

Dissociative Electron Capture of Hydrogen-Bonded Hydroxy Groups: Molecular Dynamics and Matrix Isolation ESR Study

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While examining PFPE (perfluoropolyether)-based disk lubricants, extra lability was suspected for a hydrogen-bonded pair of hydroxy end-groups in the presence of a nucleophile (electron donor). Plausible reaction sequences upon electron capture of hydrogen-bonded methanol dimer, hydrogen-bonded ethanol dimer, and 1,2-propanediol were first examined by a molecular dynamics method based on the potential given by a semiempirical SCF molecular orbital calculation, and subsequently by matrix isolation ESR spectroscopy. In the latter experimental study, alcohol dimer anions were generated by co-trapping Na atoms and alcohol molecules in argon matrices and inducing electron transfer by photo-irradiation. In the cases of methanol and ethanol dimers, the molecular dynamics study predicted that on capture of an electron, the hydroxy hydrogen of the acceptor side would cleave as an atom, and then abstract a hydrogen atom from the nearest carbon of the proton donating alcohol. For 1,2-propanediol anion, the molecular dynamics study predicted C1–C2 bond scission followed by abstraction of the C2 hydroxy hydrogen by the C1 radical fragment. The matrix isolation ESR study revealed generation of radicals upon photo-irradiation when the alcohol concentration was sufficiently high to warrant the presence of dimers. The spectral patterns thus observed were totally consistent with the radical products predicted by the molecular dynamics calculations.

The surface of magnetic disks is coated with a thin layer (≈1 nm) of PFPE (perfluoropolyether) lubricant in order to protect the magnetic layer from corrosion and to abate the tribological impact of the head flying nominally several nanometers above the disk surface. Among the topically used or tested PFPE lubricants are Z-dol, Z-tetraol, and ZDPA shown in Chart 1. For all of these lubricants, the main backbone is a random, linear copolymer of tetrafluoroethylene oxide and difluoromethylene oxide units with a roughly equimolar ratio. The molecular weight of the lubricant is in the range of 2000–4000 corresponding to m (or n) ≈ 10–20. The backbone provides the required high hydrophobicity and good lubricity. The hydrocarbon segments containing hydroxy or amino groups are attached at the termini in order to achieve adhesion to the disk surface so that lubricant molecules would not spin off when disks rotate rapidly (5–15 K RPM) during operation.

During the course of experimentation, it was observed that a mixture of ZDPA and Z-dol and a mixture of ZDPA and Z-tetraol both became brown when heated at 200 °C overnight. No such coloring occurred when any of these lubricants was heated individually. Reaction(s) involving the tertiary amine sector (a nucleophile) of ZDPA and the hydroxy units (an electrophile) of Z-dol (or Z-tetraol) was suspected to be responsible for the coloring. GPC analyses (for molecular weight distribution) of the heat-treated mixtures revealed an emergence of a second peak corresponding to doubling of molecular weight in step with the coloring.

$R–O–[–CF_2–CF_2–O–]_m–[CF_2–O–]_n–R$

Z-dol: $R = –CF_2–CH_2–OH$

Z-tetraol: $R = –CF_2–CH_2–O–CH_2–CH(OH)–CH_2–OH$

ZDPA: $R = –CF_2–CH_2–N(-CH_2-CH_2-CH_3)_2$

Chart 1.

It has been shown that in the hydrophobic environment of PFPE backbone the hydroxy units of these lubricants are hydrogen-bonded pair-wise.[1] It is well known that when two alcohol molecules form a dimer via hydrogen-bonding, one hydroxy unit becomes a proton donor while the second unit becomes a proton acceptor as shown in Chart 2.[2] The hydroxy proton in the accepting alcohol would thus be more acidic than that of an isolated system. We postulated that such a dimeric system might be sufficiently labile and in the presence of strong Lewis base (electron donor) would undergo a dissociative electron capture yielding a radical, and that such a process was responsible for the coloring (oxidation) and molecular weight doubling observed with the lubricant mixtures discussed above. It follows that the brown-coloring reaction should occur with or without the presence of PFPE backbone. Indeed a mixture of ethanol and triethylamine and a mixture of 1,2-propanediol and triethylamine became brown on refluxing at 100 °C overnight, while each of these chemicals remained clear and colorless when refluxed at the same temperature individually.

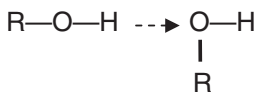

Chart 2.

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To our knowledge no study has been reported on this type of extra lability possessed by a pair of hydrogen-bonded hydroxy units. We therefore examined anionic behaviors of the hydrogen-bonded methanol pair, hydrogen-bonded ethanol pair, and 1,2 propanediol (with possible intramolecular hydrogen bonding) first by a molecular dynamics method based on the potential given by a semiempirical SCF molecular orbital calculation, and subsequently by matrix isolation ESR spectroscopy. In the latter experimental study anions were generated by co-trapping Na atoms and alcohol molecules in argon matrices and inducing electron transfer between them by photo-irradiation. In the cases of methanol and ethanol dimers, the molecular dynamics study predicted that on capture of an electron the hydroxy hydrogen of the acceptor side would cleave as an atom, and then abstract a hydrogen atom from the nearest carbon of the proton donating alcohol. For 1,2-propanediol anion, the molecular dynamics study predicted C1–C2 bond scission followed by abstraction of the C2 hydroxy hydrogen by the C1 radical fragment. The matrix isolation ESR study revealed generation of radicals upon photo-irradiation when the alcohol concentration was sufficiently high to warrant the presence of dimers. The spectral patterns thus observed were totally consistent with the radical products predicted by the molecular dynamics calculations. The results of these studies are presented in this report.

Theoretical Procedures and Experimental Methods

The molecular dynamics calculation was performed using the program implemented in HyperChem (V. 7.5).[3] As stated above, in an effort to elucidate a plausible reaction process, the potential given by the semiempirical SCF quantum mechanical method (of the PM3 level) was used. The PM3 level was chosen as it was found to yield structural and energetic aspects of hydrogen-bonded water molecules most consistent with the observed results. In the case of methanol dimer for example, the structure of the dimer was first optimized for the neutral state, and the reaction upon electron capture was followed by performing the molecular dynamics calculation after changing its charge state to -1. It is assumed here that the Born–Oppenheimer approximation stands when a neutral molecule captures an electron. The calculations were performed under the constant temperature condition with the starting and final temperature of 0 K, the heating and cooling periods of 0.1 ps, and the simulation period of 0.8 ps at a temperature of 150–400 K. The time-step size was 0.0005 ps.

An experimental setup wherein metal atoms of low ionization potential (electron donors) and molecules of interest (electron acceptors) were trapped in argon matrices at liquid helium temperature and electron transfer between them was induced by photo-irradiation of mild energy was described some time ago.[4] In the current study, Na atoms were vaporized from a resistively heated (≈250 °C) stainless steel tube and were trapped in argon matrices containing a controlled amount of a given alcohol. In the case of 1,2-propanediol, because of its low vapor pressure, it was introduced directly onto the cold finger from a reservoir. Irradiation of the resulting matrix with Na D light (580 nm) caused the desired electron transfer. The ESR spectra of the matrices were examined before and after the irradiation. All the spectra presented below were those obtained while the matrix was maintained at ≈4 K, and the spectrometer frequency was 9425 ± 2 MHz.

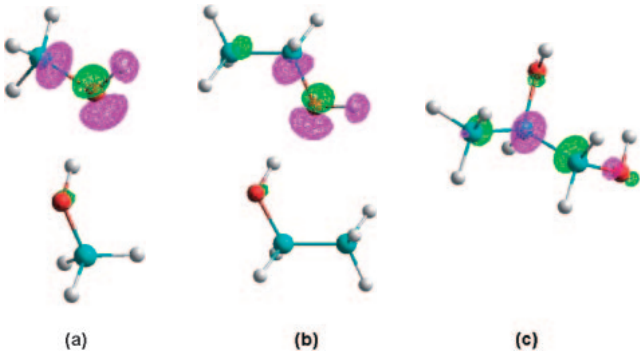

Figure 1. The LUMOs of (a) hydrogen-bonded methanol dimer, (b) hydrogen-bonded ethanol dimer, and (c) 1,2-propanediol.

Results and Discussion

Theoretical Results: Molecular Dynamics Calculations. When a neutral molecule captures an electron of thermal energy, the captured electron is expected to fall into the LUMO (lowest unoccupied molecular orbital) of the molecule. Figure 1 shows the LUMO's of the hydrogen-bonded methanol dimer, the hydrogen-bonded ethanol dimer, and 1,2-propanediol, each in its neutral state, given by the semiempirical SCF molecular orbital method. It is revealed that for the methanol and ethanol dimers the LUMO is confined within the hydrogen accepting unit, and is strongly anti-bonding for both the O–H bond and the C1–O bond. For the hydrogen bonding O_d–H···O_a–H sectors of the neutral methanol and ethanol dimers, the calculation yielded the O_d–H distance of 0.96 Å and the O_d···O_a distance of 2.78 Å. These values compare favorably with the corresponding values of 0.97 and 2.76 Å reported for solid water.[5] For neutral 1,2-propanediol, the theory yielded the O···O distance of 2.99 Å with no apparent indication of anticipated intramolecular hydrogen bonding. However, the effect of two hydroxy groups at C1 and C2 is manifested in its LUMO which is essentially an anti-bonding sigma orbital of these carbons.

It is thus anticipated that when the methanol or ethanol dimer captures an electron, the hydroxy hydrogen of the acceptor side would become loosened and oscillate with large amplitude under a given kinetic energy (i.e., heating). As stated above, the LUMO of either of these dimers is also anti-bonding for the C1–O bond of the acceptor side. However, the amplitude of the C1–O bond oscillation, on capture of an electron, would be much smaller owing to a much larger mass involved. We examined the reaction which these dimers might undergo on capture of an electron by performing the molecular dynamics calculation on each dimer starting with the structure of the neutral state and the electronic charge of -1. The calculation revealed the reaction sequence wherein the hydroxy hydrogen of the acceptor side cleaved as an atom, and then abstracted a hydrogen atom from the CH_3 unit of the donor alcohol (Chart 3). The dispositions of atoms given by the MD calculation at various stages of reactions are shown in Figures 2 and 3.

In the case of 1,2-propanediol, similar examination of the reaction following an electron capture revealed elongation of

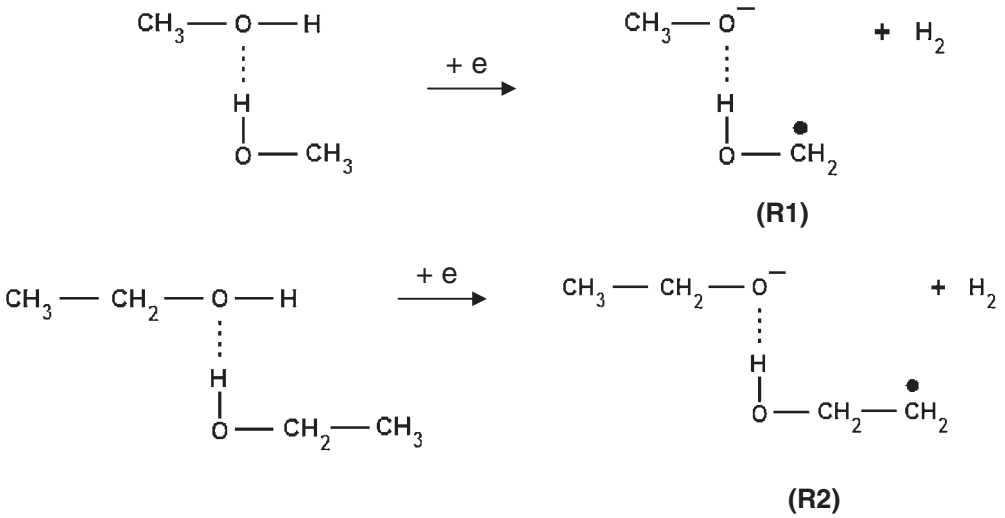

Chart 3.

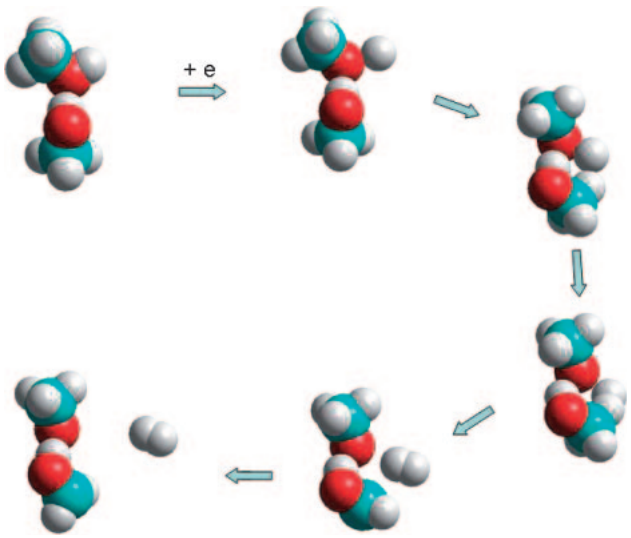

Figure 2. Dissociation sequence of methanol dimer upon electron capture predicted by MD calculation. See text for details.

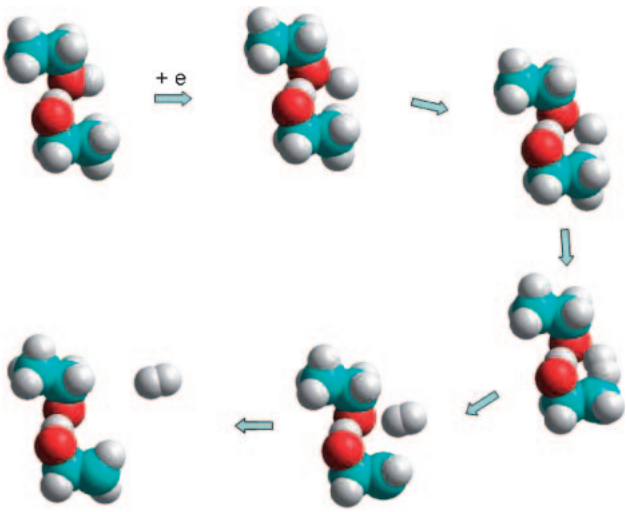

Figure 3. Dissociation sequence of ethanol dimer upon electron capture predicted by MD calculation. See text for details.

the C1–C2 bond followed by transfer of the hydroxy proton from 2-OH to the C1 carbon as shown in Chart 4. Final products are acetaldehyde anion radical and methanol. Figure 4 shows the dispositions of atoms given by the MD calculation at various stages of reaction.

In all of these MD calculations, when energized thermally, the postulated parent anion underwent various vibrations and internal rotations of various magnitudes. The O–H unit of the acceptor side of the methanol and ethanol dimers showed stretching vibration of particularly large amplitude, as expected. When by statistical chance a certain disposition of atoms favorable for the reaction was attained, the reaction commenced and proceeded to completion rapidly. For this to occur within 0.8 ps, the simulation temperature of 300, 150, and 400 K were required for the cases of methanol and ethanol dimers and 1,2-propanediol, respectively. The snap shots shown in Figures 2, 3, and 4 illustrate changes in the dispositions of atoms following the onset of such reaction. The energy levels of the final stages given by the SCF MO were lower than those of parent anions by 55, 44, and 38 kcal mol^{-1}, respectively.

Experimental Results: Matrix Isolation ESR Study. Methanol Dimer: Figure 5a shows the ESR spectrum observed, prior to photo-irradiation, from the methanol(2%)/Na/Ar system. Two sets of signals are dominant; one is due to isolated Na atoms and the other is due to Na atoms datively complexed by the alcohol via the lone pair electrons of the hydroxy oxygen. The quartet pattern arises from the hyperfine interaction with the ^{23}Na nucleus ($I = 3/2$), and the multiple splitting of individual component is ascribed to the local site effect. Sets of signals essentially identical to those were observed from argon matrices containing Na atoms and alkyl ethers and were analyzed and reported earlier.[6] Weak signals due to inadvertently formed hydrogen atoms are also recognized as indicated.

Figure 5b shows the spectrum observed from the same matrix after irradiation with yellow light (600 ± 50 nm) for 20 min. Photo-irradiation resulted in substantial diminution of

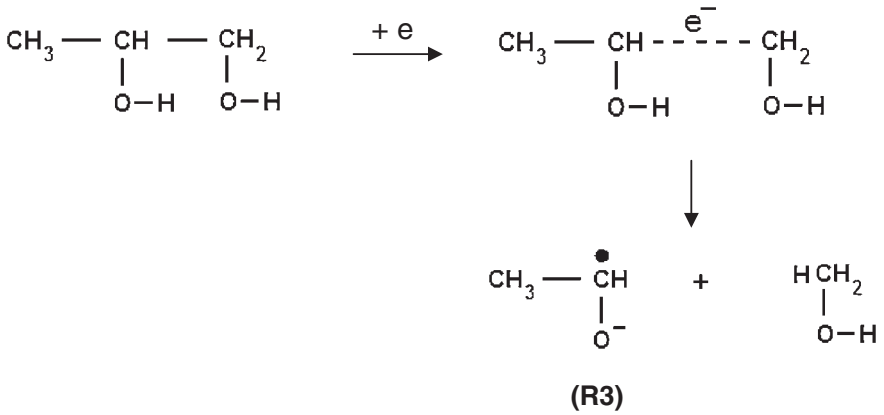

Chart 4.

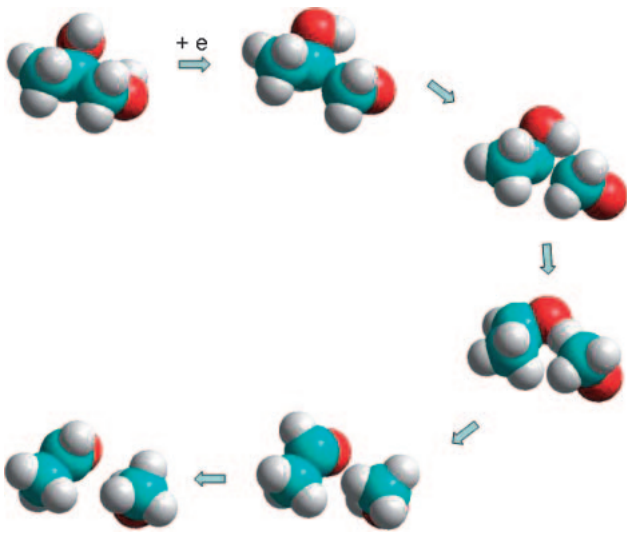

Figure 4. Dissociation sequence of 1,2-propanediol upon electron capture predicted by MD calculation. See text for details.

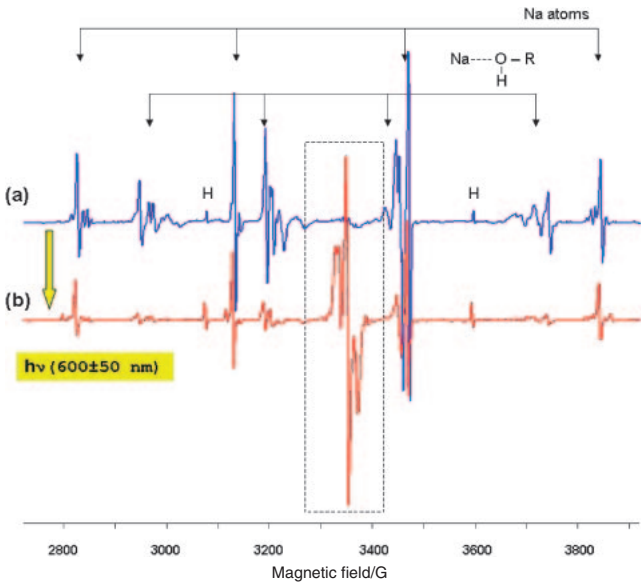

Figure 5. The ESR spectra observed from the methanol(2%)/Na/Ar system observed (a) before and (b) after irradiation of the matrix with yellow light (600 ± 50 nm).

signals due to isolated Na atoms and those due to complexed Na atoms, and generation of a strong triplet at the central section corresponding to $g = 2.00$. When the methanol concentration was halved, the intensity of the triplet decreased to 1/4, and when doubled, increased by ≈4. The photo-induced signals were thus attributed to the substituted methyl radical predicted by the MD calculation, CH_3–O^-···H–O–CH_2●. The major spectral pattern ought to depend only on the hfc (hyperfine coupling) interactions with the two α-protons.

The unpaired electron of this type of alkyl radical is localized in the p_π orbital of the α-carbon. It has been shown that the hfc tensor of the α-protons of such radicals consists of the isotropic part A_{iso} and the orientation dependent, dipolar part A_{dip}.[7] The α-proton being at the nodal plane of the p_π orbital, the isotropic part A_{iso} results from spin-polarization of the C–H σ-orbital, and is hence extremely sensitive to the presence of an oxy-substituent in its proximity. As is well known, $A_{iso} = -23$ G for a primary alkyl radical such as the methyl or ethyl radical. The dipolar part A_{dip}, on the other hand, results from direct interaction of the unpaired electron in the p_π orbital and the proton nucleus and is not affected by the presence of an oxy-substituent in its proximity. It has been shown that $A_{dip}(\|) = +11$ G, $A_{dip}(\perp,\|) = +1$ G, and $A_{dip}(\perp,\perp) = -12$ G. Here ($\|$) indicates the direction parallel to the C–H bond, and ($\perp$,$\|$), for example, indicates the direction perpendicular to the C–H bond and parallel to the p_π orbital.[8] The orientations of the hfc tensors of the two α-protons, given by $A_{iso} + A_{dip}$, would thus differ by 120 degrees within the α-CH_2 plane.

Figure 6a shows in an expanded scale the photo-induced triplet. The indicated weak quartet is due to inadvertently formed methyl radicals. Closer inspection of the spectrum reveals that the highest-field component of the triplet is narrower than the lowest-field component indicating some anisotropy of the g tensor. Examination of the SOMO by a semiempirical SCF MO method indicated a spin density of ≈0.1 at the oxygen p_π orbital. It is thus predicted that the g-value along the C–O direction may have a significant positive shift from the spin-only value (2.0023). A computer program that would simulate the spectral pattern given by an ensemble of randomly oriented radicals has been described earlier.[8] The spectral modulation due to exchange of magnetic nuclei, or

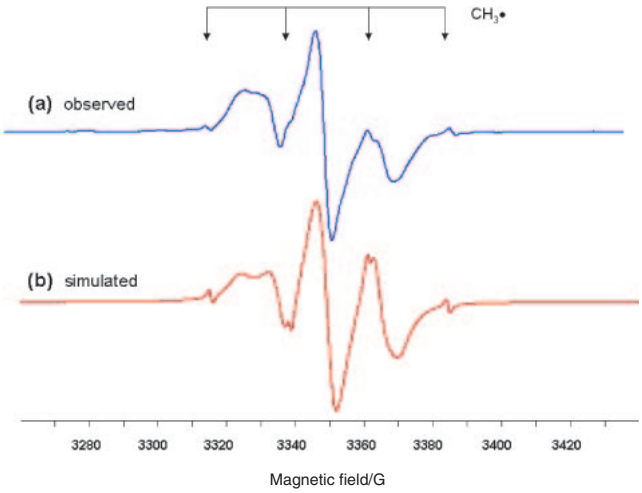

Figure 6. The central triplet photo-induced in the ESR spectrum of the methanol(2%)/Na/Ar system: (a) observed, and (b) simulated.

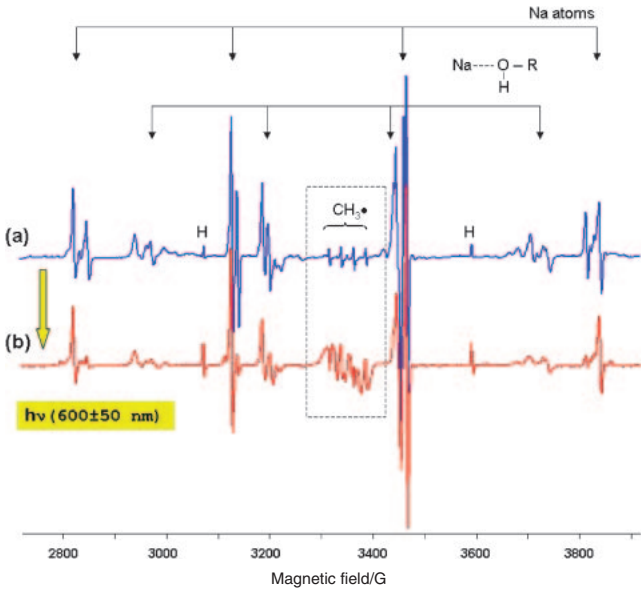

Figure 7. The ESR spectra observed from the ethanol(2%)/Na/Ar system (a) before and (b) after irradiation of the matrix with yellow light (600 ± 50 nm).

their oscillation could be addressed by modified Bloch equation.[6,9] Figure 6b shows the simulated spectrum based on (1) the α-proton hfc tensors comprising A_{iso} of -15 G and the model A_{dip} described above, (2) exchange of the α-protons at 180 MHz, and (3) the g value of 2.0040 along the C–O direction and the spin only value for the other directions. Rapid exchange of the α-protons (via tunneling) is commonly observed for this type of radical isolated in argon matrices.[6] The signals due to methyl radicals were included in the simulation as they served as the internal field calibration. The A_{iso} value of -15 G is considerably smaller than the value, -23 G, known for ordinary alkyl radicals. It is ascribed to the presence of the oxy-substituent.

Ethanol Dimer: Figure 7 shows the ESR spectra observed from the ethanol(2%)/Na/Ar system before and after photo-irradiation with yellow light (600 ± 50 nm) for 20 min. The photo-irradiation resulted in reduction of signals due to Na atoms (both isolated and complexed), and an emergence of signals in the area where the methyl signals were. This region (circumscribed by a dotted rectangle) is shown expanded in Figure 8. When the ethanol concentration was reduced to 1%, the intensity of the photo-induced signals decreased to ≈1/4, and when increased to 4%, increased by four-fold. It was thus surmised that the signals photo-induced in the methyl radical region were due to radicals generated from ethanol dimers upon electron capture.

The radical most likely to result from ethanol is the ethyl radical, CH_3–CH_2•. The ESR spectrum of ethyl radicals trapped in an argon matrix has been studied in detail.[10] The spectrum photo-induced here is definitely not due to ethyl radicals. According to the reaction scheme predicted by the MD calculation (Figure 3), the final radical would be a β-substituted ethyl radical, the spectral pattern of which is determined by the hfc tensors of the two α-protons and two β-protons. It has been shown that the hfc tensors of the β-protons are essentially isotropic and are dependent on the dihedral angle θ of the C_β–H bond relative to the p_π orbital of the α-carbon as follows: $A(H_\beta) = B_0 + B\cos^2\theta$. The B_0 and B values have been empirically determined as $B_0 = 4$ G and $B = 50$ G.[11]

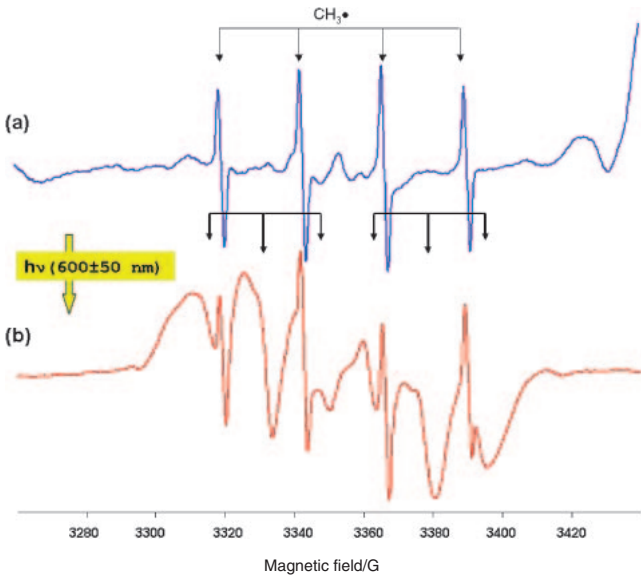

Figure 8. The central section of the spectra observed from the ethanol(2%)/Na/Ar system (Figure 7) shown expanded. The photo-induced signals are discerned as a doublet of triplet as indicated.

The two β-protons thus could have vastly different coupling constants depending on the orientation of the $C_\alpha H_2$ plane relative to the $C_\beta H_2$ sector.

The photo-induced signals revealed in Figure 8b were discerned to comprise a doublet-of-triplet pattern as indicated. They can hence be accounted for by a β-substituted ethyl radical, the triplet pattern arising from the hfc interaction of the two α-protons, and one of the β-protons having a singularly large hfc constant. Figure 9 compares the observed spectrum (Figure 8b) with the spectrum simulated based on (1) the α-proton hfc tensors consisting of A_{iso} of -13 G (adjusted for the best fit) and the model dipolar part A_{dip} described above, (2) the

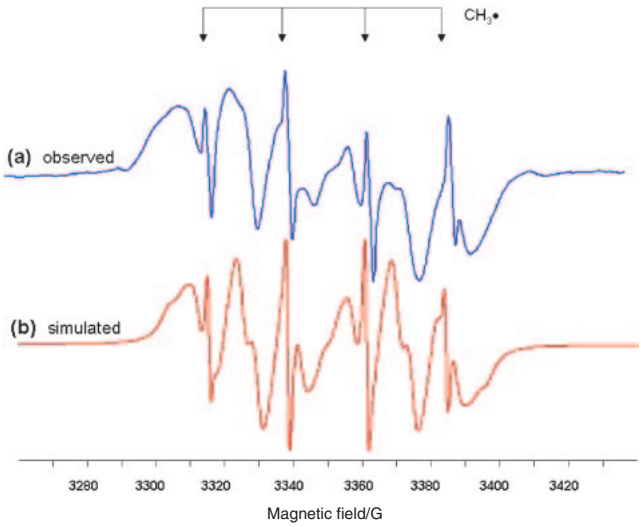

Figure 9. (a) The central section of the spectrum observed from the ethanol(2%)/Na/Ar system after photoirradiation. (b) The simulated spectrum of HO–CH_2–CH_2• radical based on the model hfc tensors given in the text. The signals due to inadvertently formed methyl radicals are superposed.

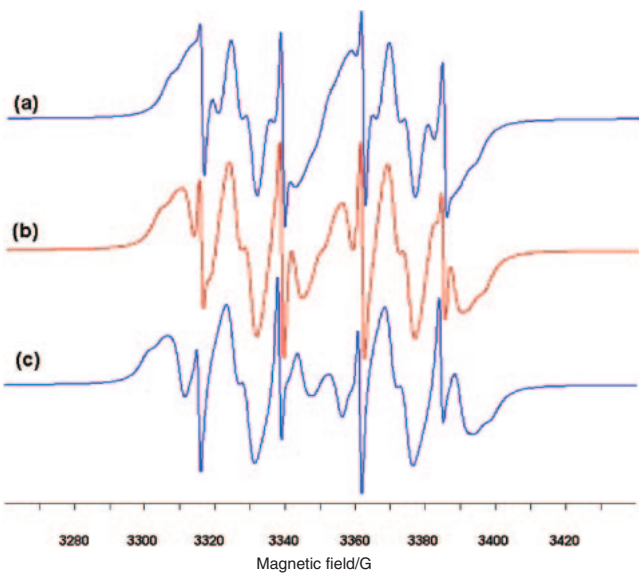

Figure 10. The simulated spectra due to HO–CH_2–CH_2• based on the model hfc tensors given in the text. Keeping all other parameters fixed, only the A_{iso} value was set at (a) −10, (b) −13, and (c) −16 G. The signals due to inadvertently formed methyl radicals are superposed.

model β-proton hfc constants with the dihedral angle of one of them chosen so as to yield the observed large doublet spacing (45 G), (3) exchange of the α-protons at the rate of 30 MHz, and (4) the isotropic g-tensor (=2.0023). The coupling constant of the second β-proton, owing to the 120° off-set of the dihedral angle, is negligibly small (≈4 G). The signals due to the methyl radical were included in the simulation. Figure 10 compares the result of simulations with the assumed A_{iso} values of −10, −13, and −16 G, respectively, keeping all other parameters fixed. The best fit was noted for A_{iso} of −13 G.

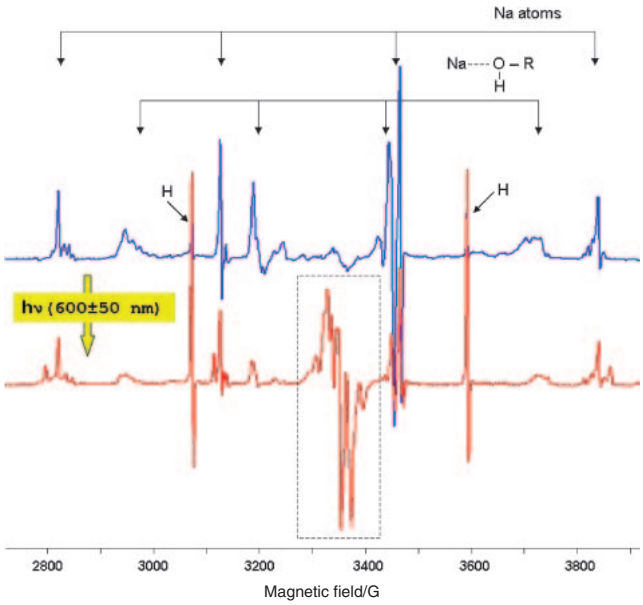

Figure 11. The ESR spectra observed from the 1,2-propanediol/Na/Ar system (a) before and (b) after irradiation of the matrix with yellow light (600 ± 50 nm).

Some discrepancy is believed due to neglect of anisotropy of the g-tensor. Here again, the A_{iso} value of −13 G is considerably smaller than the normal value of −23 G.

1,2-Propanediol: Figure 11 shows the ESR spectra observed from the 1,2-propanediol/Na/Ar system before and after photo-irradiation with yellow light (600 ± 50 nm) for 20 min. The photo-irradiation resulted in decrease of the Na signals (both isolated and complexed), a large increase of the signals due to H atoms, and an emergence of signals in the central section with an askew symmetry pattern. The latter spectrum is shown expanded in Figure 12a. As stated earlier, on account of its low vapor pressure, we could not control the concentration of 1,2-propanediol in the matrix. The spectrum has a quintet pattern as indicated. The askew symmetry of the quintet pattern indicates anisotropy in the g-tensor. These features can be accounted for by the acetaldehyde anion radical predicted by the MD calculation (Chart 4). The quintet pattern is attributed to the hfc interactions with the α-proton and the three β-protons of the rotating methyl group. Furthermore, a large increase of the H atom signal may be accounted for by photolysis of the radical as shown in Chart 5. Here the charge is borne by the resonance stabilized allylic form. The origin of the two signals indicated as of impurity is not known. Their intensity (relative to the quintet pattern) increased as the temperature of the sample reservoir was lowered.

As for the spectrum of the acetaldehyde anion, on account of the resonance between the two valence structures shown in Chart 6, it is expected that there would be a significant spin density on the oxygen atom. The semiempirical SCF calculation showed the spin density of 0.7 at the α-carbon and 0.3 at the oxygen atom. The non-bonding, lone pair electrons of the oxygen atom are in the in-plane p orbital perpendicular to the C–O bond. It is thus expected that the g-tensor of this radical would have a singularly large positive deviation (from the free

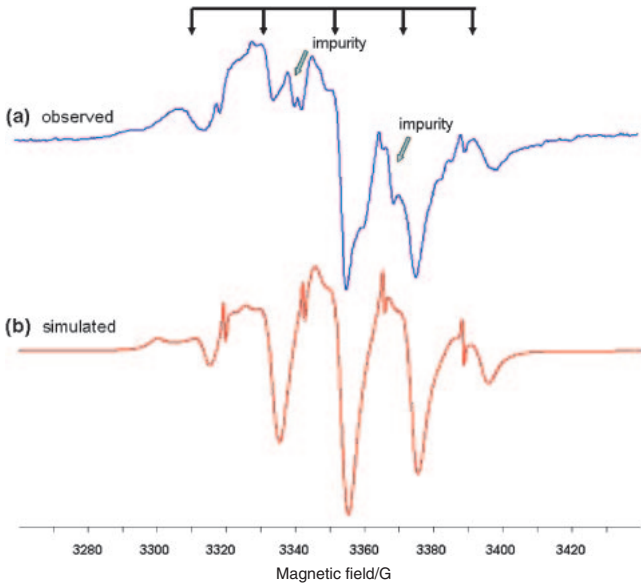

Figure 12. (a) The central section of the spectrum observed from the 1,2-propanediol/Na/Ar system after photoirradiation. (b) The simulated spectrum of the acetaldehyde anion radical, CH_3–C(–O^-)H•, based on the model hfc tensors given in the text. The signals due to inadvertently formed methyl radicals are superposed.

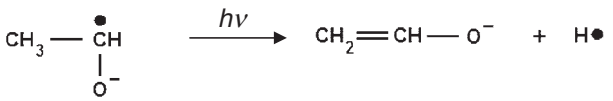

Chart 5.

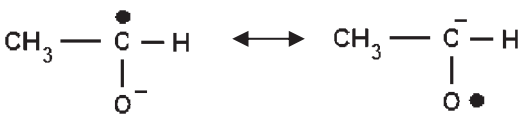

Chart 6.

spin value of 2.0023) in the direction of the C–O bond. Figure 12b is a computer simulated spectrum based on (1) the α-proton hfc tensor comprising A_{iso} of -20 G (equated to the average spacing of the quintet) and the model A_{dip} (adjusted for the spin density of 0.7 at the α-carbon), (2) the model β-proton hfc tensors (averaged for the case of rapidly rotating methyl unit and adjusted for the spin density of 0.7 at the α-carbon), (3) the g-value of 2.0083 along the direction of the C–O bond and 2.0023 along the other two principal axes, and (4) the O–C–H angle of 120 degrees.

Summary and Comments

The molecular dynamics calculations performed presently clearly revealed the anticipated extra-lability of the hydrogen-bonded hydroxy sector of methanol and ethanol dimers. Upon electron capture, the hydroxy hydrogen of the acceptor unit cleaved as an atom and abstracted a hydrogen atom of the methyl group of the donating alcohol. In the case of 1,2-propanediol, the anticipated intramolecular hydrogen bond was not found. It was learned however that the two hydroxy units at 1,2 positions caused the confinement of the LUMO in the C1–C2 region essentially as an antibonding σ-orbital, and that upon electron capture the C1–C2 bond cleaved and the resulting C1 fragment abstracted the hydrogen atom of the C2 hydroxy unit. The process thus yielded methanol and acetaldehyde anion radical. The matrix isolation ESR study confirmed generation of radicals predicted by the molecular dynamics calculations.

The A_{iso} value of the α-protons of the radical generated from the methanol dimer (R1) was -15 G, and that of the radical generated from ethanol dimer (R2) was -13 G. They are both significantly smaller than the typical value, -23 G, known for primary alkyl radicals. These α-protons being at the nodal plane of the p_π orbital, the A_{iso} results from spin-dependent polarization of the C–H σ-orbital by the unpaired electron in the p_π orbital. The A_{iso} would hence be sensitive to the presence of an oxy-substituent. The semiempirical SCF molecular orbital calculations yielded the A_{iso} value of -30 G for these radicals, and -40 G for A_{iso} of the methyl radical.

Most significantly the present study clearly elucidated the presence and mechanism of extra lability in the hydrogen bonded OH system.

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