Ion–molecular charge transfer reactions of hexafluorobenzene and cis-decalin in nonpolar solutions studied by linewidth broadening in MARY spectra

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Abstract

The effect of an external magnetic field on the radiofluorescence arising from the recombination of spin-correlated radical ion pairs (MARY spectrum) has been studied for dilute nonpolar solutions of hexafluorobenzene and cis-decalin. MARY spectra of these systems show additional local fluorescence intensity maxima at zero field and in the field equal to triple the hfi constant. The breaking down of spin coherence in the course of the ion–molecular charge transfer reaction leads to broadening of the maxima. Relations between the line broadening and the rate of charge transfer reaction have been derived. Rate constants of charge transfer reactions for hexafluorobenzene radical anion in squalane and cis-decalin radical cation in hexane have been obtained experimentally.

1. Introduction

The study of magnetic field effects on reaction yield (MARY spectroscopy) of chemical reactions provides valuable information on short-lived spin-correlated radical pairs [1,2]. As was recently demonstrated, the coherent nature of radical ion pairs generated in solution by ionizing radiation can result in the appearance of additional local fluorescence intensity maxima at zero field [3] and in the field $H^* = 3a$ equal to triple the hfi constant a [4]. The appearance of features in the fields – multiples of a
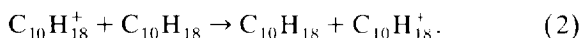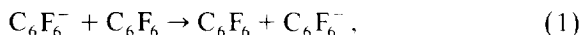
for ion radical pairs with equivalent nuclei had been predicted theoretically a while ago [5,6]. The presence of narrow lines in MARY spectra opens possibilities for the identification of short-lived paramagnetic species and the study of reactions they are involved in.

The reaction of ion–molecular resonance charge transfer between identical particles has an essential effect on spin evolution in radical ion pairs [7,8]. The breaking down of initial spin coherence in the course of charge transfer reactions should lead to broadening of narrow MARY spectrum lines, which allows the extraction of quantitative information on the rate of this process. A previous observation of exchange in MARY spectra [9] has shown zero field line broadening in the intermediate exchange situation, and line narrowing in the fast exchange limit. In the

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present work the effect of exchange on MARY spectra was studied for both zero field line and that at $H^* = 3a$. It was demonstrated that in liquid solution anions of hexafluorobenzene and cis-decalin cations take part in the reaction of resonance charge transfer to the neutral molecule,

$$C_6F_6^- + C_6F_6 \rightarrow C_6F_6 + C_6F_6^- , \tag{1}$$

$$C_{10}H_{18}^+ + C_{10}H_{18} \rightarrow C_{10}H_{18} + C_{10}H_{18}^+ . \tag{2}$$

In diluted solutions the rate of this process is proportional to the acceptor concentration and is quite close to the diffusion controlled one. Thus it is demonstrated that reactions involving short-lived radical ions can be studied basing on the effects of quantum coherence of radical pair spin systems.

2. Experimental

The experimental apparatus and sample preparation technique have been described earlier [3]. Magnetic effects under X-irradiation were taken in stationary conditions. To attain better resolution the magnetic field was modulated, hence the experimental curves are the first derivatives of the corresponding fluorescence intensities.

Solvents – squalane (99%, Aldrich) and hexane (99%, Aldrich) – were additionally purified by passing through a column with activated silica gel. The solvent purity was controlled by their UV-absorption spectra. The solvents used had an optical density equal to 1 at wavelengths of 210–215 nm.

Cis-decalin (99%, Aldrich) and hexafluorobenzene (purchased from Novosibirsk Institute of Organic Chemistry), whose hyperfine coupling constants are known, were used as hole and electron acceptors, respectively.

3. Theory

Assuming exponential recombination decay kinetics $e^{-t/\tau}$, the yield of singlet products of recombination for a singlet-born radical pair with one partner having no hyperfine interactions is given by the Laplace image of the singlet state population $\mathscr{L}[\rho_{SS}(t)]$ [7],

$$G_S = \tfrac{1}{4} + p \, \mathrm{Re}\left[\tilde{T}_{++}(p + i\omega) \right] + \tfrac{1}{2}\tilde{T}_{zz}(p), \tag{3}$$

where the components of the diagonal spin tensor $\tilde{T}(p) = \mathscr{L}[T(t)]$ completely describe the motion of the radical's spin $1/2$ in the basis (S_+, S_-, S_z), $1/\tau$ is denoted p and ω is the Larmor frequency.

The influence of an ion–molecular charge transfer reaction on the spin dynamics of one of the pair partners could be taken into consideration using the technique of averaging over realizations of Markovian processes [10,11]. In the semiclassical description of electron spin motion the final result for the fully averaged tensor $T(t)$ is given by the integral equation [7]

$$T(t) = \exp(-t/\tau_0) \, T^0(t)$$
$$+ (1/\tau_0) \int_0^t \exp[-(t-\xi)/\tau_0]$$
$$\times T^0(t-\xi)T(\xi) \, d\xi, \tag{4}$$

which gives for each tensor component with charge transfer reaction switched on

$$\tilde{T}_{ii}(x) = \frac{\tilde{T}_{ii}^0(x + 1/\tau_0)}{1 - (1/\tau_0)\tilde{T}_{ii}^0(x + 1/\tau_0)}, \tag{5}$$

where $T^0(t)$ describes the spin motion in the absence of charge transfer and τ_0 is the mean spin residence time.

For radicals containing nonequivalent nuclei the equations of spin motion should be solved numerically. However, the problem becomes much more simple for an ensemble of equivalent nuclei, where analytical solutions of the motion for each separate spin are at hand,

$$T^0(t) = \frac{1}{2}\begin{pmatrix} \langle \alpha_m \beta_{m-1}^* \rangle & 0 & 0 \\ 0 & \langle \alpha_m^* \beta_{m-1} \rangle & 0 \\ 0 & 0 & \langle |\alpha_m|^2 - |\gamma_m|^2 \rangle \end{pmatrix}, \tag{6}$$

Explicit expressions for α_m, β_m and γ_m are given in the Appendix.

Expression (3) was deduced for a radical pair with one of the pair partners containing no magnetic nuclei. Experimentally this requirement could be met quite well if deuterated substances, e.g. p-terphenyl-d_{14} (PTP-d_{14}), whose total spectrum width does not exceed 1.5 G, are used to form counterions. A similar quite simple expression could also be used when the counterion has nonzero hyperfine cou-
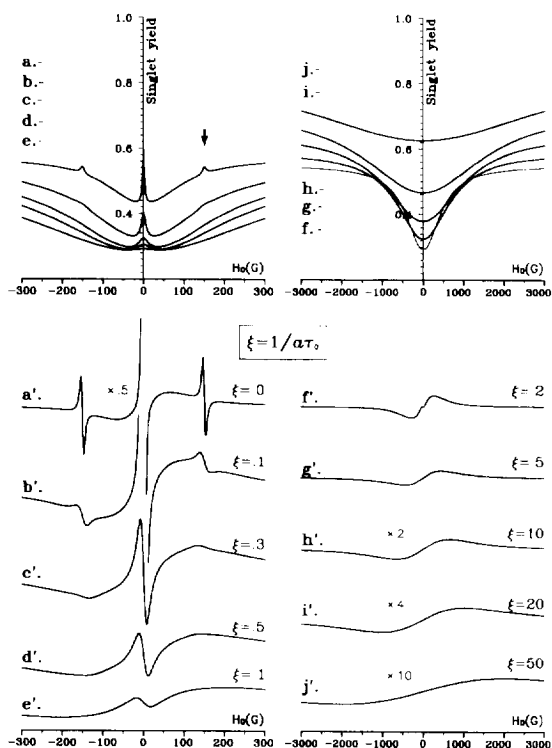
Fig. 1. Calculated dependence of singlet yield G_s (above) and $\partial G_s/\partial H$ (below) versus external magnetic field for different frequencies of charge transfer, in units $\xi = (a\tau_0)^{-1}$: (a) 0; (b) 0.1; (c) 0.3; (d) 0.5; (e) 1; (f) 2; (g) 5; (h) 10; (i) 20; (j) 50. Other parameters being $a(4H) = 50$ G, $(a\tau)^{-1} = 0.1$. The counterion has no magnetic nuclei. The arrow marks the line at $H^* = 3a$.

plings but does not participate in the charge transfer reaction (e.g. because of a low concentration of acceptor molecules in solution). In this case it is necessary to carry out averaging over all nuclear configurations in both partners. Details of this procedure will be reported elsewhere.

Fig. 1 shows the field dependence of singlet product yield G_S (so-called MARY spectra) calculated from Eq. (3) for different rates of charge transfer reaction. The curves correspond to a model radical pair with four equivalent protons (fluorines) in one of the partners, $a(4H) = 50$ G, another partner having no hyperfine couplings. Curves (a)–(j) give the yield of singlet products G_S, and their derivatives $\partial G_S/\partial H$ are shown in Figs. 1a′–1j′. For convenience the curves are split into two groups corresponding to regions of slow $((a\tau_0)^{-1} < 1$, curves (a)–(e)) and

fast charge transfer $((a\tau_0)^{-1} > 1$, curves (f)–(j)).

In the absence of charge transfer (Fig. 1i) the field dependence shows an intense maximum at zero field and an additional one in the field $H^* = 3a$ (marked by arrow), their widths being determined by the pair recombination rate if no other relaxation processes take place. Switching on the charge transfer reaction of the broad partner destroys the spin coherence in the pair which leads to a corresponding decrease in the MARY spectrum line intensities (Figs. 1b′–1c′) and a broadening proportional to the rate of this process. In the region of slow exchange (Figs. 1i′–1e′) charge transfer reaction broadens the central line as

$$1/T_2^* = 1/\tau_0 + 1/\tau \qquad (7)$$

(the line at triple the hfi constant behaves in a similar way, though we did not point it out analytically). As has already been demonstrated [3], the quantitative criterion for the existence of an interference maximum at zero field is

$$\Omega T_2^* > 1, \qquad (8)$$

where $\Omega = \sqrt{\frac{2}{3}\Sigma a_i^2 I_i(I_i + 1)} = \sqrt{2\Delta^2}$, and for $(a\tau_0)^{-1} > 1$ initial spin coherence is almost lost (Fig. 1f′). It is worth mentioning that the line in the field $H^* = 3a$ is broader and weaker than the zero field one [4] and hence it disappears earlier, at $(a\tau_0)^{-1} \approx 0.5$ (Fig. 1d′).

A further increase in migration rate casts the system in the region of fast charge transfer (Figs. 1g′–1j′). Since the transverse components of the tensor $T(t)$ are averaged down all features arising from interference disappear (Fig. 1g′), and the shape of the MARY spectrum is now determined only by the dependence of the longitudinal relaxation time T_1 on the external magnetic field. The relaxation time in the pair lengthens and this leads to an increase in the total singlet product yield (Fig. 1j), while the line-shape becomes Lorentzian,

$$G_S(\omega) = \frac{1}{4} + \frac{1}{2}(T_2^*/\tau) + \frac{1}{4}(T_1^*/\tau), \qquad (9)$$

where

$$1/T_{1,2}^* = 1/T_{1,2} + 1/\tau, \qquad (10)$$

$$1/T_1 = 2\Delta^2\tau_0/(1 + \omega^2\tau_0^2), \qquad (11)$$

$$1/T_2 = \Delta^2\tau_0 + 1/2T_1. \qquad (12)$$

Expressions (7)–(12) for non-correlated frequency migration (e.g. caused by ion–molecular charge transfer) are well known in ESR spectroscopy. Hence, MARY spectra and ESR spectra are closely analogous: both have individual lines with splittings of several hfi constants that are broadened by charge transfer reactions. However, there is also an essential difference arising from the ways the signals are observed. Since the ESR signal is actually the reaction of a spin system on transverse perturbation, an increase in migration frequency leads to a shift of the individual components towards the center of the spectrum and finally to their merging and collapsing into a single line. As could be concluded from Figs. 1a'–1d' MARY spectra do not perform such a shift. In the limiting case of fast charge transfer and in the absence of hfi in the counterion S–T transitions are frozen out which results in almost full damping of the observed signal (Fig. 1j'). Note that introducing hfi in the second partner qualitatively changes the shape of the MARY spectrum, and certain features of these changes are to be touched upon later.

4. Results and discussion

Figs. 2a–2g show MARY spectra of a solution of hexafluorobenzene in squalane at different concentrations taken at room temperature. PTP-d_{14} (5×10^{-4} M) was added as luminophore. As mentioned above, the experimental curves were recorded as first derivatives of the fluorescence intensity ($\partial G_S/\partial H$). On the given curves not only a pronounced zero field feature, but also a satellite line in the field $H^* = 3a$ (marked by arrow) is present. For convenience the inserts show this part of the spectra magnified. As follows from Fig. 2i, the positions and amplitudes of these lines completely coincide with those calculated theoretically from (3) for $a(6F) = 135$ G [12], which lets us ascribe them to the hexafluorobenzene anion MARY spectrum [4]. The central part of the spectra is shown magnified in Figs. 2a'–2g'. On increasing the C_6F_6 concentration, the charge transfer reaction (1) grows faster, leading to a corresponding broadening of the spectrum components and decrease in amplitude. In line with theoretical predictions the satellite feature disappears faster than the central one. Expression (3), taking into consideration the
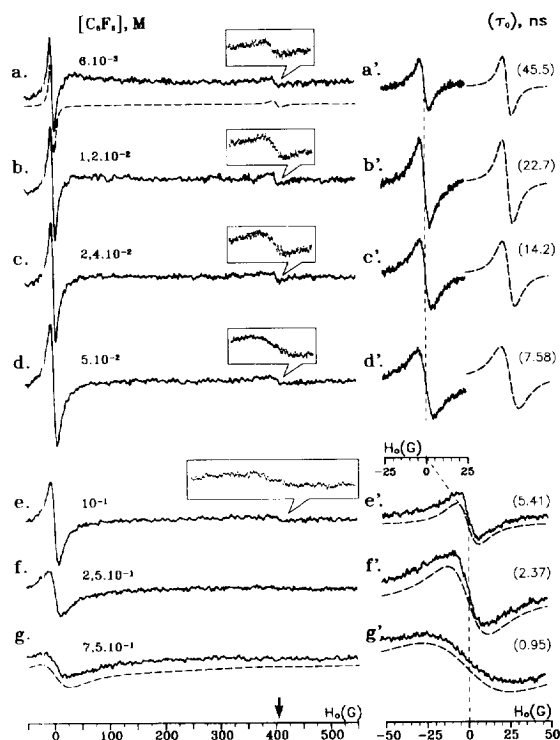

Fig. 2. Experimentally taken MARY spectra of C_6F_6 solutions in squalane for different C_6F_6 concentrations (room temperature): (a) 0.006 M; (b) 0.012 M; (c) 0.024 M; (d) 0.05 M; (e) 0.1 M; (f) 0.25 M; (g) 0.75 M. Inserts show magnified satellite line at $H^* = 3a$ (marked by arrow on the axis). Horizontal scale for inserts is the same as for curves (a')–(e'). Dashed lines were theoretically calculated from (3) for $a(6F) = 135$ G.

charge transfer reaction, completely accounts for the observed spectral transformation in the entire range of C_6F_6 concentrations, allowing one to extract the rate constant for reaction (1). As an illustration the dashed curves in Figs. 2a'–2g' show the calculated best fittings of the observed MARY spectra lines (exchange frequency being the fitting parameter). A similar simulation was also done for the satellite line.

Fig. 3 shows the dependence of the ion–molecular charge transfer reaction rate on hexafluorobenzene concentration in solution obtained via theoretically fitting the experimental curves. The reaction rates extracted from the broadening of the zero field line (circles) and line at triple the hfi constant (triangles) are seen to be almost identical. In the concentration range 0.05–0.75 M the extracted values could be fit quite well with a straight line, and the line's
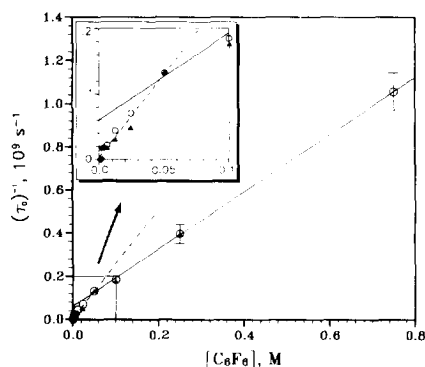
Fig. 3. Exchange frequency $(\tau_0)^{-1}$ versus hexafluorobenzene concentration in squalane at room temperature. The solid line is a linear approximation in the concentration range 0.05–0.75 M. The dashed line is the same for concentrations less than < 0.05 M.

slope gives the charge transfer reaction rate constant 1.3×10^9 M^{-1} s^{-1}. This value coincides fairly well with the known value [2] 1.2×10^9 M^{-1} s^{-1} [13], obtained using the optically detected ESR (OD ESR) technique from the broadening of individual lines in the $C_6F_6^-$ spectrum. Summing up, the entire picture of the $C_6F_6^-$ MARY spectral transformations could be completely described within the frame of ion–molecular charge transfer, and the rate constant for reaction (1) obtained by this method corresponds quite well to the known value.

It should be mentioned here that a thorough study of the region of low hexafluorobenzene concentration (< 0.05 M) gave a quite different slope for the fitting line (magnified in Fig. 3). The extracted rate constant $(2.5 \times 10^9$ M^{-1} $s^{-1})$ was found to be almost two times greater than that in the high concentration region. The reason for the change in the charge transfer reaction rate constant with hexafluorobenzene concentration is not clear. It is known that the diffusion mobility of small aromatic molecules in squalane significantly exceeds that calculated from the macroviscosity value (e.g. refer to the discussion in Ref. [14]). This anomalous diffusional mobility could be a function of hexafluorobenzene concentration. On the other hand, radical anions of fluorinated

aromatic hydrocarbons were recently shown to form dimer anions with neutral molecules [15]. This process could also impact on the broadening of MARY lines. More experiments are required to figure out the nature of the concentration dependence of the rate constant.

We have employed hexafluorobenzene to study the reaction of resonance electron transfer between the anion and neutral molecule (reaction (1)). The MARY spectra obtained a while ago of cis-decalin radical cation [4] allowed the study of resonance positive charge (hole) transfer between the radical cation and its neutral molecule (reaction (2)).

Figs. 4a–4e show experimental MARY spectra of hexane solutions of cis-decalin at different concentrations taken at room temperature. PTP-d_{14} (3 × 10^{-4} M) was added as luminophore. Since spin evolution in the cis-decalin radical cation is driven mainly by the hfi with four equivalent protons $a(4H) = 50$ G [16] its MARY spectrum demonstrates a line in the field $H^* = 3a$ [4] (marked with an arrow). In dilute solutions the charge transfer reaction is almost switched off and it is possible to observe the line (Fig. 4a). Unfortunately, small hyperfine interactions with other protons broaden the line, and we have put the corresponding part of the spectrum in a box to emphasize it. In this case the exchange reaction rate constant cannot be extracted from the width of an individual line and it is necessary to analyze the entire spectrum increasing the cis-decalin concentration, charge transfer reaction (2) goes faster leading to a corresponding broadening of the individual spectrum components and decrease in their intensities. In full agreement with theory, the satellite line disappears when $\xi = (a\tau_0)^{-1} \approx 0.5$ (Fig. 4b), and a complete breaking down of coherence and vanishing of zero field line takes place at $\xi = (a\tau_0)^{-1} > 1$ (Figs. 4c–4d). The spin system then falls into the region of fast charge transfer and all peculiarities of the spectrum disappear, turning into a single broad smashed line (Fig. 4d) that disappears in pure cis-decalin (Fig. 4e). The narrow line at zero field observed in the spectra (Figs. 4b–4e) should be ascribed to parallel processes involving radical ions of PTP-d_{14} with small overall spectrum width. In pure cis-decalin, apart from this line, an additional broad component is observed (Fig. 4e) that might arise from hole capture by some unidentified decay products, formed

[2] The different value, 1.6×10^9 M^{-1} s^{-1}, given in Ref. [14] was found to be incorrect because of a misprint in expression (28). The corrected value is also 1.2×10^9 M^{-1} s^{-1}.

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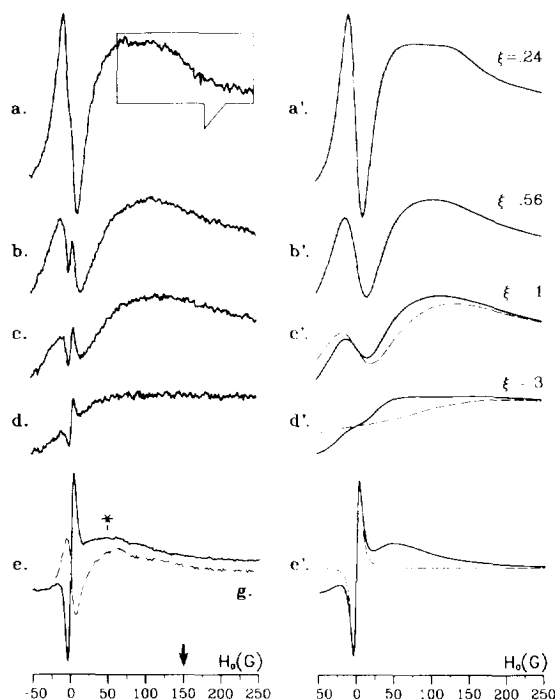

Fig. 4. (a)–(d) Experimentally taken MARY spectra of cis-decalin solutions in hexane for different cis-decalin concentrations (room temperature): (a) 0.021 M; (b) 0.09 M; (c) 0.19 M; (d) 0.47 M. p-terphenyl-d_{14} (3×10^{-4} M) was added as luminophore. For convenience the satellite line at $H^* = 3a$ is put into the frame, its position is marked by an arrow on the axis. (e) MARY spectrum of 10^{-3} M p-terphenyl-d_{14} in net cis-decalin; (g) MARY spectrum of 10^{-1} M 9,10-octalin (decalene) in cis-decalin. (a')–(d') Theoretical curves for $a_1(4H) = 50$ G, $a_2 = 0$ G, calculated from (3) for different charge transfer frequencies, $\xi = (a\tau_0)^{-1}$: (a') 0.24; (b') 0.56; (c') 1; (d') 3. (e') Theoretical curve for $a_1(2H) = 1$ G, $a_2(2H) = 1$ G, corresponding to the $(PTP\text{-}d_{14})^+/(PTP\text{-}d_{14})^-$ ion pair formed in net cis-decalin (narrow line). A broad admixture line corresponding to radiolysis products is added to fit the experimental spectra in concentrated cis-decalin solutions (curves (c')–(e')). Dashed curves show theoretical ones without the admixture line.

in the solution under irradiation. This could be, for example, molecules of 9,10-octalin (decalene) which is accumulated during radiolysis and yields an olefin cation [17]. It could also be formed immediately in the reaction of hydrogen abstraction from cis-decalin radical cation [18] prior to recombination,

$$C_{10}H_{18}^+ \rightarrow C_{10}H_{16}^+ + H_2. \tag{13}$$

For comparison, the MARY spectrum of this olefin cation, obtained earlier in squalane solution [4] is

given in the same picture (Fig. 4g, shifted vertically). More experimental work is necessary to deduce the origin of this broad line. The experiments are in progress now and the results will be reported elsewhere.

Expression (3) completely describes the observed transformations of the spectrum shape in the entire range of cis-decalin concentrations in terms of the charge transfer reaction. Figs. 4a'–4c' show calculated curves best fitting the experiment (charge exchange frequencies were adjusted). To fully fit the experiment in the range of high concentrations (Figs. 4c'–4e') a broad line whose origin has already been discussed was added to the cis-decalin spectra. The dashed curves present cis-decalin spectra without correction. The charge transfer rate constant for reaction (2) obtained via this technique, $k \sim 5.4 \times 10^9$ M^{-1} s^{-1}, is quite close to the diffusion controlled one in hexane.

Since alkanes are widely used as solvents in radiation-chemical experiments, the ability of alkane radical cations to take part in positive charge hopping is widely debated. Unfortunately, there is no direct proof for ion–molecular resonance charge transfer (reaction (2)) in saturated hydrocarbons. Very fast hole hopping was proposed to explain the conductivity measurements in cyclic hydrocarbons [19], but this explanation was questioned in subsequent publications [20]. It is generally believed that the rate of hole hopping is actually not large. This hypothesis roots in the well-known dependence of the rate constant of hole transfer from donor to acceptor on the difference of their ionization potentials ΔI [21]. The dependence shows the plateau region for $\Delta I > 1$ eV and the decrease in hole transfer rate with decreasing ΔI. For $\Delta I \rightarrow 0$ the rate constant drops by two or more orders of magnitude as compared to that for the plateau region. Attempts have already been made to figure out the cis-decalin ion–molecular charge transfer reaction from the concentration broadening of the cation's OD ESR spectra lines. However, all these attempts have failed because cis-decalin signals vanish and disappear on increasing its concentration in solution, hence not allowing the extraction of any spectral information. Therefore, this work presents the first direct spectroscopic verification of cis-decalin radical cation participation in a resonant charge transfer reaction in liquid solution.

In dilute solutions the rate of this process is proportional to the cis-decalin concentration and quite close to the diffusion controlled one.

Acknowledgement

Appendix

Similarly to equations describing the motion of spin $1/2$ in the semiclassical approach [7], one can demonstrate that for an ensemble of equivalent nuclei (protons) the components of electron spin (S_+, S_-, S_z) evolve in time as

$$\langle S_+(t) \rangle = \langle \alpha_m \beta_{m-1}^* \rangle S_-(0),$$

$$\langle S_-(t) \rangle = \langle \alpha_m^* \beta_{m-1} \rangle S_-(0),$$

$$\langle S_z(t) \rangle = \langle |\alpha_m|^2 - |\gamma_m|^2 \rangle S_z(0). \quad (A.1)$$

Angles $\langle \ \rangle_{(1,2)}$ mean averaging over all nuclear configurations in the first (second) radical,

$$\langle q_m \rangle = \sum_{I,m} \frac{W(I)}{(2I+1)} q(I, m), \quad (A.2)$$

where the summation over I, m, is carried out over all nuclear sub-ensembles with total spin I with statistical weights $W(I)$ [4]. Analytical expressions for $\alpha_m, \beta_m, \gamma_m$ read

$$\alpha_m = \cos^2\varphi_m \, \exp(iR_m t) + \sin^2\varphi_m \, \exp(-iR_m t),$$

$$\beta_m = \sin^2\varphi_m \, \exp(iR_m t) + \cos^2\varphi_m \, \exp(-iR_m t),$$

$$\gamma_m = -\tfrac{1}{2}\sin(2\varphi_m)\left[\exp(iR_m t) - \exp(-iR_m t)\right], \quad (A.3)$$

where

$$R_m = \tfrac{1}{2}\left[\omega^2 + a\omega(2m+1) + a^2\left(I + \tfrac{1}{2}\right)^2\right]^{1/2}, \quad (A.4)$$

$$\cos^2\varphi_m = \frac{1}{2R_m}\left[R_m + \tfrac{1}{2}\omega + \tfrac{1}{4}a(2m+1)\right], \quad (A.5)$$

a is the radical's hfi constant and $\omega = \gamma H$ is a Larmor frequency.

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