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ESR Study on Transient Radicals in Plastic Crystals under Electron Irradiation

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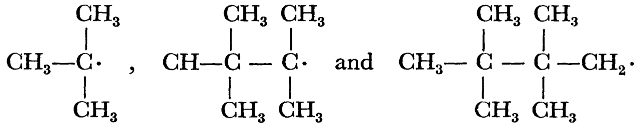
An apparatus was constructed for ESR measurements during electron irradiation, and the behavior of transient radicals in the plastic crystals of cyclohexane (CyH) and 2,2,3,3-tetramethylbutane (TMB) was investigated. It was found from the experiment that cyclohexyl radical produced by irradiation of CyH decays with a rate constant of $2\times10^{-8}\exp(-7.9\ \mathrm{kcal}/RT)\ \mathrm{cm^3/s}$. The rate constant is in good agreement with the results reported by Buben *et al.* On the other hand, radicals formed in irradiated TMB were assigned to be



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}\cdot},\quad \mathrm{CH{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{C}}\cdot}\quad \text{and}\quad \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2\cdot}$$

from the present results. It was shown from the results that the assignment made by Marx *et al.* before should be corrected to some extent. In the plastic crystals of CyH and TMB, it was suggested that the decay reactions of the observed radicals are controlled by the diffusional migration of the radicals. The analysis of radiolytic products of TMB was also made, and the results were compared with the results of ESR observation.

In order to study early stages of radiation chemical processes, it is very important to follow the dynamical behavior of transient species. The method of pulse radiolysis has been used with great success in the optical measurement of various kinds of transient species. ESR methods have been employed to give useful information about radicals produced by irradiation, but most studies were made by trapping of radicals in solids at low temperatures.

The ESR measurement of short-lived radicals under electron irradiation was first reported by Molin and his coworkers,[1)] and an extensive study has been made by Fessenden and Schuler.[2)] Recently a pulsed irradiation method in ESR spectroscopy has been developed by Smaller and his co-workers.[3)] In the present paper, we report on apparatus for ESR measurements during electron irradiation and on some recent experimental results. Since there is much to be learned about the transient behavior of radicals in solids, the experiments using the apparatus are primarily aimed at such transient species. As the first step we have tried to measure transient radicals in cyclohexane (CyH) and in 2,2,3,3-tetramethylbutane (TMB), which are known to be typical of plastic crystals. It is known that radicals produced in a plastic crystal exhibit a well-resolved ESR spectrum due to motional narrowing and that they disappear rapidly far below the melting point of the crystal. Radicals formed in irradiated cyclohexane in its plastic crystal phase have been studied by previous investigators.[4—6)]

The products formed in the radiolysis of TMB in its plastic crystal phase were analyzed chromatographically, and the results were correlated with radicals observed by ESR spectroscopy.

Experimental

Figure 1 illustrates the schematic diagram of the irradiation system. A Dynamitron accelerator was used as the irradiation source, and it was usually operated at 1.2 MeV with the beam current of 10—200 μA for ESR measurements. The focusing of an electron beam was at first difficult because of the long distance from the accelerator to the ESR cavity; the latter was located at the end of beam duct which penetrated through one of the pole pieces of ESR magnet. Several focusing magnets and a coil for the compensation of terrestrial magnetism were located along the beam duct to get a stable electron beam. When a sample of 3 mm in diameter and 7 mm in length was irradiated with an electron beam of 0.05 μA, the dose rate was about 1.5×10^8 R/hr. The dose rate was determined by the method developed by Tamura *et al.*,[7)] that is, by measuring peroxy radicals formed in irradiated

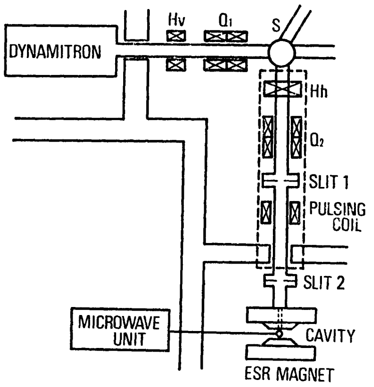


Fig. 1. Irradiation system.
Hv, Hh: Helmholtz coils for vertical and horizontal deflection. S: Switching magnet. Q_1, Q_2: Quadrupole magnets for focusing. Broken line: Coil for compensation of terrestrial magnetism.

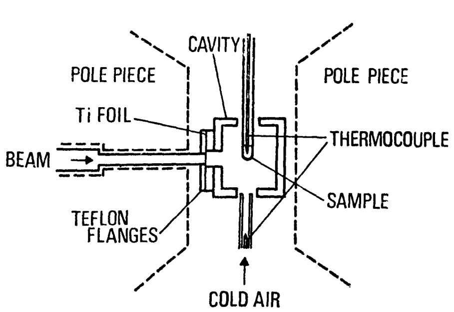


Fig. 2. ESR magnet and cavity.

polytetrafluoroethylene.

The ESR spectrometer used is a conventional X-band system with 100 kHz field modulation, and with cylindrical TE-011 mode cavity. The cavity has a 5 mm-diam. circular aperture on the wall to let an electron beam pass through it. Figure 2 is a sketch around the ESR magnet.

Dry air cooled by liquid nitrogen is used to control the temperature of the samples. Oxygen in air rapidly captures free electrons produced in the cavity and reduces their steady state concentration during irradiation. Oxygen, therefore, serves to suppress fluctuations of the resonant frequency of the cavity which would occur due to the presence of conduction electrons in the irradiated cavity if pure nitrogen was used as the coolant.

Commercial grade CyH and TMB (both above 99.9% purity) were used without further purification. Samples were degassed by a usual freeze-pump-thaw method, and were sealed off in thin-walled tubes of Spectrosil quartz.

The analysis of radiolytic products of TMB was made by a conventional gas-phase chromatograph with a flame ionization detector. Columns of squalane and of Apiezone L were used.

Results and Discussion

CyH exists in a plastic crystal phase between the transition point of −87.1 °C and the melting point of 6.3 °C. ESR studies on radicals formed in the plastic crystal of CyH under electron irradiation were already carried out by Buben *et al.*[4] and by Fessenden *et al.*,[5] and the radicals were assigned to cyclohexyl radicals. This decay was also studied by Buben *et al.*[6]

The decay characteristic of cyclohexyl radicals after the cessation of irradiation was studied more precisely in the plastic crystal phase by using our apparatus. The plots of reciprocal of radical concentration *versus* time obtained from the decay curves at different temperatures are shown in Fig. 3, where for convenience the reciprocal of each initial concentration is subtracted for each series of plots. All curves represent good fit to linear plots at the early stage of the decay. This implies that the decay is dominated by the second-order reaction, as was indicated by Buben *et al.* From the analysis of Fig. 3, the rate constant is estimated to be $2\times10^{-8}\exp(-7.9\ \mathrm{kcal}/RT)\ \mathrm{cm^3/s}$, which is a little smaller than the value of $3\times10^{-8}\exp(-8\ \mathrm{kcal}/RT)\ \mathrm{cm^3/s}$ obtained by Buben *et al.*

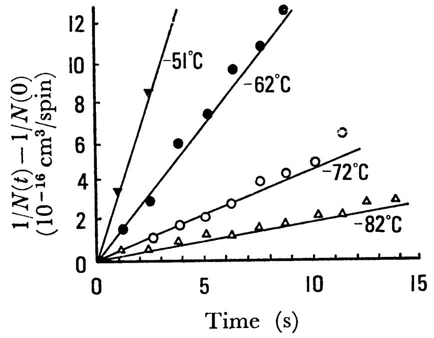
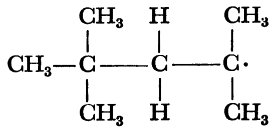


Fig. 3. Second-order plots of the decay of cyclohexyl radicals.
$1/N(t)$, $1/N(0)$: Reciprocal radical concentration at time t and zero, respectively.

As pointed out in their previous study, both the abrupt change in the rate of the decay at the transition point of −87 °C and the coincidence of the activation energy with that of self-diffusion in the plastic crystal phase, 8 kcal/mol,[8] seem to support the view that the decay reaction is controlled by the diffusional migration of the radicals. But the rate constant obtained, though smaller than the value of Buben *et al.*, seems too large compared with the one expected from Smoluchowsky equation of diffusion-controlled reaction, $2.5\times10^{-9}\exp(-8\ \mathrm{kcal}/RT)\ \mathrm{cm^3/s}$, assuming a diffusion constant of $2\times10^{-3}\exp(-8\ \mathrm{kcal}/RT)\ \mathrm{cm^2/s}$[9] and a reaction radius of 5 Å. Since it is not probable that the radicals observed are distributed homogeneously, the above-mentioned fact may indicate that the radicals are able to diffuse more easily than ordinary molecules in the crystalline matrix.

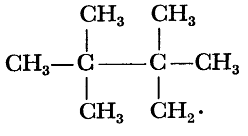
TMB (2,2,3,3-tetramethylbutane) is in the plastic crystal phase between the transition point of −120.6 °C and the melting point of 100.6 °C. The ESR spectrum of γ-irradiated TMB was recently reported by Marx *et al.*,[10] but the present study led us to different assignments of the radicals. Figure 4a is the ESR spectrum of TMB at −113 °C, which was taken after electron irradiation, since the decay is very slow at this temperature. Marx *et al.* obtained a similar spectrum, but they seem to have been unaware of two outermost lines, which are small due to the corresponding binominal coefficient. They analyzed the spectrum as having 15 lines, and attributed the spectrum to radical A of 15 lines and B of three lines, where radical A was considered to be formed by isomerization of radical B. But in fact there are 17 lines, and it is plausible that the spectrum consists of sets of ten and of seven equally spaced lines, both exhibiting the same hyperfine splitting of 23.4±0.2 G and about the same g-factor; 2.0026±0.0002 for the 10 lines, and 2.0025±0.0002 for the seven lines. The line width is about 2.5 G at this temperature. The observed ratio of the relative intensities of the ten lines is 1 : 10 : 65 : 201 : 377 : 361 : 194 : 62 : 9.5 : 1 in the order of increasing magnetic field. The 10 lines are attributable to the *tert*-butyl radical R_I, though a considerable contribution from other radicals may be inferred from the observed ratio, which should be 1 : 9 : 36 : 84 : 126 : 126 : 84 : 36 : 9 : 1 in case of the *tert*-butyl radical alone. The fact that the ratio of the

[R$_A$]



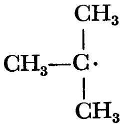
$$\begin{array}{ccccc} & CH_3 & & H & CH_3\\ CH_3- & C & - & C & -C\cdot\\ & CH_3 & & H & CH_3\end{array}$$

[R$_B$]



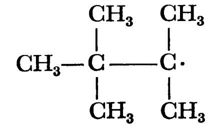
$$\begin{array}{cccc} & CH_3 & CH_3 & \\ CH_3- & C & -C & -CH_3\\ & CH_3 & CH_2\cdot & \end{array}$$

[R$_I$]

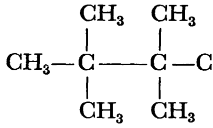


$$\begin{array}{cc} & CH_3\\ CH_3- & C\cdot\\ & CH_3\end{array}$$

[R$_{II}$]



$$\begin{array}{ccc} & CH_3 & CH_3\\ CH_3- & C & -C\cdot\\ & CH_3 & CH_3\end{array}$$

[R_{III}]


$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\cdot}$$

line next to the outermost is close to 9 : 1 indicates radical R_A contributes little to the spectrum. Moreover, it is improbable that the rate of the decay of R_A is greater than that of R_B, which must be assumed to explain the spectrum at the higher temperature. The discrepancy between the observed central part of the ratio and that expected for R_I cannot be ascribed to a definite primary radical. Part of this discrepancy may be explained by the isobutyl radical which must be formed by an addition of a hydrogen atom to R_I. The presence of this secondary addition process is also presumed from the results of the analysis of the radiolytic products, as described later. The ratio of the relative intensities of the 7 lines is 1 : 6.5 : 21 : 41 : 23 : 6.5 : 1 in the order of increasing magnetic field, and the 7 lines are attributable to the overlapping of R_{II} of seven lines and R_{III} of three lines that have about the same hyperfine coupling constant; the ratio of the concentration of the former to the latter is about 2.3 : 1.

Figure 4b is the spectrum obtained at −40 °C under electron irradiation, and it shows that the intensity of *tert*-butyl radical became smaller relative to radicals of R_{II} and R_{III}. Correspondingly the measured decay rate of the former was larger than that of the latter at the higher temperature. This seems to imply that in this case also the reaction is diffusion-controlled and that the activation energy of the diffusion of *tert*-butyl radical is smaller.

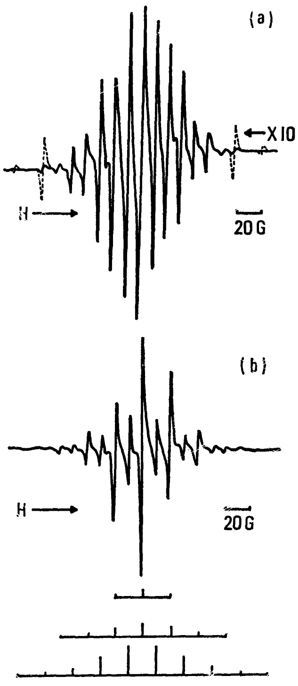


Fig. 4. ESR spectra of electron-irradiated TMB.
(a): at −113 °C after irradiation.
(b): at −40 °C during irradiation.

Table 1. Radiolysis of TMB[a] *G*-values[b]

Products	Irradiation −50 °C	Temperature −10 °C
Isobutane	0.80	1.18
Isobutene	0.30	0.17
Neopentane	0.02	0.02
2-methylbutane	0.01	0.02
2,3,3-trimethyl-1-butene	0.07	0.06
2,2,3-trimethylbutane	0.16	0.23
2,2,4-trimethylpentane	0.25	0.30
2,2,3-trimethylpentane	0.03	0.03
2,3,3-trimethylpentane	0.03	0.02

a) The dose rate was about 2 Mrad/min and samples were irradiated to about 60 Mrad. b) The absolute *G*-values may have errors of ±20% due mainly to possible errors in the dose rate measurements, but the relative *G*-values in each series are accurate with errors of ±5%.

Quantitative analysis of the decay curve was not made because of the complication brought about by the coexistence of three kinds of radicals and by the presence of secondary reactions during irradiation; these are discussed in the next section.

Table 1 shows analysis of products in the range C_4 to C_8[11] formed in samples irradiated at −50 and −10 °C. The irradiation was carried out under the same conditions as the ESR experiments.

The major products of the radiolysis are isobutane, isobutene, 2,2,3-trimethylbutane and 2,3,3-trimethyl-1-butene. These products are considered to be formed by the disproportionation reactions of R_I and R_{II}, respectively. But the ratios of the unsaturated to the saturated products are less than unity for both C_4 and C_8 products. This indicates that secondary addition reaction must have occurred during irradiation. This interpretation is consistent with the fact that the lower the temperature of irradiation, the closer the ratio approaches unity.

It must be noted that the ratio of C_4 to C_8 products is far larger than expected from the ratio of the *G*-values of R_I to R_{II}, which were estimated to be about 0.5 from the ESR measurements. This implies that a considerable fraction of C_4 products is formed by processes other than the radical mechanism.

A large *G*-value of 2,2,4-trimethylpentane is not expected directly from the assigned radicals but its presence is reasonably explained by the recombination of R_I with isobutyl radical that is thought to be formed by the addition of a hydrogen atom to isobutene. The isobutyl radical is not clearly recognized in the ESR spectrum, although the presence of such a radical is inferred from the consideration of relative intensities of the lines, as mentioned earlier.

As for products larger than C_8, two were found to have *G*-values of about 0.1~0.2. These products are presumably related to the assigned R_{III} radical, but their exact identification is difficult.

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11) Hydrogen, methane and ethane are considered to be formed in relatively high G-values, but quantitative analysis was not made.