SOLVENT EFFECTS ON THE MAGNETIC-FIELD-DEPENDENT REACTION YIELDS OF PHOTOGENERATED RADICAL ION PAIRS

H. STAERK, H.-G. BUSMANN, W. KÜHNLE and A. WELLER

Max-Planck-Institut für Biophysikalische Chemie, Abteilung Spektroskopie, D-3400 Göttingen, Federal Republic of Germany

Received 2 December 1988

A pronounced solvent viscosity and polarity dependence of the magnetic field effect was found for polymethylene-linked radical ion pairs generated by photoinduced intramolecular electron transfer in compounds of the type pyrene–$(CH_2)_n$–N,N-dimethylaniline, with $n=7$–16. This is interpreted in terms of the general radical pair mechanism, i.e. the nuclear hyperfine interaction mechanism including a spin-exchange interaction, modulated by the stochastic folding motion of the linking CH_2 chain which leads to a "motional deformation" of the reaction yield spectra.

1. Introduction

Photoinduced electron transfer reactions in polymethylene-linked donor–acceptor systems A–$(CH_2)_n$–D, in the following abbreviated by A(n)D, lead to the intermediate formation of exciplexes, $^1(A^-_{(n)}D^+)$, and radical ion pairs, $^2A^-(n)^2D^+$. Their relative (free) energies depend strongly on solvent polarity such that, generally, radical ion pairs are favoured in polar solvents, and exciplexes in non-polar solvents, as is the case in unlinked systems. Through its limited flexibility, however, the polymethylene chain governs the kinetics not only of the electron transfer but also of the back electron transfer processes, in contrast to unlinked systems with free diffusion [1–8]. In the model compounds studied here, A and D are pyrene and N,N-dimethylaniline, respectively.

In a highly polar solvent, after excitation of the acceptor molecule, A, electron transfer from ^1D to $^1A^*$ generates the radical ion pair in its overall singlet state, $^1(^2A^-(n)^2D^+)$. The formation of the radical ion pair in its overall triplet state, $^3(^2A^-(n)^2D^+)$, requires spin realignment in the pair. This is brought about by the hyperfine-coupling-induced (hfc induced) coherent spin motion of the unpaired electron spins. It can be modulated by weak magnetic fields (B) by virtue of the Zeeman effect, and by varying the exchange interaction, which is a function of the distance and the relative angles of the radicals in the pair $^2A^-(n)^2D^+$, and thus is dependent on chain length (n) and chain dynamics. The hfc induced singlet–triplet transitions can only occur between those radical pair singlet and triplet states which are degenerate within the hfc energy, ΔE_{hfc}. The magnitude of ΔE_{hfc} depends on the isotropic hfc constants a_{ik} between the nuclear spins I_{ik} and the unpaired electron spins, S_i; for the systems with A=pyrene and D=N,N-dimethylaniline one has $\Delta E_{\mathrm{hfc}} \approx 58$ G [9–12]. The spin exchange interaction, $J(r)$, between the unpaired electron spins of $^2A^-$ and $^2D^+$, splits the singlet and triplet levels of the radical ion pair by an amount $2J$, and has an important influence on the magnetic field effect and the product yield as can be shown experimentally and theoretically [1–4,13–18].

The instantaneous overall spin state of the radical ion pair determines the recombination route: back electron transfer from the singlet radical pair leads to the singlet ground state, $^1A(n)^1D$; back electron transfer from the triplet radical pair state populates the lowest excited triplet state, $^3A^*(n)^1D$. Furthermore, close association of the $^2A^-$ and $^2D^+$ moieties in the singlet radical ion pair leads to the exciplex state, as has recently been found by studying the magnetic field dependence of exciplex emission in highly polar solvents [3].

As a consequence of the distance dependence of the exchange interaction, $J(r)$, through which the time evolution of the coupled electron–nuclear spin system is affected, the intramolecular back electron transfer in radical ion pairs of compounds A(n)D is crucially influenced by the stochastic conformational changes of the polymethylene chain. In linked radical pair systems chain dynamics and spin dynamics are coupled, more or less permanently, through the exchange interaction throughout the lifetime of the radical pair. This should hold likewise for unlinked radical pairs in "supercages" (e.g. micellar systems) [19–21], but also for part of those geminate pairs of free radical pair systems in homogeneous solution which recombine at an "early" time (a few nanoseconds), i.e. geminate pairs which are released for a mean diffusional separation of say, 1–2 nm [12]. It is the *exponential* distance dependence of $J(r)$ [22] which alters the influence of the hyperfine and Zeeman interactions in a particularly sensitive way and gives rise to the prediction of a "motional shifting" effect for linked radical pairs if one changes the solvent viscosity [4].

In the experiments the absorbance $A_T(B)$ of the locally excited triplet state $^3A^*(n)^1D$ and the emission intensity $I'(B)$ of the exciplex $^1(A^{-}_{(n)}D^{+})$ were monitored spectroscopically as a function of the external magnetic field strength B by emission and absorption MODSC spectroscopy (magneto-optically detected spin conversion spectroscopy) [3,23].

Investigations have been carried out in order to study the influence of solvents of different viscosity η (0.39–38.0 cP) and constant high polarity ϵ, and on the other hand, of constant viscosity but variable ϵ (6.1–37.5), on the reaction kinetics and the magnetic-field-dependent reaction yield.

2. Experimental

Compounds A–$(CH_2)_n$–D, 1-(1-pyrene)-n-(p-N,N-dimethylaminophenyl)alkane, (abbreviated as A(n)D) with A=pyrene, D=N,N-dimethylaniline(DMA) and n=7–16 have been investigated in the solvents acetonitrile (ACN, η=0.39 cP, ϵ=37.5, Merck), in diethyleneglycol (DEG, η=38 cP, ϵ=32, Fluka) and in a neutral tenside solution (CEH). CEH is a viscous, highly polar solution of n-octyltetraoxyethylene (C_8E_4, Bachem Feinchemikalien) in water (pH≈9); its effective viscosity is intermediate between that of ACN and DEG [12,18]. Experiments have also been carried out in mixtures of ethyl acetate (ETAC, Merck) with ACN (Merck) of different mole percent, x_i, of ETAC: $x_1=0$ (η=0.39 cP: ϵ=37.5), x_2=31.2 (0.42 cP, 22.6), x_3=62.4 (0.47 cP; 13.4), x_4=90.0 (0.46 cP; 7.6) x_5=100 (0.45 cP; 6.1). The method (magneto-optically detected spin conversion spectroscopy, MODSC) for measuring magnetic-field-dependent emission and absorption signals (in this work the triplet absorption of pyrene at 415 nm and the exciplex emission at 550 nm) has been described earlier [3,14,16,23].

3. Results and discussion

Fig. 1 shows magnetic-field-dependent triplet yields $\phi_T(B)$ (with B in G) of the compound A(9)D obtained from nanosecond-laser absorption MODSC experiments at 415 nm in the solvents ACN, CEH and DEG, i.e. solvents with increasing viscosity. The triplet yield maxima show a large shift towards lower

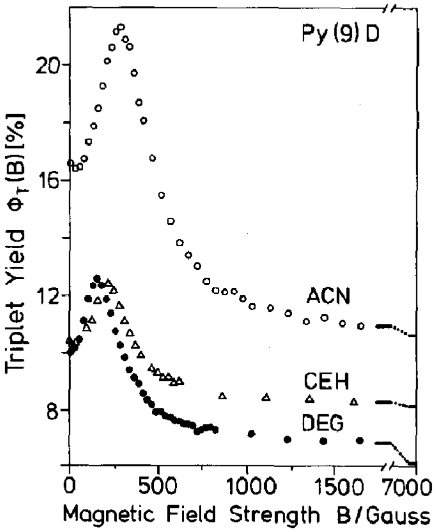

Fig. 1. Magnetic field dependence of the triplet yield $\phi_T(B)$ of pyrene–$(CH_2)_9$–N,N-dimethylaniline in solvents of high polarity but different viscosity, ACN (acetonitrile, ϵ=37.5, η=0.39 cP), CEH (viscous neutral tenside solution), DEG (diethylene glycol, ϵ=32, η=38 cP).

magnetic field strengths as one changes the solvent from acetonitrile to the viscous diethylene glycol. Such a solvent dependence is in accord with earlier predictions [4,15,22] which are related to the motional broadening/narrowing phenomenon [24], common e.g. in magnetic resonance or Mössbauer spectroscopy. The experimental results provide corroborating evidence for the important influence that the relative motion of the radicals in the pair has on the probability density distribution of the exchange interaction (the so-called "spectrum of the exchange interaction").

Fig. 2 gives examples of the relative triplet yield, $\phi_T(B)/\phi_T(0)$, of compounds A(n)D with different chain length $n=8$, 9, 10 in the solvents ACN and DEG. In each solvent, B_{max} and the width of the maxima decrease with increasing chain length n. Comparing the behaviour of the curves in the different solvents ACN or DEG for a particular chain length n, one sees that the maxima are narrower and the B_{max} values are smaller in the high-viscosity solvent DEG.

In table 1, supported by fig. 3, characteristic values of the magnetic-field-dependent relative triplet yield $\phi_T(B)/\phi_T(0)$, as obtained from MODSC experiments, are listed for a variety of chain lengths, $n=7$–16, and for the three solvents ACN, CEH and DEG. Judging by the shape of the $\phi_T(B)/\phi_T(0)$ curves, the results can be divided into two groups.

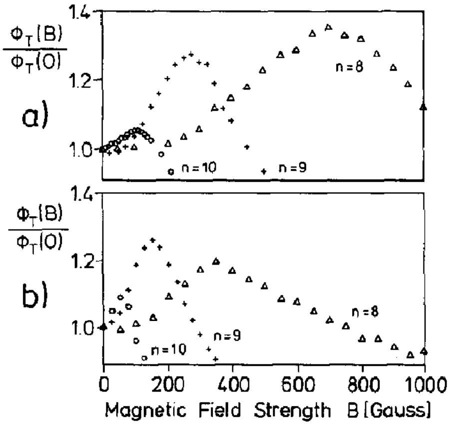

Fig. 2. Magnetic field dependence of the relative triplet yield $\phi_T(B)/\phi_T(0)$ of pyrene–$(CH_2)_n$–N,N-dimethylaniline for $n=8$, 9 and 10 in (a) acetonitrile ($\eta=0.39$ cP), (b) diethylene glycol ($\eta=38$ cP).

Those, obtained with compounds A(n)D, $n=7$–10, are clearly of the resonance type, i.e. distinct maxima in the magnetic-field-dependent triplet yield spectra are observed, where B_{max} corresponds approximately to the most probable (effective) singlet–triplet splitting energy $2J_{eff}$. For $n=12$–16 the results are of the saturation type, i.e. S-shaped curves characterized by the magnetic field strength $B_{1/2}$, at which the triplet yield has attained half its zero-field value, are observed. However, it is seen from table 1 that the shape of the curves changes *steadily* in the whole range as the length of the flexible aliphatic chain increases from $n=7$ to 16.

To obtain further experimental support for the motional shifting and motional narrowing concept, solvent mixtures with roughly the same macroscopic viscosity but varying bulk dielectric properties have been used. It is assumed that in such systems the intramolecular dynamics, i.e. the rate of relative distance and angular variation, of the radical pair remains the same, but other parameters which have an influence on the electron transfer and back electron transfer rates be varied. One example for A(9)D is given in fig. 4. The numbers 1 to 4 indicate the mole ratios of ethyl acetate in the solvent mixtures of ethyl acetate and acetonitrile. Fig. 4a shows the magnetic field dependence of the relative exciplex yield $I'(B)/I'(0)$. In highly polar solvents the exciplex is predominantly formed directly from the radical ion pair species [3] in the course of a "harpooning" reaction [2,3,13]. The exciplex fluorescence intensity therefore exhibits a magnetic field dependence with the opposite sign to that of the triplet absorbance. Relative triplet absorbance signals $A_T(B)/A_T(0)$ with x_i as parameter are shown in fig. 4b. The minima (B_{min}) in the exciplex curves (cf. fig. 4a) and the maxima (B_{max}) in the absorption curves (fig. 4b) occur at the same field strength and are most pronounced for the solvent acetonitrile (curves 1). Moreover, the curves cross the relative value of $A_T(B)/A_T(0)=1$ and $I'(B)/I'(0)=1$, respectively, at the same magnetic field strength. In the solvent mixtures with increasing mole fraction of ethyl acetate, i.e. decreasing bulk dielectric constant, the magnetic field effect gradually disappears, as other magnetic-field-independent direct channels contribute to the formation of exciplexes and molecules in the triplet state, and a solvent polarity dependence is ex-

Table 1
Characteristic magnetic field effect parameters (for definitions, see fig. 3) of pyrene–$(CH_2)_n$–N,N-dimethylaniline, abbreviated Py(*n*)D, in the solvents ACN (acetonitrile) [14], CEH (a viscous neutral tenside solution) and DEG (diethylene glycol) [16]; experimental errors ⩽ 5%

n	$B_{1/2}$ (G)	B_{max} (G)	ΔB_{HW} (G)	B_{cross} (G)	R_∞ (%) 7000 G	R_{max} (%)
in ACN						
7		1650	1270	2950	8	13
8	1400	750	510	1180	25	33
9	650	280	230	490	36	29
10	320	110	90	165	39	5.5
11	230	40		60	38	0.3
12	187				38	
13	172				37	
14	160				36	
15	147				38	
16	135				35	
in CEH						
7	4410	1120	670	2030	9	1
8	1300	515	385	795	13	7
9	490	210	148	349	22	14
10	185	74	55	110	31	7
11	114	25	30	43	34	2
12	75				26	
13	70				21	
14	75				19	
15	69				21	
16	67				17	
in DEG						
7	2380	985	780	1780	7	3
8	1380	380	345	750	29	8
9	460	150	145	288	39	12
10	185	50	48	89	37	5
11	97				32	
12	91				20	
13	100				19	
14	105				18	
15	82				17	
16	85				25	

pected for the back electron transfer rate. A magnetic field effect is not observed in pure ethyl acetate ($\epsilon = 6.1$). In the context of the motional shifting hypothesis the most interesting result of these measurements is that B_{min} and B_{max} have practically the same value (280 G for A(9)D) for all solvent mixtures. Corresponding MODSC spectra have been obtained for A(16)D with $B_{1/2} = 135$ G in the solvent mixtures x_1 to x_4 for exciplex and triplet signals.

4. Conclusion

The experimental results confirm the earlier prediction, according to which the magnetic-field-dependent signals of biradicals and polymethylene-linked radical ion pairs are not only related to the intramolecular distance and angular distribution of the radicals, but also are strongly dependent on the *rate* at which the polymethylene-linked doublet pairs convert between their various conformations [4].

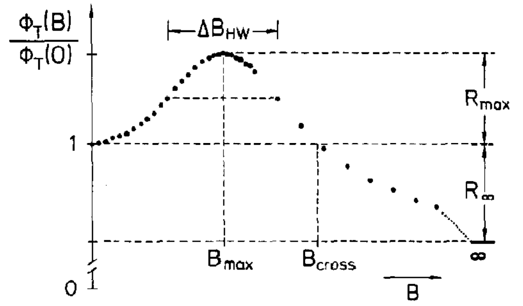

Fig. 3. Definitions of the characteristic parameters, as used in table 1, of the magnetic-field-dependent relative triplet yield $\phi_T(B)/\phi_T(0)$; only triplets which are generated by the radical pair mechanism are considered [18]. B_{max}, magnetic field strength at which $\phi_T(B)$ has a maximum; B_{cross}, magnetic field strength at which $\phi_T(0)=\phi_T(B)$; $B_{1/2}$, magnetic field strength defined by $\phi_T(B_{1/2})=\frac{1}{2}[\phi_T(0)+\phi_T(\infty)]$; ΔB_{HW}, half width in the range of the extremum between $B=0$ and B_{cross}; $R_{max}=\phi_T(B_{max})/\phi_T(0)-1$; $R_\infty=1-\phi_T(B_\infty)/\phi_T(0)$.

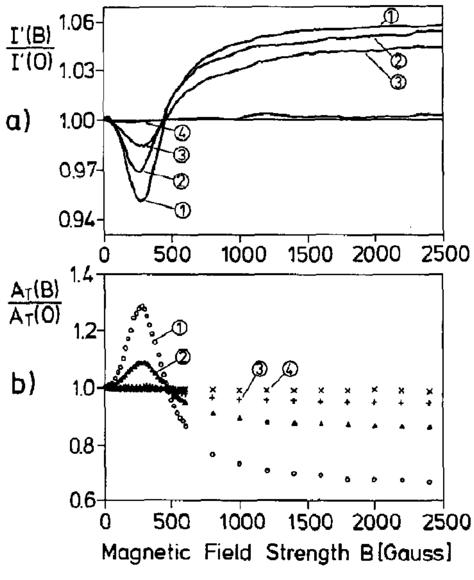

Fig. 4. Relative exciplex emission intensity $I'(B)/I'(0)$ (a) and triplet absorbance $A_T(B)/A_T(0)$ (b), as a function of the magnetic field strength B for compound pyrene–$(CH_2)_9$–N,N-dimethylaniline in mixtures of ethyl acetate/acetonitrile. 1, 0 mol% ethyl acetate, $\epsilon=37.5$; 2, 31.2 mol% ethyl acetate, $\epsilon=22.6$; 3, 62.4 mol% ethyl acetate, $\epsilon=13.4$; 4, 90.0 mol% ethyl acetate, $\epsilon=7.6$.

This prediction was made on the basis of a previous theoretical treatment of biradical CIDNP [22] and also the (static) "sub-ensemble approximation", which was applied to polymers with paramagnetic endgroups [15]. The latter theory is based on the separation of *molecular dynamics* (governing the "spectrum of the exchange interaction") and *spin dynamics* in order to reduce computational effort. In this simplified treatment, where back electron transfer is considered to be independent of A, D distance, the generally stochastic ensemble which has a time-dependent Hamiltonian, characterized by the exchange interaction $J(r(t))$, is approximated by isolated sub-ensembles with constant exchange interaction and thus time-independent Hamiltonian. The triplet yields of the sub-ensembles, $\varphi_T(B, J)$, are weighted by the spectral distribution function $w(J)$ of the exchange interaction and finally added, in order to obtain the overall magnetic-field-dependent triplet yield $\phi_T(B)$. The exchange spectrum $w(J)$ is a dynamic distribution function of exchange interactions, developed from the Kubo theory for stochastically modulated classical oscillators [24]. In some presentations, instead of J the singlet–triplet splitting energy, $2J$, has been found to be more convenient [4,18]. In essence, $w(J)$ regards the influence of the rate of conformational changes on the overall (final) molecular triplet yield.

The strongly exponential dependence of the exchange interaction on distance implies an asymmetrical "motional deformation" and "motional shifting" of the $w(J)$ spectra with changing intramolecular mobility of the radical moieties. However, it is a fundamental feature of lineshape theory [24] and of "motional narrowing" that the parameters of the probability distribution of A, D distances cannot be determined unequivocally. Even if $J(r)$ is known, they can neither be determined from the experimental triplet yield function, $\phi_T(B)$, nor from the spectrum of the exchange interaction, $w(J)$ (if it were experimentally accessible). This applies to all theoretical models used to explain the magnetic field effect of biradicals and linked radical ion pairs.

Whereas the (static) "sub-ensemble approximation" is of considerable didactic and illustrative value and is able to predict and explain the observed motional shifting, it falls short of providing quantitative triplet yields satisfactorily. Note that in fig. 1 the experimental absolute triplet yields are much higher in ACN than in CEH and DEG. A much more advanced theoretical treatment [16,18], applying an extended stochastic Liouville equation which takes into account a *distance-dependent* back electron transfer, is found to be necessary to account for quantitative details e.g. the absolute triplet yields at zero magnetic field (cf. fig. 1).

In analogy to an earlier treatment of spin and polymethylene chain dynamics [22], the temporal evolution of the spin system in radical ion pairs and the product formation in the course of back electron transfer have been calculated with the stochastic Liouville equation [16,18]. The stochastic chain dynamics, the quantum mechanical spin dynamics and the distance dependence of back electron transfer are described by the appropriate operators and the corresponding density matrix formalism of the coupled electron–nuclear spin states and the product states $^3A^*(n)^1D$ and $^1A(n)^1D$. The agreement between simulation and experiment, particularly the motional shifting and the absolute yields, suggests that the inclusion of a *distance-dependent* back electron transfer is a considerable improvement over previous models. These results which are also important for cage reactions of unlinked radical pairs are described in detail elsewhere [18].

Acknowledgement

We thank B. Frederichs and H. Meyer for technical assistance. We acknowledge discussions with Dr. J. Ihlemann and Dr. R. Treichel. This work has been supported by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich SFB 93 "Photochemistry with Lasers".

References

[1] A. Weller, H. Staerk and R. Treichel, Faraday Discussions Chem. Soc. 78 (1984) 271, 332.

[2] H. Staerk, R. Mitzkus, W. Kühnle and A. Weller, in: Springer series of chemical physics, Vol. 23. Ultrafast phenomena III, eds. K.B. Eisenthal, R. Hochstrasser and W. Kaiser (Springer, Berlin, 1982) p. 205.

[3] H. Staerk, W. Kühnle, R. Treichel and A. Weller, Chem. Phys. Letters 118 (1985) 19.

[4] H. Staerk, R. Treichel and A. Weller, in: Biophysical effects of steady magnetic fields, eds. G. Maret, J. Kiepenheuer and N. Bocarra, Springer Proc. Phys. 11 (Springer, Berlin, 1986) p. 85.

[5] H. Leonhardt and A. Weller, Z. Physik. Chem. NF 29 (1961) 277; Ber. Bunsenges. Physik. Chem. 67 (1983);
A. Weller, in: Nobel Symposium Series, Vol. 5, ed. S. Claesson (Almqvist and Wiksell, Stockholm, 1967) p. 413.

[6] A. Weller, Z. Physik. Chem. NF 133 (1982) 93, and references therein.

[7] H. Schomburg, H. Staerk and A. Weller, Chem. Phys. Letters 21 (1973) 433; 22 (1973) 1.

[8] A. Weller, in: Supramolecular photochemistry, ed. V. Balzani, NATO ASI Ser. C 214 (1987) p. 343.

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

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

[11] A. Weller, F. Nolting and H. Staerk, Chem. Phys. Letters 96 (1983) 25.

[12] H. Staerk, R. Treichel and A. Weller, Chem. Phys. Letters 96 (1983) 28.

[13] H. Staerk, W. Kühnle, R Mitzkus, R. Treichel and A. Weller, in: Springer series of chemical physics, Vol. 38. Ultrafast phenomena IV, eds. D.H. Auston and K.B. Eisenthal (Springer, Berlin, 1984) p. 380.

[14] R. Treichel, Dissertation, University of Göttingen (1985).

[15] K. Schulten and R. Bittl, J. Chem. Phys. 84 (1986) 9;
R. Bittl and K. Schulten, in: Biophysical effects of steady magnetic fields, eds. G. Maret, J. Kiepenheuer and N. Bocarra, Springer Proc. Phys. 11 (Springer, Berlin, 1986) p. 90.

[16] H.-G. Busmann, Dissertation, University of Göttingen (1987).

[17] R. Bittl and K. Schulten, Chem. Phys. Letters 146 (1988) 58.

[18] H.-G. Busmann, H. Staerk and A. Weller, J. Chem. Phys., submitted for publication.

[19] H. Hayashi and S. Nagakura, Bull. Chem. Soc. Japan 57 (1984) 322.

[20] M.B. Zimmt, Ch. Doubleday and N.J. Turro, J. Am. Chem. Soc. 106 (1984) 3363.

[21] T. Ulrich, U.E. Steiner and W. Schlenker, Tetrahedron 42 (1986) 6131, and references therein.

[22] F.J.J. de Kanter, J.H. den Hollander, A.H. Huizer and R. Kaptein, Mol. Phys. 34 (1977) 875.

[23] R. Treichel, H. Staerk and A. Weller, Appl. Phys. B 31 (1983) 15.

[24] R. Kubo, in: Fluctuation, relaxation and resonance in magnetic systems, ed. D. ter Haar (Oliver and Boyd, Edinburgh, 1962) p. 23.