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Magnetic field dependence of the deactivation rates of triplet azocumene in solution

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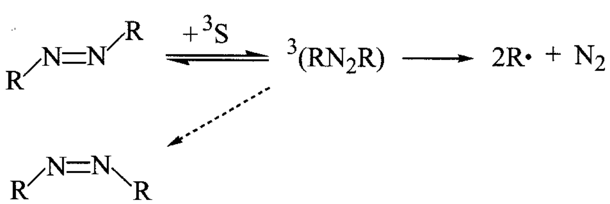
The triplet sensitized photo-decomposition of azocumene into nitrogen and cumyl radicals is investigated by time resolved EPR and optical absorption spectroscopy. It is found that the cumyl radicals carry an initial spin polarization and are formed with a yield that depends on both the solution viscosity and the strength of an external magnetic field. The phenomenon is interpreted in terms of a depopulation-type triplet mechanism, i.e. a competition between decay into radicals and fast, triplet sublevel selective intersystem crossing (ISC) back to the azocumene ground state. Analysis of the data yields relative rate constants for the ISC processes and the cleavage reaction of triplet azocumene. The energetically lower zero field triplet substate is depopulated by ISC about seven times faster than the upper one and about two orders of magnitude faster than depopulation by cleavage occurs. Cleavage probably takes place on the nanosecond time scale, while the ISC must proceed on the picosecond scale, as at elevated viscosity it becomes faster than the rotational Brownian motion of the molecule.

1. Introduction

Acyclic azoalkanes are known to possess a short lived triplet state at about $E_T \approx 226\,\mathrm{kJ\,mol^{-1}}$ above their *trans* singlet ground state. When populated via triplet sensitization it deactivates rapidly by two competing processes, radiationless return to the singlet ground state (sometimes accompanied by some *trans–cis* isomerization) and cleavage into nitrogen and two alkyl radicals, according to scheme 1, where ^{3}S is the triplet sensitizer. Not much is known about that triplet state, its structure and its lifetime. There seems to be no absorption spectrum and no phosphorescence, the state does not seem to be accessible via $S_1 \rightleftarrows T_1$ inter system crossing (ISC), and the quantum yield for radical formation is usually very low in solution [1, 2].



Scheme 1.

Recently, we have studied by time-resolved EPR (TREPR) spectroscopy the triplet quenching of acetone [3] and benzophenone [4] by AIBN (2,2′-azobis[isobutyronitrile]) in solution. It was found that during the cleavage process of triplet AIBN into nitrogen and 2-cyano-2-propyl radicals the electron spin system of the radicals becomes polarized in emission. This observation has been interpreted by assuming that the radiationless deactivation of triplet AIBN to the singlet ground state occurs faster from the energetically lower triplet substates, thus producing an overpopulation of the higher ones.

It is well known that in many photo-excited molecules the usual $S_1 \rightleftarrows T_1$ ISC process populates the zero field sublevels of T_1 with different rates, that this polarization can be partially transferred to the high field substates T_-, T_0, T_+, and that then the decay of the triplet leads to spin polarized radicals if it occurs faster than spin relaxation in the T_1 molecule. The phenomenon is called chemically induced electron polarization (CIDEP) by the triplet mechanism (TM) [5, 6]. A more specific name would be population type (p-type) triplet mechanism, because this mechanism may also work in a reversed way as a depopulation type (d-type) triplet

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mechanism. There, the sublevels of an excited triplet molecule are depopulated with different rates by state selective $T_1 \rightleftarrows S_0$ ISC to the singlet ground state. Then, radical products stemming from the triplet might be spin polarized if the ISC can compete with both radical formation and spin relaxation between the triplet substates. However, the requirements for this to happen, i.e. especially a $T_1 \rightleftarrows S_0$ ISC with rates above $10^9\,s^{-1}$, are fulfilled only in rare cases. Thus, up to now, CIDEP from a d-type triplet mechanism has been observed experimentally only for a few radicals formed from exciplexes of some excited dye molecules with heavy atom substituted electron donors [7]. The existence of a fast state selective $T_1 \rightleftarrows S_0$ ISC in these exciplexes had been postulated before by Steiner *et al.* [8, 9] to explain an observed pronounced magnetic field dependence of the radical yield in those systems.

In fact, a d-type triplet mechanism will almost always show up in both a spin polarization and a magnetic field effect (MFE) on the radical yield. Observation of both effects gives ultimate proof for that mechanism and, if analysed quantitatively, may allow one to determine the depopulation and decay rates of the triplet as well as its zero field splitting. In order to prove the mechanism for an acyclic azoalkane and to obtain some information about the elusive triplet state of these compounds, we have investigated the decomposition of *trans*-azocumene (AC) after triplet sensitization with 1-nitronaphthalene (1-NN) in solvents of different viscosities. The system seems to be well suited to study the MFE on the cumyl radical yield by laser flash photolysis (LFP) and the CIDEP of the radicals by TREPR experiments.

2. Experimental

2.1. *Time resolved EPR measurements*

Cumyl radicals were generated by laser flash photolysis (Nd-YAG laser, $\lambda = 355$ nm, 10 ns pulse width, or XeCl excimer laser, $\lambda = 308$ nm, 15 ns pulse width) of benzene solutions containing 2.1 mM 1-NN and 7.5 mM *t*AC and were detected at microwave powers in the range 0.3–1 mW, using a CW EPR spectrometer without field modulation (response time 80 ns). The details of the set-up have been described previously [10]. All solutions were deoxygenated by purging with helium for about 1 hour and then pumped in continuous flow (flow rate 10 $cm^3\,h^{-1}$) through a flat quartz cell (0.7 mm optical path length) inside the EPR cavity. The laser pulse energy was kept below 5 mJ, so that the depletion of the solutions due to irradiation was negligibly small (checked by UV absorption spectroscopy before and after irradiation).

Table 1. Solvents used and their viscosities.

	$\eta/10^{-3}$ Pa s[a]
Heptane	0.41
Benzene	0.67
Nonane	0.71
Dodecane	1.50
Hexadecane	3.32
Squalane : heptane (4 : 1 vol.)	8.32
Squalane	32.4
Paraffin oil	106.7

[a] Reference [12].

2.2. *Optical measurements*

The yield of cumyl radicals in dependence on an applied external magnetic field was determined by transient optical absorption spectroscopy after laser flash photolysis (Nd-YAG laser, specifications as above) of solutions of 1-NN and azocumene, using an experimental set-up described in [11]. The solutions were deoxygenated in the same way as described above. The flat quartz cell had an optical path length of 2 mm, a flow rate of 5 $cm^3\,h^{-1}$ was chosen, and the laser pulse energy was attenuated to 6.4 mJ, since at higher energies the signal amplitudes started to saturate.

2.3. *Materials*

To perform investigations over a wide range of viscosities we used as solvents benzene and seven alkanes, listed in table 1 together with their viscosities at room temperature. *trans*-Azocumene was synthesized from cumylamine using the method described by Stowell for 2,2′-azobisisobutane [13]. Its purity was checked by NMR and HPLC and estimated to be better than 98%. Cumylamine was prepared according to [14]. 1-Nitronaphthalene and all the solvents were purchased from Fluka or Aldrich in their purest commercially available forms and were used without further purification. All measurements were performed at room temperature.

3. Results

3.1. *Time resolved EPR experiments*

Figure 1 shows the EPR spectrum observed about 3 μs after laser flash irradiation at $\lambda = 355$ nm of a benzene solution containing 1-NN (2.1 mM) and AC (7.5 mM). According to its hyperfine pattern and phase it has to be attributed unequivocally to an ensemble of cumyl radicals, which is spin polarized in emission. Under the conditions of the experiment, the species cannot stem from a direct photolysis of AC. First, the direct photolysis of azoalkanes occurs from their excited singlet state and, therefore, leads to TREPR spectra, which initially exhibit a spin polarization with enhanced

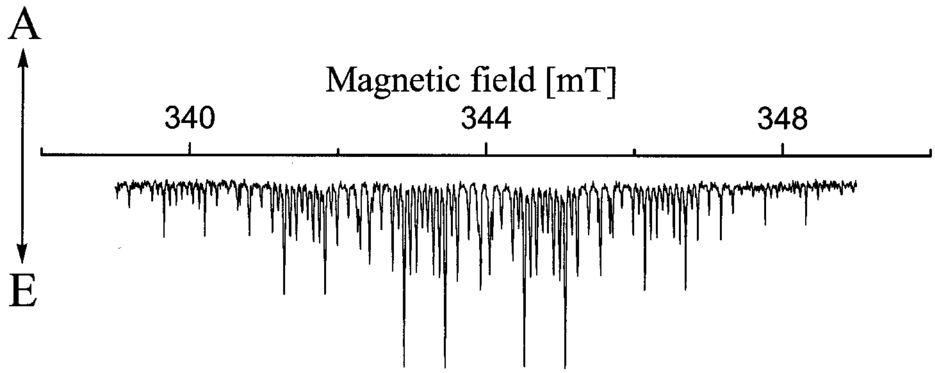


Figure 1. TREPR spectrum of cumyl radicals recorded 3 μs after triplet sensitized photolysis of azocumene in benzene. Arrows A/E designate absorption and emission, respectively.

absorption on the low field site and emission on the high field site [15]. Second, at 355 nm the absorption coefficients of 1-NN and AC are 3200 $M^{-1}\,cm^{-1}$ and 40 $M^{-1}\,cm^{-1}$, respectively. Thus, nearly all the light is absorbed primarily by 1-NN, which is known to undergo fast ISC within about 10 ps to its triplet state ^{3}(1-NN) [16]. Quenching of ^{3}(1-NN) by AC then leads to ^{3}AC, which partially cleaves into cumyl radicals and N_2. Azoalkanes are known to be efficient triplet quenchers [1, 17, 18], and the triplet energies of ^{3}(1-NN) (230 kJ/M [19]) and ^{3}AC ($\approx$226 kJ/M [1, 17, 18]) nearly match.

Regarding the observed emissive CIDEP of the cumyl radical ensemble, three sources are conceivable. First, ^{3}(1-NN) might be spin polarized by the p-type TM and transfer this polarization via ^{3}AC to the radicals. However, this source can be excluded, as the radical polarization turns out to be independent of the AC concentration, i.e. the rate of quenching. Moreover, previous quenching experiments of ^{3}(1-NN) with TEMPO radicals have given no indication of any p-type TM polarization of ^{3}(1-NN) [20]. Second, the CIDEP might be due to the radical–triplet pair mechanism (RTPM) [21, 22], i.e. it might be generated in diffusional collisions of the cumyl radicals with ^{3}(1-NN) or ^{3}AC. This is also very unlikely, because the lifetimes of both triplets are rather short in comparison with the time needed for diffusional radical–triplet collisions at the low concentrations of both species. Thus, all experimental features point to the third possibility, namely the existence of a d-type TM in ^{3}AC, i.e. a cleavage into radicals competing with a fast state selective ISC $^3\mathrm{AC} \rightleftharpoons \mathrm{AC}$ to the ground state, as has been observed previously also for the triplet state of AIBN [3, 4]. If this interpretation is correct, then the cumyl radical yield must depend on the magnetic field strength, what is investigated below using LFP with optical absorption spectroscopy.

3.2. *Optical spectra of triplet 1-nitronaphthalene and cumyl radicals*

In order to determine quantitatively the fraction of ^{3}AC which, after formation via quenching of ^{3}(1-NN), cleaves into cumyl radicals, one has to measure the concentration of initially formed ^{3}AC molecules and the concentration of cumyl radicals, which are generated from them. Doing that with optical absorption spectroscopy requires knowledge of the absorption coefficients $\varepsilon(\lambda)$ of the cumyl radicals as well as the ^{3}(1-NN) species (^{3}AC escapes direct optical observation because of its very short lifetime). Therefore, the optical absorption spectra of ^{3}(1-NN) and the cumyl radical have been taken after laser irradiation of heptane solutions containing 1-NN (0.4 mM) and AC (100 mM), respectively. The results are given in figure 2. Primarily, the experiments yielded only the optical densities OD(λ) of the transient species. For the cumyl radicals (figure 2 (*b*)) OD(λ) was scaled to $\varepsilon(\lambda)$ by adopting the literature value $\varepsilon \approx 4500$ $M^{-1}\,cm^{-1}$ for the absorption maximum [23, 24], which we found at $\lambda = 329$ nm, slightly higher than the literature information ($\lambda \approx 320$–322 nm). For ^{3}(1-NN) (figure 2 (*a*)) the optical density immediately after laser pulse excitation, $\mathrm{OD^T}(0)$, was converted to ε via

$$\varepsilon = \frac{\mathrm{OD^T}(0) \times h\nu \times N_A \times V}{E_L \times \Phi \times \left(1 - 10^{-\mathrm{OD}}\right)}.$$

The optical density OD of ground state 1-NN was known and the quantum yield $\Phi = 0.63$ could be taken from literature [25]. OD(0) was extracted by fitting the experimentally measured time profiles $\mathrm{OD^T}(t)$ with a single exponential decay (the triplet concentrations in these experiments, 10^{-5}–10^{-6} M, were low enough to neglect triplet–triplet annihilation, and at $\lambda > 450$ nm there is no overlapping absorption of ground state 1-

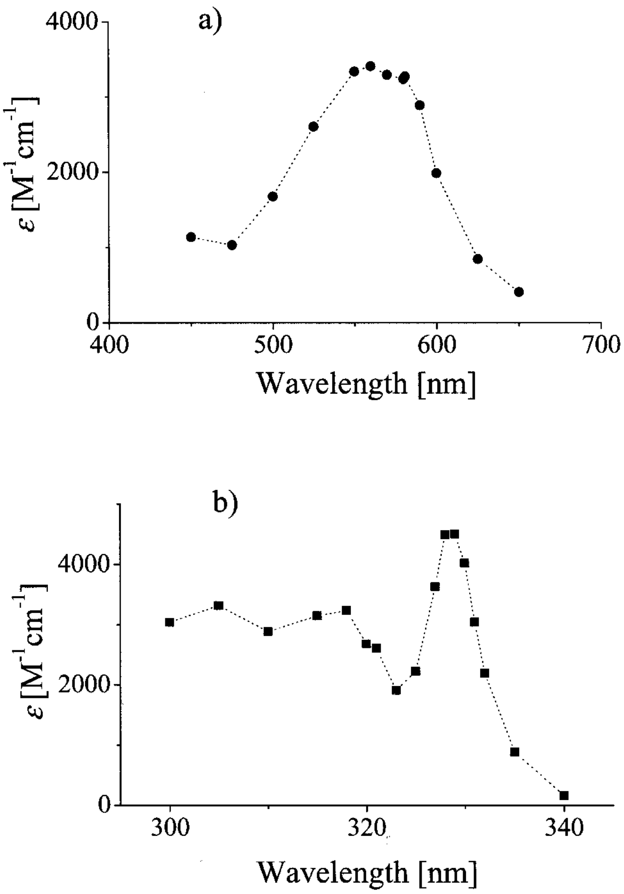


Figure 2. Optical spectra of (*a*) the triplet–triplet absorption of 1-NN and (*b*) the absorption of cumyl radicals averaged over the time interval 100–600 ns after the laser flash.

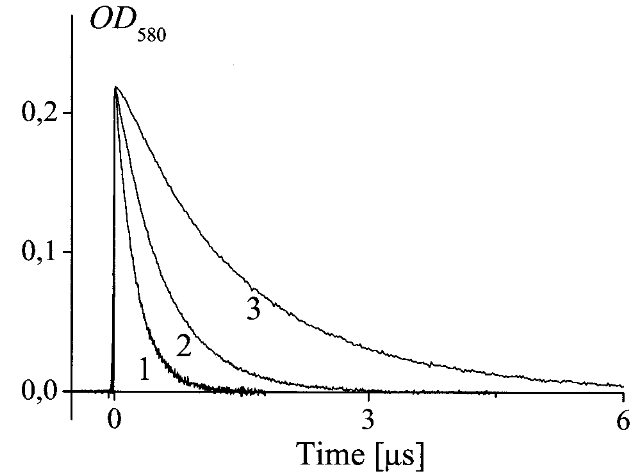


Figure 3. Dependence on time of the optical density at 580 nm after the LFP of paraffin oil solutions containing 1.2 mM 1-NN (1) and, in addition, 4.5 mM (2) and 16.5 mM (3) azocumene.

NN). The ratio of irradiated volume V to average laser pulse energy E_L was determined by actinometry using as an actinometer the photolysis of di-*t*-butyl ketone in heptane [26] (the rate constant for *t*-butyl radical self-termination in heptane was taken as $7.9 \times 10^9\ M^{-1}\,s^{-1}$ [27]).

3.3. *Quenching of triplet 1-nitronaphthalene by azocumene*

For studying the kinetics of the ^{3}(1-NN) decay, $\lambda = 580$ nm was chosen as the wavelength of detection. It is reasonably close to the absorption maximum of ^{3}(1-NN), and neither the cumyl radical nor AC nor ground state 1-NN absorbs at this wavelength. Thus the time profiles of the OD at 580 nm (OD_{580}) must reflect the kinetics of ^{3}(1-NN).

Figure 3 shows as an example the time dependence of OD_{580} obtained for solutions of 1-NN (1.2 mM) in paraffin oil containing three different AC concentrations. The decay kinetics are determined by three factors: the rate of triplet quenching by azocumene, the rate of triplet–triplet annihilation, and the residual lifetime of ^{3}(1-NN). Thus, the rate equation for the triplet concentration is

$$\frac{d}{dt}[T] = -k_{TT}[T]^2 - \left(\frac{1}{\tau_0} + k_Q[AC]\right)[T],$$

with τ_0 the residual triplet lifetime and k_Q and k_{TT} the rate constants of quenching and triplet–triplet annihilation, respectively. Integration and multiplication with the absorption coefficient at 580 nm yields

$$OD_{580}(t) = \frac{\varepsilon_{580}[T]_0\, e^{-t/\tau}}{\tau k_{TT}[T]_0\left(1 - e^{-t/\tau}\right) + 1}, \qquad (1)$$

where $[T]_0$ is the initial triplet concentration and $1/\tau = k_Q[AC] + 1/\tau_0$ represents the rate of the first-order decay. To avoid many parameter fittings in the analysis of the triplet kinetics, each time profile was divided into a short and a long term part. Triplet–triplet annihilation, being a second-order reaction, does not contribute noticeably in the long term part of the time profiles, where the triplet concentration is 5–10 times smaller than at the beginning. Thus, this part can be described by a single exponential decay with lifetime τ, i.e.

$$OD_{580}(t) \approx \frac{\varepsilon_{580}[T]_0\, e^{-t/\tau}}{1 + \tau k_{TT}[T]_0}. \qquad (2)$$

Fitting the long term part of the time profile by equation (2) yielded the parameter τ, which was then kept fixed in a subsequent fit of equation (1) to the whole curve, with $\varepsilon_{580} = 3240\ M^{-1}\,cm^{-1}$ and k_{TT} and $[T]_0$ being two variable parameters. For all the time profiles excellent agreement of fitted and experimental curves could be reached. Finally, the quenching rate k_Q was extracted as the slope of linear plots of $1/\tau = 1/\tau_0 + k_Q[AC]$ versus the quencher concentration [AC].

The results obtained for the rate constants of the triplet–triplet annihilation and the quenching process are depicted in figure 4 (a, b). As expected, the rate constant of triplet–triplet annihilation is of the order of 10^9 M^{-1} s^{-1} and varies proportionally to η^{-1}, indicating this reaction to be a diffusion controlled process. Clearly the dependence of the quenching rate k_Q on $1/\eta$ is nonlinear, approaching diffusion controlled values at high viscosities but staying below that limit at low viscosities. This observation is in full accord with the results of previous work, which also found the rate of quenching by azoalkanes with bulky substituents to be considerably diminished, probably because of steric hindrance [18].

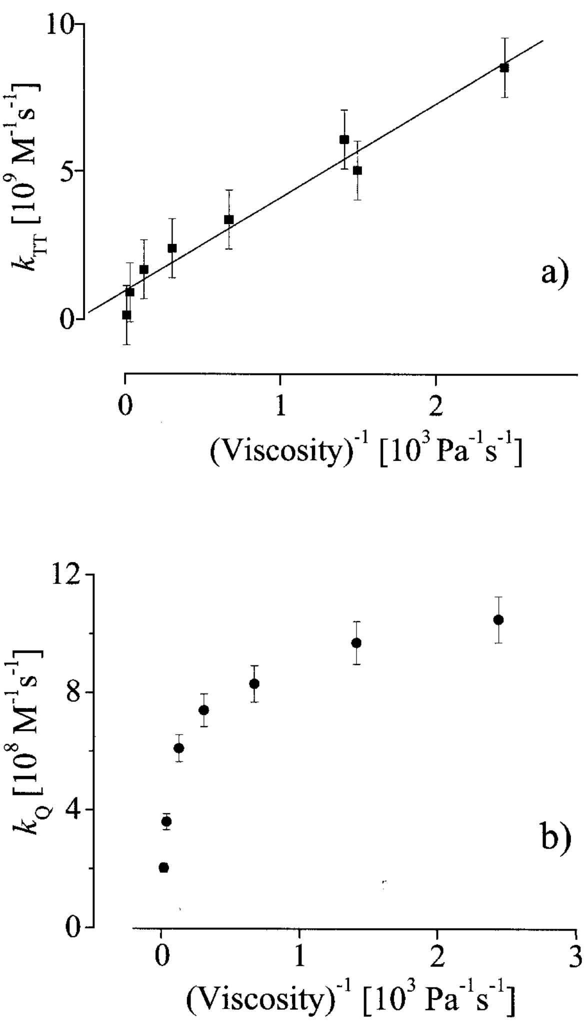


Figure 4. Dependence on viscosity of the calculated rate constants of (a) the triplet–triplet annihilation of ^{3}(1-NN) and (b) the quenching of ^{3}(1-NN) by azocumene.

Finally, it is pointed out that all the measurements of rate constants of quenching and triplet–triplet annihilation were performed in a magnetic field of 0.02 T, caused by the residual magnetization of the magnet poles in the experimental set-up. In order to test for any possible influence of magnetic fields on the decay kinetics of ^{3}(1-NN), several control experiments were carried out under a high magnetic field strength (2.94 T). No visible changes in the time profiles were observed, indicating that eventual effects of a magnetic field on the kinetics of ^{3}(1-NN) were small enough to be neglected.

3.4. *Quantum yield of cumyl radicals and magnetic field effect*

In order to obtain quantitative information about the quantum yield of cumyl radicals and its dependence on an external magnetic field, the dependence on time of the optical density at 329 nm was measured for magnetic fields between 0.02 T and 2.94 T, using solutions of 1.2 mM 1-NN and 4.5 mM AC in various alkanes and benzene. The time profiles obtained in paraffin oil at minimum (0.02 T) and maximum (2.94 T) magnetic field are given, as an example, in figure 5. $\lambda = 329$ nm corresponds to the absorption maximum of the cumyl radicals, but both ground state 1-NN and its excited triplet also have strong absorption bands at this wavelength. At sufficiently high AC concentrations the quenching of 1-NN proceeds much faster than the self-termination of the cumyl radicals. Thus, already during the laser flash the total optical density of the solution is

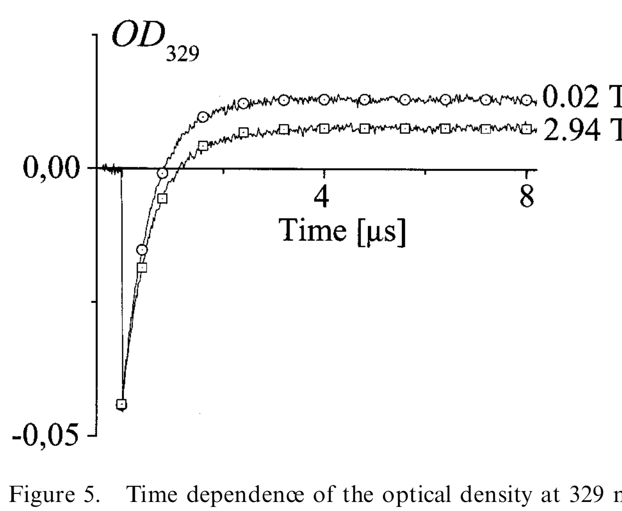


Figure 5. Time dependence of the optical density at 329 nm recorded at low and high magnetic field. Points represent their simulations by equation (3) with parameters $[R]_\infty = 1.4 \times 10^{-5}$ M, $\tau = 570$ ns for $B = 0.02$ T, and $[R]_\infty = 8.02 \times 10^{-6}$ M, $\tau = 590$ ns for $B = 2.94$ T, respectively.

lowered because of depletion of 1-NN and formation of some ^{3}(1-NN).

Afterwards, the change in optical density over a short timescale is strongly influenced by the ^{3}(1-NN) decay kinetics, and only finally over a long timescale, where the triplet concentration vanishes, is the transient absorption determined almost exclusively by the absorption of the radicals. However, there the optical density measures the amount of cumyl radicals that were generated, but part of them turned out to have been initiated via direct photolysis of AC. Despite the fact that the optical density of AC at the excitation wavelength ($OD_{355}^{AC} \approx 0.035$) was much lower than that of 1-NN ($OD_{355}^{1-NN} \approx 0.75$), the contribution of direct photolysis of AC to the total quantity of radicals amounted to about 10–15% in low viscous solvents. This noticeable contribution is explainable by the lower quantum yield of radical production from ^{3}(1-NN) compared with the direct photolysis. For quantitative estimations of the contribution of direct photolysis, time profiles obtained for solutions containing the same AC concentration, but no 1-NN, were measured and analysed. The profiles were fitted by a simple constant function and the values extracted were then corrected by multiplying with

$$\frac{OD_{355}^{AC}\left(1-e^{-OD_{355}^{AC}-OD_{355}^{1-NN}}\right)}{\left(OD_{355}^{AC}+OD_{355}^{1-NN}\right)\left(1-e^{-OD_{355}^{AC}}\right)},$$

taking into account the difference of light absorption by AC in the presence and absence of 1-NN in the solution. The estimated contributions of the direct photolysis OD_{DrPh} are collected in table 2. With increasing viscosity the influence of the direct photolysis decreased by a factor of about 3–5 because of the decrease in the radical quantum yield via direct photolysis in more viscous solvents, due to the so called 'cage effect'. This decrease is in agreement with literature data concerning the 'cage effect' for AC [28].

Taking into account these corrections regarding the direct photolysis, the curves depicted in figure 5 were fitted using the equation

$$OD_{329}(t) = OD_R(t) + \Delta OD_{1-NN}(t) + OD_{DrPh}, \qquad (3)$$

where OD_{DrPh} is the constant contribution of the direct photolysis (see table 2), $OD_R(t) = (1-e^{-t/\tau})[R]_\infty \varepsilon_{329}^R$ the optical density of the radicals formed by triplet sensitization, and $\Delta OD_{1-NN}(t) = \Delta OD_{1-NN}(t=0)\,e^{-t/\tau}$ the total change of the optical density due to excitation of ground state 1-NN to its triplet state ^{3}(1-NN). Variable parameters of the fits were $[R]_\infty$, $\Delta OD_{1-NN}(t=0)$ and τ . The parameter $[R]_\infty$ is determined mainly by the level of the plateau, which the experimental curves reach after longer times. It depends only weakly on the values of the two other parameters. For this reason it was possible to extract $[R]_\infty$ by using an approximate simple exponential decay for ^{3}(1-NN). This simplification did not affect the accuracy of the $[R]_\infty$ analysis. First, $[R]_\infty$ is very insensitive to changes in the short term part of the curve, and second, even in low viscosity solvents the contribution of triplet–triplet annihilation to the decay of ^{3}(1-NN) is only marginal.

Table 2. Corrections of OD_{329} due to the direct photolysis of azocumene.

	$OD_{DrPh} \times 10^3$
Heptane	1.8
Benzene	1.45
Nonane	1.55
Dodecane	1.6
Hexadecane	1.3
Squalane : heptane (4 : 1 vol.)	1.3
Squalane	0.6
Paraffin oil	0.4

From $[R]_\infty$ the magnetic field effect $MFE(B)$ on radical production was calculated according to $MFE(B) = \{[R]_\infty(B) - [R]_\infty(0.02\,T)\}/[R]_\infty(0.02\,T)$. In addition, the radical 'quantum yield' Φ_R was determined, i.e. the average number of cumyl radicals generated per one ^{3}AC molecule or per one ^{3}(1-NN) molecule quenched by AC. Taking into account all channels of the ^{3}(1-NN) decay (triplet–triplet annihilation, quenching by AC, and residual decay rate) the fraction ξ of triplets quenched by AC is

$$\xi = \frac{k_Q[AC]}{k_{TT}[T]_0}\ln\left\{1+\frac{\tau_0 k_{TT}[T]_0}{1+\tau_0 k_Q[AC]}\right\},$$

and therefore the yield of radical production per ^{3}AC molecule reads

$$\Phi_R = \frac{[R]_\infty}{[T]_0\xi} = \frac{[R]_\infty k_{TT}}{k_Q[AC]\ln\left\{1+\dfrac{\tau_0 k_{TT}[T]_0}{1+\tau_0 k_Q[AC]}\right\}}. \qquad (5)$$

The magnetic field effect on radical formation in various solvents is plotted in figure 6 versus the external field B. Characteristic feature of the negative $MFE(B)$ is a pronounced change in the low field region only, approaching a plateau with a maximum absolute MFE at magnetic fields $B > 1$ T. The value of the strongest reachable field effect, MFE_{max}, obviously depends on the viscosity of the solution. This dependence is given in figure 7 (a) (for MFE_{max} we have taken the average of the high field values at 1.82 T and 2.94 T). MFE_{max} sharply decreases with viscosity until $\eta \approx 30$ mPa s and then levels off at a value $MFE_{max} = -43\%$ in squalane

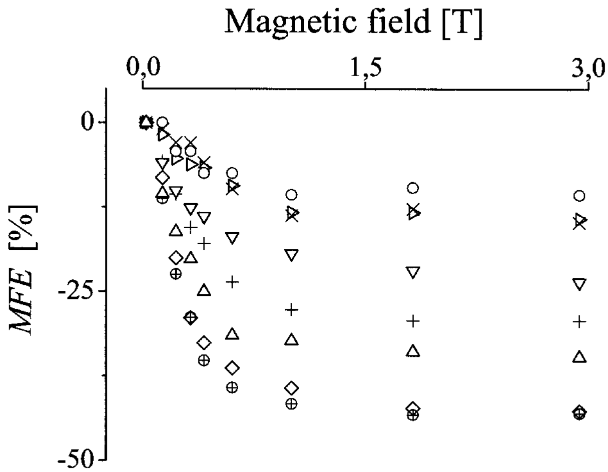


Figure 6. Magnetic field dependence of the magnetic field effect measured in heptane (○), nonane (▷), benzene (×), dodecane (▽), hexadecane (+), squalane: heptane (4:1 vol.) mixture (△), squalane (◇) and paraffin oil (⊕).

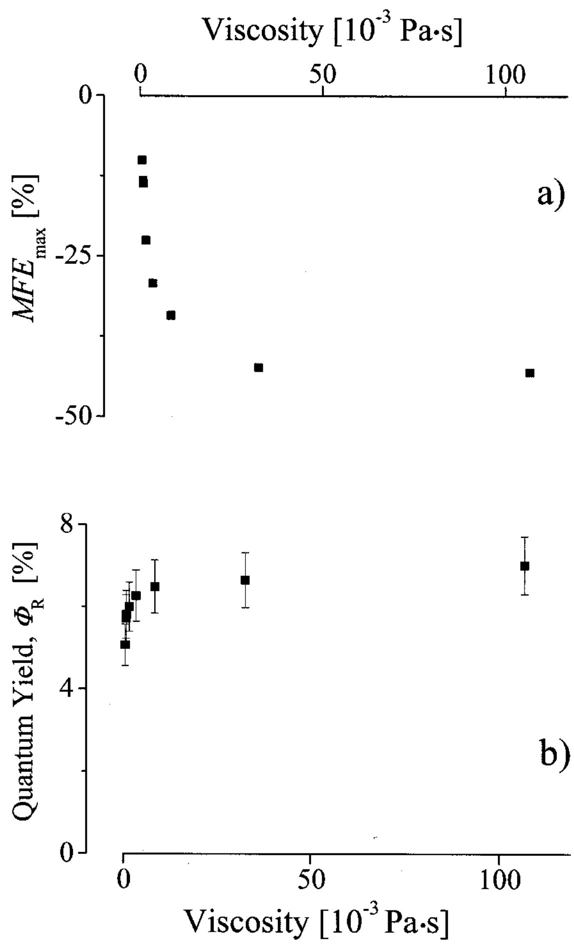
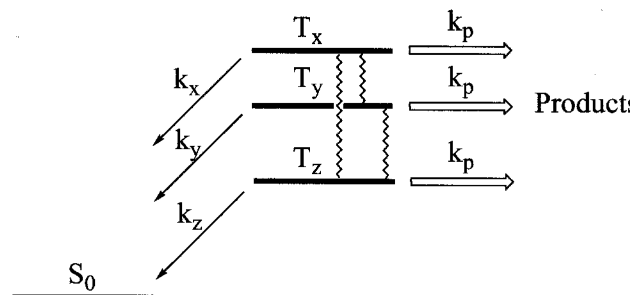


Figure 7. Dependence on viscosity of (*a*) the maximum magnetic field effect and (*b*) the cumyl radical yield per quenched triplet 1-NN.

and paraffin oil. Figure 7 (*b*) shows the dependence on viscosity of the radical quantum yield Φ_R, calculated according to equation (5) for the minimum magnetic field 0.02 T. Φ_R also levels off at high viscosities and shows a sharp decrease at low ones.

4. Discussion

The observation of a magnetic field effect in the formation of cumyl radicals from triplet azocumene plus a net spin polarization of the radicals indicates the occurrence of a d-type triplet mechanism in ^{3}AC. For a quantitative analysis of our experimental data we follow the model used by Steiner to explain the MFE on the decay of certain exciplexes [29]. We assume that ^{3}AC undergoes simultaneously spin state selective ISC to the ground state and spin state independent decay into radicals, according to scheme 2. The



Scheme 2.

spin selective ISC causes non-thermal populations of T_x, T_y, and T_z, which are partially transferred to the radical products. The quantum yield of cleavage is determined by the ratio of the decay rate k_p to the rates k_x, k_y, k_z of the ISC. An external magnetic field, combined with the rotational Brownian tumbling of the molecule, induces transitions between different spin states. That affects the total depopulation rate via the ISC and, hence, influences the quantum yield of radicals and their polarization.

For simplicity we assume for ^{3}AC axial symmetry of the zero field tensor and the ISC rate constants ($k_x = k_y = k_\perp$). This should be a good approximation, as the triplet electrons are probably localized on the two nitrogens. The interactions and processes determining the triplet spin dynamics are: Zeeman and dipole–dipole interaction, rotational diffusion, and depopulation via ISC and decay into radicals. The magnitudes of the Zeeman and dipole–dipole interaction are determined by the field B and the ZFS parameter D_{ZFS}, respectively, and the rates of the depopulation processes are described by the rate constants $k_\perp$, k_z and k_p. The diffusional tumbling is measured by the correlation time

τ_c for reorientational motion. The influence of any of these processes on the spin dynamics is determined by the ratio of the parameter measuring the process to the rate of triplet state depopulation. The value of τ_c increases with increasing viscosity. If the condition $1/\tau_c \ll \max\{k_p, \min\{k_\perp, k_z\}\}$ is met, the influence of the diffusional motion becomes negligibly small, because the molecule has simply no time to change noticeably its orientation during the lifetime of the triplet state. Then the polarization and quantum yield of the radicals become independent of the viscosity of the solution. We believe that this situation is met for ^{3}AC in the two most viscous solvents, squalane and paraffin oil, as Φ_R and MFE_{max} are nearly the same, although the viscosity differs by more than a factor of three. Thus, for these two solvents the experimental data can be analysed with neglect of rotational diffusion and assumption of a static triplet molecule, as is done in the following.

For analysis we choose a molecular frame $\{x, y, z\}$ as depicted in figure 8. Let the z axis be along the axis of symmetry of the ZFS tensor and the ISC rate constants (probably along the NN double bond), and the x axis in the plane formed by the z axis and the magnetic field vector $\vec{B}$. θ is the angle between the z axis and the field direction. In the general case, the statistical description of the quantum system requires solution of the appropriate Liouville equation. However, if the influence of diffusion is negligible, the processes can be described in terms of the Schrödinger equation. For our case it reads

$$\frac{d}{dt}\Psi = -i\hat{H}_{EFF}\Psi = -i(\hat{H}_Z + \hat{H}_{ZFS})\Psi - \frac{1}{2}\hat{k}\Psi, \quad (6)$$

In the basis $\{T_+\} = \{-(T_x + iT_y)/\sqrt{2}\}$, $\{T_0\} = \{T_z\}$, and $\{T_-\} = \{(T_x - iT_y)/\sqrt{2}\}$, quantized along the z direction, the Hamiltonian of the Zeeman interaction, $\hat{H}_Z = \omega_0(\hat{S}_z\cos(\theta) + \hat{S}_x\sin(\theta))$, can be expressed in terms of the magnetic field ω_0 and the spin operators

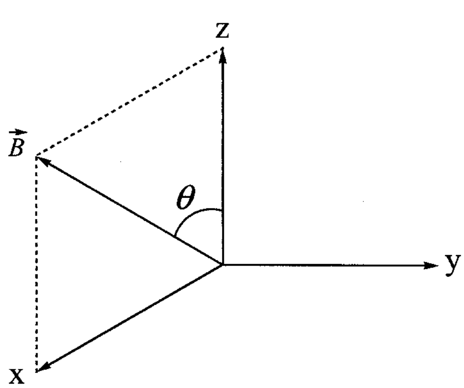


Figure 8.

$$\hat{S}_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{and} \quad \hat{S}_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

The zero field interaction and the operator describing the decay via ISC and cleavage are given by the matrices

$$\hat{H}_{ZFS} = \frac{1}{3}\begin{pmatrix} D_{ZFS} & 0 & 0 \\ 0 & -2D_{ZFS} & 0 \\ 0 & 0 & D_{ZFS} \end{pmatrix}$$

and

$$\hat{k} = \begin{pmatrix} k_\perp + k_p & 0 & 0 \\ 0 & k_z + k_p & 0 \\ 0 & 0 & k_\perp + k_p \end{pmatrix}.$$

H_{EFF} denotes the effective Hamiltonian including all interactions and processes.

The solution of the first-order linear differential equation (6) has the general form

$$\Psi(\theta, t) = C_1\vec{l}_1 e^{\lambda_1 t} + C_2\vec{l}_2 e^{\lambda_2 t} + C_3\vec{l}_3 e^{\lambda_3 t},$$

with $\vec{l}_{1,2,3}$ and $\lambda_{1,2,3}$ being the eigenvectors and corresponding eigenvalues of the matrix $-i\hat{H}_{EFF}$ and $C_{1,2,3}$ the set of arbitrary constants, which are determined by the initial conditions. For comparison with the experimental data for the quantum yield, the integration

$$\Phi_C = \frac{1}{3}\sum_{+,0,-} k_p \frac{1}{2}\int_0^\pi \sin(\theta)\, d\theta \int_0^\infty |\Psi(\theta, t)|^2\, dt \quad (7)$$

is required, because the measured quantum yield is a statistical average over all initial polarizations and orientation angles of the triplet molecule (note that Φ_C in equation (7) now is the quantum yield for cleavage, i.e. $\Phi_C = \Phi_R/2$). Unfortunately, for the general case the dependence of Ψ on θ is too complicated to permit an analytical expressions for Φ_C. Therefore, we shall consider separately two limiting cases, in which the calculations can be much simplified.

4.1. *Zero magnetic field case*

In the absence of a magnetic field, the matrix $\hat{H}_{EFF}$ is diagonal and $\{T_+\}$, $\{T_0\}$, $\{T_-\}$ are the quasi-stationary eigenstates of the triplet. The population density of the states $\{T_+\}$ and $\{T_-\}$ decays exponentially with a time constant $\tau_\perp = (k_\perp + k_p)^{-1}$, while that of state $\{T_0\}$ vanishes with $\tau_z = (k_z + k_p)^{-1}$. In the absence of any noticeable polarization transfer from triplet 1-NN the initial population of all three states is the same (1/3), so that an easy calculation delivers Φ_C, i.e. the product yield per ^{3}AC,

$$\Phi_C = k_p \frac{1}{3} \int_0^\infty \left(2e^{-t/\tau_\perp} + e^{-t/\tau_Z} \right) dt$$
$$= \frac{k_p}{3} \left(\frac{2}{k_\perp + k_p} + \frac{1}{k_z + k_p} \right). \quad (8)$$

Putting $k_\perp + k_p = \alpha k_p$ and $k_z + k_p = \beta k_p$, equation (8) can be rewritten in a form which contains only two unknown parameters α and β,

$$\Phi_C = \frac{1}{3} \left(\frac{2}{\alpha} + \frac{1}{\beta} \right).$$

According to figure 7 (*b*) the radical yield amounts essentially to about 7%, i.e. $\Phi_R \approx 0.07$. Therefore $\Phi_C = \Phi_R/2 \approx 0.035$. It is worth mentioning that, strictly speaking, the equality $\Phi_C = \Phi_R/2$ is only an approximation, because Φ_C is calculated for zero magnetic field, while Φ_R was measured at 0.02 T. However, a careful examination of the data given in figure 6 shows that the MFE at 0.02 T cannot exceed 2%. Therefore,

$$\Phi_C = \frac{1}{3} \left(\frac{2}{\alpha} + \frac{1}{\beta} \right) \approx 0.035 \quad (9)$$

is a very good approximation. In order to get a second equation for the two unknown parameters α and β, the high field case is now considered.

4.2. *High magnetic field case*

If the magnetic field is large, the effective Hamiltonian becomes dominated by the Zeeman interaction. ZFS tensor and reaction operator can then be treated as weak perturbations. Without perturbation the eigenvectors $l_{1,2,3}$ of the Zeeman Hamiltonian are the triplet states $\{T'_+\}$, $\{T'_0\}$, $\{T'_-\}$, quantized in field direction, and the corresponding eigenvalues of $-i\hat{H}_{EFF}$ become $\lambda_{1,2,3} = -i\omega_0$, 0, and $+i\omega_0$, respectively. In order to account for the ZFS and reaction operator as a weak perturbation, $\lambda_{1,2,3}$ may be written as power series

$$\lambda_{1,2,3} = \sum_{j=0}^{\infty} \lambda_{1,2,3}^{(j)} \omega_0^{1-j} \quad \text{with} \quad \lambda_{1,2,3}^{(0)} = -i, 0, +i,$$

respectively. The first correction terms then become

$$\lambda_{1,3}^{(1)} = \frac{iD_{ZFS}}{6} \left(1 - 3\cos(\theta)^2 \right) - \frac{1}{4} \left[\left(k_\perp + k_p \right) \left(1 + \cos(\theta)^2 \right) + \left(k_z + k_p \right) \sin(\theta)^2 \right],$$

$$\lambda_2^{(1)} = -\frac{iD_{ZFS}}{3} \left(1 - 3\cos(\theta)^2 \right) - \frac{1}{2} \left[\left(k_\perp + k_p \right) \sin(\theta)^2 + \left(k_z + k_p \right) \cos(\theta)^2 \right].$$

The imaginary parts of $\lambda_{1,2,3}^{(1)}$ correct the energy levels of the quasi-stationary eigenstates $\{T'_+\}$, $\{T'_0\}$, $\{T'_-\}$, and the real parts determine their lifetime. Averaging over all initial polarizations gives for the cleavage yield

$$\Phi_{C,\infty}(\theta) = \frac{k_p}{3} \left\{ \frac{1}{\left(k_\perp + k_p \right) \sin(\theta)^2 + \left(k_z + k_p \right) \cos(\theta)^2} + \frac{4}{(k_\perp + k_p)(1 + \cos(\theta)^2) + (k_z + k_p) \sin(\theta)^2} \right\}.$$

Integrating over the orientations according to equation (7) and rewriting in terms of the parameters α and β finally yields

$$\Phi_{C,\infty} = \frac{1}{3} \left\{ \frac{1}{2\sqrt{\alpha(\alpha - \beta)}} \ln \frac{\alpha + \sqrt{\alpha(\alpha - \beta)}}{\alpha - \sqrt{\alpha(\alpha - \beta)}} + \frac{4}{\sqrt{\alpha^2 - \beta^2}} \operatorname{arctg} \sqrt{\frac{\alpha - \beta}{\alpha + \beta}} \right\} \quad \text{if } \alpha > \beta, \quad (10a)$$

$$\frac{1}{3} \left\{ \frac{1}{\sqrt{\alpha(\beta - \alpha)}} \operatorname{arctg} \sqrt{\frac{\beta - \alpha}{\alpha}} + \frac{2}{\sqrt{\beta^2 - \alpha^2}} \times \ln \frac{\beta + \alpha + \sqrt{\beta^2 - \alpha^2}}{\beta + \alpha - \sqrt{\beta^2 - \alpha^2}} \right\} \quad \text{if } \alpha < \beta. \quad (10b)$$

At high magnetic fields the MFE measured in squalane and paraffin oil (see figure 7 (*a*)) levels off at about -43%. Therefore,

$$\text{MFE}_{\max} = \frac{\Phi_{C,\infty} - \Phi_{C,0}}{\Phi_{C,0}} \approx -0.43. \quad (11)$$

Expressing in equation (10) β in terms of α via equation (9), the numerical calculation of $\text{MFE}_{\max}$ as a function of α (see figure 9) gives two possible solutions for α. Equation (9) and the definition of α and β, then finally yield the following two possible parameter sets, which satisfy all the conditions pointed out above:

$$(1) \begin{cases} \alpha = 20.36 \\ \beta = 147.75 \\ k_\perp = 19.36 k_p \\ k_z = 146.75 k_p \end{cases} \quad \text{and} \quad (2) \begin{cases} \alpha = 75.5 \\ \beta = 12.72 \\ k_\perp = 74.5 k_p \\ k_z = 11.72 k_p \end{cases}.$$

As the observed spin polarization is emissive, set (1) holds if $D_{ZFS} > 0$ for ^{3}AC, i.e. if the T_z state lies energetically below the $T_{x,y}$ states. In the opposite case ($D_{ZFS} < 0$), parameter set (2) would be the correct one. For both cases our data say that the lower zero field triplet state of ^{3}AC is depopulated by the ISC about seven times faster than the upper one, and about two orders of magnitude faster than its depopulation occurs by the cleavage reaction. Absolute values for the depopulation rates might be obtainable by analysing additional information contained in the size of the spin

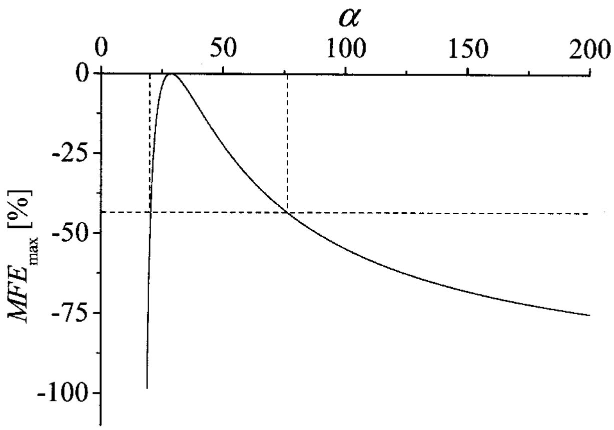


Figure 9. Dependence of MFE_{max} on the parameter α as calculated numerically from equations (9) and (10) and the definition of MFE_{max}. The dashed lines represent the two solutions resulting from the experimental value $MFE_{max} = -43\%$.

polarization. An investigation concerning this is in progress.

5. Conclusion

From the observation of both a magnetic field effect on the cleavage of triplet azocumene and a net spin polarization of the generated cumyl radicals we conclude that a d-type triplet mechanism is occurring in this excited molecule, i.e. the cleavage reaction competes with a fast, state-selective intersystem crossing to the ground state. The energetically lower zero field triplet substate is depopulated by ISC about seven times faster than the upper one, and about two orders of magnitude faster than depopulation by cleavage occurs. Cleavage probably takes place on the nanosecond timescale, while the ISC must proceed on the picosecond scale, because at higher elevated viscosities it becomes faster than the rotational Brownian motion of the molecule.

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