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An Electron Spin Resonance Study of Free Radicals in Ultraviolet-Irradiated Ethanol at 77°K.

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The electron spin resonance (e.s.r.) spectra of isotopically substituted ethyl radicals have been studied in ultraviolet-irradiated ethanol at 77°K. The observed line shapes in C_2H_5 , CH_3CD_2 , CD_3CH_2 , and C_2D_5 were in good agreement with theoretical line shapes recently calculated for the effects of anisotropic hyperfine interactions in polycrystalline media. All lines corresponding to antiparallel orientation of the α -protons or deuterons were sharp and isotropic, while other lines were weak and asymmetric owing to the anisotropic interaction of the electron with the nuclear dipoles at the α -position. In cases where hydrogen occupied the α -position in the ethanol molecule, the radical CH_3CHOH and its analogs were also produced during irradiation. When the α -hydrogen was replaced by deuterium, the only significant photolytic event was rupture of the C-O bond. The ethyl radicals decayed slowly at 77°K., apparently by hydrogen abstraction from the parent molecule which formed the matrix. After complete decay of the radicals produced during photolysis, a broad asymmetric singlet assigned to the ethoxy radical remained. An activation energy of 8-10 kcal./mole was calculated for the decay of the ethyl radicals by hydrogen abstraction.

Introduction

The electron spin resonance (e.s.r.) spectra of isotopically substituted ethyl radicals have been studied in ultraviolet-irradiated ethanol at liquid nitrogen temperatures. Several reports of applications of e.s.r. techniques to irradiated ethanol have already appeared,¹⁻⁴ although in only one of these have the spectra of ethyl radicals been found.⁴ Their appearance under the present experimental conditions is in accord with results reported in two recent studies of ultraviolet-irradiated methanol,^{5,6} and a detailed discussion of possible mechanisms of the production of radicals involving rupture of the C-O bond may be found therein. Several other radicals produced during and after the irradiation process have also been observed in the frozen ethanol matrix.

Experimental

A Varian Associates Model V 4500 e.s.r. spectrometer employing 100 kc. modulation was used to record the first derivative of the absorption spectrum. The magnetic field was monitored with a Harvey-Wells Electronic Inc. Model G-501 gaussmeter. The g -values of the spectra were determined by comparison with DPPH for which the g -value is accurately known to be 2.0036.

All irradiations were made with a low pressure mercury lamp using a Vycor filter to eliminate the 1849 Å. mercury line. Samples of liquid ethanol (C_2H_5OH , C_2H_5OD , CH_3CD_2OH , CD_3CH_2OH , C_2D_5OH) were placed in silica tubes at room temperature, frozen in a liquid nitrogen dewar, and irradiated for 30 min. before being placed in a second dewar situated in the microwave cavity. The deuterated alcohols were made by Merck Sharp and Dohme of Canada. Various precautions employed to facilitate unambiguous interpretation of results have been described earlier.⁶

Results

I. The Ethyl and Ethanol Radicals.—The observed line shapes for the radicals C_2H_5 , CH_3CD_2 , CD_3CH_2 , and C_2D_5 were in good agreement with theoretical line shapes recently calculated for the effects of anisotropic hyperfine interactions of alkyl radicals in polycrystalline media by Cochran, Adrian, and Bowers.⁷ In fact, without this theoretical framework no identification of the isotopically substituted radicals could confidently be made because of the considerable distortion of the spectral lines resulting from anisotropic interactions.

Following the usual notation we refer to the carbon adjacent to the hydroxyl group as the α -carbon and

the hydrogen (or deuterium) atoms bonded to it as α -hydrogens. The atoms of the methyl group are designated by β . It was found that all lines of the ethyl radical spectrum corresponding to antiparallel orientation of the α -protons or deuterons were sharp and showed no discernible anisotropic broadening. Other lines were weak and asymmetric owing to the anisotropic interaction of the electron with the nuclear dipoles at the α -position. In the ethyl radical the anisotropic interaction with the α -hydrogens is of the same order of magnitude as the isotropic interaction while the anisotropic interaction with the β -hydrogens is negligible.

In cases where hydrogen occupied the α -position in the ethanol molecule, the radical CH_3CHOH and its analogs were also produced during irradiation. No detailed observations could be made on these radicals since it was found impossible to separate their spectra from the ethyl radical spectra. In cases where the α -hydrogen was replaced by deuterium the only significant photolytic event was rupture of the C-O bond. This type of isotope effect in irradiation was reported previously in ultraviolet-irradiated methanol.⁶ There was also evidence for some rupture of the C-C bond during photolysis, but this effect is quite small.

The spectrum of irradiated C_2H_5OH contained the "quartet of triplets" first observed by Smaller and Matheson and an underlying quintet assigned to the ethanol radical (CH_3CHOH). The ethyl radical spectrum (Fig. 1) in ethanol at 77°K. appears to be nearly identical with that obtained by Cochran, Adrian, and Bowers from the photolysis of ethyl iodide in argon at 4.2°K.⁷ The lines corresponding to antiparallel orientation of the α -protons are sharp and isotropic. In the line reconstruction below, these prominent lines are labeled according to the scheme ($M_{1\alpha}, M_{1\beta}$), where $M_{1\alpha}$ is the net magnetic quantum number of the α -protons and $M_{1\beta}$ is that of the β -protons. The hyperfine splitting between the isotropic lines is 27 gauss. All lines corresponding to parallel orientation of the α -protons are seen to be weak and asymmetric.

The underlying quintet of the CH_3CHOH radical is poorly resolved and adds to the difficulty of interpreting the spectrum. However, Fig. 1 also includes the spectrum of C_2H_5OD in which may be seen a decided sharpening of the lines of the quintet. This effect supports the choice of CH_3CHOD instead of $(C_2H_4)^+$ as the cause of the resonance.

The spectrum of irradiated CH_3CD_2OH contains four prominent lines which have a 1:3:3:1 intensity ratio and a 27-gauss hyperfine splitting (Fig. 2). Theoretically each of these lines is the central component of a quintet, but the anisotropic hyperfine interaction has broadened the other lines to such an

(1) C. F. Luck and W. Gordy, *J. Am. Chem. Soc.*, **78**, 3240 (1956).(2) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).(3) H. Zeldes and R. Livingston, *ibid.*, **30**, 40 (1959).

(4) L. H. Piette, "NMR and EPR Spectroscopy," Pergamon Press, New York, N. Y., 1960, p. 221.

(5) P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **84**, 1 (1962).(6) P. J. Sullivan and W. S. Koski, *ibid.*, **85**, 384 (1963).(7) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **34**, 1161 (1961).

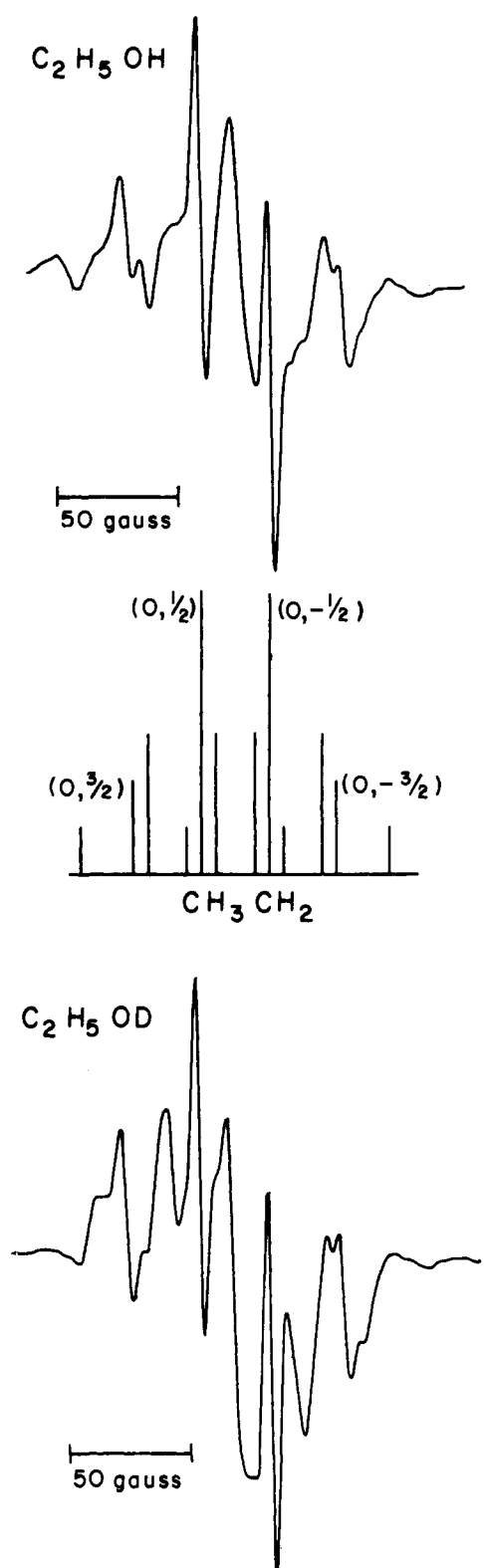


Fig. 1.—E.s.r. spectra of C_2H_5OH and C_2H_5OD after 30-min. ultraviolet irradiation at $77^\circ K$.

extent that the quartet could easily be mistaken for the methyl quartet except for the larger splitting. The symmetry of the spectrum indicates that there has probably been little production of a CH_3CDOH radical, since a 22-gauss splitting would be expected for the prominent lines of the spectrum of this radical.

Irradiation of the alcohol deuterated at the methyl position produced a central septet of about 4-gauss hyperfine splitting and an unresolved resonance on either side (Fig. 2). The distortion of the ethyl radical

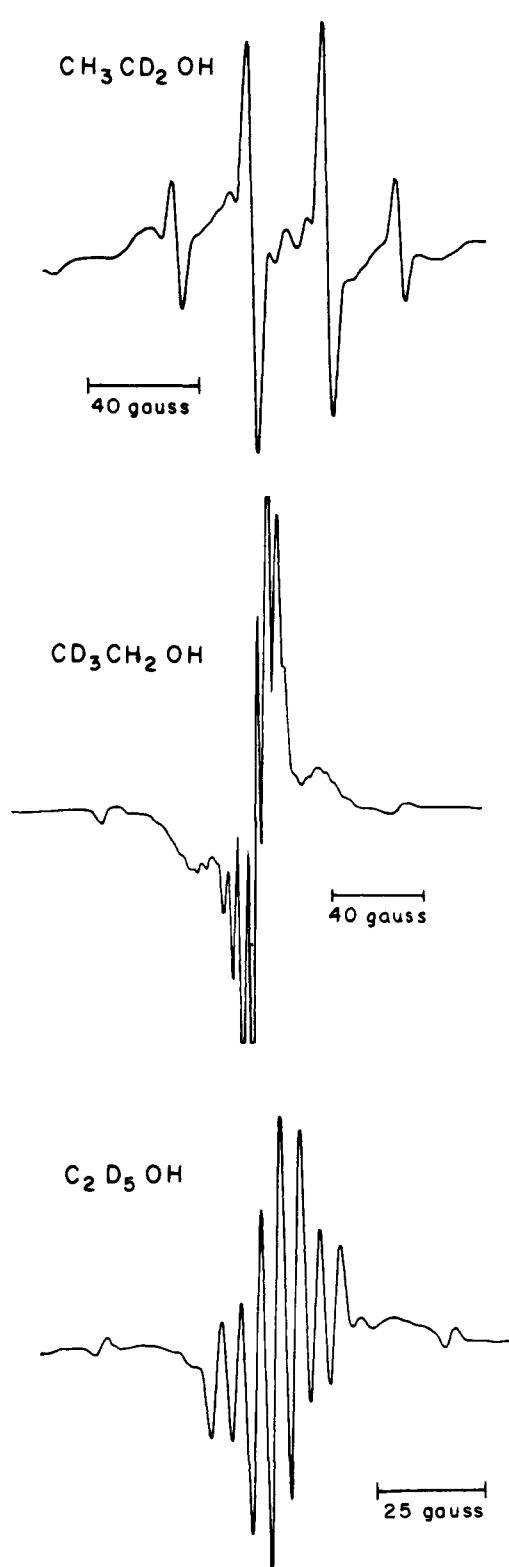


Fig. 2.—E.s.r. spectra of CH_3CD_2OH , CD_3CH_2OH , and C_2D_5OH after 30-min. ultraviolet irradiation at $77^\circ K$.

spectrum indicates that there has been some production of a CD_3CHOH radical during irradiation. Here also is seen some evidence that there is rupture of the C-C bond during irradiation. The two small lines marked in the wings of the spectrum have the correct 130-gauss splitting and anisotropic appearance to be assigned to the formyl radical. Studies on methanol, made both in our own laboratory and by Alger, Anderson, and Webb,⁸ have shown that the radical CH_2OH is quickly

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

reduced to the formyl radical by ultraviolet light in the 2500 Å. region. Rupture of the C-C bond in C_2H_5OH would also then result in production of CHO radicals, but in this case the formyl spectrum is hidden under the outer components of the ethyl radical. Similarly, in the ethanol where deuterium occupies the α -position, the lines of the deuterated formyl radical would be masked by resonances with similar splittings.

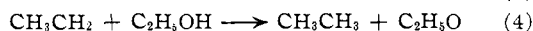
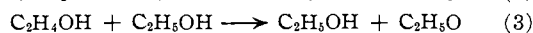
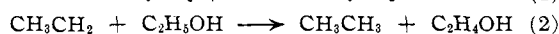
Figure 2 also shows the spectrum of the fully deuterated ethyl radical. Again the symmetry of the spectrum indicates that there is no other prominent spectrum underlying the septet. Each line of the septet is theoretically the central component of a quintet, and at the sides of the spectrum some of these weaker lines can be observed, though most of them are masked by the strong components. The two lines at the extremes of this spectrum have an 80-gauss splitting and an isotropic appearance. The problem of impurities has been considered in some detail, and small quantities of possible impurities such as acetaldehyde have been added to alcohol samples without affecting the productions of radicals thought to arise from the alcohol itself. In the present case, it is known that the CH_3CD_2OH alcohol is exceptionally radiation-sensitive (there are always higher yields of ethyl radicals from this alcohol, sometimes by a factor of 5 or 10) and the CH_3CD_2 radical appears to be a possible cause of the two weak outer lines. Complex line systems formed by impurities of other partially deuterated species may be proportionally less prominent because of overlap with the strong central spectrum and the smearing effect of the anisotropic interaction.

II. Stability of the Radicals: The Ethoxy Radical.—

Observations made over a period of time revealed that at 77°K. most of the radicals produced by photolysis were relatively short lived. The ethyl radicals in C_2H_5OH decayed with a 2-hr. half-life at 77°K., while the fully deuterated radical had a 2-day half-life at the same temperature. Plots of signal intensity *vs.* time showed some curvature at first (attributed to decay by recombination) then straightened out to show first-order kinetics. A gradual increase in the first-order decay rate with increasing deuterium in the matrix appeared to support the conclusion reached in the methanol studies⁶ that the primary decay mechanism was the abstraction of hydrogen or deuterium from the parent molecule which formed the matrix. A variable temperature study yielded an estimate of 8–10 kcal./mole for the activation energy of the hydrogen-abstraction process for ethyl radicals.

The ethanol radical, CH_3CHOH , had a 1–2-day half-life at 77°K., and CD_3CHOH seemed slightly more stable. This behavior suggested that these radicals also decayed by hydrogen abstraction.

As the radicals produced by photolysis decayed, the center of the spectrum became distorted by the growth of a new signal which, after the complete decay of the less stable radicals, appeared to be a broad asymmetric singlet. This relatively stable single line was assigned to an ethoxy radical. Its appearance can be explained on the basis of the following series of competitive reactions taking place in the solid phase. (In this scheme R represents any radical; only the possibilities for C_2H_5OH are shown.)



Reaction 1 is not highly important and is assumed to occur only during a short period after irradiation. Reaction 2 results in the production of unstable radicals

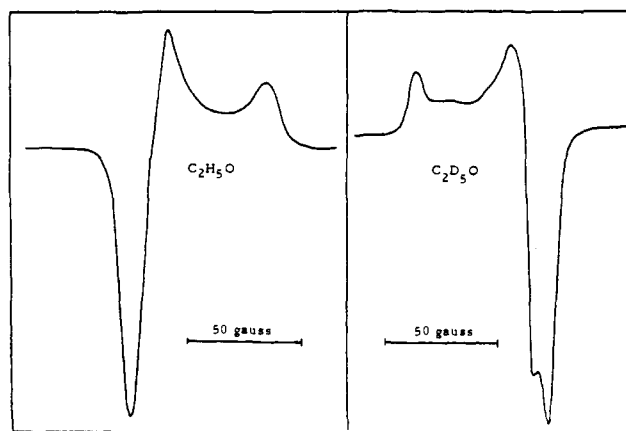


Fig. 3.—E.s.r. spectra due to ethoxy radicals.

which will in turn react with the matrix, as indicated in reaction 3. Reactions 3 and 4 result in relatively stable end products. The half-life of the ethoxy radical was a period of weeks or months at 77°K.

The ethoxy radicals showed the same variation in their spectra which was noted in the methoxy radicals (Fig. 3). The spectrum of C_2H_5O appears to have the characteristics of a radical of two *g*-values, while the spectrum of C_2D_5O indicates three *g*-values.⁹ The better resolution in the second case is attributed to the smaller magnetic interactions of the deuteron in the various processes which contribute to line broadening. Assuming a *Z*-axis along the C-O bond, the experimental *g*-values may be assigned qualitatively as follows. A *g*-value with a large positive shift, $g_z = 2.034$, occurring when the magnetic field lies parallel to the C-O bond, arises from the promotion of one of the non-bonding electrons into the half-filled orbital of the unpaired electron. When the direction of the magnetic field is perpendicular to the plane containing the C-O bond and the orbital of the unpaired electron, a *g*-value with a small positive shift, $g_x = 2.007$, probably results from the promotion of an electron from the C-O bond into the half-filled orbital. An undeviated *g*-value, $g_y = 2.002$, corresponds to a magnetic field parallel to the orbital of the unpaired electrons. Within the limits of accuracy imposed by the method of measurement, these *g*-values are the same as those of the methoxy radical. The unpaired electron, largely isolated in the oxygen orbital, is apparently little influenced by substitution of the methyl group for a hydrogen on the α -carbon. A detailed comparison of line shapes, however, revealed characteristic variations in line width which permitted a clear distinction among the resonances variously assigned to CH_3O , CD_3O , C_2H_5O , and C_2D_5O .

Conclusion

This study shows that, on ultraviolet irradiation of frozen ethanol at 77°K., the ethyl, ethanol, and ethoxy radicals are the principal intermediates formed which give rise to the spin resonance signal. The ethyl radical decayed by hydrogen abstraction from the parent molecule which constituted the matrix. An activation energy of 8–10 kcal./mole was obtained for this reaction. After complete decay of the radicals produced during photolysis, a broad asymmetric singlet remained and it was associated with the ethoxy radical. The results closely paralleled a similar study of irradiated methanol.

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(9) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).