Study of interaction of aliphatic alcohols with primary radical cations of *n*-alkanes using MARY spectroscopy

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MARY spectroscopy (the radical ion pair level crossing technique) was employed to probe the reaction of proton transfer from primary radical cations of *n*-alkanes to alcohol molecules in liquid solution. Alcohols were demonstrated to react with the primary radical cation of the solvent, leaving the counterion of the radical ion pair unaffected. The broadening of the zero field MARY line, tentatively attributed to the proton transfer reaction, was found to be independent of the proton affinity of the species in the studied systems, estimated from gas-phase data. The rate constant of the reaction is close to the diffusion controlled limit within the experimental accuracy for all the studied alcohol/solvent combinations.

1. Introduction

Primary radical cations, or holes, forming in liquid alkanes under ionizing irradiation, determine to a significant extent further chemical processes in the solution, which makes them one of the most important intermediates in the radiation chemistry of alkanes. However, the exceptionally high reactivity of the holes complicates their experimental investigation and at present there is still no single and universal method of studying primary alkane radical cations, and the understanding of their properties and reaction pathways is far from complete. The existing experimental techniques take advantage of certain particular properties of the radical cations and, to varying extents, their charge and spin, and work best for a special subclass of systems or experimental conditions. Several of the more common methods are briefly described below.

1.1. Experimental techniques used to study solvent holes Conductivity experiments are best suited for situations where the mobility of solvent holes differs substantially from the mobility of other charge carriers present in the solution to enable separation of the hole contribution to the overall conductivity of the sample. This is the case for very viscous squalane [1] and for cyclic alkanes, such as cyclohexanes and decalins, where the solvent hole is highly mobile and has a lifetime as long as microseconds [2]. A recent finding is the observation of highly mobile holes in liquid cyclooctane [3]. The technique

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of time-resolved microwave [4] and dc [5] conductivity, which has been developed during the past few years into the elaborate 'hole injection' method [6], has led to a breakthrough in understanding the properties and chemistry of 'free' holes of cyclic alkanes. Another recently suggested technique along the same direction, the time-resolved electric field effect in recombination fluorescence, enables investigation of the geminate stage of radical ion pair evolution by applying a static external electric field to X-irradiated samples [7].

Electron spin resonance (ESR) techniques have provided a great body of information on solvent radical cations stabilized in neat frozen solutions [8], and alkane radical cations stabilized in Freon [9] or zeolite [10] matrices. A single report of the ESR spectrum of the solvent hole in liquid *n*-pentadecane should also be mentioned [11]. ESR and its extensions, reaction yield detected magnetic resonance (RYDMR) [12], Optically detected ESR (ODESR) [13], and fluorescence detected magnetic resonance (FDMR) [14], can yield the most detailed information about the spin-bearing species, provided that the radical has moderate relaxation rates and lives long enough to be affected by the microwave field of the spectrometer, the approximate correspondence being 100 ns of lifetime per 1 G of the B_1 field in the resonator.

The universal technique applicable to any system is *optical absorption spectroscopy* [15], which has provided a wealth of available experimental data on alkane radical cations, though it often has to deal with broad structureless spectra that are rather difficult to interpret without additional arguments [16]. Although

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the featureless optical absorption spectra of radical cations of n-alkanes span almost the entire visible range [17] and overlap with spectra of excess electrons, excited molecules, and olefin and solute radical ions produced under radiolysis, it is this method that still provides the major volume of our knowledge about the elusive species.

Despite big efforts put into their study, primary radical cations of *n*-alkanes that have neither very high mobility nor signature optical absorption spectra and live as short as nanoseconds still remain much less well characterized than primary radical cations of cyclic alkanes, and require specialized methods for their study. In this work, to detect the holes of *n*-alkanes in neat liquids we used a relatively new spin-sensitive technique, MARY (magnetically affected reaction yield) spectroscopy, which is a stationary counterpart to the timeresolved techniques of quantum beats in magnetic field effects [18, 19] that have been successfully applied to the study of cyclic and n-alkanes. Additional qualitative information was also gained from a conventional magnetic field effect experiment [20]. Recently, its time-resolved counterpart has also provided new insights into the properties of the short-lived holes of *n*-alkanes [21].

1.2. Solvent hole deprotonation and hole transfer to alcohols

Among the possible processes that could account for the fast decay of solvent holes in liquid alkanes is usually mentioned deprotonation:

$RH^{\bullet+} + RH \rightarrow R^{\bullet} + RH_2^+$.

In solids, alkane radical cations are known to be strong acids, readily losing the proton from the C-H bond with maximum spin density [22]. Proton transfer was demonstrated to take place between an *n*-alkane radical cation and a neutral n-alkane molecule stabilized next to each other in a zeolite matrix [23], and between a cyclohexane primary hole and appropriate solutes [24], and was called up to explain the shorter lifetime of the *n*-alkane radical cation as compared to its partner anion [25], just to name a few relevant examples. ESR and chromatographic studies of y-irradiated mixtures of guest *n*-alkanes in host *n*-alkane crystals and in Freon matrices at 77 K helped to establish the sites of preferential proton loss (the chain-end methyl group) from the radical cation and proton gain (the penultimate methylene group) to the neutral molecule in the stretched all-trans configuration of the n-alkane molecules [26, 27]. In this work we tried to tune the rates of proton transfer from primary n-alkane radical cations in

liquid solutions by introducing aliphatic alcohols into the solution to accept protons from solvent holes:

$$RH^{+} + R'H \rightarrow R^{+} + R'OH_2^+$$

and followed it using the MARY spectroscopy technique.

Alcohols and other hydroxy compounds added to alkane liquids have been extensively studied in connection with the properties of the hydrogen bond [28, 29]. In radiation chemistry major attention used to be paid to the interaction of polar additives with excess electrons [30], which turned out to be captured by clusters, or associates, of polar molecules. Recently, however, the interest of researchers has shifted to reactions of polar molecules or clusters with solvent radical cations, which are much less straightforward. Thus, it was shown that radical cations of decalins in liquid decalins form fairly stable complexes with aliphatic alcohols, which accounts for the peculiarities of the proton transfer from solvent holes in these systems [31]. Similarly, it was demonstrated that phenols and other hydroxy aromatic compounds can accept either charge or a proton from solvent radical cation depending on the geometry of their encounter [32]. To avoid difficulties associated with several concurrent reactions, we tried to make proton transfer the dominan channel of reaction of the solvent primary radical cation with the alcohol molecule in our experiments. To this end, we selected alcohols with appropriate values of proton affinity (PA) relative to the PA of solvent-derived alkyl radicals, and kept the alcohol concentration below or near to the association threshold to preclude clustering and electron solvation. Charge transfer from solvent radical cations to alcohol molecules was blocked by choosing alcohols with an ionization potential (IP) higher than the IP of the solvent molecules.

2. Materials and methods

2.1. Summary of the MARY spectroscopy technique

Since no single published source for the details of MARY (Magnetically Affected Reaction Yield) spectroscopy as applied here is yet available, in this subsection we briefly summarize the method. The MARY spectrum is essentially a conventional stationary magnetic field effect (MFE) curve—the dependence of the yield of recombination fluorescence from radical ion pairs in irradiated solutions on an external static magnetic field—with sharp lines in zero and low field owing to degeneracy of the spin energy levels of the pair (as schematically shown in figure 1) [33]. To amplify the weak and narrow zero field MARY line against the slowly changing background of the MFE, magnetic field modulation with lock-in detection of the signal and



Figure 1. A schematic pattern of the energy levels of radical ion pairs in an external magnetic field (above) and the magnetic field effect curve with MARY lines in the fields of level crossing (below). For reference, the right-hand part of the graphs gives the energy levels and the resonance line for the X-band ODESR case (high field behaviour of the system). The zero field MARY line is discussed in the text.

symmetric passage through the zero of the field is used, producing a first derivative experimental spectrum resembling continuous wave ESR lines [34, 35]. The general look of MARY spectra can be found elsewhere [33, 36].

Since the spin evolution in the pair leading to the observed effect is driven by hyperfine interactions in the pair partners, rather than by the B_1 field of a spectrometer, the radical cation partner of the pair living as short as nanoseconds can be readily registered by supplying the anion partner with large hyperfine couplings, for example radical anions of hexafluorobenzene $(A_{6F} = 135 \text{ G})$ [37] or perfluorocyclobutane $(A_{8F} = 151 \text{ G})$ [38], provided that one of the partners yields a fluorescing excited state upon recombination. The technique is sensitive only to spin-correlated radical ion pairs and is thus best suited to study the reactions of geminate radical ions on the time scale from nanoseconds to tens of nanoseconds. In this work we took advantage of the dominating hyperfine couplings in one pair partner (anion), the situation in which the shape and width of the line are determined solely by the kinetic parameters of the system, without complication from the unknown hyperfine structure of the hole.

It was earlier demonstrated that the width of MARY lines is determined by chemical decay and spin relaxation of radical ions and the processes of geminate radical ion pair recombination, and the former two give additive contribution to the width, assuming that they are exponential [39]. Computer simulations have provided a recipe to take into account the non-exponential kinetics of radical ion pair recombination when interpreting

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experimental MARY spectra: the kinetics leads to apparent scaling of the exponential processes (decay and relaxation), which is accounted for by dividing the measured peak-to-peak width of the experimental line by a constant factor, typically equal to 2 in our experimental conditions [40]. Thus the obtained figure corresponds to the width of an imaginary Lorentzian contour determined by the exponential processes in the radical ion pair. MARY spectroscopy has been employed to estimate the lifetimes of primary radical cations of *n*-alkanes in neat liquids, which varied from 1 to 30 ns in the series *n*-pentane to *n*-hexadecane [41], as opposed to microseconds in cyclic alkanes.

2.2. Experimental

Detailed description of the experimental set-up can be found elsewhere [33]. About 1 cm³ of degassed solution in a quartz cuvette is placed in the field of a Bruker ER-200D ESR spectrometer equipped with an offset coil with a separate dc power supply to provide 'negative' shift of magnetic field, an X-ray tube for sample irradiation (Mo, $45 \text{ kV} \times 30 \text{ mA}$), and a photomultiplier tube assembly to detect fluorescence (FEU-130). The external magnetic field was modulated at a frequency of 12.5 kHz with an amplitude of up to 20 G. A Stanford SR-810 lock-in amplifier and computer averaging over 5-20 scans were used to get the presented MARY lines as the first derivatives of the actual field dependencies. (A modulation-free MARY study in irradiated alkane solution has also been reported in the literature [42, 43].) No microwave power was applied to the samples. All experiments were carried out at room temperature. Hexafluorobenzene C₆F₆ was used as a fluorescing electron acceptor with large hyperfine couplings in the anion radical (vide supra). The solvents-n-hexane, *n*-nonane, *n*-dodecane and *n*-hexadecane—were stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. Hexafluorobenzene, *p*-terphenyl- d_{14} , benzene- d_6 , and methyl, ethyl, isopropyl and *tert*-butyl alcohols were used as received.

Experimental series were always started from zero concentration of alcohol in the sample. Experiments that differed only by concentration of one of the solutes $(C_6F_6 \text{ or alcohol})$ were carried out in one sample by stepwise increase of the solute concentration. No noticeable build-up of reaction products or depletion of the reagents occur within the time scale of the experiment (several hours) [44]. The widths of the (isolated) MARY lines measured as a peak-to-peak distance of the first derivative registered in the experiment are plotted versus concentration in Stern–Volmer type plots in the figures below. Figure 2 shows an example of a typical MARY line in zero magnetic field



Figure 2. A typical experimental MARY line recorded as its first derivative at room temperature for a solution of $1.2 \times 10^{-2} \text{ M C}_6\text{F}_6$ in *n*-decane at zero (a) alcohol concentration and (b) its broadening when $2.8 \times 10^{-2} \text{ M}$ of isopropyl alcohol is added.

measured as a first derivative at (*a*) zero concentration of alcohol and (*b*) the line broadened by alcohol at a concentration of 2.8×10^{-2} M. After correction for non-exponential recombination kinetics the width of the line is converted to exponential time using the relation for the Lorentzian contour τ [ns] = $66/\Delta H_{pp}$ [G]. The slope of the linear part of the dependence gives the rate constant of the reaction, and the *y*-axis intercept reflects the lifetime of the spin-correlated radical ion pair at zero concentration of the solute. The estimated accuracy of the linewidth measurements is 10%.

3. Results and discussion

3.1. Rate constants of reactions with alcohols

The reaction of irreversible proton transfer from solvent holes shortens the lifetime of the radical cation partner of the spin-correlated radical ion pair, thus shortening the lifetime of the pair, which in turn determines the width of the zero field MARY line. Therefore the reaction of proton transfer can be detected as a broadening of the line. Since different alcohols, as well as different solvent-derived alkyl radicals, have different proton affinities, the proton transfer reaction rate had been expected to depend on the solvent/alcohol combination, and correlate with the proton affinity values of the species. The measured proton affinities of the relevant species for these specific conditions are difficult to come by, and gas-phase thermodynamic data were used as guidance. The gas-phase proton affinities of the alcohols [45] are given in table 1.

We failed to find any information on proton affinities of n-alkyl radicals in the literature save for those of methyl and ethyl radicals [45] which are irrelevant to this work. Therefore proton affinities of the alkyl radicals derived from the solvents used were roughly estimated

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Table 1. Gas-phase proton affinities and ionization potentials of alkyl radicals and alcohol molecules.

	Gas-phase IP (eV)	Gas-phase PA_A/PA_R (eV)
<i>n</i> -C ₆ H ₁₄	10.13	7.64
$n - C_8 H_{18}$	9.80	7.97
<i>n</i> -C ₉ H ₂₀	9.71	8.06
<i>n</i> -C ₁₀ H ₂₂	9.65	8.12
$n-C_{16}H_{34}$		
CH ₃ OH	10.84	7.82
C ₂ H ₅ OH	10.48	8.05
<i>i</i> -C ₃ H ₇ OH	10.17	8.22
t-C ₄ H ₉ OH	9.90	8.32

PA, gas-phase proton affinity of alcohol molecules [30].

 $PA_{\rm R}$, gas-phase proton affinity of alkyl radicals estimated from ionization potentials of the parent alkane molecules as $PA_{\rm R} = I_{\rm H} (13.6 \,\text{eV}) + D_{\rm CH} (4.17 \,\text{eV}) - IP_{\rm RH}$ with $IP_{\rm RH}$ taken from [30].

IP, gas-phase ionization potentials [30]; IPs of possible products of monomolecular decay of alkane radical cations, e.g., olefins, are lower than IPs of parent alkane molecules.

using the thermochemical cycle [46] from gas-phase data on ionization potentials using the relation

$$PA_R = I_H(13.6 \,\text{eV}) + D_{CH} - IP_{RH},$$
 *(1)

where $I_{\rm H}$ is the ionization potential of the hydrogen atom, IP_{RH} is the ionization potential of the parent alkane molecule, and D_{CH} is the C—H bond cleavage energy. As an estimate the value of 4.17 eV, corresponding to breaking the weakest interior bond in a long hydrocarbon molecule and fairly constant for the studied alkanes, was taken [47]. Although the terminal methyl group C—H bond cleavage was found to be preferable at low temperatures, this fact is due to specific spin density distribution in the favourable stretched all-trans conformation of the alkane radical cation in these conditions. In liquids, where more conformational freedom is allowed, the weaker interior bonds may also participate in the deprotonation giving the distribution of alkyl radical yields that is closer to the statistical distribution [48]. The thus obtained values are also given in table 1. Although in liquid solution the absolute value of proton affinities will be apparently different from these values owing to solvation of the reactants, it is believed that they can still be used as a guide in the estimation of the feasibility of the reaction, which is driven by the difference of the proton affinities of the species. It was expected that the difference in PA, the thermodynamic driving force of the reaction in question, will be only slightly modified by solvation owing to differences in sizes and charge distributions (delocalized charge in



Figure 3. The dependence of the peak-to-peak width $\Delta H_{\rm pp}$ of the zero field MARY line in *n*-hexane on the concentration of four different alcohols (∇ , methyl alcohol; \odot , ethyl alcohol, \Box , isopropyl alcohol, \diamondsuit , *tert*-butyl alcohol). The effect is independent of the type of the alcohol and has a rate $k \approx 2 \times 10^{10} \,\mathrm{M^{-1} \, sc^{-1}}$ that is close to the diffusion-controlled one $(k_{\rm D} = 2 \times 10^{10} \,\mathrm{M^{-1} \, s^{-1}})$.

the σ -radical cation vs. localised charge of the OH₂⁺ group of the protonated alcohol) of the reactants.

To check this expectation, the rate constant of the reaction was measured experimentally for four alcohols in *n*-hexane (the plots of linewidth versus concentration are shown in figure 3). More alcohol/solvent combinations were discussed elsewhere [49]. Surprisingly, the reaction rate was found to be close to the diffusioncontrolled limit even for systems where proton transfer had been predicted to be least feasible (e.g., methanol/ hexane in this set; see also the methanol/hexadecane pair later on). Apparently, either the gas-phase estimates for the driving force are inapplicable here, or the effect of alcohol in the solution has a more complex pattern than just one-step straightforward proton transfer from the solvent hole. Although differences in gas-phase ionization potentials are the standard measures of the feasibility of charge transfer in liquid non-polar solutions, other similar estimates should apparently be taken with a grain of salt until unequivocally established. In this work we rather concentrated on the other alternative and explored the possible channels of alcohol interaction with the pair that might lead to PAindependent diffusion-controlled reaction with alcohol.

3.2. Possible channels of reaction with alcohol other than solvent hole deprotonation

A trivial explanation for the fact that the reaction rate is the same for different alcohols could be reaction with the water that is always present in any alcohol, rather

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than with the alcohol it comes with. Although the PH of the water molecule is lower than the PA of the alcohols used in this study, efficient H-bonding and the resulting clusterising to form $(H_2O)_n$ with higher PA makes water a very effective proton acceptor, for example in wateralcohol mixtures it is water rather than the alcohol molecules that are protonated. Water dimers were shown to accept protons from radical cations of *n*-butane and higher alkanes in the gas phase, when a conventional bimolecular proton transfer is thermodynamically blocked [50]. However, the observed linewidth grows linearly with the increase in absolute value of the alcohol concentration, giving a rate constant close to the diffusion-controlled limit when reduced to the concentration of alcohol, not to the several per cent of water it might contain. Highly mobile solvent holes are generally considered unlikely to occur in *n*-alkanes. Had the effect been caused by water, the line would have broadened at a much slower rate with the increase in alcohol concentration. Similar reasoning excludes other possible impurities in alcohols or solvents, and forces to attribute the observed effects to the alcohols themselves.

Another possible explanation is the formation of a complex of an alcohol molecule with a solvent hole, and further proton transfer from the complex to another alcohol molecule, the process that has recently been demonstrated for cyclic alkanes [31]. Similar termolecular proton transfer reactions assisted by ionic hydrogen bond formation have also been reported for deprotonation of aromatic cations to alcohols in the gas phase [51]. A dimer of alcohol molecules has a far higher PA (by as much as 1 eV) than a single molecule, and can readily take a proton from an alkane radical cation for all the alkane/alcohol combinations studied, assuming the validity of the gas-phase estimates. This gain in energy is enough to cover the variation in the single-molecule PA from one alcohol to another. However, in our systems, where radical cations decay after as short a time as a few nanoseconds (2–5 ns for *n*-hexane, as opposed to microseconds in cyclic alkanes), kinetic factors rather than pure thermodynamics take on the major role, and two alcohol molecules do not have enough time to encounter the radical cation before it decays. According to a simple kinetic scheme estimation, the fractions of the solvent holes that live long enough to encounter one and two alcohol molecules in solution are given by the expressions

$$\frac{k_{\text{diff}}[\text{Alc}]}{k_{\text{decay}} + k_{\text{diff}}[\text{Alc}]}$$

$$\frac{k_{\rm diff}^2 [\rm Alc]^2}{\left(k_{\rm decay} + k_{\rm diff} [\rm Alc]\right)^2}$$

[FIRST PROOFS]

and

respectively, where [Alc] is the concentration of the alcohol, $k_{\rm diff}$ is the diffusion-controlled rate constant, and k_{decay} describes the disappearance of the holes via channels other than reaction with alcohol. It is assumed here for simplicity that solvation by the first alcohol molecule does not change the decay rate of the radical cation. In our experimental conditions, taking $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for k_{diff} , $2 \times 10^8 \text{ s}^{-1}$ for k_{decay} , and 10^{-2} M for [Alc] for a typical solution of alcohol in hexane, these fractions are about 50% and 25%, with larger divergence for smaller concentrations of alcohol. Since we observe a linear concentration dependence of the linewidth with diffusion-controlled rate constant at low concentrations of alcohols, such complexes with a second alcohol molecule either are not formed or are relatively unimportant for this type of experiment.

By now only the cation itself has been considered as a target for alcohol attack. However, it should be remembered that ultimately the width of the MARY line is determined by the lifetime of the spin-correlated radical ion pair, rather than the lifetime of the radical cation *per se.* Thus, it is also possible that alcohol shortens the lifetime of the radical pair through a reaction with the other partner, that is an electron sibling produced in the ionization of the alkane molecule, or hexafluorobenzene radical anion formed after its capture. In this case the PA of the alcohol as compared to that of the solvent-derived alkyl radical is not a critical parameter.

The only known relevant reaction of electrons with polar molecules is electron capture by pre-existing alcohol clusters [30], which were shown to arise in *n*-alkane solutions starting from concentrations of about $2-3 \times 10^{-2}$ M [52]. The effect of such a capture is slowing the 'free' electron down to normal diffusional molecular mobility. Nothing is known about the rates of paramagnetic relaxation of electrons in the cluster, but judging by ODESR signals readily obtained from the 'solvated electron' in squalane and pentadecane [53], the relaxation is moderate on the time scale of MARY experiments (tens of nanoseconds). The capture provides extra electrons escaping fast recombination with their parent molecules and living as long as hexafluorobenzene radical anions. The pair 'solvated electron'-'solvent hole' is not directly seen in experiment, since there is no luminophore in it. However, if such a cluster encounters a C₆F₆ molecule, it will deliver its electron to the acceptor, a process demonstrated for pyrene [52], to produce an observable pair. Thus, the neat result of the electron solvation in these systems and for this experiment is mediated transfer of electrons to C₆F₆. The important fact is that, neglecting hyperfine couplings in the solvent hole, spin evolution in the pair is mostly driven by very large hyperfine interactions in the C_6F_6 radical anion, and thus 'switches on' only at the instance



Figure 4. Dependence of the width of the MARY line in zero magnetic field a for a solution of $1.2 \times 10^{-2} \,\text{M C}_6\text{F}_6$ in *n*-hexane on the concentration of isopropyl alcohol.

of the charge delivery. This process of delayed switching of spin evolution in the pair leads to a distribution and effective shortening of the time available for spin evolution within the physical lifetime of the pair. This process is currently being specifically studied both theoretically and on model systems, but qualitatively it produces line broadening.

Thus, the expected pattern for alcohol affected via solvation of a 'free' electron is no effect until the association threshold and then additional broadening. However, the pattern produced in experiment is diffusion-controlled broadening and then plateau starting at about the association threshold (figure 4), or just the opposite to what is expected. The used alcohol (isopropyl alcohol) readily dissolves in hexane at these concentrations, so the trivial explanation of the plateau that the concentration of alcohol in solution simply does not increase any more does not work. The conclusion is that the observed pattern cannot be explained by interaction of the alcohol with the 'free' electron. Another additional complication met when working above the association threshold is a nonlinear dependence of the actual total concentration of the polar species (monomers, dimers and higher associates) on the stoichiometric concentration of alcohol expressed as monomers [54]. Further on, to avoid complications connected with solute association, we tried to keep the alcohol concentration below or near the association threshold. Thus, it is believed that the effects reported in this work come solely from reactions with alcohol monomers.

Another possibility is complexation of neutral hexafluorobenzene molecules by the alcohol molecule or solvation of the hexafluorobenzene radical anion by

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the alcohol molecule. Experimental observations of weakly bound $(1-2 \text{ kcal mole}^{-1})$ dipolar-quadrupolar complexes of polar molecules, for example acetonitrile, with neutral hexafluorobenzene molecules were recently reported in the literature [55]. Although not much is known about the equilibrium constants of the formation of such complexes, as a cautious estimate we compare such a complexation with hydrogen bonding in alcohol solutions. For typical values of H-bonding energy of 5 kcal mole^{-1} [28] the onset of alcohol association is at about $2-3 \times 10^{-2}$ M (vide supra). Since the concentrations of both alcohol and hexafluorobenzene were below or near this value, and the reported bonding energy of the complex is several times lower than the H-bond energy, complexation of neutral hexafluorobenzene molecules by alcohols is not expected in our experimental conditions.

On the other hand, solvation of the hexafluorobenzene radical anion by an alcohol molecule via ion-dipolar interaction is rather feasible. The problem of 'coagulation' of a dipolar molecule with a charge in non-polar liquid solution was treated in [56]. For a molecule with dipolar moment $\mu = 2D$ in cyclohexane solution at room temperature ($\varepsilon = 2$ and $\eta = 0.97 \,\text{cP}$) the coagulation time was estimated as τ [ns] = $0.005 \times [M]^{-1.29}$, where [M] is the concentration of the dipolar molecules. The dipolar moment of the hydroxyl group is 1.51 D, and typical dipolar moments for alcohols are in the range 1.66-1.70 D for primary alcohols C_3H_7OH to $C_{10}H_{21}OH$ [57]. The given viscosity approximately corresponds to decane ($\eta = 0.92 \,\mathrm{cP}$ at room temperature). The cited estimate gives coagulation time of 19, 7.8, and 4.6 ns for solute concentration 0.01, 0.02, and 0.03 M respectively, which is comparable with the time scale of experiment and with the lifetime of the decane hole (7 ns as lower estimate).

One of the consequences of the formation of such a complex will be the exclusion of the hexafluorobenzene radical anion from the resonance reaction of charge transfer to a neutral hexafluorobenzene molecule, which is known to be nearly diffusion-controlled under these conditions [41]. Taking again decane for comparison, the rate constant of the charge transfer reaction in which is about $3 \times 10^9 \, M^{-1} \, s^{-1}$ [41], the mean residence time of the radical anion is about 30 ns at $10^{-2} \, M$ of $C_6 F_6$ in solution, and depends as 1/[M] on the concentration of $C_6 F_6$. Another possible consequence of complexation is reduction of the intramolecular relaxation processes in the radical anion by lowering the symmetry of a symmetric Jahn–Teller active radical [58].

Because of its large hyperfine couplings, the hexafluorobenzene radical anion in the used concentration range is always in the region of slow charge transfer, and the resonance charge transfer reaction leads to

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additional line broadening which can be as large as 6G at 10^{-2} M of C₆F₆ in hexane. Lower concentrations of hexafluorobenzene are not practical because of its low quantum yield of fluorescence (about 4% in our experimental conditions). The indication of the internal relaxation is the residual width of 3-5G in all experiments with C₆F₆ even after extrapolation to zero concentration and accounting for the decay of the counterion. However, solvation of the C₆F₆ radical anion by alcohol molecules would exclude these additional sources of relaxation and thus lead to line narrowing, again giving the pattern opposite to that observed in experiment (although it might explain the plateau in figure 4-further studies are on their way at the moment). A process that would produce line broadening is an irreversible reaction of alcohol with the radical anion shortening its lifetime as a partner in the spin-correlated radical ion pair or giving nonfluorescing products, for example abstraction of the proton from an alcohol molecule by the radical anion to produce an alcohol anion and a neutral radical. However, we failed to find discussion of such processes in alkane liquids in the literature.

3.3. Further MARY study of the anion channel

With such a complex set of possible reactions to be taken into account, we sought for a way to register and study them separately. To check whether alcohol takes part in any reaction with the hexafluorobenzene radical anion, the width of the zero field MARY line was plotted versus the concentration of alcohol at various concentrations of hexafluorobenzene. An example of this procedure for isopropyl alcohol in *n*-nonane is shown in figure 5. This experiment shows that alcohol



Figure 5. Dependence of the width of the MARY line in zero magnetic field on concentration of isopropyl alcohol at various concentrations of C_6F_6 . \checkmark , 0.6×10^{-2} M; $_{\odot}$, 1.8×10^{-2} M, \square , 5.4×10^{-2} M.

just gives a linear concentration dependence of the linewidth that we attribute to the proton transfer reaction, and variation of the concentration of hexafluorobenzene just leads to a monotonic parallel shift of the curves owing to the reaction of resonance charge transfer from a radical anion to a neutral hexafluorobenzene molecule, with both rates close to the expected values. No indication of the interference between the two solutes, for example depending on the C_6F_6 concentration a decrease in the linewidth because of the anion solvation, was found in these and similar experiments. The results shown in figure 5 are consistent with independent effects of the two solutes. Thus we failed to obtain evidence of alcohol interference with the anion fate, although this experiment cannot be taken as a guarantee that such interference does not take place.

3.4. *MFE study*

The price for the easiness of kinetic studies using MARY spectroscopy as applied here is the impossibility of directly telling what are the partners of the recombining pair, since no structural information is contained in the zero field MARY line. To understand which of the radical ions of the pair is affected by alcohol, we turned to 'normal' magnetic field effect portions of the experimental spectra—the regions of monotonic change of the reaction yield with increasing field. In the field modulation experiment the position of the original MFE curve) is roughly close and proportional to the $B_{1/2}$ field determined by the effective hyperfine couplings in the partners $A_{1,2}$ through the expression [59]

$$B_{1/2} = 2\frac{A_1^2 + A_2^2}{A_1 + A_2}.$$

To exploit the sensitivity of the MFE to hyperfine couplings, we studied alkane solutions of *p*-terphenyl d_{14} (PTP- d_{14}). PTP- d_{14} is a solute that readily accepts both electrons and solvent holes, forming in irradiated alkane solutions radical ions with narrow EPR spectra (widths below 1 G). When PTP- d_{14} is added in a proper concentration, two sorts of radical ion pairs are formed in the solution, $(RH)^{+}/(PTP-d_{14})^{+}$ and $(PTP-d_{14})^{+}/$ $(PTP-d_{14})^{\bullet-}$. In the former radical ion pairs, the solvent hole acts as a partner with a wide ESR spectrum as compared to the $(PTP-d_{14})^{-}$ radical anion (the ratio of widths is about 10:1 or larger). The MFE curve yielded by this sort of pair has a relatively wide peak-to-peak 'normal' MFE and a sharp 'inversion' in the zero field (MARY line) [33]. In the (PTP- d_{14})^{•+}/(PTP- d_{14})^{•-} pairs both partners have narrow spectra, thus giving only a normal narrow MFE without inversion near the zero of the field. Adjusting the concentration of PTP- d_{14} , it is

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Figure 6. Magnetic field effects from (above) pairs $(n-C_{16}H_{34})^{\bullet+}/(PTP-d_{14})^{\bullet-}$ (broad background) and $(PTP-d_{14})^{\bullet+}/(PTP-d_{14})^{\bullet-}$ (sharp line) and (below) their transformation when MeOH is added. The concentration of *p*-terphenyl- d_{14} is 2.5×10^{-3} M, the concentration of MeOH is 5×10^{-2} M.

now possible to record spectra from two distinct types of pairs, only one of which includes the solvent hole, simultaneously.

Figure 6 (top curve) shows the spectrum for a solution of 2.5×10^{-3} M PTP- d_{14} in *n*-hexadecane. Together, the two sorts of radical ion pairs yield the magnetic effect curve with a sharp narrow MFE from the (PTP- d_{14})^{•+}/ (PTP- d_{14})^{•-} pairs against a background of the wider MFE from the (RH)^{•+}/(PTP- d_{14})^{•-} pairs, both looking 'normal'. Hexadecane was used as the solvent for its pronounced zero field MARY line, the high signal-tonoise ratio it produces, and the lowest 'driving force' for proton transfer as estimated from gas-phase data. In this particular system, the 'inverted' MARY line contained in the wider MFE curve has about the same width as the narrower 'normal' MFE, and therefore only the more intense 'normal' narrow MFE is seen.

When 5×10^{-2} M of methyl alcohol is added to the sample (bottom curve of figure 6), the general look of the spectrum does not change, except for the relative intensity of the two effects. This can be explained by reducing the relative amounts of radical ion pairs that contribute to the wider MFE and the 'inverted' MARY line, on the one hand, and to the narrower MFE, on the other hand, owing to interaction with alcohol. This effect shall be attributed to the irreversible reaction of the solvent hole with alcohol, most probably to proton transfer from the primary radical cation of *n*-alkane to an alcohol molecule. Had the alcohol interacted with the radical anion (PTP- d_{14})^{•-}, which is the same in the two types of radical ion pairs contributing to the spectrum, a change in both MFEs should have been observed. The gas-phase estimates indicate that the presented combination of hexadecane/methyl alcohol is the worst case for proton transfer in the systems under study, and



Figure 7. Magnetic field effects from (top curve) pairs $(n-C_6H_{14})^{\bullet+}/(PTP-d_{14})^{\bullet-}$ (broad background and narrow inverted line) and $(PTP-d_{14})^{\bullet+}/(PTP-d_{14})^{\bullet-}$ (sharp line) and (middle and lower curve) their transformation when MeOH is added $(1.8 \times 10^{-2} \text{ M})$ and $3.6 \times 10^{-2} \text{ M}$). The concentration of *p*-terphenyl- d_{14} is 10^{-3} M .

similar effects are observed for other alkane/alcohol combinations.

The conclusion drawn is further exemplified by changing the solvent from *n*-hexadecane to *n*-hexane, where the inverted MARY line is wider owing to a shorter lifetime of the solvent hole, while the narrow 'normal' MFE from the (PTP- d_{14})^{•+}/(PTP- d_{14})^{•-} radical ion pairs determined by the hyperfine couplings in the partners is approximately the same. The two narrow signals now do not compete and can be observed simultaneously, although the signal-to-noise ratio is poorer than in hexadecane solution. The experimental MFE curves for this system are shown in figure 7. The spectrum consists of the three features in the vicinity of the zero field: (1) a wide MFE in the 'positive phase' coming from the (RH)^{•+}/(PTP- d_{14})^{•-} pair, (2) a narrow MARY line in the 'negative phase' coming from the $(RH)^{\cdot+}/(PTP-d_{14})^{\cdot-}$ pair, and (3) a still narrower MFE in the 'positive phase' from the pairs (PTP- d_{14})⁺/ $(PTP-d_{14})^{-1}$. In the sample with added methyl alcohol the first two features become weaker and eventually disappear, which is explained by the detrimental effect of the alcohol on the radical cations forming the affected signal, that is primary solvent radical cations.

3.5. Bridging the gap with MARY

By making the radical cation the partner with the dominant hyperfine couplings in the pair, the described MFE experiments helped to qualitatively establish that

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alcohol removes the solvent hole from spin evolution, but leaves the $(PTP-d_{14})^{\bullet-}$ radical anion intact. However, quantitative kinetic studies are most comfortably performed in the hexafluorobenzene solutions, where just the widths of the isolated zero field MARY line can and have been measured and interpreted. To extend the above conclusion to our initial systems, that is to alkane solutions of hexafluorobenzene, the following experiment was performed. A connection of 10^{-2} M of positive charge acceptor C₆D₆ was introduced into the solution of 10^{-2} M of C₆F₆ in *n*-dodecane. Deuterobenzene does not capture electrons in our systems and forms the relatively stable radical cation $C_6D_6^{\bullet+}$ with narrow ESR spectrum that does not lose the proton, or rather deuteron (the proton affinity of the phenyl radical C_6H_5 is 211.3 kcal mol⁻¹ [45], or 9.16 eV, and should not change appreciably upon deuteration). Although benzene in principle can accept the proton, as can other aromatic compounds, the experimental experience says that if both charge and proton transfer are thermodynamically possible, the lighter particle, that is the electron, is invariably transferred. Thus, a pair $C_6F_6^{\bullet-}/C_6D_6^{\bullet+}$ with a stable radical cation was produced, and the effect of alcohol on such a system was observed.

The obtained transformations of the MARY spectra from dodecane solutions of C_6F_6 after addition of C_6D_6 and then MeOH are shown in figure 8: the line narrows after addition of C_6D_6 and does not change after further addition of the alcohol. The narrowing of the line after adding C_6D_6 is explained by substitution of the rapidly decaying solvent hole for a stable radical cation—a technique introduced in the studies of lifetimes of



Figure 8. Zero field MARY line for (a) a solution of 10^{-2} M C_6F_6 in *n*-dodecane and its transformation when (b) 10^{-2} M C_6D_6 and then (c) 2×10^{-2} M MeOH (c) is added.

solvent holes in liquid *n*-alkanes [41]. The concentration of the alcohol is close to (and even higher than) the concentration of deuterobenzene, so the two solutes are competing for the primary radical cation of the solvent, and again the pairs of two types are present in the solution. However, in this case the broadening due to interaction of solvent holes with alcohol is not observed because of the peculiarities of the modulation experiment, which amplifies the narrower signal and buries the wider signal proportionally to the square of the ratio of the widths. The observed line belongs to the $C_6 F_6^{\cdot -}/$ $C_6 D_6^{\bullet+}$ pairs and is not sensitive to the presence of alcohol in the solution, which supports the suggestion that the only channel for an alcohol to affect the radical ion pair in these systems is reaction with the radical cation. We did not perform the concentration scan since the range of usable concentrations is limited on the lower end by the necessity to capture solvent holes, and on the upper end by the desire to avoid association of alcohol, and offers only a narrow window at around 10^{-2} M.

3.6. Possibility of hole solvation instead of deprotonation

The sum of the described MARY/MFE experiments indicates that monomers of aliphatic alcohols interact with primary solvent radical cations with diffusioncontrolled rates. However, to infer from these results properties of the reaction of the hole with alcohol solvent, the possibility of the hole solvation rather than deprotonation should be considered.

It has been recently demonstrated [60] that the ESR spectrum widths of the isolated radical cations of guest *n*-alkanes in alkane liquids are much smaller (by a factor of 3-4) than their widths in low-temperature matrices [61], which was attributed to fast conformational motion of the carbon chain of the molecule. The work also shows that reaction of the degenerate charge transfer from the guest alkane radical cation to its neutral molecule, although having rate constants about two orders of magnitude below the diffusion-controlled limit, can put *n*-alkane radical cations into the region of exchange ESR spectrum narrowing, especially for longer alkanes (with smaller initial spectrum widths) and in neat liquids. Thus, it is expected that both fast conformational motion and fast charge transfer increase paramagnetic relaxation times of the primary solvent radical cation in *n*-alkane liquids, narrowing the zero field MARY line. Hole solvation would block or impede these processes, thus shortening relaxation times and producing the experimental pattern of increasing linewidth with increasing alcohol concentration-just as observed in practice.

To check this option, it is necessary to isolate the channel of (possible) hole solvation from other channels

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of hole interaction with the additives. Unfortunately, it is difficult to find a good solvating agent for the solvent hole that will not be happy to accept a proton from the radical cation. On the other hand, the specifics of the MARY experiment as applied here are that the actual hyperfine structure of the radical cation is not a critical parameter, so it is possible to substitute the solvent hole to emulate its solvation. However, hole scavenging in *n*-alkanes is a relatively slow diffusion-controlled process, and rather high concentrations of acceptors are required for hole substitution, which in turn leads to appreciable exchange broadening owing to the reaction of degenerate charge transfer for the hole scavenger in the region of slow transfer, which also proceeds with a diffusion-controlled rate. As an example figure 9 shows the result of adding the hole acceptor *p*-xylene to a solution of hexafluorobenzene in n-dodecane. No alcohol was added to the solution in this and the next described experiment. The spectra clearly display broadening by about 12G, which in this case can be completely accounted for by degenerate charge transfer involving the *p*-xylene radical cation.

The problem of obtaining fast hole scavenging and simultaneously slow degenerate charge transfer for a solute in an *n*-alkane can be experimentally approached by using 2,2,4-trimethylpentane (isooctane) as a hole scavenger. The important properties of this solute are diffusion-controlled hole capture, no noticeable self-exchange even at concentrations of up to 0.1 M [62] because of the significant structural distortions of



Figure 9. Zero field MARY line for (a) a solution of $2.4 \times 10^{-2} \, \text{M C}_6\text{F}_6$ in *n*-dodecane and (b) its transformation owing to addition of $1.5 \times 10^{-2} \, \text{M}$ *p*-xylene.



Figure 10. Zero field MARY line for (a) a solution of $1.2 \times 10^{-2} \text{ M C}_6\text{F}_6$ in *n*-hexane and its transformation owing to addition of (b) $2 \times 10^{-2} \text{ M}$ isooctane and (c) $9 \times 10^{-2} \text{ M}$ isooctane.

the branched carbon skeleton after hole capture, and reduced conformational mobility of the branched structure in the radical cation as compared to the linear carbon chain. The results of adding isooctane to *n*-hexane are shown in figure 10, and we can see that the thus performed emulation of hole solvation produces at most a narrowing of the zero field line opposite to the expected effect. The conclusion is that the possibility of solvation of the primary solvent radical cation by alcohol monomers should also be ruled out as not important under our experimental conditions.

4. Conclusions

In this work the interaction of aliphatic alcohols with primary radical cations of *n*-alkanes in neat liquids was studied using quantitative zero field MARY experiments and qualitative $B_{1/2}$ checks for the systems CH₃OH to C₄H₉OH in C₆ to C₁₆ alkanes. It was found that radical anions of hexafluorobenzene and *p*-terphenyl- d_{14} and the secondary radical cation $C_6 D_6^{++}$ are 'stable' and not affected by alcohols in the studied systems under these experimental conditions. Alcohol monomers interact with primary solvent radical cations and remove them from the coherent spin evolution of the radical ion pair, which yields luminescent products upon recombination, with diffusion-controlled rates in all studied alcohol/ alkane combinations. No apparent dependence on the differences of proton affinities of the alcohols and the solvent-derived alkyl radical, estimated from gas-phase data, was found for this range of alkane/alcohol combinations. Owing to the nature of the observation technique, which requires both correlated spin and charge, it is difficult to draw conclusions about the actual mechanism of the interaction with alcohol after the initial contact, but the most reasonable inference is that alcohol monomers extract protons from primary solvent radical cations of *n*-alkanes at a diffusion-controlled rate.

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