

Magnetic Field Dependence of the Geminate Recombination of Radical Ion Pairs in Polar Solvents

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With 4 figures

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Pairs of radical ions are generated in polar solvents by nanosecond laser flashes in a singlet electron spin state via photoinduced electron transfer. The recombination monitored spectroscopically with a time resolution ~ 3 ns can be resolved into a fast geminate (~ 10 ns) and a slow homogeneous (~ 1000 ns) process. It has been observed for the system pyrene + 3,5-dimethoxy-dimethylaniline in methanol that triplet products appear already during the geminate phase of the recombination. The yield of these fast triplet products is reduced by an external magnetic field of 500 Gauss to about 80% of its zero field value. The magnetic field dependence of this effect in the range 0–500 Gauss has been measured under stationary conditions. The results are found to be in agreement with a theoretical model based on the assumption that the change of spin multiplicity of the initial radical pairs originates from the hyperfine coupling between unpaired electron spins and nuclear spins within each radical.

Bei der Fluoreszenzlöschung mit Elektron-Donoren und -Akzeptoren werden in polaren Lösungsmitteln Radikationenpaare im Singlett-Elektronenspinzustand erzeugt. Ihre Rekombination, die spektroskopisch mit einer zeitlichen Auflösung von ~ 3 ns verfolgt wird, setzt sich aus einer schnellen (~ 10 ns) geminalen Reaktion und einer langsameren (~ 1000 ns) homogenen Reaktion zusammen. Im System Pyren + 3,5-Dimethoxy-Dimethylanilin in Methanol entstehen Triplettrekombinationsprodukte schon wenige Nanosekunden nach Erzeugung der Radikationenpaare. Die Ausbeute dieser frühen Triplettprodukte wird durch ein äußeres Magnetfeld von 500 Gauss auf ungefähr 80% des Nullfeldwertes verringert. Die Abhängigkeit dieses Effektes von der magnetischen Feldstärke wurde im Bereich 0–500 Gauss unter stationären Bedingungen gemessen. Die experimentellen Ergebnisse befinden sich in Übereinstimmung mit theoretischen Vorhersagen, die sich auf einen Einfluß der Hyperfeinwechselwirkung zwischen den (ungepaarten) Elektronenspins und den Kernspins auf den Wechsel der Spinmultiplizität bei der geminalen Rekombination gründen.

1. Introduction

Radical ion pairs can be generated in polar solvents via photo-induced electron transfer [1]. The radical ion pairs subsequently undergo recombination processes [2, 3]. For suitable donor-acceptor pairs in strongly polar solvents as for example the system pyrene (Py) and 3,5-dimethoxy-N,N-dimethylaniline (DMDMA) in methanol studied in this paper recombination is energetically allowed to either the triplet excited state ${}^3\text{Py}^* + {}^1\text{DMDMA}$ or the ground state ${}^1\text{Py} + {}^1\text{DMDMA}$ [4]. The solvated radical ion pairs being generated from singlet precursors have their unpaired electron spins in a singlet state initially. They may then immediately recombine to the ground state. For many systems studied the transition probability to the ground state is small enough to allow singlet radical pairs to separate [2, 4]. In this respect, a large energy difference between ground and radical ion pair states renders the transition Franck-Condon forbidden. The smaller energy gap between the triplet and the radical ion pair states favours a recombination to triplet products. For this to occur, the colliding radical ion pair needs to be in a triplet state.

Following the initial laser flash the radical ions and the triplet recombination products can be monitored spectroscopically. Evidently, there exist a slow and a fast recombination process. A fast "geminate" recombination process occurring within a few ns follows the separation and re-encounter of the initially generated radical ion pairs. This process is much influenced by the surrounding solvent medium. Radical ion pairs may also separate completely to diffuse into the solvent bulk, encounter members of other pairs and recombine. The time required for this second order "homogeneous" recombination process depends on the reactant concentrations and is typically of the order of 1000 ns.

The unpaired electron spins of radicals originating from different pairs are randomly aligned, i.e. the homogeneous recombination process encompasses 75% triplet and 25% singlet encounters. Since triplet collisions lead with greater probability to recombination than do singlet collisions the actual ratio of homogeneous triplet and singlet products will exceed 75:25 (see also below). Thus, the long time component of triplet production is readily explained. However, the short component has been subject to much debate, and the question arose by which mechanism the spin multiplicity of the radical ion pairs is changed within the short time range of a few nanoseconds. There is no firm theoretical basis for the very fast formation of so-called

"prompt" triplets supposedly originating from an unrelaxed pair state as suggested earlier [5].

Mechanisms known to induce changes of spin multiplicity in radical pairs are the hyperfine coupling between unpaired electron spins and nuclear spins, and spin lattice relaxation. Since spin lattice relaxation times are of the order of μs the latter mechanism must be disregarded for fast geminate processes. The action of the hyperfine coupling in such processes is testified, however, by the electron and nuclear spin polarization in ESR and NMR spectra [6].

The hyperfine coupling induces transitions between the degenerate S_0 and T_0, T_1, T_{-1} electron spin states of the radical pairs. An external magnetic field, however, lifts the degeneracy between the S_0 and $T_{\pm 1}$ states. For field strengths of the order of the hyperfine coupling constants the transition probabilities between these states will be reduced and will vanish for large fields. Such magnetic hyperfine modulation has been found under stationary conditions for dye sensitized delayed fluorescence in organic crystals by GROFF et al. [7]. The theory of the hyperfine induced spin dynamics of radical pairs has recently been treated in more detail by BROCKLEHURST [8]. Magnetic field effects as observed in electrogenerated chemiluminescence experiments [9] require fields much higher than necessary for the hyperfine modulation and do not have to be considered here.

In this paper we wish to report that the triplet yield of recombining radical ion pairs in polar solvents is reduced by weak external magnetic fields. In a time resolved experiment the magnetic field effect is demonstrated to be built up over the geminate phase of the recombination process. The magnetic field dependence of the triplet yield is found to be in agreement with the prediction of a theoretical model based on the hyperfine mechanism of geminate radical recombination. We believe to give the first unequivocal evidence in two different experimental approaches for spin multiplicity changes in geminate recombination processes of radical pairs in solution to originate from the hyperfine interaction.

2. Experimental methods

2.1. Materials

Pyrene (puriss. Fluka) was degassed to 10^{-6} Torr, then zone refined under nitrogen atmosphere in 80 passes and finally recrystallized from very pure ethanol. 3,5-dimethoxy-N,N-dimethylaniline (DMDMA) has been synthesized in this laboratory. Methanol (Merck, Uvasol for

fluorescence spectroscopy) was used without further purification. Samples were degassed by the usual freeze-pump-thaw technique, applied five times to a final pressure of 10^{-6} Torr.

2.2. Time resolved experiment

In the time resolved experiments the quencher concentration was 0.05 mol dm^{-3} so that the pyrene fluorescence was more than 99% quenched. The measurements were performed with a laser absorption spectrophotometer similar to the one used earlier [2]. The laser (337.1 nm) was a pulsed 100 kW N_2 superradiant device (Avco C950) with 8 ns pulse width (FWHM). The detection system, comprising a pulsed high pressure Xenon arc (Osram 150 W), specially wired photomultiplier RCA 4832 and matching optics, was optimized to provide the high sensitivity of 5×10^{-3} extinction change at a time resolution of about 3 ns [10]. Laser and monitoring light beam at right angle crossed part of the sample volume which was permeated by the magnetic field of $B \sim 500$ Gauss from a steel magnet. The magnetic field was measured with a Hall probe gaussmeter (Bell 620).

2.3. Photostationary experiment

In the photostationary experiment carried out in methanol pyrene fluorescence was quenched to 20% by DMDMA. The quenching constant for pyrene in methanol at 23°C is $3240 \text{ dm}^3 \text{ mol}^{-1}$ [4]. The sample was placed between the pole pieces of an electromagnet (Bruker B-E10) which could be adjusted between $B_0 = 6.4$ Gauss (zero current remanence) and 104 Gauss. Excitation light and delayed emission were separated using a phosphoroscope arrangement with the rotating discs driven by synchronous motors. The excitation source was a current stabilized Hg/Xe 1000 W Hanovia lamp. The sample was irradiated with 334 nm light through a Jarrell-Ash 250 mm monochromator. Delayed emission intensity was measured through a double monochromator ($2 \times$ Jarrell-Ash 250 mm in a tandem arrangement) with the photoncounting technique, applying a cooled EMI 6256 D photomultiplier, ORTEC amplifiers, and in addition an electronic gate to minimize the dark count rate. Finally the counts were summed up over time intervals with the magnetic field on and off in turns of 1 min.

3. Experimental results

The results of the time-resolved experiment in methanol are shown in Fig. 1. Fig 1a presents the emission of the ${}^1[\text{Py-DMDMA}^+]$

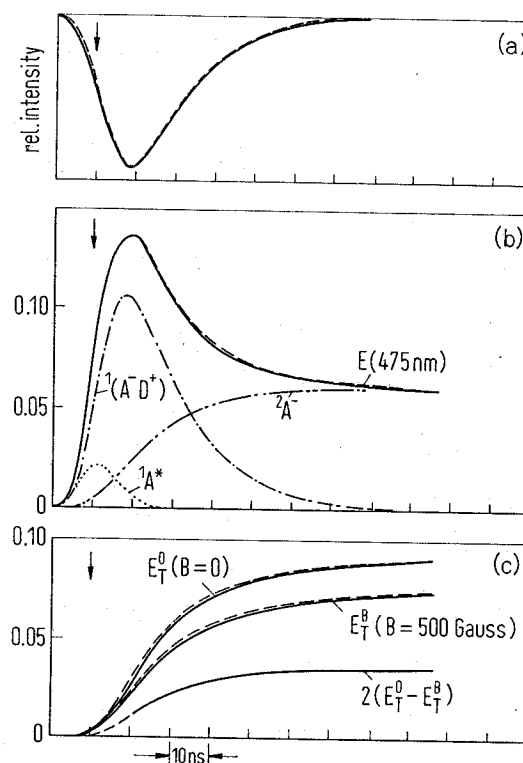


Fig.1. Transient signals of the system pyrene/DMDMA in methanol at room temperature: (a) — exciplex fluorescence signal at 532 nm (arbitrary units), simulated exciplex fluorescence signal; (b) — total measured extinction at 475 nm (averaged over 9 measurements), total simulated extinction (see text), ---- simulated exciplex extinction, ---- simulated ${}^2\text{Py}^-$ extinction, simulated ${}^1\text{Py}^*$ extinction; (c) — triplet extinction with and without an external magnetic field of 500 Gauss (averaged over 9 measurements). The signal is corrected for the ${}^2\text{Py}^-$ extinction at 412 nm, i.e. $E_T = E^{412} - 0.39 E^{475}$ simulated triplet extinction. The arrows indicate the maximum of the laser pulse

exciplex which is assumed to precede the generation of the radical ion pair. Fig.1b shows the time development of the 475 nm extinction mainly due to exciplex and ${}^2\text{Py}^-$ absorption. Absorption measurements at 475 nm have been preferred over those at 491 nm (the maximum of ${}^2\text{Py}^-$ absorption) because at 475 nm exciplex and ${}^2\text{Py}^-$ ion extinction coefficients can be assumed to be equal [4]. The signal exhibits a fast and a slow fall-off. The fast fall-off comprises the decay of the

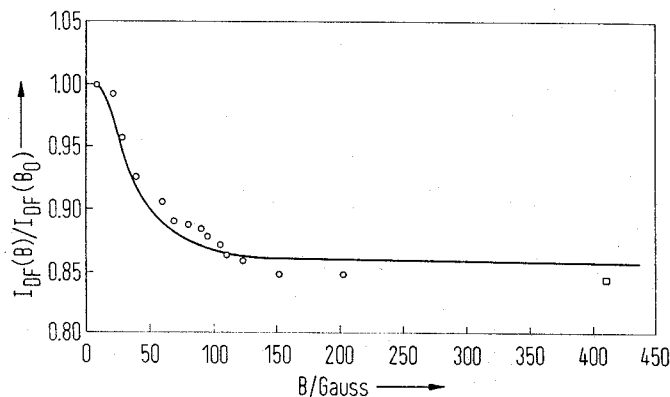


Fig. 2. Magnetic field dependence of the delayed pyrene fluorescence. $B_0 = 6.4$ Gauss is the remanence of the electromagnet at zero current, \circ measured relative fluorescence intensity $I_{DF}(B)/I_{DF}(B_0)$, absolute accuracy ± 0.01 ; \square average value of five data points obtained in the range between 400–1500 Gauss; — field dependence as obtained from the theoretical model described in the text

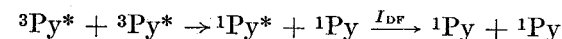
exciplex to triplet and ground state products and its separation to the ion pair followed by fast geminate recombination. The slow fall-off is due to the homogeneous recombination of the radical ions. As presented in Fig. 1c the triplet extinction signal E_T of $^3\text{Py}^*$ also appears with a fast and a slow component. The slow component arises from the homogeneous recombination of the radical ions. The fast rise of the triplet product is complementary to the 475 nm exciplex-ion pair decay.

With the aid of the magnetic field effect it is possible to distinguish between the two possible ways of triplet formation: intersystem crossing in the exciplex or geminate recombination of the solvated radical ion pairs formed by dissociation of the exciplex. As outlined in the introduction changes of the spin multiplicity of radical pairs are effected by the hyperfine coupling which can be modulated by external magnetic fields. Magnetic fields do, however, not influence the intersystem crossing in the exciplex. Magnetic field effects on the fast triplet production are, hence, indicative of triplets formed by geminate recombination. Fig. 1c compares the time evolution of triplet products with ($B = 500$ Gauss) and without a magnetic field. The magnetic field is seen to reduce the formation of triplet products. The

difference of the triplet extinction at 0 and 500 Gauss, $E_T^0 - E_T^B$, builds up parallel to the fast triplet formation until about 60 ns. At longer times ($E_T^0 - E_T^B$) is constant although triplet products are still being formed through the homogeneous recombination route.

A similar magnetic field effect has been found with the system pyrene/diethylaniline in methanol. When methanol is replaced by acetonitrile as solvent the absolute magnetic field effect which is a measure of the geminately formed triplets is significantly reduced.

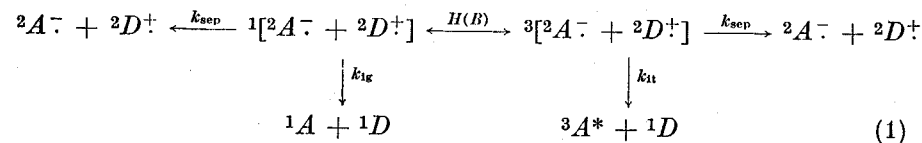
The results of the photostationary experiment described in Section 2.3 are presented in Fig. 2. The intensity of the delayed fluorescence brought about according to



is proportional to the square of the triplet concentration $[^3\text{Py}^*]^2$. Fig. 2 demonstrates how the yield of the triplet products depends on the strength of the applied magnetic field. The emission intensity of delayed fluorescence decreases rapidly with increasing magnetic field strength. Already at ~ 50 Gauss ($B_{1/2}$) the intensity drop is half of its saturation value at $B \geq 200$ Gauss.

4. Theoretical treatment

A most simple kinetic model for the geminate recombination of radical ion pairs is outlined in scheme (1) where A corresponds to pyrene and D to DMDMA:



We consider an ensemble of initially formed solvated radical ion pairs. The separation of the radical pairs is taken to be a first order process with a time independent rate constant k_{sep} . Once separated the radical pairs are assumed not to re-encounter again. Radical pairs not separated are supposed to recombine by first order processes to either the ground or the triplet excited state with rate constants k_{ig} and k_{it} , respectively. The recombination route depends on the spin multiplicity of the pair. Initially the pairs produced from singlet precursors are in a singlet

spin state. The subsequent electron spin motion is governed by the Hamiltonian

$$H(B) = \sum_k a_{1k} \mathbf{I}_k \cdot \mathbf{S}_1 + \sum_l a_{2l} \mathbf{I}_l \cdot \mathbf{S}_2 + \mu_B \mathbf{B} \cdot (g_1 \mathbf{S}_1 + g_2 \mathbf{S}_2) + J(R_{A-D}) \left(\frac{1}{2} + 2 \mathbf{S}_1 \cdot \mathbf{S}_2 \right). \quad (2)$$

(In our calculations we neglect the smaller nuclear Zeeman terms and also all anisotropic terms as the radicals are assumed to be freely rotating in the solvent cage.) The first term describes the hyperfine interaction (governed by the coupling constants a_{1k} , a_{2l}) acting between the unpaired electron spins \mathbf{S}_1 , \mathbf{S}_2 and the nuclear spins \mathbf{I}_k , \mathbf{I}_l . The second (electron Zeeman) term describes the interaction between the electron spins and the applied magnetic field \mathbf{B} . The third term represents the exchange interaction (singlet-triplet splitting) of the unpaired electrons.

The time evolution of the radical ion pair spin states may be described by the spin density matrix $\rho_0(t)$.

$$\rho_0(t) = \exp\left(-\frac{i}{\hbar} Ht\right) \rho_0(0) \exp\left(\frac{i}{\hbar} Ht\right). \quad (3)$$

The diagonal elements $[\rho_0(t)]_{ii}$ give the probability of pairs to be in the electron-nuclear spin state $|i\rangle$ at time t .

For a system of M nuclear spins $\frac{1}{2}$ there are 2^{M+2} electron-nuclear spin states to be considered which amounts to a number of more than a million for the system Py + DMDMA. We assume for the solvated radical ion pairs the exchange interaction to be negligible. Under this assumption the motion of electron and nuclear spins in the two radicals are mutually independent. Furthermore we approximate the actual hyperfine coupling of ${}^2\text{Py}^-$ and ${}^2\text{DMDMA}^+$ described by the two sets of coupling constants (in Gauss)

$${}^2\text{Py}^-: 4 \times (a_H = 2.13); 4 \times (a_H = 4.83); 2 \times (a_H = 1.04) [11]$$

$${}^2\text{DMDMA}^+: 6 \times (a_H^{\text{CH}_3} = 5.4); 3 \times (a_H = 6.0); 1 \times (a_N = 5.4) [12] \quad (4a)$$

by the more symmetric coupling situation of the sets

$${}^2\text{Py}^-: 4 \times (a_H = 2.3); 4 \times (a_H = 5.2)$$

$${}^2\text{DMDMA}^+: 6 \times (a_H^{\text{CH}_3} = 5.6); 3 \times (a_H = 5.6); 1 \times (a_N = 5.6). \quad (4b)$$

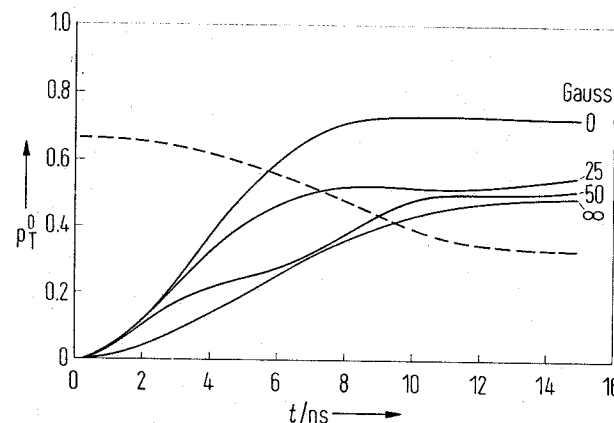


Fig. 3. — Calculated time evolution of the triplet probability $p_T^0 = \text{tr}(Q_T \rho_0 Q_T)$ of pyrene-/DMDMA⁺ radical ion pairs initially formed in a singlet state for various magnetic field strengths, - - - - relative magnetic field effect

$$\frac{p_T^0(0) - p_T^0(\infty)}{p_T^0(0)}$$

Under these assumptions the Hamiltonian assumes a convenient block diagonal form which renders possible its diagonalization and the evaluation of the spin density matrix (3). Still, numerical calculations are quite extensive since they involve expansions of initial and final states in terms of all eigenvectors of the system. The replacement (4b) leaves the total sum of coupling constants unchanged. This assures a small effect on the hyperfine induced singlet-triplet transition probability. We present in Fig. 3 the probability $p_T^0(t)$ to find the ${}^2\text{Py}^- + {}^2\text{DMDMA}^+$ pair in a triplet state:

$$p_T^0(t) = \text{tr}[Q_T \rho_0(t) Q_T] \quad (5)$$

where $Q_T = \frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2$ ($Q_S = 1 - Q_T$) is the projection on the manifold of triplet (singlet) states. The probability to find the pair in a singlet state is $p_S^0 = 1 - p_T^0$. $\text{tr}(A)$ stands for the trace of operator A . For the initial pair we assumed a density matrix $\rho_0(0) = Q_S$ (i.e. a random formation of all nuclear spin states with singlet electron spin alignment). From Fig. 3 one observes that after a time range of 5 ns the larger part of the pairs are to be found in a triplet state. Upon application of external magnetic fields the probability to find the pair in the triplet state is reduced. The detailed time behaviour of the relative magnetic field effect $\frac{p_S^0(0) - p_S^0(\infty)}{p_S^0(0)}$ is also illustrated in Fig. 3.

The time evolution of radical pairs undergoing recombination and separation can be described by the Liouville equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] - k_{\text{sep}} \rho - L(t) [K\rho + \rho K] \quad (6)$$

where

$$2K = k_{\text{ig}} Q_S + k_{\text{it}} Q_T.$$

The first term of the r.h.s. of Eq. (6) accounts for the electron-nuclear spin motion, the second term for the pair separation and the third term for the recombination to singlet and triplet products. The function $L(t)$ describes random collisions of the radicals. At the instant of an encounter [$L(t) \neq 0$] the radical pair singlet and triplet states are coupled to a manifold of singlet and triplet product states through the rate matrix K . This results in an energy broadening $\hbar k_{\text{ig}}$ for the singlet radical pair state and $\hbar k_{\text{it}}$ for the triplet radical pair state. It may be noted that if $|\hbar(k_{\text{ig}} - k_{\text{it}})|$ exceeds the energy of the hyperfine coupling the hyperfine induced spin transitions will be momentarily suppressed.

The duration of radical collisions measured by the function $L(t)$ can be evaluated from the Smoluchowski diffusion equation for radical ion pairs. This will be the subject of a future publication [13]. Without a detailed description of the diffusion process one may adopt two extreme views concerning $L(t)$:

(A) The radical ion pairs are coupled throughout their geminate phase to the product states, i.e. $L(t) = \text{const.}$

(B) The radical ion pair states are not coupled to the product states except at the instance of recombination collisions.

In case (A) the hyperfine induced spin transition is suppressed if $k_{\text{ig}} \neq k_{\text{it}}$. Using the above hyperfine coupling constants for the system pyrene/DMDMA and the rate constants $k_{\text{ig}} = 3.0 \times 10^7 \text{ s}^{-1}$, $k_{\text{it}} = 1.5 \times 10^{10} \text{ s}^{-1}$ and $k_{\text{sep}} = 2.5 \times 10^8 \text{ s}^{-1}$ a calculation for high field strengths (see Appendix) gives only a triplet product yield of 0.84%.

In case (B) the spin motion is independent of the coupling to the product states described by K . The Liouville equation can then be greatly simplified. For the probabilities p_S and p_T to have singlet and triplet radical ion pairs

$$p_S = \text{tr}(Q_S \rho Q_S)$$

$$p_T = \text{tr}(Q_T \rho Q_T)$$

we have approximately

$$\begin{aligned} \frac{dp_S}{dt} &= (p_S + p_T) \frac{dp_S^0}{dt} - (k_{\text{ig}} + k_{\text{sep}}) p_S \\ \frac{dp_T}{dt} &= (p_S + p_T) \frac{dp_T^0}{dt} - (k_{\text{it}} + k_{\text{sep}}) p_T. \end{aligned} \quad (7)$$

In these rate equations the first term describes the spin motion of the radical pairs and the second term their recombination and separation. p_S^0 and p_T^0 defined in Eq. (5) are the probabilities in the absence of recombination to find the radical pair in the singlet and triplet states, respectively. The product yields φ_S^{gem} and φ_T^{gem} of geminate recombination to the singlet ground and the triplet excited states, respectively, are obtained from the expressions,

$$\begin{aligned} \varphi_S^{\text{gem}} &= \int_0^\infty dt k_{\text{ig}} p_S(t) \\ \varphi_T^{\text{gem}} &= \int_0^\infty dt k_{\text{it}} p_T(t). \end{aligned} \quad (8)$$

There are two approximations involved with Eq. (7):

1. The fact that singlet and triplet pair states are depleted with different rates is neglected for the spin motion described by the first term of the Liouville equations, i.e. one assumes $[H, \rho] = (p_S + p_T)[H, \rho_0]$.

2. It is assumed that at all times $p_S + p_T$ has the same average value for all nuclear spin states. It should be noted that for $k_{\text{ig}} = k_{\text{it}}$ Eq. (7) holds exactly.

On the basis of Eq. (7) one obtains with the same rate constants as given before a zero field triplet product yield of 20.3% and a high field triplet product yield φ_T^{gem} of 10.4%. This latter value should be compared with the value 0.84% obtained for model (A). Explicit consideration of each nuclear spin configuration gives a triplet yield of 9.4%. This shows that assumption (2) is justified to a good approximation.

5. Interpretation of experimental results

In this section we wish to demonstrate that the possibility of calculating product yields of the geminate recombination process for various magnetic field strengths renders possible a detailed interpretation of the experimental results. In Fig. 4 are defined the reaction rates of the processes following the laser pulse $I(t)$. Quenching of the

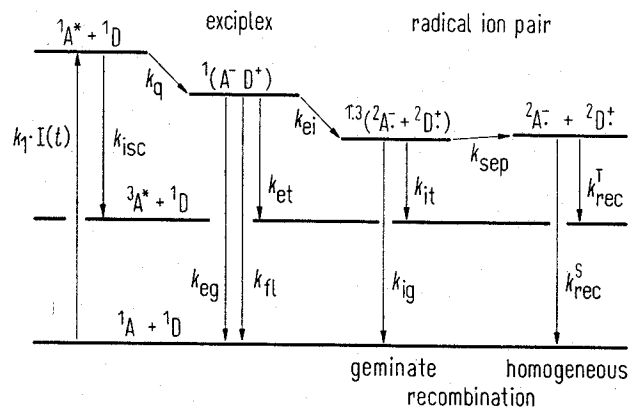


Fig. 4. Overall reaction scheme for the system pyrene/DMDMA in methanol

excited singlet state of pyrene $^1A^*$ by the donor 1D (DMDMA) leads to the singlet exciplex $^1(A-D^+)$ with the rate constant $k_q = (1.1 \pm 0.1) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [4]. Intersystem crossing in the $^1A^*$ and $^1(A-D^+)$ states gives triplet products $^3A^* + ^1D$ with the rate constants k_{isc} and k_{et} , respectively. The exciplex decays to the ground state $^1A + ^1D$ by internal conversion with the rate constant k_{eg} or by fluorescence with the rate constant $k_{fl} = 5 \times 10^5 \text{ s}^{-1}$ [4] and to the solvated radical ion pair $^2A^- + ^2D^+$ with the rate constant k_{ei} . The radical ion pair either experiences a fast geminate recombination to the singlet ground state $^1A + ^1D$ or to the triplet excited state $^3A^* + ^1D$, or it separates into the solvent bulk. The separated ion pairs $^2A^- + ^2D^+$ undergo homogeneous recombination processes to the singlet and triplet product states with the second order rate constants k_{rec}^S and k_{rec}^T , respectively. The total recombination rate constant $k_{rec} = k_{rec}^S + k_{rec}^T$ amounts to $(5.5 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

To prove that the reaction scheme of Fig. 4 is consistent with the observations we evaluate the time development of the concentrations of the reaction intermediates $[^1A^*]$, $[^1(A-D^+)]$, $[^2A^-]$ and $[^3A^*]$. This can be done by numerical integration of the rate equations corresponding to the reaction scheme in Fig. 4. In order to simplify these calculations we note that the geminate recombination phase of the radical ion pair lasts for a time which is short compared with the exciplex lifetime of 14 ns (see below) and the separated radical ion recombination time $1/(k_{rec}[^2A^-]) \approx 10^3 \text{ ns}$. One may therefore assume the geminate recombination to be instantaneous and characterize the

geminate reaction routes by relative yields rather than rates. φ_S^{gem} gives the yield for geminate recombination to the singlet state, φ_T^{gem} the yield of triplet products and $\varphi^{\text{sep}} = 1 - \varphi_S^{\text{gem}} - \varphi_T^{\text{gem}}$ the yield of separated radical ion pairs. In the following rate equations $I(t)$ represents the profile of the laser pulse as measured with the detection system described in Sec. 2.2. $\tau_0 = 295 \text{ ns}$ is the lifetime of unquenched $^1A^*$ in CH_3OH [4]. $\tau_{\text{exc}} = (k_{eg} + k_{et} + k_{ei} + k_{fl})^{-1}$ is the lifetime of the exciplex $^1(A-D^+)$, k_{ann} is the triplet-triplet annihilation rate constant and τ_T the time constant of the first order triplet decay. B is the strength of an external magnetic field.

$$\frac{d}{dt} [^1A^*] = k_1 I(t) - \left(k_q [^1D] + \frac{1}{\tau_0} \right) [^1A^*] \quad (9a)$$

$$\frac{d}{dt} [^1(A-D^+)] = k_q [^1D] [^1A^*] - \frac{1}{\tau_{\text{exc}}} [^1(A-D^+)] \quad (9b)$$

$$\frac{d}{dt} [^2A^-] = k_{ei} \varphi^{\text{sep}} [^1(A-D^+)] - k_{\text{rec}} [^2A^-]^2 \quad (9c)$$

$$\begin{aligned} \frac{d}{dt} [^3A^*] = & k_{isc} [^1A^*] + [k_{et} + k_{ei} \varphi_T^{\text{gem}}(B)] [^1(A-D^+)] \\ & + k_{\text{rec}}^T [^2A^-] [^2D^+] - k_{\text{ann}} [^3A^*]^2 - \frac{1}{\tau_T} [^3A^*]. \end{aligned} \quad (9d)$$

The exciplex lifetime τ_{exc} is determined by fitting the numerical solution of Eqs. (9a), (9b) for the time dependence of $[^1(A-D^+)]$ to the experimental exciplex emission signal (see Fig. 1a). The result is [4]

$$\tau_{\text{exc}} = (14 \pm 1.5) \text{ ns.}$$

To describe the 475 nm extinction signal of Fig. 1b the contributions from the excited acceptor, the exciplex and the free ion $^2A^-$ must be determined. The extinction coefficients [4]

$$\epsilon [^1A^*, 475 \text{ nm}] = 1.1 \times 10^7 \text{ cm}^2 \text{ mol}^{-1}$$

$$\epsilon [^1(A-D^+), 475 \text{ nm}] \approx \epsilon [^2A^-, 475 \text{ nm}] = 1.5 \times 10^7 \text{ cm}^2 \text{ mol}^{-1}$$

yield

$$E(475 \text{ nm}) = d(1.1 [^1A^*] + 1.5 [^1(A-D^+)] + 1.5 [^2A^-]) \times 10^4$$

where $d = 0.4 \text{ cm}$ is the optical pathlength and the concentrations are given in mol dm^{-3} . To evaluate this expression the rate equations (9a)–(9c) have to be solved. The only unknown rate constant $k_{ei} \varphi^{\text{sep}}$ and the amount of excited pyrene molecules $[^1A^*]_0 = k_1 \int_0^\infty I(t) dt$ can

be determined by fitting the simulated to the experimental curve. The values $[^1A^*]_0 = 3.3 \times 10^{-5} \text{ mol dm}^{-3}$ and $k_{ei} \varphi^{\text{sep}} = 2.25 \times 10^7 \text{ s}^{-1}$ give the close agreement shown in Fig. 1b. It is evident, that the relatively long-lived exciplex intermediate is necessary to obtain the pronounced initial peak of the extinction curve. If the solvated radical ion pair would originate directly from the $^1A^*$ precursor a distinct short time fall-off would not be discernable. This result is independent of the choice of the above parameters. $k_{ei} \varphi^{\text{sep}}$ only affects the relative height of the initial peak, $[^1A^*]_0$ only influences the bimolecular processes.

In order to describe the time development of the triplet products in Fig. 1c and to estimate the contributions of the various pathways of triplet production we neglect the very small deactivation terms in Eq. (9d) and assume $k_{\text{rec}}^T \approx k_{\text{rec}} = 5.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see below), $k_{\text{isc}} = 1.0 \times 10^6 \text{ s}^{-1}$ and $\varepsilon_T (412 \text{ nm}) = 2.7 \times 10^7 \text{ cm}^2 \text{ mol}^{-1} [4]$. The unknown term $k_{\text{et}} + k_{ei} \varphi_T^{\text{gem}} (B)$, which is decisive for the total yield of "fast" triplets, can be obtained for $B = 0$ and $B = 500$ Gauss by fitting the simulated to the experimental curves. The result is

$$k_{\text{et}} + k_{ei} \varphi_T^{\text{gem}} (0 \text{ Gauss}) = 1.63 \times 10^7 \text{ s}^{-1}$$

$$k_{\text{et}} + k_{ei} \varphi_T^{\text{gem}} (500 \text{ Gauss}) = 1.32 \times 10^7 \text{ s}^{-1}. \quad (10)$$

For an estimate of the rate constant k_{et} the ratio $\varphi_T^{\text{gem}} (0)/\varphi_T^{\text{gem}} (500)$ has to be known. It can be calculated from Eqs. (7) and (8) if appropriate rate constants k_{ig} , k_{it} and k_{sep} are chosen. Taking again $k_{\text{ig}} = 3.0 \times 10^7 \text{ s}^{-1}$, $k_{\text{it}} = 1.5 \times 10^{10} \text{ s}^{-1}$, $k_{\text{sep}} = 2.5 \times 10^8 \text{ s}^{-1}$ one obtains

$$\varphi_T^{\text{gem}} (0)/\varphi_T^{\text{gem}} (500) \approx 2.0.$$

This ratio actually is insensitive to the choice of the above parameters. From Eq. (10) we now have

$$k_{\text{et}} \approx 1.0 \times 10^7 \text{ s}^{-1} \text{ and } k_{ei} \varphi_T^{\text{gem}} (0) \approx 0.63 \times 10^7 \text{ s}^{-1}.$$

With the yield of exciplex formation Φ_{exc} being unity at the high quencher concentrations used the yields of triplet products from the exciplex Φ_T^{exc} and via the solvated radical ion pair $\Phi_T^{\text{gem}} (B)$ are

$$\Phi_T^{\text{exc}} = k_{\text{et}} \tau_{\text{exc}} \approx 0.14$$

$$\Phi_T^{\text{gem}} (0) = k_{ei} \varphi_T^{\text{gem}} (0) \tau_{\text{exc}} \approx 0.088$$

and

$$\Phi_T^{\text{gem}} (500) \approx 0.044.$$

Thus, at zero field about 40% of the fast triplet products is due to the hyperfine coupling mechanism acting during the geminate recombination phase.

We now want to estimate the (2nd order) rate constant k_{rec}^T for homogeneous recombination to triplet products. For radical ions originating from different pairs 75% of all encounters are in a triplet and 25% in a singlet state. One can assume that all triplet encounters lead to triplet products. Singlet encounters also lead to triplet products through the hyperfine mechanism. The probability at zero field it $\varphi_T^{\text{gem}} = 0.20$ and at high fields $\varphi_T^{\text{gem}} = 0.10$ (theoretical values). Hence, each encounter has a probability $x = 0.75 + 0.25 \times 0.20 = 0.80$ (0.775 at high fields) for triplet recombination to occur and $y = 0.25 \varphi^{\text{sep}} = 0.18$ for separation without recombination. $\varphi^{\text{sep}} = 0.72$ is assumed to be independent of the external magnetic field because no field effect on the free ion yield φ_{ion} has been observed. In our simple kinetic model of the geminate recombination processes this assumption would require $k_{\text{ig}} = k_{\text{it}}$. However, k_{it} has to be larger than k_{sep} to assure sufficient triplet production; k_{ig} has to be smaller than k_{sep} , otherwise the free ion yield would be too small. This inconsistency is probably due to the oversimplification of the diffusion process in this model.

The total probability for homogeneous triplet product formation is then $x + yx + y^2x + \dots = x/(1-y) = 0.98$ (0.95 at high fields), i.e. the 2nd order triplet recombination rate constant is

$$k_{\text{rec}}^T = 0.98 k_{\text{rec}} \quad (\text{zero field})$$

$$k_{\text{rec}}^T = 0.95 k_{\text{rec}} \quad (\text{high fields}).$$

Thus, in the absence of a magnetic field about 98% of the separated ion pairs will recombine to give triplet products and only a very small magnetic field effect on the triplet production should be observed during the homogeneous recombination process. This is in agreement with the experimental result as can be seen from Fig. 1c. The quantum yield of triplet formation from homogeneous recombination now is

$$\Phi_T^{\text{hom}} = 0.98 \tau_{\text{exc}} k_{ei} \varphi^{\text{sep}} = 0.31$$

for zero field and 0.30 for high fields.

For a final test of the hyperfine coupling model we shall compare the experimental field dependence of the delayed fluorescence

$$\frac{I_{DF}(B)}{I_{DF}(B_0)} = \left[\frac{[{}^3A^*]_{\text{stat}, B}}{[{}^3A^*]_{\text{stat}, B_0}} \right]^2 \quad (11)$$

with that predicted on the basis of Fig. 4. In Eq. (11) $[{}^3A^*]_{\text{stat}, B}$ stands for the stationary triplet concentration at field strength B . For its evaluation one has to solve the Eqs. (9a)–(9d) under stationary conditions. The annihilation term $k_{\text{ann}}[{}^3A^*]^2$ can be neglected in Eq. (9d) for triplet concentrations as prevailing in the stationary experiment. One then obtains:

$$\frac{I_{DF}(B)}{I_{DF}(B_0)} = \left[\frac{(1 - \Phi_{\text{exc}}) \Phi_T^A + \Phi_{\text{exc}} \left(\Phi_T^{\text{exc}} + \Phi_T^{\text{hom}} + \Phi_T^{\text{gem}}(B_0) \frac{\varphi_T^{\text{gem}}(B)}{\varphi_T^{\text{gem}}(B_0)} \right)}{(1 - \Phi_{\text{exc}}) \Phi_T^A + \Phi_{\text{exc}} (\Phi_T^{\text{exc}} + \Phi_T^{\text{hom}} + \Phi_T^{\text{gem}}(B_0))} \right]^2 \quad (12)$$

Thus, the magnetic field dependence of the delayed fluorescence in the stationary experiment is expressed through quantum yields known from the dynamic experiment and with the ratio $\varphi_T^{\text{gem}}(B)/\varphi_T^{\text{gem}}(B_0)$ which can be calculated theoretically from Eqs. (7) and (8). Using the quantum yields $\Phi_T^{\text{gem}}(B_0) = 0.088$, $\Phi_T^{\text{exc}} = 0.14$, $\Phi_T^{\text{hom}} = 0.31$, $\Phi_{\text{exc}} = 0.80$ (the ${}^1A^*$ fluorescence is quenched by 80% in the stationary experiment, see Sec. 2.3) and $\Phi_T^A = 0.30$ [4] (Φ_T^A is the triplet quantum yield of the unquenched ${}^1A^*$ state) one obtains the theoretical curve shown in Fig. 2. The small field dependence of Φ_T^{hom} is neglected in this simple treatment. It may easily be verified, that its inclusion results in a maximum magnetic field effect of 17% instead of 14% shown in Fig. 2. Of course, the qualitative magnetic field dependence of the delayed fluorescence is not affected by this approximation. As already mentioned, the ratio $\varphi_T^{\text{gem}}(B)/\varphi_T^{\text{gem}}(B_0)$ which is decisive for the field dependence of Eq. (12), is insensitive against the parameters in Eqs. (7) and (8). We therefore believe that the good agreement between the experimental and theoretical field dependence of the delayed fluorescence unequivocally shows that the hyperfine coupling is responsible for the magnetic field effect and, thus, for the triplet production in the geminate recombination process.

Conclusions

It has been shown for the system pyrene/DMDMA in methanol that after excitation triplet products are formed via four pathways:

- (1) intersystem crossing in the excited pyrene,
- (2) intersystem crossing in the exciplex,
- (3) geminate recombination of solvated radical ion pairs,
- (4) homogeneous recombination of radical ions.

Only the geminate triplet production, which is due to the hyperfine coupling between unpaired electron and nuclear spins in the radicals, is affected by external magnetic fields. This magnetic field dependence may be calculated from a model based on the hyperfine coupling mechanism. Comparison of the theoretical and the measured magnetic field effects in time resolved experiments renders possible the discrimination of the various processes.

A magnetic field effect even larger than for pyrene/DMDMA has been found for the system pyrene/*N,N*-diethylaniline (DEA) in methanol. This is in agreement with theoretical predictions, because the hyperfine coupling is stronger in the DEA radical cation than in DMDMA⁺ [12].

A more detailed understanding of the geminate processes requires, however, a theory which includes the diffusion of the radical ions in their mutual Coulomb field [13]. The geminate processes depend much on the solvent microenvironment of the radical pair. One may therefore expect to learn from such experiments about solvent structural effects in recombination processes. A first evidence for a solvent effect is given by the experimental finding that the magnetic field effect on the triplet production is reduced when methanol is replaced by acetonitrile. This obviously is due to faster separation of the radicals in this solvent of lower viscosity.

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Appendix: Spin motion of radical pair permanently coupled to product states; limit of large magnetic fields

In the limit of large magnetic fields the Liouville Eq. (6) reduces to uncoupled 2×2 Eqs.

$$\dot{\rho} = -\frac{i}{\hbar} \left[\begin{pmatrix} 0 & a \\ a & 0 \end{pmatrix}, \rho \right] - k_{\text{sep}} \rho - \frac{1}{2} L(t) \left[\begin{pmatrix} k_{\text{ig}} & 0 \\ 0 & k_{\text{it}} \end{pmatrix}, \rho \right] \quad (A1)$$

in the basis of S_0, T_0 electronic spin states connected with a single nuclear spin configuration $N(m_{11}, m_{12}, \dots, m_{21}, m_{22}, \dots)$. The hyperfine coupling is described through

$$a = \frac{1}{2} \sum_k a_{1k} m_{1k} - \frac{1}{2} \sum_l a_{2l} m_{2l}.$$

We employ the notation $[A, B]_- = AB - BA$. The case of permanent coupling to product states is characterized through $L(t) \equiv 1$.

Eq. (A1) together with an initial condition $\varrho(0)$ is readily solved. Set

$$\begin{aligned} \varrho(t) &= F(t) \sigma(t) \\ F(t) &= \exp \left[- \left(k_{\text{sep}} + \frac{k_{1g} + k_{1t}}{2} \right) t \right] \end{aligned} \quad (\text{A2})$$

to get

$$\dot{\sigma} = A_1 \sigma + \sigma A_2 \quad (\text{A3})$$

where

$$\begin{aligned} A_{1,2} &= -\kappa \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \mp \frac{i}{\hbar} a \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \kappa &= (k_{1g} - k_{1t})/4. \end{aligned} \quad (\text{A4})$$

The solution of (A3) is known to be $[\sigma(0) = \varrho(0)]$

$$\sigma = \exp(A_1 t) \varrho(0) \exp(A_2 t). \quad (\text{A5})$$

Noting that

$$A_{1,2}^2 = (\kappa^2 - a^2/\hbar^2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (\text{A6})$$

the exponential operators are readily evaluated through Taylor expansion

$$\begin{aligned} \exp(A_{1,2} t) &= \cosh \Omega t + \frac{\sinh \Omega t}{\Omega} A_{1,2} \\ \Omega &= (\kappa^2 - a^2/\hbar^2)^{1/2} \end{aligned} \quad (\text{A7})$$

(A7) together with (A2), (A4) and (A5) establishes the desired solution.

For the initial condition

$$\varrho(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

i.e. all pairs initially in a singlet electron spin state one has

$$\begin{aligned} \varrho_{11}(t) &= p_S(t) = F(t) [\cosh \Omega t - (\kappa/\Omega) \sinh \Omega t]^2 \\ \varrho_{22}(t) &= p_T(t) = F(t) (a/\hbar\Omega)^2 \sinh^2 \Omega t. \end{aligned} \quad (\text{A8})$$

For $\kappa^2 \gg a^2/\hbar^2$ corresponding to a large difference between the singlet and triplet recombination constants k_{1g} and k_{1t} holds

$$p_T(t) \sim [a/\hbar(k_{1g} - k_{1t})]^2$$

and transitions to the triplet state are suppressed.

The singlet and triplet recombination yields are evaluated as

$$\begin{aligned} \varphi_S^{\text{gem}}(N) &= k_{1g} \int_0^\infty p_S(t) dt \\ \varphi_T^{\text{gem}}(N) &= k_{1t} \int_0^\infty p_T(t) dt \end{aligned} \quad (\text{A9})$$

where N indicates the dependence on the nuclear spin configuration. One obtains explicitly

$$\begin{aligned} \varphi_S^{\text{gem}}(N) &= k_{1g} \left\{ \frac{c^2}{k_{\text{sep}} + (k_{1g} + k_{1t})/2 - 2\Omega} + \frac{2c(1-c)}{k_{\text{sep}} + (k_{1g} + k_{1t})/2} \right. \\ &\quad \left. + \frac{(1-c)^2}{k_{\text{sep}} + (k_{1g} + k_{1t})/2 + 2\Omega} \right\} \end{aligned} \quad (\text{A10})$$

$$\begin{aligned} \varphi_T^{\text{gem}}(N) &= k_{1t} (c^2 - c) \left\{ \frac{1}{k_{\text{sep}} + (k_{1g} + k_{1t})/2 - 2\Omega} - \frac{2}{k_{\text{sep}} + (k_{1g} + k_{1t})/2} \right. \\ &\quad \left. + \frac{1}{k_{\text{sep}} + (k_{1g} + k_{1t})/2 + 2\Omega} \right\} \end{aligned} \quad (\text{A11})$$

$$c^{-1} = 1 - [\hbar\kappa/a + (\hbar^2\kappa^2/a^2 - 1)^{1/2}]^2.$$

Assuming that initially all nuclear spin configurations are equally populated one has for the total of singlet and triplet products

$$\varphi_S^{\text{gem}} = \frac{1}{Z} \sum_N \varphi_S^{\text{gem}}(N) \quad (\text{A12})$$

$$\varphi_T^{\text{gem}} = \frac{1}{Z} \sum_N \varphi_T^{\text{gem}}(N) \quad (\text{A13})$$

where Z is the total number of nuclear spin configurations.

References

1. H. LEONHARD and A. WELLER, *Z. physik. Chem. Neue Folge* **29** (1961) 277; *Ber. Bunsenges. physik. Chem.* **67** (1963) 791.
2. H. SCHOMBURG, H. STAERK and A. WELLER, *Chem. Phys. Letters* **21** (1973) 433; **22** (1973) 1.
3. M. OTTOLENGHI, *Accounts Chem. Res.* **6** (1973) 153.
4. H. SCHOMBURG, Dissertation, Göttingen 1975.
5. C. GOLDSCHMIDT, R. POTASHNIK and M. OTTOLENGHI, *J. physic. Chem.* **75** (1971) 1025. — N. ORBACH, R. POTASHNIK and M. OTTOLENGHI, *J. physic. Chem.* **76** (1972) 1133. — N. ORBACH, J. NOVROS and M. OTTOLENGHI, *J. physic. Chem.* **77** (1973) 2831. — D. M. GOODALL, N. ORBACH and M. OTTOLENGHI, *Chem. Phys. Letters* **26** (1974) 365. — N. ORBACH and M. OTTOLENGHI, in: *The Excipies*, M. GORDON and W. R. WARE (editors). Academic Press Inc. New York 1975, p. 75.
6. A. R. LEPLEY and G. L. CLOSS, Eds., *Chemically Induced Magnetic Polarization*. John Wiley, New York 1973.
7. R. P. GROFF, R. E. MERRIFIELD, A. SUNA and P. AVAKIAN, *Phys. Rev. Letters* **29** (1972) 429. — R. P. GROFF, A. SUNA, P. AVAKIAN and R. E. MERRIFIELD, *Physic. Rev. B* **9** (1974) 2655.
8. B. BROCKLEHURST, *Chem. Phys. Letters* **28** (1974) 357.
9. L. R. FAULKNER, H. TACHIKAWA and A. J. BARD, *J. Amer. chem. Soc.* **94** (1972) 691.
10. H. MEYER, H. SCHOMBURG, M. SCHULZ and H. STAERK, to be published.
11. H. W. BROWN and R. C. JONES, *J. chem. Physics* **36** (1962) 2809.
12. B. M. LATTA and R. W. TAFT, *J. Amer. chem. Soc.* **89** (1967) 5172.
13. Z. SCHULTEN, K. SCHULTEN, A. WELLER and H.-J. WERNER, to be published.