Spin–Orbit Coupling Induced Magnetic Field Effects in Electron-Transfer Reactions with Excited Triplets: The Role of Triplet Exciplexes and Radical Pairs in Geminate Recombination

Ulrich E. Steiner* and Werner Haas

Fakultät für Chemie, Universität Konstanz, D-7750 Konstanz, FRG (Received: April 19, 1990)

The magnetic field dependence of free-radical yield in the electron-transfer quenching of methylene blue triplet by p-iodoaniline has been determined between 0.00 and 3.30 T in methanol/ethylene glycol mixtures of various viscosities by using laser flash spectroscopy and a photostationary flow technique. The observed decrease of the free-radical yield with the magnetic field is interpreted by heavy-atom-induced spin-orbit coupling causing magnetic field sensitivity according to the triplet mechanism (TM) in intermediate triplet exciplexes and to the Δg type radical pair mechanism (RPM) in geminate triplet radical pairs originating from dissociation of the triplet exciplexes. Analytical expressions are provided for a treatment of a combination of both mechanisms including the case of reversible formation of the triplet exciplex from the geminate radical pair. The formalism of Pedersen developed for the high field radical pair mechanism and modified by Vollenweider and Fischer to account for effects of exchange interaction is generalized to include various boundary conditions for the electron spin density matrix suggested in the literature to describe the effects of encounters and chemical reaction. With a physically consistent choice of TM and RPM parameters model calculations provide a very good quantitative fit of the observed magnetic field and viscosity dependence of the yield of free radicals.

1. Introduction

Magnetic field effects (MFEs) in chemical and photochemical kinetics result from the intriguing interplay of the motion of unpaired electron spins with molecular motion and reaction dynamics. During the past 20 years the growing theoretical understanding of such effects has added a great deal to our knowledge of reaction mechanisms particularly where radical pairs are involved as intermediates. For a survey of these mechanisms cf. refs 1–3.

An important pathway for radical pair (RP) formation is photoelectron transfer, resulting in a spin *and* charge separation. Though spatially separated, the unpaired electron spins originating in such a process must be assumed at first to retain their original correlation; i.e., radical pairs with total singlet or triplet spin are formed in electron-transfer reactions between closed-shell donors or acceptors with excited singlets or triplets, respectively. These radical pairs which, if they are in direct contact and exhibit appreciable electronic overlap, adopt the characteristics of exciplexes⁴ are usually of high energy and will tend to relax by efficient back electron transfer⁵⁻⁸ yielding singlet ground-state products or, in favorable cases, even locally excited triplet products.⁹⁻¹¹

The required spin correlation between the spin state wherein the radical pair (or exciplex) is produced and the final product state represents a kinetic selection rule discriminating between spin-allowed and spin-forbidden reactions. There are two basic interactions, spin-orbit coupling (SOC) and hyperfine coupling (HFC), capable of moderating these selection rules and hence becoming kinetic determinants in a reaction mechanism involving radical pairs. SOC is only effective in mixing states differing in spin *and* orbital part of the wave function. Thus, whereas stationary states of appreciably spin-mixed character do not occur unless there is orbital degeneracy, e.g., in transition-metal complexes of high symmetry.¹² SOC can effectively contribute to make excited states nonstationary by inducing radiationless ISC processes $(S_1 \rightarrow T, T_1 \rightarrow S_0)$ where spin and orbital changes occur simultaneously.¹³ Within exciplexes, the processes ${}^{1}CT \rightarrow {}^{3}LE$ (charge transfer to locally excited state) and ${}^{3}CT \rightarrow S_0$ are of this type.

In a pair of well-separated radicals SOC cannot induce radiationless transitions connected with orbital changes since, individually, the radicals are in their doublet ground states.¹⁴ Only in the case of a *direct contact* between the radicals, i.e., when they form *one* electronically excited system, can SOC support processes involving both a spin and orbital change, e.g., recombination of a ³RP to a singlet ground-state product. $^{15-17,68}$

The effect of HFC can be represented by local magnetic fields to which the unpaired electron spins are exposed in the individual radicals.¹⁸ These local fields are characterized by an isotropic part (IHFC) independent of radical orientation and an anisotropic part (AHFC) which is modulated by molecular rotation. The interaction with the hyperfine fields allows the electron spin to change (reorient) without a change of orbital motion so that overall

(2) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. Spin Polarization and Magnetic Effects in Radical Reactions; Elsevier: Amsterdam, The Netherlands, 1984.

(4) Gordon, M., Ware, W. R., Eds. *The Exciplex*; Academic Press: New York, 1975.

(5) Rehm, D.; Weller, A. Ber. Bunsen-Ges. Phys. Chem. 1969, 73, 834.
(6) Iwa, P.; Steiner, U. E.; Vogelmann, E.; Kramer H.E.A. J. Phys. Chem. 1982, 86, 1277.

(7) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. J. Am. Chem. Soc. 1988, 110, 1991. Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. Ibid. 1987, 109, 3794.

(8) Kakitani, T.: Mataga, N. J. Phys. Chem. 1986, 90, 993. Mataga, N.; Kanda, Y.; Okada, T. Ibid. 1986, 90, 3880.

(9) Schulten, K.; Staerk, H.; Weller, A.; Werner, H-J.; Nickel, B. Z. Phys. Chem. 1976, 101, 371.

(10) Michel-Beyerle, M. E.; Haberkorn, R.; Bube, W.; Steffens, E.; Schröder, H.; Neusser, H. J.; Schlag, E. W. Chem. Phys. 1976, 17, 139. (11) Hoff, A. J. Q. Rev. Biophys. 1981, 14, 599.

(12) Steiner, U. E.; Wolff, H.-J.; Ulrich, T.; Ohno, T. J. Phys. Chem. 1989, 93, 5147.

(13) Mc Glynn, S. P.; Azumi, T.; Kinoshita, M. Molecular Spectroscopy of the Triplet State; Prentice Hall: Englewood Cliffs, NJ, 1969.

(14) SOC may induce changes in electronic spin orientation of a radical by virtue of the spin-rotational interaction. This mechanism provides a coupling to stochastic molecular motion and thus results in T_1 and T_2 type spin relaxation. Since such processes are not generally correlated between two radicals of a pair they also cause $T \rightleftharpoons S$ spin relaxation of the radical pair. In homogeneous solution of low viscosity, however, the rate of this process is usually slower than the rate by which the RP decays into uncorrelated free radicals.

 (15) Zimmt, M. B.; Doubleday, Ch., Jr.; Gould, I. R.; Turro, N. J. J. Am. Chem. Soc. 1985, 107, 6724. Zimmt, M. B.; Doubleday, Ch., Jr.; Turro, N. J. J. Am. Chem. Soc. 1986, 108, 3618.

(16) Steiner, U. E. Schweratome als molekulare Sonden zum Nachweis und Studium des Verhaltens von Triplettexciplexen; Hochschulverlag: Freiburg, 1979.

(17) Steiner, U. E.; Winter, G.; Kramer, H.E.A. J. Phys. Chem. 1977, 81, 1104.

(18) Schulten, K.; Wolynes, P. J. Chem. Phys. 1978, 68, 3292. Knapp, E.-W.; Schulten, K. J. Chem. Phys. 1979, 79, 1878.

⁽¹⁾ Steiner, U. E.; Ulrich, T. Chem. Rev. 1989, 89, 51.

⁽³⁾ Gould, I. R.; Turro, N. J.; Zimmt, M. B. Adv. Phys. Org. Chem. 1984, 20, 1.

^{*} Author to whom correspondence should be addressed.

singlet and triplet spin states of a radical pair may be converted into each other. The corresponding processes induced by the IHFC are coherent ones and require that the spin states to be mixed have an energy separation not greatly exceeding the HFC interaction responsible for the coupling. Provided this condition is met, they are quite efficient with effective rate constants of 10^8-10^9 s⁻¹ in typical organic radical pairs. The AHFC provides a mechanism of incoherent mixing of the RP spin states by virtue of its stochastic modulation by rotational diffusion. These incoherent processes (spin relaxation) due to AHFC are usually by at least 1 order of magnitude slower than the coherent ones due to IHFC.^{19,20}

By applying external magnetic fields the unpaired electron spins become subject to the Zeeman interaction and the microscopic kinetics, as far as it depends on SOC and HFC effects, may be modified in specific ways.

With respect to SOC, in triplet exciplexes the so-called triplet mechanism^{21,22} (TM) can take action. This mechanism depends on selective ISC rates from the different zero-field substates T_x , T_y , T_z of a triplet. Since the Zeeman interaction in randomly oriented molecules mixes the substates T_x , T_y , T_z the ISC selectivity is averaged out during one Larmor period with the effect that (for an initially uniform population of triplet sublevels) the overall ISC process becomes more efficient and competes more successfully with non-spin-selective processes, e.g., exciplex dissociation into free radicals. The mechanism has been established and investigated in some detail in previous work from this laboratory.^{23,24} A characteristic feature of the TM is that the magnetic field effect saturates when the Larmor frequency exceeds the sum of the largest substate-specific ISC rate constant and the relaxation rate constant among the zero-field substates.

In RPs a combined action of SOC and Zeeman interaction can take place which is absent in zero field. It is due to a difference between the g factors of the two radicals and will be enhanced by heavy atom substituents in only one of the radicals. In such a case the different Larmor frequencies at the two radicals bring about a periodic dephasing and rephasing of the transverse spin components corresponding to periodic transitions $T_0 \leftrightarrow S$ of the RP. The rate of these transitions increases linearly with the magnetic field. According to the radical pair mechanism (RPM) recombination or escape product yields depend on the combined action of $T \leftrightarrow S$ spin motion and geminate reencounters. Since, however, the time dependence of reencounters of geminate RPs is not monoexponential but corresponds to a rather broad spectrum of first reencounter times, a saturation limit of magnetic field effects on product yields is approached only very gradually, when this mechanism is operating.25

With respect to HFC in radical pairs it is important that the Zeeman splitting of the triplet components caused by the external magnetic field goes along with a suppression of coherent $T_{\pm} \leftrightarrow$ S transitions. Such effects approach a saturating limit if the field exceeds several times a characteristic quantity $B_{1/2}$ related to the effective HFC of the radicals involved. Typical $B_{1/2}$ values are on the order of several millitesla and are by 1 or 2 orders of magnitude smaller than the fields where SOC-induced magnetic field effects according to the TM and the Δg RPM usually become apparent. An external magnetic field will also affect the rates of incoherent relaxational processes as induced by AHFC and g-tensor anisotropy.^{19,20,26} Such processes will, however, not be considered of importance in the present investigation since they are too slow to compete effectively with the other processes determining the reaction yields.

In this paper we describe investigations on the magnetic field dependence of free-radical formation in the electron-transfer reaction between methylene blue triplet and p-iodoaniline, a system

(19) Hayashi, H.; Nagakura, S. Bull. Chem. Soc. Jpn. 1984, 57, 322.
(20) Lüders, K.; Salikhov, K. M. Chem. Phys. 1987, 117, 113.
(21) Atkins, P. W.; Evans, G. T. Mol. Phys. 1974, 27, 1633.
(22) Steiner, U. E. Chem. Phys. Lett. 1980, 74, 108.
(23) Steiner, U. E. Ber. Bursen-Ges. Phys. Chem. 1981, 85, 228.
(24) Ulrich, T.; Steiner, U. E.; Föll, R. E. J. Phys. Chem. 1983, 87, 1873.
(25) Schulten, K.; Epstein, I. R. J. Chem. Phys. 1979, 71, 309.

with strong SOC in the electron donor moiety so that magnetic field effects according to the TM and to the Δg RPM are possible. We expected that from a detailed analysis of precisely determined magnetic field dependences in solvents of varying viscosities the contributions of both mechanisms could be assessed and hence interesting information on the roles of triplet exciplexes and geminate radical pairs in the course of free-radical formation might be obtained. One particular point of interest is the question to what extent dissociation of a triplet exciplex into a radical pair is reversible. In the case of singlet electron-transfer reactions such reversible exciplex formation has been demonstrated by magnetic field modulation of exciplex fluorescence intensity.^{27-29,41} In these cases the effects observed were due to the HFC mechanism in the RP. Such a kind of luminescence probing is not possible in the case of short-lived triplet exciplexes since their phosphorescence is not detectable in liquid solutions. Utilizing the TM, however, in short-lived exciplexes with strong SOC provides a specific method for the triplet case.

2. Experimental Section

2.1. Materials. Methylene blue from the stocks of the laboratory was purified by an extraction method according to the procedure by Bergmann and O'Konski.³⁰ The purity was checked by elemental analysis and by thin layer chromatography. In methanol the molar extinction coefficient at $\lambda_{max} = 650$ nm was 84 500 M⁻¹ cm⁻¹.

Aniline (Merck, p.a.) was distilled in vacuo, p-iodoaniline (Fluka, 98%) was recrystallized twice from petroleum ether (bp 35-80 °C). Solvents used were methanol (Merck, p.a.) and ethylene glycol (Merck, p.a.). Buffer materials used were phenylacetic acid (Roth, puriss.) and sodium methylate prepared by dissolving sodium metal in methanol and determining the exact concentration by volumetric titration.

2.2. Instrumentation. For the time-resolved experiments a nanosecond laser flash spectrometer with an excimer/dye laser combination and described in more detail in refs 31 and 32 was used. The laser dye was rhodamine 6G tuned at 582 nm. For investigating magnetic field effects by continuous illumination experiments, the technique described by Schlenker und Steiner³³ was applied. Details on the equipment may be found in ref 31. In both types of experiments, time resolved and stationary, the magnetic field was varied between 0.0 mT (±0.1 mT) and 3.3 T by means of a Bruker Model B-E 15 electromagnet equipped with a current reverse unit to compensate for the remanent magnetization of the pole pieces when the zero-field value is adjusted.

2.3. Specific Conditions. In the time-resolved experiments signal averaging over 32 single-pulse events was applied.

Both time-resolved and stationary experiments were carried out in flow-through systems. For deaeration the solutions were flushed in the supply vessels with Suprapur N_2 for 1.5 h (500 mL solution) for stationary experiments and for 0.5 h (100 mL solution) for laser measurements. The Teflon flow lines were surrounded by polyethylene tubes flushed with nitrogen. In some of the laser experiments the solutions were buffered in order to protonate the dye semiquinone for better optical detectability (cf. ref 24). For this purpose the solutions were 0.015 M in phenylacetic acid and 0.005 M in sodium methylate, corresponding to a $pH^* = 8.6$ in methanol.³⁶ In order to vary the solvent viscosity, mixtures of

- (32) Ulrich, T. Dissertation, Universität Konstanz, 1986. (33) Schlenker, W.; Steiner, U. E. Ber. Bunsen-Ges. Phys. Chem. 1985,
- 89, 1041.
- (34) Wolff, H.-J. Diploma Thesis, Universität Konstanz, 1988.
 (35) Wiedorn, M. Diploma Thesis, Universität Konstanz, 1988.
 (36) Broser, W.; Fleischhauer, H. Z. Naturforsch. B 1970, 25, 1389.

⁽²⁷⁾ Petrov, N. Kh.; Shushin, A. I.; Frankevich, E. L. Chem. Phys. Lett. 1981, 82, 339.

⁽²⁸⁾ Basu, S.; Nath, D.; Chowdhury, M. J. Chem. Soc., Faraday Trans. 2 1987, 83, 1325. Nath, D. N.; Chowdhury, M. Chem. Phys. Lett. 1984, 109, 13.

⁽²⁹⁾ Staerk, H.; Kühnle, W.; Treichel, R.; Weller, A. Chem. Phys. Lett. 1985, 118, 19.

 ⁽³⁰⁾ Bergmann, K.; O'Konski, C. T. J. Phys. Chem. 1963, 67, 2169.
 (31) Ulrich, T.; Steiner, U. E.; Schlenker, W. Tetrahedron 1986, 42, 6131.



Figure 1. Transient signals of MB• radical absorbance observed at 430 nm on laser photolysis of a $[MB^+] = 10^{-5}$ M solution in oxygen-free methanol with 10^{-2} M aniline or *p*-I-aniline.

methanol and ethylene glycol (EGLY) were used as solvents.

3. Results

The triplet of methylene blue (MB⁺) is quenched by aniline very efficiently via electron transfer with formation of the methylene blue semiquinone radical (MB[•]).³⁹ In methanol we found a quenching rate constant of $k_q(An) = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The corresponding quenching constant for *p*-iodoaniline $(k_q(p-I-An) = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ was found similar to that of aniline, indicating that both quenchers have about the same electrondonating potential as is also expected from their one-electronoxidation potentials.37 This similarity in their behavior toward ³MB⁺ is in line with earlier observations in this laboratory on the quenching of thionine triplet.37,38

The semiquinone radical originating from the quenching may be observed by its absorption band with a maximum at 415-430 nm. When high concentrations of the donors are applied, so that the triplet decay is fast and occurs almost exclusively through the bimolecular quenching process, the initial radical absorbance after triplet decay provides a measure for the efficiency of free-radical formation in the quenching (η_{FR}) . The corresponding absorption signals for methanol as a solvent are shown in Figure 1. Here the triplet decay is complete after a fraction of 1 μ s and the largely different efficiencies of radical formation for aniline and piodoaniline become apparent. From the initial absorbance at 0.5 μ s after the laser flash we determine a value of $\eta_{FR} = 0.12$ for *p*-iodoaniline relative to aniline, for which an absolute value of 0.84 has been reported in the literature.³⁹ Thus the absolute value for p-I-An in MeOH is taken to be 0.10.

The radicals produced (MB[•], An^{•+}, or *p*-I-An^{•+}) decay mainly by second-order recombination. In Figure 1 the relative initial decay rates of the radicals appear much larger with aniline than with p-I-aniline. This is a consequence of the different concentration of radicals and the second-order nature of the decay. Determining the effective second-order rate constants under conditions of equal amounts of radicals produced, we found $k_b = 5.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for MB[•] + An^{•+} and $k_b = 9.8 \times 10^9 \text{ M}^{-1}$ s^{-1} for MB[•] + p-I-An^{•+}. This demonstrates not only that the efficiency of free-radical formation is smaller with the heavyatom-substituted donor but also that the recombination of free radicals is more efficient with the latter.

In order to investigate the viscosity dependence and magnetic field dependence of the efficiency η_{FR} of free-radical formation which is fairly low with the heavy-atom-substituted donor, a more sensitive method of radical detection was applied, utilizing the protolytic conversion reaction $MB^{*} + H^{+} \rightarrow MBH^{*+}$ to form the radical MBH ** which has a strong absorption band in the longwavelength region ($\lambda_{max} = 880$ nm). This technique has been



Figure 2. Transient absorbance observed at 840 nm on laser photolysis of solutions buffered at $pH^* = 8.6$ and containing $[MB^+] = 5 \times 10^{-5} M$, $[p-I-An] = 5 \times 10^{-3}$ M. Solvents were methanol/ethylene glycol (EGLY) mixtures with volume percentage of EGLY as indicated. The initial absorbance spike is due to ³MB⁺, whereas the subsequent signal rise corresponds to the formation of MBH++ by protonation of the MB+ radical originating in the triplet quenching reaction.



Figure 3. Magnetic field dependence of radical formation efficiency in the triplet quenching of MB^+ by p-I-An. The solvent is methanol, buffered at $pH^* = 8.6$. For the explanation of the time dependence cf. Figure 2 and text. The order of the field values corresponds to that of the curves (highest radical yield in zero field).

TABLE I: Efficiencies n_{FR} of Free-Radical Formation from ³MB⁺ Reaction with p-I-An in MeOH/EGLY Solvent Mixtures

% EGLY	η _{FR}	η/cP^a	
0	0.100	0.600	
10	0.085	0.828	
20	0.066	1.155	
40	0.042	2.143	

^a Dynamic viscosity at 20 °C, from ref 65.

described in previous work from our laboratory.^{24,38} By choosing a suitable buffer concentration (cf. section 2) the protonation can be made fast enough to convert all the MB* radicals into MBH*+ and still not to interfere with the triplet quenching reaction ³MB⁺ $+ D \rightarrow MB^{\bullet} + D^{\bullet+}$

In Figure 2 are shown absorbance signals recorded for fast quenching of ³MB⁺ by p-I-An in mixtures of methanol and ethylene glycol (EGLY) observed at 840 nm where both ³MB⁺ and MBH*+ absorb strongly but MB* and p-I-An*+ do not absorb. The initial sharp peak is due to the triplet which is rapidly quenched. The protonation of the MB[•], a species which cannot be seen at this wavelength, occurs within $1-3 \mu s$ (depending on the viscosity of the solution) and a long persistent plateau of absorbance of MBH*+ indicates the efficiency of free radicals formed. Using the absolute value of $\eta_{FR} = 0.100$ for neat methanol, the ratios of plateau values in Figure 2 yield the values given in Table I, where also the dynamic viscosities of the solvent mixtures are listed.

The magnetic field dependence of η_{FR} with p-I-An as electron donor is demonstrated in Figure 3. As the field is increased the

⁽³⁷⁾ Steiner, U. E.; Winter, G. Chem. Phys. Lett. 1978, 55, 364.
(38) Waschi, H. P. Dissertation, Universität Stuttgart 1983.
(39) Kayser, R. H.; Young, R. H. Photochem. Photobiol. 1976, 24, 395.
(40) Burri, J.; Fischer, H. Chem. Phys. 1989, 139, 497.
(41) Hamilton, C. A.; Hewitt, J. P.; McLauchlan, K. A.; Steiner U. E. Mol. Phys. 1988, 65, 423.



Figure 4. Magnetic field dependence of relative change R of free-radical formation efficiency in the quenching of ³MB⁺ by p-I-An, determined by the continuous photolysis technique. Solvents are MeOH/EGLY mixtures with (●) 0%, (○) 10%, (■) 20%, and (□) 40% of EGLY. The solid lines are the best fits obtained by model calculations described in sections 4 and 5. Parameters used for the TM are given in Table III (case $F_{TM} = 0$). Parameters used for the RPM are $\lambda_s = 1$, $\lambda_T = 0$, a =7 Å, $\sigma = 0.1$ Å, $\Sigma_{hfc} = 0.6$ mT, $\Delta g = 0.015$, $J_0 = 0$, D = (2.15, 1.56, 1.12, 0.6) × 10^{-5} cm² s⁻¹ for 0, 10, 20, 40% EGLY, respectively. Reaction term (P) was used.





value of η_{FR} decreases. The magnetic field dependence of η_{FR} was measured for the four solvent mixtures indicated in Figure 2.

In addition to the laser experiments the magnetic field effect was also investigated by a continuous-illumination/continuous-flow technique, whereby the permanent bleaching of the dye is monitored in a special apparatus described in detail in ref 33. The quantum yield of permanent bleaching is by about 1 order of magnitude lower than the quantum yield of free-radical formation. However, the relative magnetic field effects for both quantities are the same. Since the continuous flow method is the more accurate one (error in magnetic field effect < 1%), the diagram in Figure 4 shows the data points obtained with the latter method.

In the diagram a logarithmic field scale has been used. With this type of representation three regions of field dependence can be distinguished as follows: In the low-field region (below 200 G) no magnetic field effects have been detectable. In the second region above 200 G (20 mT) the curves drop and then run with parallel straight slopes, whereby an increase of solvent viscosity shifts the curves to lower fields. The beginning of the third region is at about 5000 G (0.5 T) where the lines bend to continue as straight lines with a decreased slope. The end of this region is not yet reached at 3.3 T, the highest field applied.

The solid curves shown in Figure 4 result from model calculations, described and discussed in section 5.

4. Theory

General Situation. The mechanism that will be adopted for the formation of free radicals is represented in Scheme I. Electron transfer in the encounter of excited triplet ³A⁺ and electron donor D is mediated by formation of a triplet exciplex^{16,42} $(^{3}(AD^{+}))$ SCHEME II



which may undergo deactivation to the singlet ground-state pair of reactants by SOC-induced intersystem crossing (ISC), or may dissociate to a geminate radical pair ³(²A[•]···²D^{•+}) where, initially, the unpaired electrons are in a triplet spin alignment. Dissociation of the triplet exciplex should be considered as a reversible process (cf. several investigations with luminescing singlet exciplexes²⁷⁻²⁹), so that the geminate ³RP can recombine via reversible triplet exciplex formation. On the other hand, spin evolution during the lifetime of the geminate RP will eventually transform the spin state to singlet so that electron back-transfer to form the singlet educts can directly occur in geminate reencounters. Due to the lack of Coulomb attraction, the major fraction of the RPs will, however, undergo final diffusive separation to free radicals, homogeneously distributed in the bulk of the solution.

We note that it would cause no problem to extend our treatment to a reaction scheme including also direct formation of RPs in the triplet quenching. However, this quenching channel is not considered important in the present system of investigation.⁴³

The rates of two processes in Scheme I can be affected by an external magnetic field. The first is the SOC-induced ISC process of the triplet exciplex which is based on triplet sublevel specific kinetics and may be accounted for theoretically in terms of the TM. The second is spin conversion of the radical pair which may be dealt with by the theories developed for the RPM.

Treatment of the Triplet Mechanism. In the treatment of the triplet mechanism we will follow the method applied in previous work from this laboratory.²⁴ It has been shown that the kinetic behavior of triplet exciplexes of the present type is adequately described in terms of Scheme II. Due to the local symmetry at the substitution site of the heavy iodine atom in the electron donor moiety of the exciplex, SOC at this center will enhance ISC from two substates (denoted T_x and T_y) only (rate constant k_{ISC}). On the other hand, the rate constant k_{ER} of radical formation from the triplet exciplex is not likely to be different for the three sublevels. Transitions between the zero-field substates T_x , T_y , and T_z are due to the rotational diffusion of the exciplex (incoherent process) and to the Larmor precession of the total electronic spin around the external magnetic field vector (coherent process). Due to the latter the efficiency of radical formation in a single dissociation step from the exciplex ($\eta_{\rm FR}$) becomes magnetic-field dependent. The theory of this magnetic field effect has been worked out in some detail comprising a numerical solution of the stochastic Liouville equation²⁴ and two analytical approximations.^{23,24,44} Of these the first one, developed by Steiner²³ and modified by Ulrich, Steiner, and Föll (USF²⁴), will be used here. It reproduces the exact solutions of the SLE very well if the condition

$$D < k_{\rm ER} + (2/3)k_{\rm ISC} + 6D_{\rm r} \tag{1}$$

is satisfied. Here D is the (axial) zero-field splitting parameter of the triplet and D_r the coefficient of rotational diffusion. It will be shown below that the present case is in accord with this condition.

⁽⁴²⁾ Winter, G.; Steiner, U. E. Ber. Bunsen-Ges. Phys. Chem. 1980, 84, 1203.

⁽⁴³⁾ This argument is based on the quantitative analysis of strong effects of heavy-atom substituents on the absolute yields of free-radical formation for triplet reactions of thionine, ^{16,37} a dye akin to methylene blue.

⁽⁴⁴⁾ Serebrennikov, Yu.A.; Minaev, B. F. Chem. Phys. 1987, 114, 359.

The basic relations to calculate $\eta_{\rm ER}(B_0)$ according to the USF method are given here in terms of the relative parameters

$$k'_{\rm ISC} = k_{\rm ISC} / k_{\rm ER} \tag{2}$$

$$D'_{\rm c} = D_{\rm c} / k_{\rm EP} \tag{3}$$

$$\omega'_0 = \omega_0 / k_{\rm ER} \tag{4}$$

with ω_0 , the Larmor frequency of the triplet, given by

$$\omega_0 = g\mu_{\rm B}B_0/\hbar \tag{5}$$

For equal initial populations of the triplet sublevels the exact zero-field result for $\eta_{\rm ER}$ is

$$\frac{\eta_{\text{ER}}}{(1+(1/3)k'_{\text{ISC}}+6D'_{\text{r}})[(1+k'_{\text{ISC}})(1+4D'_{\text{r}})+2D'_{\text{r}}]^{-1}} (6)$$

The USF approximation for general fields (not only intermediate fields as written in ref 24) consists in replacing $D'_{\rm f}$ in (6) by $D'_{\rm r,B}$

$$D'_{r,B} = s(1 - sp_s)(6sp_s - 2)^{-1}$$
(7)

with

$$s = 1 + (2/3)k'_{1SC}$$
 (8)

and p_s the Laplace transform of the spin correlation function in the molecular frame of reference. 1

$$p_{s} = \frac{1}{15} \left\{ \frac{5}{s} + \frac{2}{s + 6D'_{r}} + \frac{4(s + 6D'_{r})}{(s + 6D'_{r})^{2} + \omega'_{0}^{2}} + \frac{4(s + 6D'_{r})}{(s + 6D'_{r})^{2} + 4\omega'_{0}^{2}} \right\}$$
(9)

Note that $D'_{r,B} \rightarrow D'_{r}$ as $B_0 \rightarrow 0$. Treatment of the Radical Pair Mechanism Including Reversible Exciplex Formation. Since the magnetic field effects dealt with in this investigation are typical high-field effects, i.e., occur at fields were $B_0 \gg \bar{B}_{\rm IHFC}$, we confine our explicit treatment to that of $T_0 \leftrightarrow S$ processes only. In order to estimate any low-field effects we may assume that the recombination efficiency of radical pairs produced with triplet spin and recombining only with singlet spin is by about 70% higher in zero field than in the high-field limit, if only the isotropic HFM is operating. This estimate can be adopted from model calculations by Purtov and Salikhov⁴⁵ for neutral radical pairs. In our treatment of radical pair recombination we apply the random flight model developed by Noyes.46 The parameters to be used are the reaction diameter a, the diffusional step width σ , the probability p of another reencounter after a reactionless contact, and the reaction probabilities λ_s or λ_T during one contact of a singlet or triplet RP, respectively. Whereas $\lambda_{\rm S}$ refers to a spin-allowed electron-transfer process, which may occur even with solvent-separated reactants if the energetic conditions are favorable, λ_T applies to a case of spinforbidden recombination which requires the assistance of SOC and can only become efficient if the reactants are in close contact, a situation that we will assume to correspond to a re-formation of the triplet exciplex. The relation of λ_s and λ_T to other kinetic parameters characterizing the reaction system will be discussed in more detail below. To calculate the reencounter probability p for small values of σ/a the relation⁴⁷

$$p = 1 - (\frac{1}{2} + \frac{3a}{2\sigma})^{-1}$$
(10)

was used.

In the high-field limit of the HF-RPM and when spin relaxation processes are neglected, the recombination of T_{\pm} RPs is kinetically decoupled from that of T_0 RPs. The recombination yield F_{TM} of T_{\pm} RPs after an infinite series of reencounters is

$$F_{\rm TM} = \lambda_{\rm T} [1 - p(1 + \lambda_{\rm T})]^{-1}$$
(11)

For RPs originating in the T_0 spin state $T_0 \leftrightarrow S$ spin evolution is possible between reencounters and will be accounted for by the

formalism developed independently by Pedersen⁴⁸ and by Purtov and Salikhov.49 Here we follow more closely the treatment of Pedersen which has been extended by Vollenweider and Fischer⁵⁰ for including the effects of exchange interaction in a semiempirical analytical way. One further extension added in our treatment is to include the possibility of reactions occurring due to the triplet exciplex regeneration from reencounters of RPs in the T₀ spin state. Another extension refers to various forms of the reaction operator. According to Pedersen spin motion in the T_0/S spin space may be represented by the reduced spin density vector

$$\bar{\rho} = \begin{pmatrix} 2 \operatorname{Im} (\rho_{\mathrm{ST}_{0}}) \\ \rho_{\mathrm{T}_{0}\mathrm{T}_{0}} \\ \rho_{\mathrm{SS}} \end{pmatrix}$$
(12)

were ρ_{ii} are the matrix elements of the corresponding spin density matrix. Following Pedersen we can write the result for the recombination yield F_{T_0} after an infinite series of reencounters with spin evolution between them in the form

$$F_{T_0} = (0, \lambda_T, \lambda_S) [\hat{\mathbf{1}} - \hat{\mathbf{M}} \hat{\mathbf{Q}}]^{-1} (0, 1, 0)_t$$
(13)

Here M is the spin evolution superoperator averaged over the distribution of first reencounter times. The elements of \hat{M} are given by Pedersen.⁴⁸ The reaction superoperator \hat{Q} projecting the density matrix of unreacted RPs after a contact is represented by a diagonal matrix for which, in the spirit of Pedersen, we would have to use

$$\hat{\mathbf{Q}}_{(\mathbf{P})} = \text{diag} (1, 1 - \lambda_{\mathrm{T}}, 1 - \lambda_{\mathrm{S}})$$
(14)

This form of $\hat{\mathbf{Q}}$ does not affect the off-diagonal matrix elements of the spin density matrix. As has been shown by Haberkorn,⁵¹ this can lead to physically unreasonable values of the density matrix. Therefore, we also used the alternative versions

$$\hat{\mathbf{Q}}_{(H)} = \text{diag} \left(\left[(1 - \lambda_{S})^{*} (1 - \lambda_{T}) \right]^{1/2}, 1 - \lambda_{T}, 1 - \lambda_{S} \right)$$
 (15)

which corresponds to the anticommutator reaction term recommended by Haberkorn, and

$$\hat{\mathbf{Q}}_{(S)} = \text{diag} (0, 1 - \lambda_{T}, 1 - \lambda_{S})$$
(16)

implying complete S/T_0 phase randomization in a RP contact according to the effect of strong exchange interaction. The latter form has been applied by Salikhov.² It is also in compliance with the criteria listed by Haberkorn. The solution of eq 13 is

$$F_{T_0} = \frac{1}{2N} \{ \lambda_{S} [py(1-c) + p^2 xy(c^2 + s^2 - c)] + \lambda_{T} [2 - p(2xc + z(1+c)) + p^2 xz(c^2 + s^2 + c)] \}$$
(17)

with

$$N = 1 - \frac{p}{2}[(y + z) + c(y + z + 2x)] + p^2 \left[\frac{x}{2}(y + z)(c^2 + s^2 + c) + cyz\right] - p^3 xyz[c^2 + s^2]$$
(18)

Here x, y, z correspond to the elements of the general reaction superoperator

$$\mathbf{Q} = \operatorname{diag}(x, y, z) \tag{19}$$

where x, y, z may be specified according to $\hat{\mathbf{Q}}_{(P)}$, $\hat{\mathbf{Q}}_{(H)}$, or $\hat{\mathbf{Q}}_{(S)}$. For radicals diffusing in steps and starting at the reaction diameter the quantities c and s have been given by Vollenweider and Fischer.⁵⁰ (We neglect contributions of spin relaxation to Z.)

$$c = \exp(-Z) \cos(Z) \tag{20}$$

$$s = \exp(-Z) \sin(Z) \tag{21}$$

$$Z = (3/2)[(1-p)^2/p](a/\sigma)(a^2/D)^{1/2}Q^{1/2}$$
(22)

Here D is the sum of the diffusion constants of the radicals and

- (48) Pedersen, J. B. J. Chem. Phys. 1977, 67, 4097.
 (49) Purtov, P. A.; Salikhov, K. M. Theor. Exp. Chem. 1980, 16, 413, 530.
 (50) Vollenweider, J.-K.; Fischer, H. Chem. Phys. 1988, 124, 333.
 (51) Haberkorn, R. Mol. Phys. 1976, 32, 1491.

⁽⁴⁵⁾ Purtov, P. A.; Salikhov, K. M. Theor. Exp. Chem. 1980, 16, 413.
(46) Noycs, R. M. J. Chem. Phys. 1956, 78, 5486.
(47) Kaptein, R. J. Am. Chem. Soc. 1972, 94, 6251.

Electron-Transfer Reactions with Excited Triplets

Q is the S/T₀ coupling matrix element given by

$$Q = \frac{1}{2\hbar} (\Delta g \mu_{\rm B} B_0 + \sum_{i(1)} a_i m_i - \sum_{j(2)} a_j m_j)$$
(23)

where $\Delta g = g_1 - g_2$ is the g-factor difference of the two radicals and the a_i, m_i, a_j, m_j are the isotropic hfc constants and magnetic quantum numbers of nuclei of radicals 1 and 2, respectively. In order to account for effects of exchange interaction J(r) depending on the interradical distance r as

$$J = J_a \exp[-(r - a)/r_J] = J_0 \exp[-r/r_J]$$
(24)

where J_0 and r_j are characteristic parameters, and J_a is the value of J at r = a, Vollenweider and Fischer suggested to replace c and s in the expression for F_{T_0} with c' and s' related to c and s by

$$c' = (c + x)/(1 + x)$$
 (25)

$$s' = s/(1+x)$$
 (26)

and x given by

$$\kappa = (5r_J/3a) \ln (1 + J_a a r_J/D) \ln (1 + \delta^{0.9})$$
(27)

and

$$\delta = (a^2 Q / D)^{1/2}$$
(28)

Combining the effects of TM and the RPM, the following final result for the efficiency of free-radical formation in the triplet quenching process is obtained

$$\eta_{\rm FR} = \eta_{\rm ER} [1 - (2F_{\rm TM} + F_{\rm T_0})/3]$$
(29)

In order to assess various contributions to F_{T_0} it will be useful to decompose it as

$$F_{\mathrm{T}_{0}} = F_{\mathrm{TM}} + \Delta F_{\mathrm{SM}} \tag{30}$$

where ΔF_{SM} is the contribution of spin motion $(T_0 \rightarrow S)$ induced recombination in excess to the pure triplet RP recombination probability.

5. Model Calculations

5.1. Radical Pair Mechanism Only. It will be instructive firs. to consider magnetic field effects due to the radical pair mechanism only, i.e., with no magnetic field effect on the primary yield of radical pair present and with no regeneration of the triplet exciplex in radical pair reencounters. Our choice of parameters is as follows.

Diffusion Coefficient D and Reaction Diameter a. Since experimental values of diffusion coefficients of the radicals involved are not available, they were estimated by using the empirical procedure by Othmer and Thakar.⁵² Thus a sum of D = 2.15 $\times 10^{-5}$ cm² s⁻¹ was obtained for methanol as solvent. Together with a reaction diameter of a = 7 Å, which is commonly used for fast spin-allowed electron-transfer reactions in solution,⁵ the Smoluchowski equation would yield a value of $k_{\rm diff} = 1.13 \times 10^{10}$ M^{-1} s⁻¹. This estimate appears very reasonable. In fact the fastest rate constants reported in the literature³⁹ for ³MB⁺ quenching in MeOH by excellent electron donors (e.g., dimethylaniline), reactions which are expected to be diffusion-controlled, is $1.5 \times$ 10^{10} M⁻¹ s⁻¹. Given the value for D in methanol the values for the solvent mixtures were chosen to be inversely proportional to the dynamic solvent viscosity η .

Reaction Probability for Singlet Encounters λ_s . For spinallowed electron-transfer reactions with moderately negative free energy change, λ_s is expected to be close to 1. In this case homogeneous radical recombination reactions are expected with rate constants of $(1/4)k_{diff}$, if the contribution of random triplet spin encounters to the recombination is negligible. This should be the case, e.g., in the recombination between MB[•] and An^{•+} radicals where no heavy atom effects will assist the recombination of RPs with triplet spin. Experimentally, the effective second-order



Figure 5. Theoretical magnetic field dependence of R according to the RPM only. Experimental data points as in Figure 4. Common parameters of curves 1-6 are $\lambda_{\rm S} = 1$, a = 7 Å, $\sigma = 0.1$ Å, $D = 2 \times 10^{-5}$ cm² s⁻¹, $\Sigma_{\rm hfc} = 0.6$ mT, $\Delta g = 0.015$. Types of exchange interaction and reaction term: (1) $J_0 = 0$, (P): (2) $J_0 = 0$, (H) or (S); (3) J(KS), (P); (4) J(K), (P); (5) J(BF), (P); (6) J(VF), (P).

rate constant of MB[•] radical decay observed directly after a laser pulse, when the concentration of MB[•] and An^{•+} should be equal, was found to be 5.8×10^9 M⁻¹ s⁻¹ which amounts to about 1/2instead of 1/4 of the diffusion-controlled value cited above. In fact it may be assumed to correspond to the sum of two reactions: MB[•] + MB[•] (disproportionation) and MB[•] + An^{•+} (recombination), so that each of it could contribute 1/4 of the diffusioncontrolled value.

Diffusional Step Width σ . A value of 0.1 Å was used which practically corresponds to the continuous diffusion limit. It should be noted that in this limit the maximum magnetic field effect is obtained. Noticeable changes in the results are not obtained unless $\sigma \gtrsim 1$ Å.

Hyperfine Coupling. Due to the presence of an appreciable number of nuclear spins coupled to the electron spins in the radicals MB[•] and p-I-An^{•+} the geminate recombination yield has to be averaged over a large number of nuclear spin states. This task was solved in a simplified way by approximating the distribution of coupling strength $Q_{\rm HFC}$ by a Gaussian distribution with the same rms deviation $\Sigma_{\rm HFC}$ given as

$$\Sigma_{\rm HFC} = \left(\frac{1}{12}\sum_{i}a_{i}^{2}I_{i}(I_{i}+1)\right)^{1/2}$$
(31)

Here the sum is extended over the nuclei of both radicals. The hyperfine couplings of MB[•] which are not experimentally available were assumed to be the same as for thionine semiquinone,⁵⁴ with

 $1 \times (a_{\rm N} = 0.73 \text{ mT}); \quad 2 \times (a_{\rm H} = 0.24 \text{ mT});$ $2 \times (a_{\rm H} = 0.14 \text{ mT})$

The hyperfine couplings of p-I-An⁺⁺ were estimated from a HMO/McLachlan calculation⁵³ as

$$1 \times (a_{\rm N} = 0.80 \text{ mT}); \quad 2 \times (a_{\rm H} = 0.86 \text{ mT})$$

 $2 \times (a_{\rm H} = 0.50 \text{ mT}); \quad 2 \times (a_{\rm H} = 0.12 \text{ mT})$

From these data a value of $\Sigma_{\rm HFC}$ = 0.6 mT is obtained.

Difference of g Factors. For TH[•] the experimental value is $g = 2.0042^{54}$ and may be assumed to apply also for MB[•]. For *p*-I-An⁺⁺ a value of $g \approx 2.017$ may be estimated from the experimental value published for the 5-iodouracil radical⁵⁵ when allowing for the different spin densities at the halogen substituent in both radicals. Thus $\Delta g \approx 0.013$. A rounded value of $\Delta g =$

 ⁽⁵²⁾ Othmer, D. F.; Thakar, M. S. Ind. Eng. Chem. 1953, 45, 589.
 (53) McLachlan, A. D. Mol. Phys. 1960, 3, 233.

⁽⁵⁴⁾ Schmidt, H. Private communication.

⁽⁵⁵⁾ Sevilla, M. D.; Swarts, S.; Riederer, H.; Hüttermann, J. J. Phys. Chem. 1984, 88, 1601

⁽⁵⁶⁾ De Kanter, F. J. J.; Kaptein R. J. Am. Chem. Soc. 1982, 104, 4759. (57) De Kanter, F. J. J.; den Hollander, J. A.; Huizer, A. H.; Kaptein, R. Mol. Phys. 1977, 34, 857

⁽⁵⁸⁾ Schulten, K.; Bittl, R. J. Chem. Phys. 1986, 84, 5155.

0.015 was used in our present calculations.

In Figure 5 we show the magnetic field dependence of the free-radical yield as obtained theoretically for various forms of the reaction term (P, H, S) without extra consideration of exchange interaction and for reaction term (P) with several parameter sets (J_0, r_J) of the exchange interaction that have been suggested in the literature:

$$J_0 = 4.5 \times 10^{18} \text{ rad s}^{-1} \qquad r_J = 0.37 \text{ Å}(\text{KS})^{56}$$

$$J_0 = 1.7 \times 10^{17} \text{ rad s}^{-1} \qquad r_J = 0.47 \text{ Å}(\text{KS})^{57,58}$$

$$J_0 = 1.0 \times 10^{18} \text{ rad s}^{-1} \qquad r_J = 0.46 \text{ Å}(\text{BF})^{40}$$

$$J_0 = 3.2 \times 10^{16} \text{ rad s}^{-1} \qquad r_J = 0.92 \text{ Å}(\text{VF})^{50}$$

The two-parameter representation (J_o, r_J) of J(r) may be translated into a more instructive one by quoting the range of r wherein Jincreases from 1 to 100 G. The corresponding figures are 10.7-8.6 Å (K), 9.7-8.0 Å (KS), 11.4-9.3 Å (BF), and 19.6-15.3 Å (VF). The sets K and KS have been used in theoretical work on magnetic field dependent reaction of biradicals whereas the BF and VF sets have been suggested in connection with the analysis of CIDNP effects due to freely diffusing RPs.

It is clear from Figure 5 that all of the theoretical curves obtained by considering the RPM only are far from a correct modeling of the experimental data. Whereas the onset of the observed effects is at about 0.02 T the onset of the theoretical Δg RPM effect appears at fields larger than 0.1 T. Comparing the curves corresponding to reaction terms (P), (H), and (S), we note that the magnetic field effect is reduced when taking the S/Tdephasing effect during reactive contacts into account. For λ_{S} = 1, the case shown in Figure 5, the results with reaction terms (H) and (S) are of course equivalent, but for $\lambda_{s} < 1$ case (H) is intermediate between (S) and (P). In the limit of small λ_S case (H) becomes identical with case (P). As λ_s is decreased the ratio of high-field magnetic field effects for case (S) and (P) remains at a constant value of about 0.8. The transition of case (H) between the limits (S) and (P) is not uniquely determined by $\lambda_{\rm S}$ but depends also on the reencounter probability p. The quantity that really matters is given by

$$\Lambda_{\rm S} = \lambda_{\rm S} / (1 - (1 - \lambda_{\rm S})p) \tag{32}$$

It corresponds to the overall reaction probability of a singlet RP in an infinite series of reencounters. For $\Lambda = 0.9$ the magnetic field effect for case (H) is found to be about halfway between (S) and (P).

Introducing explicit exchange interaction, it is seen that the parametrization according to VF has an effect much stronger than reaction term (S), whereas parametrization of J(r) according to K or KS, or BF has only weak effects compared to the plain reaction term (P). The statement of Vollenweider and Fischer⁵⁰ that the Salikhov boundary condition corresponds to a rather poor representation of the effect of exchange interaction is not generally true.

With $r_J = 0.47$ Å (KS) and the other parameters of the RPM chosen as in Figure 5 we investigated which value of J_0 would be necessary for a given reaction radius *a* to obtain the same magnetic field effect on the free-radical yield with reaction term (P) including explicit exchange interaction ($J_0 \exp[-r/r_J]$) as with reaction term (S) without extra exchange interaction. It was found that reaction term (S) becomes equivalent to reaction term (P) including explicit exchange interaction when J_0 is chosen such that treaction term (S) becomes equivalent to reaction term (P) including explicit exchange interaction when J_0 is chosen such that the centre of the 1–100 G range is about 4 Å outside reaction radius *a*. Thus, whereas for $a \approx 5$ Å reaction term (S) is equivalent to (P) with exchange parameter set (KS), for a < 5Å the exchange effect of reaction term (S) is smaller than that of (KS), and for a > 5 Å it is larger. These results are valid for $D \approx 2 \times 10^{-5}$ cm² s⁻¹. When D is decreased by a factor of 4, the equivalent exchange frontier of 1–100 G approaches the contact radius to about 3 Å.

One might wonder whether the parameters of the RPM could be adjusted at all to give a reasonable fit of the experimental results. Using reaction term (P) which yields the strongest



Figure 6. Theoretical magnetic field dependence of R according to the RPM only. Experimental data points as in Figure 4. Common parameters of curves 1-4 are $\lambda_{\rm S} = 1$, a = 7 Å, $\Sigma_{\rm hfc} = 0.6$ mT, $\Delta g = 0.1$. D parameter values in cm² s⁻¹ are (1) 2 × 10⁻⁵; (2₁) 1.6 × 10⁻⁵; (3) 8 × 10⁻⁶; (4) 4 × 10⁻⁶.

TABLE II: Parameters for Optimum Fits When Applying the TM $Only^{\alpha}$

 solvent	Γ _{TM}	k _{ER} ^b	k _{ISC} ^b	D _r ^b		
MeOH	0	2.19	38.3	6.81		
10% EGLY	0	1.48	31.6	5.16		
20% EGLY	0	1.05	30.2	4.54		
40% EGLY	0	0.44	20.6	3.04		
MeOH	0.46	4.57	38.8	6.44		
10% EGLY	0.47	3.02	31.2	4.86		
20% EGLY	0.48	2.14	29.9	4.25		
40% EGLY	0.49	0.91	20.7	2.94		

^a Both sets (with $F_{TM} = 0$ and $F_{TM} = 0.46$, ..., 0.49) yield identical sets of curves, shown in Figure 7. ^bIn units of 10⁹ s⁻¹.

magnetic field effects and choosing $\Delta g = 0.1$, which is certainly not realistic for the system under consideration, the curves shown in Figure 6 are obtained for a series of *D* values modeling the change of solvent viscosity. Whereas the onset behavior could be adapted to the experimental results the slope of the effects is still too flat. Thus it may be concluded that the RPM alone is clearly inadequate to explain the observed effects.

5.2. Triplet Mechanism Only. To see the explanatory potential of the pure triplet mechanism we determined the optimum values of the triplet exciplex parameters $k_{\rm ISC}$, $k_{\rm FR}$, and $D_{\rm r}$. Since there is no independent experimental information available on these quantities our approach was to obtain suitable values from an unrestricted best fit to the experimental data and to discuss the physical significance of the parameter values subsequently (cf. Discussion).

The following procedure yields a unique set of parameters. Starting with a trial value of k'_{ISC} the value of D'_r is fixed by the absolute experimental value of η_{ER} (note that in this section it will be assumed that $\eta_{ER} = \eta_{FR}$ the latter being determined experimentally).

$$D'_{\rm r} = (1 + k'_{\rm ISC}/3 - \eta_{\rm ER}(1 + k'_{\rm ISC}))/(\eta_{\rm ER}(6 + 4k'_{\rm ISC}) - 6)$$
(33)

Then the relative magnetic field effect $R_{ER}(\omega'_0) = [\eta_{FR}(\omega'_0) - \eta_{FR}(0)]/\eta_{FR}(0)$ is calculated by eqs 6-9. The relative Larmor frequency ω'_0 is related to the absolute Larmor frequency ω_0 by $\omega'_0 = \omega_0/k_{FR}$. Hence, plotting $R_{ER}(\log \omega'_0) = R_{ER}(\log \omega_0 - \log k_{FR})$ versus ω'_0 yields a curve displaced against the experimental one by log (k_{FR}) from which k_{FR} and the absolute values of k_{ISC} and D_r are obtained. Thus the actual fitting procedure corresponds to the free variation of *one* parameter only and the best fit obtained in this way will represent the best fit of the complete set of parameters (Table II).

It is in this way that the curves shown in Figure 7 have been obtained. Up to fields of about 0.3 T the theoretical results fit the experimental ones excellently. There is, however, a systematic discrepancy at higher fields where the theory of the TM predicts



Figure 7. Theoretical field dependence according to the TM only. Parameter sets used are given in Table II. Experimental data points as in Figure 4.



Figure 8. Theoretical field dependence obtained from a combination of the TM (parameters according to the first set in Table II, case of irreversible exciplex dissociation) and the RPM (parameters as in Figure 4). Experimental data points as in Figure 4.

a saturation behavior, whereas the experimental magnetic field effects continue to increase. This high-field discrepancy becomes most pronounced at higher solvent viscosities where the saturation behavior according to the TM commences at lower fields.

From the analysis presented so far it has become clear that, on its own, neither of the two mechanisms, TM and RPM, can satisfactorily account for the observed magnetic field effects. On the other hand, it has been demonstrated that the TM is suitable up to medium fields where the effect of the Δg RPM just becomes apparent. Thus in a combination both mechanisms should supplement each other in an ideal way.

5.3. Triplet Mechanism Combined with Recombination of Geminate RPs. (a) The Case $\lambda_T = 0$. In Figure 8 we show the theoretical curves obtained when combining the TM using parameters according to Figure 7 with the standard set of RP parameters and using reaction term (P). The improvement of the fit as compared to versions with TM or RPM only is striking. The high-field part of the curves has the correct shape, which would be too flat when reaction term (S) is used. The fit can still be improved by slightly readjusting the TM parameters. The final parameter values are collected in Table III, and the corresponding curves are shown in Figure 4. A similar quality of the fit can be obtained with reaction term (S) if Δg is increased to 0.035. Application of exchange interactions using parametrization K, KS, or BF does not significantly influence the results. Using, however, exchange interaction parameters VF leads to a strong decrease of the RPM contribution which cannot be compensated with a reasonable Δg value.

(b) The Case $\lambda_T > 0$. If generation of triplet exciplexes from radical pairs is of any importance this should be borne out in a difference of the second-order recombination constants $k_{rec}^{(2)}$ in the systems MB[•]/An^{•+} and MB[•]/p-I-An⁺⁺. Such SOC effects on homogeneous radical recombination have also been reported by

TABLE III: Parameters for Optimum Fits with Combined TM and RPM

solvent	F _{TM}	k _{ER} ^a	k _{ISC} ^a	D,ª	Δg^b	
MeOH	0	2.19	37.5	7.45	0.015	
10% EGLY	0	1.48	30.8	5.68	0.015	
20% EGLY	0	1.05	29.5	4.89	0.015	
40% EGLY	0	0.44	20.6	3.04	0.015	
MeOH	0.46	4.57	37.5	7.45	0.05	
10% EGLY	0.47	3.02	30.2	5.52	0.05	
20% EGLY	0.48	2.13	28.9	4.98	0.05	
40% EGLY	0.49	1.04	23.6	3.45	0.05	

^a In units, of 10^9 s^{-1} . ^b For other parameters of RPM cf. caption of Figure 4.

Kikuchi et al.⁵⁹ On the basis of spin statistics this recombination rate constant is

$$k_{\rm rec}^{(2)} = ((1/4)\Lambda_{\rm S} + (3/4)\Lambda_{\rm T})k_{\rm diff}$$
(34)

where Λ_S and Λ_T are the total recombination probabilities (including reencounters) for geminate singlet or triplet RPs, respectively, originating at the reaction diameter r = a that is related to the diffusion-controlled rate constant k_{diff} . A reasonable approximation for our systems is to set $\Lambda_S = 1$ and $\Lambda_T = F_{TM}$, i.e., to assume diffusion-controlled reaction rate for singlet RPs and to attribute any significant contributions of triplet RPs to the effect of SOC in encounters generating an exciplex-type configuration.

In methanol the observed values for $k_{rec}^{(2)}$ are 5.8×10^9 M⁻¹ s⁻¹ for MB[•]/An^{•+} and 9.8×10^9 M⁻¹ s⁻¹ for MB[•]/p-I-An^{•+}. If we assume that these are exclusively due to the recombination reactions MB[•] + An^{•+} (MB[•] + p-I-An^{•+}) and that $F_{TM} = 0$ for MB[•] + An^{•+}, we obtain $F_{TM} = 0.23$ for MB[•] + p-I-An^{•+}. If it is assumed that both rate constants contain a diffusion-controlled contribution from the reaction MB[•] + MB[•] (for which we assume $\Lambda_S = 1$, $\Lambda_T = 0$), we obtain $F_{TM} = 0.46$ for MB[•]/p-I-An⁺⁺. In order to see a potential effect of ³RP recombination most clearly we used the larger one of these values of F_{TM} for our model calculation.

From $F_{\rm TM}$ in methanol one can obtain $\lambda_{\rm T}$ by solving eq 11 for the latter. To obtain a realistic solvent viscosity dependence of $\lambda_{\rm T}$ a relation with the experimentally determined values of $\eta_{\rm FR}$ was established. Introducing the probability $p_{\rm E}$ of exciplex formation when a RP has an "encounter", i.e., whenever the separation becomes equal to a, we have

$$\lambda_{\rm T} = p_{\rm E}(1 - \eta_{\rm ER}) \tag{35}$$

On the other hand

$$\eta_{\rm FR} = \eta_{\rm ER} (1 - \Lambda_{\rm T}) \tag{36}$$

Thus $p_{\rm E}$ can be determined from the values of $\Lambda_{\rm T} \approx F_{\rm TM} = 0.46$ and $\eta_{\rm FR} = 0.100$ in methanol. The probability of exciplex formation $p_{\rm E}$ in one encounter was assumed to be independent of solvent viscosity. Then from $p_{\rm E}$ as determined with $F_{\rm TM} = 0.46$ for methanol and the particular value of η_{FR} for each solvent, the parameter λ_{T} could be obtained from the combination of eqs 11, 35, 36. The absolute values of $p_{\rm E}$ and $\lambda_{\rm T}$ depend on the reencounter probability p which itself depends on the chosen step width σ . However, the theoretical results for $\eta_{FR}(B_0)$ do not depend on σ as long as we stay in the continuous diffusional limit $(a/\sigma \gg$ 1). What is also independent of the choice of σ is the value of $F_{\rm TM} \approx \Lambda_{\rm T}$. It is given in Table III for the different solvents. We see that it is not very strongly viscosity dependent. The reason for this is that even in the solvent of lowest viscosity the probability of deactivation of the exciplex is higher than the probability η_{ER} that it dissociates to a radical pair again. Hence, although $\eta_{\rm ER}$ varies approximately as the inverse of the solvent viscosity, F_{TM} does not change very much.

Introducing $\lambda_T > 0$ means that the TM will contribute to Λ_T and hence, even when considering the TM only, $\eta_{ER} > \eta_{FR}$ (cf.

⁽⁵⁹⁾ Kikuchi, K.; Hoshi, M.; Abe, E.; Kokubun, H. J. Photochem. 1988, 45, 1.



Figure 9. Theoretical field dependence obtained from a combination of the TM (parameters according to the second set in Table II, case of reversible exciplex dissociation) and the RPM (parameters as in Figure 4).

eq 36). The magnetic field effects caused by the TM are mainly determined by $\eta_{ER}(B_0)$. Therefore, after introducing the effect of $\lambda_T > 0$, i.e., possible regeneration of exciplexes after dissociation into radicals, the exciplex parameters k_{ISC} , k_{FR} , D_r have to be newly adjusted for an optimum fit of the observed $\eta_{FR}(B_0)$ relation. We note here that identical curves of $\eta_{FR}(B_0)$ can be generated with the TM formalism for different values of λ_T and that the required change of parameters $(k_{FR}, k_{ISC}, D_r)_{\lambda_T=0} \rightarrow (k_{FR}, k_{ISC}, D_r)_{\lambda_T}$ is unique. Thus using the Λ_{TM} values given in Table III the second parameter set given in Table III has to be used to obtain the same curves as in Figure 7 representing an optimum fit if only the TM is applied.

Combining the TM with the RPM and using the standard set of Figure 5 for the latter the result shown in Figure 9 is obtained. It is found that due to the effect of triplet RP recombination (F_{TM}) the contribution of the RPM (based on spin motion and recombination of singlet RPs only) is attenuated. Now the slope in the high-field region is too flat and cannot be improved unless the Δg parameter is increased. To obtain the same quality of the fit as shown in Figure 4 it is necessary to have $\Delta g \ge 0.05$. For Δg = 0.05 the slightly readjusted parameters of the TM given in Table III have to be used.

In concluding this section we mention that for combining $F_{\text{TM}} \approx 0.5$ with reaction term (S) the theoretical curves can be fitted to the experimental ones only if unrealistically high values of Δg are used.

6. Discussion

In our general treatment the efficiency of free-radical formation η_{FR} is influenced by the efficiency η_{ER} of triplet radical pair formation from the exciplex, by the efficiency F_{TM} of recombination of such pairs due to reversible formation of the exciplex, and by the excess contribution ΔF_{SM} of geminate recombination of singlet radical pairs originating in the course of RP spin evolution. For an analysis it will be useful to decompose the observed overall MFE R_{FR} on η_{FR} into various contributions. Defining the relative magnetic field effect of any quantity x as

$$R_x(B_0) = \frac{x(B_0) - x_0}{x_0} \tag{37}$$

where x_0 is the corresponding quantity at zero field, the following equation can be derived from eqs 29 and 30.

 $R_{\rm FR} =$

$$R_{\rm ER} - \frac{\eta_{\rm ER,0}}{\eta_{\rm FR,0}} (1 + R_{\rm ER}) F_{\rm TM} R_{\rm FTM} - \frac{\eta_{\rm ER,0}}{\eta_{\rm FR,0}} (1 + R_{\rm ER}) \Delta F_{\rm SM} R_{\Delta F}$$
(38)

where R_{ER} , R_{FTM} , and $R_{\Delta F}$ are the relative magnetic field effects on η_{ER} , F_{TM} , and ΔF_{SM} , respectively. Note that according to the definition in eq 37 R_{ER} is negative but R_{FTM} and $R_{\Delta F}$ are positive. The three terms in eq 38 correspond to the contributions of



Figure 10. Viscosity dependence of the parameters $k_{\rm ISC}$, $k_{\rm ER}$, D_r determined for the triplet exciplex ³(MB *p*-I-An)⁺ (cf. Table III). Full symbols, results obtained from the fits assuming irreversible exciplex dissociation; open symbols, for reversible exciplex dissociation.

one-step triplet exciplex dissociation (R_{ER}) , reversible triplet exciplex formation $(R_{Ex,RP})$, and spin motion in the radical pairs (R_{SM}) , i.e. by definition

$$R_{\rm FR} = R_{\rm ER} + R_{\rm Ex-RP} + R_{\rm SM} \tag{39}$$

From eq 38 it follows that the various contributions summing to R_{FR} in eq 39 are not completely independent of each other.

The results of our model calculations presented in the last section provide evidence that both TM and Δg RPM make substantial contributions to the MFEs observed. Furthermore, it has become clear that the field regions, where these mechanisms exhibit their effects most prominently, overlap only partially. Therefore, the parameters obtained when first fitting the TM that dominates the initial region of magnetic field sensitivity are only slightly modified when the Δg RPM mechanism, dominating the high-field behavior, is added. Thus we may discuss the parameters obtained for the TM without special regard to the RPM part of the effect.

(a) The Triplet Mechanism. Let us first consider the influence of reversible exciplex formation which was not explicitly taken into account in our previous treatment²⁴ of this mechanism. From Tables II and III we see that the rate constant of dissociation $k_{\rm ER}$ has to be significantly modified if the same experimental results are to be accounted for by the model with reversible exciplex formation from the RP. Actually, if reversible exciplex formation is allowed for, this corresponds to a subdivision of the total dissociation lifetime of the exciplex whereby the actual number of divisions is not relevant if the total lifetime is unchanged. Thus it is not surprising that, if $F_{\rm TM} \approx 0.5$, which means that $\eta_{\rm FR} \approx$ $0.5\eta_{\rm ER}$ (cf. eq 36), the dissociation rate constant must be about 2 times larger than if the same $\eta_{\rm FR}$ is achieved in a one-step dissociation mechanism.

In general, application of the TM alone does not suffice to make a definite conclusion as to what extent reversible exciplex formation does accur. However, since from the analysis of homogeneous radical recombination $F_{\rm TM} \approx 0.5$ seems to be an upper limit, the actual values of $k_{\rm ER}$ are expected to be intermediate between those obtained for the extremes $F_{\rm TM} = 0$ and $F_{\rm TM} = 0.5$. Analyzing for the relative contributions of $R_{\rm ER}$ and $R_{\rm Ex-RP}$ by use of eqs 38 and 39 we find that, even for $F_{\rm TM} \approx 0.5$, $R_{\rm ER}$ still accounts for about 90% of the magnetic field effect observed.

The viscosity dependence of k_{ER} as obtained with or without exciplex regeneration from the RP is shown in Figure 10b, where k_{ER} is plotted versus $1/\eta$. Straight lines extrapolating through the origin are obtained in both cases.

For $F_{\rm TM} \approx 0.5$ the equation of the correlation line is

Electron-Transfer Reactions with Excited Triplets

$$k_{\rm ER} = 2.6 \times 10^9 (1/\eta) \, {\rm s}^{-1} \, {\rm cP}$$
 (40)

It is interesting to note that this relation comes close to the one established by Weller who found a slope of 2.3×10^9 s⁻¹ cP for the dissociation of polar singlet exciplexes into free-radical ions.⁶⁰

The rate parameters $k_{\rm ISC}$ and $D_{\rm r}$ are only little affected if exciplex regeneration is taken into account. The reason for this is that the magnetic field effect R_{ER} is independent of k_{ER} as long as $k_{\rm ER} \ll k_{\rm ISC}$ and $k_{\rm ER} \ll 6D_r$, where $6D_r$ corresponds to the effective rate constant of equilibration of the substates T_x , T_y , and T_z. In the theory of the TM the coefficient of rotational diffusion D, of the triplet exciplex appears since this process is considered as the essential mechanism by which the equilibrium among the triplet substates is established. According to Debye⁶² the following relation should be expected for D_r

$$D_{\rm r} = \frac{kT}{8\pi R^3 \eta} \tag{41}$$

with η the solvent viscosity and R the effective hydrodynamic radius of the rotating species. The plot of D, versus $1/\eta$ (cf. Figure 10b) yields a straight line, however, not extrapolating to the origin but to $D_{\rm r} \approx 1.5 \times 10^9 \, {\rm s}^{-1}$ at $1/\eta = 0$. An interpretation of this finding could be that, in addition to molecular rotation, there is also some other mechanism contributing to spin relaxation which is independent of the bulk solvent viscosity. Thus, e.g., vibrations associated with conformational changes of the exciplex might contribute. Equating the *slope* of the D_r vs $1/\eta$ line with kT/η $(8\pi R^3)$ we obtain a value of 3.6 Å for R which seems a very reasonable estimate with regard to the possible dimensions of the exciplex (cf. ref 24).

The value of $k_{\rm ISC}$ shows the weakest viscosity dependence (cf. Figure 10a) as might be expected for an intramolecular radiationless deactivation process. That there is a viscosity dependence at all (the extrapolated value for $n \rightarrow \infty$ is about half of the value in methanol) might indicate that the ISC process by which the exciplex returns to the singlet ground state of the donor/acceptor pair depends on the mutual orientation of donor and acceptor moiety and that the rate of establishing conformational equilibrium might have some bearing on $k_{\rm ISC}$. The order of magnitude determined for $k_{\rm ISC}$ in the (MB[•]/p-I-An^{•+}) exciplex is similar to that found in the (TH[•]/p-I-An^{•+}) case.²⁴ It should be conceived as characteristic of a fast back electron transfer in a contact pair of radical ions including a spin flip which becomes quasi-allowed by virtue of the strong SOC of the iodine atom.

The validity of the approximation applied for the TM may be assessed now by checking the condition in eq 1. With the parameters given in Tables II and III, the lowest value of the right-hand side is 3.2×10^{10} s⁻¹ corresponding to an allowed upper limit of $D \approx 0.17 \text{ cm}^{-1}$ for the zero-field splitting parameter D of the triplet exciplex. Such a value is higher by a factor of 2-3than what is be to expected for typical CT complexes.^{66,67} Thus we may assume the condition of eq 1 to be fulfilled for the present systems.

(b) The Radical Pair Mechanism. It is striking to see how well the observed MFE can be modeled (cf. Figure 4) if the TM is supplemented by the RPM. This is most remarkable in view of the fact that the parameters used to characterize the RPM (D,a, Δg , λ_s , Σ_{HFC}) were fixed by reasonable arguments prior to any curve fitting. It is particularly gratifying that the $1/\eta$ dependence

demic Press: New York, 1975; p 23

adopted for the diffusion constant D represents the observed behavior in different solvents very well.

What needs to be discussed are the roles of exchange interaction (J(r)), of reaction term ((P) versus (H) or (S)), and of reversible exciplex formation from the radical pair (F_{TM}) . Furthermore, the low-field effect to be expected due to a suppression of $T_{\pm} \rightarrow$ S spin transitions when B_0 exceeds the typical $B_{1/2}$ (about 3 mT in our system) but not observed experimentally deserves a critical comment.

The effects of both J(r) and F_{TM} reduce any MFEs due to the RPM. Analysis of the various factors involved in R_{SM} (cf. eqs 38 and 39) reveals that this reduction of the MFE is mainly due to changes in ΔF_{SM} , i.e., the excess fraction of radical pairs recombining due to $T_0 \rightarrow S$ spin evolution. The reason for this is evident in the case of exchange interaction, since the T_0/S energy gap introduced by J decreases the efficiency of $T_0 \rightarrow S$ transitions. The reason why the introduction of $F_{\rm TM}$ leads to a decrease of $\Delta F_{\rm SM}$ is less obvious. To explain it, one must note that the contributions of reversible exciplex formation and of recombination after $T_0 \rightarrow S$ spin transitions in the RP are not simply additive. For this reason ΔF_{SM} , the "contribution" to RP recombination due to spin motion, had to be defined as an excess quantity. It is reduced if reversible exciplex formation leading to recombination of triplet RPs is turned on, because (i) the success of $T_0 \rightarrow S$ transitions is less pronounced than in the case where T_0 -RPs cannot recombine directly and (ii) the net rate of $T_0 \rightarrow S$ transitions is reduced if the population of T_0 is kept lower due to direct T-RP recombination through exciplex regeneration.

As for the modifications (H) and (S) of the reaction term compared to the original Pedersen version (P), it has been shown that their effect corresponds to combining application of (P) with considerable exchange interaction. Both terms, (S) and (H), could be adapted, however, to the observed magnetic field dependences when using Δg values exceeding our estimated one by a factor of 2 or less which is certainly within the uncertainty limits of our estimate of Δg .

The reasonable order of magnitude of Δg also limits the acceptable degree of reversible exciplex formation. While interpretation of the homogeneous radical recombination rate constant would allow a maximum of $F_{TM} = 0.5$ this value is already too high if the magnetic field effect shall be reproduced with the theoretically best founded reaction term (H) or (S) and with an acceptable Δg value.

The magnetic effect due to the suppression of the hyperfineinduced $T_{\pm} \rightarrow S$ transitions has not been explicitly taken into account in the present treatment where, as far as the RPM is concerned, our main interest has been in the interpretation of Δg -induced high-field effects. An order-of-magnitude estimate of the low-field effect to be expected may be obtained in a semiempirical way by using results from model calculations for neutral triplet radical pairs reported by Purtov and Salikhov,45 according to which the ratio of recombination yield at zero field and high field is about 1.7. By this estimate we expect a positive low-field effect on η_{FR} between 1.3 and 2.6% for the range of viscosities applied in our experiments if we use reaction term (P) with $F_{\rm TM} = 0$ and 0.8-1.5% with $F_{\rm TM} = 0.5$.

Experimentally, no MFE was observed, however, in the low-field region $(B_0 < 200 \text{ G})$ and as soon as effects started to become detectable their sign was negative. On the other hand, when experimentally investigating the RP MB[•]/An^{•+} in 40% EGLY solvent by the stationary illumination technique, we were able to show that positive effects on the order of 1% could be definitely detected. Here the MFE was found to be $+1.8 \pm 0.4\%$ at $B_0 =$ 400 G, and even intermediate values $\approx 0.9 \pm 0.3\%$ at 50 G were clearly detectable. This order of magnitude of effects found for the MB[•]/An^{•+} system, where no heavy atom effect enhances ISC in the triplet exciplex, is in accord with the estimates given above and hence provides an argument of the basically correct application of the RPM to the present systems. From these control experiments we conclude that the low-field HFC-RPM effect in the MB^{\bullet}/p -I-An^{•+} must be smaller than 0.5%, a result which is not accounted for by any of the estimates quoted above. This could

⁽⁶⁰⁾ Weller, A. Z. Phys. Chem. 1982, 130, 129

⁽⁶¹⁾ Weller applied an extended form of eq 40 including a Boltzmann factor to account for Coulomb interaction in the exciplex. For our case of charge distribution (+/0) this factor is equal to 1.
(62) Debye, P. Polar Molecules; Dover Publications: New York, 1945.
(63) Busmann, H.-G.; Staerk, H.; Weller, A. J. Chem. Phys., in press.
(64) Weller, A. In The Exciplex; Gordon, M., Ware, W. R., Eds.; Aca-

mean that either F_{TM} or J is larger than reasonably assumed which, on the other hand, is not in accord with the size of effects observed in the high-field region where the Δg RPM is effective.

Another possibility that the low-field HFC-RPM effect is theoretically overestimated in our MB[•]/p-I-An^{•+} system could be sought in the nonapplicability of the semiempirical factor of 1.7 relating $\Delta F_{\rm SM}$ ($B_0 = 0$) and $\Delta F_{\rm SM}$ ($B_0 \gg B_{1/2}^{\rm HFC}$). Whereas this may be a good estimate if no direct recombination of triplet RPs can occur (i.e., if $\Delta F_{SM} = F_{T_0}$), it may not be so if spinmotion-induced recombination and direct triplet RP recombination interfere. In this paper only the T₀-S spin motion has been explicitly taken into account; a full treatment of the $T_{\pm,0} \rightarrow S$ process might be necessary to clarify the problem of the low-field effect for RPs with appreciable SOC.

7. Conclusion

The quantitative study up to high fields of the heavy-atominduced magnetic field effect on the yield of free radicals has allowed us to differentiate the contributions of the triplet exciplex and the geminate radical pair to fast electron back-transfer in triplet electron-transfer reactions producing radicals devoid of Coulombic attraction.

The magnetic field dependence exhibited at high fields where the contributions due to the triplet mechanism are expected to be close to saturation is well accounted for by the radical pair mechanism employing Δg -induced T₀/S mixing. A refined version of Pedersen's analytical result for the radical pair mechanism taking also into account reaction-induced S/T dephasing and reversible exciplex formation has been derived. In effect these modifications correspond to an enhancement of exchange interaction. The influence of these modifications, which increases with the reaction diameter, can be compensated by assuming a larger Δg value. At present the accuracy of our knowledge of the g factors of the radicals studied in this work limits the information on the effects related to exchange interaction that can be gained from an analysis of the experimental results.

In zero field 90% of the triplets quenched by electron transfer do not reach the stage of free radicals because they follow the heavy-atom-enhanced ISC path in the triplet exciplex. The contribution of back electron transfer in geminate radical pairs originating through dissociation of the exciplex is very low at zero field.

In a field as high as 3.3 T where the rate of Δg -induced magnetic T_0/S mixing in the radical pair corresponds to an effective field difference of about 200 G between both radicals, fractions of 7% (MeOH) to 11% (40% EGLY mixture) of the geminate radical pairs undergo recombination after ISC by the Δg mechanism.

From the magnetic field effect contribution due to the triplet mechanism, the decay constants of the extremely short-lived exciplexes that should actually be conceived as contact radical pairs have been obtained as a function of solvent viscosity η . The dissociation rate constant has been found to be inversely proportional to η with the same slope as previously determined for fluorescing singlet exciplexes.⁶⁰ The effective rate constant of rotational diffusion also varies as $1/\eta$, however, with an η -independent contribution pointing to some participation of spin relaxation mechanisms other than rotation of the exciplex as a whole.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Diffusion-Limited Reactions at Solid–Liquid Interfaces: Effects of Surface Geometry

Joshua Samuel, Michael Ottolenghi,* and David Avnir*

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel (Received: April 23, 1990; In Final Form: September 4, 1990)

The diffusion-controlled reaction between a molecule (excited $Ru(bpy)_3^{2+}$) adsorbed at the irregular surface of porous silicas and a reactant (anthracene) diffusing from an intrapore liquid phase was studied by nanosecond laser excitation. It was found that the reaction is controlled by the short-range irregularity of the surface but not by the average pore diameter (in the 40-1000-Å range). It is suggested that the chemical reactivity correlates with the fractal dimension of the surface accessible for adsorption.

Introduction

A large variety of natural and man-made chemical processes take place at solid interfaces. A quantitative assessment of the reaction kinetics of such systems requires understanding of the effects imposed by the complex geometrical features associated with most porous and amorphous solids. These are described by empirical parameters such as pore size, particle size, and formalisms involving fractal¹ or spectral² dimensions. Recent work, both theoretical and experimental, has demonstrated the applicability of the fractal formalism to a variety of problems in heterogeneous chemistry and in surface science.³ The effects of

pore size^{4,5} and of surface fractality⁶⁻¹² on photoprocesses have been studied in several laboratories. In spite of the wide interest

0022-3654/91/2095-1890\$02.50/0 © 1991 American Chemical Society

⁽¹⁾ Mandelbrot, B. B. The Fractal Geometry of Nature; Freeman: San Francisco, 1982.

^{(2) (}a) Alexander, S.; Orbach, R. J. Phys. Lett. 1982, 43, 626. (b) Rammal, R.; Toulouse, G. J. Phys. Lett. 1983, 44, L13.

⁽³⁾ The Fractal Approach to Heterogeneous Chemistry: Polymers, Colloids, Surfaces; Avnir, D., Ed.; Wiley: Chichester 1989.
(4) (a) Turro, N. J.; Zimmt, M.; Gould, I.; Mahler, W. J. Am. Chem. Soc.
1985, 107, 5826. (b) Turro, N. J. Tetrahedron 1987, 43, 7, 1589.
(5) (a) Avnir, D.; Busse, R.; Ottolenghi, M.; Wellner, E.; Zacchariasse, K. J. Phys. Chem. 1985, 89, 3521. (b) Wellner, E.; Ottolenghi, M.; Avnir, D.; Hugnert, D. (angenuir 1986, 26, 6619. (c) Bicenburg H: Avnir, D.; D.; Huppert, D. Langmuir 1986, 2, 616-619. (c) Birenbaum, H.; Avnir, D.; Ottolenghi, M. Langmuir 1989, 5, 48-54.

^{(6) (}a) Grätzel, M. In Photochemical Energy Conversion; Norris, J., Meisel, D., Eds.; Elsevier: Amsterdam, 1989; p 284. (b) Vlachopoulus, N.; Liska, P.; Augustinski, J.; Grätzel, M. J. Am. Chem. Soc. 1988, 110, 1216.

⁽⁷⁾ Yang, C.-L.; El-Sayed, M. A.; Squib, S. L. J. Phys. Chem. 1987, 91, 4440

⁽⁸⁾ Pines, D.; Huppert, D. Chem. Phys. Lett. 1989, 156, 223.
(9) Takami, A.; Mataga, M. J. Phys. Chem. 1987, 91, 618.

⁽¹⁰⁾ Even, U.; Redeman, K.; Jortner, J.; Maor, N.; Reisfeld, R. Phys. Rev. Lett. 1984, 52, 2164.