

MARY-detected ESR spectrum of solvent radical cations (holes) in squalane

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Abstract

The technique of magnetic field modulation of reaction yield (MARY) spectroscopy was employed to obtain the ESR spectrum of squalane holes that are formed under the action of ionizing radiation at room temperature. The spectrum is shown to consist of a single line which is homogeneously narrowed due to resonance charge transfer over the solvent molecules with the rate constant exceeding the diffusion-controlled one. © 1997 Published by Elsevier Science B.V.

1. Introduction

Radical cations of alkanes have been extensively studied both in Freon matrices with the ESR method [1–3] and in hydrocarbon solutions using the optically detected ESR (OD ESR) technique in CW [4,5] and time-resolved (fluorescence detected magnetic resonance, FDMR) [6–8] variants. They are readily observable by ESR in dilute ($< 1\%$) Freon solutions that have been frozen and γ -irradiated at low temperatures, and the spectra can be studied up to the matrix melting point (140–170 K depending on the halocarbon used). The OD ESR/FDMR technique allows taking the spectra of radical cations in glassy as well as in liquid solutions. The technique is based on the effect of a change in the recombination fluorescence yield of the solution when the Zeeman transitions within the radical ion pair are pumped by a resonance microwave field. The time resolution of the technique is determined by the attainable microwave power in the resonator of the spectrometer and for a typical machine would not exceed 100 ns.

An alkane with a higher ionization potential is used as a matrix, and the substance of interest is added in small ($< 10^{-2}$ M) concentrations as an admixture. Thus, the OD ESR spectra of cis-decalin radical cations in cyclohexane [9] and squalane [10] were observed for dilute solutions even at room temperature. However, all efforts to observe the signals of solvent radical cations (holes) in nondilute solutions at room temperature using this technique have failed. In the case of cis-decalin, for example, the signals of the radical cation vanish and disappear when the decalin concentration is raised above ca. 0.1 M [9,10]. The holes of squalane are not an exception from this rule. Although their OD ESR spectra can be readily detected in frozen matrices [5], all attempts to trail the cations at room temperature led to nothing [11]. This failure to detect the holes resulted in a hypothesis that some fast hole decay is responsible for the absence of any signal. Actually, experiments on pulse radiolysis [12] have demonstrated that the primary species in nondilute squalane have a mean lifetime of ca. 20 ns at room temperature.

which renders them practically inaccessible by conventional OD ESR techniques.

As has been recently demonstrated, the effect of level crossing in spin-correlated radical ion pairs [13] allows taking the ESR spectra of radical cations without microwave pumping [14]. The pair is formed in a spin-correlated (e.g. singlet) state, which is generally not a stationary state of the Hamiltonian. Consequently, several eigenstates of the system are populated simultaneously and evolve, keeping the phase memory of the initial moment. As a result, the observed singlet state population oscillates in time. Since the eigenlevels of the spin Hamiltonian are magnetic field dependent, they can be tuned by varying the external magnetic field and can be forced to cross, which leads to peculiarities in the spin dynamics of the system, and to resonance-like features in stationary experiments. In magnetic field modulation of reaction YIELD (MARY) spectroscopy experiments spectra are recorded as a magnetic field dependence of the fluorescence yield of the recombination products (MARY spectrum). The signals in MARY spectra appear as an increase in the fluorescence intensity in fields where the electron–nuclear levels of the pair cross. Since it is the hyperfine interaction within the pair that drives the spin evolution in the low fields of interest, the time resolution of the technique is determined by the hyperfine couplings in the partner radicals and can significantly exceed that of the ESR one at practically no cost, because of a proper choice of partners.

For the registration of the ESR spectra a special choice of counterion in the pair is required. Fortunately, in the case of a radical cation, the radical anion of hexafluorobenzene containing six equivalent fluorines with large hyperfine coupling constants is available. Equivalent nuclei build up a simple level structure with scarce but pronounced crossing points, and this allows the observation of narrow MARY signals due to level crossing at zero field and in a field equal to triple the hexafluorobenzene coupling constant $H^* = 3a$ [13]. The hyperfine couplings of the pair radical cation modify the energy levels and split the crossing points, yielding the spectrum of the cation at the $3a$ line of the MARY spectrum. An explicit correspondence between the MARY spectrum and the radical cation ESR spectrum has been demonstrated [14], opening the possi-

bility of taking ESR spectra without microwave pumping. As an example (though not a knocking down one) the ESR spectra of naphthalene- h_8 and - d_8 radical cations were taken via this MARY–ESR technique at room temperature [14] and were shown to be identical to those obtained by the conventional OD ESR technique.

In this Letter the MARY–ESR technique was employed to obtain the ESR spectrum of the squalane radical cation (hole) at room temperature in a nondilute solution. It is demonstrated that the ESR spectrum of the solvent radical cation is narrowed due to the resonance ion–molecular charge transfer reaction $S^+ + S \rightarrow S + S^+$. (1)

It is also demonstrated that the charge transfer reaction increases the rate of diffusion over the molecular one, and this inference comes in line with the data from pulse radiolysis experiments.

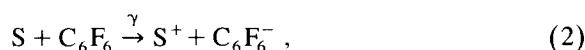
2. Experimental

The MARY spectroscopy approaches has been described elsewhere [13]. About 1 ml of a sample solution in a quartz cuvette is put in the magnetic field of a BRUKER ER-200D ESR spectrometer equipped with an X-ray tube (Mo, 45 kV $\times$ 50 mA) for sample irradiation and a photomultiplier tube with a quartz light guide for the registration of recombination fluorescence. The signal is monitored through a light filter (2500–3200 Å) to leave only the fluorescence from the luminophore excited singlet state. To increase the signal to noise ratio, the experiments are carried out in the modulation regime, when the photomultiplier signal is fed to the inlet of a lock-in detector, and the scanned magnetic field is modulated at 12.5 kHz, being the base frequency for the detector, yielding the first derivative of the actual signal. No microwave pumping is applied to the sample. Hexafluorobenzene, whose hyperfine parameters are known from the literature, was used as a luminescing electron acceptor. The solvent-squalane (2,6,10,15,19,23-hexamethyltetracosane, 99%, Merck) was treated with concentrated sulfuric acid and then passed through a column with silica gel activated with silver nitrate (20%), the resulting purity being checked by a UV absorption spectrum. For the sample preparation the fraction with optical den-

sity equal to unity in a 1 cm layer at a wavelength 210 nm was used. Prior to the experiments the samples were degassed to $\approx 10^{-3}$ Torr. All experiments were carried out at room temperature.

3. Results and discussion

Fig. 1a shows the experimental MARY spectrum of a 1.2×10^{-2} M solution of hexafluorobenzene in squalane. The formation of $S^+/C_6F_6^-$ radical ion pairs under irradiation of the solution and the subsequent recombination to yield excited molecules can be described by an ultimately simplified scheme



where S^+ stands for the solvent hole. The concentration of hexafluorobenzene was taken rather low to avoid broadening of the $C_6F_6^-$ lines due to electron exchange. According to available data [15], the exchange contribution to the overall linewidth is below 1 G under our experimental conditions. The most interesting part of the presented curve is the satellite line at $H^* = 405$ G = $3a_{C_6F_6^-}$ (marked by arrow), which identifies the spectrum as belonging to the hexafluorobenzene radical anion [16], the hyperfine coupling constants of which are known to be a $(6F) = 135$ G [17]. Our aim is to figure out its partner, the radical cation constituent of the pair. Since the MARY spectrum is built up for systems with $\Omega\tau > 1$ ($\Omega = \sqrt{\frac{2}{3}} \sum a_i^2 I_i(I_i + 1)$ is the effective spectral width of the partner that drives the evolution, and τ is the time available for evolution), i.e. for systems that are dynamical enough to exhibit resonance-like behavior [16], partners living as short as several nanoseconds can be (and are) detected. To avoid hole scavenging, the solvent was thoroughly purified from traces of impurities with lower ionization potential (arenes and olefins), and the high ionization potential of hexafluorobenzene precludes hole acceptance from a solvent molecule. Since the observed MARY spectrum is formed in the process of the recombination of spin-correlated radical ion pairs, and the solution was intentionally freed from possible hole acceptors, only the solvent holes should be considered as possible counterions to $C_6F_6^-$.

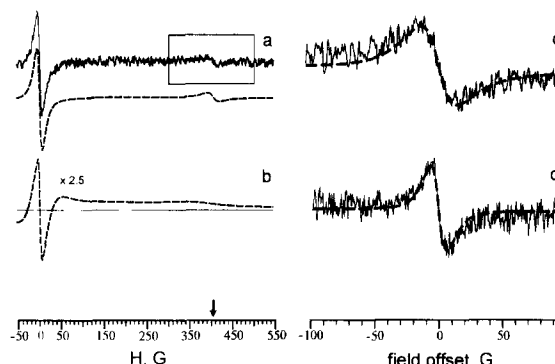


Fig. 1. (a) MARY spectrum of 1.2×10^{-2} M solution of hexafluorobenzene in squalane. The dashed line gives the calculation for squalane holes $\Delta = 10.6$ G in the limit of fast charge transfer $(\tau_{res})^{-1} = 3 \times 10^9$ s $^{-1}$. The satellite line at $H^* = 3a$ is put in a box and marked with an arrow at the axis. (b) Theoretical calculation for a squalane-derived olefin, $\Delta = 25.2$ G, $(\tau_{res})^{-1} = 0$. (c) MARY-taken ESR spectrum of squalane holes. Bottom axis – field offset ($H - H^*$), to obtain the ESR sweep scale the spectrum should be shrunk three times. (d) as (c) but with added 10^{-3} M *p*-terphenyl- d_{14} . All spectra taken at room temperature.

However, these arguments are not sufficient for the ultimate identification of the solvent hole as a counterion to $C_6F_6^-$ in the pair. The products of monomolecular squalane hole decay (olefin cations) [12,18] can also play this role.

The judging argument in favour of the hole assignment of the cation is the shape of the spectral lines. As has been recently demonstrated [14], the lines of the MARY spectrum are sensitive to the distribution of magnetic nuclei over the pair partners. The presence of hyperfine couplings in the cation splits the hexafluorobenzene satellite line in the field $H^* = 3a$ by projections of the total nuclear spin M_Z in the cation, and for an unresolved spectrum leads to broadening and attenuation of the line. The width of the central line in the field $H^* = 0$ stays practically unaltered, reflecting just the relaxation properties of the system [19]. Thus, the entire MARY spectrum of the pair helps establish unequivocally the inhomogeneous contribution to the overall width of the spectrum of the cation. It is clear that when there is no HFI in the cation or when it is effectively averaged down to zero due to fast ion–molecular charge transfer the ratio of the widths of the lines is determined solely by the slopes of intersecting terms in the crossing points $H^* = 0$ and $H^* = 3a$. For

hexafluorobenzene the main contribution to the MARY signal at $H^* = 3a$ comes from the subensemble with total nuclear spin $I = 2$, and this ratio is close to 3. Were the cation ESR spectrum inhomogeneous, it would result in a broader satellite line, increasing the ratio. The value extracted from the spectrum in Fig. 1a is close to 3 within experimental error ($< 15\%$), testifying that the spectrum of the cation is a single homogeneous line.

The dashed line in Fig. 1a shows the theoretical calculation for squalane radical cation assuming fast charge transfer over the solvent molecules $(\tau_{\text{res}})^{-1} = 3 \times 10^9 \text{ s}^{-1}$, where τ_{res} is the mean residence time of a hole at a solvent molecule. The OD ESR spectrum of squalane radical cation in a solution frozen to 77 K is known to be a single inhomogeneous Gaussian-type line with width $\Delta = (\sum a_k^2 I_k(I_k + 1)/3)^{1/2} = 10.6 \text{ G}$ [5], which was taken as the inherent spectrum of S^+ . The calculation procedure has been described elsewhere [15]. To assess the contribution from the $C_6F_6^-$ charge transfer reaction, the diffusion-controlled rate of the reaction was taken [15]. As can be concluded from Fig. 1a, the theory fits the experiment well if one assumes that the HFI from S^+ are completely averaged by fast charge transfer. Given such a rate of exchange, the charge transfer contribution to the overall linewidth is not large, $\Delta^2 \tau_{\text{res}} \approx 0.65 \text{ G}$, and the observed width is determined mainly by the mean lifetime of holes prior to recombination $\tau^* = 9 \text{ ns}$. This value is lower than the lifetime of holes measured in pulse radiolysis experiments [12], because it corresponds to the lifetime of a spin-correlated radical ion pair, and not only the hole monomolecular decay processes, but also intratrack recombination (and spin relaxation, if fast enough) contributes to it.

The structure of the olefin radical cation which is formed during the radiolysis of squalane [11,12,18] is not known precisely, but its FDMR spectrum was shown to consist of a broad unresolved line with width $\Delta = 25.2 \text{ G}$, no charge transfer is expected. To test this alternative candidate, similar calculations were performed, and the results are presented in Fig. 1b. As could have been predicted, an inhomogeneous contribution to the cation spectrum width leads to an abrupt drop in the amplitude of the satellite line, and the ratio of the widths of the lines exceeds 10. The observation that an olefin radical cation should live

longer than the primary hole only eases the binary choice between the two possible candidates, since the homogeneous linewidths become smaller stressing the inhomogeneous contribution. The comparison of theoretical calculations of Fig. 1a,1b with experiment leads to the unambiguous conclusion that the ESR spectrum of the pair cation is a narrow or a homogeneously narrowed line. From known acceptors with low ionization potentials only the radical cations of deuterated compounds possess such a narrow spectrum, but they were not present in the solution. Because of the special care taken the concentration of aromatic impurities also did not exceed 10^{-4} M . Squalane-derived olefin radical cation would give an inhomogeneous broad line. Thus, we are bound to ascribe the observed MARY spectrum to the $S^+/C_6F_6^-$ pair, where S^+ is the squalane hole.

The MARY-taken ESR spectrum of the squalane hole is given in Fig. 1c, being just the vicinity of the satellite line of the MARY spectrum (boxed in Fig. 1a). According to the results of our previous work [14], under conditions of no charge transfer this part of the MARY spectrum reproduces the ESR spectrum of the counterion (save for threefold scaling), i.e. the ESR spectrum of the squalane hole (vide supra). It should be stressed that, as opposed to OD ESR/FDMR techniques, where the central line of the spectrum is usually hidden by the signal of the fluorescing counterion, the MARY spectrum belongs exclusively to the positive radical ions of the pair. The horizontal field axis gives the offset from the centre of the line $H^* = 405 \text{ G}$. The corresponding ESR field scale can be obtained by shrinking the spectrum three times to reflect the slope of terms at the crossing point. The ESR spectrum of the squalane hole is a homogeneous (Lorentzian) line with width of about 8 G HWHM, coming mostly from the rate of intratrack recombination and the rate of monomolecular decay of the holes. Furthermore, although the concentration of hexafluorobenzene was taken rather low, the exchange broadening of the $C_6F_6^-$ lines contributes about 1 G to the overall spectrum width. The dashed line in Fig. 1c shows the results of theoretical calculations with the parameter set from Fig. 1a. It can be seen that with the given set of parameters the agreement is satisfactory. The slight deviations at the maxima result from a line

overmodulation ($\approx 10\%$) because of the poor signal to noise ratio in the experiment (no corrections for this effect were incorporated in the calculations). The possible background that develops at the wings of the spectrum must arise from the signal of an olefin cation, the product of radiolysis (cf. Fig. 1b). An addition of the olefin cation signal with weight $\approx 50\%$ to the calculated MARY spectrum enhances the agreement between the calculated and the observed spectra.

According to data on the pulse radiolysis of squalane, the lifetime of the monomolecular decay of the holes is about $\tau_0 = 20 \pm 5$ ns [12]. This value agrees well with the value of 19 ns obtained by the technique of quantum beats in strong magnetic fields [20]. Thus, the presented technique allows the registration of the ESR spectra of short-lived (< 20 ns) solvent holes in liquid solutions, while the conventional techniques (time resolved ESR and OD ESR) are confined to times longer than 50–100 ns. To our knowledge, this is the first observation of ESR signals from such short-lived (≈ 9 ns) chemical reaction intermediates.

The high rate of charge transfer is also revealed as an anomalously high rate of hole scavenging by acceptors. Fig. 1d shows the MARY–ESR spectrum of a 1.2×10^{-2} M solution of hexafluorobenzene in squalane with added 10^{-3} M of *p*-terphenyl- d_{14} , taken in experimental conditions identical to those of Fig. 1c. It can be clearly seen that the addition of a minor amount of the acceptor leads to a nearly twofold decrease in the overall spectral width. The hyperfine parameters of the *p*-terphenyl- d_{14} radical cation are known; in liquid alkane solution its spectrum consists of a single line of width $\Delta = 0.85$ G. Furthermore, hole capture at low acceptor concentrations effectively switches off the charge transfer reaction, slowing down the recombination and lengthening the lifetime of the pair. Hence, a narrower spectrum in Fig. 1d implies an effective charge transfer from the primary holes to acceptor molecules



where *P* stands for a *p*-terphenyl- d_{14} molecule. Such a rapid hole capture cannot be explained within the framework of the diffusion-controlled limit of reaction (RE₄). Actually, the diffusion-limited rate

of scavenging in squalane falls well within the range $k_D \approx (1.4\text{--}0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for a wide variety of acceptors [12]. Accordingly, only $\tau_0 k_D [P] \approx 2\%$ of the positive charges would have been captured within the hole lifetime. Even taking into consideration the high quantum yield of fluorescence of *p*-terphenyl φ_P , exceeding almost 10 times that of hexafluorobenzene φ_F , such a low yield of reaction (4) cannot account for such a pronounced appearance of P^+ signals in the spectrum. It is clear that the rate of primary holes scavenging by *p*-terphenyl molecules must exceed the diffusion-controlled limit several times. An almost intuitive estimate for a required rate constant can be suggested $k \approx (\varphi_F/\varphi_P)(\tau_0[P])^{-1} \approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which agrees well with the data on the pulse radiolysis of squalane with various aromatic acceptors added, where the values $(3.8\text{--}6.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the rate of hole scavenging were obtained [12].

The dashed line in Fig. 1d shows the results of theoretical calculations for the radical cations of *p*-terphenyl- d_{14} ($\Delta = 0.85$ G). Again the theory fits the experiment well, and the deviations at the wings, similar to those in Fig. 1c, should be ascribed to an admixture of an olefin cation signal.

The high frequency of hole hopping should correlate with the high rate of scavenging by acceptors. Assuming the diffusional motion of holes over the closest neighbours, the hopping contribution to the rate constant of reaction (1) can be readily estimated

$$k = 4\pi R_C D = \frac{4R_C}{d} \frac{\pi d^3}{6} \frac{1}{\tau_{\text{res}}} \approx \frac{4R_C}{d} \frac{V_{\text{mol}}}{\tau_{\text{res}}}, \quad (5)$$

where R_C and d are the hole capture radius and the length of jump, respectively, V_{mol} is the molar volume, and the rate constant is converted to molar units in the last expression. For typical values of $R_C/d \approx 1$, $V_{\text{mol}} = 0.5 \text{ M}^{-1}$ and $(\tau_{\text{res}})^{-1} = 3 \times 10^9 \text{ s}^{-1}$, expression (5) estimates the rate constant to be $k \approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which quantitatively agrees with the experimental value.

4. Conclusions

The MARY–ESR technique allows the registration of short-lived (< 20 ns) solvent holes in nondilute liquid solutions. In the present work the tech-

nique was employed to obtain the ESR spectrum of squalane holes. The spectrum constitutes a single homogeneous line narrowed by fast resonance charge transfer over the solvent molecules. The holes can be captured by acceptor molecules with lower ionization potential to produce secondary radical cations of acceptors, the rate of this process exceeding the diffusion-controlled one several times. The results obtained completely agree with the known data on the temperature-activated mobility of alkane holes in frozen solutions [5,21], pulse radiolysis data [12], and the data from time-resolved OD ESR in squalane [11].

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