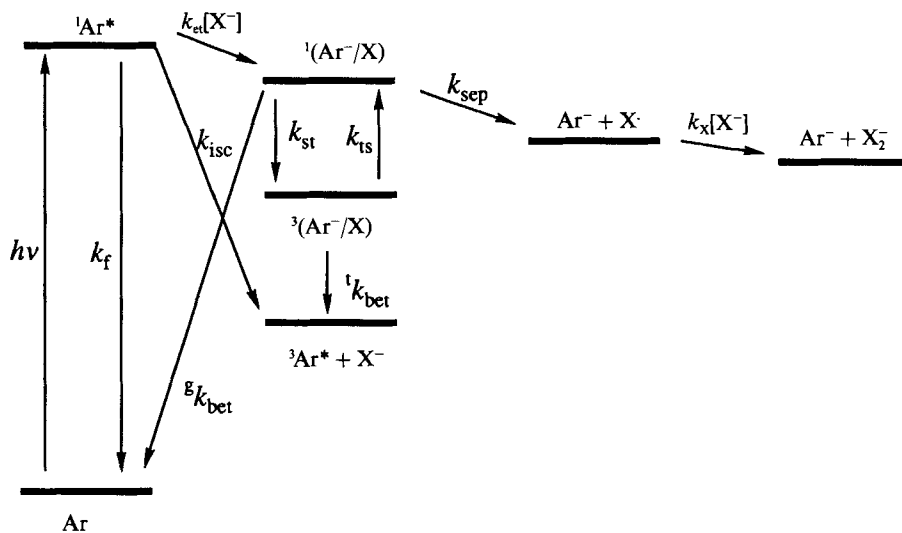
$$k_{et} = A \exp\left(-\frac{(\Delta_{et}G^\circ + \lambda)^2}{4\lambda kT}\right), \quad (3)$$

where  $\Delta_{et}G^\circ$  is the free-energy gap between the initial and the final state, and  $\lambda$  is the solvent-reorganization energy. The preexponential factor  $A$  depends on the dynamic properties of the system. Formulae for this pre-exponential factor are given in [22–24]. The parameter  $\lambda$  depends on the dielectric and geometric properties of the system and has the form

$$\lambda = \frac{N_A e^2}{4\pi\epsilon_0} \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right), \quad (3a)$$

where  $a_1$  and  $a_2$  are the radii of the reactants,  $r$  is the distance between the centres of the two reactants, and  $\epsilon_\infty$  and  $\epsilon_s$  are the optical and static dielectric constants, respectively.

*Scheme 2<sup>a)</sup>*



- <sup>a)</sup> Ar: aromatic molecule in the ground state  
 $^1\text{Ar}^*$ : aromatic molecule in the singlet excited state  
 $^1(\text{Ar}^-/\text{X})$ : CT complex in the singlet state  
 $^3(\text{Ar}^-/\text{X})$ : CT complex in the triplet state  
 $^3\text{Ar}^*$ : aromatic molecule in the triplet state  
 $\text{Ar}^- + \text{X}$ : separated radicals
- } gap exaggerated for clarity

The reaction rate constants refer to the following processes:  $k_f$ : fluorescence;  $k_{et}$ : forward electron transfer,  $k_{isc}$ : intersystem crossing;  $^1k_{bet}$ : back electron transfer to the triplet state;  $^gk_{bet}$ : back electron transfer to the ground state;  $k_{ts}$  and  $k_{st}$ : spin interconversion;  $k_{sep}$ : radical separation,  $k_X$ : complexation of X by  $\text{X}^-$ .

Let us consider the quenching mechanism depicted in *Scheme 2*. Kinetic analysis of *Scheme 2* for the limiting case of high quencher concentration (complete fluorescence quenching) gives the following expression for the ion-separation quantum yield,  $\Phi_{\text{sep}}$

$$\Phi_{\text{sep}} = \frac{k_{\text{sep}}}{k_{\text{sep}} + {}^1k_{\text{bet}} \frac{k_{\text{st}}}{k_{\text{ts}} + {}^1k_{\text{bet}}} + {}^3k_{\text{bet}}} \quad (4)$$

In the special case of  ${}^1k_{\text{bet}} \ll k_{\text{ts}}$  and  $k_{\text{ts}} \approx k_{\text{st}}$  (negligible energy gap between singlet and triplet radical pairs), *Eqn. 4* is simplified to *Eqn. 4a*.

$$\Phi_{\text{sep}} = \frac{k_{\text{sep}}}{k_{\text{sep}} + {}^1k_{\text{bet}} + {}^3k_{\text{bet}}} \quad (4a)$$

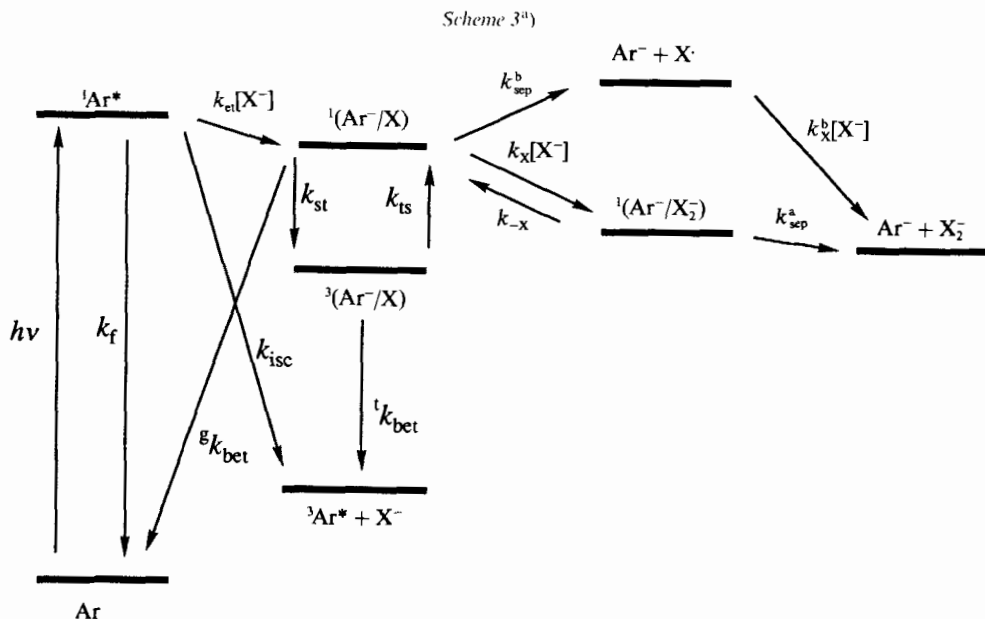
It was assumed that inorganic anions such as  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$  induce intersystem crossing only through the electron-transfer path, because these simple anions possess no orbital momentum [10]. A 'direct' enhancement of intersystem crossing by heavy-atom inorganic ions may play a role in the fluorescence quenching in some special cases such as the fluorescence quenching of anthracene by  $\text{I}^-$  and  $\text{SCN}^-$  anions in alcohols [25] or in the endothermic  $\Delta_{\text{et}}G$  region, when the electron-transfer reaction is slow [5].

Hence, the quantum yield of ion separation should increase with decreasing rates of the competing back electron-transfer processes,  ${}^1k_{\text{bet}} + {}^3k_{\text{bet}}$ . Increasing quantum yields  $\Phi_{\text{sep}}$  were found in the following order: naphthalene < *p*-terphenyl < 1-CNN < 9,10-DCA with  $\text{I}^-$  as a quencher (*Table 2*). If we assume that the rate of separation of the singlet CT complexes,  $k_{\text{sep}}$ , is constant in the series, these results imply that  ${}^1k_{\text{bet}} + {}^3k_{\text{bet}}$  increases in the order 9,10-DCA < 1-CNN < *p*-terphenyl < naphthalene. Let us correlate these observations with some thermodynamic properties of the above systems. *Table 2* shows the relation between ion-separation quantum yields and the energy gaps between the CT state and the triplet and ground states. It is seen that the intensity of the observed transient species  $\text{I}_2^-$  increases with increasing free-energy change between the charge-transfer state and the triplet and ground state.

Table 2. Dependence of the Fluorescence ( $\Phi^{\text{fl}}$ ) and Triplet-State ( $\Phi^{\text{tr}}$ ) Quantum Yields on the Energy Gap between the CT and Ground ( $\Delta_{\text{bet}}^{\text{g}}G$ ) or Triplet ( $\Delta_{\text{bet}}^{\text{t}}G$ ) States, Respectively, Measured at 0.04M NaI Concentration in MeCN

System	$\Delta_{\text{bet}}^{\text{g}}G/\text{eV}$	$\Delta_{\text{bet}}^{\text{t}}G/\text{eV}$	$\Phi_{[\text{Q}]=0}^{\text{fl}}$	$\Phi^{\text{fl}}$	$\Phi^{\text{tr}}$	$\lambda_{\text{obs}}/\text{nm}$
9,10-DCA + $\text{I}^-$	-1.80 [11] [17]	-0.0 [17]	0.88 [11]	0.06	0.0	450
1-CNN + $\text{I}^-$	-2.88 [16] [17]	-0.4 [16] [17]	0.37 [15]	0.04	0.65	470
<i>p</i> -Terphenyl + $\text{I}^-$	-3.20 [3]	-0.68 [3]	0.93 [17]	0.35	0.54	450
Biphenyl + $\text{I}^-$	-3.56 [3] [17]	-0.64 [3] [17]	0.49 [3]	0.06 [3]	0.74 [1]	
Naphthalene + $\text{I}^-$	-3.49 [16] [17]	-0.85 [16] [17]	0.25 [16] [17]	0.02	1.00	420

It remains to be shown why we do not observe similar species for the quenching of the previously mentioned aromatics by  $\text{SCN}^-$  and  $\text{Br}^-$ , although  $\Delta_{\text{et}}G^{\ominus}$  of back electron transfer is of similar magnitude. For an explanation, we consider *Scheme 3* which differs from *Scheme 2* in one respect: charge separation is also induced by association of the halide radical in  ${}^1(\text{Ar}^-/\text{X})$  with an additional inorganic ion [10].



- a) Proposed kinetic scheme to explain all photophysical processes after electron transfer in the investigated systems. The reaction rate constants refer to the following processes:  $k_x$ : association rate constant of the ionic radical pair by anions;  $k_{-x}$ : dissociation rate constant of  $^1(\text{Ar}^-/\text{X}_2^-)$  to  $^1(\text{Ar}^-/\text{X}) + \text{X}^-$ ;  $k_{\text{sep}}^a$ : separation rate constant of  $^1(\text{Ar}^-/\text{X}_2^-)$ . Other rate constants as in Scheme 2.

Analysis of Scheme 3 yields the following formula for the quantum yield of ion separation (Eqn. 5 is derived in the Appendix),

$$\Phi_{\text{sep}} = \frac{\alpha}{\beta} \left( k_{\text{sep}}^b + k_{\text{sep}}^a \frac{k_x[\text{X}^-]}{k_{-x} + k_{\text{sep}}^a} \right), \quad (5)$$

where  $\alpha = \frac{K_{\text{sv}}[\text{X}^-]}{1 + K_{\text{sv}}[\text{X}^-]}$  is the efficiency of fluorescence quenching and

$$\beta = {}^gk_{\text{bet}} + k_{\text{sep}}^b + k_x[\text{X}^-] \frac{k_{\text{sep}}^a}{k_{-x} + k_{\text{sep}}^a} + {}^1k_{\text{bet}} \frac{k_{\text{st}}}{k_{\text{is}} + {}^1k_{\text{bet}}}.$$

If  $k_{\text{sep}}^b$  is much smaller than  $k_{\text{sep}}^a \frac{k_x[\text{X}^-]}{k_{-x} + k_{\text{sep}}^a}$ , and the dissociation of  $^1(\text{Ar}^-/\text{X}_2^-)$  into  $^1(\text{Ar}^-/\text{X})$  and  $\text{X}^-$  is negligible, i.e., if the halide ions are formed predominantly through irreversible trapping of the CT complex  $^1(\text{Ar}^-/\text{X})$  with a second halide ion (path a), the above equation is simplified as follows:

$$\Phi_{\text{sep}} = \alpha \frac{k_x^a[\text{X}^-] + k_{\text{sep}}^b}{{}^gk_{\text{bet}} + {}^1k_{\text{bet}} \frac{k_{\text{st}}}{k_{\text{is}} + {}^1k_{\text{bet}}} + k_{\text{sep}}^b + k_x[\text{X}^-]}. \quad (6)$$

This situation applies for high concentration of the quenchers [10].



If the rate of dissociation of  $(Ar^-/X_2^-)$ ,  $k_{-X}$ , is much greater than that of ion separation,  $k_{sep}^a$ , then

$$\Phi_{sep} = \alpha \frac{k_{sep}^a K[X^-] + k_{sep}^b}{{}^s k_{bet} + {}^t k_{bet} \frac{k_{st}}{k_{ts} + {}^t k_{bet}} + k_{sep}^b}, \quad (7)$$

where  $K$  is the equilibrium constant of the formation of  ${}^1(Ar^-/X_2^-)$  from  ${}^1(Ar^-/X)$  and  $X^-$ .

Assuming that the formation of  $I_2^-$  ion in MeCN is diffusion controlled and occurs with a rate constant approaching  $2 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$ , we are able to calculate the sum of the rates of back electron transfer to the triplet and ground states and the separation rate constant of  $(Ar/X^-)$ ,  $k_{sep}^b$ .

The value of  $k_{sep}^b$  obtained from a nonlinear least-squares fit to *Eqn. 6* is one order of magnitude smaller than the charge separation rate constant assumed by *Gould et al.* [11] to explain the results of back electron transfer in the  $(9,10\text{-DCA}^-/Ar^+)$  couple and may be neglected as a significant contribution to ion separation even at low quencher concentrations. Neglecting  $k_{sep}^b$ , *Eqn. 6* is transformed to *Eqn. 8*.

$$\frac{\alpha}{\Phi_{sep}} = 1 + \frac{{}^s k_{bet} + {}^t k_{bet} \frac{k_{st}}{k_{ts} + {}^t k_{bet}}}{k_x} \frac{1}{[X^-]} \quad (8)$$

The dependence of the inverse of  $\Phi_{sep}$  on the inverse of the quencher concentrations has a linear form (*Fig. 6*).

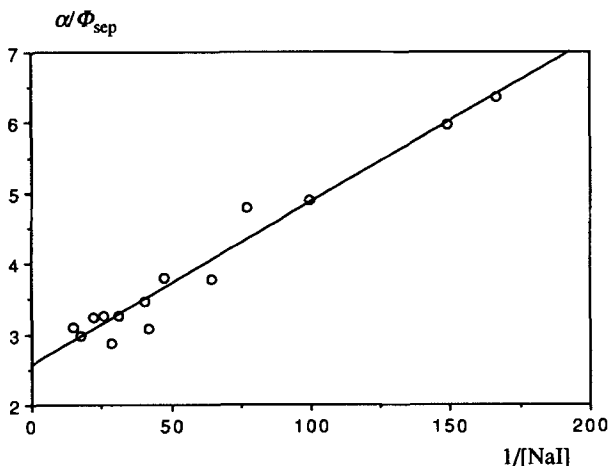


Fig. 6. Dependence of the inverse of the ion-separation quantum yield on the inverse of molar concentration of the quencher for 1-CNN and NaI in MeCN (*Eqn. 8*)

The calculated back electron-transfer rate constants for 9,10-DCA, 1-CNN, *p*-terphenyl, biphenyl, naphthalene, and NaI in MeCN are collected in *Table 3*. The lack of  $X_2^-$  formation with  $Br^-$  and  $SCN^-$  as quenchers may be attributed to the greater energy gap between the CT and ground state compared to those with  $I^-$  as a quencher.

Table 3. Dependence of Back Electron-Transfer Rate Constants on the Energy Gap between CT and Triplet States in MeCN

System	$\Delta_{\text{bet}}^{\ddagger}G/\text{eV}$	${}^1k_{\text{bet}}/(10^9 \text{ s}^{-1})$
9,10-DCA + I <sup>-</sup>	0.0	< 0.1 <sup>a</sup> )
1-CNN + I <sup>-</sup>	-0.4	0.48 ± 0.07 <sup>b</sup> )
<i>p</i> -Terphenyl + I <sup>-</sup>	-0.68	3.8 ± 1.3 <sup>b</sup> )
Biphenyl + I <sup>-</sup> [1]	-0.64	3.6
Naphthalene + I <sup>-</sup>	-0.85	> 10

<sup>a</sup>) The analysis may not be appropriate for this system, because the sum of the quantum yields of the singlet, triplet, and ion separation may be smaller than 1 due to fast recombination to the ground state.

<sup>b</sup>) The errors were estimated using the propagation of errors method assuming 10% errors in the absolute fluorescence (or intersystem crossing) quantum yields of the unperturbed aromatic molecules in polar solvents. The standard errors in the measurements of relative triplet yields never exceeded 10%. The measurements of the relative fluorescence quantum yields were relatively precise (1–2% standard errors).

As mentioned in the *Introduction*, the electron-transfer reaction between ketones or quinones with inorganic ions in H<sub>2</sub>O was the subject of investigations by *Treinin* and coworkers [10]. They observed the X<sub>2</sub><sup>-</sup> radicals in their transient absorption measurements, but only at very high concentrations of the quenchers. Moreover, they observed dihalide radicals also for SCN<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup> anions in the same quencher concentration range. On the other hand, *Kemp* and *Martins* [7] observed the diiodide and dithiocyanide anion radicals in electron transfer triplet quenching of 5-nitro-2-furoic acid at low iodide concentration (*ca.* 0.01M) in MeCN but at 0.21M KSCN in acetone.

Two processes may be considered, both contributing towards faster back electron transfer in MeOH than in MeCN. In alcohols, the charge-transfer states for the investigated systems are lying *ca.* 0.2–0.3 eV higher than in MeCN [2]. The larger energy gap between the CT and molecular triplet state accelerates back electron transfer to the triplet state (*normal* Marcus region) in alcohols compared to MeCN. Furthermore, we should expect a contribution from the finite rates of solvation of the complexes formed in the forward electron transfer. The solvation of dipoles and charges in MeCN is faster than in MeOH solutions (the longitudinal dielectric relaxation times for MeCN and MeOH at room temperature are 0.2 [26] and 3.6 ps [27], respectively). If we assume that back electron transfer competes with the solvation processes, which are slower in MeOH compared to MeCN, the *dynamical* energy gap between CT and triplet states will be greater in MeOH.

Moreover, if we assume that complexation of (Ar<sup>-</sup>/X) by X<sup>-</sup> is diffusion-controlled, the complexation rate constant in MeOH should be *ca.* two times lower than in MeCN. The above reasons may be responsible for the decrease of the ion separation yield in MeOH. Reversibility of the formation of (Ar<sup>-</sup>/X<sub>2</sub><sup>-</sup>) in alcohols cannot be ruled out.

The back electron-transfer rate constants measured for 9,10-anthraquinone-2-sulphonate and inorganic anions in H<sub>2</sub>O [10] are much higher than those measured in this work due to the larger energy gap between the <sup>3</sup>CT and ground states (*ca.* 1.5 eV), hence higher anion concentrations were needed to observe the radicals in flash photolysis experiments. For 5-nitro-2-furoic acid and I<sup>-</sup> in MeCN, where this energy gap is equal 0.55 eV, the diiodide radical anion appears at lower concentration (0.01M) [7].

*Treinin* and coworkers [10] observed a heavy-atom effect in triplet radical pairs. The rate constant of back electron transfer depended on the spin-orbit coupling parameter of the halogen or S-atom ( $X_2^-$  radicals have no orbital *momentum*, so back electron transfer in  $Ar^-/X_2^-$  leading to  $Ar + 2X^-$  may be excluded). In our case, we do not observe such a correlation (assuming intra-radical spin-orbit interaction, we expect preference for  $X_2^-$  formation for  $SCN^-$  and  $Br^-$  rather than for  $I^-$ ). A possible explanation is that spin inversion in the radical pair is much faster than the spin-allowed electron transfer from the triplet radical pair to the molecular aromatic triplet. Then, the back electron transfer is rate-limiting for the decay of  $^1(Ar^-/X)$ . In the systems investigated by *Treinin* and coworkers [10], the spin-allowed back electron transfer from  $^1(Ar^-/X)$  to the ground state was much faster than spin inversion in the radical pair due to the relatively large energy gap between the mentioned states. Hence, the decisive step in ion separation was spin inversion.

The assumption made by *Treinin* and coworkers [10], that complexation of  $^1(Ar^-/X)$  radical pairs and halide or thiocyanide radicals at high concentrations of inorganic anions is governed by the same rules seems to be inadequate for the systems investigated in the present work.

Table 3 shows that our estimates for the values of the back electron-transfer rates change with the free energy of back electron transfer to the triplet state. To obtain these estimates, we assumed that back electron transfer to the ground state can be neglected due to the large energy gap between the CT and ground states.

In summary, radical ions formed in fluorescence quenching of aromatic molecules by inorganic ions in MeCN were to our knowledge observed for the first time. The delicate balance between back electron-transfer rates in  $^1(Ar^-/X)$  and the rates of formation and dissociation of  $^1(Ar/X_2^-)$  in various systems is held responsible for the widely different yields of radical ions observed by various investigators [7] [10].

**Experimental.** – 1-CNN and 9,10-DCA were crystallized from MeOH and toluene, respectively. Solvents were of spectroscopic grade. All measurements were performed after degassing by the freeze-pump-thaw technique. Transient absorption measurements were performed by excitation with 308- or 351-nm pulses (pulse width *ca.* 20 ns) from an excimer laser (*Lambda-Physik EMG 101*). The fluorescence measurements were recorded on a *Spex Fluorolog 2* (Model 111C) with a multialkali R928 photomultiplier tube operated as a quantum counter. There was no appreciable absorption of any of the quenchers at the excitation wavelength of 308 nm. To ensure that radicals were produced only by electron transfer from anions to excited aromatic molecules and not by direct excitation of the anions, the following experiment was performed. For measurements with 9,10-DCA, the samples were very concentrated (*ca.*  $3.2 \cdot 10^{-4}$  M) due to very low absorption of 9,10-DCA at 308 nm. With 0.06M NaI in MeCN, we observed a strong absorption band around 450 nm (the tail of the  $I_2^-$  absorption band) and a band above 600 nm (the radical anion absorption [11] [20]). When we repeated the measurements with a tenfold diluted solution of 9,10-DCA, no absorption bands were detected under otherwise identical conditions. This experiment excludes electron ejection from excited anions as a significant contribution to the production of radical anions.

Absorption spectra showed no changes due to added quencher at excitation wavelengths  $\lambda \geq 308$  nm. Fluorescence emission and excitation spectra showed no changes in spectral distribution, only decreasing intensity of emitted light was observed upon the addition of the quenchers. *Stern-Volmer* plots were constructed from integrated fluorescence intensities, and the *Stern-Volmer* constants were obtained by linear regression. If the *Stern-Volmer* plots were nonlinear, as for 9,10-DCA and 1-CNN with  $I^-$  and  $SCN^-$  as quenchers, the initial slopes were taken as the *Stern-Volmer* constants. The relative triplet quantum yields were estimated from initial absorbances of the triplet decays  $A_{[Q]}^{I=0}/A_{[Q]}^{I=0}$ .

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**Appendix.** – *Derivation of Eqn. 5.* From *Scheme 3*, we obtain the following equation for the rate of formation of the charge-separated species  $\text{Ar}^- + \text{X}_2^-$

$$\frac{d[\text{Ar}^- + \text{X}_2^-]}{dt} = k_{\text{sep}}^a [{}^1(\text{Ar}^-/\text{X}_2^-)] + k_{\text{X}}^b [\text{X}^-] [\text{Ar}^- + \text{X}] \quad (\text{A1})$$

For the intermediate states we assume the steady state approximation.

$$[\text{Ar}^- + \text{X}] = \frac{k_{\text{sep}}^b [{}^1(\text{Ar}^-/\text{X})]}{k_{\text{X}}^b [\text{X}^-]} \quad (\text{A2})$$

$$[{}^1(\text{Ar}^-/\text{X}_2^-)] = \frac{k_{\text{X}} [\text{X}^-] [{}^1(\text{Ar}^-/\text{X})]}{k_{\text{sep}}^a + k_{-\text{X}}}$$

$$[{}^1(\text{Ar}^-/\text{X})] = \frac{k_{\text{et}} [\text{X}^-] [\text{Ar}^*] + k_{-\text{X}} [{}^1(\text{Ar}^-/\text{X}_2^-)] + k_{\text{is}} [{}^3(\text{Ar}^-/\text{X})]}{k_{\text{st}} + k_{\text{sep}}^b + k_{\text{X}} [\text{X}^-] + {}^g k_{\text{bet}}}$$

$$[{}^3(\text{Ar}^-/\text{X})] = \frac{k_{\text{st}} [{}^1(\text{Ar}^-/\text{X})]}{k_{\text{is}} + {}^t k_{\text{bet}}}$$

Simple algebraic rearrangement of the above equations leads to the equation

$$\frac{d[\text{Ar}^- + \text{X}_2^-]}{dt} = \frac{k_{\text{et}} [\text{X}^-] [\text{Ar}^*]}{\beta} \left( k_{\text{sep}}^b + k_{\text{sep}}^a \frac{k_{\text{X}} [\text{X}^-]}{k_{-\text{X}} + k_{\text{sep}}^a} \right) \quad (\text{A3})$$

$$\text{where } \beta = {}^g k_{\text{bet}} + k_{\text{sep}}^b + k_{\text{X}} [\text{X}^-] \frac{k_{\text{sep}}^a}{k_{-\text{X}} + k_{\text{sep}}^a} + {}^t k_{\text{bet}} \frac{k_{\text{st}}}{k_{\text{is}} + {}^t k_{\text{bet}}}$$

To analyze the results from flash photolysis, we integrate up to a time  $T$  which is assumed to be large on the time scale of fluorescence, but small on the time of transient radical decays.

$$[\text{Ar}^- + \text{X}_2^-]_T = A \int_0^T k_{\text{et}} [\text{X}^-] [\text{Ar}^*] dt \quad (\text{A4})$$

$$\text{where } A = \left( k_{\text{sep}}^b + k_{\text{sep}}^a \frac{k_{\text{X}} [\text{X}^-]}{k_{-\text{X}} + k_{\text{sep}}^a} \right) \frac{1}{\beta}$$

Now, we assume that concentration of  $\text{Ar}^*$  decays exponentially, according to the formula

$$[\text{Ar}^*] = [\text{Ar}]_0 \exp\left(-t \frac{1}{\tau^0} + k_{\text{et}} [\text{X}^-]\right) \quad (\text{A5})$$

where  $\tau^0$  is the fluorescence lifetime of the unperturbed aromatic molecule. By solving of above integral (A4), we obtain

$$[\text{Ar}^- + \text{X}_2^-]_T = \frac{k_{\text{et}} [\text{X}^-]}{\frac{1}{\tau^0} + k_{\text{et}} [\text{X}^-]} A, \quad (\text{A6})$$

and the last equation may be rewritten as

$$\frac{[\text{Ar}^- + \text{X}_2^-]_0}{[\text{Ar}]_0} = \Phi_{\text{sep}} = \frac{\alpha}{\beta} \left( k_{\text{sep}}^b + k_{\text{sep}}^a \frac{k_{\text{X}} [\text{X}^-]}{k_{-\text{X}} + k_{\text{sep}}^a} \right) \quad (\text{A7})$$

where  $\alpha = \frac{K_{\text{sv}} [\text{X}^-]}{1 + K_{\text{sv}} [\text{X}^-]}$  is the efficiency of fluorescence quenching.

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