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ELECTRON PARAMAGNETIC RESONANCE OF TRIMETHYLENEMETHANE FORMED BY RADIOLYSIS OF METHYLENECYCLOPROPANE

Tetsuo YAMAGUCHI, Masahiro IRIE, and Hiroshi YOSHIDA
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo, 060

Trimethylenemethane was formed by the radiolysis of methylenecyclopropane at 77°K, and its epr spectrum was studied. From the $\Delta M_S = 1$ spectrum epr parameters were determined as $T_{ZZ} = 9.17 \pm 0.05$G, $D = (2.37 \pm 0.01) \times 10^{-2}\mathrm{cm}^{-1}$ and $E = 0$. The $\Delta M_S = 2$ transition showed seven hyperfine lines with a separation of 9G.

Trimethylenemethane, a molecule in a ground triplet state, has long been attracting the interest of theoretical chemists. Its zero-field splitting constants and spin density distribution were studied on the basis of several MO treatments.[1) However, its spectroscopic observation has been so far reported only by Dowd and his coworkers.[2) They produced trimethylenemethane by photolizing 4-methylene-Δ^1-pyrazoline or 3-methylenecyclobutanone and observed its electron paramagnetic resonance (epr) spectra. For trimethylenemethane trapped in a single crystal of 3-methylenecyclobutanone, they reported the angular dependence of the spectra suggesting the zero-field splitting constant of $D = 0.0244\mathrm{cm}^{-1}$ and the principal value of hyperfine coupling tensor along the molecular axis, T_{ZZ}, of 8.9G.[2c)

During the course of radiation chemical study of methylenecycloalkanes, Takeda et al. examined epr of γ-irradiated methylenecyclopropane and suggested the formation of trimethylenemethane by the opening of the three membered ring.[3) The study was extended to confirm its formation and to determine its epr parameters so precisely as to be compared with the theoretical predictions. Fortunately, trimethylenemethane formed by the radiolysis of polycrystalline methylenecyclopropane exhibited a well-resolved hyperfine structure. This enabled us to determine some of the epr parameters unambiguously, which will be briefly reported in this communication. The results may complement the previous results obtained by Dowd et al. in understanding the nature of trimethylenemethane.

Methylenecyclopropane was synthesized from methacrylchloride[4)], sealed in a sample tube of pure quartz under vacuum, frozen in liquid nitrogen into polycrystalline state, and irradiated with ^{60}Co γ-rays to a dose of 2×10^{6} rad at 77°K. The purity of synthesized methylenecyclopropane was estimated to be 95% or better from its nmr spectrum. The irradiated sample was subjected to epr measurements at 77°K with a conventional X-band spectrometer using 100Kc field modulation and a normal

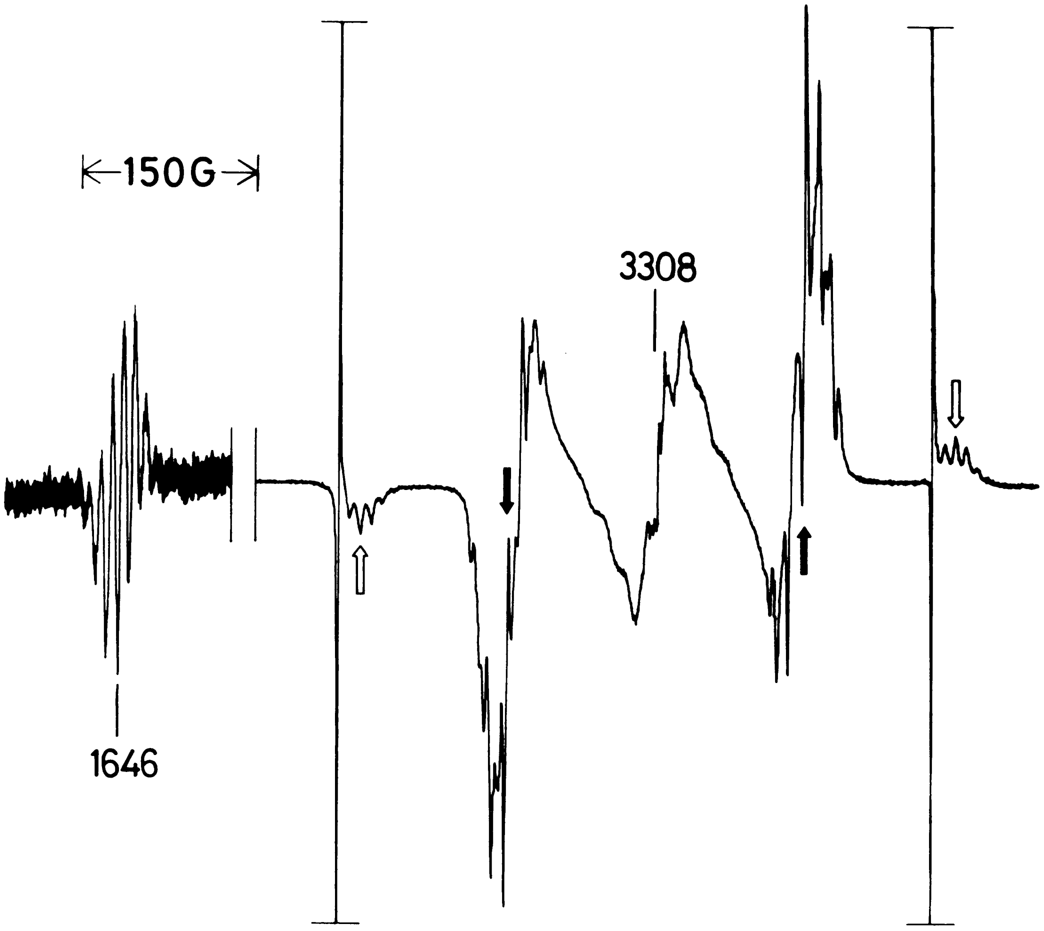

Fig. 1. Epr signal recorded from methylenecyclopropane irradiated by γ-rays to a dose of 2×10^{6} rad at 77°K. Mocrowave frequency: 9276 MH_z (calculated from the resonance field of DPPH, 3308G). The white and black arrows indicate the spectrum of $\Delta M_S = 1$ transition of trimethylenemethane. Amplifier gain for the spectrum of $\Delta M_S = 2$ transition is ten times as high as that for the spectrum of $\Delta M_S = 1$ transition.

cylindrical TE_{011} cavity. Therefore, H_1 was perpendicular to the static magnetic field. The resonance field was calibrated with reference to the proton resonance frequencies for the spectrum of $\Delta M_S = 1$ transition. The calibration for the spectrum of $\Delta M_S = 2$ transition was made with reference to the spectra of triphenylene and naphthalene in triplet state dissolved in rigid matrix under photoirradiation, though it was not very precise.

Epr signal shape recorded from irradiated methylenecyclopropane is illustrated in Fig. 1. It indicates a spectrum typical to the $\Delta M_S = 1$ transition (indicated by black and white arrows) and that of the $\Delta M_S = 2$ transition (around 1646 G) of a triplet molecule, as well as a spectrum of doublet free radicals (around 3308G, the magnetic field of DPPH) and a pair of sharp lines of hydrogen atom trapped probably on the surface of the sample tube. If one reasonably assumes that trimethylenemethane is a plane molecule with a sp^2 conformation, six protons in the molecule are expected to be equivalent only when the molecule is so oriented that the external magnetic field is parallel with the molecular axis (taken as Z-axis). This is really the case. The Z-components of the $\Delta M_S = 1$ spectrum indicated by white arrows show equally-spaced seven hyperfine lines with the binomial intensity ratio, though two of them are superimposed on the intense spectrum of trapped hypergen. The separation between the hyperfine lines is determined to be 9.17±0.05G, which is the principal value, T_{ZZ}, of the hyperfine coupling tensor along the Z-axis. The X,Y-components of the spectrum are complex because of the inequality of the protons and the mixing of forbidden transition lines in these orientations of the molecule.5) The $\Delta M_S = 2$ spectrum also shows the equally-spaced seven hyperfine lines with the binomial intensity ratio and with the separation of 9G. The zero-field splitting constant D is determined to be $(2.37\pm0.01)\times10^{-2}\text{cm}^{-1}$ from the separation between the Z-components of 507±1G. For reference, the separation between the two lines of the trapped hydrogen spectrum was determined to be 505G, a reasonable value, on the basis of the magnetic field calibration made in this study. If one takes the strongest hyperfine lines indicated by the black arrows as the center of the X,Y-components, the separation between them is just one half of 507G and provides an evidence for E = 0.

The spectrum of $\Delta M_S = 1$ transition shows the shape essentially the same as that of photochemically produced trimethylenemethane in rigid glassy matrices,2a, 2b) except that the present spectrum is better resolved. Thus D is slightly smaller, while T_{ZZ} is bigger than those obtained in the previous investigation.[2)] The slight difference may be given by the different environments in which trimethylenemethane is trapped. Slight twisting of the CH_2 groups could occur in one experiment and not in the other but more information will be needed before a definitive conclusion could be available.

Finally, radiation chemical data will be mentioned very briefly. Trimethylenemethane is formed very efficiently by the radiolysis of solid methylenecyclopropane. Its yield is 2 for 100eV energy absorbed. From the epr signal, free radicals formed are predominantly trimethylenemethane. The yield of doublet radicals seems to decrease with the increasing purity of methylenecyclopropane. No decrease in intensity of the trimethylenemethane spectrum was observed, at least, in a week when the irradiated sample was kept at 77°K.

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