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Magnetic field effect study of solvent hole deprotonation in X-irradiated liquid *n*-alkanes

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Abstract

Stationary magnetic field effects including MARY spectroscopy (radical ion pair level crossing technique) were employed to unequivocally establish primary radical cations of *n*-alkanes as targets for aliphatic alcohol attack, with indication of diffusion-controlled deprotonation of the radical cation. For *n*-alkanes C₆...C₁₆ and four alcohols from MeOH to *t*-BuOH the broadening of the zero field MARY line, attributed to the proton transfer reaction, was found to be independent of the proton affinity of the alcohol monomer and alkyl radical.

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1. Introduction

Solvent radical cations, or holes, are the key intermediates in many radiation chemical processes. However, because of their short life span (ns to tens of ns), normal molecular ion mobility, and the lack of characteristic optical spectra, the radical cations of *n*-alkanes are difficult to study using conventional conductivity, ESR and optical spectroscopic techniques. A suitable alternative is spin chemistry methods whose advantage is the hole being a partner of a spin-correlated radical ion pair, in particular the time-resolved and stationary magnetic field effects and their coherent extensions, quantum beats and level crossing (MARY) spectroscopy. In this work stationary magnetic field effect including MARY spectroscopy was applied to study the rates and targets of interaction with alcohols in X-irradiated liquid *n*-alkanes.

Deprotonation is usually mentioned high in the list of possible channels of rapid decay of solvent holes in *n*-alkanes. Here we tried to tune the rate of proton transfer by introducing aliphatic alcohols in the solution to accept protons from solvent holes for several *n*-alkanes in the series C₆...C₁₆ and four alcohols from MeOH to

t-BuOH. The alkane/alcohol combinations were chosen to preclude charge transfer to alcohol (high IP of the solute) and adjust the driving force for proton transfer (the difference of PA of the alcohol and the solvent-derived alkyl radical). The relevant parameters are given in Table 1. Alcohol concentration was kept below or near the association threshold ($2\text{--}3 \times 10^{-2}$ M, Pimentel and McClellan, 1960) to avoid complications due to clusterization of the solute (Kenney-Wallace and Jonah, 1982).

2. Experimental

A detailed description of MARY spectroscopy as applied here to follow solvent holes in *n*-alkanes, living as short as nanoseconds, can be found in Sviridenko et al. (1998). About 1 cm³ of degassed solution in a quartz cuvette was 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 kV × 30 mA), and a photomultiplier tube assembly to detect fluorescence (FEU-130). Field modulation at frequency 12.5 kHz, lock-in detection and computer averaging over 5–20 scans were used to get

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Table 1

Gas phase ionization potentials (IP) of alcohol and alkane molecules, and gas phase proton affinities (PA) of alcohol molecules and solvent-derived alkyl radicals

	Gas phase IP, eV	Gas phase PA _A /PA _R , eV
CH ₃ OH	10.84	7.82 ^a
C ₂ H ₅ OH	10.48	8.05 ^a
<i>i</i> -C ₃ H ₇ OH	10.17	8.22 ^a
<i>t</i> -C ₄ H ₉ OH	9.90	8.32 ^a
<i>n</i> -C ₆ H ₁₄	10.13	7.64 ^b
<i>n</i> -C ₈ H ₁₈	9.80	7.97 ^b
<i>n</i> -C ₉ H ₂₀	9.71	8.06 ^b
<i>n</i> -C ₁₀ H ₂₂	9.65	8.12 ^b
<i>n</i> -C ₁₁ H ₂₄	9.56	8.21 ^b

^a Gas phase proton affinity of alcohol molecules PA_A taken from the NIST database (Webbook).

^b Gas phase proton affinity of alkyl radicals PA_R estimated from gas phase ionization potentials of the parent alkane molecules IP_{RH}, ionization potential of hydrogen atom *I*_H, and C–H bond cleavage energy for a long-chain *n*-alkane *D*_{CH} as PA_R = *I*_H (13.6 eV) + *D*_{CH} (4.17 eV) - IP_{RH}. All IP values taken from Webbook. Data for alkanes not present in the table were interpolated/extrapolated.

MARY lines in zero field, in which reactions with additives were visualized as line broadening. The peak-to-peak width of the line ΔH_{pp} was then converted into the effective rate of exponential decay of the spin-correlated radical ion pair K_{exp} , that includes chemical decay of the cation as one of the additive contributions, via the expression $K_{exp} \text{ (ns}^{-1}\text{)} = \Delta H_{pp} \text{ (G)}/(2 \times 66)$. Hexafluorobenzene C₆F₆ was used as a fluorescing electron scavenger with large hyperfine couplings in the radical anion. *n*-Alkane solvents were stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. Hexafluorobenzene, *para*-terphenyl-*d*₁₄ (PTP), benzene-*d*₆, methyl-, ethyl-, isopropyl-, and *tert*-butyl-alcohols were used as received.

3. Results and discussion

An extensive scan for *n*-alkanes from C₆ to C₁₆ and alcohols from MeOH to *t*-BuOH with careful provisions for solvent purity yielded diffusion-controlled rates of the C₆F₆^{•−}/Solvent⁺ pair decay for all studied alkane/alcohol combinations. An example of the Stern-Volmer-type plot of K_{exp} vs. [Alcohol] for four alcohols in *n*-hexane, used to obtain the rate constant of interaction with alcohol, is shown in Fig. 1. Surprisingly, no correlation was found between the rate and the $\Delta(\text{PA})$ of the expected proton transfer reaction, extrapolated

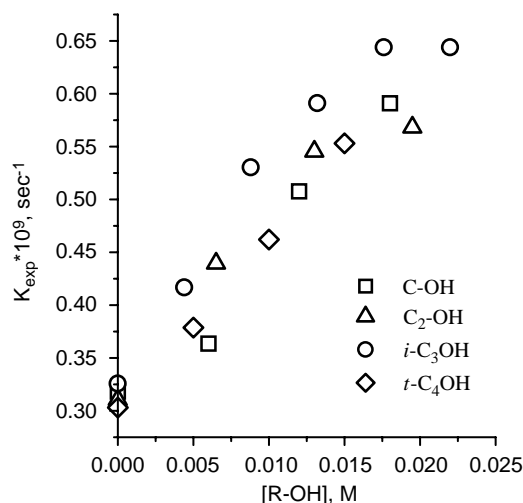


Fig. 1. Total rates of exponential processes of decay of the spin-correlated radical ion pair C₆F₆^{•−}/Solvent⁺, including chemical decay of the solvent hole, for solutions of 1.8×10^{-2} M C₆F₆ in *n*-hexane for four alcohols vs. concentrations of the alcohols, room temperature. The rates were obtained from analysis of the zero field MARY line. Rate constant $k \sim 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is close to the diffusion-controlled limit in *n*-hexane ($k_D = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

from gas phase data. One possible explanation is that the differences in sizes and charge distributions of the two cations can make a substantial (and hardly accountable) solvation contribution to the driving force of the reaction even in these non-polar solvents. Another option is that other reaction channels, e.g., interaction with the radical anion partner of the pair, are possible, or proton transfer in these systems is not a straightforward single-step process (Shkrob et al., 2000).

To clarify the matter, in this work we isolated and separately checked the radical anion and the radical cation channels of the alcohol attack. To this end, in the former case the hole was substituted for a stable C₆D₆⁺ radical cation not prone to proton transfer under these conditions, and the effect of adding alcohol was qualitatively evaluated (left part of Fig. 2). As can be seen, hole capture (“a” to “b”) leads to narrowing of the line due to stabilization of the radical cation (decrease in K_{exp}) and production of the pair C₆F₆^{•−}/C₆D₆⁺, which is indifferent to further addition of alcohol (“b” to “c”). Thus, the radical anion is not effectively attacked by alcohol monomers.

To isolate and visualize the radical cation channel of alcohol attack, “normal” magnetic field effect portions of the experimental spectra—the regions of monotonous change of the reaction yield with increasing field (further referred to as MFE) were employed. In the field modulation experiment the position of the maxima of its first derivative (the inflection point of the original magnetic field effect curve) is roughly close and

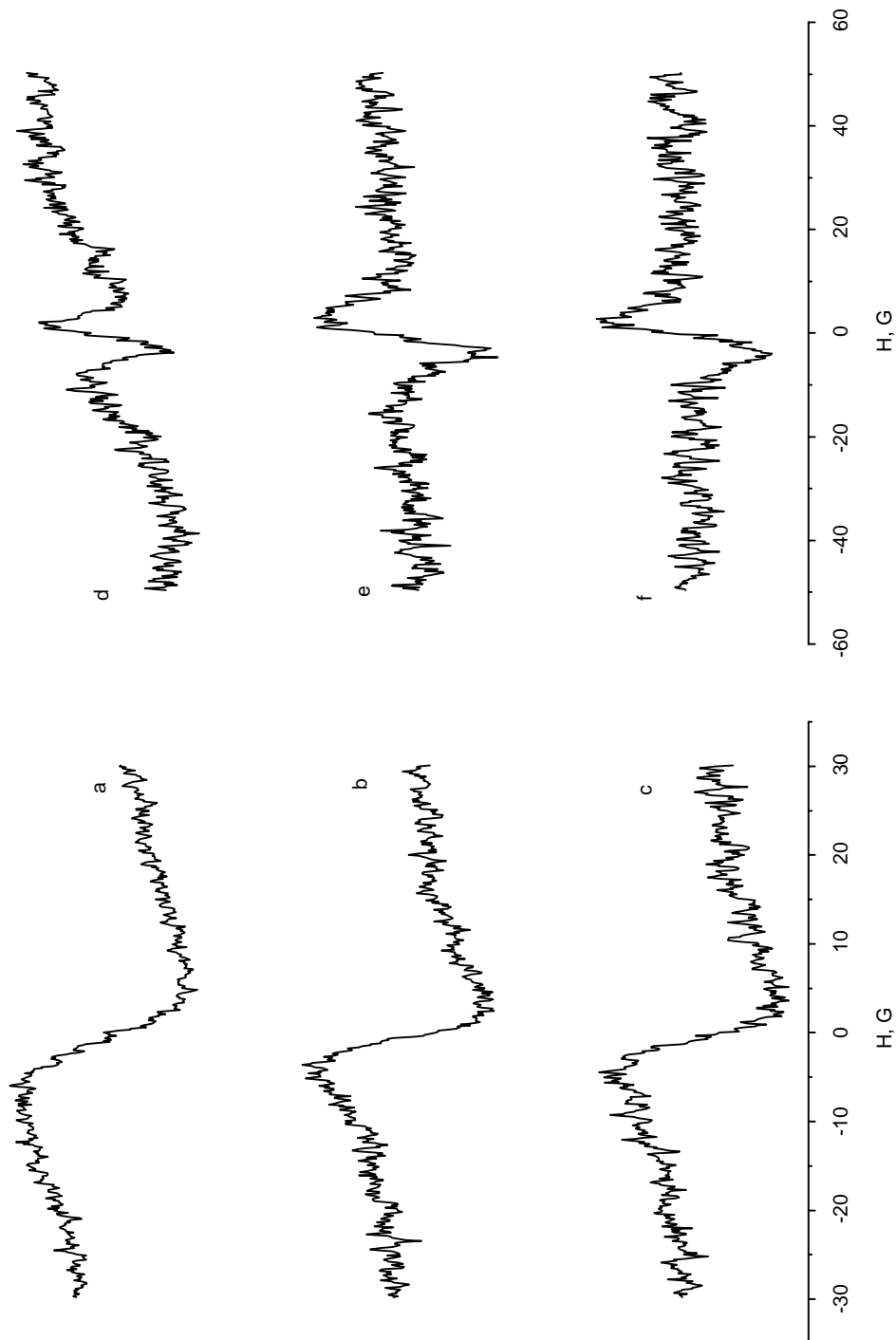


Fig. 2. Checking the radical anion/cation channels of alcohol attack. Left: zero field MARY line for a solution of 1.2×10^{-2} M C_6F_6 in *n*-dodecane (a), and its transformation after adding first 1.2×10^{-2} M C_6D_6 (b), and then 2.5×10^{-2} M methanol (c). Right: magnetic field effect for the solution of 10^{-3} M *para*-terphenyl- d_{14} in *n*-hexane (d), and its transformation after adding 1.8×10^{-2} M (e) and 3.6×10^{-2} M (f) methanol to solution.

proportional to the $B_{1/2}$ field, determined by the effective hyperfine couplings in the partners $A_{1,2}$ through expression (Weller et al., 1983) $B_{1/2} = 2(A_1^2 + A_2^2)/(A_1 + A_2)$, most suitable for qualitative check when $A_1 \gg A_2$.

To exploit the sensitivity of MFE to hyperfine couplings, we studied alkane solutions of *para*-terphenyl- d_{14} (PTP), a solute that readily accepts both electrons and solvent holes, forming in irradiated alkane solutions radical ions with narrow EPR spectra (below 1 G). When PTP is added in a proper concentration, two sorts of radical ion pairs are formed in the solution, “Solvent⁺/PTP⁻” and “PTP⁺/PTP⁻”. In the former radical ion pairs, solvent hole acts as a partner with a wide ESR spectrum as compared to the PTP⁻ radical anion (the ratio of widths is 10:1 or greater for all alkanes). Magnetic field effect curve yielded by this sort of pairs has a relatively wide peak-to-peak “normal” magnetic field effect and a narrower “inversion” in zero field (MARY line) (Stass et al., 1995). In the “PTP⁺/PTP⁻” pairs both partners have narrow spectra, thus producing only a “normal” and still narrower magnetic field effect without inversion near the zero of the field. Adjusting the concentration of PTP, it is now possible to simultaneously record spectra from two distinct types of pairs, only one of which includes the solvent hole.

As an example of this approach the experimental curves for solutions of 10^{-3} M PTP in *n*-hexane are shown in the right part of Fig. 2. The initial spectrum (curve “d”) displays all the three features listed above. Addition of alcohol (“d” to “e” and then to “f”) removes both features coming from the “Solvent⁺/PTP⁻” pair, and leaves the narrow signal from the “PTP⁺/PTP⁻” pairs intact. Since the pairs differ only in the radical cation partner, the detrimental effect of alcohol on the solvent hole is unequivocal.

4. Conclusions

Alcohol monomers were shown to react with primary radical cations of *n*-alkanes in neat alkane liquids at room temperature. For *n*-alkanes C₆...C₁₆ and four alcohols from MeOH to *t*-BuOH the rate of removal of solvent radical cations from the coherent spin evolution is diffusion-controlled and does not depend on the

driving force $\Delta(\text{PA})$ of the expected proton transfer reaction, as estimated from gas phase data. Due to the nature of the observation technique (need of correlated spin and charge), it is difficult to draw conclusions about the actual mechanism of the interaction after the initial contact, but the most probable reaction is solvent hole deprotonation to alcohol. More experimental evidence for this, and more detailed discussion of other possible channels, including clusterization of the solutes, concerted action of two alcohol molecules, and hole solvation rather than deprotonation, is a subject of a more extended publication now in preparation.

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