SPIN-SELECTIVE DEPOPULATION OF TRIPLET SUBLEVELS
IN RAPIDLY ROTATING TRIPLET EXCIPLEXES DETECTED
BY A HEAVY-ATOM-INDUCED MAGNETIC FIELD EFFECT

Ulrich STEINER
Institut für Physikalische Chemie der Universität Stuttgart, D-7000 Stuttgart 80, Germany

A mechanism is presented explaining a reported heavy-atom-induced magnetic field effect as a consequence of non-equilibrium triplet sublevel population in an intermediate exciplex. The triplet exciplex spin polarization is induced by sublevel-selective intersystem crossing from the exciplex triplet to its singlet ground state and is decreased by an external magnetic field. The theory accounts almost quantitatively for the observed influence of magnetic field strength and heavy-atom substituents

1. Introduction

Recently we reported a magnetic field effect on the radical yield of electron-transfer reactions between a dye triplet and heavy-atom-substituted electron donors [1]. As a possible explanation we suggested that it might be due to a magnetic field modulation of geminate radical pair recombination according to the Δg-mechanism. Though this explanation is qualitatively reasonable it is not supported by a quantitative application of current radical-pair theories. In a recent analysis of the Δg-mechanism, applied to the singlet recombination yield of geminate radical pairs produced in the triplet state [2], Schulten and Epstein [3] showed that with $\Delta g = 0.01$ and a magnetic field of 10 kG, the singlet recombination yield is of the order of 1.5%, whereas we observe a magnetic field effect of about 12% at 4 kG with a system where the g-factor difference is not likely to be greater than 0.01.

In this letter we give a preliminary presentation of a mechanism which can quantitatively account for the heavy-atom-induced magnetic field effects.

2. Kinetic model

As previously demonstrated [4] a triplet exciplex, $^3(AD^+)$, of radical-pair-like structure has to be assumed as the primary product in the electron-transfer reaction between dye triplet ($^3A^+$) and electron donor (D):
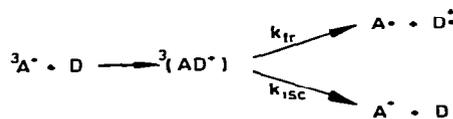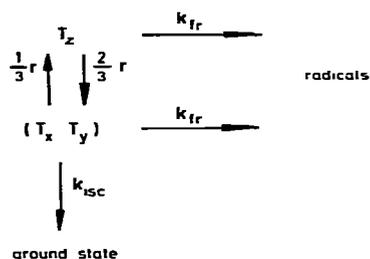

Scheme I.

Therefore, if a radical-pair mechanism fails to explain the magnetic field effect, it is tempting to invoke a magnetic field effect on the dynamics of the triplet exciplex.

Considering the intersystem crossing process leading from the triplet to the singlet ground state, we have to regard the contributions of the triplet sublevels separately. As will be shown in a forthcoming paper [5], the three triplet substates of the exciplex are not equally effective in intersystem crossing and for simplicity we assume here that intersystem crossing occurs only from two substates (denoted T_x and T_y) and is negligible from the third substate (T_z). Of

course the zero-field splitting of the exciplex triplet substates is rather small. Because of the dominating charge-transfer character in the cases under considera- tion [4], the D-value is expected to be of the order of 0.02 cm^{-1} [6], corresponding to a Zeeman split- ting in a magnetic field of about 200 G. In solutions at room temperature these levels are populated equal- ly. However, if there is a fast intersystem crossing from two of these levels, comparable in its rate or faster than the relaxation of the triplet sublevel popu- lation, a non-equilibrium distribution over the triplet sublevels will be maintained during the decay of the exciplex.

The radical yield obtained under such conditions will be higher than under equilibrium conditions, since the dissociation rate constant is not expected to be spin selective. If in such a case the rate of relaxa- tion among the triplet sublevels can be increased by some external influence, the radical yield will de- crease. Since an external magnetic field has the effect of mixing the triplet sublevels of the randomly orient- ed rotating triplet exciplexes, it provides an effective additional relaxation mechanism with the consequence that the radical yield decreases with increasing mag- netic field strength.

An exact treatment of the proposed mechanism should be based on the solution of the appropriate stochastic Liouville equation and will be presented elsewhere [5]. Here we treat the problem in a simple but more illustrative kinetic approximation described by:

Scheme II.

It is assumed that the equilibrium of the triplet sub- level population can be described by a single rate con- stant r, k_{isc} denotes the intersystem crossing rate con- stant for the substates T_x and T_y, k_{fr} is the rate con- stant for exciplex dissociation into radicals and is as- sumed to be equal for T_x, T_y and T_z. Since T_x and

T_y are not distinguished kinetically we treat them as one common state.

Assuming equal population of the triplet sublevels when the exciplex is formed, with scheme II we arrive at the following expression for the radical yield Φ_{fr},

$$\Phi_{\mathrm{fr}} = k_{\mathrm{fr}} \frac{k_{\mathrm{fr}} + \frac{1}{3}k_{\mathrm{isc}} + r}{(k_{\mathrm{fr}} + k_{\mathrm{isc}})(k_{\mathrm{fr}} + \frac{2}{3}r) + \frac{1}{3}rk_{\mathrm{fr}}} . \qquad (1)$$

As will be shown in detail elsewhere [5], the effective relaxation rate constant of the triplet sublevels in the presence of an external magnetic field is given by

$$r = r_0(1 + 5x^2 + 4x^4)/(1 + 3x^2 + 0.8x^4) , \qquad (2)$$

where r_0 is the relaxation constant in the absence of an external field and x is defined by

$$x = g\mu_B B\hbar^{-1}/r_0 . \qquad (3)$$

Here B is the magnetic field strength, g the gyromag- netic ratio and μ_B is the Bohr magneton. In the deriva- tion of eq. (2) the zero-field splitting of the exciplex has been neglected, so that one might expect some discrepancy between theoretical and experimental re- sults at fields below 1 kG.

The relaxation constant r_0 of the triplet sublevels in zero field can be obtained by the following argu- ment. The zero-field splitting of the exciplex corre- sponds to a characteristic time of approximately 300 ps which is much longer than the orientational corre- lation time to be expected for the exciplex in a solvent like methanol. Hence it will be a good approximation to assume that during the rotational diffusion of the exciplex the spin remains almost fixed in the labora- tory system. As a consequence the triplet sublevel relaxation time $1/r_0$ should be well approximated by the orientational relaxation time τ_D which can be cal- culated by the Debye formula [7]

$$1/r_0 \approx \tau_D = \frac{4}{3}\pi r_D^3 \eta/kT , \qquad (4)$$

where r_D is the Debye radius, η is the solvent viscosity, T the absolute temperature and k Boltzmann's con- stant.

3. Comparison with experiment

To compare the predictions of our model with the experimental results we shall proceed in the following way. As expressed in eq. (1), Φ_{fr} is a function of k_{fr},

k_{isc} and B. We have determined Φ_{fr} for a series of exciplexes with thionine as electron acceptor and various halogen anilines as electron donors [4]. As was demonstrated, halogen substitution of the aniline leaves the dissociation rate constant k_{fr} of the exciplex approximately unaffected but changes k_{isc} significantly. So, if we could guess the dissociation rate constant k_{fr} and assume a reasonable value for r_D in eq. (4), we could calculate k_{isc} from the radical yield at zero field (henceforth denoted as $\Phi_{fr}(k_{isc}, 0)$) by use of eqs. (1)–(4) and predict the magnetic field effect R, defined by

$$R = 100[\Phi_{fr}(k_{isc}, B) - \Phi_{fr}(k_{isc}, 0)]/\Phi_{fr}(k_{isc}, 0) , \quad (5)$$

as a function of k_{isc} and B. It is indeed possible to obtain a reasonable fit of our experimental data assuming the same value of k_{fr} for all systems investigated. The best fit is obtained with $k_{fr} = 1.1 \times 10^9$ s^{-1} whereby the relative accuracy of the magnetic field effects detected limits the accuracy of k_{fr} to $\pm 30\%$. Our calculations are based on a value of 25×10^9 s^{-1} for $r_0 = 1/\tau_D$, corresponding to a Debye radius of about 4 Å in methanol.

Fig. 1 shows the magnetic field effect R measured and calculated as a function of magnetic field strength for the thionine/p-iodoaniline triplet exciplex. Since we neglected the influence of the zero-field splitting, we expect a discrepancy between theory and experiment in the region of low magnetic fields. Roughly
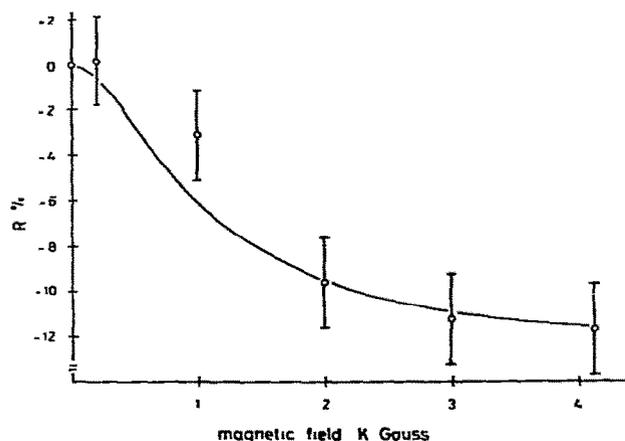
Fig. 1. Relative magnetic field effect R as a function of magnetic field strength for the triplet exciplex thionine/p-iodoaniline. Solid curve, calculated as described in text.
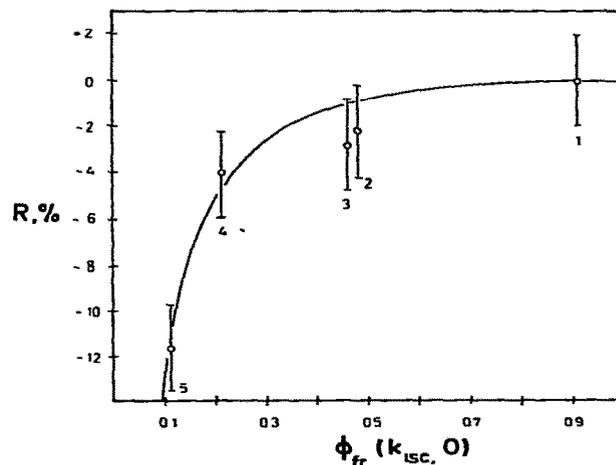
Fig. 2. Relative magnetic field effect R as a function of radical yield at zero field $\Phi_{fr}(k_{isc}, 0)$. The numbers refer to the different electron donors listed in table 1. Solid curve, calculated as described in text.

the influence of the zero-field splitting should be that the magnetic field affects the sublevel kinetics only at values $\geqslant D$, so that, as a first-order correction, we should shift our calculated curve ≈ 200 G to higher fields. This might explain the deviation of the point at 1 kG where the magnetic field dependence has its steepest descent.

In fig. 2 we compare theory and experiment with respect to the influence of k_{isc} on the magnetic field effect. Since we obtain k_{isc} from Φ_{fr} measured at zero field, we plot the magnetic field effect directly against $\Phi_{fr}(k_{isc}, 0)$ rather than against k_{isc}. Again theory and experiment compare favorably.

In order to justify the applicability of our model, it remains to be discussed whether the order of magnitude which had to be assumed for the exciplex dissociation rate constant is reasonable. Weller and co-workers [8] observed a dissociation rate constant of 3×10^7 s^{-1} for the pyrene/3,5-dimethoxy-dimethylaniline singlet exciplex in methanol. In this case the exciplex dissociates into a pair of oppositely charged radical ions, whereas in our case only the donor radical is positively charged, so that the dissociation is not hindered by Coulomb attraction. This may explain the faster dissociation in our case where the exciplex bonding is probably only due to a resonance stabilization of the charge-transfer state by the locally

excited triplet state, $(^3A^+D) \leftrightarrow {}^3(AD^+)$ [9,10]. Thus $k_{fr} \approx 10^9$ s^{-1} appears physically reasonable and the good agreement between experimental and theoretical results as demonstrated in figs. 1 and 2 supports the validity of our model.

4. Concluding remarks

It may be anticipated that spin—orbit-coupling-enhanced magnetic field effects of the kind reported here will become a valuable tool to study the properties and dynamics of short-lived triplet exciplexes. Since the orientational relaxation time provides an absolute time basis for all rate processes shown in scheme II, we can now obtain absolute rate constants for the intersystem crossing of the triplet exciplexes. The values obtained for the systems described in this paper are listed in table 1, their relative accuracy, as in the case of k_{fr}, amounting to ±30%.

Refining the theoretical treatment and improving the experimental accuracy should allow determination of the zero-field splitting parameter of these and similar systems which cannot be studied by ESR experiments. Thus detailed information on the electronic structure of short-lived intermediates in electron-transfer reactions with excited triplet states may become available.

It should be noted that scheme II provides a general mechanism for magnetic field effects; it is not necessarily restricted to triplet exciplexes but may involve any triplet-state species provided it decays by a fast sublevel-selective intersystem crossing process com-

peting with a non-sublevel-selective second decay mechanism. Whereas in our case the second decay channel is provided by the exciplex dissociation into radicals, processes like hydrogen-atom or proton-transfer may function as the second channel in other cases.

Finally we point out that the model presented here bears a close relation to a mechanism of electron spin polarization in photochemically generated radicals as suggested by Atkins and Evans [11]. In their mechanism the different *population* rate constants of the spin sublevels of a reacting triplet are chiefly important. Significant effects ensue if the quenching reaction of the triplet, leading to radical formation, is faster than the relaxation of the triplet Zeeman level population (T_1). In our case, however, the sublevel population of the precursor triplets $(^3A^+)$ has already obtained thermal equilibrium when the exciplexes are formed (in order to avoid reaction of the excited dye singlets we generally choose fairly low donor concentrations so that the effective lifetime of $^3A^+$ is ≈100–1000 ns). The non-equilibrium sublevel population of the exciplex triplet, $^3(AD^+)$, is produced by its own spin-selective *depopulation* process. It may be concluded, however, that in our case, too, the radicals formed should show spin polarization, and it might be of interest to look for CIDEP effects in these systems.

Table 1
Radical yields Φ_{fr} and intersystem crossing rate constants k_{isc} for triplet exciplexes between thionine and various electron donors

Donor [a]	Φ_{fr} [b]	k_{isc} [c]
aniline (1)	0.91	0.15
p-Br-aniline (2)	0.48	1.8
m-I-aniline (3)	0.46	2.0
o-I-aniline (4)	0.21	6.8
p-I-aniline (5)	0.11	16.3

[a] Numbers in parentheses refer to data points in fig. 2.
[b] Measured at zero field.
[c] 10^9 s^{-1}, accuracy ±30%, calculation based on $k_{fr} = 1.1 \times 10^9$ s^{-1}.

References

[1] U. Steiner, Z. Naturforsch. 34a (1979) 1093.
[2] H. Staerk and K. Razi Naqvi, Chem. Phys. Letters 50 (1977) 386.
[3] K. Schulten and I.R. Epstein, J. Chem. Phys. 71 (1979) 309.
[4] U. Steiner and G. Winter, Chem. Phys. Letters 55 (1978) 364.

[5] U. Steiner, to be published.

[6] H. Beens, J. de Jong and A. Weller, Colloque Ampère 15, ed. P. Averbuch (North-Holland, Amsterdam, 1969) pp. 289–292;
H. Hayashi, S. Iwata and S. Nagakura, J. Chem. Phys. 50 (1969) 993.

[7] P. Debye, Polare Molekeln (Leipzig, 1929).

[8] K. Schulten, H. Staerk, A. Weller, H.-J. Werner and B. Nickel, Z. Physik. Chem. NF 101 (1976) 371,

H.-J. Werner, H. Staerk and A. Weller, J. Chem. Phys. 68 (1978) 2419.

[9] A. Weller, in: The exciplex, eds. M. Gordon and W.R. Ware (Academic Press, New York, 1975) pp. 23–30.

[10] U. Steiner, Schweratome als molekulare Sonden zum Nachweis und Studium des Verhaltens von Triplettexciplexen (Hochschulverlag, Freiburg, 1979).

[11] P.W. Atkins and G.T. Evans, Mol. Phys. 27 (1974) 1633.