TABLE XI: Kinetic Parameters of RCHBrCH₃ at 340.0 °C (613.15 K)

R	$10^4 k_1$, s ⁻¹	$E_{\rm a}$, kJ/mol	$\log A$, s ⁻¹	ref
CH ₃	3.86	199.9	13.62	3
CH ₃ CH ₂	10.46ª	183.2	12.63	6
		195.8 ^b		6
	6.09ª	190.3	13.00	7
		198.6 ^b		7
	9.23ª	194.4	13.53	8
		196.3 ^b		8
	8.87ª	196.6	13.70	9
	9.88	188.3 ± 0.6	13.04 ± 0.05	с
		196.1 ^b		с
CH ₃ CH ₂ CH ₂	13.99	187.0 ± 2.7	13.08 ± 0.23	С
		194.2 ^b		с

^a Analysis of isomeric butene products was not made. ^b This E_a value results from adjusting the A factor to 13.7. ^c This work.

Arrhenius parameters obtained by using the least-squares procedure. The errors were estimated to 80% confidence limits.

Adjusting the A factor of this work to 13.70^9 as well as those from ref 6-8 (Table XI) would raise the energy of activation E_{a} to about 196 kJ/mol, which is in good agreement with the work reported in ref 9.

The literature cites a work of Maccoll and Ross on the kinetics of the hydrogen bromide catalyzed isomerization of 1-butene to 2-butene in the gas phase.¹² As a difference from that work, the present study aimed to investigate which factor affects the dehydrobromination process during elimination of some secondary alkyl bromides. Since the olefin formation from the pyrolyses of 2-bromobutane and 2-bromopentane does not proceed by kinetic control (Tables III-V), an adequate assessment of the factor by which either the R or CH_3 group in RCHBrCH₃ (Table XI) affects the direction of elimination is not feasible. However, an increase of R from CH₃ to CH₃CH₂CH₂ in RCHBrCH₃ leads to a small augmentation in the overall rate (Table XI). Such a result suggests that the effect of the alkyl groups is polar (+I electron release), thus stabilizing the C-Br bond polarization, in the direction of $C^{\delta+}$...Br^{\delta-}, in the transition state. This argument is associated with the results of the alkyl substituent effect in the pyrolysis of primary alkyl bromides in the gas phase, where a good correlation of log k/k_0 against σ^* values was obtained.¹³

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Registry No. HBr, 10035-10-6; 2-Bromobutane, 78-76-2; 2-bromopentane, 107-81-3; 1-butene, 106-98-9; cis-2-butene, 590-18-1; trans-2butene, 624-64-6; 1-pentene, 109-67-1; cis-2-pentene, 627-20-3; trans-2-pentene, 646-04-8.

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Geminate Recombination Kinetics of Triplet Radical Pairs in Glycerol: Magnetic Field Effect

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Laser flash technique has been used to record the geminate recombination kinetics of triplet radical pairs (RP) generated from benzophenone photoreduced with p-cresol in the viscous glycerol/p-cresol binary solvent. The RP decay kinetics fits fairly into the first-order law. At the same time the kinetics curve features a manifest slow descending "tail" that follows the $\varphi_{\infty} - \varphi(t) \sim t^{-1/2}$ relationship, where φ_{∞} is the (total) cage effect and $\varphi(t)$ is the time-dependent cage effect. The geminate recombination kinetics is closely described in the entire time range ($0 \le t \le 10 \ \mu s$) by the function originating from Noyes' treatment of molecular dynamics, $\varphi(t) = \varphi_{\infty} \operatorname{erfc}(k_{N}t^{-1/2})$, where k_{N} is a constant. An increase of solvent viscosity (decrease of temperature) causes an increase of φ_{∞} and deceleration of RP dissociation. The geminate recombination kinetics is described by mutual diffusion coefficients smaller than the sum of the diffusion coefficients of individual radicals. The probable reason of such behavior is that there is a strong correlation between the molecular motions of radicals positioned within several molecular diameters from each other. Application of an external magnetic field ($H \le 0.34$ T) results in inhibited geminate recombination and decrease in φ_{∞} by 10-50%. The extent of the magnetic effect heavily depends on H when $H \lesssim 0.1$ T and is practically independent of H when $0.1 \leq H \leq 0.34$ T. The mechanisms of the singlet-triplet evolution of the investigated RP and the magnetic effect are discussed. The S-T evolution of RP proceeds via the four mechanisms: in a separated pair the hyperfine coupling (hfc), Δg , and the relaxation mechanisms are active; in contact RP the spin-orbit coupling mechanism dominates. The latter mechanism is more or less effective in the entire range of field strengths. For $H \lesssim 0.1$ T, the magnetic field acts by the hfc mechanism and by slowing the paramagnetic relaxation due to the hfc anisotropy and dipole-dipole coupling between unpaired electrons.

Introduction

The dynamics of the cage effect in liquids has been attracting invariable attention of both theoreticians and experimenters (cf., e.g., ref. 1-6). Quite a few theories have been proposed to account for the cage effect,¹⁻⁵ but the situation is aggravated by scarcity of the relevant data that is also often too inaccurate. The pioneering work⁷ on geminate recombination of iodine atoms invoked considerable interest. Later it was found however that the observed

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Triplet Radical Pairs in Glycerol

spectral effects were due not only to the geminate recombination of iodine atoms but also to the relaxation of the vibrationally excited I2.5 Bagdasaryan et al.8 recorded geminate recombination of the radical ions and Khudyakov et al.9 the geminate recombination of neutral organic radicals.

The investigator of geminate recombination immediately faces the question, what kinetic order does it follow? This question remained open thus far. Theoretical treatments which are based on different assumptions regarding the reactivities of the reagents, the nature of their motion in the cage, initial positions, etc. led to different kinetic laws.^{4,5} A reliable registration of the dynamics of the cage effect, determination of the kinetic order of the process, and experimental verification or disproving of one model or another would have deepened our understanding of the cage effect.

In this work we have opted for the photoreduction of benzophenone with p-cresol in a viscous solvent as a most appropriate model. This reaction which generates triplet radical pairs (RP) had been studied previously in nonviscous solvents and micellar solutions.10,11

Application of a moderate magnetic field affected both the radical geminate recombination kinetics and the cage effect values. The effect of an external magnetic field upon the geminate recombination of triplet RP had mostly been studied in micellar solutions (cf., e.g., ref 11 and 12); the field effect on the geminate recombination rate in a homogeneous medium has not been identified. Obviously, experiments concerning the magnetic field effect should provide further data regarding the laws controlling the geminate recombination. The magnetic field effect should also be studied from the standpoint of magnetochemistry.

The objects pursued in this work were as follows: (1) record the geminate recombination kinetics of RP generated in the triplet state; (2) establish the kinetic laws governing geminate recombination; (3) establish the factors controlling the geminate recombination kinetics; (4) investigate the effect of the external magentic field on the reaction and establish its mechanism.

Experimental Section

A laser flash photolysis apparatus with a kinetic spectrometer (8-ns resolution) has been used. Excitation was effected with an LN 1000 nitrogen laser (337.1 nm, PRA, Canada) operating in the repetitive regime. To reduce error the results are averaged over 128-1024 flashes. The apparatus used for the purpose was BIOMATION 6500 waveform recorder coupled to an Apple IIe computer. The system permitted signals with a repetition rate of 10 Hz to be stored. The kinetics were recorded at 1024 points with a time spacing of 2, 5, or 10 ns. A total of 79 points with a constant time interval of 24, 60, or 120 ns were used for approximation of the experimental kinetic curves. The best parameter fits were obtained by minimization of the sum of the squared differences between the calculated and experimentally observed variables (Q); calculations procedure details have been published elsewhere.13

A 1×1 cm cross section quartz cell was used which in the magnetic field effect experiments was placed in a permanent magnet. The poles of the magnet could be displaced relative to one another; in their closest position (15 mm), H = 0.34 T. All solutions had been deoxygenated by prolonged evacuation on a vacuum pump line. The solutions were thermostated with a temperature error within ± 1 °C. The experiments were conducted in the temperature range of 253–303 K. Solvent viscosities (η) at different temperatures were measured with a Höppler viscometer: at 293 K, $\eta = 10.7 \pm 0.3$ P.



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Figure 1. The absorption spectra of the intermediates formed from benzophenone in glycerol/p-cresol mixtures under laser flash photolysis, recorded immediately after the flash (black circles) and 10 μ s after the flash (empty circles).



Figure 2. Variation of the optical density of the ketyl radical of benzophenone following a laser flash under a magnetic field of 0.34 T (1) and under zero magnetic field (2) at 293 K. Solid lines, approximation by the exponential law (5); the respective parameters are given in Table I.



Figure 3. Variation of the optical density of the ketyl radical of benzophenone following a laser flash under a magnetic field of 0.34 T at 293 K (1) and at 253 K (2). Solid lines, approximation by the Noyes function (7); dashed lines, approximation by the exponential law (5). The respective parameters are given in Table I.

Benzophenone (B) was purified by sublimation in vacuo, pcresol (PhOH) by distillation in vacuo. Soviet commercially available "chemically pure" grade glycerol was used without further purification. The glycerol solutions contained 1×10^{-3} M of B and 1.0 M of PhOH.

Results

Photoexcitation of B in the presence of PhOH initiates the well-known series of processes¹⁰

$$B + h\nu \rightarrow B_{S}^{*} \longrightarrow B_{T}^{*} \xrightarrow{\text{PhOH}} {}^{3}[BH^{\bullet}, PhO^{\bullet}] \qquad (1)$$

where the brackets enclose the radical pair (RP). The laser photolysis of B in pure glycerol or under low concentrations of PhOH (<0.01 M) has led to generation and decay of two intermediates: B_T^* and BH[•]. The radical is formed through reaction of B_T^* with the solvent. At [PhOH] = 1.0 M the lifetime of B_T^* becomes shorter than the laser flash duration, and immediately after the flash the absorptions of BH• and PhO• are registered (Figure 1). The extinction coefficients of BH[•] and PhO[•] are known, cf., e.g., ref 10. It may be safely assumed that, within

TABLE I: Cage Effects, Rate Constants, Diffusion Coefficients, and Sums of Squared Approximation Errors for Geminate Recombination at Different Temperatures with and without Magnetic Field^k

<i>T</i> , K	<i>Н</i> , Т	φ∞ ^{E a}	φ _∞ ^{N b}	$\varphi_{\infty}^{\text{expt} \mid c}$	$k_{\text{obsd}} \times 10^{-6}$, $a \text{ s}^{-1}$	$k_{\rm rec} \times 10^{-6}$, $d {\rm s}^{-1}$	$k_{dis} \times 10^{-6}$, $k_{dis} \times 10^{-6}$	$Q^{\rm E} \times 10^{3 e}$	$Q^{N} \times 10^{3f}$	$\frac{D^{\rm E} \times 10^{9,8}}{\rm cm^2/s}$	$D^{\rm N} \times 10^{9,h}$ cm ² /s	$\frac{D^{\rm SE} \times 10^{\rm 9,i}}{\rm cm^2/s}$	
						Approximat	ion at $t \leq 1$.	75 μs					
293	0	0.47	0.59	0.50	4.9	2.3	2.6	17.3	3.64	3.7	1.4	12	
293	0.34	0.34	0.43	0.36	3.8	1.3	2.5	8.42	2.69	3.5	1.9	12	
						Approxima	ation at $t \leq 1$	5 μs					
293	0.34	0.37	0.45	0.36	2.4	0.9	1.5	21.6	2.49	2.1	1.3	12	
253	0.34	0.87	1.05	0.80	2.1	1.8	0.3	48.6	20.0	0.4	j	0.2	

^a Value obtained as approximation by eq 5. ^b Value obtained by approximation with (7). $c_{\varphi_{\infty}}$ estimated from the experimental relationships $\varphi(t)$ at $t = 1.75 \,\mu s$ (see the text). The rms error of determination of φ_{∞}^{expd} is not beyond 5% of the value. ^d The constant based on the calculated values of φ_{∞}^{E} and k_{obsd} and eq 3 and 4, see text. ^e The sum of squared of differences between the theoretical and experimental optical densities peculiar to approximation by eq 5. ^f The sum of squared differences between the theoretical and experimental optical densities peculiar to approximation by eq 5. ^f The sum of squared differences between the theoretical and experimental optical densities peculiar to approximation by eq 7. ^g Coefficient of mutual diffusion of radicals obtained on the basis of the calculated k_{dis} and eq 12, see text. ^h Coefficient of mutual diffusion of radicals obtained by using the results of approximation by eq 7, see text. ⁱ Sum of coefficients of diffusion of radicals BH^{*} and PhO^{*}, each calculated by formula 13. ^j The value of D^N is indeterminate since $1 - \varphi_{\infty}^{N}$ in eq 10 is close to zero. ^k The rms error in determination of $\varphi_{\infty}^{E}, \varphi_{\infty}^{N}$, and k_{obsd} does not exceed 5% of the quantity and that of the constants k_{rec} and k_{dis} 10%.

experimental accuracy, the initial concentrations of BH[•] and PhO[•] are equal and BH[•] is formed only via reaction 1 with PhOH.¹

Decay Kinetics. Kinetic measurements were carried out at λ 400 nm (the absorption maximum of PhO[•]) and at λ 545 nm (the absorption maximum of BH[•]), cf. Figure 1. The oscilloscopic traces of optical density due to the radical absorption at these two wavelengths coincide to within the ratio of the extinction coefficients of PhO[•] and BH[•] in the time range of 0–10 μ s, considering the experimental error. Most recordings were made at λ 545 nm where only BH[•] absorbs.

The oscilloscopic traces contained the fast component ($t \leq 5 \mu s$, Figures 2 and 3) which corresponded to radical decay through geminate recombination, and the slow component ($t \gg 10 \mu s$) reflecting radical decay in the bulk of solvent. The plateau segment ($5 \leq t \leq 10 \mu s$) represents absorption of BH[•] that have escaped into the bulk of a solvent (Figure 3). Immediately after the flash the absorption spectrum of the radicals is practically identical with that at moment $t = 10 \mu s$ (Figure 1).

At time t = 0 let the radicals be produced in pairs and let their concentration in solution be C_0 . With time the concentration C(t) decreases on account of the geminate recombination. The fraction of radicals decayed in cage at time t is

$$\varphi(t) = (C_0 - C(t))/C_0$$

The magnitude of the cage effect (i.e., the fraction of the radicals decayed in cage during the entire cage recombination period) φ_{∞} is given by $\varphi(t)$ when $t \to \infty$.

The simplest kinetic description of RP behavior is in terms of the exponential model: the RP recombine (disproportionate) at $k_{\rm rec}$ (s⁻¹) and dissociate at $k_{\rm dis}$ (s⁻¹)

$$[BH^{\circ}, PhO^{\circ}] \xrightarrow{K_{obsed}} B + PhOH$$

$$(2)$$

$$(2)$$

$$(2)$$

In this approach

$$k_{\rm obsd} = k_{\rm rec} + k_{\rm dis} \tag{3}$$

$$\varphi_{\infty}^{E} = k_{\rm rec} / k_{\rm obsd} \tag{4}$$

$$\varphi(t) = \varphi_{\infty}^{E} (1 - \exp(-k_{\text{obsd}}t))$$
(5)

The superscript E signifies, here and hereafter, that the value pertains to the exponential model.

The measured geminate recombination rates in the time range of $0 \le t \le 2 \mu s$ (Figure 2) fitted into the law (5) with fair accuracy. The rates in the time interval $0 \le t \le 1.75 \mu s$ approximated by formula 5 (k_{obsd}) are presented in Table I together with φ_{∞}^{E} . The corresponding k_{rec} and k_{dis} have been calculated from these values by using eq 3 and 4 (see Table I). The exponential law (5) does not give as accurate results in the wider time range of $0 \le t \le$ 5 μs (Figure 3); the value of Q increases and the constant k_{obsd} decreases in this cases (Table I). The geminate recombination curve has a manifest slow "tail" portion (Figure 3). Obviously in such a case the kinetics is much better described not by one but by two exponents:

$$\varphi(t) = \varphi_{\infty}^{(1)}(1 - \exp(-k_1 t)) + \varphi_{\infty}^{(2)}(1 - \exp(-k_2 t))$$
(6)

However, rate constants k_1 and k_2 as well as $\varphi_{\infty}^{(1)}$ and $\varphi_{\infty}^{(2)}$ values are heavily dependent upon the time range; see for details ref 13. It seems to be pointless to search for a physical sense in the description by formula 6. This formula may be successfully used for a practical purpose—to describe a kinetic curve with good accuracy by any function.

According to Noyes'^{1,2} treatment of molecular dynamics, for reagent pairs with the sum of the van der Waals radii σ generated at distance L from each other and reacting upon encounter with the probability β' , we have

$$\varphi(t) = \frac{\sigma}{L} \int_0^t h(t') dt' = \varphi_{\infty}^{N} \operatorname{erfc} \left(k_{\mathrm{N}} t^{-1/2} \right)$$
(7)

where h(t) is the nominal probability density of reaction, $\varphi_{\infty}^{N} = (\sigma/L)\beta'$, and k_{N} [s^{1/2}] is a constant. For k_{N} is true

$$k_{\rm N} = (1 - \beta')\sigma/2(\pi D^{\rm N})^{1/2}$$
(8)

where D^{N} is the coefficient of the mutual diffusion of the

$$D^{\mathrm{N}} = D_1 + D_2 \tag{9}$$

reagents. The superscript N signifies, here and hereafter, that the value pertains to the Noyes model (7).

Equation 7 describes the experiment with sufficient accuracy in the time range of both $t \le 1.75 \ \mu s$ and $t \le 5 \ \mu s$ (Figure 3); the parameters φ_{∞}^{N} , Q and k_{N} are practically independent of the time range (cf. Table I).

The table also contains D^N values obtained from eq 8 by using the calculated φ_{∞}^N and k_N :

$$D^{\rm N} = (1 - \varphi_{\rm m}^{\rm N})^2 \sigma^2 / 4\pi k_{\rm N}^2 \tag{10}$$

For the viscous solvent used in the experiments we may assume $\sigma/L \simeq 1.^{2.5}$ The van der Waals radii (ρ) of BH[•] and PhO[•] were taken to be 3.5 and 3.0 Å, respectively, and $\sigma = 6.5$ Å. The ρ values had been estimated by the procedure described in ref 14.

Equation 7 is expected to be valid for freely diffusing reagents. In a more general case reagents may form complexes with each other, i.e., to exist in a potential hole with an arbitrary depth. This case has been considered recently in ref 4. The following equation has been obtained:⁴

$$\varphi(t) = \frac{k_{\text{rec}}}{k_{\text{rec}} + k_{\text{dis}}} \left\{ 1 - e^{-\tau'} + \frac{\delta}{\pi^{1/2}} [\tau'^{1/2} - (1 + 2\tau')F(\tau')^{1/2}] + \frac{\delta\tau'^2}{2} e^{-\tau'} \right\}$$
(11)

⁽¹⁴⁾ Burshtein, A. I.; Khudyakov, I. V.; Yakobson, B. I. Prog. React. Kinet. 1984, 13, 221.



Figure 4. Dependence of the cage effect φ_{∞}^{exptl} and the recombination rate constant k_{rec} on external magnetic field strength at 293 K.



Figure 5. Arrhenius temperature dependence of the recombination and dissociation constants of RP: (1) k_{rec} at H = 0; (2) k_{rec} at H = 0.34 T; (3) $k_{\rm dis}$.

Here k_{rec} and k_{dis} are rate constants of recombination and dissociation of a pair, respectively; $\tau' = (k_{rec} + k_{dis})t$; $F(X) = e^{-x^2} \int_0^x t^{2s} dt$ e^{t^2} dt (Doson integral); δ is a constant, $0 < \delta < 1$. In contrast to the exponential model (cf. eq 5) a part of the reagent pairs equal to δ participates in a random wandering. The anisotropy of reagent reactivity is also taken into account in the model."

The bulky formula (11) which contains three fitting parameters describes the geminate recombination kinetics as well as the rather simple formula (7) that contains two parameters; see ref 13 for details. All this renders the Noyes model^{1,2} (eq 7) more attractive than model in ref 4 (eq 11).

Thus there are possible differing, though closely, estimates of φ_{∞} (see Table I). For φ_{∞} it is convenient to use the value $\varphi_{\infty}^{\text{expti}}$ experimentally measured from the oscilloscopic traces and equal to $\varphi(t)$ at $t = 1.75 \ \mu s$ (Figure 2). It may be measured with a small relative error (cf. Table I and Figure 4). Obviously, $\varphi_{\infty}^{E} \leq \varphi_{\infty}^{exptil}$ $\lesssim \varphi_{\infty}^{N}$ (cf. Table I).

Temperature Effect. Variation of the solution temperature has a strong effect on φ_{∞} . Thus at 303 K, $\varphi_{\infty} \simeq 0.3$, and at 273 K $\varphi_{\infty} \simeq 1$. From the log φ_{∞} versus 1/T relationship we have found the corresponding activation energy 4 ± 1 kcal/mol. Figure 5 shows the Arrhenius plots for k_{rec} at H = 0 and H = 0.34 T, and k_{dis} . The respective activation energies are 1.5 ± 0.5 , 0 ± 0.5 , and 11 ± 1 kcal/mol. The activation energy for the viscous flow of the glycerol/PhOH mixture is $E_{\eta} = 16 \pm 1$ kcal/mol.

In cooler solutions the magnetic effect is abated which is manifested in the smaller difference between the φ_{∞} values measured with and without field and the constants k_{rec} (Figure 5).

Discussion

Geminate Recombination Kinetics. The k_{dis} constant which is used in the exponential model may be evaluated by, e.g., the formula proposed in ref 15

$$k_{\rm dis} = 3D^{\rm E}/\sigma^2 \tag{12}$$

where D^{E} is the coefficient of mutual diffusion; cf. eq 9. Table I gives the $D^{\rm E}$ calculated by formula 12 on the basis of the $k_{\rm dis}$

(15) Eigen, M. Z. Phys. Chim. (Munich) 1954, 1, 176.

values calculated on the assumptions of the exponential model. We will now determine the coefficient of the mutual diffusion of radicals (eq 9) using the diffusion coefficients for each of the radicals calculated by the Stokes-Einstein formula:

$$D_{1(2)} = kT/6\pi\eta\rho \tag{13}$$

This value of the coefficient of mutual diffusion denoted as D^{SE} is given in Table I. As it follows from the table, D^{N} , $D^{E} \leq D^{SE}$.

It is known, moreover, that eq 13 usually underestimates $D_{1(2)}$; the true values are χ times higher than predicted by eq 13.^{14,16} The factor χ is particularly large in viscous media: according to ref 16 it is as high as $\chi \simeq 40$ for molecular-size particles in viscous alcohols. Further, the experimental data on the diffusion coefficients of the stable nitroxyl radical, having a close van der Waals radius $\rho = 3.3$ Å, in glycerol solutions show that the experimental values are 1-2 orders of magnitude greater than the corresponding predictions by eq 13.17

The conclusion therefore must be that the coefficients of the mutual diffusion D^{N} or D^{E} describing the geminate recombination kinetics are each smaller than the sum of the individual diffusion coefficients of the radicals in a given solution. In other words, while the obvious equality 9 is valid for radicals widely parted in space, for radicals in a cage we must assume

$$D^{\mathrm{N}}(D^{\mathrm{E}}) \ll D_1 + D_2 \tag{14}$$

The reason for the inequality apparently consists in the interplay of the molecular motions in cage of radicals being in juxtaposition or separated not more than a few molecular diameters. We believe that inequality 14 is an experimental ground for a statement made by Noyes in 1956:¹ "Although the assumption of completely random diffusive displacements is undoubtedly satisfactory for molecules that are separated by more than a few molecular diameters [cf. eq 9], two molecules that are almost in juxtaposition will certainly exhibit a nonrandom selectivity in the direction of displacements". More recent works on molecular dynamics calculations indicate that there is more or less strong correlation between the molecular motions (see a review in ref 5 and 14). There is no reason to hold this rule as universal but it ought to be implied for the present case.

The slower than expected geminate recombination and exit from the cage may be due to an alternative reason, namely, that the RP is originally formed as a complex bonded by a weak chemical bond which then relatively slowly dissociates and recombines:

$$[BH^{\circ} \cdots PhO^{\circ}] \xrightarrow{K_{obsd}} B + PhOH$$

$$(15)$$

$$(15)$$

$$K_{dis} = BH^{\circ} + PhO^{\circ}$$

As was mentioned above, such a situation is described by eq. 11.⁴ The parameter δ of eq 11 which is under determination depends upon the mutual diffusion coefficient D^{δ} . Thus D^{δ} may be calculated in a similar way as D^{N} (eq 10) or D^{E} (eq 12).¹⁸ After this calculation we have obtained once more that $D^{\delta} \ll D_1$ $+ D_2$ (cf. eq 14).

The existence of substantial magnetic field effects for a given RP (see Figures 2, 4, and 5 and the Table I) means that a significant part of RPs are being generated initially as complexes participate in random wandering.¹⁹ In fact, if the RP may exist as a complex there must be a strong exchange interaction between the radicals in the RP and virtually no magnetic effect.²⁰

Consider the slowly descending portion of the kinetic curve (the "tail"), Figure 3. At $t \rightarrow \infty$ the functions 7 and 11 which give

1983 (in Russian). (18) We have omitted here details of D^{δ} calculation. They may be found in ref. 13.

⁽¹⁶⁾ Schuh, H.-H.; Fischer, H. Helv. Chim. Acta 1980, 61, 2130.

⁽¹⁷⁾ Tarasoff, V. F. Ph.D. Thesis, Institute of Chemical Physics, Moscow,

⁽¹⁹⁾ δ -values equal to 0.2–0.6 have been obtained.¹³

⁽²⁰⁾ Zimmt, M. B.; Doubleday, C.; Turro. N. J. J. Am. Chem. Soc. 1985, 107, 6726.

a good description of the experiment may be approximated with^{1,2,4}

$$\varphi_m - \varphi(t) \sim t^{-1/2} \tag{16}$$

The law (16) is a well-known one: the probability of the contact of particles random-wandering in three-dimensional space, i.e., h(t) (cf. eq 7), is proportional to $t^{-3/2}$, and $\varphi(t)$ obeys (16).^{1,2} An exact analysis of the law controlling the shape of the tail of geminate recombination is difficult for an obvious reason-the experimental error increases nonproportionally. The log $(\varphi_{\infty}{}^{\mathrm{N}}$ – $\varphi(t)$ versus log t relationships are linear at large enough times and have a slope as, considering experimental accuracy, predicted, namely -0.5

To conclude this section of the paper we note that the complex composition of the solution used in the study may also have had a certain effect on the observed geminate recombination kinetics. The glycerol/p-cresol binary mixture contains a variety of molecular associates formed by the agency of hydrogen bonds, including the photogenerated RP. The RP contained in different associates may possess different reactivities and polychromatic kinetics may result.

Elementary Steps of Reactions 1 and 2. The recombination of BH[•] and PhO[•] in the bulk of such a viscous solvent must be limited by molecular mobility.²¹ The geminate recombination of RP involves the singlet-triplet transition because the RP is born in the triplet state and the products are in a singlet state. The spin evolution of the spatially separate RP occurs, in the absence of magnetic field, by the hfc mechanism and for aromatic radicals is characterized by $\tau_{\text{S-T}} \simeq A_{\text{hfc}}^{-1} \simeq 10^{-8} \text{ s}$ (see below), which is much smaller than k_{rec}^{-1} (cf. Table I).

Therefore, when the radicals in a pair find themselves in a favorable orientation, they recombine with a unit probability or its $k_{\rm rec} \gg k_{\rm dis}^{22}$ Yet the experiment shows both $k_{\rm rec}$ and $k_{\rm dis}$ to be of the same order of magnitude (Table I). It remains to assume therefore that the radicals are generated in a mutual orientation that does not favor the reaction.

Some portion of the energy released due to hydrogen abstraction may go to overcome the viscous drag which prevents the radicals from rotating relative one another and/or departing from each other (the increasing of L in the Noyes model (7)). Thanks to molecular motion the radicals in a pair may achieve the orientation required for the reaction of recombination or escape of radicals out of cage (dissociation). As η decreases the radicals rotate (or depart) by an ever larger angle (distance L). At the same time the decreasing η enhances molecular motions. Compensation of the two effects results in a situation where $k_{\rm rec}$ is little dependent upon temperature (Figure 5). Thus the temperature dependence of φ_{∞} is mainly due to the variation of k_{dis} in the exponential model (5) or L in the Noyes model (7).

A contrary extreme opinion holds that it is the intersystem crossing of RP, occurring by one mechanism or another (see below), which controls the RP recombination. Then $k_{\rm rec}$ will be limited by the rate of the intersystem crossing of RP that is weakly dependent on temperature or viscosity (see Figure 5, lines 1 and 2). As expected, k_{dis} decreases with decreasing T (increase of η), and φ_{∞} increases (see Figure 5, line 3).

The truth, as usual, lies in between the two extremes. The RP consist of both separated and contacting pairs. The recombination rate of separated pairs is determined by the molecular dynamics and that of contact pairs by the rates of the intersystem crossing (see the next section).

Magnetic Field Effect. Imposition of magnetic field leads, as expected for triplet RP,^{11,12} to increase of φ_{∞} and inhibition of geminate recombination (Table I; Figures 2 and 4). It means that there are S-T transitions sensitive to magnetic field in the RP.

The effect is particularly tangible for H < 20 mT, typically of the hfc mechanism.^{12,20} (According to hfc mechanism one expects that φ_{∞} at $H \gg A_{\rm hfc}$ will be equal to one-third of the zero-field value). However, the field effect versus H dependences (Figure 4) become flat only at $H \gtrsim 0.1$ T which is much in excess of the effective hfc constant for given RP ($A_{\rm hfc} \simeq 2 \ {\rm mT}^{23,24}$ or $A_{\rm hfc}^{-1}$ $\simeq 2 \times 10^{-8}$ s). Delayed field effect curves had been repeatedly observed for recombination of RP including those containing radicals of related nature in micelles.^{11,12} This is due to the relaxation transitions $T_{\pm}-T_0$,S in RP occurring with the rate of paramagnetic relaxation:^{12,25}

$$1/T_1 = 2\tau_{\rm c} |V|^2 / \hbar^2 (1 + \omega^2 \tau_{\rm c}^2) \tag{17}$$

Here V is the off-diagonal matrix element of transition due to the hfc anisotropy, anisotropy of the g factor, or still the dipole-dipole spin coupling of the radicals; τ_c is the rotational correlation time; the frequency $\omega = g\beta H/\hbar$ (g is the mean value of the isotropic g factors of radicals). As a simple model we may according to ref 12 consider an RP each of the partners of which has a hyperfine splitting with only one nucleus having the spin 1/2. In this model RP the following equation is suggested in ref 12 to describe the relaxation transitions (k_{rel}) from T_{\pm} to T_0 and S states

$$k_{\rm rel} = [\tau_c/\hbar^2 (1 + \omega^2 \tau_c^2)] \times [\Delta A_{\rm hfc}^2 / 18 + (\Delta g \beta H)^2 / 15 + 3g^4 \beta^4 / 10R^6]$$
(18)

where ΔA_{hfc}^2 is the sum for two radicals of the values $(A_{hfc}^{\parallel} A_{\rm hfc}^{\perp})^2$ which characterizes the hfc anisotropy; $(\Delta g)^2$ is the sum for two radicals of the values $(g^{\parallel} - g^{\perp})^2$ which characterizes the anisotropy of the g factor, and the last term in (18) describes the T_{+} -T₀ transitions due to the dipole-dipole interaction between the unpaired electrons. Here the signs || and \perp denote the main tensor component parallel and perpendicular to its axis of symmetry; R is the effective distance between the radicals in RP; β is the Bohr magneton.

It is assumed in this approximate treatment that τ_c is the same for both radicals and for the dipole-dipole interaction. As follows from eq 18 the relaxation transitions due to the hfc anisotropy and the dipole-dipole coupling are retarded as H increases. (The relaxation due to the g anisotropy is much slower and may be ignored.¹²) At the same time the estimates reported in ref 12 show that for the relatively nonviscous micellar solutions the corresponding $k_{\rm rel}$ value under a strong magnetic field ($H \simeq 0.3$ T) is low, $k_{\rm rel} \simeq 10^5 \, {\rm s}^{-1}$. In the viscous glycerol solutions characterized by higher τ_c one may expect an even smaller k_{rel} under a strong field. Thus in a strong magnetic field the relaxation transitions proceed 3 orders of magnitude slower than recombination (cf. Table I and Figure 5, line 2) and can hardly contribute any to the recombination rate. Indeed, the experimental studies of the paramagnetic relaxation of BH* in solvents of different viscosity at H = 0.33 T (the X-range ESR) showed that BH[•] relaxation in viscous media is controlled chiefly by the anisotropy of the g factor and hfc.^{26,27} Then, according to ref 26, $k_{rel} \sim T/\eta$; at η $\simeq 10 \text{ P} k_{\text{rel}} = 1/T_1 \simeq 5 \times 10^3 \text{ s}^{-1}$. Hence, under a strong magnetic field only the T_0 -S transitions due to the isotropic hfc and the difference of the g factors of the radicals (the Δg

⁽²¹⁾ A high rate constant of 1.0×10^8 M⁻¹·s⁻¹ has been obtained for the reaction between BH* and aroxyl radical 2,6-diphenyl-4-methoxyphenoxyl in ethanol at 293 K (Khudyakov, I. V.; Levin, P. P., unpublished results). At $\eta \gtrsim 1$ P the reaction any between BH[•] and any sterically nonhindered aroxyl will no doubt be limited by molecular mobility.

⁽²²⁾ This statement must be valid under proviso that τ_{S-T} is much shorter than the characteristic time in which a pair can acquire an orientation favorable for the reaction.

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1978, 36, 1397. (b) Atkins, P. W.; McLauchian, K. A.; Percival, P. Mol. Phys. 1973, 23, 281.

⁽²⁷⁾ We appeal here to paramagnetic relaxation of BH[•] in view of the existence of pertinent published data. Aroxyl radicals have T₁ values equal to several microseconds in nonviscous solvents [(a) Chen, K. S.; Wan, J. K. S.; Kochi, J. K. J. Phys. Chem. 1981, 85, 1726. (b) Adeleke B. B.; Wan J. K. S. J. Chem. Soc., Faraday Trans. 1 1976, 1799] T_1 values of aroxyls are ca. 5 times less than the corresponding values of BH^{*} in nonviscous solvents. T_1 values of aroxyls increase with the solvent viscosity increase.^{27b} It may be expected that in viscous solvents T1 values of BH* and PhO* are of the same order of magnitude.

mechanism²⁸) are effective in separated RP. The characteristic time of these transitions $\tau_{S-T_0} \simeq \tau_{S-T} \simeq 2 \times 10^{-8}$ s (see above).

Therefore, if there had been no alternative S-T evolution routes in RP only the RP generated in the T_0 state might be expected to recombine under a strong field. Under these circumstances one would observe very high magnetic effects; for example, under H = 0.34 T the φ_{∞} would have been 1/3 of the zero-field value (see above). Yet the real effect of the field is weaker (cf. Table I and Figure 4). Besides, at 253 K nearly all the RP recombine in the magnetic field (Table I, Figure 3) and the latter has practically no effect on the recombination rate (Figure 5, lines 1 and 2). As noted, the field effect curves reach the plateau at $H \gtrsim 0.1$ T (Figure 4). Hence there must be an alternative channel of the S-T evolution for given RP in a viscous solvent and the rate of it must be independent of the field strength.

Examining literature for suggested alternative mechanisms of the S-T crossings and intersublevel transitions we find that the rate of relaxation due to the spin-rotation coupling is independent of field strength.²⁹ However, the spin-rotation relaxation effective in nonviscous solvents²⁹ can hardly have any efect on the decay of the RP in question.

A lower magnetic effect may also be expected if the T_-S transitions (or T₊-S transitions, depending on the exchange integral sign) are due to the exchange repulsion of the terms. CIDEP data provide important evidence in favor of their important role in viscous media.^{30,31} But if this mechanism were accepted we would have to expect the extremum nature of the field effect curves^{20,32} which is not so in fact (Figure 4).

Our opinion is that to explain the observed relationships (Figure 4) we have to take into account the spin-orbit coupling (SOC) in contact RP where the SOC may induce the intersystem crossings leading to recombination. Such transitions are obviously the reason for the smaller than unity yield of radicals in quenching of B_T^* with phenols even in nonviscous solvents.¹⁰ This means that the intersystem crossings have an opportunity to occur in a primary contact RP within its lifetime. The SOC is the controlling factor in recombination of certain triplet biradicals.³³ A ponderous argument in favor of such T-S transition mechanism in RP in glycerol is the internal heavy atom effect: $k_{\rm rec}$ and φ_{∞} increase when a Br atom is introduced into B and/or PhOH as substituent.34

Thus the following kinetic scheme may be considered to give a so far most comprehensive description of the magnetic effects in the system under discussion:

³[BH[•]····PhO[•]]
$$\implies$$
 ³[BH[•], PhO[•]] \implies BH[•] + PhO[•]
 \downarrow soc $\uparrow \downarrow$ hfc (19)
B + PhOH \implies ¹[BH[•], PhO[•]] \implies BH[•] + PhO[•]

where [BH•...PhO•] is the contact RP or "complex"; [BH•,PhO•] is a sufficiently separated RP where the hfc is effective; BH[•] + PhO[•] are radicals out of the cage.

Earlier, such a scheme had been used with effect for describing magnetic phenomena in exciplex-containing systems.^{32,36} Α decrease of temperature shifts the equilibrium toward the complex resulting in a smaller magnetic effect (Figure 5). The value of k_{SOC} is weakly dependent upon temperature or upon the applied moderate magnetic field.

Scheme 19 has been presented to underline the magnetically sensitive stage. With the aim of usual kinetic analysis scheme 19 may be reduced to eq 15 and the kinetics is well described by eq 11, see above.

Thus according to scheme 19 the triplet-singlet transitions in RP under a zero field are SOC-induced (in contact pairs) and hfc-induced (in spatially separated pairs). Imposition of a weak magnetic field suppresses the T_{\pm} -S transitions (the hfc mechanism) and amplifies the relaxation mechanism in separated pairs. In a strong magnetic field ($H \gtrsim 0.1$ T) the relaxation transitions cannot occur within the pair lifetime. In this field the T-S crossings take place in contact pairs under effect of SOC and the T_0 -S transitions in separated pairs under effect of HFC and Δg .

The magnitude of k_{rel} may supposedly be determined from the field relationship of k_{rec} (Figure 4). According to ref 12 and 36 we may assume that $k_{\rm rel}$ is approximately equal to the difference between the limiting value of $k_{\rm rec}$ at H = 0.34 T and the $k_{\rm rec}$ observed under $H > A_{hfc}$. Using this assumption and eq 17 we may now rely on the field relationship of $k_{\rm rec}$ (Figure 4) to obtain two estimates: 12,36 $\tau_c \simeq 1 \times 10^{-9}$ s and $2\tau_c |V|^2 / \hbar^2 \simeq 1 \times 10^7$ s⁻¹. Putting these parameters in eq 17 we come up with $k_{\rm rel} \simeq$ 3×10^3 s⁻¹ at H = 0.33 T. This value of k_{rel} is close to $1/T_1$, obtained for BH[•] by ESR in a solvent of similar viscosity (see above). Unfortunately, it is not possible to put much significance in the closeness of these calculated and the experimental values. The calculation of τ_c and $2\tau_c |V|^2 \hbar^2$ based on the data of Figure 4 can be done with low precision. So, one can expect the coincidence of calculated and experimental values within ca. 1 order of magnitude.

In such a way, τ_c too corresponds, to within 1 order, with the rotational correlation time of stable nitroxyl radicals in glycerol solutions of close viscosity.37

Using the obtained relaxation parameters and eq 18 we may calculate the corresponding $\Delta A_{\rm hfc}$ and R. The parameters that result are reasonable and noncontradictory. If relaxation is induced only by hfc anisotropy, then $A_{\rm hfc}/g\beta = 2.4$ mT (compare ref 12), but if the dipole-dipole coupling is more effective we obtain 12 Å for R.

The available data do not make possible an unambiguous conclusion regarding the relaxation mechanism in the investigated RP. It may be due to two alternative mechanisms: hfc anisotropy or dipole-dipole coupling between the unpaired electrons.

Conclusions

When homogeneous solvents of sufficient viscosity ($\sim 10 \text{ P}$) are used, the triplet radical pairs generated under a light flash have a rather long lifetime ($\sim 1 \ \mu s$). It is therefore possible to obtain direct records of the kinetics of geminate recombination. Geminate recombination kinetics comes out as an important new branch of liquid-phase kinetics which had not been accessible for measurement just one decade before.

For the investigated radicals the geminate recombination kinetics is closely described by the formulas 7 and 11. At longer recording times the kinetics obeys the well-known law (16). The simplest approximation of the geminate recombination kinetics of triplet radical pairs is given by the exponential law (5) and is satisfactory in many cases. The approximation has been and will apparently be used for describing the cage effect.

Solvent viscosity is the major factor influencing geminate recombination rate. The higher the viscosity the greater is the cage effect value. For geminate recombination the coefficients of mutual diffusion are smaller than the sum of the diffusion coefficients of the individual reagents. A possible explanation of this fact consists in the correlation existing between the molecular

⁽²⁸⁾ The characteristic time of the S-T₀ evolution of RP due to the dif-ference of the g factors of the radicals under study $(g_1 - g_2 \simeq 2 \times 10^{-3})^{23,24}$ is ca. 2×10^{-8} s at H = 0.3 T.

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motions of the closely spaced radicals and (or) in the existence of an attractive potential between radicals of pair. Both effects retard the radicals recombination and escape from cage.

Our purpose has been to provide an unambiguous explanation of the totality of data available to date. Strictly speaking, such topics as the mechanism of molecular diffusion in liquids, the elementary mechanism of the photogeneration of free radicals in a liquid remain open. They remain a constant challenge for both theoreticians and experimentors.

The hfc, relaxation, and Δg are the mechanisms that make substantial contribution to the singlet-triplet evolution of the investigated radical pairs. Yet, in very viscous and cool solvents it is not so much these three mechanisms as another H-independent mechanism peculiar to the relatively long-lived contact pairs which controls this evolution. The latter mechanism is the intersystem crossing induced by the spin-orbit coupling in contact pairs.

Registry No. Benzophenone, 119-61-9; p-cresol, 106-44-5.

Quantitative Assessment of Solvent-Sorting Effects. 1. A Menschutkin Reaction in **Mixed Solvents**

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The second-order rate constant k_{app} for the reaction between $(C_2H_5)_3N$ and CH_3I has been determined at 30.0 °C in cyclohexane and in mixtures of cyclohexane with variable amounts (up to ca. 0.3 M) of the following cosolvents (S): N,N-dimethylacetamide, cyclohexanecarbonitrile, cyclohexyl methyl ketone, butanone, tetrahydrofuran, ethyl acetate, cyclohexyl chloride, methyl cyclohexanecarboxylate, cyclohexyl methyl ether, dibutyl ether, nitrobenzene, N,N-dimethylbenzamide, benzonitrile, acetophenone, benzophenone, methyl benzoate, diphenylmethane, anisole, chlorobenzene, fluorobenzene, 1,2-diphenylethane, triphenylmethane, benzene, 1,4-dichlorobenzene, toluene, and p-xylene. Within the limits of experimental error, the following have been found: (1) The activity coefficients of the reagents are practically unaffected by the added cosolvent. (2) For low cosolvent concentrations, k_{app} is related to the concentration of S by the equation $k_{app} = k_0 + k_c[S]$, where k_0 is the reaction rate in pure cyclohexane. (3) In all cases, the catalytic effect of S is quite large: it amounts to ca. 50% of the lowering of the activation free energy of the reaction, observed on going from pure cyclohexane to pure S. (4) This major effect is largely underestimated by the Onsager-Kirkwood model. (5) The catalytic efficiency of aromatic cosolvents of low or zero dipolarity is over 1 order of magnitude larger than predicted by this model. This is traced to electrostatic interactions involving higher multipoles and to London forces. (6) Although a fraction of the catalytic effect can be attributed to a "general dielectric" contribution, these and other results strongly suggest that this reaction can proceed through a true termolecular channel.

Introduction

This paper is the first of a series aimed at providing experimental information leading to a quantitative analysis of the solvation of dipolar transition states (TS), particularly regarding the process of formation of their first "solvation shell". Here, the kinetics of a reaction proceeding through a highly dipolar TS is studied in pure cyclohexane and in mixtures of cyclohexane with a variety of dipolar and/or highly polarizable cosolvents (S), the objective being the study of the stepwise solvation of the TS by the cosolvent. In doing so we also intend to give a quantitative basis to the somewhat fuzzy concept of "solvent sorting".

As a reaction model we have selected a typical Menschutkin⁴ reaction, involving triethylamine and methyl iodide (process 1):

$$(C_2H_5)_3N + CH_3I \rightarrow CH_3N^+(C_2H_5)_3I^-$$
 (1)

The reasons for this choice are as follows: (1) A great deal of effort has been devoted to the kinetic and thermodynamic study of the Menschutkin reactions with emphasis on the analysis of the structure and properties of their TS.⁵ Studies were on, for example, (i) the influence of the bulk solvent on the thermodynamic properties of reactants, products, and TS,6 (ii) the influence of electronic⁷ and steric⁸ characteristics of the reactants, and (iii)

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