

ring-size effects, which are much smaller than corresponding factors for thermolysis of symmetric *cis*-azo-1-methylcycloalkanes (A. Schulz, N. T. Glac, and C. Rüchardt, *Tetrahedron Lett.*, 845 (1977)) and which do not follow the same trend, suggest that N-4 to C-5 bond breaking is not part of the rate-determining step in thermolysis of 1d-g. We thank Dr. C. Rüchardt for suggesting the use of ring-size effects to probe for concertedness in oxadiazoline thermolysis.

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- (28) For example, *cis*- and *trans*-stilbene oxides are photochemically interconverted in competition with irreversible formation of deoxybenzoin: G. A. Lee, *J. Org. Chem.*, **41**, 2656 (1976). α -Cyano-*cis*- and *trans*-stilbene oxides also form carbonyl ylide intermediates reversibly: V. Markowski and R. Huisgen, *J. Chem. Soc., Chem. Commun.*, 439 (1977); R. Huisgen and V. Markowski, *ibid.*, 440 (1977).
- (29) The enol ether was not actually detected, but its intermediacy was postulated in a reasonable mechanism to account for the product that was obtained: I. J. Lev, K. Ishikawa, N. S. Bhacca, and G. W. Griffin, *J. Org. Chem.*, **41**, 2654 (1976).
- (30) A poor yield of product from trapping need not point to a carbonyl ylide intermediate but instead to the interception of some 7.
- (31) Compound 1j was at least 95% deuterated, as determined by analysis of the mass spectrum. It gave deuterated 4b.
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Received July 18, 1977

Electron Spin Resonance of Methoxy Radicals Trapped in Methanol X-Irradiated at 4.2 K

Sir:

Methoxy radicals are one of the most important radical intermediates in organic chemistry, especially in radiation and photochemistry. Nevertheless, the direct ESR observation of trapped $\text{CH}_3\text{O}\cdot$ has not been successful except for the very recent detection by laser magnetic resonance in the gas phase,¹ which did not give details of the magnetic interaction parameters.

In the present study, we have directly observed the ESR spectra arising from $\text{CH}_3\text{O}\cdot$ which is trapped in polycrystalline methanol x-irradiated at 4.2 K. The hyperfine coupling constant and the g factor have been determined for the first time. The experimental setup is the same as that reported in our previous papers.²⁻⁴ It is believed that the direct evidence for the formation and trapping of $\text{CH}_3\text{O}\cdot$ in irradiated methanol must be invaluable in radiation chemistry. Its trapping at 4.2 K provides us a further way to study the detailed behavior of this important radical intermediate.

Figure 1 shows the ESR spectrum obtained from polycrystalline CH_3OD x-irradiated and measured at 4.2 K. CH_3OH gave essentially the same spectrum with a slightly broader line width than that from CH_3OD . The signals at around the free spin g value indicated by the arrows and the circles in Figure 1 are due to $\dot{\text{C}}\text{H}_3$ and $\dot{\text{C}}\text{H}_2\text{OD}$, respectively. The weak hyperfine structure on the low-field tail arises from $\text{CH}_3\text{O}\cdot$ which is characterized by its highly positive g shift. The overlay spectrum is measured with 10 times higher gain. The hyperfine structure on the g_{max} component consists of seven lines which is characteristic of the CH_3 group undergoing tunneling rotation at low temperature. The stick diagram indicates the splitting of the A and E lines.^{5,6} The spacing of the A line, 52 G, corresponds to the hyperfine coupling constant of the methyl protons. The spacing of the E lines (47 G) is slightly smaller

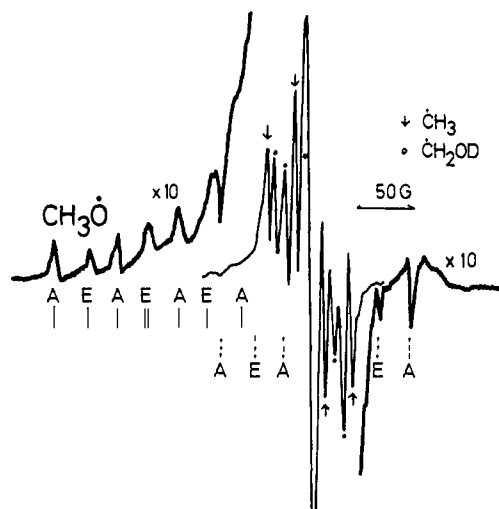


Figure 1. X-band ESR spectra of polycrystalline methanol (CH_3OD) x-irradiated and measured at 4.2 K. The overlay spectrum is recorded with 10 times higher gain. The other spectrometer conditions are the same: microwave power = $6 \mu\text{W}$, field modulation width = 1.5 G.

Table I. CH_3 Proton Coupling Constant and g Tensor Elements of $\text{CH}_3\text{O}\cdot$ Trapped in Polycrystalline CH_3OD X-Irradiated and Measured at 4.2 K

| | g factor | $a_{\beta}(\text{CH}_3)$, G |
|------------------|-----------------------------|------------------------------|
| g_{max} | $2.088 (2.076 \pm 0.014)^a$ | 52 (52) ^b |
| g_{int} | $(2.006 \pm 0.001)^a$ | |
| g_{min} | $1.999 (1.998 \pm 0.002)^a$ | |

^a The numbers in parentheses are the average values reported for substituted alkoxy radicals.¹¹ ^b The calculated values from the $B_0 + B_2 \cos^2 \theta$ rule.¹¹ See text.

than that of the A lines, suggesting that there is a contribution from the term other than that depending upon $\cos^2 \theta$, where θ is the conformation angle for β -proton coupling.⁶ The two outermost lines of the hyperfine structure on the g_{min} component can be seen in the high-field end of the spectrum as shown by the dotted lines. The spacing of the two lines is nearly the same as that of the two outermost lines on the g_{max} component. This indicates that the hyperfine coupling is nearly isotropic and is consistent with the assignment to the rotating methyl group. Thus, the g_{max} and g_{min} values are ascertained to be 2.088 and 1.999, respectively. These results are tabulated in Table I.

The large positive g shift is characteristic of the oxygen centered radicals in which the unpaired electron is in the nonbonding oxygen p_{π} orbital. The g_{max} value of 2.088 for $\text{CH}_3\text{O}\cdot$ is in nearly the same range as that reported by us for the OH radicals trapped in organic crystals.^{7,8} The β -proton coupling of 52 G in the rotating methyl group is considerably larger than ~ 25 G in carbon-centered π radicals, but is rather similar to that found in some nitrogen-centered π radicals. For example, nitrogen-centered π radicals $\text{H}_2\text{N}\dot{\text{C}}\text{H}_2\text{R}$ found by us in irradiated glycine exhibited a large β coupling with $B_2 = 99$ G in the $B_2 \cos^2 \theta$ rule.⁹ This gives 50 G for the freely rotating methyl group. The oxygen-centered π radical may be rather similar to the nitrogen-centered π radicals.

Since Lee and Box¹⁰ have first observed the substituted alkoxy radical in a single crystal of serine x-irradiated at 4.2 K, a number of other examples of the substituted alkoxy radicals have been found in irradiated nucleosides and nucleotides. Very recently their g tensors and β -proton couplings have been well characterized by Bernhard et al.¹¹ According to their Table III of ref 11, the g_{max} and g_{min} values are given as 2.076 ± 0.014 and 1.998 ± 0.002 , respectively, in an agreement with those of $\text{CH}_3\text{O}\cdot$. They have also summarized the hyperfine

coupling of C-H_β protons in the substituted alkoxy radicals and proposed that $B_0 = 5$ G and $B_2 = 94$ G for the $a_\beta = B_0 + B_2 \cos^2 \theta$ rule. These constants give $a_\beta = 52$ G for a freely rotating methyl group in an excellent agreement with our value for CH₃O•. In addition, if the contribution from the anisotropic coupling is neglected, the E line splitting is expected to be 47 G from these constants in agreement with the observed splitting of 47 G. These results indicate that substituted alkoxy radicals found in very different crystals such as nucleosides and nucleotides have essentially the same electronic structure as that of the most fundamental species CH₃O• in methanol crystals.

CH₃O• in polycrystalline methanol is unstable at 77 K and disappeared after annealing for a few minutes at 77 K. During the annealing at 77 K, CH₃ radicals also disappeared with a concomitant increase of CH₂OD radicals, suggesting that both the CH₃O• and CH₃ radicals were converted into CH₂OD. Besides these isolated radicals, we have also found from the $\Delta M_s = \pm 2$ spectra that radical pairs between CH₃ and CH₂OD are formed. After annealing at 77 K, CH₃ in this radical pair was converted into CH₂OD forming a pair between two CH₂OD radicals. This is consistent with the radical conversion of isolated CH₃ radicals. The details of the results obtained from the species other than CH₃O• will be reported elsewhere.

Acknowledgment. We wish to thank Mr. H. Muto for his assistance in the low temperature experiments.

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Received December 6, 1977

²⁵Mg Hyperfine Coupling in the Bacteriochlorophyll Radical Cation

Sir:

Much of our understanding of the nature of the reactants which take part in the primary electron-transfer steps in photosynthesis has come from applications of magnetic resonance techniques (EPR and ENDOR). For instance, it was shown that the reversible photo-EPR signal observed in green plants and photosynthetic bacteria (signal I) arises from photooxidation of a pair of chlorophyll molecules known as the "special pair".^{1,2} Subsequently, much effort has been spent on elucidating the electronic structure of the π -cation radicals of chlorophyll and related systems.²⁻⁵ The possibility that spin density on ²⁵Mg (10.05% natural abundance) might contribute to the EPR spectrum of the chlorophyll a radical cation was recently investigated.⁶ No difference was observed in comparing EPR line widths of the chlorophyll a radical cation

containing the natural abundance of ²⁵Mg with chlorophyll a highly enriched in ²⁵Mg. It was concluded that the ²⁵Mg hyperfine coupling constant was <1 G. It was shown in that work that the contribution to the second moment of the EPR line from sources other than protons is ~15%. On the other hand, a similar analysis shows that the contribution to the second moment of the EPR line from sources other than deuterons in fully deuterated chlorophyll a radical cations is ~74%! Thus, by using fully deuterated chlorophyll highly enriched in ²⁵Mg it should be possible to detect any contributions of a ²⁵Mg coupling to the second moment. We have carried out this experiment using perdeuterobacteriochlorophyll a (²H Bchl) and ²H Bchl enriched to 92% in ²⁵Mg, and have found that there is indeed a small interaction with the magnesium.

The techniques for growing fully deuterated *Rhodospirillum rubrum* have been described.⁷ For isotopic enrichment the growth medium contained 97.9% ²⁵Mg as MgO⁸ as the sole magnesium source. Bacteriochlorophyll was extracted by the method of Strain and Svec.⁹ It was found to contain 92% ²⁵Mg by mass spectrometric techniques.

Bacteriochlorophyll cations were produced by I₂ oxidation in methanol-methylene chloride (1:1). Spectra were recorded on a Varian E9 spectrometer on line with the Argonne Chemistry Division Sigma 5 computer. Modulation amplitudes did not exceed 0.1 of the line width, and microwave powers were 0.5 mW at room temperature and 2 μ W at 77 K. Temperature regulation was achieved with an Air Products Helitran system used with an Oxford Instruments temperature controller.

Samples of the fully deuterated bacterium *R. rubrum* containing either natural abundance or 92% ²⁵Mg were made either in 0.1 M tris-DCl (pH 7.4) or 0.01 M glycylglycine buffer (pH 7.4) or 50% buffer-50% glycerol. Light of wavelength greater than 530 nm was used to produce signal I.

For ²H Bchl radical cation one expects the contribution to the second moment from sources other than deuterons to be ~66%. These other contributions are the source of slight asymmetries observed in the low-temperature EPR signal of this species so that in these experiments it is necessary to carry out a numerical integration^{10,11} in order to determine the second moments of the EPR spectra.

To obtain the ²⁵Mg hyperfine coupling we have

$$\langle \Delta H^2 \rangle^{25\text{Mg}} = (1/0.8195) (\langle \Delta H^2 \rangle^{2\text{H}, 25\text{Mg}(92\%)} - \langle \Delta H^2 \rangle^{2\text{H}, 25\text{Mg}(10\%)})$$

and

$$\langle \Delta H^2 \rangle^{25\text{Mg}} = (35/12) A_{25\text{Mg}}^2$$

where $\langle \Delta H^2 \rangle^{2\text{H}, 25\text{Mg}(x\%)}$ is the total second moment observed for ²H Bchl cation containing the given percent of ²⁵Mg, and $\langle \Delta H^2 \rangle^{25\text{Mg}}$ is the calculated contribution of the ²⁵Mg coupling to the second moment. $A_{25\text{Mg}}$ is the root-mean-square ²⁵Mg hyperfine coupling constant.

Furthermore

$$[(12/35) \langle \Delta H^2 \rangle_{25\text{Mg}}^{300\text{K}}]^{1/2} = (a^2)^{1/2}$$

and

$$[(12/35) \langle \Delta H^2 \rangle_{25\text{Mg}}^{77\text{K}}]^{1/2} = \left(a^2 + \frac{1}{3} \sum_{\substack{i=x, \\ y,z}} b_{ii}^2 \right)^{1/2}$$

where a is the ²⁵Mg isotropic hyperfine coupling constant and b_{ii} represents the components of the dipolar coupling tensor. Measurements made at the two temperatures allow one to determine both a and b_{ii} . The results are given in Table I.

Using the mean values in Table I the analysis yields

$$|a_{25\text{Mg}}| = 0.23 \text{ G}$$

$$\mathbf{T} = \pm(0.69, 0.69, -0.69 \text{ G}) \text{ or } \pm(0.23, 0.23, -1.15 \text{ G})$$