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COMPARISON OF PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF AROMATIC CARBONYL VS. CYANO COMPOUNDS WITH ELECTRON DONORS IN CONDENSED PHASE: THE IMPORTANCE OF THE SPIN STATE OF THE GEMINATE ION PAIR FOR OBTAINING HIGH ION YIELDS.

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Dedicated to Professor M.J.S. Dewar on the occasion of his 70th birthday, in grateful appreciation of his outstanding contributions to chemical science and to the formation of young chemists.

ABSTRACT

Photoinduced electron transfer reactions in acetonitrile with benzophenone, anthraquinone, 9-cyanoanthracene and 9,10-dicyanoanthracene as electron acceptors, and with 1,4-diazabicyclo[2,2,2]octane and N,N-dimethylaniline as electron donors have been studied with ns-laser flash photolysis and fluorescence quenching measurements. For these systems the resulting free ion yield depends on the spin state of the geminate ion pair: its separation is very efficient if formed in a triplet state (carbonyl compounds/donors), while it is very inefficient if formed in a singlet state (cyanoanthracenes/donors). In the triplet systems, geminate back electron transfer is limited by the rate of spin flip

PRELIMINARIES : Relationship between the work of Professor M.J.S. Dewar and the present work.

The technique of UV-photoelectron spectroscopy (PE-spectroscopy) was recognised by Professor M.J.S. Dewar shortly after its development in the mid sixties as a decisive tool for justifiying the model of Molecular Orbital Theory. In 1968, Professor Dewar had already installed a corresponding experimental research group, its first report dealing with the PE-spectrum of cis-1,3-butadiene [1a]. Simultaneously his theoretical research group elaborated MO-programs generating orbital energies of all kinds of molecules. The bridge between experimental and theoretical advances was provided by Koopmans theorem, one of the most direct links existing between Hartree-Fock-type quantum calculation and experimental chemistry. The work of Professor Dewar and his collaborators widely supported the validity of that link, an early report being cited in [1b].
PE-spectroscopy however is not limited to these types of investigations : it also allows a better understanding of the nature of the electronic states of the studied compounds [2] as well as a direct experimental insight into some of the electronic states of the corresponding open-shell cations [3]. The latter species are increasingly recognised as intermediates in all kinds of important chemical transformations where charge-transfer steps are involved. While these take place commonly in condensed phases, PE-spectroscopy provides data about the isolated ions in the gas phase. In order to gain information about the ions in condensed phase, various techniques for ionising the neutrals have been developed, among them bimolecular photoactived charge-transfer from an excited donor (D) to a ground

state acceptor (A), or vice versa in solution (Weller–route). The present paper considers in detail the experimental conditions required to obtain high free ion yields in condensed–phase electron transfer reactions, this being a prerequisite for obtaining reliable data on these species.

SPECIFIC OUTLINE OF THE PROBLEM

A large number of theoretical and experimental studies have been performed on electron transfer processes starting from neutral precursors [4], as these represent one of the most important elementary chemical steps. A high separation efficiency of the geminate ion pair formed in the primary process is clearly the crucial condition to obtain a high free ion yield. The question arises, what are the factors which influence this separation efficiency? It has been suggested [5] that the energy gap between the ion pair state and the ground state may have an influence on the charge separation efficiency: a small gap would favour charge recombination and thereby decrease the separation probability. On the contrary, a large gap would slow down the rate of recombination and increase the ion yield. Indeed, Iwa et al.[6] have observed a linear dependence between the free enthalpy of reaction and the ion yield in a series of closely related systems.

In the present paper, we report a study of electron acceptors benzophenone (BP), anthraquinone (AQ), 9–cyanoanthracene (CNA) and 9,10–dicyanoanthracene (DCNA) with 1,4–diazabicyclo [2,2,2]octane (DABCO) and N,N–dimethylaniline (DMA) in acetonitrile (MeCN) by laser flash photolysis and fluorescence measurements. The acceptors have been chosen for their different triplet yields Φ_T: the two carbonyls are known to have $\Phi_T \approx 1$, whereas the two cyanoanthracenes have $\Phi_T \approx 0$. We have focused our attention in particular on the reason why in some electron donor(D)/acceptor(A) systems the charge separation efficiency is close to unity, while in others it is very low.

RESULTS

BENZOPHENONE (BP)

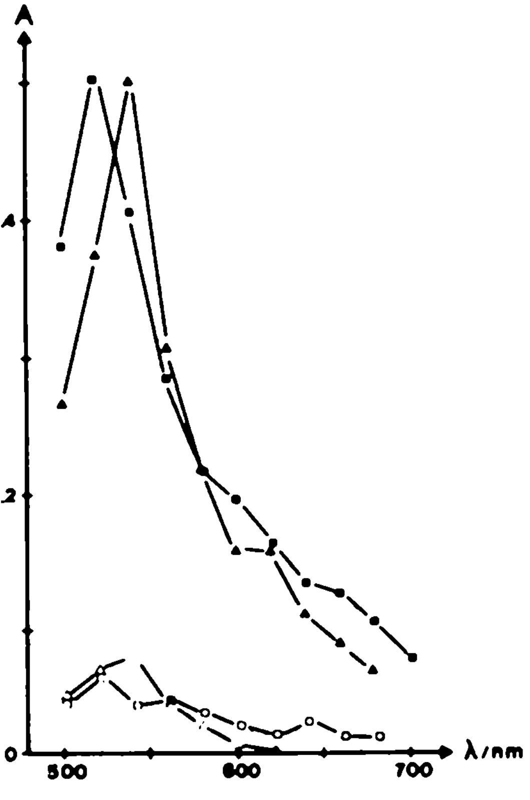


Fig. 1. *Transient spectra obtained from solutions of BP in MeCN (■) and in benzene (▲) directly after laser pulse (■▲) and after 9 µs (□△).*

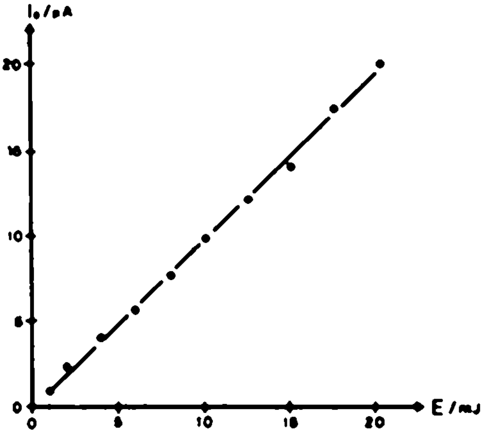


Fig. 2. *Initial transient photocurrent* I_0 *observed in a solution of BP in MeCN as a function of the laser light energy* E.

The transient absorption of a 8x10^{-5}M deoxygenated solution of BP in MeON and in benzene irradiated at 355 nm with a 25 ns laser pulse has been measured between 500 and 700 nm. In MeON the spectrum of the initial transient absorption corresponds mostly to triplet–tAfter 3 μs, a small band appears at 630 nm in MeCN, while it is not present in benzene (Figure 1). It corresponds to the radical anion absorption (BP^{-})[8]. In the presence of oxygen, the decrease of the other bands is very pronounced, as expected for a T–T absorption. The presence of charged species is confirmed by measurement of the transient photocurrent which increases linearly with the excitation light intensity, indicating a monophotonic process (Figure 2). A biphotonic process is unlikely since a plot of I_0 vs. E is a straight line which passes through the origin [9].

With DABCO addition, the photocurrent increases by a factor of 40. The behaviour of the transient absorption at 630 nm is very similar : with small addition of this donor, the ion yield enhancement is very strong, and at higher DABCO concentration the ion absorption reaches a maximum value which keeps constant even at very high DABCO concentration (Figure 3 and 4). Concurrently the T–T absorption is quenched.

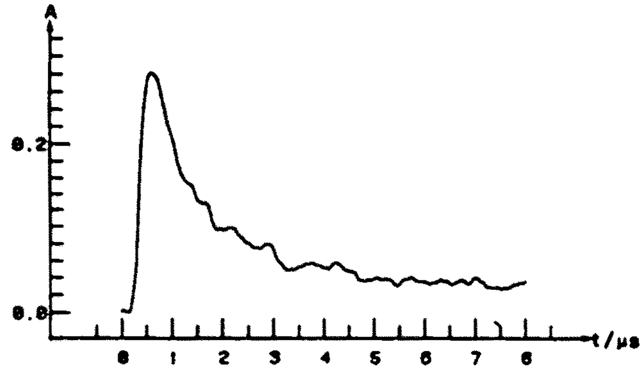


Fig.3. *Transient absorption of the radical anion BP^{-}* (at 630 nm) *in MeCN* (*DABCO* mole fraction X_D=0.137)

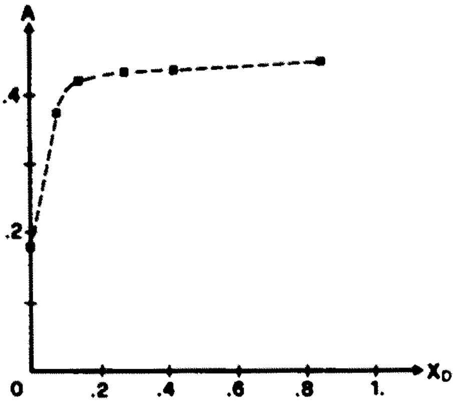


Fig.4. *Initial absorbance of BP^{-}* (at 630 nm) *as a function of the DABCO mole fraction* (X_D).

From the molar decadic extinction coefficient of BP^{-} at 630 nm [8] and the number of absorbed photons, we have estimated the free ion yield Φ_{ion} = 0.95±0.10.

Kinetic studies of BP^{-}/DABCO^{+} free ion recombination show that within our time resolution (>20 ns) the process is second order with an observed rate constant k_{rec}= 2.06±0.30x10^{10} M^{-1}s^{-1}. This value is close to the diffusion rate constant in MeCN calculated from the Debye equation:

$$k_{dif} = \frac{8 \cdot R \cdot T}{3000 \cdot \eta} = 1.91 \times 10^{10}\ M^{-1}s^{-1} \qquad (1)$$

R being the gas constant in erg mol^{-1}K^{-1}, T the absolute temperature and η the solvent viscosity in centipoises. In the case of charged species however, this equation needs a modification according to Debye [10] and Eigen [11] for the electrostatic interaction:

$$k_{dif} = \frac{2 \cdot R \cdot T}{3000 \cdot \eta} \cdot \frac{(r_A + r_D)^2}{r_A \cdot r_D} \cdot \frac{b}{e^{b} - 1} \qquad (2)$$

where $b = z_A z_D e^2/\varepsilon k_B T(r_A + r_D)$.

r_D and r_A being the ionic radii, z_A and z_D the ionic charges, ϵ the solvent static dielectric constant, and k_B the Boltzmann constant. For the present systems, assuming that the electron transfer takes place at contact distance, a mean value of $k_{dif}=4.2\times10^{10}$ $M^{-1}s^{-1}$ is then obtained, i.e. about twice that of k_{rec}.

When DMA is used instead of DABCO, the 680 nm transient absorption disappears. This is due to a photochemical reaction. The irreversible photoreduction of $BP^{\cdot-}$ by $DMA^{\cdot+}$ is well established [12] involving H–transfer from the cation to the anion. This process is favorable due to formation of a 3e⁻–2 center bond in the resulting cation. In the case of DABCO, however, the same process would not lead to formation of such a bond due to the orthogonality between the n–orbital at the N–atom and the ensuing 2p–orbital at the adjacent trigonal C–atom; it is therefore energetically less favorable.

ANTHRAQUINONE (AQ)

A 2×10^{-3} M deoxygenated solution of AQ in MeCN shows a weak transient absorption in the same region as the radical anion prepared by γ–irradiation in a MTHF glass. Its optical density at 543 nm corresponds to an ion yield $\Phi_{ion} = 0.02$ under the same conditions, the transient photocurrent being weak as well.

With DABCO addition to the AQ–solution, the transient absorption increases in the same way as occurs for the BP–solution, the maximum ion yield being $\Phi_{ion} = 0.88 \pm 0.09$. Concurrently, the T–T absorption is also quenched. Figures 5 and 6 show the close analogy between the transient spectrum and the electronic absorption spectrum of $AQ^{\cdot-}$ prepared by γ–irradiation in a rigid glass. The photocurrent increases by a factor of 20. Replacing DABCO by DMA leads to very similar results: the ion yield is $\Phi_{ion} = 0.90 \pm 0.09$ and the photocurrent increases by a factor of 20. The kinetics of free ion recombination are second order for both donors with rate constants of $2.03 \pm 0.10\times10^{10}$ $M^{-1}s^{-1}$ for DABCO and of $1.90 \pm 0.20\times10^{10}$ $M^{-1}s^{-1}$ for DMA.

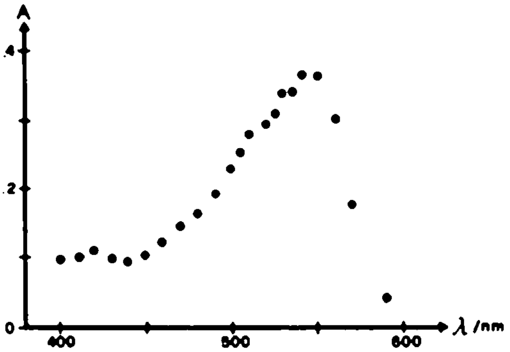


Fig.5. *Initial transient absorption spectrum of a solution of AQ in MeCN following laser excitation (DABCO* mole fraction, X_D=0.91)

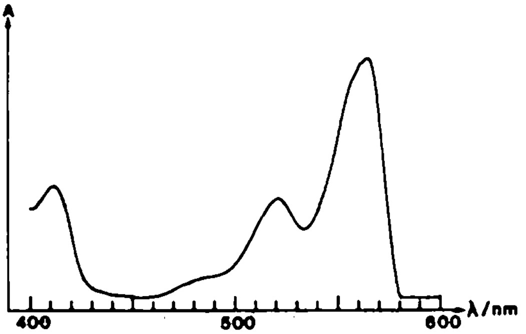


Fig.6. *Electronic absorption spectrum of the radical anion of AQ prepared by γ–irradiation in a MTHF glass*

CYANO–COMPOUNDS

In order to know the regions of electronic absorption of $CNA^{\cdot-}$ and $DCNA^{\cdot-}$, these species have been prepared by γ–irradiation in MTHF glass. The reaction is [13]:

$$MTHF \xrightarrow{\gamma\text{-irrad.}} MTHF^{\cdot+} + e^-$$

$$M + e^- \longrightarrow M^{\cdot-} ,$$

M being the solute molecule.

The G value of total scavengeable electrons for this kind of glass has been estimated as 2.58 [14]. The absorbed dose being known, the molar decadic extinction coefficient is then easily determined. Knowledge of this value is essential for making an estimation of the ion yield in flash photolysis experiments.

Figure 7 shows the electronic absorption spectra of CNA$^{\cdot}$ and DCNA$^{\cdot}$ obtained in these experiments.

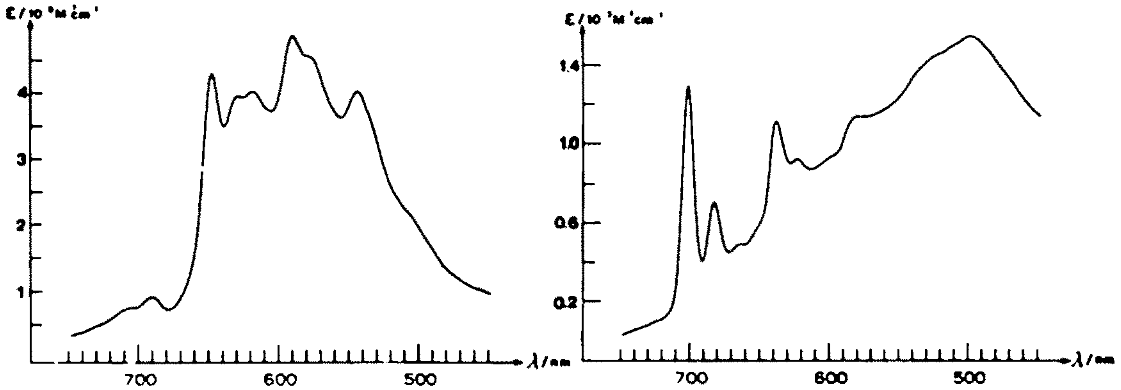


Fig. 7. *Electronic absorption spectra of CNA$^{\cdot}$*(left) *and DCNA$^{\cdot}$*(right) *prepared by γ-irradiation in a MTHF glass.*

9-CYANOANTHRACENE (CNA)

A deoxygenated solution of 2×10^{-4}M CNA in MeCN irradiated at 355 nm shows a weak transient absorption at 596 nm. On irradiation in the presence of DABCO, the optical density increases very weakly by a factor of 1.2 and the ion yield does not exceed 0.08.

The CNA fluorescence is strongly quenched by DABCO, the quenching rate constant being 1.66×10^{10} $M^{-1}s^{-1}$. Even in a non-polar solvent like cyclohexane, no exciplex emission has been observed.

Using DMA instead of DABCO, the results are similar and the quenching rate constant is 1.56×10^{10} $M^{-1}s^{-1}$.

9,10-DICYANOANTHRACENE (DCNA)

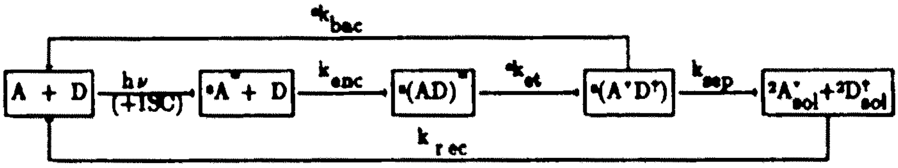
Systems with DCNA show a very similar behaviour to those with CNA. The observation of the radical anion absorption is difficult since the triplet-triplet absorption lies very close to the anion absorption region. In the absence of a donor, no transient absorption at 700 nm nor any photocurrent have been detected. With DABCO or DMA additions, there is still no detectable transient absorption but a very small photocurrent is observed. It is 150 times smaller than in the BP/DABCO system.

DCNA fluorescence is quenched by DABCO and by DMA, the quenching rate constants being 2.13×10^{10} $M^{-1}s^{-1}$ and 2.43×10^{10} $M^{-1}s^{-1}$, respectively.

DISCUSSION

As already mentioned in the introduction, the electron acceptors have been selected to fall into two distinct classes: BP, AQ : $\Phi_T \approx 1$, and CNA, DCNA : $\Phi_T \approx 0$.

Clearly, for the first class the donor will quench the triplet state, while for the second class it will quench the singlet state. Accordingly, the encounter complexes and the ensuing geminate ion pairs will be formed with the corresponding multiplicities. The reaction sequence can then be summarised simply according to the scheme below with s=3 (i.e. triplet) for the first and s=1 (i.e. singlet) for the second class.



Note that k_{enc}, k_{sep} and k_{rec} do not depend on the multiplicity by reasons given below.

Turning now to the results, they show clearly the very different behaviour of the carbonyl and the cyano–aromatic compounds. In all four cases electron transfer takes place and a geminate ion pair must be generated. In the cases of CNA and DCNA only a very small part separates into free solvated ions, whereas with BP and AQ essentially all ion pairs separate. For these last two systems, the kinetics of free ion recombination are second order with rate constants very close to the diffusional limit. This suggests that back electron transfer occurs essentially at the first encounter between the two ions.

A first question arises which to our knowledge has never been considered explicitely : Why then do these ions separate in the first place, only to recombine at the first encounter afterwards with subsequent back–electron transfer? Several factors can be considered:

- The excess energy liberated in forward electron transfer is concentrated strongly in the mode linking the two ions since this degree of freedom will suffer the strongest changes upon this reaction. This outcome will lead to particulary fast dissociation (within half of a vibrational period) since quenching of the excess energy by the medium may in this case be less competitive;
- The energy balance of the back electron transfer in the cage can influence its rate ;
- The spin state of the geminate ion pair can favour either separation or back electron transfer;
- The Coulombic forces: For electron transfer between phenothiazines and viologen, a linear dependence between the free ion yield Φ_{ion} and the Coulombic work term between products (p) and reactants (r), $w_p - w_r$, has been reported [15]:

$$w(\mathrm{erg^{-1}mol}) = \frac{{}^{s}A\,{}^{s}D\,e^{2}N}{\epsilon\sigma(1+k\sigma)}\ ,\ k(\mathrm{cm^{-1}}) = \left(\frac{8\pi N^{2}e^{2}\mu}{1000\epsilon RT}\right)^{1/2} \qquad (3)$$

where σ is the distance between the centers of the ions and μ the ionic strength.

The energy balance for electron transfer reactions are calculated with the Rehm–Weller equation [16] using the modified Coulomb term of [17]:

$$\Delta G_{et} = E_{ox}(D) - E_{red}(A) - E^{*} + C \qquad (4)$$

$$C = -\frac{e^{2}}{2n^{2}(r_{A}+r_{D})}$$

applicable in cases of Van–der–Waals contact between donors and acceptors. The values of the different parameters are listed in the following table for the different possible reactive states of the molecules considered in this work.

TABLE 1: Values of the reduction potential E_{red}, the excited state energy E^{*}, the Coulomb term C, the free energy of electron transfer reaction ΔG_{et} calculated from eq.(4), and the observed free ion yield Φ_{ion} for the different donor/acceptor systems (E_{ox}(DABCO)=0.56 vs. SCE [18], E_{ox}(DMA)=0.79 vs. SCE [19]). Energies in eV and redox potentials in V.

Acceptor(A)		$E_{red}(A)$	$E(A^{*})$	Φ_T	C	D=DABCO ΔG_{et}	Φ_{ion}	C	D=DMA ΔG_{et}	Φ_{ion}
BP	(T_1)	-1.73[20]	3.0	1.0[23]	-0.477	-1.19	0.95±0.10	-0.523	-1.01	a)
	(S_1)		3.2			-1.39			-1.21	a)
AQ	(T_1)	-0.94[21]	2.7	0.9[23]	-0.483	-1.68	0.88±0.09	-0.529	-1.50	0.88±0.09
	(S_1)		2.9			-1.88			-1.70	
CNA	(T_1)	-1.58[22]	≈1.8	≤0.07[24]	-0.480	-0.14		-0.526	0.04	
	(S_1)		3.04			-1.38	<0.08		-1.20	≤0.08
DCNA	(T_1)	-0.98[22]	≈1.8	≤0.1[24]	-0.470	-0.73		-0.519	-0.55	
	(S_1)		2.89			-1.82	≤0.05		-1.64	≤0.05

a) Not determined due to chemical reaction, see text.

The results show that no correlation exists between the energy balance of the photoinduced electron transfer processes and Φ_{ion}. If the excess energy were the driving force for ion separation, the CNA/donor and DCNA/donor reactions should have a much higher Φ_{ion}. The results show furthermore no correlation between Φ_{ion} and the magnitude of the Coulomb term.

Note that a linear dependence between free enthalpy and separation efficiency has been reported in [6]. In this case however, the two components (oxonine–ion and a neutral donor) do not acquire opposite electric charges after electron transfer. The Coulombic force has not to be overcome and for this reason the separation of the particles is easier than in the cases considered in the present paper.

Ion separation certainly depends on the rate of the competing back electron transfer process in the geminate ion pair as implied in the scheme shown above:

$$^{s}\Phi_{ion}=\frac{k_{sep}}{^{s}k_{bac}+k_{sep}} \quad (s=1 \text{ or } 3) \tag{5}$$

noting that k_{sep} is considered to be independent of the spin state of the geminate pair, being determined only by diffusion [25](i.e. 5×10^{8} s^{-1} under our conditions). It is therefore possible to calculate $^{s}k_{bac}$ (Table 2).

TABLE 2: Values of ΔG_{bac} calculated from eq (6) and of approximate values for k_{bac} calculated from eq.(5). Energies in eV.

ACCEPTOR	ΔG_{bac}(DABCO)	ΔG_{bac}(DMA)	$^{s}k_{bac}$ ($M^{-1}s^{-1}$)	s
BP	−1.81	−1.99	$\simeq 5 \cdot 10^{7}$	3
AQ	−1.02	−1.20	$\simeq 10^{8}$	3
CNA	−1.66	−1.84	$\simeq 10^{10}$	1
DCNA	−1.07	−1.26	$\simeq 2 \cdot 10^{10}$	1

According to the semiclassical Marcus–Hush model [4a,4i], $^{s}k_{bac}$ in principle depends on the free reaction enthalpy ΔG_{bac}:

$$\Delta G_{bac} = -E_{ox}(D) + E_{red}(A) - C \tag{6}$$

The values of ΔG_{bac} calculated from equations (4) and (6) for the different reactions are found in table 2.

It follows that there is no relationship $k_{bac} = f(\Delta G_{bac})$ discernable. Indeed, the results fall clearly into two classes which correspond to those defined above for the acceptors. For CNA and DCNA which react from the singlet state, the rate of back electron transfer is too high to allow the geminate ion pair to separate, hence $\Phi_{ion} \approx 0$. For the carbonyl compounds, there must be a factor that slows down the back electron transfer and this must be clearly the spin state of the geminate ion pair. The rate constant $^{s}k_{bac}$ is then limited by the spin flip rate constant which is of the order of the electronic spin lattice relaxation time, 10^{-7} s or more. The ions will therefore separate and the spin correlation will eventually be lost. The observed values of k_{bac} are about half those for k_{dif} calculated with the

Debye–Eigen equation (eq. 2). A smaller value of k_{rec} with respect to k_{dif} is expected since theoretically only 25 % of the homogenous encounters lead to a singlet ion pair which can decay to ground state neutrals by back electron transfer.

Note that in the singlet systems considered in this paper the values of ΔG_{bac} stay between −1 and −2 eV, which corresponds to the top region of the Marcus curve $k_{bac} = f(\Delta G_{bac})$ [26]. For more exergonic reactions k_{bac} is expected to fall off ('inverted region'). k_{sep} becomes increasingly competitive, leading to increasing Φ_{ion}.

CONCLUSION

We have investigated donor/excited acceptor systems for which the final ion yields are very different. In all these cases, the electron transfer takes place by the diffusion controlled quenching of the excited states, but the ion pair separation into free ions does not occur in every case. The excess energy does not seem to be a decisive driving force for the separation, nor is the ion yield dependent on the free reaction enthalpy of geminate back electron transfer ΔG_{bac}.

The crucial parameter for ion separation appears to be the spin state of the geminate ion pair. In the case of a triplet pair, the back electron transfer is limited by the spin flip hence allowing the ions to separate with high yield. In the case of the singlet pair, the ion yield depends strongly on the rate of geminate back electron transfer, which is much faster than for the triplet pair. Hence, for the present systems, the ion yield is low.

EXPERIMENTAL

BP (*Fluka*) was recrystallised twice from ethanol. AQ (*Fluka*), CNA (*Aldrich*) and DCNA (*Kodak*) were recristallised twice from chloroform. DMA (*Fluka*) was distilled using a *Fischer* column under Ar and DABCO (*Fluka*) was sublimed under vacuum. MTHF (methyl–tetrahydrofuran) (*Fluka*) was purified according to [27]. Benzene and MeCN (*Fluka* UV grade) were used without further purification. All solutions were degassed by bubbling N_2 for 10 to 15 min.

The laser–flash apparatus and the data acquisition system were described earlier [28][29].

Electronic absorption spectra of the radical anions were obtained by exposing frozen solutions (T=77 K) of the cyano–compounds in MTHF to 1.3 MeV γ–radiation from a ^{60}Co–source (0.18 Mrad/h) for 8 h. Optical spectra were recorded on a *Perkin–Elmer Lambda 9* UV/VIS/NIR spectrophotometer interfaced to a *PE 3600* microcomputer which was itself connected to a *Olivetti M24* personal computer where the spectra were worked up digitally.

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