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MAGNETOKINETIC INVESTIGATIONS OF SPIN-FORBIDDEN ELECTRON BACK TRANSFER IN EXCIPLEXES AND RADICAL PAIRS

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Abstract

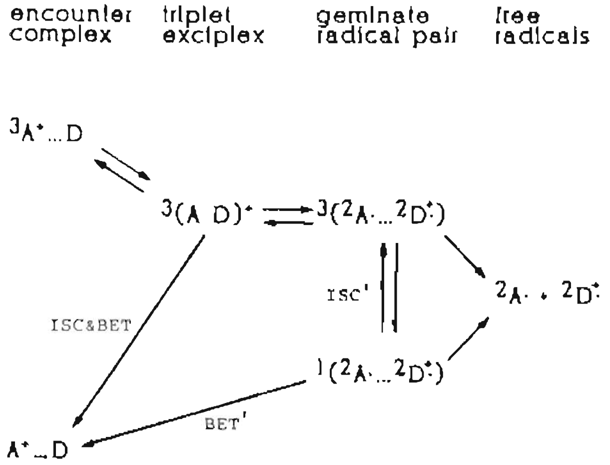
In this paper we report on spin-orbit coupling induced magnetokinetic effects on the free radical yield of triplet electron transfer reactions. From the magnetic field dependence observed in a variety of mixed solvents the solvent dependent dynamics of short-lived triplet exciplexes is quantitatively deduced.

1. Introduction

One of the most important aspects of photoinduced electron transfer is its superior potential for achieving fast conversion of electronic excitation energy into chemical energy. A separation of the transferred electron from the hole it left behind is a crucial step in natural and artificial light energy conversion systems. In liquid solution such a separation is usually achieved by diffusional motion, whereby a primary pair of redox products separates into free radicals. Since the pioneering work of Weller, Mataga and others [1] intermediates of photoelectron transfer reactions in solution, viz. exciplexes and radical (ion) pairs (cf. Scheme 1) and their dynamics have been studied intensively [2]. Time-resolved fluorescence and laser-flash induced excited state absorption spectroscopy have been the most important experimental techniques in these studies. One important kinetic requirement for a direct, time-resolved study of the dynamics of exciplexes and correlated radical pairs is that formation of these species can be made faster than their decay. This condition is easily met if the electron transfer reactions involve excited singlet states since the time of their production is only limited by the duration of the excited light pulse or the initial photoelectron transfer step. In the case of reacting triplets the intramolecular ISC process following optical excitation usually causes a time lag not much shorter than about a nanosecond before the excited state of interest can react. It is therefore difficult to obtain direct information on subnanosecond dynamics of short-lived electron transfer intermediates in such cases.

This is exactly the situation encountered when studying photoelectron transfer reactions with typical sensitizer dyes as, for example, the phenothiazine dyes thionine or methylene blue in which we have been interested for some time [3-6]. These dyes are cations and acting as photoelectron acceptors they form neutral radicals so that no Coulombic interaction prevents the primary redox pair from dissociation. Furthermore, since rather polar solvents must be used with them, the bonding interaction due to resonant charge delocalization is weak because solvation in polar solvents tends to stabilize localized charge. Thus the primary intermediate of photoelectron transfer reactions with such reactants are very short-lived species with decay times comparable to or shorter than the S_1-T_1 ISC process in the dye.

We will describe here, how the method of magnetokinetics [8,9] in combination with the internal heavy atom effect can be utilized for obtaining quantitative information on the solvent dependent dynamics of the short-lived redox intermediates in such systems. The basis of our method is the kinetic competition between dissociation of the primary redox product (in general a two-step process leading from the triplet exciplex to a solvent-shared radical pair (RP) and furtheron to uncorrelated free radicals) and backward electron transfer (BET) either from the exciplex or the geminate RP. Since, according to the principle of spin conservation, the primary redox product originates with triplet spin and BET leads to the singlet ground state



Scheme 1

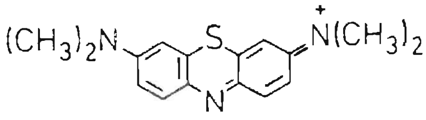
of the pair a spin conversion has to take place before or synchroneously with the BET process. Control of this spin conversion by the internal heavy atom effect and its modulation by an external magnetic field is reflected (in a time-integrated manner) by a corresponding change in the yield of free radicals that can be conveniently measured on a long time scale. If the details of the magnetic field dependent processes are quantitatively understood it is possible to determine the dynamics of the intermediate redox pair from the magnetic field dependence of the free radical yield.

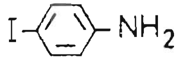
2. Solvent Dependence of Free Radical Yield

To a good approximation spin-orbit coupling (SOC) as induced by internal heavy atoms in the reacting species is only effective if the primary redox pair is in close contact, i.e. on the stage of the exciplex [7]. Spin conversion (ISC) and BET cannot be separated on this stage and the rate constant of the combined process, to be considered in more detail below, will be denoted k_{isc}. Using k_{er} as the rate constant of exciplex dissociation into radicals and neglecting at this stage of approximation BET contributions due to possible reencounters in the diffusion of the correlated geminate RP, we can represent the yield of free radicals from the exciplex as

$$\Phi_{fr} = k_{er}/(k_{er} + k_{isc}) = 1/(1+k_{isc}/k_{er}) \qquad (1)$$

indicating that this experimental quantity may be used e.g. as an indicator of solvent effects on k_{er} or k_{isc}. Note, however, that relative changes of these rate constants are reflected as changes of Φ_{fr} only if $k_{isc} > k_{er}$. For this reason the application of heavy atom substituents proves to be most useful [6].


methylene blue (A^+)


p-I-aniline(D)

The experimental results reported and analyzed in this paper have been obtained by investigating the electron transfer reaction between methylene blue triplet and p-I-aniline, the iodine substituent providing for a strong SOC in the redox pair. Observations of free radical yield were made by ns-time-resolved laser flash spectroscopy (for details cf. [7]). The quantity Φ_{fr} has been measured in a series of solvents including, in particular, binary solvent mixtures allowing for a fairly steady change of solvent properties. A survey of the results obtained is given in Table 1.

The variation of Φ_{fr} extending between 0.017 and 0.255 is considerable. A simple analysis might be based on eq (1) from which one obtains

$$k_{isc}/k_{er} = 1/\Phi_{fr} - 1 \qquad (2)$$

Since from Φ_{fr} only the ratio of k_{isc} and k_{er} can be obtained the individual solvent dependence of each of these parameters remains ambiguous. Nevertheless one might assume that k_{er} mainly reflects solvent viscosity effects, whereas k_{isc} characterizing a process that involves electron transfer (BET) should also depend on solvent polarity. It was on the basis of these assumptions that a reasonable interpretation of the solvent dependence of Φ_{fr} for the reaction of thiopyronine triplet with p-I-aniline and p-Br-aniline could be given previously [6]. As will be shown in the following, however, with the help of the magnetokinetic technique one can determine the absolute values of the rate parameters of the triplet exciplex and, in addition, assess the relative importance of BET within the exciplex and the correlated RP.

Table 1
Characteristics of solvents used and free radical yield Φ_{fr}, observed in zero magnetic field

Solvent v/v (%)	Polarity[a)] E_T (kcal)	Viscosity (cP)	free rad. yield Φ_{fr}
MeOH/EGLY			
100/ 0	55.5	0.600	0.100
90/ 10		0.828	0.085
80/ 20		1.155	0.066
60/ 40		2.143	0.042
MeOH/ACN			
50/ 50	55.3	0.337	0.113
30/ 70	54.8	0.332	0.165
25/ 75	54.5	0.330	0.174
10/ 90	52.9	0.330	0.211
2/ 98	50.2	0.332	0.239
0/100	46	0.341	0.255
MeOH/H_2O			
90/ 10	56.0	0.84	0.059
80/ 20	56.5	1.09	0.038
70/ 30	57.0	1.30	0.021
60/ 40	57.5	1.47	0.017
MeOH/Dioxane			
80/ 20	54.4	0.580	0.103
50/ 50	52.2	0.653	0.107
25/ 75	49.4	0.799	0.121
ACN/H_2O			
98/ 2	50.4	0.35	0.191
90/ 10	53.5	0.41	0.110
80/ 20	54.9	0.50	0.090
75/ 25	55.4	0.55	0.070
50/ 50	56.8	0.80	0.040

a) cf. ref [14]

3. Magnetokinetic Effects on Spinforbidden BET

Various types of spin-inversion mechanisms (cf [8,9]) must be considered when analyzing the spinforbidden BET in Scheme 1. In the triplet exciplex the exchange interaction leads to a considerable T_1-S_1 energy splitting and the combined spininversion/BET process takes place as a SOC induced T_1- S_0 radiationless process governed by the SOC properties of the heayy atom substituent. This process is magnetic field dependent according to the triplet mechanism (TM, cf. Figure 1). In the solvent-separated geminate RP T and S spinstates are in effect degenerate and the independent motions of the two unpaired electron spins will eventually lead to a change of radical spin correlation

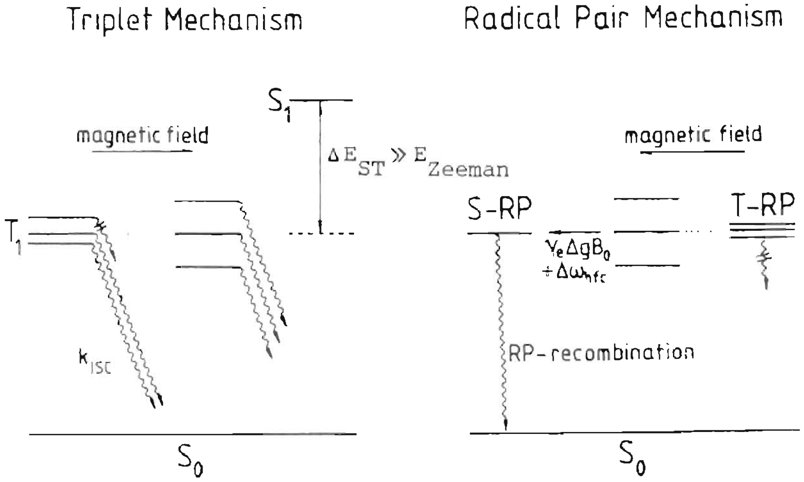


Figure 1. Two cases of SOC induced magnetokinetic effects. In the radical pair mechanism recombination to a singlet product is only possible form the radical pair singlet substate. A magnetic field may support recombination of triplet radical pairs by Δg-dependent mixing of radical pair T_0 and S spin substate. The triplet mechanism, applying e.g. to heavy atom containing triplet exciplexes, requires that fast direct SOC-induced transitions from triplet substates to the singlet ground state can occur. Due to symmetry selection rules SOC does not affect the triplet substates equally and they decay at different rates. In a magnetic field the zero-field triplet substates are mixed. Thereby their kinetic distinction is lost. Increasing uniformity of triplet sublevel decay enhances the overall efficiency of the T - S_0 process. The excited singlet state is not involved in case of this mechanism because the T/S energy splitting is too wide. Note that the splitting of the triplet levels is represented in a strongly enlarged scale as compared to the T/S_0 energy gap.

from T to S, so that a fast (now spin-allowed) BET may take place in the next re-encounter. It may be reasonably assumed [7] that of the various mechanisms of radical spin motion the T_0-S mixing due to the difference in Larmor frequencies (Δg- or Zeeman mechanism, cf. Figure 1), which increases linearly with the magnetic field, is the only one strong enough to become clearly detectable even for rapidly separating RPs. Thus our analysis of the magnetic field effect (MFE) is based on a combination of the TM in the triplet exciplex and the Δg-type RPM in the geminate RP. The mathematical details can be found in ref [7]. Here we will confine ourselves on defining the model parameters entering into the calculations and on a few demonstrations of how these parameters affect the observable magnetic field effect R(B) (eq.(3)) on the yield of free radicals.

$$R = [\Phi_{fr}(B) - \Phi_{fr}(0)]/\Phi_{fr}(0) \qquad (3)$$

The parameters characterizing the TM are k_{isc}, k_{er} and D_r. Here k_{isc} is the rate constant of the T_1-S_0 process for two of the exciplex triplet substates, the rate constant for the third one being considered as negligible; k_{er} is the rate constant of exciplex dissociation into a solvent-shared, spin-correlated geminate RP; D_r is the rotational diffusion constant of the exciplex, entering as a parameter to describe spin relaxation among the zero-field triplet substates of the exciplex [10].

The parameters characterizing the Δg-type RPM are Δg, D, a, Λ_S, Σ_{hfc}. Here Δg is the difference of electronic g-factors of the two radicals estimated as 0.015 for the present system [7], and D is the sum of the translational diffusion constants estimated as $3.7\text{x}10^{-5}\eta^{-1}cm^2s^{-1}cP$, with η the dynamic viscosity of the solvent. Parameter 'a' denotes the reaction distance for BET in a singlet spin correlated RP, and Λ_S the probability for a singlet RP at distance 'a' to react in this or any following re-encounters. The quantity Σ_{hfc} (6 Gauss for the present system) denotes the rms deviation of longitudinal hyperfine field differences between the two radicals for all possible nuclear spin configurations.

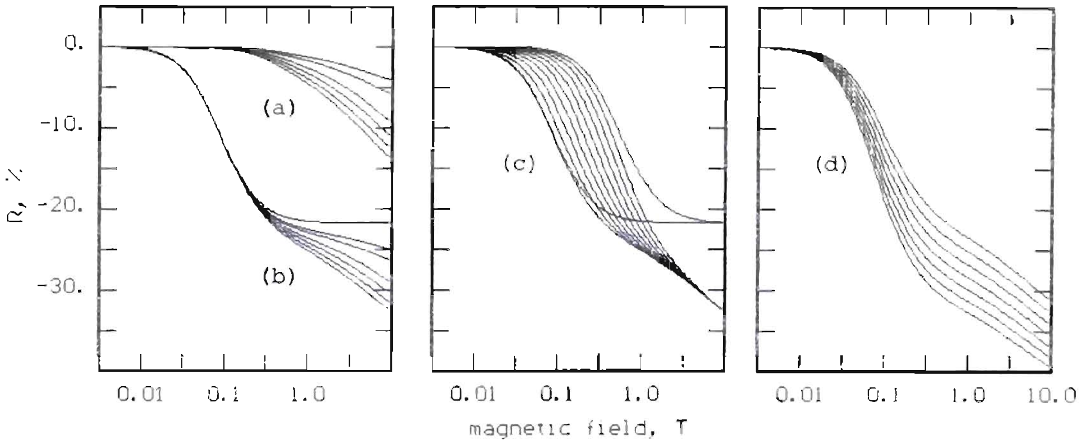


Figure 2. Theoretical parameter dependence of magnetic field effect on free radical yield.

(a) Pure RPM contribution, for curves from below values of (a/Å, Λ_S) are: (7, 1.0), (6, 1.0), (5, 1.0), (4, 1.0) (4, 0.65), (4, 0.5). Other RPM-parameters are $D=2\times10^{-5}cm^2s^{-1}$, $\Delta g= 0.015$, $\Sigma_{hfc}= 6$ Gauss.

(b) upper curve: pure TM ($k_{isc}=2\times10^{10}s^{-1}$, $k_{er}=10^9s^{-1}$, $D_r= 8\times10^9s^{-1}$), other curves: TM in combination with RPM, parameters as in (a).

(c) Variation of TM for Φ_{fr} fixed to 0.1. Parameters for curves from left to right are $\log(k_{er}/s^{-1})$ = 9.0, 9.1, 9.2, 9.3, 9.4, 9.5, 9.6, 9.7, $k_{isc}= 18.5\ k_{er}$, $D_r= 2.6\ k_{er}$. The RPM contribution is constant corresponding to a=0.7nm, $\Lambda_S=1.0$. The first and the last case are also shown without contribution of the RPM.

(d) Variation of TM: $k_{er}= 10^9s^{-1}$, other parameters for curves from left to right are $k_{isc}=$ (1.80,1.85, 1.90, 1.95, 2.00, 2.05)$\times10^{10}s^{-1}$; $D_r=$ (2.83, 2.61, 2.42, 2.27, 2.14, 2.03, 1.93)$\times10^9s^{-1}$ is determined such that $\Phi_{fr}= 0.1$ remains constant. Parameters of the RPM are as in (c).

In order to provide a feeling for how the two mechanisms contribute to the overall MFE, results of some model calculations employing various sets of the characteristic parameters are presented in Figure 2. Here set (a) of curves demonstrates the effect of the RPM only. The lowest curve (strongest MFE) in the set shown corresponds to the most favorable conditions of electron transfer that can be reasonably assumed (unity reaction probability at 0.7 nm separation). It is noteworthy that in the system considered the RPM does not contribute significantly to a MFE below 0.1 Tesla and does not exceed an absolute value of 8% at 3.5 Tesla the highest field investigated. Set (b) in Figure 2 shows the typical behaviour of the MFE due to the TM with a characteristic sigmoid dependence of R on log(B), implying saturation at high fields (cf. top curve in set (b), case of pure TM). Combining the TM with the RPM (cf. other curves of set (b)), the high field saturation behaviour is absent.

When fitting the TM to the experimental R(B) curve, only two parameters of the set k_{isc}, k_{er} and D_r are actually free to choose, if the additional constraint of the absolute experimental value of Φ_{fr} at zero field is taken into account. Thus, choosing k_{isc} and k_{er} the value of D_r is uniquely determined from $\Phi_{fr}(B=0)$ [11]. The effects of a variation of k_{isc} and k_{er} for a fixed value of Φ_{fr} are demonstrated by the sets (c) and (d) of curves in Figure 2. Changing k_{er} and keeping the ratio k_{isc}/k_{er} and D_r/k_{er} fixed (so that $\Phi_{fr}(0)$ remains constant) that part of the magnetic field depencence which is due to the TM undergoes a horizontal shift (if a log(B) scale is applied). The limiting behaviour at high fields (determined by the RPM), however, is independent of k_{er}. A change of k_{isc} at constant k_{er} with D_r adjusted such that Φ_{fr} at zero field is constant, leads to the variation of MFE demonstrated by set (d) in Figure 2. It appears that such a change has a major influence on the amplitude of the MFE.

In the following the experimental results of the MFE on Φ_{fr} in the solvents quoted in Table 1 are reported and analyzed in terms of the magnetokinetic mechanisms described above. As a general remark to the experimental technique for determining the magnetic field dependence of Φ_{fr} (actually defined as the efficiency of free radical formation from every triplet quenched by electron transfer) we note here that the results from the laser flash technique have been corroborated by applying also a more accurate, though more indirect, photostationary technique [7, 12] yielding the MFE at rather precision even for low absolute values of Φ_{fr}. The data points shown are from the latter experiments.

4. Solvent Viscosity Dependence of Magnetic Field Effect

The solvent series of methanol/ethylene glycol (EGLY) mixtures was chosen with the intention to realize a variation of solvent viscosity without a simultaneous change of polarity. This assumption seems to be fairly well justified in view of the chemical structures and the similar values of DK (32.7/37.7) or polarity parameter E_T (55.5/56.3) of the neat solvents. The MFEs observed in this series of solvents together with their theoretical simulations are shown in Figure 3. The parameters of the RPM correspond to the case of a diffusion controlled electron transfer reaction for BET with a reaction distance of 0.7 nm. The change of solvent viscosity is accounted for by the $D \sim 1/\eta$ relation mentioned above. The solvent viscosity dependence of the TM parameters obtained from the theoretical fit of the experimental MFE is displayed in the diagrams of Figure 4. The rate constant k_{er} shows a good proportionality to $1/\eta$ with a slope of about 20 times lower than to be expected for free diffusional separation of a pair of particles at 0.5 nm separation on the basis of the Eigen equation [13]. Therefrom we estimate a binding energy for the triplet exciplex of about 11 kJ mol^{-1}.

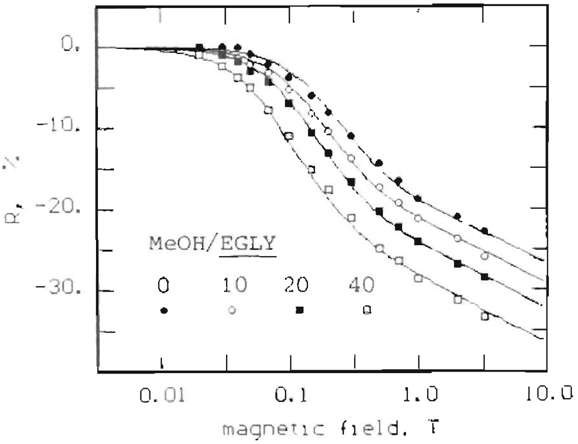


Figure 3. Magnetic field effect in MeOH/EGLY mixtures. Volume percentages of EGLY are assigned. The solid lines represent best fits using the TM parameter values indicated in Figure 4. The parameters of the RPM correspond to those of set (d) in Figure 2, except for D which is adapted to solvent viscosity as given in the text.

The rotational diffusion constant D_r is almost proportional to the inverse of the solvent viscosity. Applying Debye's expres-

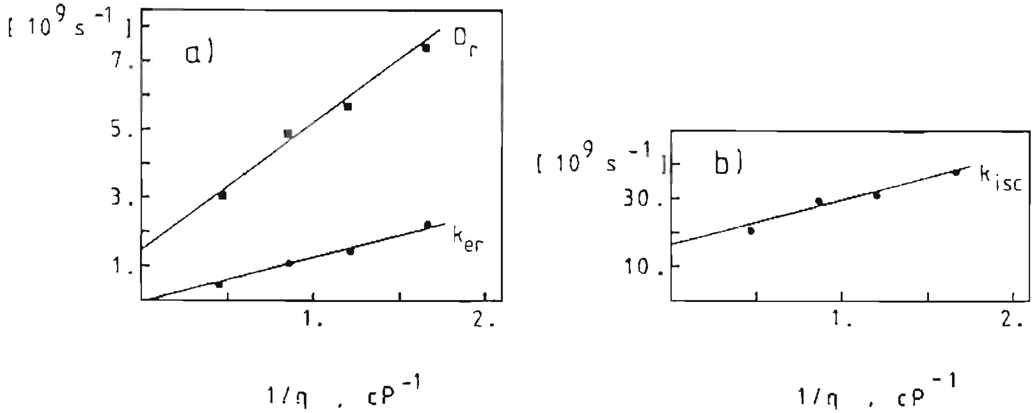


Figure 4. Viscosity dependence of the parameters k_{isc}, k_{er}, D_r determined for the triplet exciplex $^3(MB\cdot\cdot p\text{-}I\text{-}An)^+$.

sion for the rate constant of rotational diffusion one can estimate an effective hydrodynamic radius of the exciplex of about 0.36 nm [7] which fits rather well with what one expects from a molecular model. The rate constant of ISC in the exciplex has the weakest dependence on solvent viscosity, as expected. The value of about 3×10^{10} s^{-1} corresponding to 30 ps lifetime is very fast for an ISC process. It is due to the strong internal heavy atom effect of the iodine substituent.

5. Solvent Polarity Dependence of Magnetic Field Effect

On the basis of the present method of evaluation no preassumptions have to be made when analyzing for the solvent dependence of the various parameters characterizing the dynamics of the triplet exciplexes. This may be demonstrated with the magnetokinetic results for the other solvents listed in Table 1, where the variations of k_{isc}, k_{er} and D_r causing the solvent dependence of Φ_{fr} are less obvious than in the solvent viscosity series described above. The MFE curves observed (cf. Figure 5) span a large range of variations. The kinetic parameters evaluated for the triplet exciplexes are presented in plots versus $1/\eta$ the inverse of solvent viscosity or versus the empirical solvent polarity parameter E_T (Figures 6 and 7).

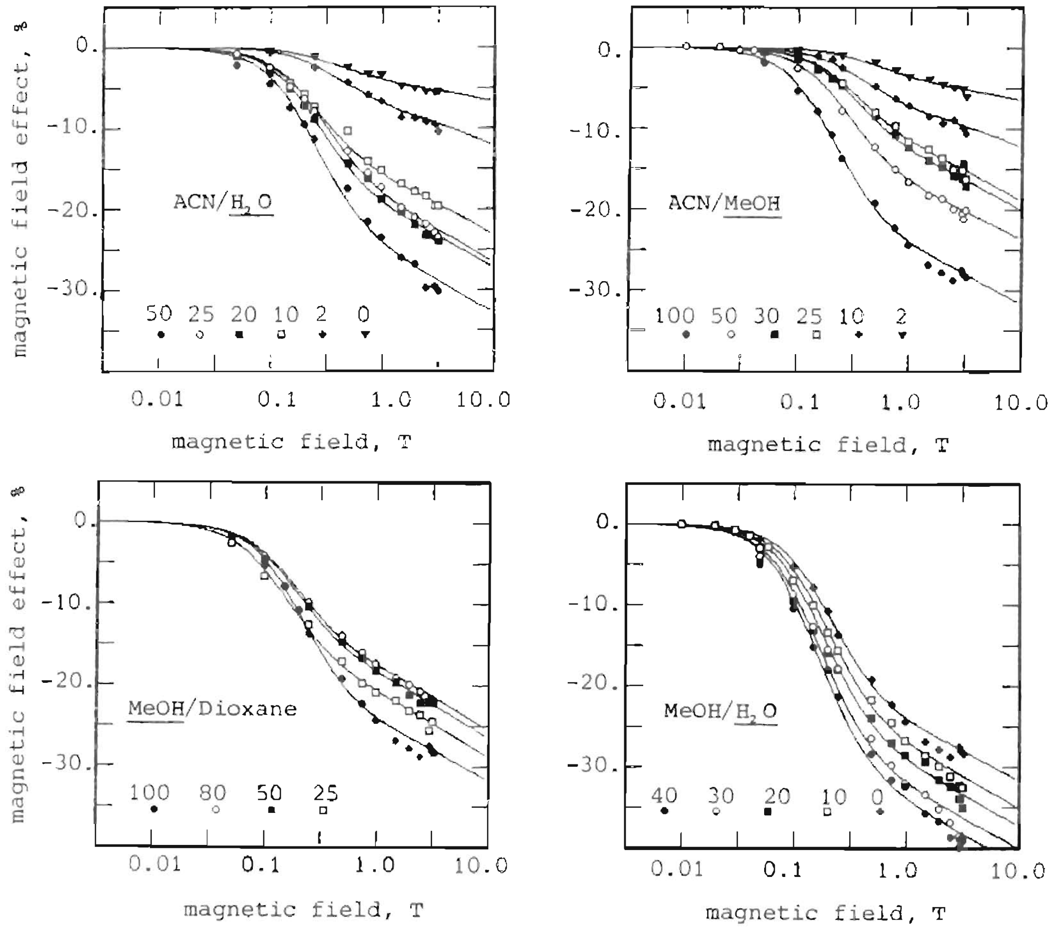


Figure 5. Magnetic field effect on the free radical yield in various solvent mixtures. Volume percentages of the underlined solvent components are indicated for each series of mixtures. The solid lines represent best fits using the TM parameters plotted in Figure 6. The parameter values for the RPM are those of set (d) in Figure 2, except for neat ACN (a= 4Å, Λ_S= 0.4), ACN/2% H_2O (a= 4Å, Λ_S= 0.8), ACN/2% MeOH (a= 4Å, Λ_S= 0.4), ACN/10% MeOH (a= 4Å, Λ_S= 0.8).

From the MFE in the H_2O/MeOH mixtures we obtain that k_{isc} is constant, with a very high value of about 4×10^{10} s^{-1}. The change in Φ_{fr} and in its magnetic field dependence is mainly due to changes in k_{er}, varying linearly with $1/\eta$ (Figure 6) which, along with the variation of D_r, is in line with the $1/\eta$ dependence of the MeOH/ EGLY mixtures.

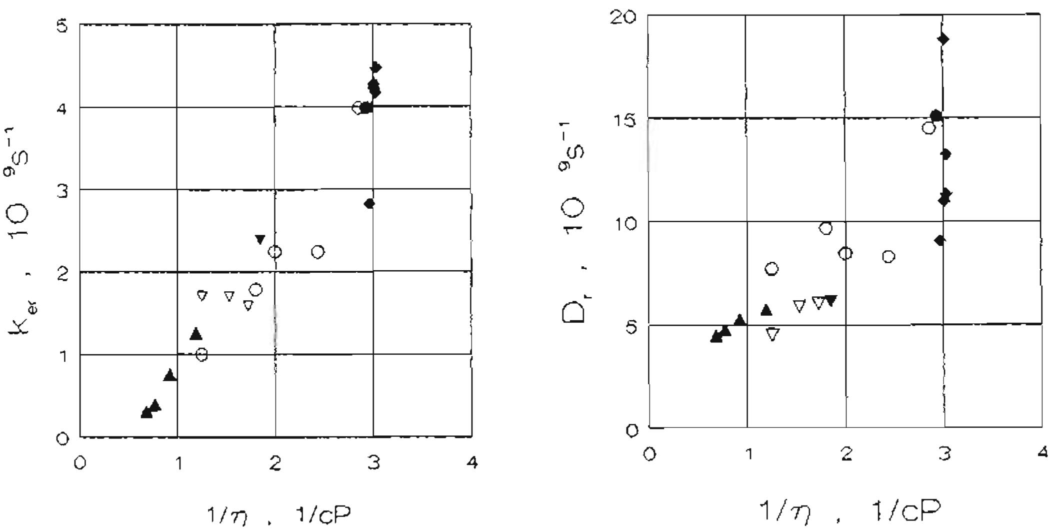


Figure 6. Correlation of exciplex paramters k_{er} and D_r with the inverse of solvent viscosity $1/\eta$.
Symbols are assigned as follows:
● ACN, ○ ACN/H_2O, ◆ ACN/MeOH, ▲ MeOH/H_2O, ▽ MeOH/Dioxane, ▼ MeOH

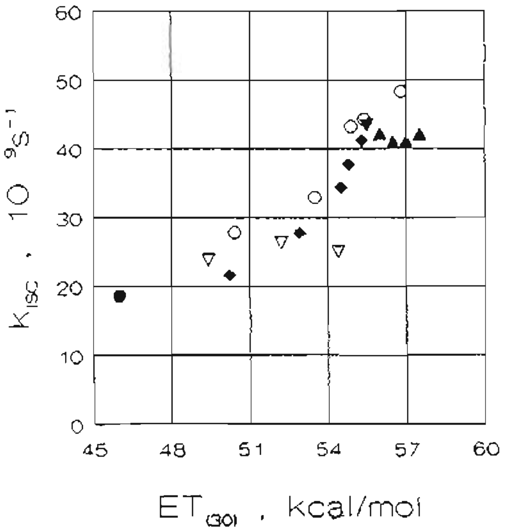


Figure 7. Correlation of exciplex parameter k_{isc} with solvent polarity parameter E_T. Assignment of solvents as in Figure 6.

The MFE curves obtained with ACN and its mixtures with H_2O or MeOH (Figure 5) span sets that are clearly different from those of the H_2O/MeOH mixtures. From the evaluation of the MFE it follows that with increasing amount of ACN k_{isc} is diminished whereas k_{er} and D_r increase. The trends of k_{isc} and k_{er} support each other in their effect on Φ_{fr} adopting its largest value in neat ACN. In the ACN mixtures k_{isc} shows a good correlation with the po-larity parameter E_T, whereas k_{er} and D_r fit the general $1/\eta$ trend although their scatter is considerable. It should be noted that for the small MFE in ACN rich solutions the TM and the RPM are no longer clearly separated on the log(B) axis. So the accuracy at which the triplet exciplex parameters can be determined is only about 30% in these cases, whereas it is better than about 10% in the others.

The mixtures of MeOH/Dioxan, in spite of an appreciable variation in E_T, do not show a great variation either in Φ_{fr} nor in the MFE on it. The rate parameters of the triplet exciplex determined from the MFE curves fit, however, into the general correlation of k_{isc} with E_T and of k_{er} and D_r with $1/\eta$.

In concluding, we point out that the determination of absolute values of individual rate constants characterizing the decay of the short lived triplet exciplexes, as has been demonstrated in this paper, confirms our previous interpretation of the solvent viscosity and polarity dependence of Φ_{fr} [6]. The argument provided for an increase of k_{isc} with solvent polarity was that increasing the solvent polarity should have a decreasing effect on the Franck-Condon energy gap between exciplex and ground state pair of reactants.

Acknowledgement

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DISCUSSION

Rettig

You showed strong magnetic field effects in exciplex systems (radical cation and neutral radical) with presumably strong exchange interaction. Would you expect that a similarly strong magnetic field effect might be observable in TICT systems with charge shift (radical cation of neutral radical need together by a single band)? What about TICT systems with charge separation?

Steiner

The essential condition for observing a triplet-mechanism type magnetic field effect is that the triplet under consideration undergoes a rapid, spin-sublevel selective intersystem crossing decay. Spin-sublevel selectivity is the usual property of spin-orbit coupling and not a very restrictive condition. The rate of the ISC process, however, must be faster or at least comparable to the rate of spin-relaxation among the zero-field substates. In liquid solution this process occur at a rate approximately equal to the orientational relaxation rate of the molecule. Comparably fast ISC usually requires enhanced spin-orbit coupling as may be achieved by heavy atom substituents.

The value of the exchange interaction (energy gap to configurationally related singlet) is not of relevance in the triplet mechanism.

In the case of linked donor-acceptor systems or TICT states the triplet mechanism can operate as in triplet exciplexes. The effect could be observed as a magnetic-field dependent shortening of the triplet lifetime or, if another decay channel besides ISC exists, as a magnetic field effect on the yield into this channel (analogous to the free radical yield in our triplet exciplex case). In the case of linked system such a monitoring channel might perhaps be realized by some fast photochemical reaction.

Matsuo

It is a pity that you did not have enough time to discuss $Ru(bpy)_3^{2+}$-viologen system. I would like to hear about the effects of the ligand and acceptor on the magnetokinetic parameters. Could you explain them quickly?

Steiner

Photoelectron transfer between $Ru(bpy)_3^{2+}$ and methylviologen is followed by efficient backward electron transfer (BET), such that only about 25% of free radicals are formed. By a magnetic field of 3.5T the BET is enhanced such that the free radical yield is reduced by 23%. Replacing the bipyridine (bpy) ligand by 4,4'-diethoxycarbonyl-bpy (dce) reduces this magnetic field effect to 6%. When mixing the two types of ligands it appears that the magnetic field effect reflects independent additive contributions of the ligands. Recent results suggest that this behavior might be attributed to the different contributions of the ligands to electron spin relaxation in the Ru(III) complex. The validity of this assumption will be investigated by ^{1}H-NMR of the paramagnetic Ru(III) complexes. Since electron spin relaxation in Ru(III) complexes is due to vibrational modulation of the g-tensor, our magnetokinetic results may provide a novel access to information about the bonding potential of the ligands in such complexes.

Ohno

I am interested in the dependence of k_{isc} on solvent polarities. You mentioned the polarity of solvent shifted ΔE to smaller one. My question is concerned with ΔE-dependence of k_{isc}, which may display the maximum of k_{isc} at higher ΔE. What is the energy gap involved in the spin converted ET process?

Steiner

The free energy change driving the spin-inverted backward electron transfer may be approximated as the negative free energy of the reaction $A^{+}\cdots D \longrightarrow A\cdots D^{+}$. In methanol this amounts to about 1.2 eV.