Electron Spin Resonance Study of X-Irradiated Binary Mixtures of Benzene and Alcohols[1]

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Abstract: Binary mixtures of benzene with methanol and ethanol have been irradiated with X-rays at 77°K. and studied by e.s.r. and mass spectral methods. Using isotopic labeling of the benzene and the various positions in the alcohols, it was found that on X-irradiation the hydroxyl hydrogen was liberated. It then added to the benzene molecule to form $C_6H_7\cdot$ or abstracted an α hydrogen from the alcohol to form the corresponding alcohol radical. A mechanism is discussed for the process.

High-energy radiation effects of organic compounds have attracted much interest in recent years, and considerable effort has been channeled toward the determination of the degree and type of damage experienced by the parent molecule.

Radiation will be absorbed almost entirely by interaction with electrons.[2] For X-rays and low-energy γ rays, the photoelectric effect predominates, while in the 0.1- to 2-Mev range, Compton scattering is important. In the case of X-ray irradiation of the alcohols, one might expect electron ejection to take place in the neighborhood of the oxygen nucleus because of its higher charge. However, the eventual bond rupture does not appear to involve the oxygen bond but rather the α-carbon atom. Vapor phase chromatographic and mass spectral analysis of products formed by radiolysis of methanol and ethanol show a large yield of H_2 and vicinal glycols. The presence of these products is compatible with e.s.r. studies of irradiated solid methanol and ethanol where intermediate free radicals such as $\cdot CH_2OH$ and $CH_3\dot{C}HOH$ are observed.[3,4] An interesting question that arises in these systems involves the mechanism of the reactions taking place. In the case of methanol, is the $\cdot CH_2OH$ radical intimately involved with the primary electron ejection step, or does it represent a single step of a series of events? Indeed the latter may be suspected to be the case if electron ejection actually takes place in the environment of the oxygen atom. It is to this aspect of the problem that this study has addressed itself, and this paper presents the pertinent results obtained.

Experimental Section

All chemicals used were reagent grade and used without further purification. The isotopically substituted compounds were obtained from Volk RadioChemical Co. and have a minimum isotopic purity of 98 atom %.

Frozen, clear glassy spheres were formed for irradiation by dropping small droplets of a 5 mole % benzene in alcohol solution from a syringe into liquid nitrogen. The sample spheres rested on a copper block immersed in liquid nitrogen and they were irradiated with a G.E. Maxitron 250 therapeutic X-ray unit for several hours. Doses of over 1 Mr. were given; however, the maximum number of free radicals attainable reached a steady state at doses of somewhat less than 1 megarad.

Preliminary tests had shown that when the sample was thoroughly outgassed, vacuum distilled into a quartz sample tube, sealed off, frozen, and irradiated, the results were unchanged.

The mass spectral data of the irradiated CD_3OH were taken on a CEC Type 21-103C spectrometer.

The e.s.r. equipment was a Varian Model 4500-10 spectrometer employing 100-kc./sec. modulation and a 6-in. magnet equipped with liquid nitrogen dewar and variable temperature accessories. Magnetic field measurements were made on a Harvey-Wells Electronic Inc. Model G-501 gaussmeter using DPPH as a standard.

Results and Discussion

Irradiation of a 5 mole % benzene–methanol glass at 77°K. produced an e.s.r. spectrum that consisted of a strong triplet superimposed on another spectrum, four small lines of which could be seen on either side of the triplet. The deep red-purple color of the irradiated sample could be bleached by sunlight or ultraviolet light. After bleaching, the center line of the triplet decayed significantly, altering the intensity of this triplet to 1:2:1. The four satellite lines on each side of the triplet remained unchanged. The bleaching phenomena have been associated with the solvated electron, and the triplet observed has been assigned to the methanol radical $\cdot CH_2OH$.

As the sample temperature was permitted to increase, the methanol radical triplet decayed and finally disappeared at ~114°K. The satellites that were present on each side of the triplet remained unchanged. Figure 1 shows the spectrum obtained after the complete disappearance of the methanol radical. It consists of a 1:2:1 triplet with a 47.5-gauss splitting. Each line of the triplet is further split into a 1:3:3:1 quartet with a 10.4-gauss spacing, and each of the latter lines are split into a 1:2:1 triplet of 2.5 gauss. This latter splitting is not evident in Figure 1. This spectrum has been shown by others[5-7] to be due to the cyclohexadienyl free radical which is formed by the addition of a hydrogen atom to the benzene ring. The large splitting is due to the two hydrogens on the sp^3 carbon. The quartet is due to the nearly equivalent hydrogens positioned *ortho* and *para* to the sp^3 carbon, and the two *meta* hydrogens give rise to the 1:2:1 triplet with the 2.5-gauss splitting.

Ohnishi and co-workers[5] have reported that γ irradiation of benzene at 77°K. produces a phenyl radical

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[1] This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

[2] R. O. Bolt and J. G. Carroll, Ed., "Radiation Effects on Organic Materials," Academic Press Inc., New York, N. Y., 1963.

[3] R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959).

[4] H. Zeldes and R. Livingston, *ibid.*, **30**, 40 (1959).

[5] S. Ohnishi, T. Tanei, and I. Nitta, *ibid.*, 37, 2402 (1962).

[6] H. Fischer, *Kolloid-Z.*, **180**, 64 (1964).

[7] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).

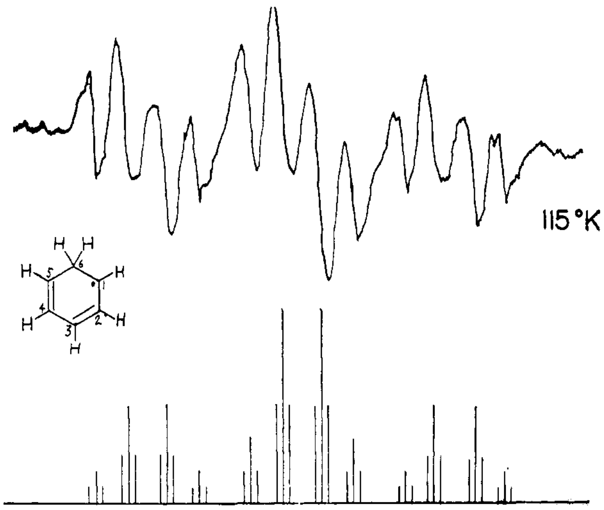

Figure 1. The e.s.r. spectrum of an irradiated 5 mole % benzene in methanol solution at 115 °K.

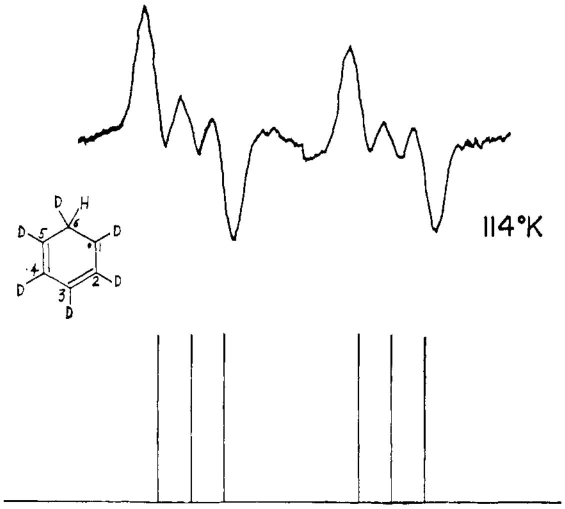

Figure 2. The e.s.r. spectrum of an irradiated 5 mole % perdeuteriobenzene in methanol solution at 114 °K.

and the resulting hydrogen atom adds to benzene to produce the cyclohexadienyl free radical. The spectrum obtained is similar to that shown in Figure 1 except that the center portion is distorted by the presence of a superimposed broad single line due to the phenyl radical which is stable up to 0°, whereas the hydrogen addition product decays at about −50°. In view of the small concentration of the benzene in the methanol matrix, and in view of the absence of any distortion in the spectrum in Figure 1, we conclude that the phenyl radical is not present and the observed spectrum is due to the presence of the cyclohexadienyl free radical produced by the reaction of benzene with a hydrogen atom from the methanol matrix.

The above experiment was repeated under the same conditions except that perdeuteriobenzene was used, and the results are shown in Figure 2. A doublet with a spacing of 48.5 gauss is obtained and each component of the doublet is split into a triplet with a spacing of 7.9 gauss. This spectrum is compatible with the assumption that a hydrogen atom from the methanol matrix has added to a deuterated benzene molecule. Again there is no evidence of the phenyl radical.

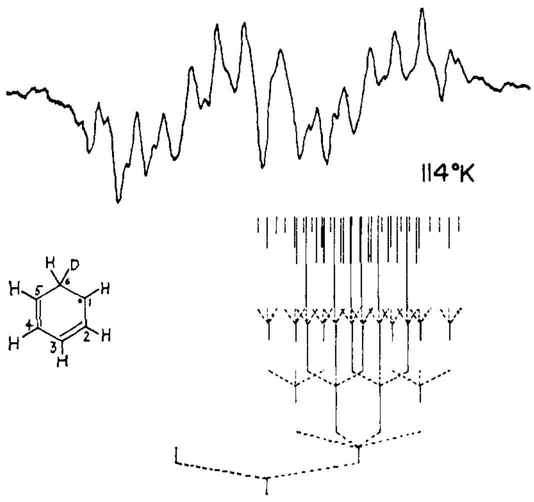

Figure 3. The e.s.r. spectrum of an irradiated 5 mole % benzene in methanol-*d* solution at 114 °K.

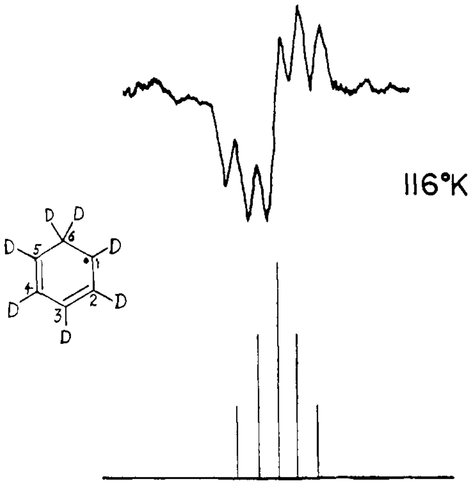

Figure 4. The e.s.r. spectrum of an irradiated 5 mole % perdeuteriobenzene in methanol-*d* solution at 116 °K.

The experiment was repeated again with a solution of normal benzene in CH_3OD. The results are shown in Figure 3. Careful examination of this spectrum reveals that this is the expected result if a deuterium atom is added to benzene. There is no clear evidence in the spectrum that any α hydrogen has added to benzene. If perdeuteriobenzene is dissolved in CH_3OD and irradiated at 77 °K., the spectrum shown in Figure 4 is obtained. Here one has a 1:2:3:2:1 quintet due to two equivalent deuterium atoms on the sp^3 carbon atom of the cyclohexadienyl free radical. The splitting is 7.9 gauss. The smaller hyperfine splittings due to the other deuterium atoms in the radical were not resolved. When irradiations were made of benzene and CD_3OH and perdeuteriobenzene and CD_3OH, the results were identical with those obtained when CH_3OH was used.

It is thus apparent that in the majority of the cases it is the hydroxyl hydrogen that is liberated by 250 kev. γ irradiation. This hydrogen atom then either adds to benzene to form the cyclohexadienyl free radical, abstracts hydrogen from a methyl group to give the methanol free radical, or combines with another hydrogen atom to give H_2. Further confirmation of these deductions was obtained from some mass spectral data.

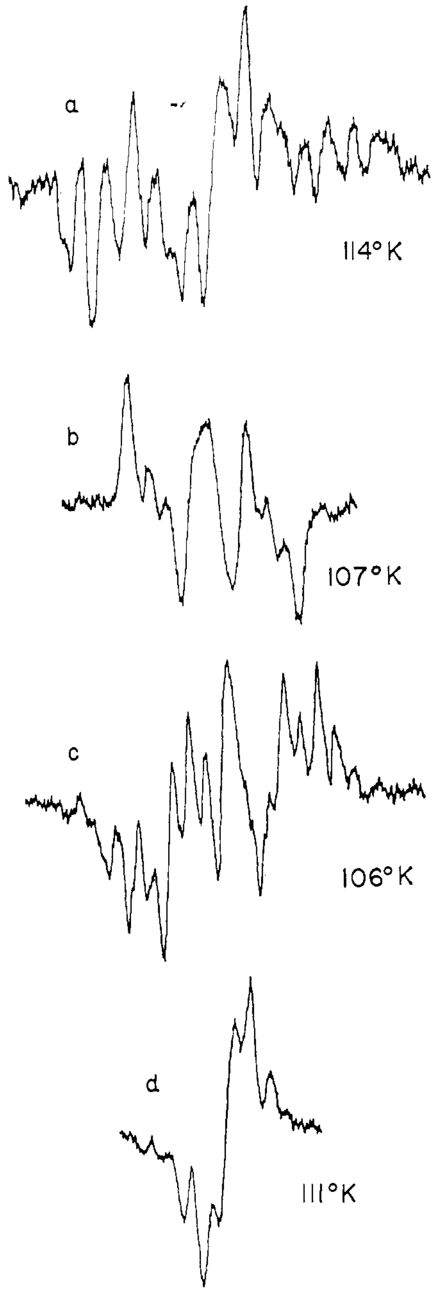

Figure 5. The e.s.r. spectra of irradiated benzene in ethanol solutions: (a) 5 mole % benzene in ethanol; (b) 5 mole % perdeuteriobenzene in ethanol; (c) 5 mole % benzene in ethanol-*d*; (d) 5 mole % perdeuteriobenzene in ethanol-*d*.

A sample of CD_3OH was thoroughly out-gassed in a vacuum system by pumping ($<10^{-5}$ mm.) and subjecting the sample to several freeze–pump–thaw cycles. The sample was then irradiated in the glassy state at 77°K. The sample was permitted to melt and was then cooled to 77°K. and the gas phase of this tube was then analyzed mass spectroscopically.

The results gave 58% HD, 30% H_2, and 12% D_2. If one ignores the isotope effect which would favor H· production, then upon X-irradiation it is, to a great degree, the hydroxyl hydrogen that is liberated and is the precursor to the methanol free radical. Assuming equal probability of OH and CD bond rupture as the sole cause of H· and D· liberation, the expected yield of deuterium would be 75% rather than the obtained ratio of $^{41}/_{59}$ of D/H since there are three deuterium atoms to every hydrogen atom in CD_3OH. The amount of hydrogen liberated from the benzene, if that were the case in the mixed sample, again would contribute only a small amount of H·. Thus, the small amount of D_2 indicates that in a much smaller number of events the α hydrogen may be liberated. Work done by Meshitsuka[8] and co-workers on the γ radiolysis of CH_3OD supports the assumption that the hydroxyl hydrogen is the most viable.

The above experiments were also carried out with ethanol–benzene mixtures. Figure 5a gives the e.s.r. spectrum obtained on irradiation of C_2H_5OH and C_6H_6. The slight distortion of the spectrum is due to the fact that the α-ethanol free radical decays just a few degrees cooler than the cyclohexadienyl radical does, so there is a small amount of contribution to the spectrum from the presence of residual $CH_3\dot{C}HOH$. However, the main features of the spectrum are easily recognizable. In Figure 5b (perdeuteriobenzene in ethanol) the two sets of triplets are readily visible and the resonance is similar to that obtained with methanol. The effects of the residual ethanol radical are again visible. Figure 5c (C_2H_5OD plus benzene) gives results which match the results obtained with CH_3OD. In Figure 5d correlation is again obtained with perdeuteriobenzene and C_2H_5OD. Benzene solutions were also run with ethanol-d_2 and ethanol-d_3 and, as in the methanol case, the results were the same as with fully protonated alcohol. A few experiments were attempted with higher alcohols, *i.e.*, 2-propanol and 1-butanol. However, because of the smaller mobility of the alcohol radicals, they persist in the spectrum at higher temperatures than the cyclohexadienyl radical, making the analyses of the spectra considerably more difficult so that this phase of the work was not pursued further.

Further evidence to support these results is found in the results obtained by Strong and Burr.[9] The γ radiolysis of 2-propanol in the liquid phase with 1% benzophenone added as a hydrogen atom scavenger shows a high degree of hydroxyl hydrogen liberation from the alcohol.

These results can be discussed with only minor changes in the mechanism proposed by Hayon and Weiss.[10] Step 1 shows the initial products formed after the high-energy photoelectron and the secondary electrons it produces have reached thermal energies.

$$CH_3OH \rightsquigarrow (CH_3OH)^+,\ (CH_3OH)^-,\ \text{and } e^-_{solv} \qquad (1)$$

Here the e^-_{solv} species is an electron held in a cage but not associated with any one alcohol molecule.[11] Step 2 represents the decay of the polarons; however, the decay of $(CH_3OH)^+$ to $\cdot CH_2OH + H^+$ would have to be minor if it is to be compatible with our mass spectral

$$(CH_3OH)^- \longrightarrow CH_3O^- + H\cdot \qquad (2a)$$

$$\begin{tikzcd}
 & \cdot CH_2OH + H^+ \\
(CH_3OH)^+ \arrow[ur] \arrow[r] \arrow[dr] & CH_3O\cdot + H^+ \qquad (2b) \\
 & CH_3O^+ + H\cdot
\end{tikzcd}$$

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(8) G. Meshitsuka, K. Ouchi, K. Hisota, and G. Kusumota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **78**, 129 (1957).

(9) J. D. Strong, and J. G. Burr *J. Am. Chem. Soc.*, **81**, 775 (1959).

(10) E. Hayon and J. J. Weiss, *J. Chem. Soc.*, 3962 (1961).

(11) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).

and e.s.r. results on irradiated CD_3OH. Step 3 shows a series of reactions, some of which also contribute to the over-all process.

$$H^+ + (CH_3OH)^- \longrightarrow H\cdot + CH_3OH \qquad (3a)$$

$$H^+ + CH_3O^- \longrightarrow CH_3OH \qquad (3b)$$

$$H\cdot + CH_3OH \longrightarrow \cdot CH_2OH + H_2 \qquad (3c)$$

$$H\cdot + H\cdot \longrightarrow H_2 \qquad (3d)$$

$$H\cdot + C_6H_6 \longrightarrow C_6H_7\cdot \qquad (3e)$$

$$CH_3O\cdot + CH_3OH \longrightarrow CH_3OH + \cdot CH_2OH \qquad (3f)$$

After appropriate combination of these steps, one is left with three paramagnetic species: the methanol radical, the cyclohexadienyl radical, and the solvated electron; and an ionic species, probably $(CH_3OH_2)^+$. According to Smith and Pieroni[11] there is an average of 40–50 Å. distance separating the trapped electron and the positive ion, and there probably is a significant coulombic attraction between these species. Consequently, on bleaching as represented in step 4 there is a release of the electron and neutralization of the positive ion leaving the observed radicals $\cdot CH_2OH$ and $C_6H_7\cdot$. Other conjugated aromatic ring systems such as toluene and naphthalene are under study, and preliminary results indicate that here also the hydroxyl hydrogen liberated from alcohols by radiation adds to the ring.

$$(CH_3OH_2)^+ + e^-_{solv} \rightsquigarrow CH_3OH + H\cdot \qquad (4a)$$

$$CH_3O^+ + e^-_{solv} \rightsquigarrow CH_3O\cdot \qquad (4b)$$

An Electron Spin Resonance Study of the Anion Radical of Azodicarbonitrile

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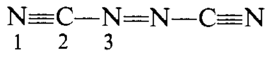
Abstract: The e.s.r. spectrum of the anion radical of azodicarbonitrile was obtained. The ^{14}N hyperfine splittings are 7.37 and 2.11 oersteds. The observed ^{14}N splittings are considered with respect to the σ–π parameters reported for other azine and nitrile anion-radical systems. The σ–π parameters of Stone and Maki, when used to calculate the azine splitting, give good agreement with the experimental value. The values of Rieger and Fraenkel for nitrile nitrogen do not yield satisfactory results, and more satisfactory values are suggested.

The isotropic nitrogen hyperfine splittings in azine radicals are of significant interest.[1] The rationalization of such splittings in terms of the relationship between π-electron spin densities and ^{14}N coupling constants based on the Karplus–Fraenkel[2] treatment of ^{13}C is of considerable concern in studies of the electronic structure of nitrogen-containing radicals.

Nitrogen hyperfine splittings arising from azodicarbonitrile (I) anion radical[3] and their rationalization in terms of the Karplus–Fraenkel treatment are reported.



$$\underset{1}{N}{\equiv}\underset{2}{C}{-}\underset{3}{N}{=}N{-}C{\equiv}N$$

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Experimental Section

The anion radical of azodicarbonitrile was prepared in 1,2-dimethoxyethane as described elsewhere.[3] The spectrometer was a Varian e.s.r. spectrometer equipped with a dual cavity, 12-in. electromagnet, and a flux stabilizer to scan the magnetic field. The spectra were obtained at room temperature.

Results

The e.s.r. spectrum of an 8×10^{-4} M solution of azodicarbonitrile anion radical consists of five lines, each further split into five lines. The relative intensities of each set are those expected for two equivalent nitrogens, *i.e.*, 1:2:3:2:1. The hyperfine splittings are 7.37 and 2.11 oersteds. Assignment of the splitting constants is based upon LCAO–MO calculations and the knowledge that nitrile nitrogens yield small splittings, *i.e.*, in the range 0.5 to 3 oersteds.

Discussion

A. Possible Structures of the Anion Radical. Azodicarbonitrile exists in *cis* and *trans* isomeric forms.[3] The observed e.s.r. spectrum of the anion radical could arise from any of the following structural forms: *cis*, *trans*, linear, or a mixture of *cis* and *trans* isomers. If the e.s.r. spectrum arises from a mixture of *cis* and *trans* isomers, the two isomers either have identical resonance spectra or they undergo interconversion at frequencies larger than the difference between the spectral positions (expressed in units of frequency) associated with each isomer. Finally, a comment about the linear structure: one could conjecture that increased conjugation of the type $^-N{=}C{=}N{-}N{=}C{=}N\cdot$ might lead to stabilization of the linear over the *cis* and *trans* forms. Unfortunately the results of this study cannot allow more to be said with regard to the anion-radical structure.

B. MO Calculations. Both simple Hückel and McLachlan[4] MO-SCF calculations of π-spin densities were made. The results are shown in Table I. In

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[1] D. H. Geske and G. R. Padmanabhan, *J. Am. Chem. Soc.*, **87**, 1651 (1965), and references cited therein.

[2] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[3] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **87**, 1819 (1965).

[4] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).