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Heavy Atom Substituents as Molecular Probes for Solvent Effects on the Dynamics of Short-lived Triplet Exciplexes

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Lösungsmitteleffekte / Photochemie / Schweratomeffekte / Triplettexciplexe

The influence of heavy atom substituents (Br, I) in the electron donor aniline on the electron transfer reaction with thiopyronine triplet is investigated by flash spectroscopy in solvents of different viscosity and polarity. Triplet quenching constants and radical yields are determined. The results are analysed in terms of decay constants of an intermediate triplet exciplex where the heavy atom substituents significantly enhance the intersystem crossing process leading to singlet ground state formation and thus diminishing the radical yield due to exciplex dissociation. The sensitivity of the radical yield to solvent effects is strongly enhanced by heavy atom substitution though the solvent effects proper on the exciplex dynamics are substituent independent. The heavy atom effect is used to study the solvent cage effect on exciplex dissociation by means of viscosity variation. The exciplex dissociation lifetime is proportional to solvent viscosity, however, it contains a constant contribution which may be attributed to exciplex bonding. By means of the heavy atom probes it is found that increasing solvent polarity intersystem crossing in the exciplex is favored over exciplex dissociation into radicals. A tentative explanation is given in terms of solvent polarity dependence of the electronic energy gap between exciplex and corresponding Franck-Condon ground state.

Der Einfluß von Schweratomsubstituenten (Br, I) im Elektronendonor Anilin auf die Elektronentransferreaktion mit dem Thiopyronintriplett wurde blitzspektroskopisch in Lösungsmitteln verschiedener Viskosität und Polarität untersucht. Es wurden die Triplettlöschkonstanten sowie die Radikalausbeuten bestimmt. Mit Hilfe dieser Ergebnisse wurden relative Zerfallskonstanten eines intermediär gebildeten Triplettexciplexes ermittelt, in dem die Schweratomsubstituenten den zum Singlettgrundzustand führenden Intersystem-Crossing-Prozeß signifikant verstärken und so die Radikalausbeute, die aus der Exciplexdissoziation resultiert, vermindern. Die Empfindlichkeit der Radikalausbeute für Lösungsmitteleffekte wird durch die Schweratomsubstituenten gesteigert, obwohl der eigentliche Lösungsmitteleffekt auf die Exciplexdynamik substituentenunabhängig ist. Mit Hilfe des Schweratomeffekts läßt sich die Variation des Cage-Effektes des Lösungsmittels auf die Exciplexdissoziation bei steigender Lösungsmittelviskosität verfolgen. Die Dissoziationslebensdauer des Exciplexes wächst linear mit der Viskosität, enthält jedoch einen viskositätsunabhängigen Beitrag, der sich der Exciplexbindung zuschreiben läßt. Mit zunehmender Lösungsmittelpolarität wird der Intersystem-Crossing-Prozeß im Vergleich zur Exciplexdissoziation in Radikale begünstigt. Zur Erklärung wird eine Polaritätsabhängigkeit des Franck-Condon-Faktors des strahlungslosen Prozesses diskutiert.

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1. Introduction

Since the formation of exciplexes, i.e. excited molecular complexes formed in a reaction of an electronically excited molecule and a ground state molecule, was discovered by Leonhardt and Weller [1] many subsequent investigations have shown that exciplex formation is a quite general phenomenon and is of fundamental importance as a photochemical primary reaction (for recent reviews see Refs. [2–5]). Whereas singlet exciplexes are normally detected by their fluorescence which is characteristically different from that of their isolated components, information on triplet exciplexes in fluid solution is more difficult to obtain. Although there are many investigations on the phosphorescence of excited EDA-complexes in rigid matrices [7, 8], spectroscopic evidence of dynamically formed triplet exciplexes is quite rare. Weller reports a case of delayed exciplex fluorescence indicative of an intermediate triplet exciplex [9]. From flash spectroscopic as well as phosphorescence measurements Whitten and coworkers obtained information on triplet exciplex formation in the quenching of metallo-porphyrin triplets [10, 11]. Spectroscopically, the latter triplet exciplexes behaved quite similar to the uncomplexed triplets from which the exciplexes can be distinguished mainly by kinetic means, the lifetime of the triplet exciplexes being in the region of a few microseconds.

Apart from these few examples our direct information on triplet exciplexes is quite poor and can in no way be compared with the vast information available for singlet exciplexes.

Most of the prominent exciplex studies have been performed in non-polar or weakly polar solvents. One reason for this is the drastic decrease of exciplex fluorescence in polar solvents due to (a) exciplex dissociation into a non-fluorescent radical ion pair [12] combined with a decrease in the exciplex fluorescence rate constant [13] or (b) due to direct formation of the radical ion pair in the fluorescence quenching reaction without intermediate exciplex formation [12]. Nevertheless, in recent investigations weak exciplex fluorescence was detected even in solvents as polar as methanol and acetonitrile [14–16] demonstrating that the radical ion pairs are formed at least in part via the exciplex. In these cases the exciplex lifetime amounts to only a few nanoseconds.

In photochemistry excited triplet states of dyes are of special importance as sensitizers [17]. There are two basic sensitizing mechanisms: Electronic energy transfer or electron transfer between the dye triplet and some substrate (for a competition of both see e.g. Ref. [18]). To elucidate the redox mechanism reactions with several dye triplets and many electron donors have been investigated in this laboratory during the last years [19, 20]. Observations on physical triplet quenching by electron donors accompanying the radical formation process lead us to assume that triplet exciplexes are important intermediates in these reactions [21].

Since in polar solvents exciplexes usually separate into radicals within a few nanoseconds it appears unlikely that triplet exciplexes can be detected by their phosphorescence under such conditions. In a recent paper [22] we provided indirect evidence for the formation of triplet exciplexes as intermediates in electron transfer reactions. We studied the reaction of thionine triplet as an electron acceptor with aniline and its monohalogen derivatives as electron donors in methanol. In these reactions the halogen substituents have systematic influence on the radical yield (extrapolated to complete triplet quenching) which could be explained satisfactorily by the following mechanism, strongly supported by a recently determined magnetic field effect [23]:

$$\begin{tikzcd} {}^3\dot{A}^+ + {}^1D \arrow[r, "k_q"] & {}^3(\dot{A}\dot{D}^+) \arrow[r, "k_{fr}"] \arrow[d, "k_{isc}"] & {}^2A^\cdot + {}^2D^{\cdot+} \\ & {}^1(A^+D) & \end{tikzcd}$$

The rate determining step in the quenching of the excited cationic dye triplet (${}^3\dot{A}^+$) by the electron donor (D) is the formation of a triplet exciplex with *radical-pair-like* electronic structure (${}^3(\dot{A}\dot{D}^+)$). The triplet exciplex has two decay channels: dissociation to the free radicals (rate constant k_{fr}) and intersystem crossing with back transfer of the electron to the donor leading to the formation of the ground state of the reaction partners (rate constant k_{isc}). The radical yield observed is determined by the two decay constants of the exciplex:

$$\Phi_r = \frac{k_{fr}}{k_{fr} + k_{isc}} \tag{1}$$

The analysis of the radical yields showed that substituting aniline by one halogen atom has no significant influence on the rate constant k_{fr}. The rate constant k_{isc} can be written as a product of a factor F_{el}, describing the electronic coupling strength, and a factor F_{FC} which is mainly determined by the Franck-Condon weighted density of vibrationally excited ground state levels isoenergetic with the exciplex (Eq. (2))

$$k_{isc} = F_{el} \cdot F_{FC} \,. \tag{2}$$

The halogen substituents have significant influence on the electronic factor F_{el} only. The latter can be approximately described by:

$$F_{el} \propto \zeta^2_{Hal}\, c^2(\mathrm{pos}_{Hal}) \,, \tag{3}$$

where ζ_{Hal} is the atomic spin-orbit coupling constant of the halogen and $c^2(\mathrm{pos}_{Hal})$ is the Hückel spin density transferred to the position of the halogen atom by the electron transfer. The latter factor readily explains the positional dependence of the substituent effect (para > ortho > meta).

1.1. The Probe Function of Heavy Atom Substituents

From Eqs. (1) and (2) it follows that the radical yield is determined by three factors, characterizing the behaviour of the triplet exciplex (Eq. (4))

$$\Phi_r = \frac{1}{1 + F_{el}\dfrac{F_{FC}}{k_{fr}}} \,. \tag{4}$$

The experiments described in Ref. [22] demonstrate, how F_{el} can be modified by halogen substitution, F_{FC} and k_{fr} being approximately unaffected by this measure. As will be shown, however, the halogen substituents are very useful tools in studying e. g. solvent influences on k_{fr} and F_{FC}.

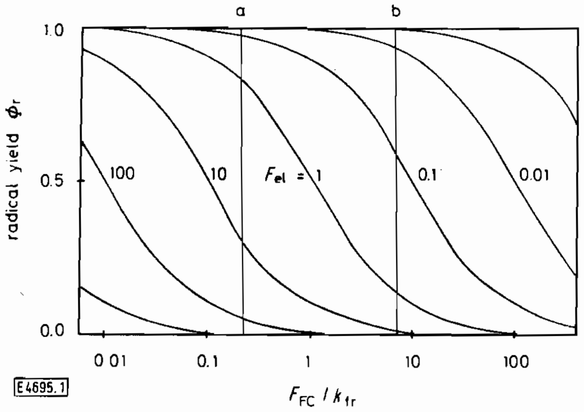


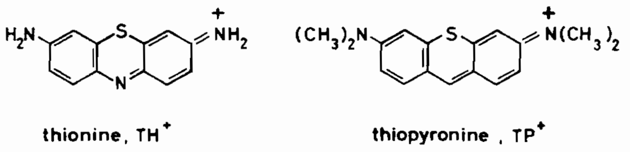
Fig. 1
Radical yield Φ_r (Eq. (4)) as a function of $\log(F_{FC}/k_{fr})$ with F_{el} as parameter

This is demonstrated in Fig. 1, where we plot the radical yield, given by Eq. (4) as a function of F_{FC}/k_{fr} using a logarithmic scale and treating F_{el} as a constant parameter. In this way we obtain identical but horizontally displaced s-shaped curves, their relative shift being determined by the electronic factor F_{el}. Assuming that a certain solvent change leads to a change in the exciplex behaviour corresponding to a change of F_{FC}/k_{fr} from a to b (see Fig. 1) the diagram clearly shows that the effect on the radical yield depends on the electronic factor, i. e. on the kind and position of the halogen substituent. Thus, by a suitable choice of the substituent, determining F_{el}, the radical yield can be made a most sensitive measure of changes in F_{FC} and k_{fr}, which are substituent independent and describe rather general properties of this type of exciplexes. It is in this sense that we regard the halogen substituents as probes for the dependence of the exciplex behaviour on external parameters. It may be of interest to note that the diagram (Fig. 1) is completely analogous to a diagram describing the degree of dissociation of an acid-base indicator as a function of pH of the solution. It is quite familiar that for an indication of pH that indicator will be best suited, the pK_a of which lies in the corresponding pH-range. Thus if we look upon $\log(F_{FC}/k_{fr})$ as a function of a solvent property and compare it with the pH then the electronic factor F_{el} is analogous to the pK_a of a pH-indicator.

In this paper we shall report how the concept of heavy atom probes can be used to detect effects of solvent viscosity and polarity on the behaviour of triplet exciplexes formed as intermediates in electron transfer reactions with an excited dye triplet.

1.2. Systems Investigated

Although the function of halogen substituents in aniline as probes for the exciplex behaviour has been established in the electron transfer reaction with thionine triplet as electron acceptor, for investigations with various solvents thiopyronine triplet appeared to be more convenient. In thiopyronine (TP^+) the ring nitrogen of thionine is replaced by a CH-group. Thus complications arising from the simultaneous appearance of two different protolytic forms of the semiquinone [21] are avoided.



Scheme I

In its photochemical behaviour thiopyronine is similar to thionine and methylene blue (N,N-tetramethylthionine). The photoreactions of thiopyronine have been studied in detail first by Morita and Kato [24] and later by Berg et al. [25]. The dye is of some importance in photobiology due to its very strong photodynamical efficiency [26].

To investigate the solvent influence on the reaction parameters k_q and Φ_r for a single donor-acceptor pair many measurements with different donor concentrations have to be performed in a variety of solvents. Therefore our present investigation only comprises a limited choice of the donors compared in Ref. [22]. To see the effect of heavy atom substitution most clearly, we selected the following donors: aniline, p-bromoaniline and p-iodoaniline, with almost equal one-electron oxidation potentials (0.87, 0.89, and 0.88 V, respectively, vs. s.c.e. in acetonitrile [27]).

2. Experimental

2.1. Apparatus

The flash apparatus used has been described by Kramer [28]. The flash lamp was filled with xenon (20 – 30 Torr), the electric energy of the discharge being 100 J (20 kV, 0.5 µF) the flash duration (FWHM) 3 µs. A Kodak Wratten filter No. 8 was inserted between the flash lamp and the photolysis cell to absorb light of wavelengths shorter than 450 nm. Due to the scatter of the flash intensity it was necessary to average about 10 – 15 signals to obtain radical yields with a relative accuracy of 3 – 4%.

2.2. Materials

Thiopyronine was synthesized according to a procedure described by Biehringer and Topaloff [29] and purified by several recrystallizations from concentrated hydrochloric acid. The composition of the crystals corresponds to a formula $TP^+Cl^- \cdot 1/2$ HCl. Without decomposition of the dye the hydrochloric acid can be removed to about 7 mol% by heating the material under vacuum (120 °C, 0.1 Torr). The final HCl-content was determined by conduction measurements in acetonitrile. The purified thiopyronine sample yielded a molar extinction coefficient in water (pH 7, λ_{max} = 563 nm) of $8.0 \cdot 10^4\ M^{-1}$ cm as compared to a value of $7.4 \cdot 10^4$ M^{-1} cm obtained by Morita and Kato [24] under the same conditions and of $1.02 \cdot 10^5\ M^{-1}$ cm in ethanol (λ_{max} = 565 nm) as compared to a value of $0.9 \cdot 10^5\ M^{-1}$ cm obtained by Lalitha and Haug [30] in the same solvent.

Donors: Aniline (Merck, reagent grade), distilled under vacuum, p-Bromoaniline (Merck, reagent grade) used without further purification, p-iodoaniline (Merck-Schuchardt, > 98%) recrystallized twice from petrolether (40 – 60 °C), N,N-Dimethylaniline (Merck-Schuchardt > 99%) distilled under vacuum, N,N-bromodimethylaniline (Fluka-Buchs, purum) recrystallized twice from methanol-water mixtures.

Solvents: Water, deionized and doubly distilled in a quartz apparatus, methanol (Merck, reagent grade), acetonitrile (Merck, zur Rückstandsanalyse), ethanediol (Merck, reagent grade), N-methylformamide (Fluka-Buchs, purum > 99%).

The dynamic viscosity was determined using calibrated viscosimeters according to Ubbelohde [31] at 22 °C. (For numerical values cf. upper and lower abscissa of the diagram Fig. 5).

3. Results

3.1. Photochemical Characteristics of Thiopyronine

The transient spectra obtained on flashing pure thiopyronine solutions in various solvents (see below) are similar to the ones described by Morita and Kato for aqueous solutions [24].

In oxygen- and donor-free solutions with a dye concentration of $1.5 \cdot 10^{-5}$ mol/l we find triplet lifetimes of about 80 microseconds for the solvents water, methanol and acetonitrile and 1250 µs for ethanediol. In donor-free solutions the decay of thiopyronine triplet is determined by its reaction with dye molecules in the ground state which, besides a great fraction of physical quenching, consists in a disproportionation reaction:

$$^{3}\overset{*}{\mathrm{T}}\mathrm{P}^{+} + {}^{1}\mathrm{TP}^{+} \rightarrow {}^{2}\mathrm{TP}^{\bullet} + {}^{2}\mathrm{TP}^{\dot{+}+} \qquad (5)$$

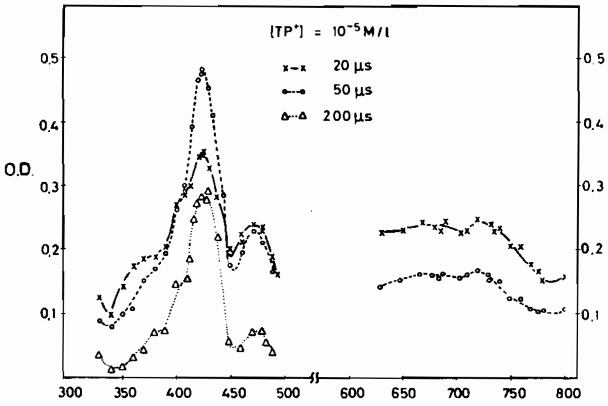


Fig. 2
Transient spectra of thiopyronine in methanol observed at different times after the excitation flash. Optical path length of cuvette 10 cm

Fig. 2 shows transient spectra obtained at different times after the flash in methanol as solvent. Whereas the absorption in the long wavelength region is due to the triplet alone, making it suitable for measurements of the triplet decay time, (molar extinction coefficients at 660 nm: ε = 4350, 4200, and 4560 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ for water, methanol and acetonitrile, respectively) the short wavelength part of the spectrum is a superposition of the spectra of triplet thiopyronine, semiquinone ($\mathrm{TP}^{\bullet}$, $\lambda_{\max}$ 425 nm) and the half oxidized radical ($\mathrm{TP}^{\dot{+}+}$, $\lambda_{\max}$ 470 nm). The absorption band due to the semiquinone radical is shown in Fig. 3 together with the absorption spectrum of thiopyronine ground state. For the determination of the radical yield the high extinction coefficient of the semiquinone radical is of great advantage.

Morita and Kato report a quantum yield of triplet formation from the first excited singlet of 0.67 for thiopyronine [24b]. This value is likely to be too high as compared to a corresponding value of 0.62 for thionine [32]. Comparing the triplet population of thionine and thiopyronine after absorption of equal amounts of light quanta at 480 nm (from a dye laser) we found that the $S_1 - T_1$ intersystem crossing efficiency in thiopyronine amounts to only 45% of that in thionine.

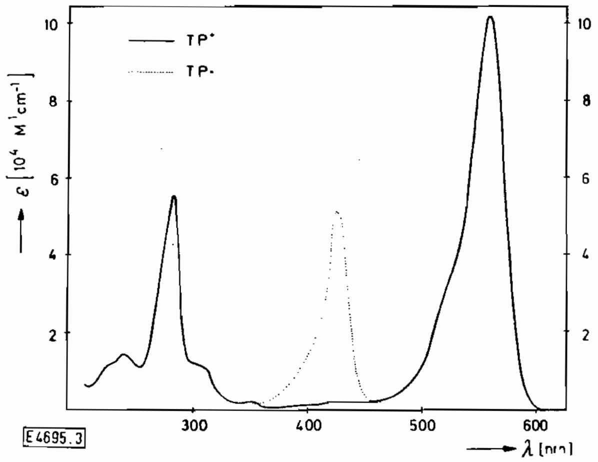


Fig. 3
Absorption spectra of thiopyronine ground state (TP^{+}) and semiquinone radical ($\mathrm{TP}^{\bullet}$) in methanol. The radical $\mathrm{TP}^{\bullet}$ was produced by reaction of $^{3}\overset{*}{\mathrm{T}}\mathrm{P}^{+}$ with diazabicyclo[2.2.2]octane ($4 \cdot 10^{-3}$ M)

For the energetics of the electron transfer reaction and the intermediate exciplex the one-electron reduction potential of thiopyronine is of interest. From polarographic measurements in water Berg et al. [25] obtained a one-electron potential of E vs. s.c.e. = −0.41 V. The authors cast some doubt on the reliability of this value since it strongly depends on the dye concentration. They assume that the electrode reaction is influenced by adsorption of dye at the electrode surface. Comparing the molecular structure of thionine and thiopyronine it would be indeed hard to understand that the potential of thiopyronine should be more positive than that of thionine (E_0 ($\mathrm{TH}^{\bullet}/\mathrm{TH}^{+}$) vs. s.c.e. = −0.49 V [19]).

A different method to determine the one-electron redox potential of thiopyronine is to use electron transfer rate constants. As was shown by Rehm and Weller for electron transfer reactions with excited singlets [33], the rate constant of these reactions are determined by their free enthalpy change. The typical Rehm-Weller relation was shown to be applicable also to electron transfer reactions with excited dye triplets by Vogelmann et al. [19]. For an electron transfer reaction of the type

$$^{3}\overset{*}{\mathrm{A}}^{+} + {}^{1}\mathrm{D} \rightarrow {}^{2}\mathrm{A}^{\bullet} + {}^{2}\mathrm{D}^{\dot{+}} \qquad (6)$$

the free enthalpy change of the reaction is given by:

$$\Delta G = E_0(\mathrm{D}/\mathrm{D}^{\dot{+}}) - E_0(\mathrm{A}^{\bullet}/\mathrm{A}^{+}) - E({}^{3}\overset{*}{\mathrm{A}}{}^{+}) \qquad (7)$$

where the E_0 are the corresponding one-electron potentials and $E({}^{3}\overset{*}{\mathrm{A}}{}^{+})$ is the triplet energy of the acceptor. Comparing the reaction of two different triplets $^{3}\overset{*}{\mathrm{A}}{}^{+}$ and $^{3}\overset{*}{\mathrm{B}}{}^{+}$ with the same donor D, we obtain the relation:

$$\begin{aligned}\Delta G({}^{3}\overset{*}{\mathrm{A}}{}^{+}) - \Delta G({}^{3}\overset{*}{\mathrm{B}}{}^{+}) &= (E_0(\mathrm{A}^{\bullet}/\mathrm{A}^{+}) - E({}^{3}\overset{*}{\mathrm{A}}{}^{+})) \\ &\quad - (E_0(\mathrm{B}^{\bullet}/\mathrm{B}^{+}) - E({}^{3}\overset{*}{\mathrm{B}}{}^{+}))\,. \end{aligned} \qquad (8)$$

The rate constant k_{et} of reaction (6) is most sensitive to ΔG in the region of positive ΔG-values. Here the Rehm-Weller relation can be simplified to the equation:

$$k_{\mathrm{et}} = k'\,\mathrm{e}^{-\Delta G/RT} \qquad (9)$$

where k' is in the order of 4 times the diffusion controlled rate constant. Eq. (9) is valid only in the limit for reaction rates far from the diffusion controlled limit. It has been successfully applied to explain the different reactivities of acid-base conjugated triplet forms (e.g. $^{3}\overset{*}{\mathrm{T}}\mathrm{H}^{+}$ and $^{3}\overset{*}{\mathrm{T}}\mathrm{H}_2^{+\,+}$) [20b, c] for which expression (8) can be determined directly and with great accuracy from the Michaelis cycle.

In Table 1 data are presented allowing the calculation of E_0 ($TP^{\bullet}/TP^{+}$) vs. s.c.e. by the use of Eqs. (8) and (9). The result of -0.67 V indicates that thiopyronine is a weaker electron acceptor than thionine as is expected from the molecular structure of these dyes.

Table 1
Data pertinent to calculation of $E_0(TP^{\bullet}/TP^{+})$ by use of Eqs. (8) and (9)

	TH^+	TP^+
$E(^3A^+)$	1.7 eV [58]	1.8 eV [30, 51]
$k_q(ATH)$[a]	$8.2 \cdot 10^6$ [20c]	$5.4 \cdot 10^5$
$k_q(KSCN)$[a]	$3.5 \cdot 10^6$	$2.0 \cdot 10^5$
$E_0(A^{\bullet}/A^{+})$[b]	-0.49 V [19]	-0.67 V[c]

[a] Triplet quenching constant with respective electron donor, $[M^{-1} s^{-1}]$, in methanol as solvent, unless otherwise stated determined in this work, ATH = allylthiourea.

[b] Versus s.c.e.

[c] Calculated by use of Eqs. (8) and (9), identical results are obtained with $k_q(ATH)$ and $k_q(KSCN)$.

With this reduction potential of thiopyronine and the oxidation potentials of the donors given above we obtain a value of about -0.25 eV for ΔG of the electron transfer reaction by the use of Eq. (7). This means that the electron transfer reactions to be observed are weakly exergonic. The value of -0.25 eV should be considered only as an approximation, however, since potentials determined in different solvents enter into its calculation. Furthermore, it is to be expected that ΔG will depend somewhat on the solvent polarity (see section 4.2.1). In any case, however, ΔG will be in an order of magnitude where the electron transfer is sufficiently fast to achieve almost complete triplet quenching with an acceptable donor concentration, i.e. where fluorescence quenching is negligible ($10^{-3}-10^{-2}$ M).

3.2. Influence of Solvent Viscosity

One purpose of the present investigations was to study the influence of solvent viscosity on the exciplex behaviour, whereby the viscosity variation should be achieved at constant temperature and as constant as possible polarity of the solvent.

To realize these conditions we used mixtures of methanol and ethanediol because of their chemical similarity. Their dielectric constants at 25 °C are 32.6 and 38.6, respectively. As shown below empirical solvent parameters as Kosower's Z-value [34] are better suited as a measure of polarity in our case than the dielectric constant. The corresponding values are 83.6 for methanol and 85.1 for ethanediol [35] indicating that the condition of constant polarity is fulfilled quite well.

The rate constant of triplet quenching was determined in the usual manner, by measuring the triplet lifetime τ as a function of the donor concentration and plotting $1/\tau$ versus the concentration of D, which yields a linear plot according to the equation:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[D]\,. \tag{10}$$

The triplet decay **was** monitored **at 810 nm** to avoid superposition of fluorescence straylight. To obtain a relative measure of the radical yield Φ_r, the optical density at the maximum (425 nm) of thiopyronine semiquinone absorption was used, where the oxidized donor radicals contribute only about 5% to the optical density ($\varepsilon \approx 2000\ M^{-1}\ cm^{-1}$ [52]). The donor concentrations used (10^{-3} to 10^{-2} M) were high enough to achieve almost complete triplet quenching, however still low enough that singlet quenching was negligible. To put these data on an absolute scale (Φ_r is the radical yield per triplet molecule quenched) the method using the observation of ground state depopulation at the maximum of ground state absorption was used. This procedure is described in detail in Ref. [21].

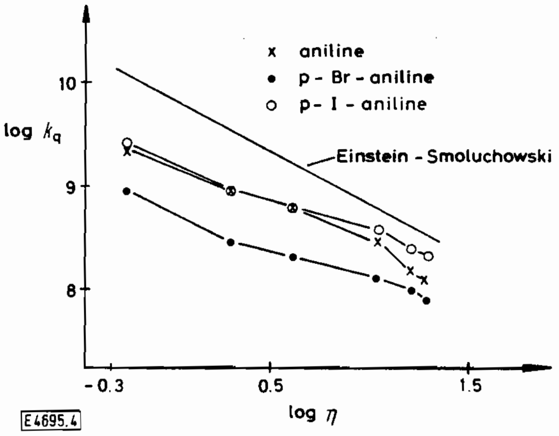


Fig. 4
Rate constant k_q of thiopyronine triplet quenching by anilines as a function of solvent viscosity η (for solvent composition see Fig. 5); the diffusion controlled limit (Eq. (11)) according to Einstein-Smoluchowski is indicated

The observed values of k_q are given in Fig. 4 as a function of solvent viscosity. It can be noticed that the rate constants are definitely below the limit given by the Einstein-Smoluchowski expression for diffusion controlled reactions [36]

$$k_{ES} = \frac{8\,RT}{3000\,\eta}\,. \tag{11}$$

The results for the radical yields obtained at different solvent viscosities under the condition of complete triplet quenching are shown in Fig. 5. As qualitatively expected the radical yields decrease with increasing viscosity, due to the solvent cage effect. As can be seen, however, the solvent influence is drastically enhanced by the heavy atom substituents.

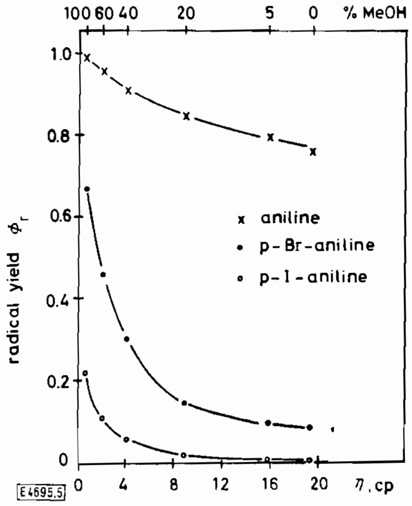


Fig. 5
Radical yield Φ_r obtained under conditions of complete quenching of thiopyronine triplet by different anilines as a function of solvent viscosity. Solvent: methanol/ethanediol mixtures, upper abscissa: volume percentage of methanol

We now want to check if the effect of the halogen substituents is explicable in terms of their 'probe-function' as expressed in Fig. 1. This would require that we know the rate constant k_{fr} and the Franck-Condon factor F_{FC} as a function of the solvent viscosity, Since a priori this information is not available, we start with one of the s-shaped curves of Fig. 1 and plot the radical yields for one of the donors (p-bromoaniline) onto this curve, thereby defining a relative value of F_{FC}/k_{fr} for each solvent composition. Now we can plot the results for the other donors too. If our concept is correct the points for the other donors should also lie on the same type of s-shaped curve with a certain shift relative to the reference s-curve. As can be seen from Fig. 6 this is indeed the case. From the relative shifts the electronic factors are obtained to be in the ratio 7.2 : 1 : 0.025 for the systems with iodoaniline, bromoaniline and aniline, respectively. The ratio between iodo- and bromo-derivative is almost identical with the value obtained with thionine triplet as an electron acceptor (7.5) Ref. [22] and is of an order of magnitude comparable to the ratio of the squares of the atomic spin-orbit coupling constants of these atoms (4.2). The ratio between bromoaniline and aniline too is consistent with the assumption of spin-orbit-coupling effects on k_{isc} in the exciplex. Assuming that the square of the atomic spin-orbit coupling constant of the heaviest atom in the exciplex under consideration determines the order of magnitude of F_{el} (Br in the TP-bromoaniline exciplex, $\zeta_{Br} = 4260$, S in the TP-aniline exciplex, $\zeta_S = 382$) we would expect F_{el} (TP-bromoaniline): F_{el} (TP-aniline) $\approx 1:0.008$.

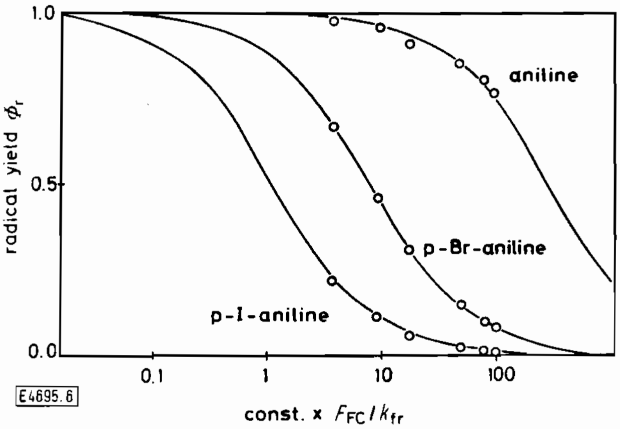


Fig. 6
Radical yield Φ_r as a function of $\log(F_{FC}/k_{fr})$ varied by solvent viscosity. Relative values of (F_{FC}/k_{fr}) are determined for each solvent by plotting the radical yield Φ_r with p-Br-aniline on a standard curve of the type shown in Fig. 1. Curves for p-I-aniline and aniline are of the same shape with relative shifts such that a best fit of the data points is obtained

3.3. Influence of Solvent Polarity

Studying the influence of solvent polarity has greatly contributed to the understanding of the exciplex phenomenon (cf. e.g. Ref. [5]). From the solvent polarity dependence of exciplex emission Weller et al. [37] determined the dipole moments of exciplexes and thus proved the charge-transfer nature of these species. Mataga and coworkers found a quantitative relationship between the yield of radical ions and the dielectric constant of the solvent [38].

Whereas, however, in most work on exciplexes and electron transfer reactions in the excited state the reacting partners are neutral molecules and the radicals are ions, so that a charge separation is involved when the exciplex dissociates, the exciplexes considered in this work are positively charged and no charge separation is necessary for a dissociation of the exciplex into a radical pair. Thus solvent polarity effects for these systems are less obvious. Nevertheless, the effects observed with the aid of the heavy atom probes are quite considerable.

For a variation of solvent polarity one has to take into account that the cationic dye is soluble only in relatively polar solvents. Solvent polarity is not a very exactly defined quantity. Besides the dielectric constant a number of different empirical solvent parameters have been used for different applications [35]. Among these Kosower's Z-value appeared to be best suited for our purposes since it is determined from the solvent dependence of the energy of an electronic charge transfer absorption in a binary complex. Therefore we selected solvents and solvent mixtures for which these Z-values can be taken from the literature. In Table 2 the different quantities relevant to our investigations are listed for the solvents and solvent mixtures used.

Table 2
Polarity parameters and viscosities of various solvents and solvent mixtures

Solvent a)	ε b)	Z d)	η f)
acetonitrile (ACN)	37.5	71.3	0.35
ACN – H_2O (9)	40	80	0.39
ACN – H_2O (25)	47	82	0.56
ACN – H_2O (50)	58.5	87.5	0.79_5
ACN – H_2O (75)	70	92	0.97
methanol (MeOH)	32.6	83.6	0.54
MeOH – H_2O (25)	47	87.8	1.21
MeOH – H_2O (50)	59	91	1.58
MeOH – H_2O (75)	69.5	93.1	1.38
H_2O	78.5	94.6	0.895
N-methylformamide	182.4 c)	81.9 e)	1.65 g)

a) Figures in parentheses indicate volume percentage of water.
b) Dielectric constant at 25 °C, data from Ref. [43] (ACN – H_2O mixtures) and Ref. [44] (MeOH – H_2O mixtures).
c) Ref. [45].
d) Kosower's Z-value at 25 °C, [kcal/mol], data for MeOH – H_2O calculated from Y-value by the correlation $Z = 2.4\ Y + 86.2$ [34], data for ACN – H_2O from Ref. [39].
e) From E_T-values in Ref. [35b] by the correlation $Z = 1.26\ E_T + 13.8$.
f) Dynamic viscosity [cp] at 25 °C, for ACN – H_2O from Ref. [40], for MeOH from Ref. [41].
g) Ref. [42].

Variation of solvent polarity was achieved by mixing acetonitrile with water or methanol with water. The results obtained for the quenching constants and radical yields with these series of solvents are shown in Fig. 7, where we have used Kosower's Z-value as a measure of solvent polarity.

Whereas there appears to be no significant difference in the influence of solvent polarity on the quenching constant when comparing aniline and its halogen substituted derivatives, the solvent polarity influence on the radical yield is significantly dependent on heavy atom substitution. With the halogen substituted donors the radical yield drastically decreases with increasing polarity (see Fig. 7). This applies likewise to the N,N-dimethylated derivatives (see Table 3). The observation is in accord with our previous results [22], where we found that there is no specific heavy atom effect on the rate of electron transfer but a marked influence on the intersystem crossing in the exciplex and hence, indirectly, on the radical yield.

It remains to be investigated if our model of the heavy atom effect leading to diagrams of the type of Fig. 1 can also explain the heavy atom dependent solvent polarity influence on the radical yield.

We use the same procedure as in the case of viscosity variation. Plotting the radical yields for p-bromoaniline in the different solvents onto the s-type curve, defines a relative value of F_{FC}/k_{fr} for the exciplex in each solvent. Now the radical yields for the other donors can be plotted also, and displaced s-curves of the same shape can be drawn through these points. In Fig. 8 we chose the same shifts as in Fig. 6 and it is observed that in the case of polarity variation, too, they lead to a reasonable fit of the observed data points, indicating that the ratio of the electronic factors is not solvent dependent.

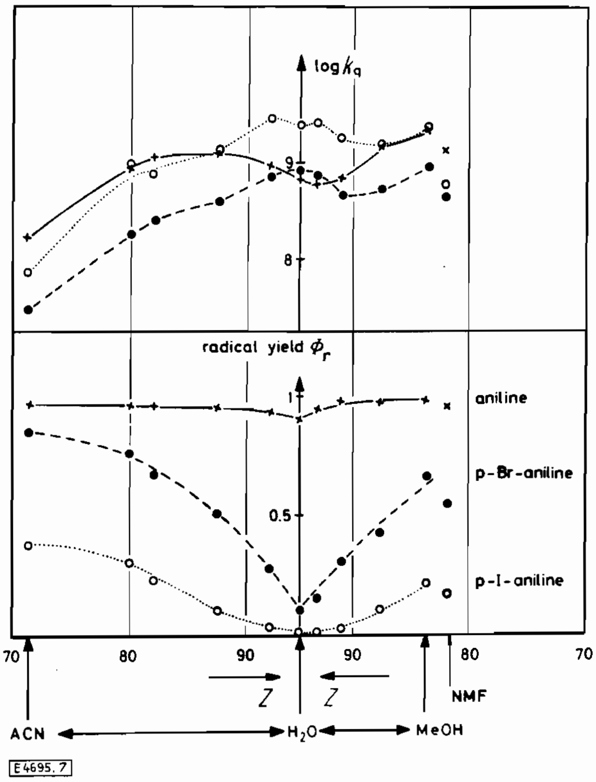


Fig. 7
Rate constants k_q (upper part) and radical yields Φ_r (lower part) observed for quenching of thiopyronine triplet by anilines as a function of Kosower's solvent polarity parameter Z. The right hand side of the diagram represents the results for methanol/water mixtures and N-methylformamide (NMF), the left hand side for acetonitrile/water mixtures. For solvent compositions see Table 2

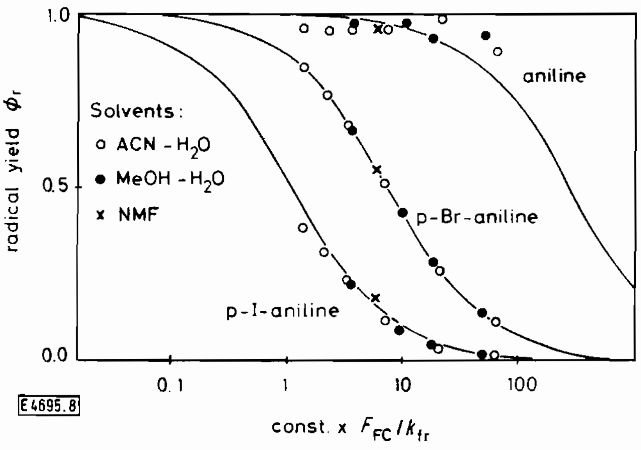


Fig. 8
Radical yield Φ_r as a function of $\log(F_{FC}/k_{fr})$ varied by solvent polarity. Determination of (F_{FC}/k_{fr}) for different solvents as in Fig. 6. Results with p-Br-aniline are used as standard, for curves of other donors the same displacements are adopted as in Fig. 6

4. Discussion

4.1. Influence of Solvent Viscosity

From a variation of solvent viscosity one expects to obtain information on diffusion dependent processes in a reaction mechanism. Thus in Scheme I the primary process between acceptor triplet and donor and the dissociation of the exciplex will be viscosity dependent.

4.1.1 Quenching Constants

The viscosity dependence of the quenching constants as shown in Fig. 4 may be compared with the Einstein-Smoluchowski behaviour of diffusion controlled rate constants, which is also shown in Fig. 4. Whereas the quenching constants observed by us behave similar for the different donors they are definitely below the Einstein-Smoluchowski limit.

This cannot be explained, however, by an activation controlled process in the encounter pair, independent of solvent viscosity, since in this case the viscosity dependence would be weakest at low viscosities. A possible explanation for the observed viscosity dependence could be, that the quenching reaction requires formation of a very specific steric configuration which can be formally described by a reaction diameter smaller than the encounter diameter used in the Einstein-Smoluchowski theory. The specific configuration may be a requirement of exciplex formation.

4.1.2 Radical Yields

As demonstrated by Fig. 6 the apparently different viscosity dependence of the radical yield with the different donors, displayed in Fig. 5, is a consequence of the heavy atom 'probe function' and is in accord with a substituent independent viscosity effect on the exciplex parameter F_{FC}/k_{fr}. Since it appears unlikely that the Franck-Condon factor is viscosity dependent the variation of F_{FC}/k_{fr}, causing the change in Φ_r, is probably mainly due to the viscosity dependence of k_{fr}, i.e. the solvent cage effect. Plotting $1/\Phi_r$ versus viscosity η yields fairly straight lines (Fig. 9), so that we can extrapolate to zero viscosity, thus obtaining values for a hypothetical solvent without cage effect. Assuming k_{isc} to be viscosity independent and using Eq. (1) the linear relation shown in Fig. 9 is expressed as follows:

$$\frac{1}{\Phi_r} = 1 + \frac{k_{isc}}{k_{fr}} = 1 + k_{isc}\,\tau_{o,D} + k_{isc}\,a\,\eta\,, \qquad (12)$$

where we inferred from Fig. 9 that

$$\frac{1}{k_{fr}} = \tau_{o,D} + a\,\eta \qquad (13)$$

$\tau_{o,D}$ and a being viscosity independent. The quantity $\tau_{o,D}$ may be interpreted as dissociative lifetime of the exciplex due to exciplex bonding forces alone, the quantity $a\,\eta$ as the solvent cage effect contribution to the dissociative lifetime.

From Eq. (12) we see that heavy atom substitution (F_{el} in k_{isc}) affects the slope as well as the intercept of the straight lines. Here the halogen substituents exhibit their useful probe function: with increasing atomic number of the substituent slope and intercept increase, so that they can be determined with better accuracy. For aniline $k_{isc} \cdot \tau_{o,D}$ is too small to be determined from Fig. 9, for p-bromoaniline and p-iodoaniline values for $k_{isc} \cdot \tau_{o,D}$ of 0.17 and 1.26 are obtained.

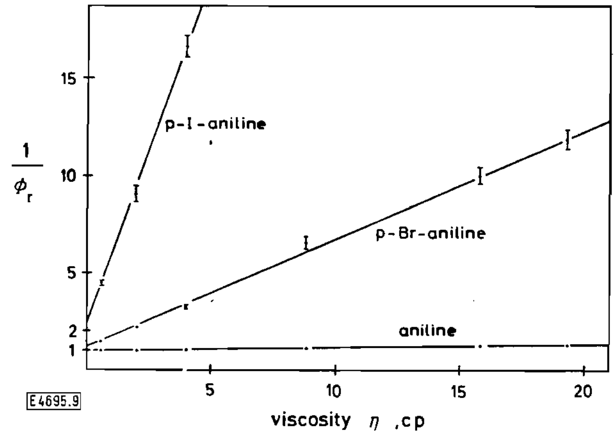


Fig. 9
Viscosity dependence of the observed radical yields Φ_r: extrapolation of $1/\Phi_r$ to zero viscosity

To evaluate $\tau_{o,D}$ the k_{isc} values have to be known. Recently we succeeded in determining these parameters for the respective exciplexes with thionine triplet as acceptor by means of a magnetic field modulation of the exciplex triplet sublevel relaxation [23]. We obtained $k_{isc} \approx 1.8 \cdot 10^9\ s^{-1}$ and $16.3 \cdot 10^9\ s^{-1}$ for the triplet exciplexes between thionine and p-bromoaniline and p-iodoaniline, respectively. Adopting these values for the thiopyronine exciplexes, too, we calculate $\tau_{o,D}$ to be about 0.1 ns. It should be noted, however, that in a solvent of the viscosity of e.g. methanol the cage effect contribution $(a\eta)$ already supercedes $\tau_{o,D}$ (see Fig. 9).

Eq. (13) is of purely heuristic nature. To achieve a certain mechanistic understanding it is to be clarified if the constant a is in some way related to the exciplex stability as characterized by $\tau_{o,D}$. We consider the following, grossly simplified, kinetic model of the dissociation process:

$$^3(\dot{A}D^+) \underset{k_2}{\overset{k_1}{\rightleftarrows}} {}^3(A^{\cdot}\_\_D^{\dot{+}}) \xrightarrow{k_\eta} {}^2A^{\cdot} + {}^2D^{\dot{+}}\,, \tag{14}$$

where we separate the dissociation process into two steps, the first of which is regarded to be viscosity independent. This step leads to an activation of the dissociative vibration of the exciplex, $^3(A^{\cdot}\_\_D^{\dot{+}})$ being the corresponding activated state. The second step is the separation of the exciplex components by a solvent molecule or, in other words, the escape from the primary solvent cage. Using the steady state approximation for the activated state one obtains:

$$\frac{1}{k_{fr}} \equiv \tau_D = \tau_{o,D}\left(1 + \frac{k_2}{k_\eta}\right), \tag{15}$$

where $\tau_{o,D} = 1/k_1$. If k_η is proportional to $1/\eta$, which has been rationalized by Eyring [46], then the expression (15) is equivalent to our heuristic Eq. (13):

$$\frac{1}{k_{fr}} = \tau_{o,D} + \tau_{o,D}\,a'\eta\,. \tag{16}$$

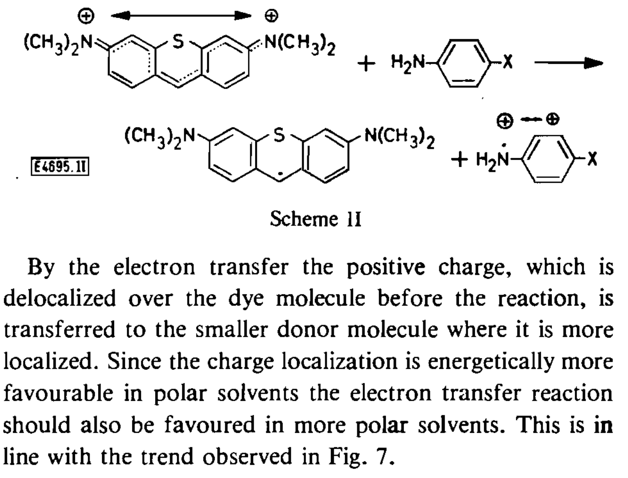
As a consequence of the model it follows that the cage effect contribution ($a\eta$ in Eq. (13)) to the exciplex dissociative lifetime is not independent of the exciplex bonding contribution $\tau_{o,D}$ but is proportional to $\tau_{o,D}$. The constant a' is determined from Fig. 9 as 3.14 cp^{-1}. It will be used below to separate the viscosity effect on k_{fr} in solvents of different polarity.

In this paper the exciplex dissociation is considered as a first order rate process. To be more precise, one should note that separation of the exciplex components into a solvent shared radical pair does not necessarily lead to the free radicals observed in the microsecond time domain since the pair can recombine shortly, i.e. within a few nanoseconds after its formation (geminate recombination [47]). So far, however, geminate recombinations have been detected mainly with radical pairs subject to Coulomb attraction (see e.g. Ref. [14, 48, 49]). Without Coulomb interaction as in our systems the effects are expected to be much smaller [50].

4.2. Influence of Solvent Polarity

4.2.1 Quenching Constants

As shown in Fig. 7 (upper half) the quenching constants show little variation in the Z-region 84 to 94, but there is a systematic drop in the region Z = 80 to 70 corresponding to the transition from acetonitrile-water mixtures to pure acetonitrile. Since the electron transfer reactions considered here do not constitute charge separations we have to consider the charge redistribution in more detail (cf. Scheme II).



Scheme II

By the electron transfer the positive charge, which is delocalized over the dye molecule before the reaction, is transferred to the smaller donor molecule where it is more localized. Since the charge localization is energetically more favourable in polar solvents the electron transfer reaction should also be favoured in more polar solvents. This is in line with the trend observed in Fig. 7.

Apart from purely electrostatic considerations a possible influence of hydrogen bonding must not be overlooked. By the loss of one electron aniline becomes a weak acid of pK_a = 7 in water [52]. From the equilibrium constant of $K = 10^{-7}$ M and a maximum rate constant for the association of $10^{11}\ M^{-1}\ s^{-1}$ [53] it follows that the dissociation rate constant cannot be faster than $10^4\ s^{-1}$. Thus the acid strength is not sufficient to protonate the solvent during the geminate phase of some ns. Though, hydrogen bonding to a water or methanol molecule may lead to a better stabilization of the aniline radical than in acetonitrile, explaining the decrease of the reaction rate constant in the latter solvent. This explanation is supported by the observation that hydroquinone, which is similar to aniline in that it also becomes a moderately strong acid on one electron oxidation, reacts considerably slower with thiopyronine triplet in acetonitrile ($k_q = 4.5 \cdot 10^7\ M^{-1}\ s^{-1}$) than in methanol ($k_q = 1.1 \cdot 10^9\ M^{-1}\ s^{-1}$) whereas dimethylaniline and p-bromo-N,N-dimethylaniline (see Table 3) do not show this solvent effect. With the latter donors the quenching constant is even higher in acetonitrile than in water.

Table 3
Triplet quenching parameters of thiopyronine with N,N-dimethylated anilines (DMA)

Solvent	DMA		p-Br-DMA	
	k_q [a]	Φ_r [b]	k_q [a]	Φ_r [b]
acetonitrile	8.2	1.0	8.0	0.88
water (5% acetonitrile)	2.3	0.93	2.5	0.13

[a] Quenching constant [$10^9\ M^{-1}\ s^{-1}$].
[b] Radical yield per triplet under conditions of complete triplet quenching.

4.2.2 Radical Yields

As was demonstrated in Fig. 8 the influence of solvent polarity on the radical yield can be explained assuming the same solvent influence on the exciplex parameter F_{FC}/k_{fr} for each of the three systems investigated. It is of interest now to look for the solvent parameter which uniquely defines this exciplex quantity. In Fig. 10 we plot for comparison the exciplex parameter F_{FC}/k_{fr} against the solvent dielectric constant and the corresponding Z-value. As can be seen the dielectric constant correlates with F_{FC}/k_{fr} for each single series of solvent mixtures but for the two series different curves are obtained.

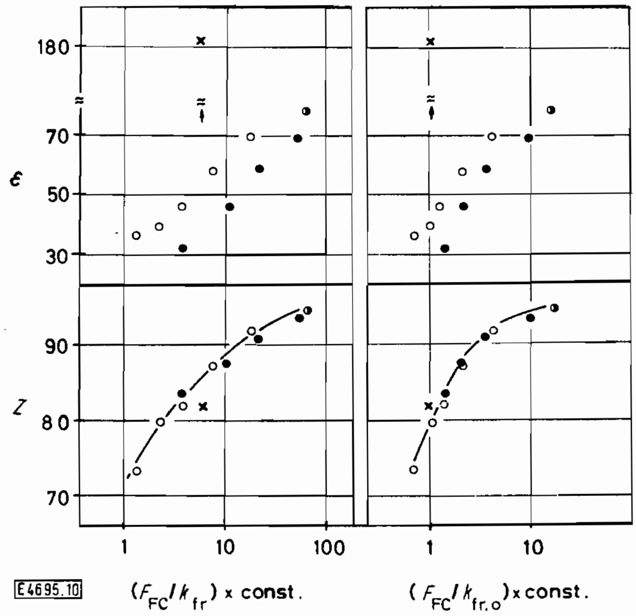


Fig. 10
Dielectric constant (ε) and Kosower's Z-values versus $\log(F_{FC}/k_{fr})$ and $\log(F_{FC}/k_{fr,o})$. Numerical values for $\log(F_{FC}/k_{fr})$ are obtained from Fig. 8. $k_{fr,o}$ is k_{fr} extrapolated to zero viscosity by means of Eq. (16). For designation of solvents see Fig. 8

The inadequacy of the dielectric constant as a universal polarity measure is most clearly demonstrated in the case of N-methyl-formamide as solvent ($\varepsilon = 182.4$). As is shown in Fig. 10 the empiric polarity parameter Z gives quite a good correlation with F_{FC}/k_{fr} independent of the kind of solvent mixture used. Even N-methylformamide behaves fairly regular.

To discuss the variation of F_{FC}/k_{fr} as caused by the change of solvent the parameters k_{fr} and F_{FC} have to be investigated individually. As was shown in the preceding section, k_{fr} is quite sensitive to changes in solvent viscosity. Assuming that the viscosity dependence of k_{fr} can be described by Eq. (16) and using the value of a', determined above, k_{fr} can be reduced to zero viscosity. In this way the correlations displayed on the right hand side of Fig. 10 are obtained. We notice that only a small fraction of the change observed for F_{FC}/k_{fr} is due to viscosity variation and that after the influence of viscosity has been accounted for, the parameter Z still shows a better correlation with F_{FC}/k_{fr} than the dielectric constant, though the correlation with the latter has improved.

Discussing a polarity dependence of k_{fr} it has to be noted again that there is no charge separation involved when the exciplex dissociates into the radicals. If there is any polarity dependence of k_{fr} to be expected its value should increase when going from acetonitrile to water since the aniline radical is increasingly better solvated as argued above. This trend of k_{fr}, however, would be at variance with what is observed for F_{FC}/k_{fr} and leads to the conclusion that F_{FC} increases still more with increasing solvent polarity than F_{FC}/k_{fr}. Thus we arrive at the conclusion that the Franck-Condon factor of the exciplex intersystem crossing rate constant increases strongly with increasing solvent polarity.

Very little has been reported in the literature on the solvent polarity dependence of exciplex intersystem crossing rate constants. Recently Werner et al. [15] gave evidence that k_{isc} in the pyrene-dimethylaniline singlet exciplex increases at least by a factor of 2–3 when going from hexane to methanol. In our case the effect points into the same direction but is much more pronounced, k_{isc} increasing by a factor of about 40 when going from acetonitrile to water.

Werner et al. [15] discuss a solvent polarity dependence of the electronic factor determining k_{isc}. Though comparing the diagrams Fig. 8 and Fig. 1 suggests that the electronic factor is not polarity dependent in our case, it should be noted that, as a consequence of the way diagram Fig. 9 is constructed, s-shaped curves with the same displacements would be obtained also with polarity dependent electronic factors, if only their *ratio* were polarity independent.

According to Ref. [22] the electronic factor is related to the charge-transfer structure of the exciplex. Thus a variation of charge-transfer character in the exciplex may cause a variation of the electronic factor (F_{el} in Eq. (4)). Since we observe fast radical formation, however, in all solvents investigated, we may assume that the charge-transfer character of the exciplex is always ≥ 50%. Hence an increase of charge-transfer character by more than a factor of two seems improbable and thus cannot account for the strong polarity dependence of the radical yield observed.

For a polarity dependence of the Franck-Condon factor the following explanation can be suggested. Since the intersystem crossing in the exciplex, leading to the singlet ground state of its components, involves a back-transfer of the electron from the acceptor to the donor it also represents a strongly exothermic electron transfer reaction ($\Delta G \approx -145$ kJ). This reaction requires transformation of excess electronic energy into vibrational energy of its components. Since this process is governed by the Franck-Condon principle, the transfer of the electron is followed by a solvent relaxation whereby the solvent reorganization energy will be the larger the more polar the solvent (cf. Fig. 11). As a consequence the electronic energy gap which has to be transformed to vibrational energy in the electronic transition becomes smaller, which according to general experience in radiationless transitions leads to an increase of the Franck-Cordon factor (see e. g. Ref. [54]).

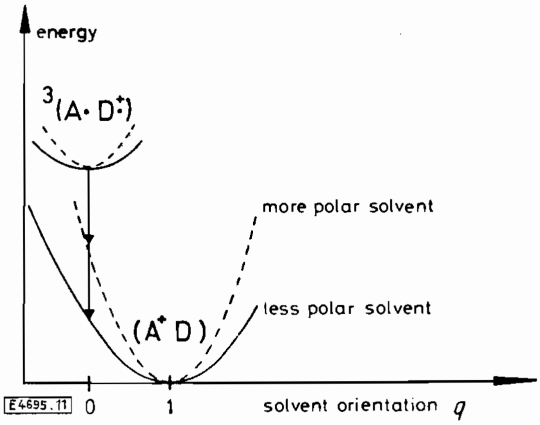


Fig. 11
Energy of exciplex and ground state encounter pair as a function of solvent orientation parameter q, corresponding to equilibrium solvation of the hypothetic charge distribution ($A^q D^{1-q}$)

We shall now consider whether this explanation can account for the order of magnitude of the observed effect. The influence of solvent polarity on the energy of electronic transitions has been treated theoretically by several authors (for a review see Ref. [55]). Principally most of the treatments are based on Onsager's concept of the reaction field [56] by which a surrounding dielectric acts back on a polarizing ion or dipolar molecule. The influence on the energy of electronic transitions can be calculated as the energy which the electron loses during the transition, due to the electrostatic work in the orientational part of the reaction field which is kept fixed during the electronic transition (Franck-Condon principle).

If the reaction field is due to an electric dipole and the effect of the electronic transition is to discharge this dipole then, neglecting the polarizability of the molecule, according to the simple Onsager model the work to be performed in the reaction field during the transition is given by:

$$W_{+-} = e^2 a^2 \left\{ \frac{2}{R^3} \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{1}{R^3} \frac{(n^2 - 1)}{(2n^2 + 1)} \right\}, \qquad (21)$$

where the molecule is considered to fill a spherical cavity of radius R in the dielectric and the molecular dipole strength is (ea) (cf. Fig. 12a). ε is the dielectric constant and n the refractive index of the dielectric.

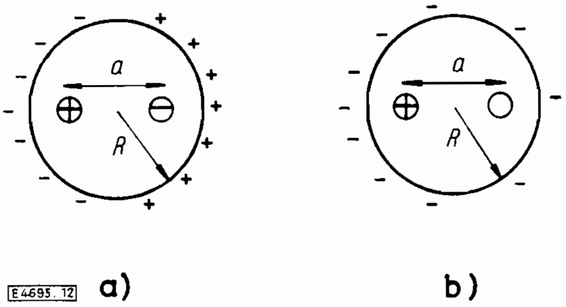


Fig. 12
Definition of charge distribution of reacting molecules and surrounding dielectric used in Eqs. (21) and (22).
a) (+ −)-type, b) (+ ○)-type

In our case, however, the situation is different. The reaction field is due to a positive charge, localized on the donor molecule. During the transition the positive charge migrates from the donor molecule to the acceptor molecule (cf. Fig. 12b). The corresponding work term in this case is:

$$W_{+0} = e^2 a^2 \frac{1}{R^3} \frac{(\varepsilon - 1)}{(2\varepsilon + 1)}, \qquad (22)$$

which for polar solvents is about half of the corresponding quantity in the dipole case.

Equations of the type (21) have been applied successfully e. g. for the determination of dipole moments of exciplexes in solvents of dielectric constants smaller than about 10 [5, 49]. For solvents with higher dielectric constants these equations fail since $(\varepsilon - 1)/(2\varepsilon + 1)$ approaches a limiting value of 0.5, whereas even in the region of ε between 30 and 80 drastic solvent shifts of charge transfer transitions can be observed. These effects have been used to define empirical solvent polarity parameters [34]. As described above, Kosower's Z-value refers to a transition whereby a dipolar complex is discharged, the corresponding transition energy increasing by about 100 kJ when going from acetonitrile to water. Though the simple Onsager-type formulas (Eqs. (21, 22)) cannot apply to very polar solvents it may be a reasonable assumption that the actual work terms for transitions of type (+ −) and (+0) (Fig. 12a and 12b) are still in the ratio 2:1. Then we can deduce from the Z-value difference of acetonitrile and water (the Z-value corresponds to a type (+ −) transition) that the corresponding energy shift for a type (+0) transition (as in our case) should be about 50 kJ or $4 \cdot 10^3$ cm^{-1}.

To estimate the change of the Franck-Condon factor of radiationless transitions going along with this energy shift we refer to a paper of Dreeskamp et al. [57] where the rate constant of k_{ST} of a heavy atom induced singlet-triplet transition is determined as a function of the corresponding electronic energy gap ΔE. The data can be described by the relation:

$$k_{ST} \propto e^{-\alpha \Delta E} \qquad (23)$$

with $\alpha \approx 10^{-3}$ cm. This relation can be interpreted as directly reflecting the energy gap dependence of the corresponding Franck-Condon factor. Substituting our energy shift of about $4 \cdot 10^3$ cm^{-1}, we obtain that the Franck-Condon factor should be increased by a factor of about 50 which is in the order of magnitude of the effect observed in our case, where the energy gap is assumed to be modified by the solvent polarity. It should be noted, however, that if we apply the same type of calculation to the system of Werner et al. [15], representing a (+ −)-type charge transfer, a much greater polarity effect on k_{isc} is to be expected than in our case. Thus the observation of Werner et al. would be at variance with our interpretation of a polarity dependent Franck-Condon factor. At present we cannot give a consistent explanation for both systems and information from further investigations will have to be awaited.

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