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MARY and Optically Detected ESR Spectroscopy of Radical Cations of *cis*- and *trans*-Decalin in Nonpolar Solutions

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Optically detected ESR and magnetic field effect on recombination luminescence yield (MARY) spectroscopy of spin-correlated radical ion pairs were used to study *cis*- and *trans*-decalin radical cations in nonpolar solutions. The differences observed in *cis*- and *trans*-decalin spectra are demonstrated to agree with the existence of temperature-activated intramolecular dynamic transitions in *trans*-decalin radical cation. In diluted solutions with decalin added as acceptors, the MARY spectroscopy technique yields the spectra of the corresponding radical cations even at room temperature. Under these conditions, the fast limit of dynamic transitions in *trans*-decalin radical cation takes place. It is demonstrated that both *cis*- and *trans*-decalin radical cations take part in ion–molecular charge transfer to a neutral molecule, the rate constant being close to the diffusion-controlled one.

Introduction

Radical cations of *cis*- and *trans*-decalin have been studied in Freon matrices and zeolites by ESR,^{1–4} as well as in hydrocarbon solutions by optically detected ESR (OD ESR) in CW^{5,6} and time-resolved^{7–9} variants. Radical cations derived from both isomers are fairly well stabilized in frozen Freon matrices and zeolites, yielding resolved ESR spectra. However, for hydrocarbon solutions their OD ESR spectra behave in a dramatically different manner. The *cis*-decalin radical cation OD ESR spectra in diluted cyclohexane¹⁰ and squalane¹¹ solutions were observed at temperatures up to ambient, but the signals of *trans*-decalin can be obtained only below 40 K.^{7,8,9} All efforts to detect signals of the decalin radical cations (i.e., solvent holes) in nondiluted solutions at room temperatures have failed. In the case of *cis*-decalin its lines vanish and disappear at concentrations higher than 0.1 M.^{10,11}

On the basis of such a behavior of the OD ESR signals, it was assumed⁹ that in hydrocarbon solutions radical cations are quickly deprotonated



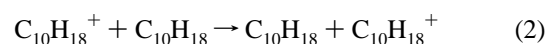
trans-decalin reacting much faster than the *cis*-decalin isomer. However, by employing the pulse radiolysis technique, it was demonstrated¹² that the *trans*-decalin radical cation lifetime exceeds 100 ns even at room temperature. Thus, the decay reactions cannot be responsible for the failure in getting its OD ESR spectra.

ESR in Freon matrices³ and zeolites⁴ helped in determining that the radical cations of both *cis*- and *trans*-decalin have a couple of nearly degenerate electronic states with different ESR spectra. The quantum calculations³ predict minor differences in the electronic structures of *cis*- and *trans*-decalin radical cations. Accordingly, the ESR spectra of both states for *cis*- and *trans*-decalin were observed in zeolites.⁴ The energy gap between the two quasi-degenerate highest occupied molecular orbital states is comparable with the energy of interactions with the media, and these states may be involved in intramolecular dynamic transitions.³ We suggest that the observed temperature transformations of the *trans*-decalin radical cation OD ESR

spectrum be assigned to the activation of transitions between two nearly degenerate electron states.

In contrast with zeolites, in Freon matrices the two states and the dynamic transitions between them have so far been observed only for *trans*-decalin radical cation,³ but the *cis*-decalin radical cations do not demonstrate such peculiarities. We suppose that the same is true for hydrocarbon matrices as well, which let us quantitatively describe all the experimental data. The analysis of MAGnetic field effect on Recombination luminescence Yield (MARY spectra) provides additional arguments in favor of such an explanation.

Besides, in dilute solutions the radical cations of both conformers are shown to take part in the resonance charge transfer reaction



with the rate constant being quite close to the diffusion-controlled one.

Experimental Section

The OD ESR spectra were taken under stationary conditions using an experimental setup¹³ modified for conducting low-temperature experiments. The sample, containing about 1 mL of solution in a quartz cuvette, was put into the microwave cavity of a BRUKER ER-200D ESR spectrometer equipped with an X-ray tube for sample irradiation and a photomultiplier tube (PMT) with a quartz light guide for fluorescence detection. The fluorescence was monitored through a light filter ($\lambda < 360$ nm) to cut off sample phosphorescence. The PMT signal was fed to a phase-sensitive detector. The scanned magnetic field was modulated by a small alternating one at 170 Hz (the reference frequency of the lock-in detector). The microwave field amplitude for the clystron operation at 200 mW amounted to $H_1 \approx 0.45$ G.

The technique of OD ESR spectra registration at 77 K has been described elsewhere.⁶ A special Dewar flask with a flat bottom, serving as an output window for fluorescence, was used. To take spectra at 4 K, a special double-wall Dewar flask of ~ 2 dm³ capacity was used. The external nitrogen coat was made of polyurethane, the working end being cooled by the film of freely flowing liquid nitrogen (Figure 1). The sample

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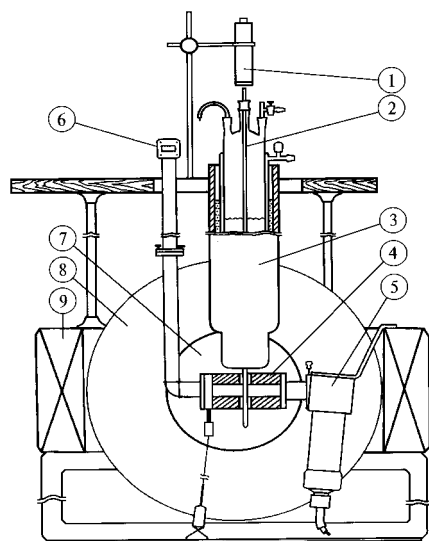


Figure 1. Liquid helium OD ESR experimental setup: (1) PMT; (2) light guide; (3) helium Dewar; (4) MW cavity; (5) X-ray tube; (6) MW power input; (7), (8), (9) magnet poles, coils, and yoke, respectively.

fluorescence was led out by a quartz light guide, drowned in liquid helium. A single load of helium Dewar sufficed for 2–3 h of continuous work. In the temperature range 6–40 K the sample temperature was varied by blowing helium, evaporating from a small helium cryostat fastened right under the microwave cavity. The setup scheme is close to that described earlier.⁸ The sample temperature was controlled using a calibrated Fe–Au thermocouple.

The MARY spectra (sample fluorescence yield vs applied external magnetic field) under X-irradiation were taken under stationary conditions as described earlier,¹⁴ with magnetic field modulation at 12.5 kHz and lock-in detection. Spectra are recorded as first derivatives.

The solvents used, *cis*- and *trans*-decalin (99%, Aldrich) and cyclohexane (99%, Aldrich), were purified by passing through a column with activated silica gel. Cyclohexane was also distilled prior to column. The purity was tested by UV absorption in the range 215–225 nm. Prior to experiments the samples were degassed to $\sim 10^{-3}$ Torr by repeated freeze–pump–thaw cycles.

OD ESR Studies

The OD ESR technique^{15,16} has proven to be a highly effective method for studying short-lived radical ion pairs born under the action of ionizing radiation in hydrocarbon solutions.^{17,18} In typical experimental conditions, the radical ion pairs with lifetimes longer than ~ 100 ns can be easily detected.

Figure 2 shows the OD ESR spectra of *cis*- and *trans*-decalin solutions in squalane at different temperatures (4–77 K) with naphthalene-*d*₈ added as electron acceptor and fluorescing partner. The spectra of *trans*-decalin (Figure 2a–d) and *cis*-decalin (Figure 2a'–d') were taken in similar conditions. The spectra obtained for both *cis*- and *trans*-decalin are in general similar to those obtained using the time-resolved fluorescence detected magnetic resonance technique^{7–9} at temperatures about 15–45 K. The 50 G quintet (4 H) in the spectrum of *cis*-decalin solution in squalane at 77 K (Figure 2a') has already been identified^{6,19} as pertaining to *cis*-decalin radical cation [(*c*-DEC)⁺]. An intense single line at the center of spectrum arises from naphthalene-*d*₈ radical ions. As the temperature decreases from 77 K to 4 K, the amplitude of (*c*-DEC)⁺ signals does not change (Figure 2a'–d'). With *trans*-decalin being a positive charge acceptor, the situation is quite different (Figure

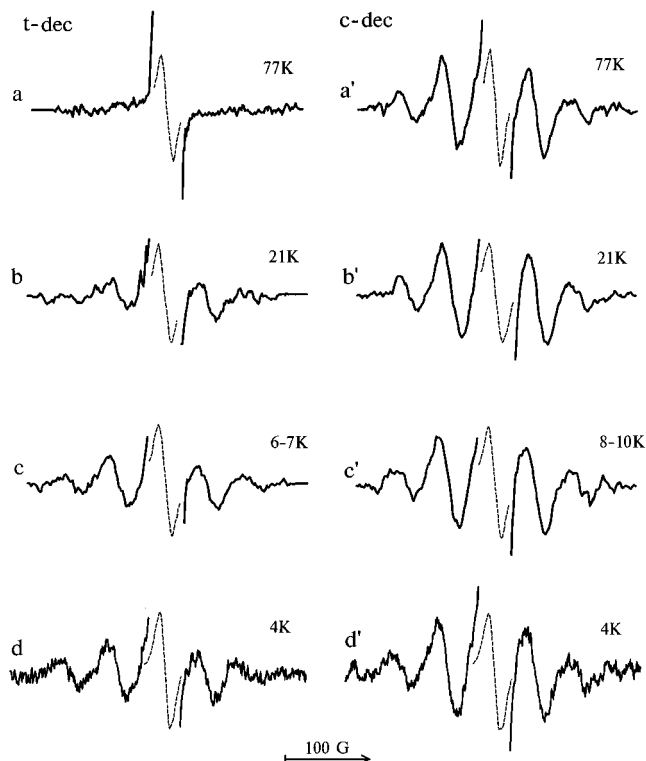


Figure 2. Temperature transformations of the OD ESR spectra for glassy solutions of 8×10^{-3} M naphthalene-*d*₈ in squalane with added (a–d) 0.3 M *trans*-decalin or (a'–d') 0.3 M *cis*-decalin.

2a–d). At 77 K the OD ESR spectrum of *trans*-decalin solution in squalane consists of a single narrow central line due to naphthalene-*d*₈ radical ions. At 21 K the lines of quintet ≈ 50 G (4 H) arise, growing more intensive with temperature decrease. The spectrum observed at 4 K is identical to that observed for the *trans*-decalin radical cation in Freon matrix,¹ which allows it to be ascribed to *trans*-decalin radical cation [(*t*-DEC)⁺]. Having lower ionization potential than squalane, the molecules of both *cis*- and *trans*-decalin effectively capture matrix holes.⁶ However, one should mention that at 4 K the spectrum of (*t*-DEC)⁺ is about 30% less intense than that of (*c*-DEC)⁺ when normalized to the central line.

Since in Freon the *cis* and *trans* isomers give similar ESR spectra at nitrogen temperatures,¹ the dramatic difference observed in their OD ESR spectra in alkane matrices deserves special consideration. It is well-known that in radical cations of many cyclic alkanes (e.g., cyclohexane) the intramolecular dynamic transitions between degenerate Jahn–Teller states can take place.^{2,20,21} The latter leads to the modulation of hyperfine coupling constants, which should reveal itself in the OD ESR spectra. It is believed that a strong anisotropy and large shift of *g*-factor, typical of these Jahn–Teller active radical cations, result from the admixture of orbital state,²² which also shortens the spin–lattice relaxation times. It is reasonable to assume that the observed transformation of resolved (*t*-DEC)⁺ spectrum with temperature elevation also roots in these reasons: the dynamical averaging of hfi and the shortening of pair spin relaxation time.

ESR in Freon matrices³ and zeolites⁴ helped in determining that the radical cations of both *cis*- and *trans*-decalin have a couple of nearly degenerate electronic states with different ESR spectra (Table 1). Quantum chemical calculation³ results that the two highest occupied molecular orbitals (HOMOs) in decalin neutral molecule have low symmetry (correspondingly *a*_G and *b*_G for *trans* and *a*₁ and *a*₂ for *cis* conformer). Thus, in this case the Jahn–Teller theorem could not be directly applied.

TABLE 1: Hyperfine Coupling Constants for *cis*- and *trans*-Decalin Radical Cations

cation	matrix ^a	T, K	hfi, G	g-factor	ref
(c-DEC) ⁺ Na-Ω -5	ZSM-34	77	50 (4 H)		4
		77	29.5 (4 H)		4
	CCl ₃ F	77–140	51.8 (4 H)	2.0032	3
	c-C ₆ F ₁₂	77–140	50.3 (4 H)		3
	SQ	290	50 (4 H)		11
	c-C ₆ H ₁₂	290	51 (4 H)		10
	n-C ₅ H ₁₂	180	51 (4 H)		10
	3-MP	140	50 (4 H)		5
	c-DEC	77	50 (4 H)		6
	SQ	4–77	50 (4 H)		this work
(t-DEC) ⁺	ZSM-34	77	51.5 (4 H)		4
	Na-Ω -5	77	29.8 (4 H)		4
	CCl ₃ F	77–140	51.3 (4 H)	2.0032	3
	c-C ₆ F ₁₂	77–140	34.6 (4 H)	(2.0080) _⊥ (1.9988)	3
	CF ₃ -cC ₆ F ₁₁	4–77	52 (4 H) ↔ 0 (4 H) 0 (4 H) ↔ 34.6 (4 H)		3
	SQ	14–45	52 (4 H)		7
	SQ	4–77	52 (4 H) ↔ –3 (4 H) [2] 5 (4 H) ↔ –3 (4 H) –1 (4 H) ↔ 35 (4 H)		this work

^a ZSM-34, Na-Ω -5 = zeolites; SQ = squalane; 3-MP = 3-methylpentane; c-DEC = *cis*-decalin. ^b hfi constants accepted for OD ESR spectra simulation.

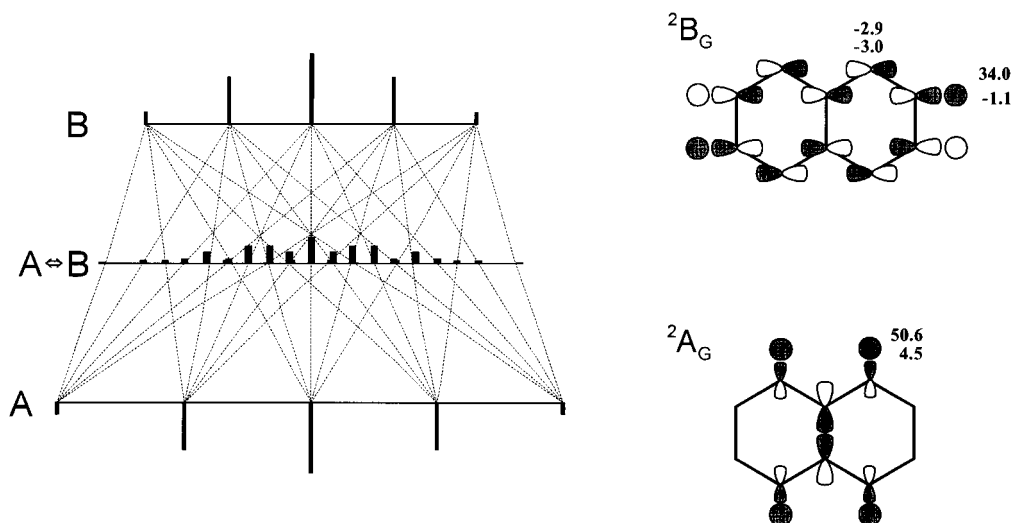


Figure 3. ESR stick diagram and schematic representation of HOMOs for two nearly degenerate states of (t-DEC)⁺.³ Quantum chemically obtained hfi constants are given in gauss. Only significant hfi were taken to demonstrate the effect of dynamic averaging.

However, the level splitting is not large, and the levels could be treated as nearly degenerate. The HOMOs of (t-DEC)⁺, corresponding to two different electronic states are presented in Figure 3. The spin density of the lower state ²A_G is concentrated on the central C–C bond, resulting in large hyperfine interaction (hfi) couplings with four equatorial *trans*-β-protons. The electron density of the higher state ²B_G is delocalized on side C–C bonds, yielding smaller hyperfine couplings in the radical cation. As has been experimentally demonstrated,^{3,4} either the ²A_G or ²B_G (t-DEC)⁺ state may be observed depending on the matrix used, and moreover, under certain conditions (elevated temperature and relevant matrix) the dynamical transitions ²A_G ↔ ²B_G could be experimentally observed. The calculations for *cis*-decalin show that the energy gap between two HOMOs in neutral molecule is also quite small. Accordingly, the ESR spectra of both states for *cis*- and *trans*-decalin were observed in zeolites.⁴ However, in contrast with zeolites, in Freon matrices only the lower state of (c-DEC)⁺ is experimentally observed (Table 1). One may assume that the same is true for hydrocarbon matrices as well. Summing up, we suppose that the experimentally observed differences in *cis*- and *trans*-decalin OD ESR spectra (Figure

2) originate from the dynamic averaging of (t-DEC)⁺ spectrum structure and promoting spin–lattice relaxation.

The analysis of the (t-DEC)⁺ OD ESR spectrum transformation is presented in Figure 4. The curves Figure 4a–d are the numerically integrated experimental curves from Figure 2a–d, normalized to the central line. With increasing temperature (4–21 K), (t-DEC)⁺ spectra evidently change: the amplitude of the sidemost *M*_I = ±2 lines drops as compared to the *M*_I = ±1 lines (Figure 4a–c), and the pits between the lines are smashed. At 77 K the resolved structure vanishes and the spectrum turns into a broad featureless background (Figure 4d). The observed spectrum transformation may be theoretically described in terms of the model of thermally activated dynamic transitions between two states of (t-DEC)⁺. The curves Figure 4a'–d' present the theoretically calculated OD ESR spectra with two-site intramolecular exchange²³ taken into consideration, ²A_G ↔ ²B_G. The exchange was assumed to take place between two groups of protons with the hfi constants taken close to quantum chemically calculated for (t-DEC)⁺ (see Table 1). The ratio of forward and back reaction rates was supposed to depend exponentially on the temperature. In order to account for the intensity

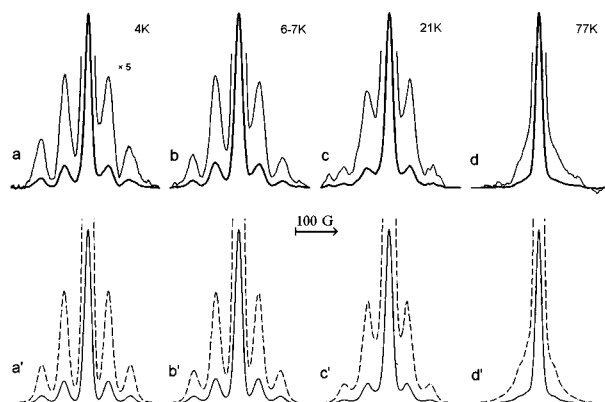


Figure 4. Temperature transformation of the OD ESR spectra of 0.3 M *trans*-decalin in glassy squalane solutions: (a–d) integrated experimental curves; (a'–d') spectra calculated with two-site exchange taken into consideration, exchange rates and T_1 being (a') $k_{AB} = 10^6 \text{ s}^{-1}$, $k_{BA} = 5 \times 10^7 \text{ s}^{-1}$, $T_1 = 8 \text{ } \mu\text{s}$; (b') $k_{AB} = 10^7 \text{ s}^{-1}$, $k_{BA} = 1.25 \times 10^8 \text{ s}^{-1}$, $T_1 = 2 \text{ } \mu\text{s}$; (c') $k_{AB} = 1.7 \times 10^8 \text{ s}^{-1}$, $k_{BA} = 3.3 \times 10^8 \text{ s}^{-1}$, $T_1 = 1 \text{ } \mu\text{s}$; (d') $k_{AB} = 5 \times 10^8 \text{ s}^{-1}$, $k_{BA} = 5 \times 10^8 \text{ s}^{-1}$, $T_1 = 0.1 \text{ } \mu\text{s}$. Microwave field amplitude $H_1 = 0.45 \text{ G}$. Central line of naphthalene ions added for visual correspondence.

decrease, the relaxation time was supposed to decrease with temperature.

Figure 4a (see also Figure 2d) shows that at 4 K the ratios of *trans*-decalin spectrum line amplitudes substantially differ from the statistical ones—the sidemost lines are unusually strong. This phenomenon has already been observed in the OD ESR spectra of alkane radical cations in alkane matrices^{23–25} and was shown to arise from the spectral migration between the components of hyperfine structure, revealing itself under strong microwave pumping. In neat alkanes the migration is provided via ion–molecular charge transfer (holes hopping) between the matrix molecules. In diluted solutions studied a positive charge is stabilized on the acceptor molecule and the effect of ion–molecular charge transfer may be neglected. Thus, the anomalous distribution of *trans*-decalin spectrum line amplitudes should be completely ascribed to intramolecular transitions. Remarkably, the spectrum of *cis*-decalin, where no transitions take place, exhibits no anomalies (Figure 2d').

As could be concluded from Figure 4, the assumption of intramolecular dynamic transitions allows one to describe the main peculiarities of the (t-DEC)⁺ spectrum shape transformation. These results lead to the conclusion that the temperature transformations of (t-DEC)⁺ spectrum are rooted in the dynamic transitions, and the experimentally observed decreases in the *trans*-decalin OD ESR spectra intensity are the consequences of a faster spin relaxation due to electron energy level degeneracy. Furthermore, an assumption that some other cyclic alkanes lack the OD ESR spectra (see Discussion) for the same reasons seems quite reasonable. The data obtained show that the increase in sample temperature up to the ambient one will lead to the total dynamic averaging of hyperfine couplings in (t-DEC)⁺, the resulting spectrum being formed by two groups of protons $a_1(4 \text{ H}) \approx 25 \text{ G}$ and $a_2(4 \text{ H}) \approx 17 \text{ G}$ (see Table 1). However, the short relaxation times of (t-DEC)⁺ at these temperatures are likely to make the spectrum registration impossible. Assuming that in the high-temperature limit the degenerate states are equally populated, it is quite easy to calculate the predicted second moment of (t-DEC)⁺ spectrum. As will be further demonstrated, this value agrees fairly well with that extracted from the experimental (t-DEC)⁺ MARY spectra taken at room temperature.

MARY Studies

As has been recently demonstrated,^{14,26–28} the coherent nature of spin-correlated radical ion pairs allows both the identification and reaction studies of short-lived pair partners by their MARY spectra. For a singlet-born radical ion pair the theoretical calculations predict the nonmonotonous dependence of singlet products yield vs external magnetic field in the region of weak fields^{29–33} due to level degeneracy and the resulting interference of different S–T conversion channels. For a sufficiently long-lived radical ion pair in the field where levels cross, the average singlet state population turns out to be greater than in its vicinity, resulting in narrow lines in MARY spectrum. The level crossing points H^* are determined by the set of hyperfine coupling constants in both of the pair partners. In particular, the effect of interference will announce itself at zero field for an arbitrary set of magnetic nuclei in one of the pair partners provided that the hyperfine couplings of the other are negligibly small.¹⁴ For radical ion pairs where the hyperfine interactions are substantial only for equivalent nuclei in one of the pair partners, local maxima in nonzero fields could also be observed. For systems with an integer total spin (e.g., for an even number of protons) the most intensive maximum would be found in the field equal to triple the hfi constant ($H^* = 3a$).^{27,32,34} In addition to the narrow lines the MARY spectra demonstrate a broad background, related to the effective spectrum width of the broad partner $\Omega = \sqrt{(2/3)\sum a_i^2 I_i(I_i+1)} = \sqrt{2\Delta^2}$.

Figure 5 shows the experimental MARY spectra of *cis*- (Figure 5a–e) and *trans*-decalin (Figure 5a'–e') solutions in cyclohexane at different concentrations taken at room temperature. Since the effects of coherence should be particularly pronounced for pairs with negligibly small hfi in one of the partners, *p*-terphenyl-*d*₁₄ (PTP) was chosen as electron scavenger and luminophore. Because of magnetic field modulation the spectra are first derivatives of the corresponding signals. In the absence of decalin in the solution (Figure 5a,a') the spectrum constitutes a narrow single line at zero field, pertaining to the (PTP)⁺/(PTP)[−] pair with no broad signals. The width of the zero field line corresponds to the second moment of *p*-terphenyl-*d*₁₄ ions, and its phase reflects an increase in fluorescence intensity with increasing magnetic field. Thus, there are neither lines related to coherent effects nor broad background signals in neat cyclohexane, which makes it a suitable solvent for these experiments.

When *cis*-decalin is added to solution, the signal of its radical cation appears (Figure 5b'), whose MARY spectrum in hexane was identified earlier.²⁷ The latter consists of an inverted intense line at zero field, $H^* = 0 \text{ G}$, and a satellite line in the field $H^* = 150 \text{ G}$ superimposed on the background with the total width corresponding to the second moment of the (c-DEC)⁺ ESR spectrum. Since the spin evolution in *cis*-decalin radical cation is mostly driven by four equivalent protons with $a(4 \text{ H}) = 50 \text{ G}$ (Table 1), its MARY spectrum can be unambiguously identified by a line in the field $H^* = 3a$. The corresponding spectrum part (Figure 5b') is put into box for the sake of clarity. The lines in the fields $H^* = 0$ and $H^* = 3a$ result from the initial spin coherence in the radical ion pair (t-DEC)⁺/(PTP)[−] leading to observable features in the fields where spin energy levels cross.

In general, the obtained MARY spectra of *cis*-decalin in cyclohexane and their concentration transformations resemble those for hexane solutions.²⁸ As has been demonstrated,²⁸ the observed transformations of MARY spectrum shape (Figure 5b'–d') are due to the ion–molecular charge transfer reaction that the radical cations of *cis*-decalin take part in (reaction 2). With concentration increasing, the reaction grows faster, result-

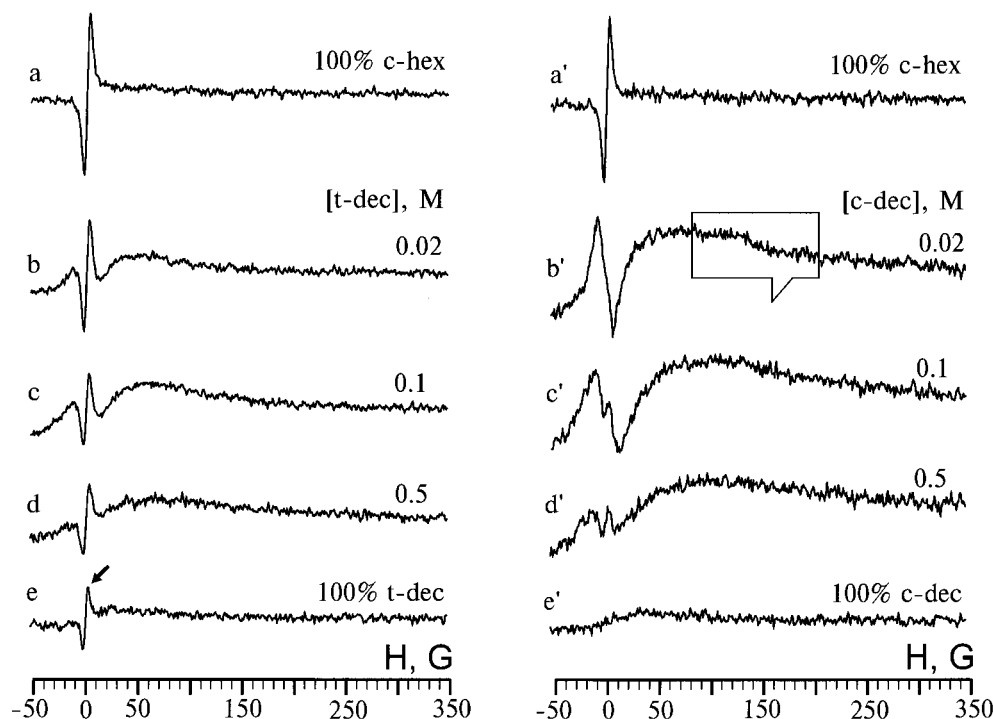
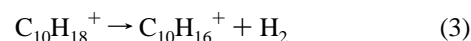


Figure 5. Experimental MARY spectra of *cis*- and *trans*-decalin solutions in cyclohexane at different concentrations. 10^{-3} M *p*-terphenyl- d_{14} added as luminophore. All spectra taken at room temperature. The satellite line of the *cis*-decalin radical cation at $H^* = 3a$ is boxed. Arrow marks narrow line of $(\text{PTP})^+ / (\text{PTP})^-$ pair.

ing in the corresponding broadening of individual spectrum components and the decrease of their intensities. The transformations are fairly well described by the theory.²⁸ The width of MARY lines is directly determined by the $(\text{c-DEC})^+$ exchange time τ_0 : $\Delta H \approx \Delta^2 / \tau_0$, which allows the study of this process. In line with the theory, in the region of slow charge transfer the satellite line at $H^* = 3a$ broadens and becomes unobservable at $(a\tau_0)^{-1} \approx 0.5$ (Figure 5c'), and the total breaking down of coherence and vanishing of the line at zero field requires that $(a\tau_0)^{-1} > 1$ (Figure 5d'). The spin system is then cast in the region of fast charge transfer. All spectrum peculiarities disappear, merging into a single structureless broad line which completely disappears in neat *cis*-decalin (Figure 5e'). The weak normal phase line at zero field observed in spectra of Figure 5c', d' is analogous to that in neat cyclohexane (Figure 5a') and pertains to the parallel processes involving *p*-terphenyl- d_{14} radical ions. Extracted by numerical simulation, the charge transfer rate constant for reaction 2 in diluted solutions is found to be $k \sim 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, being quite close to the diffusion-controlled one.

The MARY spectra of *trans*-decalin solutions in cyclohexane (Figure 5a–e) qualitatively resemble those of *cis*-decalin. However, some significant differences could be noticed. The broad line in the *trans*-decalin spectrum has somewhat less width, and there is no satellite line in nonzero fields. The inverted line at zero field is substantially suppressed, being overwhelmed by a much stronger narrow $(\text{PTP})^+ / (\text{PTP})^-$ line in normal phase. To get rid of this signal due to the hole capture by *p*-terphenyl molecules, experiments with lowered (10^{-4} M) *p*-terphenyl concentrations were carried out (Figure 6). In diluted *trans*-decalin solutions, where charge transfer reaction is practically turned off (Figure 6a), an intense central line ($H^* = 0$) of the MARY spectrum is observed. The following considerations let one ascribe the observed signal to the *trans*-decalin radical cations: (i) the spectrum does not practically depend on the solvent used; (ii) the spectrum transformation with increasing *trans*-decalin concentration testifies that the spectrum does not belong to the products of monomolecular

decay of *trans*-decalin radical cations (olefins):



(iii) the broad line observed corresponds to the second moment $\Omega = \sqrt{2\Delta^2} = 44 \text{ G}$ expected from the OD ESR experiments. The absence of a satellite line is also quite natural, taking into consideration the nonequivalence of protons in the high-temperature limit (see above).

In line with theoretical predictions the increase in *trans*-decalin concentration (similar to *cis*-decalin) leads to the loss of spin coherence in the pair, resulting in zero field MARY line broadening and the corresponding decrease of its amplitude (Figure 6a–d). The theory describes the observed spectrum transformation quite well provided that the hyperfine interactions in *trans*-decalin radical cation are driven by a set of nonequivalent nuclei (semiclassical description) with the total spectrum width $\Omega = 44 \text{ G}$.²⁸ Actually, as has already been discussed, the *trans*-decalin radical cation may be found in two close energy states with possible transitions between them. In these states the $(\text{t-DEC})^+$ hyperfine interactions are mostly due to two groups of protons with $a_1(4\text{H}) = 52 \text{ G}$ and $a_2(4\text{H}') = 35 \text{ G}$, respectively (Table 1). At low temperature the $^2\text{A}_g$ state is predominantly populated. The temperature elevation activates the dynamic transitions $^2\text{A}_g \leftrightarrow ^2\text{B}_g$, and the cation hfi will be $a_1(4\text{H}) \approx 25 \text{ G}$ and $a_2(4\text{H}') \approx 17 \text{ G}$ in the fast-exchange high-temperature limit. The $(\text{t-DEC})^+$ ESR spectrum experimentally observed in $\text{CF}_3\text{-cC}_6\text{F}_{11}$ at 77 K is quite close to $a(8\text{H}) \sim 22 \text{ G}$.³

To achieve a full correspondence between the experimental and theoretical MARY spectra, it turned out to be necessary to introduce quite a short intrinsic spin relaxation time ($T_1 \sim 7 \text{ ns}$) in the radical cation, not related to the charge transfer process (see solid and dashed lines in Figure 6a'). Under these assumptions the theory reproduces the experimentally observed transformation of $(\text{t-DEC})^+$ MARY spectrum with concentration (Figure 6a–d), and the derived charge transfer rate constant

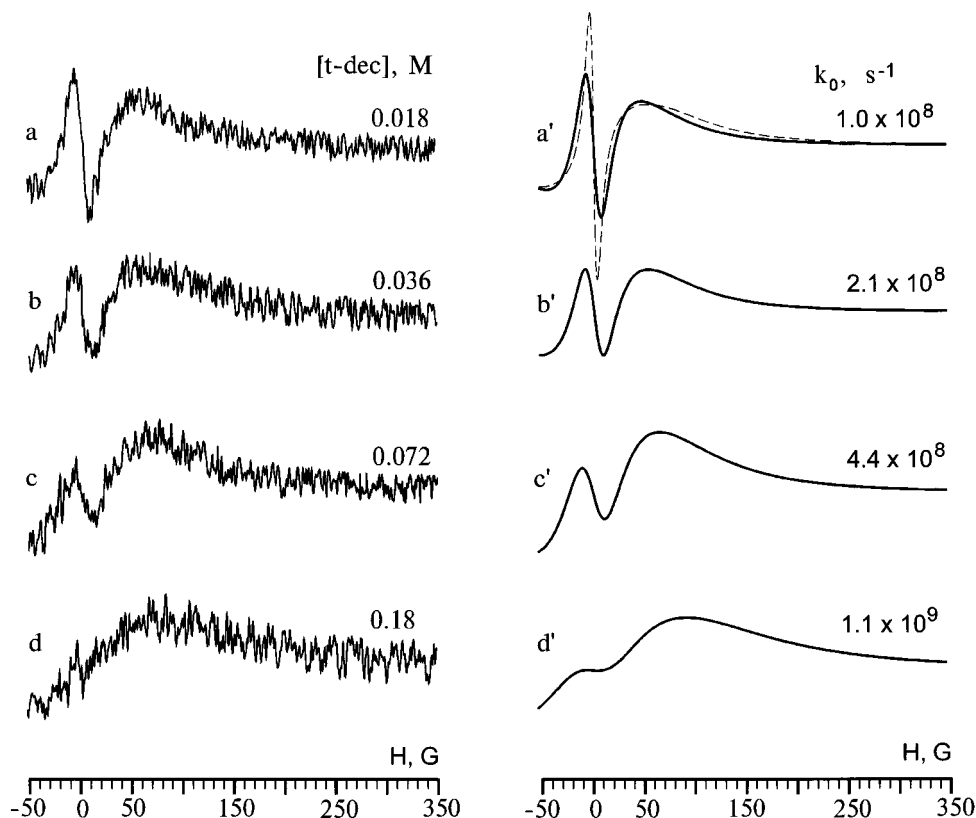


Figure 6. MARY spectra of *trans*-decalin solutions in cyclohexane at different concentrations: (a–d) experiment, all spectra taken at room temperature; (a'–d') calculated for different cation exchange rate $k_0 = 1/\tau_0$ with (t-DEC)⁺ ESR spectrum width $\Omega = 44$ G. Spin relaxation time $T_1 \sim 7$ ns in radical cation, not related to charge transfer processes, was introduced. Dashed curve (a') presents calculation in the absence of this relaxation. 10^{-4} M *p*-terphenyl-*d*₁₄ added as luminophore.

TABLE 2: Correlation between Existence of Dynamic Transitions and the Observability of OD ESR Signals for Radical Cations of Cyclic Alkanes

cation	<i>T</i> , K	type of motion	ref ^a	OD ESR (<i>T</i> , K)	ref
(c-C ₃ H ₆) ⁺	4–102	transitions between three states	2	none	this work
(c-C ₅ H ₁₀) ⁺	4–110	inversion/pseudorotation	2	none	9, 25
(c-C ₆ H ₁₂) ⁺	18–140	transitions between two or three states	2	none	10, 25 ^b
(Me-cC ₅ H ₉) ⁺	4–110	no transitions	2	present	25 ^b
(Me-cC ₆ H ₁₁) ⁺	4–173	transitions between two states	35	none (>77)	10 ^b
				present (35)	9
				present (4)	this work
(1,2-Me ₂ -cC ₆ H ₁₀) ⁺	4–173	no transitions	35	present	9
(1,4-Me ₂ -cC ₆ H ₁₀) ⁺	4–173	no transitions	35	present	9
(c-DEC) ⁺	4–170	no transitions	3	present	5 ^b
(t-DEC) ⁺	4–125	transitions between two states	3	none (>77)	7 ^b
				present (4–45)	7 ^b

^a Studied by ESR in Freon matrix. ^b This work also.

for reaction 2 $k = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is quite close to the diffusion-controlled one in cyclohexane.

Discussion

The analysis demonstrates that the peculiarities of the *trans*-decalin OD ESR and MARY spectra at high temperatures root in the quasi-degeneracy of electron levels and the related dynamic transitions and spin relaxation due to strong spin–orbital interaction. We consider this fact to be important for understanding the temperature transformations of the OD ESR spectra of other cyclic alkane radical cations in nonpolar solutions.

It is well-known that the highest occupied molecular orbital in radical cations with certain elements of symmetry (methane, ethane, some cyclic alkanes) is degenerate. Because of the instability of degenerate electron states these cation radicals are cast to distorted geometry of a lower symmetry (the Jahn–Teller

effect). The dynamic transitions between close potential wells existing in these cations can be experimentally observed using ESR.² The activation energy of the transitions is typically not large, 0.2–0.3 kcal/mol. The introduction of substitutes can eliminate orbital degeneracy.

Table 2 summarizes the knowledge about the degenerate states in cyclic radical cations obtained by ESR in Freon matrices, as well as the information about the observation of their OD ESR spectra in alkane solutions. These data demonstrate that the absence of degeneracy in radical cations should be treated as the necessary condition for observation of its OD ESR spectrum. In fact, the table shows that introducing two methyl groups into the C₆ ring completely eliminates degeneracy (dimethylcyclohexane). There are no dynamic transitions in this system, and the corresponding OD ESR spectra may be readily obtained even in liquid solution.⁹ The presence of a single methyl group eliminates degeneracy only partially, and the

intramolecular dynamic processes just grow a bit slower. In this case the OD ESR signals amplitude appears to be temperature dependent, and the lines of the corresponding radical cations arise at temperatures below the nitrogen one (methylcyclopentane, methylcyclohexane). In highly degenerate systems (cyclohexane, cyclopropane) no OD ESR signals can be observed even at 4 K. Therefore, one could conclude that the degeneracy in the system of electron levels leading to spin relaxation in radical cation due to strong spin-orbital interaction is responsible for the absence of the signals of cyclic alkane radical cations at high temperatures. The argument in favor of a strong spin-orbital interaction is the anomalous shift of *g*-factor, typical of all cycloalkanes studied.²² *trans*-Decalin seems to be an intruder in this group since in its case the degeneracy results from an accidental coincidence of electron level energies rather than from the presence of some required elements of symmetry.

The closeness of the rate constants for ion-molecular charge transfer reaction in *cis*- and *trans*-decalin solutions to the diffusion-controlled one should be explicitly mentioned. It is well-known that the rate constant for hole transfer from donor to acceptor with lower ionization potential depends on the difference in their ionization potentials ΔI .^{36,37} In the region of small ΔI the reaction of hole transfer from donor to acceptor slows down, and when $\Delta I \rightarrow 0$ its rate drops by many orders of magnitude because of the energy expenses on media reorganization and the tuning of intramolecular bonds of reagents. Obviously, the charge transfer between identical molecules of *cis*- or *trans*-decalin does not obey this law and proceeds much faster. This result agrees with the known fact^{12,38-40} that in neat *cis*- and *trans*-decalin the holes have super high mobility. It is generally believed that this mobility is provided by the holes hopping due to ion-molecular charge transfer, which yields higher mobilities as compared to common molecular diffusion.

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