An ESR Study of Irradiated Cyclic Hydrocarbons in Solid State

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Fessenden and Schuler have recently studied the ESR spectra of free radicals, in liquid hydrocarbons involving cycloalkanes, which were being produced by the irradiation of electron beams.[1] According to their results, all the cycloalkyl radicals except the cyclohexyl have four equivalent β-protons because of rapid internal motions. In solid state at lower temperatures, however, unequivalent β-protons might be expected to exist owing to the restriction of molecular motions.

In the present investigation, various cycloalkanes and cycloalkenes were irradiated at −196°C and changes with raising temperature in the obtained ESR spectra were followed. Interest was focused on the structures of radicals trapped in matrices of parent molecules.

Experimental

Cyclopropane, cyclopentane, cyclohexane, cycloöctane and cycloöctene were obtained from commercial sources. Cyclobutane,[2] cyclopentene,[3] cyclohexene,[4] cycloheptane[5] and cycloheptene[6] were prepared according to the methods described in the literature. After purifications these materials were shown to be at least of more than 95% purity by gas chromatographic analyses. Degassed samples were prepared in the usual manner. These samples were irradiated at −196°C with an electron beam from a Van de Graaff accelerator (1.5 MeV, 100 μA) to a dose of 15 Mrad. ESR measurements were made at various temperatures from −196°C to near the melting point of the samples, using X-band Varian V-4500 spectrometer with its accessories.

Results and Discussion

TABLE 1. SUMMARY OF HYPERFINE COUPLING CONSTANTS FOR CYCLOALKYL RADICALS (gauss)

Radical	Temp. °C	A_α	A_{β_1}	A_{β_2}	A_γ
$c\text{-}C_4H_7\cdot$	−133	24	37	37	—
	(−80	21.20	36.66	36.66	1.12)
$c\text{-}C_5H_9\cdot$	−196	24	48	24	—
	(−80	21.48	35.16	35.16	0.53)
$c\text{-}C_6H_{11}\cdot$	−196	24	42	∠5	—
	(+10	21.15	41	5	0.71)
$c\text{-}C_7H_{13}\cdot$	−196	24	24	20	—
	−135	21.0	31.4	21.0	—
	(−6	21.78	24.69	24.69	—)
$c\text{-}C_8H_{15}\cdot$	−196	24	{ 48 {∠5	{∠5 { 24	—

The values quoted in parentheses are those found in liquid state by Fessenden and Schuler.

Spectra of Irradiated Cycloalkanes. Some of the spectra obtained for irradiated cycloalkanes are shown in Fig. 1(a)—(g). Except the complex spectrum for irradiated cyclopropane, the others could reasonably be assigned to the corresponding cycloalkyl radicals. The hyperfine coupling constants for α- and β-protons determined by the analyses of these spectra are summarized in Table 1. For comparison, the results obtained in liquid state by Fessenden and Schuler[1] are also given in parentheses.

In solid state, the hf constants of α-proton were about 24 gauss, whereas those values in liquid state were reported to be 21 gauss. This difference would be explained as being due to the anisotropic hyperfine interaction in polycrystalline solid matrix. In the spectrum of cycloheptyl radical with a notable motional narrowing at −135°C (see Fig. 1(f),) the value was found to be 21 gauss, nearly equal to that obtained in liquid state. The temperature dependence of this spectral changes might show that of an interconversion between two forms of the cycloheptyl radical.

As for the hf constants of β-protons in solid and liquid state, fair coincidences were seen for cyclohexyl and cyclobutyl radicals. This would mean the temperature independence of conformation about the carbon skeleton; a chair form for the former and a planer form for the latter. In the other cases, however, two sets of different coupling constants of β-protons were obtained in solid state, suggesting that these radicals are locked in a highly twisted configurations with respect to the β-methylenic groups.

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[1] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
[2] J. D. Roberts and C. W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).
[3] B. B. Corson and V. N. Ipatieff, "Organic Syntheses," Coll. Vol. II, p. 153 (1948).
[4] G. H. Coleman and H. F. Johnstone, *ibid.*, Coll. Vol. I, p. 183 (1941).
[5] L. Ruzicka, *Helv. Chim. Acta*, **19**, 424 (1936).
[6] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

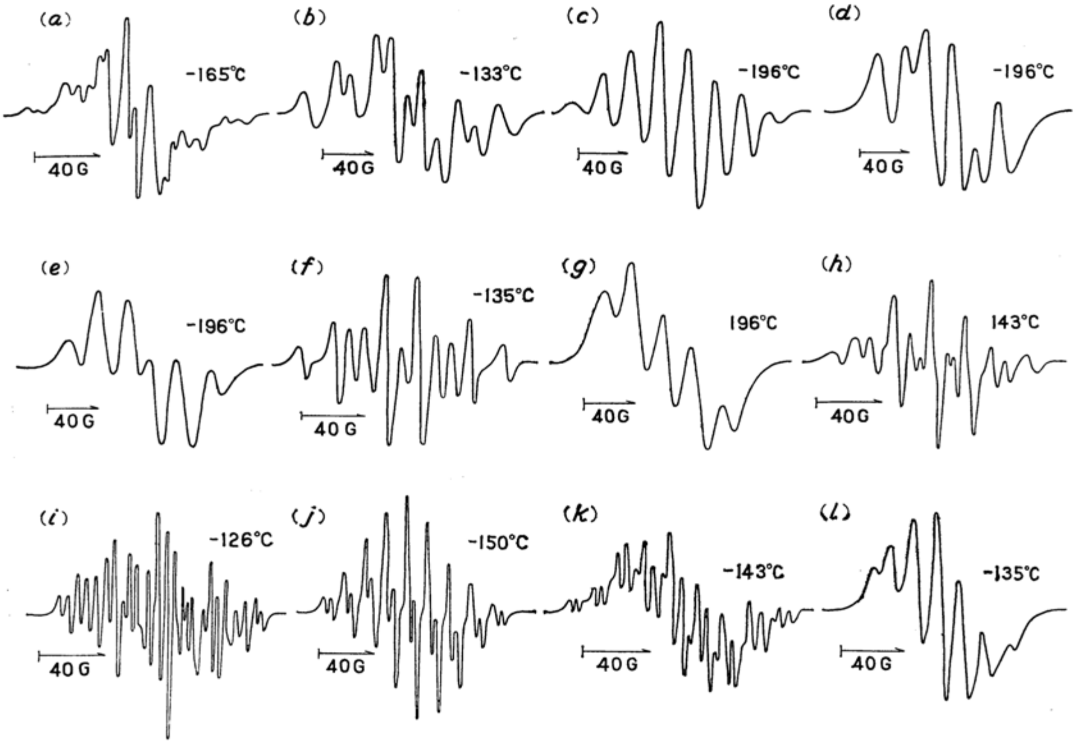

Fig. 1. ESR spectra of irradiated cycloalkanes and cycloalkenes: (a), cyclopropane; (b), cyclobutane; (c), cyclopentane; (d), cyclohexane; (e) (f), cycloheptane; (g), cycloöctane; (h), cyclopentene; (i), cyclohexene; (j) (k), cycloheptene; (l), cycloöctene. Temperatures of measurement are shown with each spectrum.

Spectra of Irradiated Cycloalkenes. Typical spectra obtained from irradiated solid cycloalkenes are shown in Fig. 1(h)—(l). The spectrum for irradiated cyclohexene has been previously obtained by Ohnishi *et al.*⁷⁾ They gave the detail discussion that the main species are the cyclohexenyl radical, the β-methylenic configuration of which is nearly the same as that in cyclohexyl radical. With this in mind, the spectra shown in Fig. 1(h)—(l) except (k) could also be attributed to the corresponding 3-cycloalkenyl radicals with assumption of the sets of hf constants given in Table 2.

TABLE 2. SUMMARY OF HYPERFINE COUPLING CONSTANTS FOR 3-CYCLOALKENYL RADICALS (gauss)

Radical	Temp. °C	A_α	$A_{\alpha'}$	A_{β_1}	A_{β_2}
c-$C_5H_7\cdot$	−143	14.2	~0*	23.1	23.1
c-$C_6H_9\cdot$	−126	15.6	4.2	21.6	8.4
c-$C_7H_{11}\cdot$	−150	13.8	4.6	13.8	27.5
c-$C_8H_{13}\cdot$	−135	15.0	~0*	15.0	15.0

* Not observed owing to the inclusion in line width.

The equivalence among four β-protons in cyclopentenyl radical suggests the planer structure of the radical as is expected.

In contrast with this, the cycloheptenyl radical seems to be locked in a non-planer form below −145°C. On warming this sample up to a slightly higher temperature (−143°C), the nine doublet lines (Fig. 1(j)) suddenly disappeared and a completely different spectrum (Fig. 1(k)) was remained in a radical concentration of about 10%. The remained spectrum is composed of 26 lines and, what is very interesting, quite similar to that assigned by Ohnishi *et al.*⁸⁾ to an allyl-type radical produced in irradiated polyethylene film at −196°C; $A_\alpha=20.5$, $A_{\alpha'}=5.5$, $A_{\beta_1}=30.0$ and $A_{\beta_2}=11.0$ gauss. The present observation may be justified by considering some ring-opening process to produce the allyl-type radical analogous to that in polyethylene. It is noteworthy that the rapid decay of cycloheptenyl radical occurred at a temperature just below the transition point of cycloheptene (about −150°C) determined by the differential thermal analysis in the present work.

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7) S. Ohnishi and I. Nitta, *J. Chem. Phys.*, **39**, 2848 (1963).

8) S. Ohnishi, S. Sugimoto and I. Nitta, *ibid.*, **37**, 1283 (1962).

In discussing the spectrum for irradiated cycloöctene, we have no evidences to reject the possibility of being due to some ring-opened radical, for the seven-line spectrum is very similar to that reported for allyl-type radical produced in irradiated *n*-hexadecene-1.⁹⁾

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9) I. Nitta, S. Ohnishi and Y. Nakajima, *Ann. Rept. of Japanese Association for Radiation Research on Polymers*, **3**, 339 (1961—1962).