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Electron Spin Resonance Study of Irradiated Methanol[1]

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The electron spin resonance spectra of ultraviolet irradiated isotopically substituted methanol were investigated. Studying the spectra as a function of isotopic substitution, time of irradiation and temperature permitted the identification with considerable certainty of these radicals, $\cdot CH_2OH$, $\cdot CH_2OD$, $\cdot CH_3$, $\cdot CD_3$, $\cdot CHO$ and $\cdot CDO$. Evidence also was obtained for the radicals $\cdot CD_2OH$, $\cdot COD$, $\cdot COH$, $CH_3O\cdot$ and $CD_3O\cdot$.

Introduction

A study of the electron spin resonance (e.s.r.) spectrum of $C^{14}H_3OH$ has motivated an extensive investigation of ultraviolet irradiated isotopically-substituted methanol. Irradiated methanol has been studied previously by e.s.r. methods,[2-4] but in the present work detailed observations on the stability of the radicals as a function of time and of temperature, and an interesting isotope effect permit the identification of several previously unobserved radicals, and answer some questions left undecided by earlier work.

Experimental

A Varian Associates Model V 4500 e.s.r. spectrometer 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 1,1-diphenyl-2-picrylhydrozyl (DPPH) for which the g-value is accurately known to be 2.0036.[5] All line widths were measured from the maximum to the minimum of the first derivative curve.

One millimole of one millicurie of $C^{14}H_3OH$ was sealed in a tube and kept frozen for several weeks in liquid nitrogen. It was examined at intervals in the spectrometer.

All other samples were placed in quartz tubes and then in a Dewar of liquid nitrogen which was situated in the microwave cavity. The deuterated methanols were made by Volk Radio Chemical Co., Chicago. The quick cooling of the sample usually resulted in partial crystallization; attempts to determine differences between a crystallized sample and a supercooled clear sample were inconclusive since the latter always were partially crystallized after irradiation and removal from the cavity. Addition of several per cent. water to absolute methanol other than CH_3OD did not noticeably affect the spectra.

The 0.5 cc. samples were irradiated in the microwave cavity by ultraviolet light from a low pressure mercury lamp. Filtering showed that it was the 2536 Å. line which produced the spectra. The relatively low energy was assumed to rule out the formation of detectable amounts of ionized species.[6] The spectra were recorded during irradiation and at intervals afterward, since both the development pattern and the decay were significant in identifying the spectral lines. The glassware was checked periodically for a signal, but none was observed near $g = 2$. Irradiation periods lasted 10 min. to 1 hr.

Results

Figure 1 gives typical results obtained from ultraviolet irradiated CH_3OH and CH_3OD and a spectrum of $C^{14}H_3OH$ frozen at liquid nitrogen temperature. In the latter case, the free radicals are produced by the β-rays from the decay of C^{14}. Irradiation of CH_3OH (Fig. 1-A) produced a quartet characterized by a 1:3:3:1 intensity ratio, a 23.5 gauss hyperfine splitting, and a line width of 3–4 gauss. Underlying the quartet is a triplet with an approximately 1:2:1 intensity ratio, an 18 gauss splitting and an 11 gauss line width. The triplet is seen clearly in Fig. 1-B where, at 1.5 hr. after irradiation, the quartet has almost completely decayed. Both spectra show a strong doublet of 130 gauss splitting which appeared first as the spectrum was recorded during irradiation. These lines are asymmetric with the high field component exhibiting more apparent asymmetry. There also appears to

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[1] This work was done under the auspices of the United States Atomic Energy Commission.

[2] C. F. Luck and W. Gordy, *J. Am. Chem. Soc.*, **78**, 3240 (1956).

[3] (a) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958); (b) H. Zeldes and R. Livingston, *ibid.*, **30**, 40 (1959).

[4] The NMR-EPR Staff of Vairan Associates, "NMR and EPR Spectroscopy," Pergamon Press, Inc., New York, N. Y., 1960, Chap. 20, p. 250.

[5] A. N. Holden, W. A. Yager and F. R. Merritt, *J. Chem. Phys.*, **19**, 1319 (1951).

[6] C. P. Poole and R. S. Anderson, *ibid.*, **31**, 346 (1959).

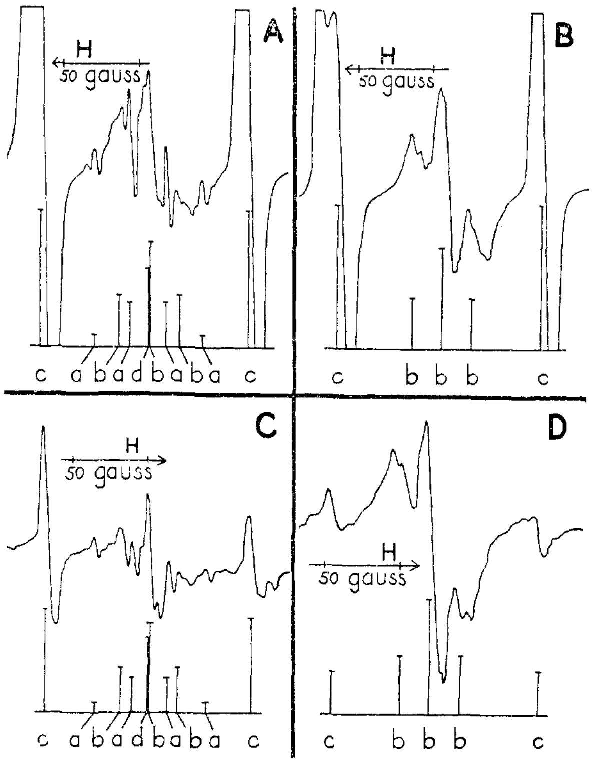

Fig. 1.—Electron spin resonance spectra of free radicals produced in irradiated methanol: (A) CH_3OH irradiated for 30 minutes at 77°K. and recorded immediately; (B) same as (A), but recorded 1.5 hr. after termination of irradiation at 77°K.; (C) CH_3OD, same conditions as (A); (D) 1 mmole of 1 mcurie of $C^{14}H_3OH$ kept at 77°K. for one week. In the line reconstruction below each spectrum, (a) labels the lines of the quartet, (b) the triplet, (c) the doublet, (d) a singlet.

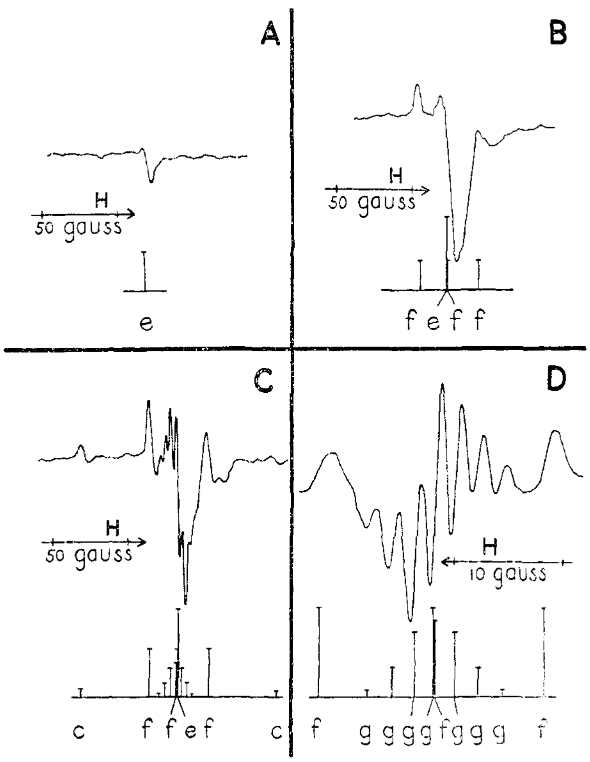

Fig. 2.—Electron spin resonance spectra of free radicals produced in irradiated CD_3OH: (A) CD_3CH after 10 minutes irradiation at 77°K.; (B) same as (A) after 20 minutes irradiation; (C) same as (A) after 30 minutes irradiation (the doublet marked (c) is due to the 1% residual hydrogen in the CD_3OH; the septet here is unlabeled); (D) same as (C), with instrumental conditions adjusted to optimize presentation of spectrum of CD_3 radical. In the line reconstructions, (e) labels a singlet, (f) an equal intensity triplet, (g) the septet.

be a narrow singlet superimposed on the central line of the triplet.

Irradiation of CH_3OD (Fig. 1-C) gives a spectrum similar to that of CH_3OH. Two differences were noted—the lines of the triplet were somewhat sharper, and the singlet superimposed on the center peak was very prominent before the triplet became strong. From the radioactive sample (Fig. 1-D) one obtains a strong triplet with a 19 gauss splitting and a weaker doublet with a 130 gauss separation.

On irradiation of CD_3OH at 77°K., the first line to appear was an asymmetric singlet (Fig. 2-A) which continued to grow on further irradiation while an equal intensity triplet with a 19.5 splitting gradually appeared (Fig. 2B). Finally, as the irradiation continued, a seven-line spectrum with a 3.5 gauss splitting became superimposed on the central peak of the triplet (Fig. 2-C, 2-D). All spectra were centered around the free electron g-value.

Discussion

These observations give fairly reliable identification to some of the free radicals present. The 1:3:3:1 quartet observed has the correct intensity ratio and hyperfine splitting to be assigned unequivocally to $\cdot CH_3$. Its instability at 77°K. has been observed previously.[3,7]

Sufficient data are now available to make an identification of the radical producing the 1:2:1 triplet. Three lines with 18 gauss hyperfine splitting have been observed by Luck and Gordy,[2a] Smaller and Matheson, and Zeldes and Livingston[3] from samples of methanol. These investigators used high energy radiation, *i.e.*, Co gamma rays and 40 kev. X-rays. Some ambiguity existed as to whether the radical was $\cdot CH_2^+$ or $\cdot CH_2OH$; however, chemical evidence favored the latter. Because of the low radiation energy used in the present experiment, $\cdot CH_2OH$ appears to be the correct choice. Fujimoto and Ingram irradiated a mixture of CH_3OH and HOOH with ultraviolet at 3650 Å. wave length which provided only enough energy to produce OH radicals.[8] The resulting three lines could be ascribed in this case to $\cdot CH_2OH$, assuming abstraction of an alpha hydrogen by ·OH. It is interesting to note in the $C^{14}H_3OH$ case that on β-ray bombardment the ion $^+CH_2OH$ is preferentially formed, since the most intense line in the mass spectra of methanol corresponds to mass 31.[9]

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(7) W. Gordy and C. G. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956).

(8) M. Fujimoto and D. J. E. Ingram, *Trans. Faraday Soc.*, **54**, 1304 (1958).

(9) A. Friedel, J. L. Shultz and A. G. Sharkey, *Anal. Chem.*, **28**, 926 (1956).

However, apparently in the condensed state this ion is neutralized rapidly to produce the $\cdot CH_2OH$ radical.

The doublet present in CH_3OH and $C^{14}H_3OH$ results from the interaction of the odd electron with a single proton. Deuterium substitution confirms this conclusion, since the equal intensity triplet in CD_3OH must arise from the splitting of the electron resonance by a single deuteron. The fragment $\cdot CHOH$ is not expected to be paramagnetic in the ground state, so that the remaining possibilities which could account for a doublet are $\cdot CHO$ and $\cdot COH$. It is noteworthy that in electron bombardment of methanol, the mass spectra show that the peak due to mass 29 is a prominent one. In view of the large splitting of the e.s.r. spectrum, the formyl radical is selected as the most likely candidate for this assignment. Miyagawa and Gordy[10] have observed a doublet of 135 gauss splitting from the irradiation of formic acid which they attributed to $\cdot CHO$. They also reported shoulders at 40 gauss separation from the irradiation of CDOOD, but a possible central line was obscured by other resonances so that the identification of a triplet from $\cdot CDO$ remained inconclusive. Their results and interpretation appear to be in harmony with those of the present experiments.

The asymmetry of the doublet due to $\cdot CHO$ and the triplet of $\cdot CDO$ is typical of a radical with axial symmetry, and using the method of Sands,[11] Searles[12] and Kneubühl,[13,14] $g_\perp$ and $g_\parallel$ were evaluated as 2.003 and 1.998, respectively. The same values within experimental error were obtained for both $\cdot CHO$ and $\cdot CDO$.

The implied axial symmetry of the formyl radical calls for some comment since this radical has been studied by optical spectroscopic techniques by Herzberg and Ramsay.[15] They reported that $\cdot CHO$ is bent in the ground state and linear in an excited state. This observation can be reconciled with the e.s.r. measurements if one assumes that the bent $\cdot CHO$ is free to rotate rapidly about the axis around which the moment of inertia is smallest. This then would give the axially symmetric situation indicated in the e.s.r. spectra.

In a comparison of the spectra of $C^{14}H_3OH$ and CH_3OH in which the $\cdot CH_2OH$ triplet has approximately the same intensity, it was found that the doublet in the latter case was much stronger. This difference in the doublet intensity has at least two possible explanations. On the one hand, if the absorption coefficient of $\cdot CH_2OH$ is high, hydrogens can be removed by successive photolytic events giving rise to $\cdot CHO$. In the case of β-interaction, the probability of multiple bond rupture in the same molecule is small.

A second possible explanation is that on ultraviolet interaction, when bond rupture occurs, the energy imparted to the hydrogen atom is small so that it remains in the vicinity of the parent radical and abstracts hydrogen from it. In the β-interaction case, the recoil imparted to the hydrogen may be large enough so that it is out of reaction range with the parent radical. This latter assumption would picture the formyl radical as arising in the ultraviolet case from secondary processes involving hydrogen abstractions by the various reactive species produced in the primary events.

The septet observed in the CD_3OH spectrum is easily explained. The radical $\cdot CD_3$ is expected to give seven lines with a 1:3:6:7:6:3:1 intensity ratio and an approximately 4 gauss hyperfine splitting, and $\cdot CD_2OH$ five lines with a 1:2:3:2:1 intensity ratio and a 3 gauss splitting. Because of the small difference in the calculated splittings, one might expect to find the two systems superimposed and indistinguishable. It is not useful to measure exactly the observed intensities of the seven-line spectrum because of the broader underlying spectrum, but the appearance is not incompatible with the theoretical 1:4:8:10:8:4:1 intensity ratio. Attempts to separate the septet and the quintet by storage and by gradual warmup were inconclusive.

Variations in the spectra as a function of time and temperature indicated the possible presence of several other radicals. Samples of irradiated CH_3OH which were kept for some time showed a single asymmetric line at $g = 2$ which became more prominent as the triplet decayed. This singlet also appears along with the doublet due to $\cdot CHO$ when CH_3OH is irradiated at 95°K., no other lines being evident. This suggests that this resonance is due to a radical containing oxygen, since in this study it has been found that such radicals have a longer lifetime and greater stability, presumably because they are stabilized by hydrogen bonding. A similar line is the first to become visible during the irradiation of CD_3OH (see Fig. 2A), and though also present in CH_3OD is never prominent. The asymmetry and breadth (45 gauss in CH_3OH) of this line suggest that it is due to $CH_3O\cdot$ with the odd electron localized to a large extent in the oxygen. The rapid appearance of the asymmetric singlet due to $CD_3O\cdot$ in CD_3OH is attributed to an isotope effect, since it has become increasingly apparent throughout this study that it is easier to break the O–H bond than the O–D bond in methanol. A similar effect has been reported by Rexroad and Gordy[16] in their irradiation studies of water.

This isotope effect also appears to explain the sharp singlet in the CH_3OD spectrum. Preferential removal of the hydrogens on the methyl group would leave the fragment $\cdot COD$, which will give a single line if the electron interacts to a negligible extent with the deuteron, as is the case in the $\cdot CH_2OD$ radical. A singlet, 4–5 gauss in width, also apparently is present in the CH_3OH spectrum, where it is more difficult to distinguish because it is masked by other resonances. Possibly it arises from a $\cdot COH$ radical.

The various radicals that have been observed as a result of this study are tabulated in Table I with their observed widths and hyperfine splittings.

[10] I. Miyagawa and W. Gordy, *J. Am. Chem. Soc.*, **83**, 1036 (1961).

[11] R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

[12] J. W. Searles, R. C. Smith and S. J. Wyard, *Proc. Phys. Soc. (London)*, **74**, 491 (1959).

[13] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

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[15] G. Herzberg and D. A. Ramsay, *Proc. Roy. Soc. (London)*, **233A**, 34 (1955).

[16] H. N. Rexroad and W. Gordy [Session: Spins IV, K 2], Bulletin of the Am. Phys. Soc., 1961 Spring Meeting.

Table I

Radicals Observed in Ultraviolet Irradiated Methanol at 77°K.

Radical	Lines	Observed line width (gauss)	Observed hyperfine splitting (gauss)
$\cdot CH_2OH$	Triplet	11	18
$\cdot CH_2OD$	Triplet	7–8	17
$\cdot CH_3$	Quartet	3–4	23.5
$\cdot CHO$	Doublet	8–10	130
$\cdot CDO$	Triplet	5–6	19.5
$\cdot CD_3$	Septet	1.7	3.5
$\cdot CD_2OH$	Quintet	1–2	3–4
$\cdot COD$	Singlet	3–4	. . .
$\cdot COH$	Singlet	4–5	. . .
$CH_3O\cdot$	Singlet	45	. . .
$CD_3O\cdot$	Singlet	18	. . .

The radicals above the line are those identified with considerable certainty, whereas the ones listed below the line are identified with somewhat less certainty. It will be noted that $\cdot CH_2OH$ gives a triplet of about the same hyperfine splitting as $\cdot CH_2OD$, but the line width is less in the latter case, indicating some influence of the hydroxyl hydrogen or deuterium. Such narrowings of lines can come about if deuterium is present in the crystal but not bound in the radical itself. These effects have been discussed previously by Zeldes and Livingston.[3]

In conclusion, some comments should be made about relative stabilities for the radicals observed in this investigation. In general it was found that oxygen-containing radicals had considerably longer lifetimes than non-oxygenated radicals such as $\cdot CH_3$. The formyl radical and $\cdot CH_2OH$ can be produced at 90°K., whereas $\cdot CH_3$ did not even appear under our conditions. The oxygen-containing radicals could be kept indefinitely at 77° K.; however, $\cdot CH_3$ decayed within 2 hr. under such conditions. The $\cdot CH_3$ radical apparently can tumble rapidly as evidenced from its sharp line symmetrical spectrum. The motion of $\cdot CHO$ exhibited considerable hindrance as indicated by its asymmetric spectrum. These differences probably arise because of the hydrogen bonding in the case of oxygen-containing radicals.

There is also a good indication that the deuteriated radical $\cdot CD_3$ is more stable than $\cdot CH_3$. For example, $\cdot CD_3$ in methanol was kept for 4 days at 77°K. without any pronounced change in its seven line spectrum; and gradual warmup did not weaken the spectrum appreciably until the temperature rose above 95°K.

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[Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Canada]

The Structure of Substituted C_7 Ions from Benzyl Derivatives at the Appearance Potential Threshold

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The appearance potentials of ions of the general formula $RC_7H_6^+$ have been measured from a number of *meta* and *para* substituted benzyl derivatives $RC_6H_4CH_2X$. The combinations studied were R = CH_3 (X = H and Br), R = F (X = H and Br), R = OH (X = H and CH_3) and R = CH_3O (X = Cl). From a comparison of the effect of substitution in the *meta* and *para* position it is suggested that when R is CH_3, F, or OH the ion formed at the threshold has the symmetrical tropylium structure, but that when R is CH_3O the ion at the threshold has the benzyl structure. The heats of formation of the $CH_3C_7H_6^+$ and $FC_7H_6^+$ ions are estimated and compared with heats of formation calculated for the isomeric substituted benzyl ions. The appearance potentials of $RC_6H_4O^+$ ions from *meta* and *para* substituted anisoles have been shown to follow a linear relation with the σ^+ values for the substituents.

Introduction

Considerable evidence has been presented[1-4] indicating that the $C_7H_7^+$ ion found in abundance in the mass spectra of toluene and other benzyl derivatives is the symmetrical tropylium ion rather than the benzyl ion. This evidence has been obtained chiefly through carbon-13 and deuterium labelling and is based on the observation that the ring and side-group carbon and hydrogen atoms become indistinguishable in the $C_7H_7^+$ ion. This conclusion is based on the distribution of the label in the $C_5H_5^+$ ion which is formed from the $C_7H_7^+$ ion by the process

$$C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2$$

These results refer therefore to $C_7H_7^+$ ions which have sufficient energy to undergo further decomposition and do not provide information of the structure of the $C_7H_7^+$ ion at the appearance potential threshold. Furthermore, recent electron impact work[5] on tropylium derivatives has led to the conclusion that the heat of formation of the tropylium and benzyl ions are the same within experimental error, with the consequence that the structure of the $C_7H_7^+$ ion at the appearance potential threshold cannot be established on the basis of the heat of formation of the ion.

The mass spectra of ring-substituted benzyl derivatives $RC_6H_4CH_2X$ frequently show large peaks for the ion $RC_7H_6^+$ analogous to the $C_7H_7^+$ ion in benzyl compounds. The present work reports the

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(2) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(3) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

(4) S. Meyerson, P. N. Rylander, E. L. Eliel and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(5) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960).