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Highly Mobile Solvent Holes in Viscous Squalane Solutions As Detected by Quantum Beats and MARY Spectroscopy Techniques

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The quantum beats and magnetic field effect on the reaction yield spectroscopy techniques were employed to study the formation of diphenyl sulfide radical cations in squalane solutions under ionizing irradiation. It is demonstrated that the precursors of diphenyl sulfide radical cations are short-lived primary solvent radical cations (holes) with the electron spin resonance spectrum narrowed by the resonance charge transfer reaction. The rate constant of hole scavenging by diphenyl sulfide molecules was measured directly and amounts to 6.1×10^9 M^{-1} s^{-1}, exceeding the diffusion-controlled one several times. The obtained value is well in line with the data on pulse radiolysis of squalane solutions with optical monitoring of the highly mobile precursor, supporting the hypothesis about the hole nature of the latter.

Introduction

Highly mobile positive charge carriers in hydrocarbons were discovered by Warman[1] when studying pulse radiolysis of the cyclic alkanes, cyclohexane, and *trans*-decalin. The microwave conductivity experiments yielded the mobilities of the carriers exceeding 20−40 times the diffusion-controlled ones, with the lifetimes of tens to hundreds of nanoseconds in the absence of scavengers. The existence of these species in cyclohexane was also confirmed by the dc conductivity experiments with laser multiphoton ionization.[2,3] The recent progress in the pulse radiolysis technique allowed for obtaining the optical absorption spectra of the short-lived intermediates and for measuring the rate constants of their scavenging by acceptors.[4,5] All these experiments demonstrate an extremely high reactivity of the cations, accenting their importance for the primary radiation chemistry transformations in hydrocarbons. Apart from cyclic alkanes, similar highly mobile solvent cations have recently been detected in the long-branched hydrocarbon squalane by the pulse radiolysis technique.[6] Although the experimentally observed mobility is lower than that of cyclohexane by an order of magnitude, it is still several times higher than the diffusion-controlled limit for squalane.

Most of the investigators today tend to accept the hypothesis[1] that the highly mobile primary positive species forming in the alkane radiolysis are the solvent radical cations (holes), *e.g.*, $C_6H_{12}^{+\bullet}$. Fast (resonance) ion−molecule charge transfer of the latter can generally lead to a hyperdiffusional transport in solution. The extremely high mobility of holes in cyclic alkanes is usually related to the presence of a rigid six-member ring in the molecular skeleton, favoring the resonance transfer. According to this mechanism, both the hole positive charge and its spin are localized on the same molecule. However, an alternative point of view has been put forward[7] for when a cation being a product of the molecular transformations of the solvent holes serves as a mobile carrier. In this case the charge transport proceeds *via* the proton H$^+$ (a spinless species) transfer between a solvent molecule and its protonated counterpart (*e.g.*, $C_6H_{13}^+$).

Techniques based on the effects of spin coherence[8,9] in the recombination of radical ion pairs can provide unambiguous confirmations to the hypothesis on the hole nature of the highly mobile positively charged species in irradiated alkanes. These techniques are sensitive exclusively to processes involving cation and anion radicals, completely ignoring any spinless ions.

It is well known that in a radical pair the dynamic transitions between the levels of different multiplicities take place. The transitions result from the coherent initial state of the pair. Being nonstationary, it leads to singlet−triplet oscillations in the system, making it possible to directly observe the spin dynamics in the pair by monitoring the recombination fluorescence kinetics of the sample.[10] Employing this principle, two new techniques to study the primary processes in alkane radiolysis have been designed: the quantum beats spectroscopy[11−13] and the Zeeman level crossing, or magnetic field effect on the reaction yield (MARY) spectroscopy.[14−16]

Quantum beats have thus far been observed in the recombination of spin-correlated radical ion pairs generated by ionizing radiation in saturated hydrocarbons with added electron and hole acceptors.[11−13,17] As has been recently demonstrated on the example of isooctane,[18] the method allows extraction of the hole-scavenging rate constant from the phase shift of the oscillations, provided that the electron spin resonance (ESR) spectrum of the holes is narrowed by fast charge transfer.

As opposed to the quantum beats technique, yielding kinetic information, the effect of the spin-correlated radical ion pair level crossing[15] can be utilized for an identification of radicals involved in a magnetosensitive reaction. Furthermore, a modification of the technique (MARY−ESR) allows taking the ESR spectra of radical cations without microwave pumping.[19] This method has recently been employed to detect the ESR spectrum of squalane holes at room temperature.[20] So an opportunity to compare the pulse radiolysis data and the data from the quantum beats method on hole scavenging without any *a priori* assumptions about the spectrum structure has emerged for the first time.

In the present work the rate constant for squalane hole scavenging by a diphenyl sulfide molecule is directly obtained

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using the quantum beats technique. The value obtained agrees quite well with the data on pulse radiolysis of squalane solutions,[6] giving stronger background to the hypothesis about the hole nature of the highly mobile solvent cations in squalane.

Experimental Section

The recombination fluorescence was monitored using the photon-counting technique as described elsewhere.[18] The radioactive isotope ^{90}Sr with activity of about 5 μCi served as a source of ionizing radiation. The external magnetic field was provided by a Varian (E-3) electromagnet with pole concentrators, giving the field of up to 9600 G with inhomogeneity better than 2 G at the sample location. Photons were detected by a fast microchannel photomultiplier tube (PMT) with the single-photon pulse rise time less than 200 ps. The fluorescence from the luminophore excited singlet state was separated by a cutoff light filter, $\lambda < 350$ nm. Time resolution of the setup was about 700 ps, and the fluorescence kinetics were reproducible with an accuracy allowing extraction of the time lag of the beats within 200 ps.

The following procedure was adopted to extract the phase of the beats. To separate the oscillating contribution, the kinetics $I(t)$ was taken two times for each sample: in a strong field H_{MAX} (9600 G), where the oscillations are rather pronounced, and in a weak one H_{MIN}, where the oscillations are virtually absent. The weak field used (170 G) was close to the residual field of the magnet. For the analysis of the phase shift of the beats the ratio of the kinetics $I_{MAX}(t)/I_{MIN}(t)$ was used. As has already been demonstrated, such a processing technique allows one not to consider the complex kinetic profile of the intratrack counterion recombination.[18] Since under β-particle irradiation, the fluorescence results from the consequential events of the counterion recombination and the radiative deactivation of the excited recombination products; the observed time profile is actually a convolution of the kinetics with the luminophore fluorescence lifetime. For a luminophore with a short radiative time (p-terphenyl) the following expression approximately holds

$$I_{MAX}(t)/I_{MIN}(t) \propto W'_{MAX}(t)/W'_{MIN}(t) \tag{1}$$

where $W'(t)$ is the convolution

$$W'(t) = \tau_{fl}^{-1} \int_0^t e^{-(t-\xi)/\tau_{fl}} W_S(\xi) \, d\xi \tag{2}$$

Here $W_S(t)$ is the singlet state population of the radical ion pair at time t. The convolution was performed numerically. The fluorescence lifetime τ_{fl} measurements were carried out with the same samples. The fluorescence was excited by the pulses of Čerenkov light, arising from electrons passing through a 45 mm quartz converter. In the absence of diphenyl sulfide the fluorescence lifetime of PTP-d_{14} amounted to 1.23 ± 0.04 ns, agreeing well with the known literature value of 1.19 ns.[21] No fluorescence quenching was observed when raising the diphenyl sulfide concentration, and this value remained constant within the accuracy of the experiment. The fluorescence lifetime thus obtained was then used to determine the phase shifts and the capture times.

The MARY spectroscopy setup has been described elsewhere.[15] About 1 mL of the sample solution in a quartz cuvette was put into the magnetic field of a BRUKER ER-200D ESR spectrometer, equipped with an X-ray tube for irradiation and a PMT. The fluorescence was registered with modulating the external magnetic field at 12.5 kHz and lock-in detection, yielding the first derivative of the signal. No microwave pumping was applied.

Diphenyl sulfide-d_{10} (DPS-d_{10}) and p-terphenyl-d_{14} (PTP-d_{14}) were used as acceptors for quantum beats experiments. To avoid hole scavenging by p-terphenyl-d_{14} molecules, the concentration of the latter was taken rather low (10^{-3} M). The experiments with this concentration of PTP-d_{14} and with 2×10^{-4} M of PTP-d_{14} appeared to give identical results. MARY spectra were taken using hexafluorobenzene C_6F_6 as an electronacceptor with equivalent nuclei. The hexafluorobenzene concentration in the solution was taken sufficiently low to suppress the $C_6F_6^-$ line broadening due to charge transfer reaction. In our experimental conditions its contribution to the overall line widths was about 1 G. The solvent, squalane (2,6,-10,15,19,23-hexamethyltetracosane, 99%, Merck), was purified on a chromatographic column with alumina activated with silver nitrate (10%). The solvent purity was monitored by its UV absorption spectrum, the fraction used had its optical density equal to 1 in a 1 cm layer at the wavelength 210 nm. We estimate the amount of unsaturated impurities (particularly, olefins) in the fresh purified solvent is less than 10^{-4} M. Diphenyl sulfide was purified by distillation. The solutions were degassed to $\sim 10^{-3}$ Torr by repeated freeze−pump−thaw cycles and sealed off in thin-walled quartz cuvettes. All experiments were carried out at ambient temperature. The values of g-factors (2.00 28) and spectrum widths $\Delta = (\sum a_k^2 \, I_k(I_{k+1})/3)^{1/2} = 0.68$ G for (PTP-d_{14})$^-$ and 2.00 39 and 10.6 G, respectively, for squalane radical cations, necessary for simulations, were taken from the literature.[22,23] The g-factor value of 2.00 82 for (DPS-d_{10})$^+$ was found from the frequency of oscillations.

Results and Discussion

The Quantum Beats Study. In the primary event of solvent ionization a free electron and a solvent hole are formed. The electron spins of the counterions are correlated, and the initial (singlet) state of the pair is nonstationary. In a static external magnetic field the dynamics of the singlet−triplet (S−T) transitions are governed by Zeeman and hyperfine interactions (HFI) of electron spins, and the multiplicity of the forming excited products [1,3]P* corresponds to the multiplicity of the pair (S, T) at the moment of recombination. Electron capture by acceptor (PTP-d_{14}) molecules proceeds rather fast because of their high mobility, but the holes are scavenged in a slower reaction

$$S^+ + D \xrightarrow{k_0} S + D^+ \tag{3}$$

where S stands for a solvent molecule and D for the hole acceptor (DPS-d_{10}), respectively. As a result, the oscillations in a (DPS-d_{10})$^+$/(PTP-d_{14})$^-$ radical ion pair start with a certain offset in time, resulting in a phase shift of the beats and damping of the beats amplitude. Monomolecular decay of the holes, track recombination with counterions, and spin relaxation all compete with this process, diminuating the phase shift and diminishing the observed amplitude of the beats.

To obtain a quantitative description of the radical ion pair spin dynamics the equations for density matrix were solved numerically. The simulation procedure allowed consideration of the finite spectrum widths, ion−molecular charge transfer rates, and lifetimes of the pair partners, as well as hole-scavenging processes in the track. On the other hand, as has already been pointed out,[18] it is possible to provide a simple analytical description of the quantum beats profile given that the HFI in S$^+$ are averaged down to 0 by fast charge transfer, and there are no HFI in (DPS-d_{10})$^+$. Under these conditions the numerical calculations and a simple exponential model yield quite similar results. For brevity, below only the analytical

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description of the beats profile is presented, the details of the numerical procedure will be presented elsewhere.

Assuming homogeneous spectra for both S^+ and $(DPS\text{-}d_{10})^+$, the singlet yield from the pairs $S^+/(PTP\text{-}d_{14})^-$ and $(DPS\text{-}d_{10})^+/(PTP\text{-}d_{14})^-$ is given by[18]

$$G_{13} = \frac{1}{2}[e^{-(k_0+k_1)t} + e^{-(k_0+k_1^*)t}\delta\cos(\omega_{13}t)] \qquad (4)$$

$$G_{23} = \frac{k_0}{2k_{12}^*}[R(t) + e^{-k_2^*t}\delta\cos\varphi\cos(\omega_{23}t - \varphi)] \qquad (5)$$

respectively, $\omega_{ij} = (g_i - g_j)\beta H\hbar^{-1}$ being the frequencies of the beats in the static external magnetic field H, and indices "1", "2", "3" referring to S^+, $(DPS\text{-}d_{10})^+$, and $(PTP\text{-}d_{14})^-$, respectively. $k_0 = k[D]$, where k is the rate constant for bimolecular hole scavenging and $[D]$ is the DPS concentration. $k_{12} = k_0 + k_1 - k_2$, where k_1 and k_2 are the total rates of depletion of holes and acceptor cations, respectively, in the course of track recombination and monomolecular decay reaction, $k_{12}^* = k_0 + k_1^* - k_2^* = k_0 + k_{dec}$, where $k_i^* = k_i + 1/T_2^{(i)}$ are the observed rates of the beats' decay for the first and the second channel. $\varphi = \arctan(\omega_{12}/k_{12}^*)$ is the angle of the phase shift of the oscillations. $\delta = \exp(-0.5\Delta_3^2 t^2)$ is the oscillations' damping factor due to the inhomogeneous spectrum width of $(PTP\text{-}d_{14})^-$, and finally, $R(t)$ is a smooth background

$$R(t) = \frac{k_{12}^*}{k_{12}}(1 - e^{-k_{12}t}) - e^{-(k_0+k_1^*)t}\delta\cos\varphi\cos(\omega_{13}t - \varphi) \qquad (6)$$

The total yield of pairs recombining to give singlets in both recombination channels is

$$W_S(t) = [G_{13}(t) + G_{23}(t)]\Theta + \frac{1}{4}(1 - \Theta) \qquad (7)$$

where it has been taken into account that singlet correlated pairs comprise only a fraction $\Theta \leq 1$ of the total number of recombining pairs (*e.g.*, refer to ref 24).

It should be noted that quantum beats from the primary pairs $S^+/(PTP\text{-}d_{14})^-$, given by the G_{13} term, could be observed in strong fields even without any acceptor (DPS).[17] However, the contribution of this channel to the total fluorescence yield of the sample decays exponentially with the time constant of the hole scavenging (decay), so only the beats from the pairs involving acceptor molecules $(DPS\text{-}d_{10})^+/(PTP\text{-}d_{14})^-$ will remain at longer ($t > 20$ ns) times. In this time domain the singlet yield oscillates with the frequency ω_{23}, and the phase shift is determined only by the rate of hole scavenging and by the g-factor shift (ω_{12})

$$\omega_{12}\cot\varphi = k[D] + k_{dec} \qquad (8)$$

Thus, the hole-scavenging rate constant can be extracted from the slope of the concentrational dependence of $\omega_{12}\cot\varphi$. The expression (eq 8) is the basis for determining the rates of primary short-lived solvent holes scavenging by acceptors with lower ionization potentials. The experimentally measured phase shift values φ unambiguously determine the scavenging rate, since g-factors of the corresponding radicals are known. When the acceptor concentration is decreased, $k_0 \rightarrow 0$, the phase shift tends to its maximum value, $\varphi_{max} = \arctan(\omega_{12}/k_{dec})$, making it possible to also obtain the hole lifetime in the absence of scavengers k_1^*, since the value of k_2 could be extracted from the experimentally observed damping of the oscillations.

Figure 1a–c shows the quantum beats from the solutions of 10^{-3} M PTP-d_{14} and DPS-d_{10} at different concentrations in
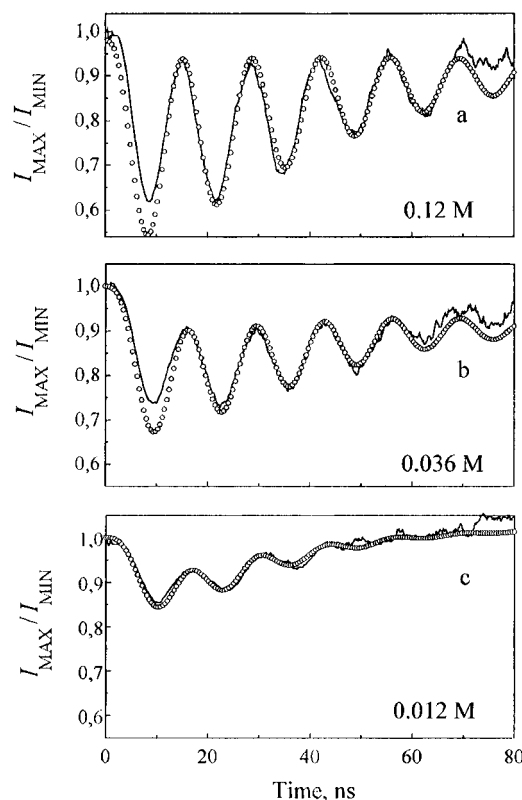
Figure 1. Quantum beats for the solutions of 10^{-3} M *p*-terphenyl-d_{14} in squalane and different concentrations of DPS-d_{10}: (a) 0.12 M; (b) 0.036 M; (c) 0.012 M. Solid lines indicate values taken from experiment, and circles represent those from simulation. The solution was held at ambient temperature.

squalane, taken at room temperature. The presented curves are the ratios of the recombination fluorescence kinetics I_{MAX}/I_{MIN} and clearly demonstrate the transformations of spin dynamics with slowing hole scavenging. At high concentrations of DPS-d_{10} (Figure 1a) the hole capture is almost instant. Correspondingly, the beats' amplitude reaches its maximum and no phase shift is observed, implying that almost all radical cations− precursors of $(DPS\text{-}d_{10})^+$ are effectively captured by acceptor molecules. When the DPS-d_{10} concentration is decreased, the beats drop in amplitude (Figure 1b) and almost vanish in strongly diluted solutions (Figure 1c). It could be noticed that parallel to the drop in amplitude, an offset (lag) of the beats emerges, its magnitude not exceeding a quarter of a period. So this picture agrees qualitatively with the predictions of the theory. Expressions 3 and 4 provide a quantitative description of the process of hole capture by an acceptor. The dots in Figure 1 give the results of the theoretical calculation according to (eq 1). All the curves were obtained using the same set of parameters: $k = 6.1 \times 10^9$ M^{-1} s^{-1}, $k_1^* = 0.11 \times 10^9$ s^{-1} ($\tau_1^* = 9$ ns), and $\Theta = 0.22$. This Θ-value is lower than that (0.6) obtained in magnetic field effect experiments.[25] The possible origin of this discrepancy is that only primary solvent holes are responsible for quantum beats in a viscous solvent while olefin cations contribute also to the magnetic field effect.[24] The observed rate of the beats' decay depends on the concentration of DPS-d_{10} in solution and within the experimental accuracy changes from $k_2^* = 0.017 \times 10^9$ s^{-1} (0.12 M) to $k_2^* = 0.03 \times 10^9$ s^{-1} (0.012 M). As the figure demonstrates, this simple theoretical model describes quite satisfactorily the transformations of kinetic profiles at long times ($t > 15$ ns) with dilution of the solution. At shorter times the theory and the experiment diverge slightly, and the amplitude of the first oscillation is lower than predicted. The discrepancy must result from an ap-
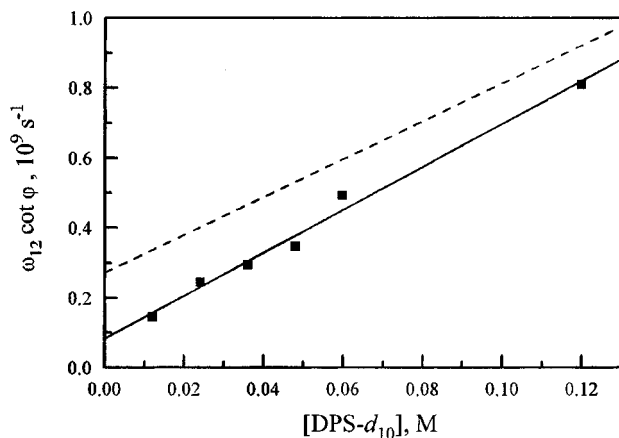
Figure 2. The dependence of $\omega_{12} \cot \varphi$ on the concentration of DPS-d_{10} in solution. Squares are experimental points. The solid line is the linear approximation. The dashed curve represents the simulation for an olefin cation with a broad spectrum, $\Delta = 25.2$ G, as a precursor of $(DPS-d_{10})^+$.

**TABLE 1: Rate Constants of Squalane Hole Scavenging by Acceptors at 293 K**

acceptor	k, 10^9 M^{-1} s^{-1}	ref
TMPD[a]	6.5	6
DPS-d_{10}	6.1	this work
triethylamine	6.0	6
biphenyl	3.8	6

[a] N,N,N',N'-tetramethyl-p-phenylenediamine.

proximate character of the expression (eq 1) in the vicinity of the abrupt recombination kinetics falloff.[18] The oscillations at times of about 1 ns arise from a drift of the fluorescence profile maximum ($\sim$200 ps) and do not cause any major aberrations at long times.

Measuring the phase shift allows one to determine the rate constant of hole scavenging by acceptor molecules and the monomolecular hole decay rate in a straightforward fashion (expression 7). The experimental dependence of $\omega_{12} \cot \varphi$ on the DPS concentration is shown in Figure 2. Within the accuracy of experiment the data points lie on a straight line, its slope yielding the scavenging rate constant and y-axis intercept giving the decay rate. For the rate constant of squalane hole scavenging by diphenyl sulfide molecules, this procedure yields $k = (6.1 \pm 1) \times 10^9$ M^{-1} s^{-1}, which agrees well with the data on pulse radiolysis for other acceptors[6] and exceeds the diffusion-controlled one several times (Table 1). The decay rate constant $k_{\text{dec}} = k_1^* - k_2^*$ is obtained from Figure 2 by a linear approximation to infinite dilution and amounts to $k_{\text{dec}} = (0.083 \pm 0.02) \times 10^9$ s^{-1}.

The simple analytical description of the beats profile, eqs 3 and 4, can be derived only if it is assumed that the hyperfine structure of the squalane hole S^+ is completely averaged out by fast spectral migration. If this is not the case, a numerical simulation making use of additional information on the ESR spectrum structure of the primary cation is required. The high experimental rates of hole scavenging seem to result from high hole mobility due to fast hopping over the solvent molecules. Assuming diffusional motion of the holes over the closest neighbors, the mean residence time can be readily estimated $\tau_{\text{res}} \approx 4 V_{\text{mol}}/k = 330$ ps, where $V_{\text{mol}} = 0.5$ M^{-1} is the squalane molar volume. It is clear that charge transfer and, consequently, fast frequency exchange will average the HFI and shrink the hole spectrum into a narrow line of the width $1/T_2^{(1)} = \Delta_1^2 \tau_{\text{res}} = 0.65$ G, thus lending support to the assumption about the homogeneity of the hole spectrum.
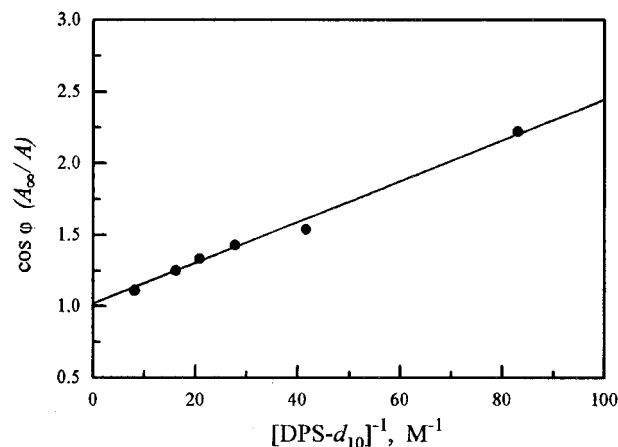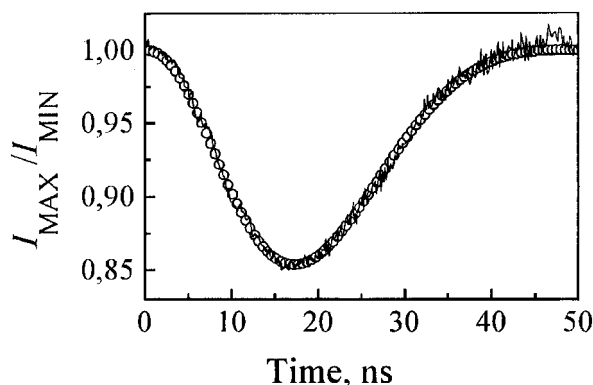

Figure 3. Stern-Volmer plot of the beats' amplitude $(A_\infty/A) \cos \varphi$ *vs* the reciprocal of the DPS-d_{10} concentration. Circles are experimental points. Solid line is the linear approximation.

For a comparison the dashed curve in the same figure shows the result of numerical calculation of $\omega_{12} \cot \varphi$ *versus* acceptor concentration, assuming that an olefinic radical cation with a broad unresolved spectrum of the width $\Delta = 25.2$ G[26] serves as a precursor to $(DPS-d_{10})^+$ and there is no charge transfer. The rates of scavenging were taken to be equal for both cases. For a fixed scavenging rate constant, the line slope deviates only slightly from the actual value ($\sim$10%) (Figure 2), justifying the application of this technique of scavenging rate constant measurement irrespective of any assumptions about the precursor spectrum structure. It could be noticed that the inhomogeneous width of the precursor appears in a greater y-axis intercept. Significantly smaller experimental intercepts (Figure 2) allow one to exclude cations of olefins from the list of possible precursors to DPS radical cations. Another reason to ignore olefins is the high value of the rate constant extracted from the slope, since the scavenging of olefin radical cations would have proceeded at rates not exceeding the diffusion-controlled one $((0.6 \div 1.5) \times 10^9$ M^{-1} s$^{-1})$.[6,16,27] The above mentioned considerations allow us to conclude that it is a squalane hole that serves as the main precursor of $(DPS-d_{10})^+$.

As follows from expression 4 the amplitude of the beats from secondary pairs depends on the acceptor concentration, reflecting both the fraction of holes captured and the phase shift of the oscillations as $A \sim (k_0/k_{12}^*)\Theta \cos \varphi$. In the limit of high acceptor concentrations, the beats' amplitude reaches the plateau A_∞, which depends only on Θ. The dependence of amplitude upon acceptor concentration follows a modified Stern−Volmer expression

$$(A_\infty/A) \cos \varphi = 1 + (k_{\text{dec}}/k)[D]^{-1} \qquad (9)$$

from which one can obtain the decay rate of the holes k_{dec} independently, provided that the scavenging constant rate is already known. The function of the beat amplitude corresponding to the left hand side of eq 9 plotted *versus* the reciprocal of the DPS-d_{10} concentration is shown in Figure 3. Experimental points fit a straight line, the slope of which yields the ratio of the decay and scavenging rate constants $k_{\text{dec}}/k = (0.014 \pm 0.001)$ M. Substituting the value of k obtained above, one finds the hole decay rate of $k_{\text{dec}} = 0.085 \times 10^9$ s^{-1}, coinciding with the phase shift analysis result. Using the known value of the beats' decay rate k_2^* and ignoring the contribution from the relaxational width of the hole, the latter yields for the hole lifetime in solution $\tau_1 = 9$ ns ($k_1 \cong k_1^* = 0.11 \times 10^9$ s^{-1}), which is close to the characteristic time of squalane hole intratrack decay, $\sim$12 ns, known from the pulse radiolysis experiments.[6]

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Figure 4. Quantum beats from the solution of 10^{-3} M p-terphenyl-d_{14} in squalane in the absence of DPS-d_{10}. Solid line indicates values taken from the experiment at ambient temperature. Dotted line indicates the theoretical calculation with parameters $\Theta = 0.2$, $\tau_1^* = 19$ ns.

According to eq 3, quantum beats could be observed even in the absence of acceptor (DPS). In this case the beats arise in the primary pair $S^+/(PTP\text{-}d_{14})^-$ due to the g-factor difference of the pair constituents. Since for squalane radical cations the difference is not large, the oscillations are degenerate in the fields below 2 T.[17] Figure 4 shows the quantum beats for the solution of 10^{-3} M PTP-d_{14} in squalane without diphenyl sulfide added. The experimental profile is just a single spike of the beats with the decay decrement being close to the beat period. The profile of the beats from primary pairs is also described by the general expression 6, but the parameter k_1^* (the rate of the beats decay) no longer has a recombinational contribution since the latter is disposed of during the normalization procedure (eq 1). Thus, the beats from the primary pairs $S^+/(PTP\text{-}d_{14})^-$ have the monomolecular decay rate as the single adjustable parameter as opposed to the beats from acceptors which bear the information about the total rate of hole decay in the processes of hole capture, track recombination, and monomolecular decay. As follows from Figure 4, the theory and the experiment can be reconciled with the following set of parameters: $\tau_1^* = 19$ ns ($k_1^* = 0.053 \times 10^9$ s^{-1}) and $\Theta = 0.2$. The fraction of spin-correlated pairs, Θ, for the primary pairs is identical to that extracted from the beats from acceptors (DPS-d_{10})$^+$/(PTP-d_{14})$^-$, and the hole lifetime τ_1^* agrees well with the data on pulse radiolysis for squalane 20 ns.[6]

The data presented show that in the case of squalane the value $\Theta = 0.22 \pm 0.02$ for the fraction of spin-correlated pairs describes satisfactorily the entire body of experimental data. At the same time, similar studies of a series of solvents[24] demonstrated that, for nonviscous alkanes (isooctane, hexane, cyclohexane, decalin), the observed fraction of singlet-correlated pairs is about two times higher ($\Theta = 0.35 \div 0.56$) than for squalane. One can hardly find any physical reasons for such a difference. Obviously, the fraction of spin-correlated pairs is determined by the track density (linear energy transfer upon ionization) and by the electron thermalization length and should be approximately the same for all hydrocarbons studied. An explanation could be that the low amplitude of the beats in squalane results from some parallel reactions, *e.g.*, the recombination of (PTP-d_{14})$^-$ with olefin radical cations forming in the track at the instance of ionization. As can be deduced from the pulse radiolysis results,[6] introducing a certain amount ($10-15\%$) of such ions at $t = 0$ improves the agreement between theory and experiment.

The MARY Spectroscopy Study. Apart from the quantum beats technique yielding kinetic information about the radicals involved in a magnetosensitive reaction, the effect of level crossing in spin-correlated radical ion pairs (dubbed the MARY
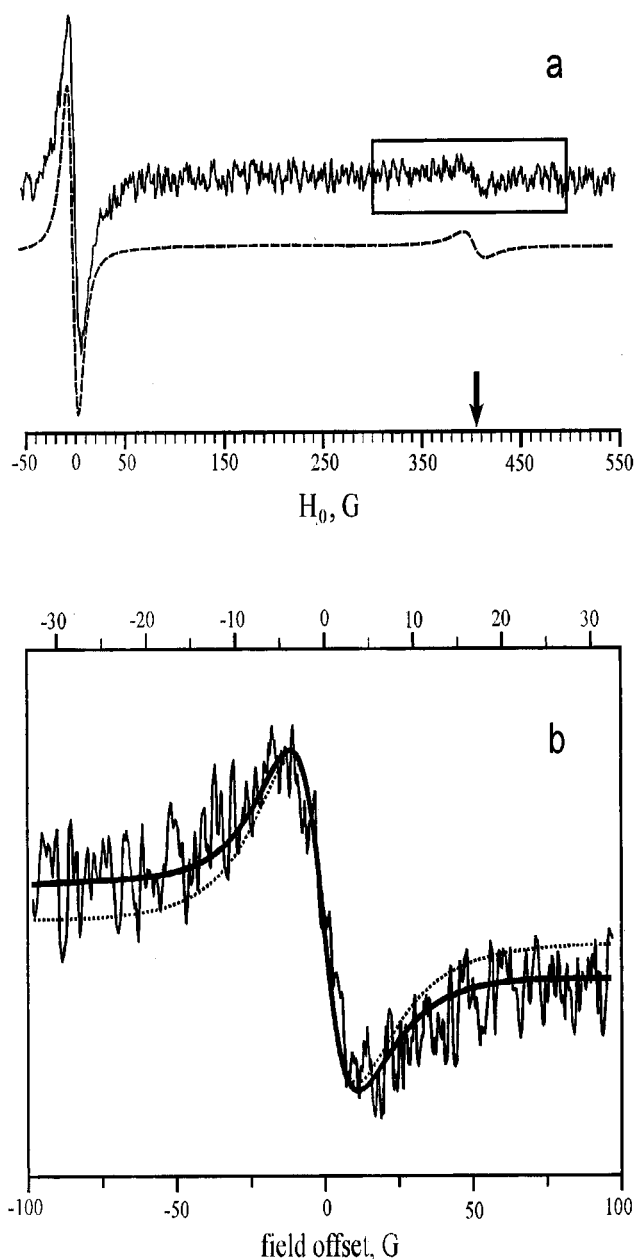
Figure 5. (a) MARY spectrum from the solution of 1.2×10^{-2} M hexafluorobenzene in squalane. Dashed line represents the simulation for squalane hole ($\Delta = 10.6$ G, $(\tau_{\text{res}})^{-1} = 3 \times 10^9$ s^{-1}). The satellite line at $H^* = 3a$ is put into the box. The center of the line is marked by the arrow at the axis. (b) MARY spectrum in the vicinity of the satellite line (MARY$-$ESR of squalane holes). Bottom axis is the field offset ($H-H^*$); top axis is the corresponding ESR field offset. Spectra were taken at ambient temperature.

spectroscopy) gives spectral information about the pair partners and, in the case of squalane, allows one to arrive at a definite conclusion about the homogeneity of the hole spectrum. Furthermore, a modification of the technique (MARY$-$ESR) helps one get the ESR spectrum of the holes.

Figure 5a shows an experimental MARY spectrum of the 1.2×10^{-2} M solution of hexafluorobenzene in squalane, taken at room temperature. Together with a pronounced signal at zero field, a satellite line dwells in the field $H^* = 405$ G (marked by an arrow). As has been recently demonstrated,[15] the line allows one to ascribe the observed spectrum to hexafluorobenzene radical anion, the hyperfine coupling constant of which is known to be $a(6F) = 135$ G.[22] Since the spectrum observed is formed in the process of the spin-correlated radical ion pair recombination, it comes naturally that the partners of $C_6F_6^-$ be

the solvent holes and the cations or radiolytic products (olefins) because we intentionally did not add any hole acceptors to the solution. To preclude the hole capture, the solvent was thoroughly purified from traces of impurities with low ionization potential (IP) (aromatics and olefins), and the high IP of the hexafluorobenzene molecule prevents positive charge transfer from a solvent molecule.

The shape of the spectrum lines (Figure 5) identifies the hole nature of the cation. As has been recently demonstrated,[19] the lines of MARY spectra are sensitive to the distribution of magnetic nuclei over the pair partners. The presence of HFI in the cation splits the satellite line of hexafluorobenzene in the field $H^* = 3a$ by the projection of the total nuclear spin M_Z in the cation, leading to broadening and to a drop in amplitude of the line. The width of the central line in the field $H^* = 0$ remains practically unchanged, reflecting only the relaxational properties of the system.[28] Consequently, the full spectrum helps conclude the homogeneity of the cation spectrum. When the HFI in the cation are completely averaged down by fast charge transfer, the ratio of the widths of the lines depends exclusively on the slopes of the pair electron terms in the crossing points $H^* = 0$ and $H^* = 3a$. For hexafluorobenzene, where MARY signals result mainly from the nuclear subensemble with total spin $I = 2$, this ratio is close to 3. Inhomogeneity of the cation ESR spectrum leads to additional broadening of the satellite line over this value.

To provide an example, the dashed curve in Figure 5a gives the result of simulations for squalane radical cation in the conditions of strong spectrum narrowing due to fast ion–molecular charge transfer over the matrix molecules. As a starting nonperturbed spectrum, a broad inhomogeneous Gaussian-type profile with $\Delta = 10.6$ G was taken. The simulation procedure is described in ref 16. As could be concluded from the figure, the theory fits the experiment quite satisfactorily given the complete averaging of HFI in S^+ by fast charge transfer with a rate $(\tau_{res})^{-1} = 3 \times 10^9$ s^{-1}. As has already been pointed out, at such high exchange rates the spectrum of the squalane holes converges to a single homogeneous line. The observed width comes from the intratrack decay rate, $k_1^* = 0.11 \times 10^9$ s^{-1}, and the charge–exchange broadening of $C_6F_6^-$, $1/T_2 = 1$ G. Within the experimental error (<15%) the ratio of the widths $\Delta H(3a)/\Delta H(0) \cong 3$, forcing a conclusion that the ESR spectrum of the cation is a single homogeneous line, which should be ascribed to S^+. Similar theoretical calculations were also carried out for an olefinic radical cation with a broad spectrum ($\Delta = 25.2$ G) with charge transfer switched off.[20] In this case the ratio of the widths exceeds 10, and the calculated spectrum does not resemble the experimental one.

As has been recently demonstrated,[19] the direct correspondence between MARY and ESR spectra of radical cations opens a possibility to take ESR spectra without microwave pumping (MARY–ESR). A MARY-taken ESR spectrum of the squalane hole is given in Figure 5b, being the relevant part of the hexafluorobenzene MARY spectrum (put in a box in Figure 5a). The bottom axis marks the field offset from the center of the line ($H-H^*$). The corresponding ESR field offset is given by the top axis: it is 3-fold scaled (shrunk) according to the slope of levels around the crossing point. This spectrum has been identified[20] as belonging to solvent holes. When an acceptor with a low ionization potential (PTP-d_{14}, naphthalene-h_8, naphthalene-d_8, tetramethylethylene, p-xylene) is added to the solution, the spectrum transforms into the spectrum of the acceptor radical cation with the rate of scavenging exceeding the diffusion-controlled one. It should be stressed that as opposed to conventional optically detected ESR/fluorescence-

detected magnetic resonance techniques, where the central line of the spectrum is often overlapped with the signal of the fluorescing counterion, in MARY–ESR the entire spectrum belongs to the cations of the pair. The ESR spectrum of the squalane hole is a homogeneous (Lorentzian) line with the width of about 8 G (half-width at half-maximum), coming mostly from the rate of intratrack hole decay k_1^*. The dashed curve (Figure 5b) presents the results of theoretical calculation with the value of k_1^* taken from the beats simulation. Taking into account that the line is slightly overmodulated ($\sim$10%), the agreement between the calculations and the experiment is quite satisfactory. At the wings of the spectrum certain deviations from the calculated curve, appearing as a broad background, can be seen, which may be due to a contribution of a broad line from olefin radical cations. Including the signal of an olefin radical cation ($\Delta = 25.2$ G) with the weight $\sim$50% into the simulations improves the agreement between calculated and experimental spectra,[20] agreeing also with the quantum beats results.

Conclusion

The techniques of quantum beats and MARY spectroscopy were employed to study the primary squalane holes forming during radiolysis in the radiation track. It was demonstrated that the latter rapidly decay in the processes of recombination with counterions and monomolecular decay. In the absence of solute the lifetime of the holes in solution is about 19 ns. In the presence of an acceptor with a low ionization potential, the holes of squalane are scavenged to form secondary radical cations of the acceptor. In the case of diphenyl sulfide the rate of scavenging, extracted from the phase shift of the beats, exceeds the diffusion-controlled one several times, amounting to 6.1×10^9 M^{-1} s^{-1}. Such a high value results from charge hopping due to ion–molecular charge transfer as opposed to molecular diffusion, yielding higher mobilities. MARY spectroscopy was used to obtain the ESR spectrum of squalane holes, being a homogeneous line with the width determined by the overall lifetime of holes in the track until recombination ($\sim$9 ns).

The results obtained agree well with the data on pulse radiolysis of squalane solutions[6] and lend confirmations to the hole nature of the track positively charged species. Although the measured mobility of squalane holes does not reach the extremely high values typical for cyclic alkanes,[1–5] our results point to the importance of hopping processes in other alkanes as well in considering the ESR spectra and possible reactions of solvent holes.

References and Notes

(1) Warman, J. M. In: *The Study of Fast Processes and Transient Species by Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; Reidel: Boston, MA, 1981; p 433.

(2) Sauer, M. C., Jr.; Schmidt, K. H.; Liu, A. *J. Am. Chem. Soc.* **1987**, *91*, 4836.

(3) Sauer, M. C., Jr.; Shkrob, I. A.; Yan, J.; Trifunac, A. D. Technical report, Argonne National Laboratory, Argonne, IL, 60439, 1996. Submitted for publication in *J. Phys. Chem.*

(4) Shkrob, I. A.; Sauer, M. C., Jr.; Trifunac, A. D. *J. Phys. Chem.* **1996**, *100*, 7237.

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(5) Shkrob, I. A.; Sauer, M. C., Jr.; Trifunac, A. D. *J. Phys. Chem.* **1996**, *100*, 6876.

(6) Shkrob, I. A.; Sauer, M. C., Jr.; Trifunac, A. D. *J. Phys. Chem.* **1996**, *100*, 5993.

(7) Trifunac, A. D.; Sauer, M. C., Jr.; Jonah, C. D. *Chem. Phys. Lett.* **1985**, *113*, 316.

(8) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.

(9) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

(10) Brocklehurst, B. *J. Chem. Soc. Faraday Trans. II* **1976**, *72*, 1869.

(11) Klein, J.; Voltz, R. *Phys. Rev. Lett.* **1976**, *36*, 1214.

(12) Anisimov, O. A.; Bizyaev, V. L.; Lukzen, N. N.; Grigoryants, V. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1983**, *101*, 131.

(13) Veselov, A. V.; Melekhov, V. I.; Anisimov, O. A.; Molin, Yu. N. *Chem. Phys. Lett.* **1987**, *136*, 263.

(14) Sukhenko, S. A.; Purtov, P. A.; Salikhov, K. M. *Khim. Fiz.* **1983**, *1*, 21 (in Russian).

(15) Stass, D. V.; Tadjikov, B. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *235*, 511.

(16) Stass, D. V.; Lukzen, N. N.; Tadjikov, B. M.; Grigoryants, V. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *243*, 533.

(17) Veselov, A. V.; Bizyaev, V. L.; Melekhov, V. I.; Anisimov, O. A.; Molin, Yu. N. *Radiat. Phys. Chem.* **1989**, *34*, 567.

(18) Grigoryants, V. M.; Tadjikov, B. M.; Usov, O. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *246*, 392.

(19) Tadjikov, B. M.; Stass, D. V.; Molin, Yu. N. *Chem. Phys. Lett.* **1996**, *260*, 529.

(20) Tadjikov, B. M.; Stass, D. V.; Usov, O. M.; Molin, Yu. N., *Chem. Phys. Lett.* **1997**, *273*, 25.

(21) Sauer, M. C., Jr.; Jonah, C. D.; Naleway, C. A. *J. Phys. Chem.* **1991**, *95*, 730.

(22) *Landolt-Börnstein. Numerical Data and Functional Relationship in Science and Technology, vol. II/17f. Magnetic Properties of Free Radicals*; Fischer, H., Ed.; Springer: Berlin, 1990.

(23) Tadjikov, B. M.; Melekhov, V. I.; Anisimov, O. A.; Molin, Yu. N. *Radiat. Phys. Chem.* **1989**, *34*, 353.

(24) Usov, O. M.; Grigoryants, V. M.; Tadjikov, B. M.; Molin, Yu. N. *Radiat. Phys. Chem.* **1997**, *49*, 237.

(25) Baker, G. J.; Brocklehurst, B.; Hayes, M.; Hopkirk, A.; Holland, D. M. P.; Munro, I. H.; Shaw, D. A. *Chem. Phys. Lett.* **1989**, *161*, 327.

(26) Shkrob, I. A.; Trifunac, A. D. *J. Chem. Phys.* **1995**, *103*, 551.

(27) Saik, V. O.; Lukzen, N. N.; Grigoryants, V. M.; Anisimov, O. A.; Doctorov, A. B.; Molin, Yu. N. *Chem. Phys.* **1984**, *84*, 421.

(28) Stass, D. V.; Tadjikov, B. M.; Molin, Yu. N. Manuscript in preparation.