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CONFORMATIONAL ANALYSIS OF THE EPR SPECTRA OF CYCLOHEXENYL RADICAL AND SOME OF ITS ALKYL DERIVATIVES

By

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DISCLAIMER

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ABSTRACT

Electron paramagnetic resonance spectra have been obtained for radicals produced by x-irradiation of cyclohexene and various alkyl-substituted cyclohexenes trapped in an adamantane matrix. Temperature variations of these spectra permits determination of the enthalpy and entropy of activation for interconversion between the conformations.

For cyclohexenyl radical, the enthalpy of activation is 6.81 $\pm$ 0.58 kcal/mole and the entropy of activation is -0.04 $\pm$ 2.38 e.u. Methyl substitution on C_1 gives a radical with activation parameters similar to the parent radical. Methyl groups attached to C_5 increase the activation parameters significantly. On the basis of these observations, it is suggested the cyclohexenyl radicals exist in two conformations of the same energy which are of the "envelope" type, with C_1, C_2, C_3, C_4, and C_6 coplanar. A model involving a planar transition state for the interconversion process is proposed which accounts for most of the experimental results.

To my sons, my husband and my parents.

ACKNOWLEDGMENTS

I express my sincerest appreciation to my research director, Dr. David W. Pratt, for his assistance and advice throughout the course of this work. Many thanks go to Mr. Henry F. Walter for his valuable and helpful cooperation.

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I. INTRODUCTION

The investigation of the conformational properties of cyclic and acyclic molecules has been considered a very important area of fundamental chemical experimentation and among the systems studied, six-membered rings, by virtue of their abundance and importance as structural units of many natural products, have received greatest attention. Magnetic resonance has been revealed to be among the best suited experimental techniques for the study of both static and dynamic properties of molecular conformations; epr spectroscopy if a molecule is paramagnetic; nmr spectroscopy if it is not paramagnetic.[1]

Prior experiments in epr studies of organic radicals have been done in many media: gases, liquids, solutions and single crystals. Each sample type has its advantages and disadvantages. Matrix isolation seems a good choice among the possible ways of studying reactive free radicals. It offers the advantages of being easily handled as a solid, and being magnetically dilute to minimize interradical interactions, but can provide possible host-guest interaction creating an unrealistic environment.

In the present work, we have used adamantane, $C_{10}H_{16}$, as a host material. It is a proton-rich compound and, therefore, has extensive dipolar interactions with guest radicals leading to rather broad spectral lines. However, by using adamantane -d_{16} as a matrix, these interactions can be minimized. Furthermore, the host is apparently not easily damaged by x-rays used to generate radicals, is easily purified and doped with the guest precursor

molecules, and may be conveniently handled in air. In addition, x-irradiation of cyclohexene and its derivatives in adamantane produces radicals in good yield.

This study reports on one aspect of the continuing investigation of organic free radicals in this laboratory; namely, a conformational analysis of the cyclohexenyl radical and some alkyl-substituted cyclohexenyl radicals through an interpretation of the temperature dependence of their epr spectra in an adamantane host.

II. EXPERIMENTAL

A. Equipment

Epr spectra were obtained with an x-band Varian E-4 spectrometer system equipped with an E-257 variable temperature accessory. Second-derivative signal presentations were employed. Temperatures reported over the range 100° to 330° K are believed to be accurate to ± 2.0° K. The temperature controller was calibrated by a thermocouple immersed in n-pentane for the lower temperature range and in glycerol for the higher temperature range. Typically, epr spectra of cyclohexenyl radicals in adamantane could be recorded at power levels up to 2 mw without noticeable saturation effects.

X-Irradiation was done using an XRD-1 X-ray generator with a Cu-target tube.

Irradiation was carried out using a special fixture which fit into the opening of the x-ray tube. The pellet was slipped into a slot on the inside of the brass fixture. The fixture was then screwed into the mount on the x-ray tube. After irradiation (usually 8 minutes), the sample was removed and placed in a quartz sample tube.

B. Chemicals

Adamantane (Aldrich, puriss grade) was recrystallized from n-heptane. Adamantane -d_{16} (97.7 atom % D) was the gift of Merck, Sharp, and Dohme of Canada, Ltd., and was used as received. Cyclohexene was purchased from Chemical Procurement Laboratories, Inc. The 1-methyl-, 3-methyl-, 4-methyl-, and 4,4-dimethylcyclohexene and methylenecyclohexane compounds were purchased from Chemical Samples Company. Each was used as received.

C. Sample Preparation

The substance was placed in a test tube (20 mm. x 135 mm.), about a quarter gram of adamantane was added; the adamantane was dissolved in the substance by heating with a heat gun, and the solution quenched by immersion in cold water. The damp crystals were suction dried on a Büchner funnel and allowed to air dry. Cylindrical pellets, about 3 mm. in diameter and 5 mm. long, were pressed on a Parr pellet press.

A vacuum line preparation was used for samples made in perdeuteroadamantane. Adamantane was placed in a glass tube and degassed with several freeze-thaw cycles. The material to be studied was likewise degassed and then condensed into the adamantane tube. The tube was sealed off under vacuum and then the materials mixed by means of repeated sublimation from one end of the tube to the other. The tube was then opened and the pellet pressed in the usual manner. Four cycles usually produced satisfactory pellets.

D. Computations

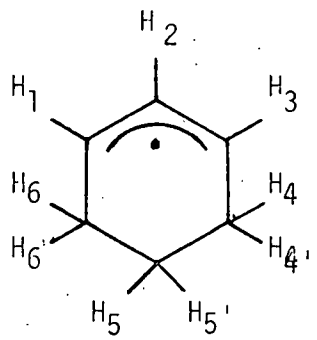
Spectra were simulated using ISOEPR on a XDS Sigma-7.[2] EXALL, EYRING, and BLEND programs were run on the University of Pittsburgh PDP-10 time sharing system in either batch mode or interactive mode. Both computer systems are equipped with Calcomp plotting facilities. Quoted errors in the activation parameters are 95% confidence limits on the average value.

III. RESULTS AND INTERPRETATION

A. Cyclohexenyl Radical

Figure 1 shows the epr spectra obtained when a sample of adamantane ($-\underline{h}_{16}$ or $-\underline{d}_{16}$) which has been recrystallized from cyclohexene is x-irradiated and examined in the E4 spectrometer at selected temperatures. Immediately apparent from these spectra is the fact that they are symmetrical and therefore characteristic of a rapidly tumbling molecule, as in the gas phase or in solution. Further, it is also obvious that a tremendous improvement in resolution is possible by utilizing the perdeutero compound. These effects have been observed before and discussed thoroughly in the literature.[3]

The low temperature spectrum of Figure 1 B can be fit by assuming that x-irradiation leads to loss of a hydrogen atom from the carbon atom adjacent to the double bond of cyclohexene and the formation of the cyclohexenyl radical, I.



I

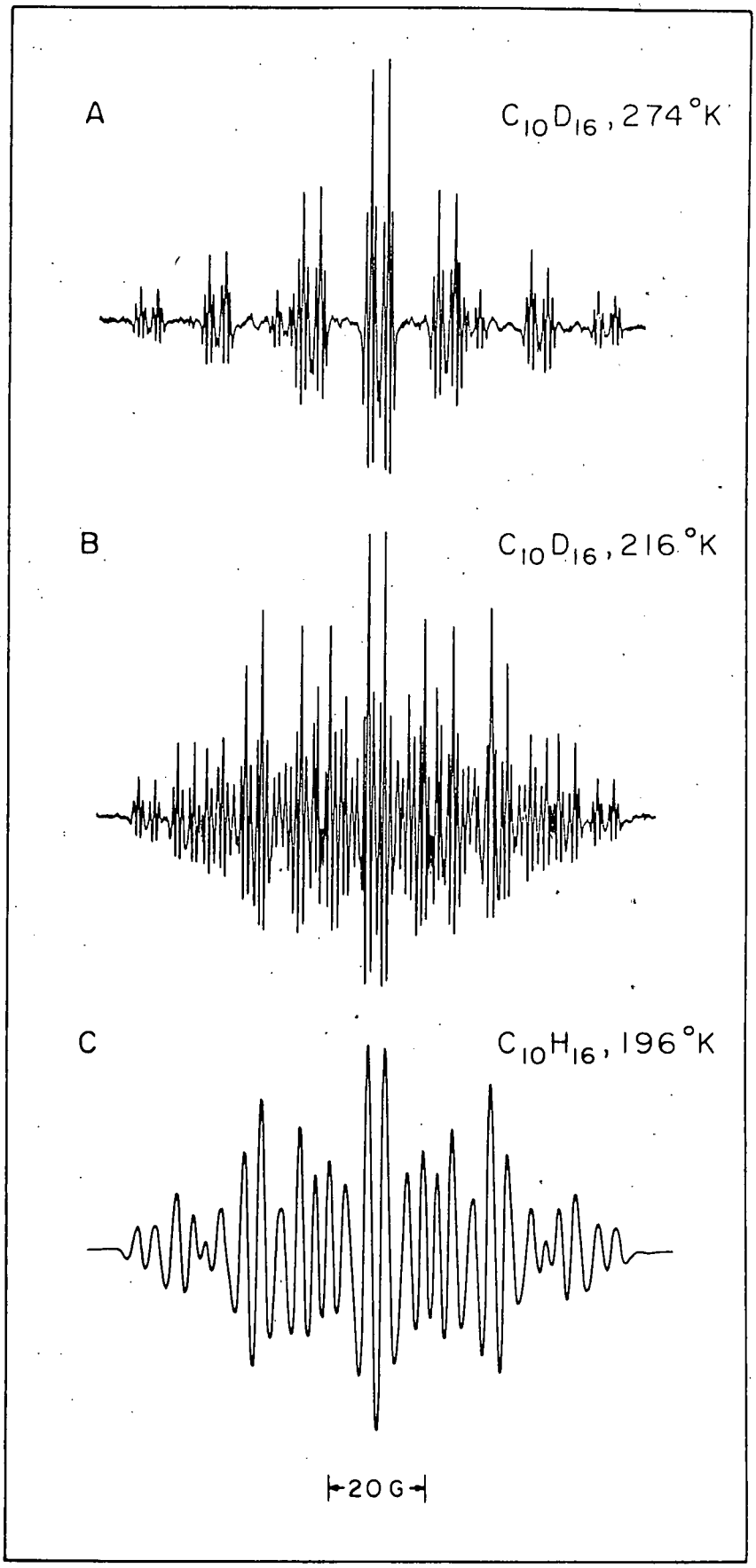


Figure 1 - Observed spectra for cyclohexenyl radical at selected temperatures

What is remarkable about the spectrum in Figure 1 B is that it exhibits hyperfine splittings (hfs) from all protons in the molecule. Thus, a computer simulation of the spectrum at 216° K yields the parameters $a^H_{1,3} = 14.63$, $a^H_2 = 3.57$, $a^H_{4,6} = 26.49$, $a^H_{4',6'} = 8.44$, and $a^H_{5,5'} = 0.89$ G.

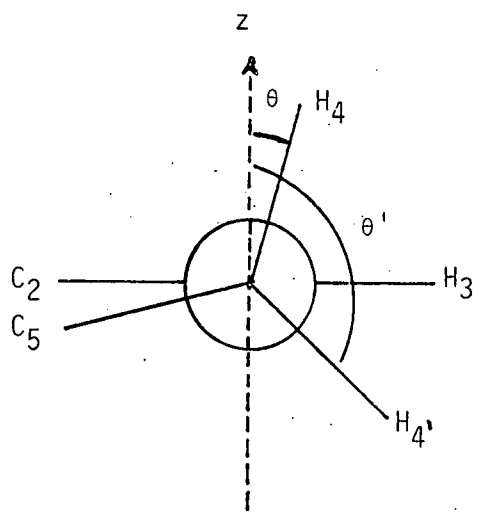
These hfs are characteristic of an allylic free radical with two pairs of magnetically-inequivalent β protons and one pair of equivalent γ protons, and are in agreement with the parameters previously obtained from solution measurements.[4] Of course, it is not known to which pair of β protons the larger hfs belongs (i.e., an alternative assignment is $a^H_{4,4'} = 26.49$, $a^H_{6,6'} = 8.44$ G.), but since the molecule is assumed to have a plane of symmetry, the above assignment seems more reasonable.

On increasing the temperature it is observed (Fig. 1 A) that some of the center lines in the spectrum broaden and eventually disappear, all the while maintaining their position relative to the other lines. In other words, the overall width of the spectrum is essentially invariant to temperature which means that the total hfs is temperature independent. This behavior is reversible and is well-known in epr spectroscopy. It is a manifestation of an exchange process caused by the interchange of the geometrical positions of the β protons, resulting in an "alternating linewidith" effect.[5]

The above behavior can be understood by considering the radical geometry and the spin states of the nuclei involved. The cyclohexenyl radical would be expected to have three sp^2 hybridized carbon atoms, C_1, C_2, and C_3, leading formally to a coplanarity of atoms C_1, C_2, C_3, C_4, and C_6, and the hydrogen atoms remaining on

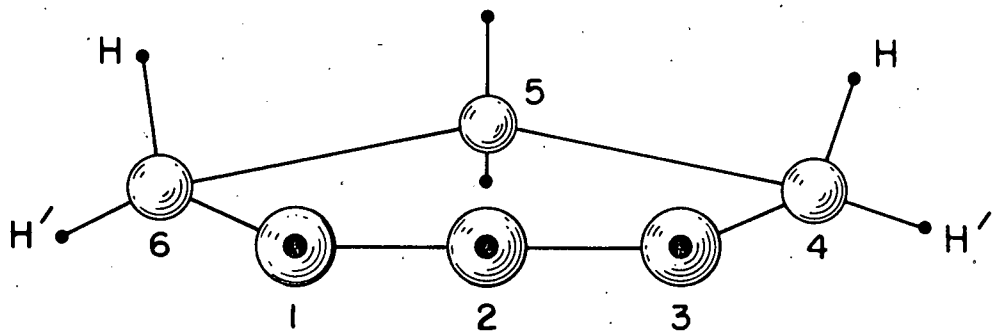
C_1, C_2, and C_3. Only C_5, among the heavier atoms, is not coplanar, and two conformations of the radical are possible, II and III. Of course, conformations II and III have the same energy since the substituents attached to C_4, C_5, and C_6 are the same in the case of the cyclohexenyl radical. However, the magnetic environments of the protons attached to C_4 and C_6 are different in the two conformations; protons H_4, $H_{4'}$ being magnetically inequivalent. It is believed that the interconversion II $\rightleftarrows$ III which interchanges the environments of protons H_4, $H_{4'}$ and H_6, $H_{6'}$ is responsible for the observed alternating linewidth effect.*

To see why the protons H_4 and $H_{4'}$ are magnetically inequivalent, the mechanism for hyperfine coupling to β protons must be considered. Structure IV shows an approximate view along the C_4 - C_3 bond axis for the conformation II. The two protons on C_4

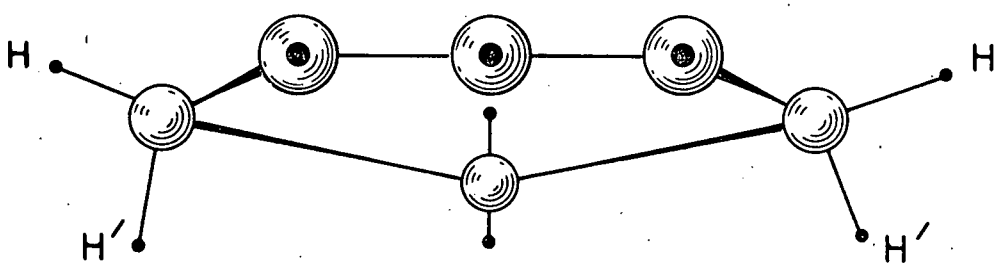


IV

*Similar effects have been observed in other radicals derived from cyclohexane[6] and cyclohexanone.[7]



II



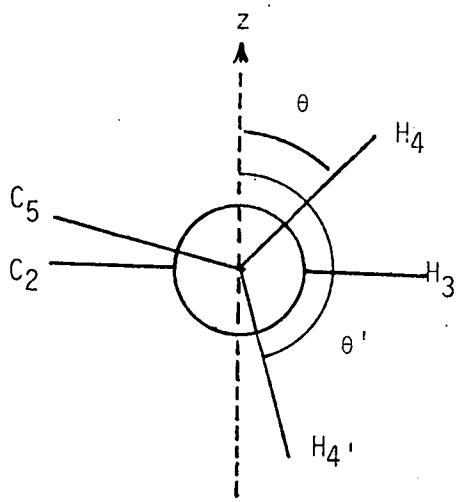
III

are approximately axial (H_4) and approximately equatorial ($H_{4'}$). The third and fourth atoms attached to C_4 are C_5 and C_3, with C_3 having spin density ($\rho = 0.589$)[8] in a $2p_z$ type orbital. This spin density is transmitted, through a hyperconjugative mechanism, to the protons on C_4, the magnitude of the observed β proton hfs following the well-known $\cos^2\theta$ relationship[9]

$$a^H_\beta = \rho^C_\alpha (B_0 + B_2 \cos^2\theta) \qquad (1)$$

where ρ^C_α is the spin density in the $2p_z$ orbital of the α carbon atom, B_0 and B_2 are empirical constants, and θ is the dihedral angle between the $2p_z$ orbital and the β proton (H_4 or $H_{4'}$ in IV). It follows then that the value of a^H_β should be a maximum when the β proton is axial ($\theta = 0$) and should be small when the β proton is equatorial, since $B_0 \ll B_2$.[9] It is this phenomenon which is responsible for the pair-wise inequivalence of the β protons in the cyclohexenyl radical at low temperatures. Thus, at 216° K, the hfs of $a^H_{4,6}$ = 26.49 G. implies that protons H_4 and H_6 are nearly axial and a hfs of $a^H_{4',6'}$ = 8.44 G. implies that protons $H_{4'}$ and $H_{6'}$ are nearly equatorial. In fact, if we assume B_0 = 1.8 and B_2 = 49.8 G.,[9] we calculate from Eq. (1) $\theta = 21.4°$ and $\theta' = 141.4°$.

There is, of course, an energetically equivalent structure V corresponding to conformation III of the cyclohexenyl radical. This is shown below. Since the angle θ of this structure is equal to θ' of structure IV, it is obvious that in conformation III, proton H_4 has the same hfs as $H_{4'}$ in conformation II. In other words, the interconversion II $\rightleftarrows$ III (or IV $\rightleftarrows$ V) leads to exchange of the proton H_4 and $H_{4'}$ (and H_6 and $H_{6'}$) between two magnetically inequivalent sites. It is this phenomenon which is responsible



V

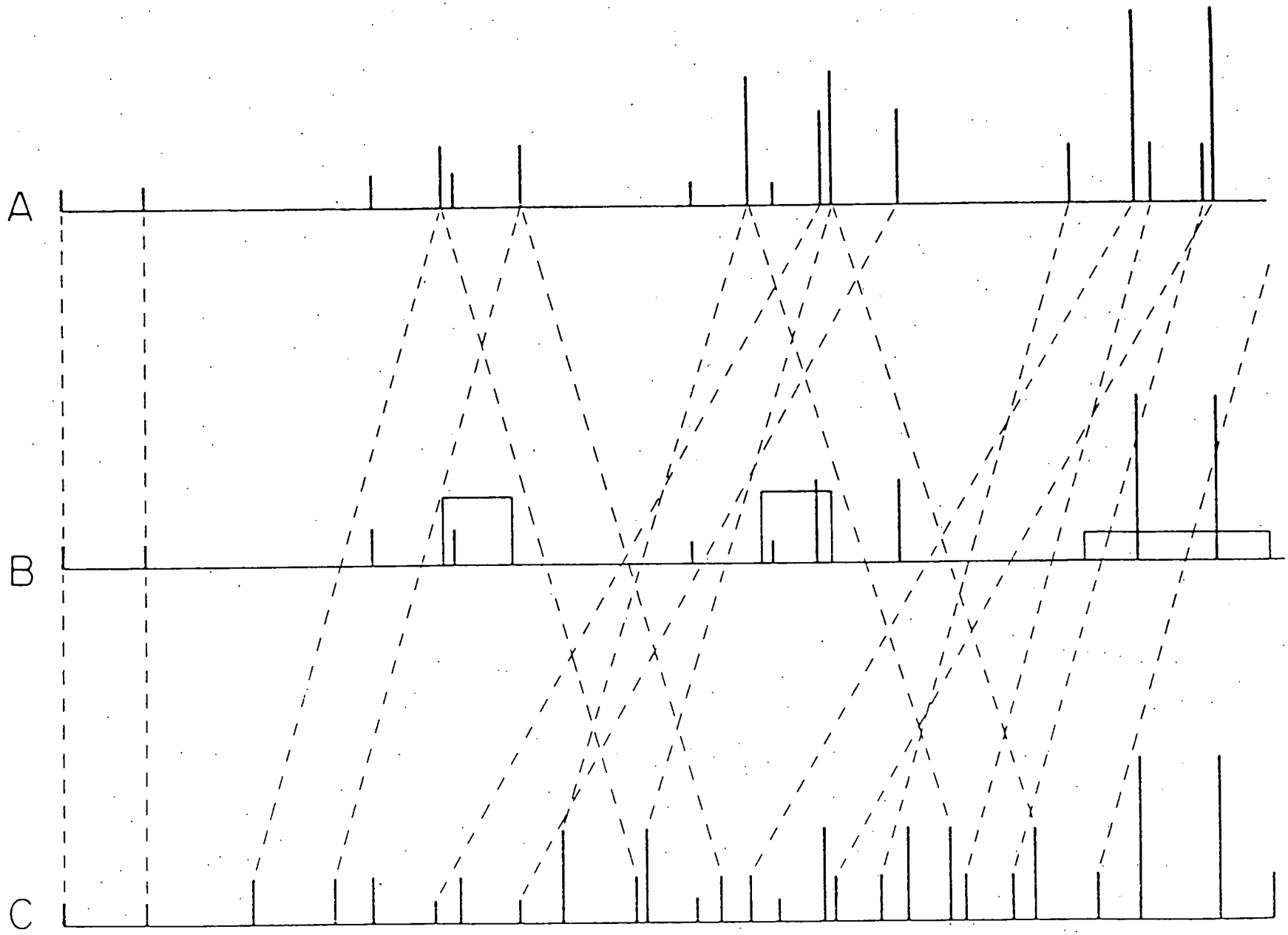
for the alternating linewidth effect.

For a spectrum centered at $H_o = h\nu_o/g\beta$, the relative position (H) of a line due to those radicals having a particular set of spin states (m_i) and coupling constants (a^H_i) is

$$H - H_o = \sum_i m_i a^H_i . \qquad (2)$$

Using Eq. (2), it is possible to construct a stick diagram corresponding to the low temperature spectrum of cyclohexenyl radical. One half of this (symmetrical) diagram is shown in Fig. 2 C where the spin wave functions of $C_{1,3}$, C_2, $C_{4,6}$ and $C_{4',6'}$ protons are shown below. The C_5 proton splittings have been omitted for clarity. From the diagram, the assignment of the spectrum of Figure 1 B is

Figure 2 - Stick diagram for the cyclohexenyl radical in the case of (A) fast, (B) intermediate, and (C) slow exchange


A
B
C
H1, 3 - - - - 0 - 0 - 0 -0 + - 0 + -0 + - 0 + - 0 - 0
H2 - + - + - - + + - - + - + - + -+ - + -+ - + + -
H4, H6 - - - - - - - - - 0- - 0 - - 0- -.0 0 - 0 0 0 0
H4', H6' - - 0 0 - + - + 0 -0 - - + - 0+ 0 0 -0 + - + 0

clear; there is a 1:2:1 triplet due to the protons H_4 and H_6, a 1:2:1 triplet due to $H_{4'}$ and $H_{6'}$, a 1:1 doublet due to H_2, and a 1:2:1 triplet due to H_5 and $H_{5'}$ (not shown).

We next consider the spectrum expected in the limit of fast exchange, i.e. when the interconversion II $\rightleftarrows$ III (or IV $\rightleftarrows$ V) is fast compared to the magnetic inequivalence of protons H_4 and $H_{4'}$ expressed in frequency units [$\Delta\nu = (a^H_4 - a^H_{4'})/g\beta h$]. In this case, although not observed experimentally, protons H_4, $H_{4'}$, H_6 and $H_{6'}$ would be expected to become magnetically equivalent. The hfs from the β protons should then be, approximately, the average value: 1/2(26.49 + 8.44) = 17.47 G., and the triplet of triplets pattern in the low temperature spectrum should be replaced by a 1:4:6:4:1 quintet at high temperatures. A stick diagram corresponding to this hypothetical situation is shown in Figure 2 A, where it is assumed that all remaining proton hfs are temperature independent (again, the C_5 proton hfs are omitted).

The behavior of the spectrum at intermediate rates of exchange is more complex and can be understood by reference to Figure 2 B. Essentially, the situation is the following. A conformational change will lead to change in line position only if the spins which are exchanging have different nuclear spin states. Thus, consider the line due to the combination of nuclear spin states $H_{1,3} = \beta\beta$, $H_2 = \beta$, $H_{4,6} = \beta\beta$, $H_{4',6'} = \beta\beta$ in the low temperature limit. Using Eq. (2), it will be at a field

(-1)(14.63) + (-1/2)(3.57) + (-1)(26.49) + (-1)(8.44) = -51.3 G.

relative to the center of the spectrum. (Here, all hfs constants are assumed positive for convenience.) When a change in

conformation occurs, the axial protons move from an environment of 26.49 G. to 8.44 G., while simultaneously the equatorial protons move from 8.44 to 26.49 G. However, the line position is invariant, i.e.,

$(-1)(14.63) + (-1/2)(3.57) + (-1)(8.44) + (-1)(26.49) = -51.3$ G.

since the exchanging spins have the same m_I value. Furthermore, the line will be in the same position in the limit of fast exchange; i.e., when $a^H_{4,6} = a^H_{4',6'} = 17.47$ G., the line is at

$(-1)(14.63) + (-1/2)(3.57) + (-1)(17.47) + (-1)(17.47) = -51.3$ G.

Consequently, no broadening of this line is expected at intermediate rates of exchange.

Now, consider the line due to the combination of $H_{1,3} = \beta\beta$, $H_2 = \beta$, $H_{4,6} = \beta\beta$, $H_{4',6'} = \alpha\alpha$. At low temperatures, it lies at

$(-1)(14.63) + (-1/2)(3.57) + (-1)(26.49) + (1)(8.44) = -34.53$ G.

After a conformation change, the line shifts to

$(-1)(14.63) + (-1/2)(3.57) + (-1)(8.44) + (1)(26.49) = 1.6$ G.

Moreover, at high temperatures, the line position is again changed, i.e.,

$(-1)(14.63) + (-1/2)(3.57) + (-1)(17.47) + (1)(17.47) = -16.4$ G.

Consequently, as the rate of exchange increases, the line will first broaden, then disappear, and then finally reappear in a new field position, first as a broad line and then as a sharp one. This phenomenon is what is represented schematically in Figure 2 B. Furthermore, it should be obvious that a careful examination of the spectra at intermediate rates of exchange should provide estimates of the conformational lifetimes (τ), their temperature dependence, and the entropies and energies of activation

for the interconversion process.

Figure 3 shows expanded scale spectra of the cyclohexenyl radical in the temperature region 216° K - 274° K together with their respective computer simulations utilizing the programs developed by Walter in this laboratory.[7] The values of the hfs and conformational lifetime τ necessary to fit these and other spectra in this range are listed in Table I. It is observed that within experimental error ($\pm$ 0.1 G.), the hfs are independent of temperature as expected. Moreover, τ decreases from 2.5×10^{-6} to 5.9×10^{-8} sec. in this range.

$\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and conformational lifetimes are related through the Eyring equation[10]

$$k_j = (kT/h)\exp(-\Delta G_j^{\neq}/RT) \tag{3}$$

$$k_j = (kT/h)\exp(\Delta S_j^{\neq}/R)\exp(-\Delta H_j^{\neq}/RT) \quad j = 1,2 \tag{4}$$

Where k is Boltzmann's constant, h is Planck's constant, and k_j is the forward rate constant for the jth conformation in the conformational change

$$A_1 \underset{\leftarrow}{\overset{\rightarrow}{}} A_2 \tag{5}$$

Also,

$$k_1 = 1/\tau_1, k_2 = 1/\tau_2 \tag{6}$$

Equation (4) can be rewritten as

$$\ln(1/T\tau_j) = \ln(k/h) + \Delta S_j^{\neq}/R + (1/T)(-\Delta H_j^{\neq}/R)$$

A plot of $\ln(1/T\tau_j)$ vs. 1/T will have a slope of $(-\Delta H_j^{\neq}/R)$ and an intercept of $[\ln(k/h) + \Delta S_j^{\neq}/R]$.

The enthalpy and entropy of activation, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for cyclohexenyl radical were calculated from an Eyring plot of $\ln(1/T\tau_j)$ against 1/T, using the data in Table I. The plot is

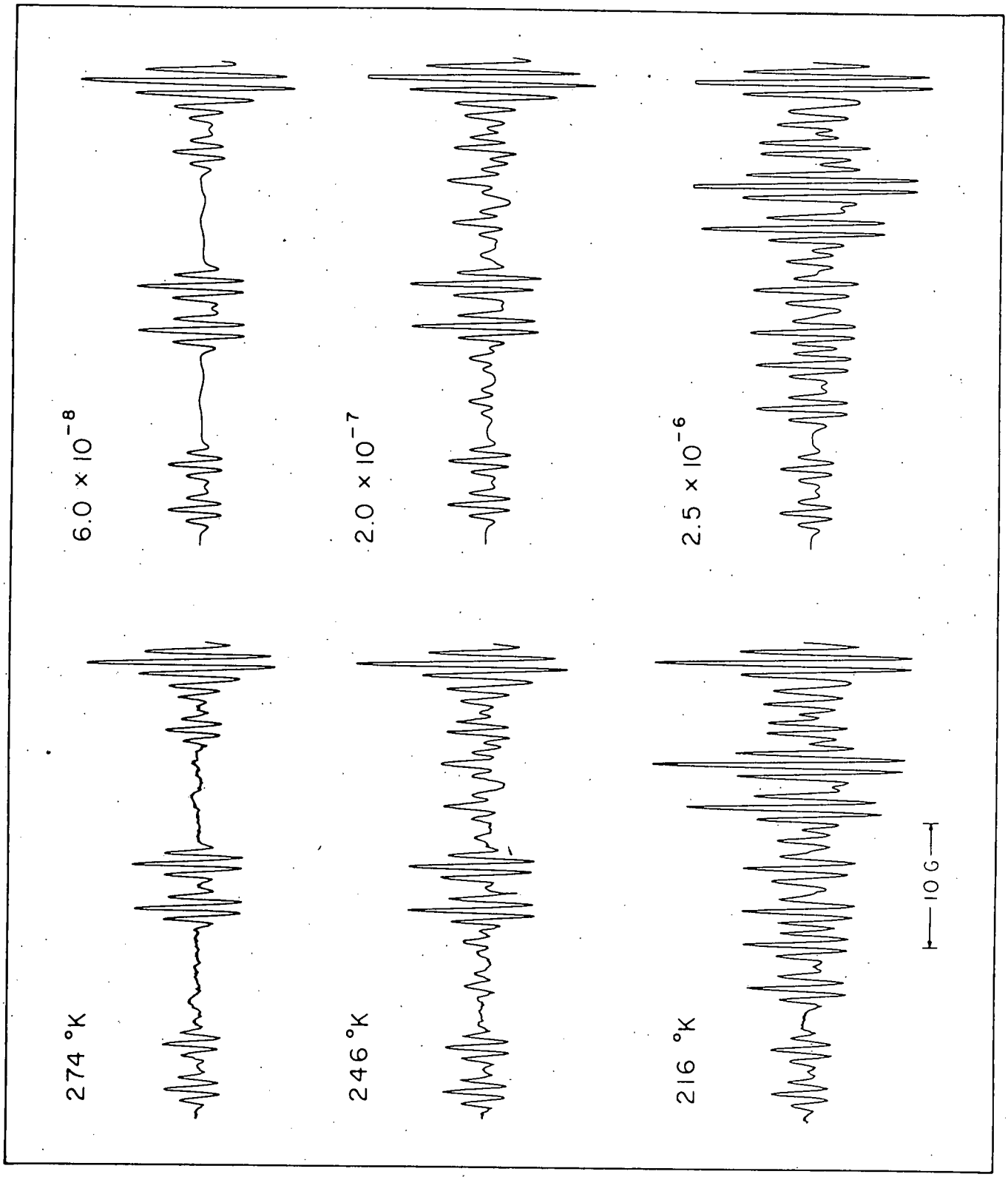


Figure 3 - Expanded scale spectra of the cyclohexenyl radical with their respective computer simulations at selected temperatures.

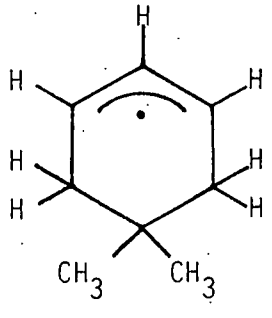
Table I. EPR parameters as function of temperature for cyclohexenyl radical.

Temperature °K	$a^H_{1,3}$	a^H_2	$a^H_{4,6}$	$a^H_{4',6'}$	$a^H_{5,5}$	$a^H_{4,6} + a^H_{4',6'}$	Lifetime, τ, sec
216	14.63	3.57	26.49	8.44	0.89	34.93	2.50×10^{-6}
227	14.63	3.52	26.49	8.44	0.90	34.93	6.60×10^{-7}
236	14.59	3.57	26.33	8.45	0.89	34.78	3.00×10^{-7}
246	14.59	3.58	26.20	8.44	0.89	34.64	2.00×10^{-7}
257	14.59	3.60	26.26	8.45	0.89	34.71	1.20×10^{-7}
264	14.59	3.60	25.95	8.58	0.85	34.53	8.00×10^{-8}
274	14.59	3.60	25.80	8.74	0.85	34.54	5.90×10^{-8}

shown in Figure 4. The resulting parameters are $\Delta H^{\neq}$ = 6.81 ± 0.58 kcal/mole, $\Delta S^{\neq}$ = -0.04 ± 2.40 e.u., and $\Delta G^{\neq}_{298}$ = 6.82 ± 0.91 kcal/mole.

B. 5,5 - Dimethylcyclohexenyl Radical

Figure 5 shows the epr spectra which were obtained when a sample of adamantane containing 4,4-dimethylcyclohexene was x-irradiated. The coupling constants which were necessary to fit the spectra are listed in Table II and are consistent with a single radical having the structure VI. In this case, the small



VI

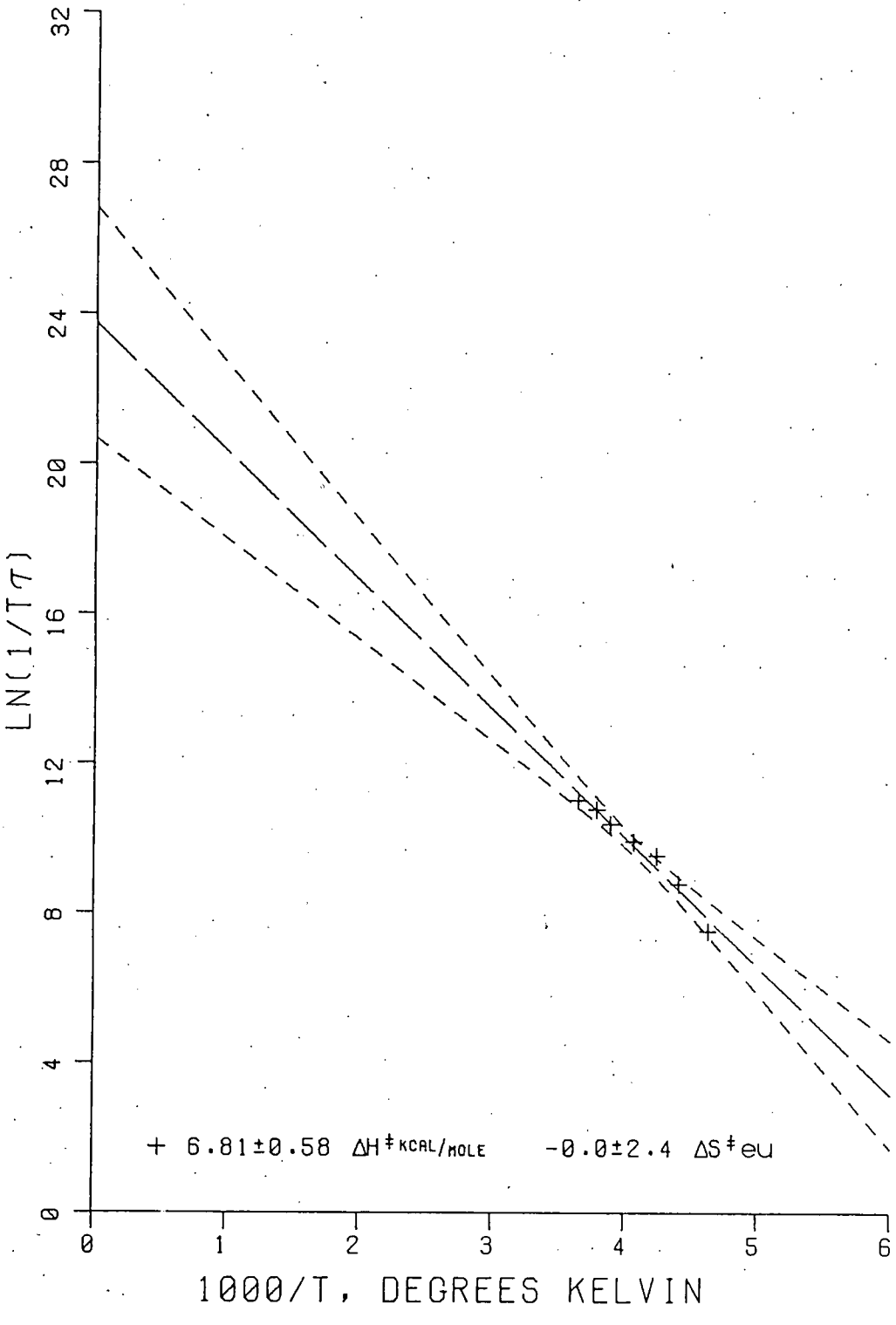


Figure 4 - Eyring plot for cyclohexenyl radical

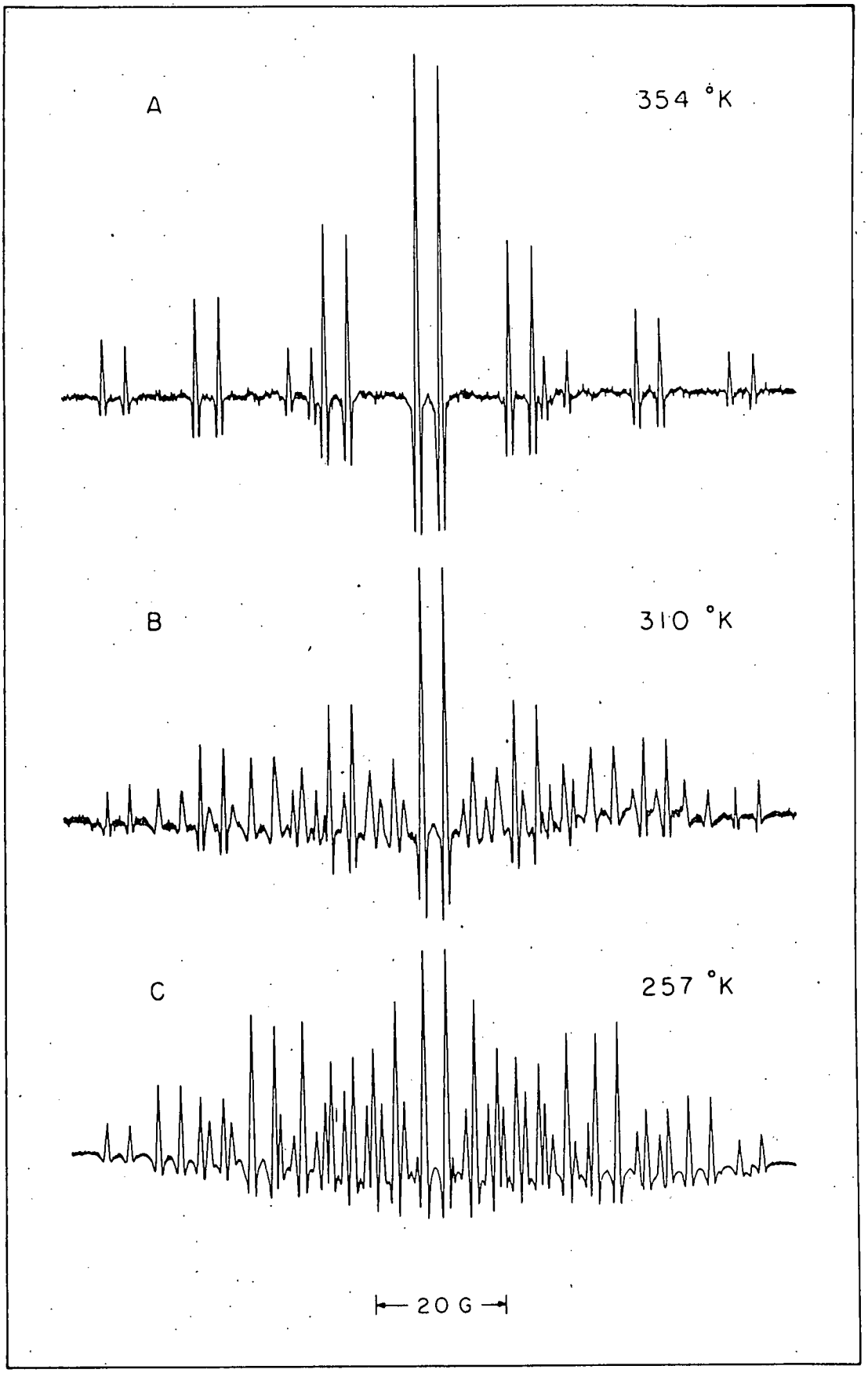


Figure 5 - Observed spectra for 5,5-dimethylcyclohexenyl radical at selected temperatures

γ-proton hfs found in the case of cyclohexenyl is not observed since these protons are replaced by methyl groups. However, since this substitution preserves the plane of symmetry of the radical, the two conformations analogous to II and III again have the same energy. Consequently, no temperature dependence of the proton hfs is expected or observed (c.f. Table II). No evidence for the 4,4-dimethylcyclohexenyl radical was obtained.

The distinguishing feature of this radical is that the temperatures required for intermediate exchange are considerably higher than those for cyclohexenyl. Thus, the epr spectrum of the 5,5-dimethylcyclohexenyl radical is essentially unchanged at temperatures of 274° K and below, and the coalescence temperature (the point at which lines disappear) is not reached until ~354° K. Otherwise, the spectra can be analyzed in an identical fashion to that described for the cyclohexenyl radical.

The high resolution spectra of 5,5-dimethylcyclohexenyl radical together with their respective computer simulations are shown in Figure 6; the values are listed in Table II. A plot of $(T\tau)^{-1}$ vs. 1/T is shown in Figure 7; the activation parameters are $\Delta H^{\neq}$ = 11.75 ± 0.46 kcal/mole, $\Delta S^{\neq}$ = 8.8 ± 1.70 e.u., and $\Delta G^{\neq}$ = 9.12 ± 0.73 kcal/mole.

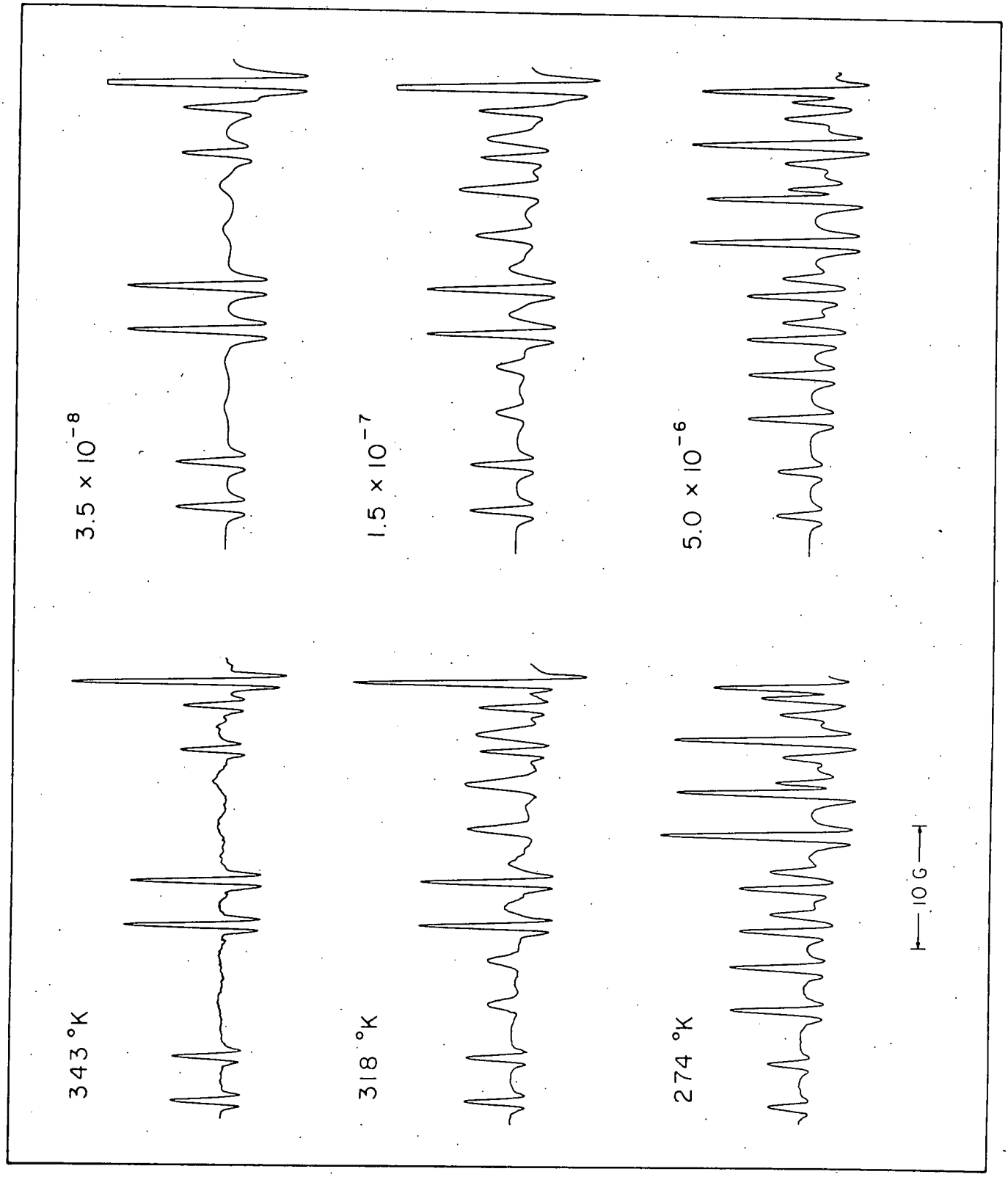


Figure 6 - Expanded scale spectra of the 5,5-dimethylcyclohexenyl radical with their respective computer simulations at selected temperatures

Table II. EPR parameters as a function of temperature for 5,5-dimethylcyclohexenyl radical.

Temperature °K	$a^H_{1,3}$	a^H_2	$a^H_{4,6}$	$a^H_{4',6'}$	$a^H_{4,6} + a^H_{4',6'}$	lifetime, τ, sec
216	14.55	3.55	26.6	7.90	34.5	6.0×10^{-6}
274	14.40	3.60	26.6	7.90	34.5	5.0×10^{-6}
293	14.40	3.60	26.6	7.90	34.5	1.0×10^{-6}
302	14.40	3.60	26.6	7.90	34.5	5.0×10^{-7}
322	14.40	3.68	26.6	7.90	34.5	1.5×10^{-7}
333	14.40	3.68	26.6	8.00	34.6	9.0×10^{-8}
343	14.40	3.68	26.6	8.00	34.3	4.8×10^{-8}
354	14.40	3.75	26.6	8.00	34.3	3.5×10^{-8}

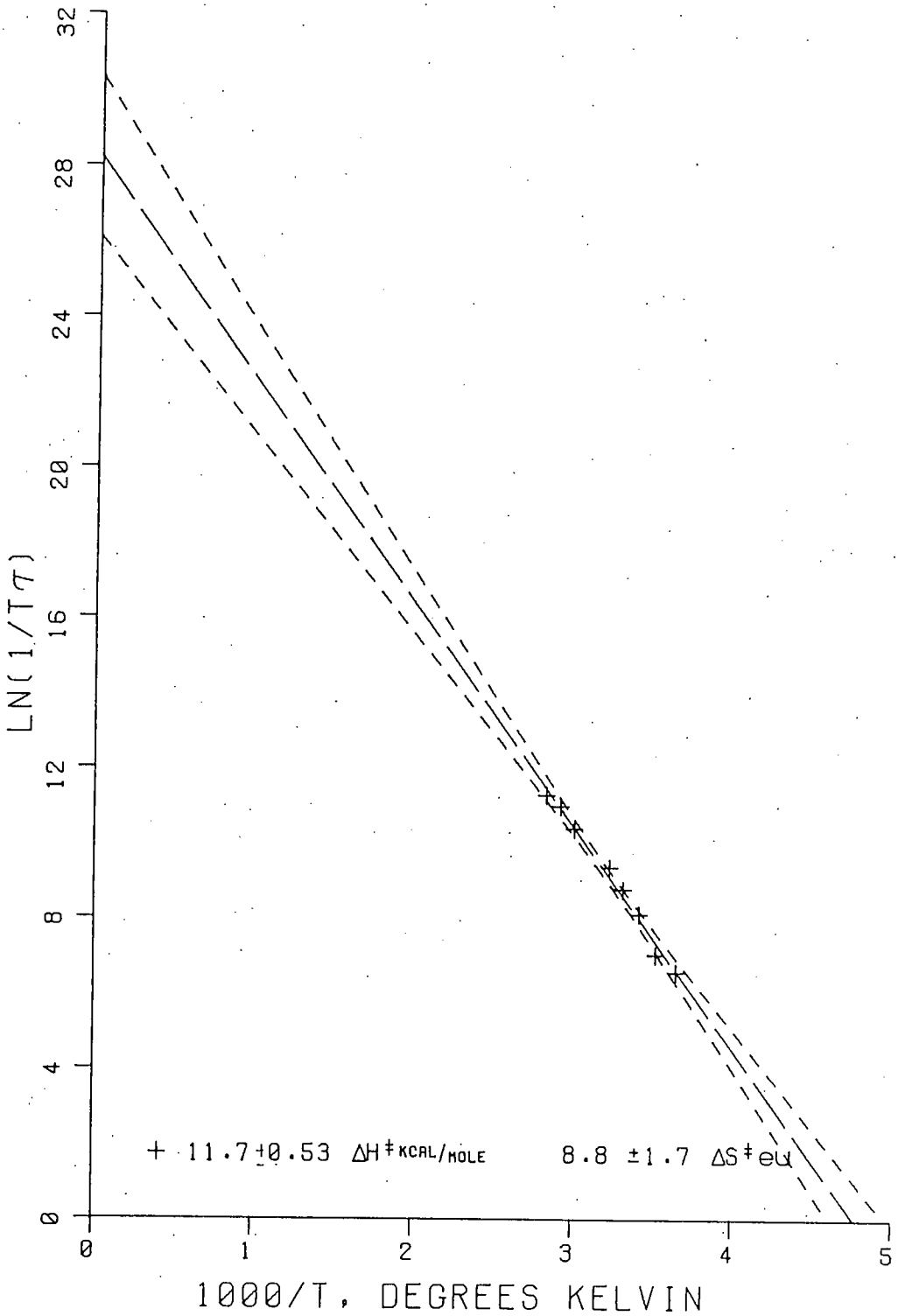
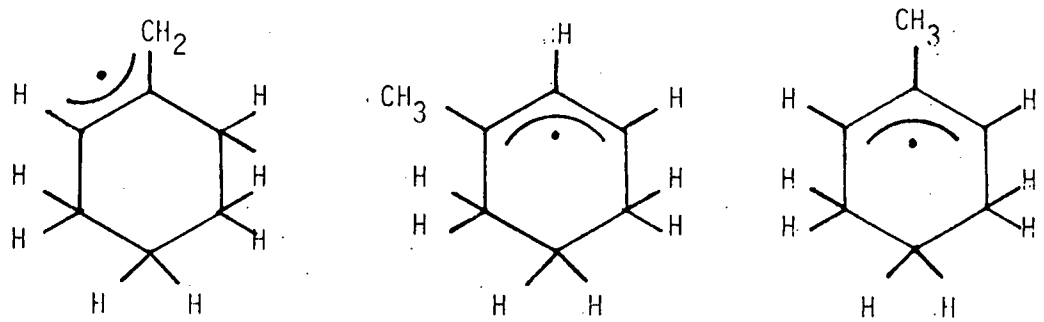


Figure 7 - Eyring plot for the 5,5-dimethylcyclohexenyl radical

C. 2-Methylenecyclohexyl and 1-Methylcyclohexenyl Radicals

X-irradiation of 1-methylcyclohexene in adamantane might be expected to produce at least three different radicals depending on the position of hydrogen-atom removal. These are shown below as structures VII - IX.



VII VIII IX

In practice, only two radicals are observed in sufficient concentration to be characterized, 2-methylenecyclohexyl (VII) and 1-methylcyclohexenyl (VIII). Fortunately, it is possible to distinguish these two experimentally, VII by the absence of the 3 - 4 G. doublet due to the C_2 proton and by the presence of a 3 - 4 G. triplet due to the C_3 protons, and VIII by the presence of the 3 - 4 G. doublet (absent in IX as well) and by the larger overall width due to the presence of the three β protons in the 1 position.

1. 2-Methylenecyclohexyl Radical

Figure 8 shows the epr spectrum of this radical in $C_{10}H_{16}$ at 293° K together with its computer simulation. This spectrum was obtained by x-irradiation of a pellet at room temperature followed by u.v.-irradiation to selectively remove lines due to the 1 methylcyclohexenyl radical (vide infra). This spectrum can be fit using the parameters a^{H}_{1} = 13.5 , $a^{H}_{2,2}$ = 14.9, $a^{H}_{3,3}$ = 3.7 and $a^{H}_{6,6}$ = 22.4 G. and shows no effects due to exchange over the temperature range examined (216° K - 328° K, anisotropic below this range). Furthermore, no additional hfs are observed in the $C_{10}D_{16}$ matrix, suggesting that there is an inhomogeneous width associated with unresolved hfs due to H_5 and $H_{5'}$. An attempt was made to generate this radical by x-irradiation of methylenecyclohexene in adamantane but the spectrum observed in this case consisted of a single 1:2:1 pattern with a coupling constant of ∿13 G. No assignment of this later spectrum was made.

2. 1-Methylcyclohexenyl Radical

As noted above, this radical (VIII) would be expected to exhibit a larger overall spectral width than VII. Consequently, it was possible to obtain information about this species even in the presence of the 2-methylenecyclohexyl radical. Figure 9 shows high resolution spectra of VIII at selected temperatures in the range 216° - 257° K and their respective computer simulations. The spectrum shows no further changes with temperatures up to the highest temperature examined (328° K).

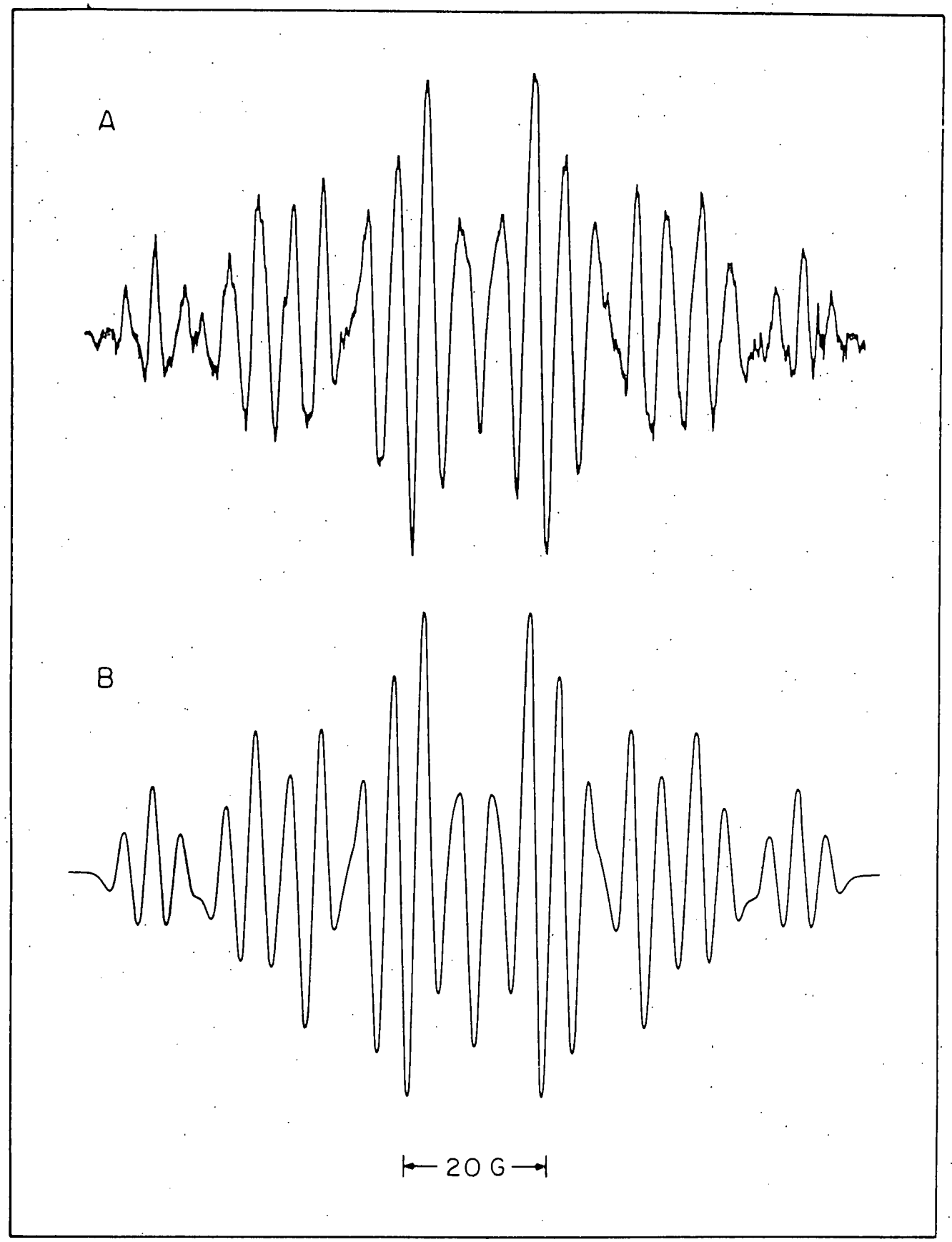


Figure 8 - Observed and synthesized spectra for 2-methylenecyclohexyl radical at 257°K

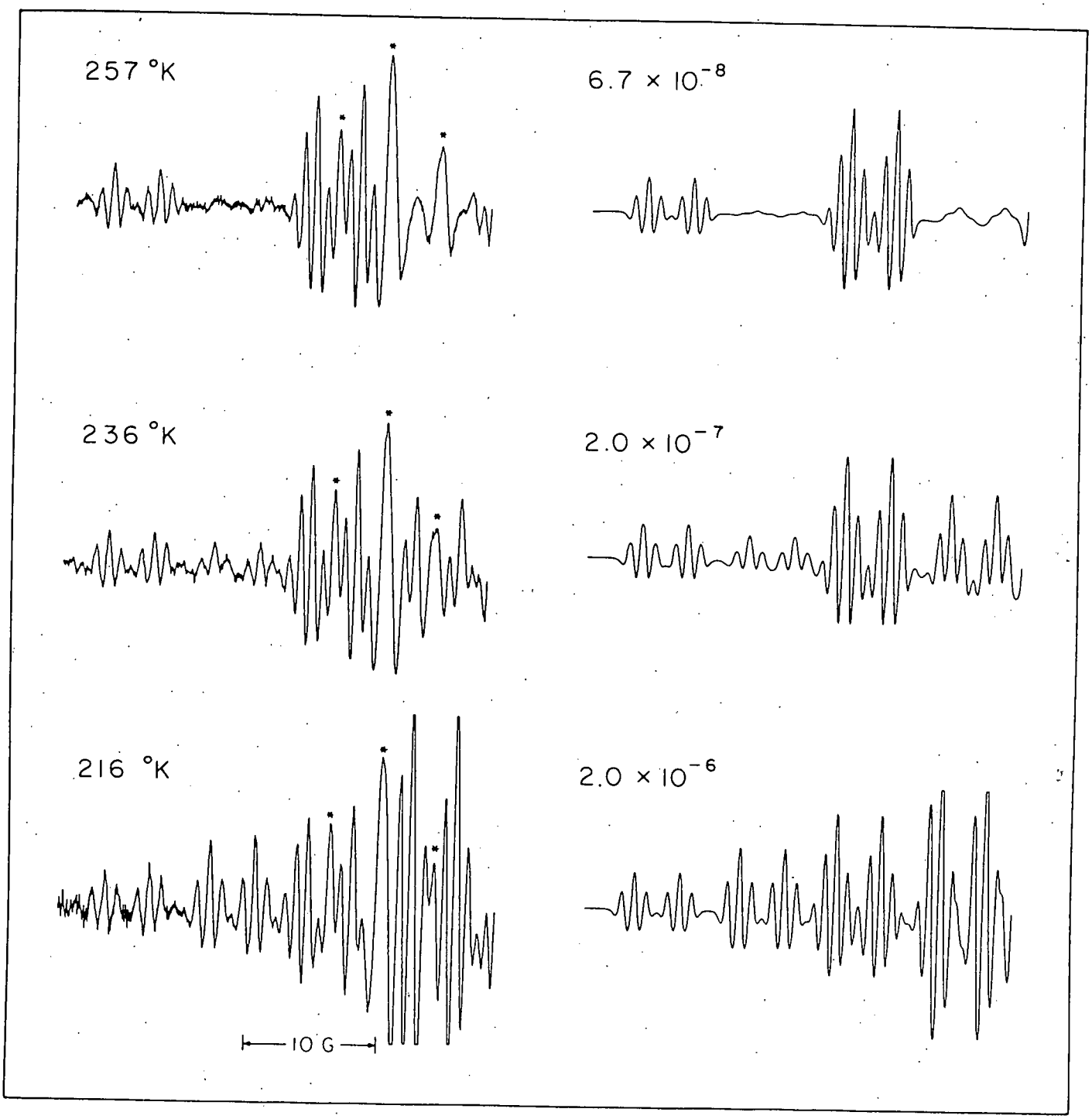


Figure 9 - Expanded scale spectra of 1-methylcyclohexenyl radical with their respective computer simulations at selected temperatures

Since the position of methyl group substitution in VIII is at a planar (or nearly planar) carbon atom, the two resulting conformations analogous to II and III are expected to be of equal energy. An examination of the parameters in Table III shows that this is the case; the parameters are similar to those of the unsubstituted cyclohexenyl radical (cf. Table I), except, of course, for the three CH_3 protons in position 1, and are essentially temperature independent. The spectra therefore exhibit an alternating linewidth effect; the resulting kinetic parameters are (Fig. 10) $\Delta H^{\neq}$ = 7.30 ± 1.24 kcal/mole, $\Delta S^{\neq}$ =-2.20 ± 5.2 e.u., and $\Delta G^{\neq}_{298}$ = 6.60 ± 1.98 kcal/mole. It should be noted that there is considerably higher uncertainty in these values because of the overlapping lines from radical VII.

D. 4- Methylcyclohexenyl Radical

X-irradiation of 3-methylcyclohexene in adamantane might again produce several different types of radicals. There are two likely candidates, 1-methylcyclohexenyl (VIII) and 4-methylcyclohexenyl (X). As can be seen from the experimental spectrum in Figure 11, the predominant radical is one which exhibits a complex multiplet pattern and has a small overall width (< 100 G.). There are weaker lines on the wings of this spectrum which are stronger in other spectra (not shown) but could not be analyzed in detail. Judging from this difference in overall widths, it is believed that this second, less intense, spectrum is due to the 1-methylcyclohexenyl radical, but further work is necessary in order to determine whether this is correct.

Table III. EPR parameters as a function of temperature for 1-methylcyclohexenyl radical.

Temperature °K	$a^H_{7,7,7}$	a^H_2	a^H_3	$a^H_{4,6}$	$a^H_{4',6'}$	$a^H_{5,5}$	$a^H_{4,6} + a^H_{4',6'}$	Lifetime τ, sec
216	15.22	3.4	14.5	24.4	7.9	0.9	32.3	2.5×10^{-6}
227	15.22	3.4	14.5	24.4	7.9	0.9	32.3	9.0×10^{-7}
236	15.22	3.4	14.5	23.92	8.0	0.9	32.3	3.0×10^{-7}
246	15.22	3.4	14.5	23.92	8.0	0.9	32.3	1.0×10^{-7}
257	15.22	3.4	14.5	23.82	8.1	0.9	32.3	9.0×10^{-8}
274	15.22	3.4	14.5	23.82	8.1	0.9	32.3	6.6×10^{-8}

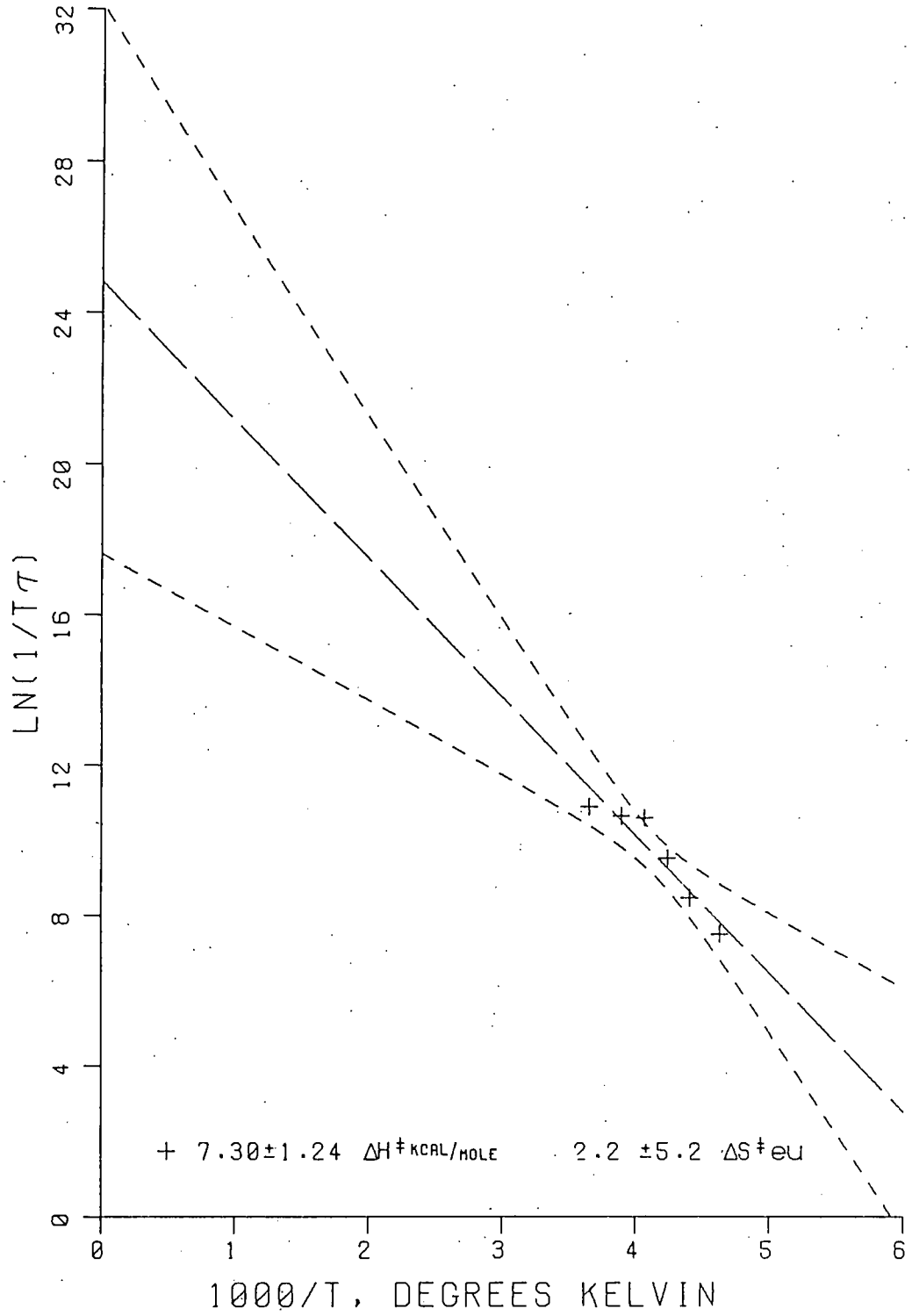


Figure 10 - Eyring plot for 1-methylcyclohexenyl radical

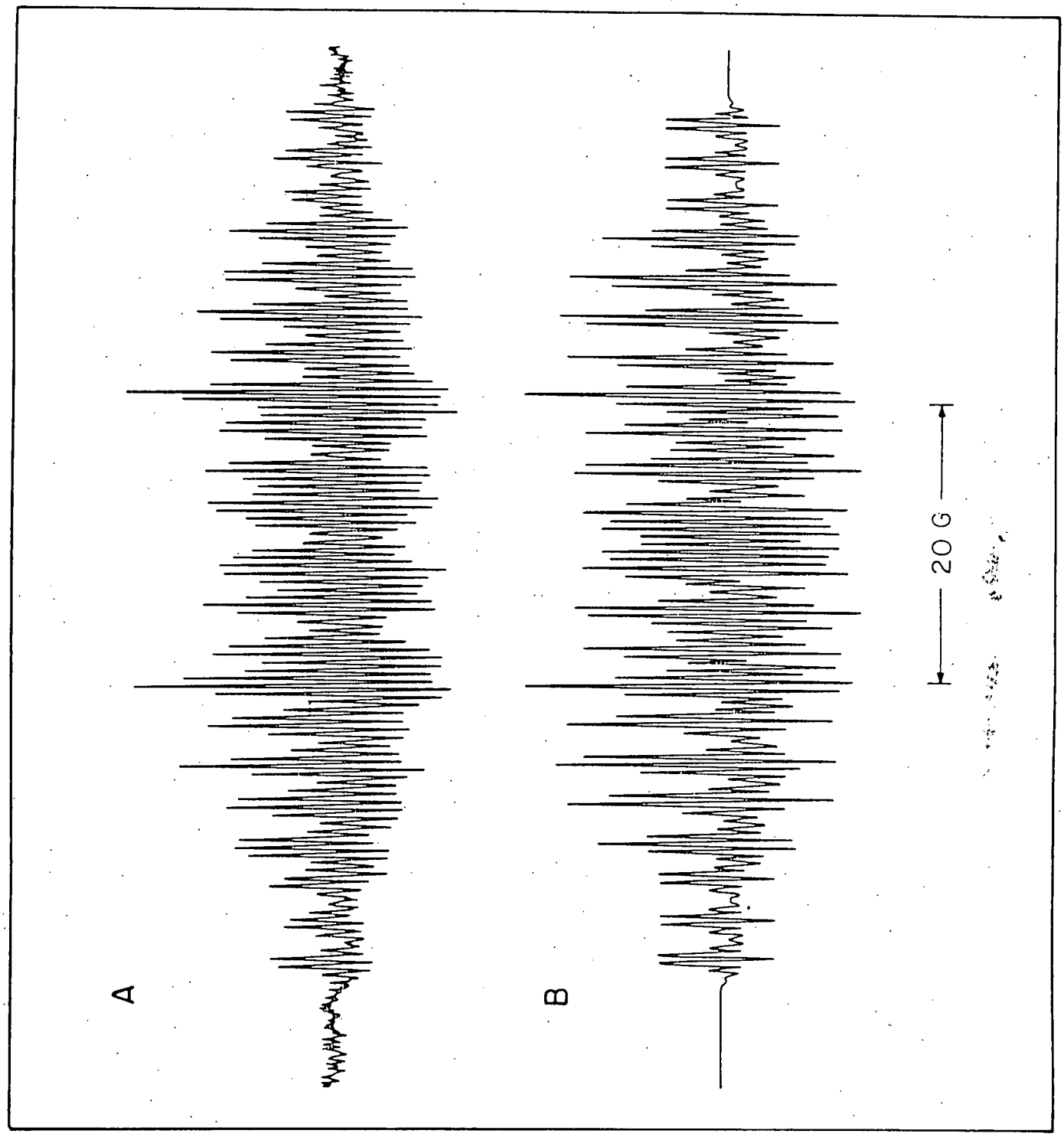
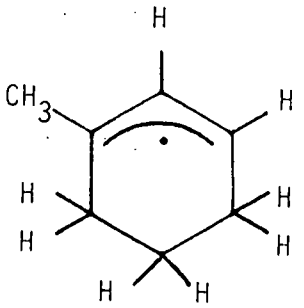
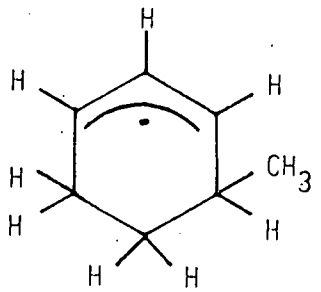


Figure 11 - Observed and synthesized spectra for 4-methylcyclohexenyl radical at 236°K



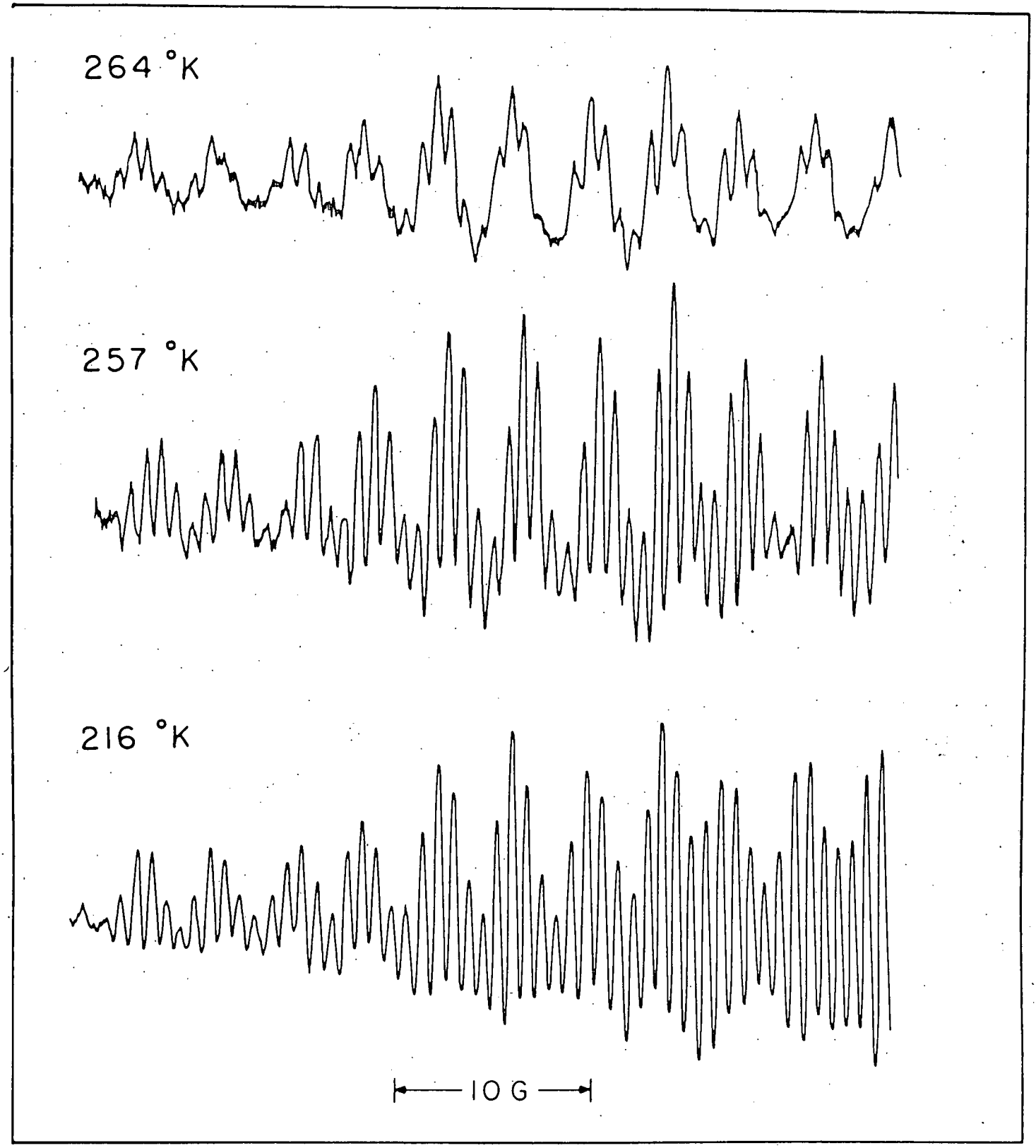
VIII



X

The major lines in Figure 11 can be assigned to the 4-methylcyclohexenyl radical (X). One unusual feature of this spectrum is that it exhibits hfs due to five γ protons; the spectrum can be assigned using the parameters $a^{H}_{1,3} = 14.50$, $a^{H}_{2} = 3,50$, $a^{CH_3}_{4} = 0.69$, $a^{H}_{4'} = 10.10$, $a^{H}_{5,5'} = 0.69$, $a^{H}_{6} = 26.05$ and $a^{H}_{6'} = 7.25$ G. Within experimental resolution, the five γ protons are observed to be magnetically equivalent, yielding a 1:5:10:10:5:1 multiplet pattern. Furthermore, the β proton attached to C_4 clearly prefers the equatorial position. This is then a six coupling constant problem and is one of the most complex epr spectra ever observed.

A second unusual feature of this spectrum is its temperature dependence. After several attempts at eliminating other lines from interfering species, a reasonably clear set of high resolution spectra were obtained. These are shown in Figure 12. On increasing the temperature, it is observed that <u>each</u> of the individual hyperfine multiplets is selectively broadened, some more

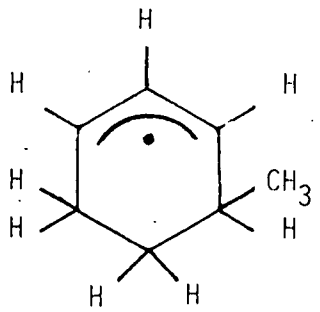


rigure 12 - Expanded scale spectra of 4-methylcyclohexenyl radical at selected temperatures

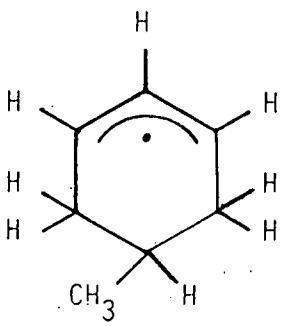
than others. This behavior is quite different from that observed in other cases where only a fraction of the lines are affected by the onset of exchange. There are several possible explanations for this behavior; the most likely is that, since exchange moves the β-methyl group from a nearly axial position to a nearly equatorial one, its average hfs is reduced and the multiplet pattern is simplified to a (somewhat broader) 1:2:1 from the two remaining protons in the 5 position. Unfortunately, this phenomenon has so far made it impossible to obtain kinetic parameters for the 4-methylcyclohexenyl radical. Further experiments on this molecule are in progress.

E. 5 - Methylcyclohexenyl Radical

When $C_{10}D_{16}$ containing 4-methylcyclohexene is x-irradiated, hydrogen atom removal from an allylic position can produce two different radicals, 4-methylcyclohexenyl (X) and 5-methylcyclohexenyl (XI). Based on the earlier results, these two radicals



X



should be most easily distinguished by a small (~ 1.0 G.) 1:2:1 triplet in the former and a small 1:1 doublet in the latter. Examination of the spectra in Figure 13 shows that the predominant species is the 5-methylcyclohexenyl radical. It should be noted, however, that these spectra were obtained only after heating the sample for 5 minutes at 328° K to remove the lines from an interfering radical which are still present to some extent, especially on the low-field side.

The spectrum of the 5-methylcyclohexenyl radical at 216° K can be fit using the parameters $a^H_{1,3}$ 14.5, a^H_2 = 3.5 , $a^H_{4,6}$ = 26.98, $a^H_{4',6'}$ = 7.85, and a^H_5 = 0.99 G. Above this temperature, the spectra again exhibit an alternating linewidth effect which was studied using the high resolution scans of Figure 14. Table IV summarizes the data obtained. As in previous cases, the hfs are essentially temperature independent. This is a somewhat surprising result because the 5-methylcyclohexenyl radical is an unsymmetrically-substituted species whose conformations should be different in energy. The absence of a temperature dependence of the hfs suggests that this difference in energy in the 5-methylcyclohexenyl radical is small; i.e., that the two conformations are essentially equally populated at all temperatures examined in this work (213° - 323° K).

An Eyring plot for the 5-methylcyclohexenyl radical is shown in Figure 15. The activation parameters are $\Delta H^{\neq}$ = 8.65 ± 0.52 kcal/mole, $\Delta S^{\neq}$ = 1.63 ± 1.78 e.u., and $\Delta G^{\neq}_{298}$ = 8.16 ± 0.74 kcal/mole.

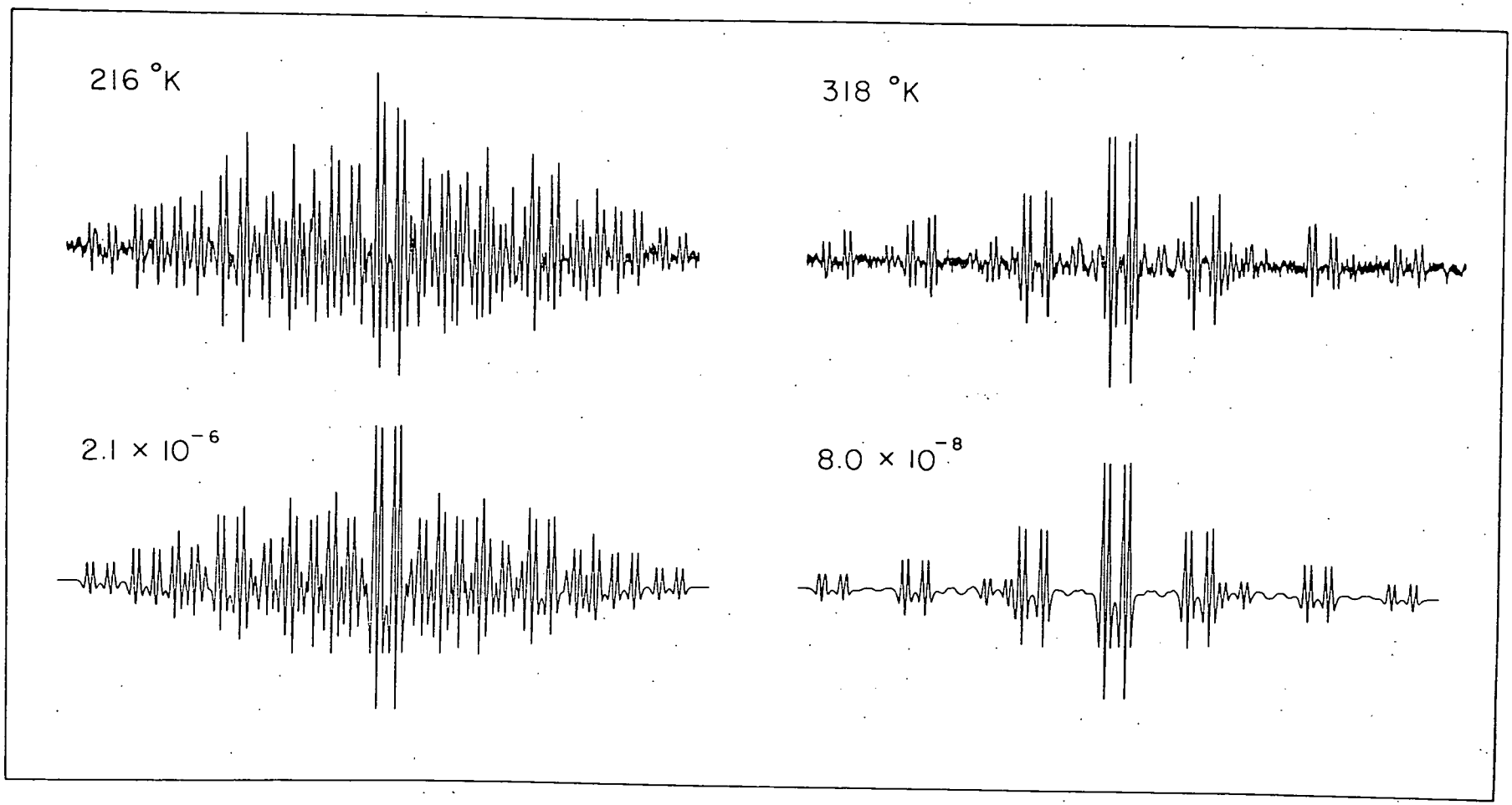


Figure 13 - Observed and synthesized spectra for 5-methylcyclohexenyl radical at selected temperatures

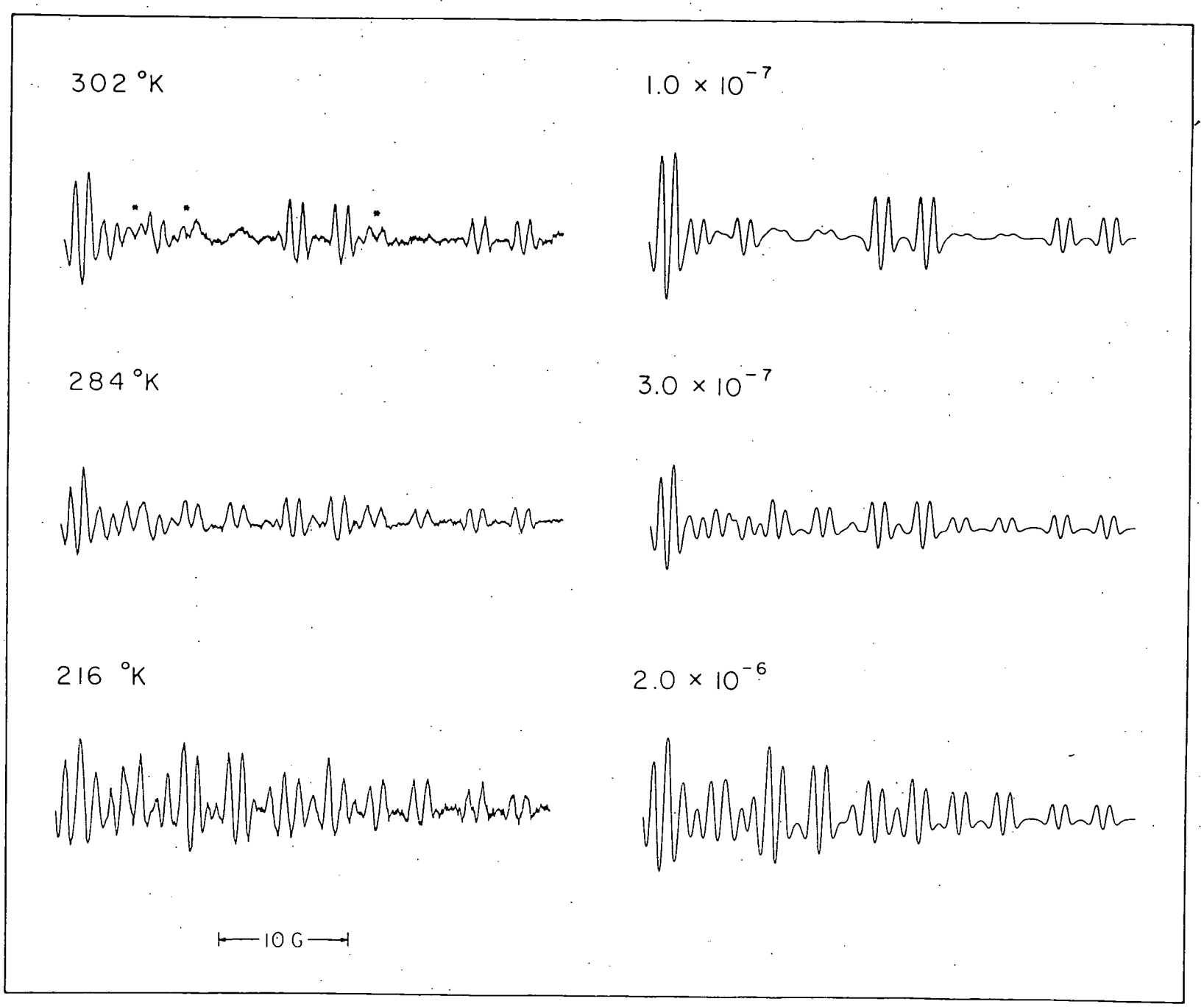


Figure 14 - Expanded scale spectra of 5-methylcyclohexenyl radical with their respective computer simulations at selected temperatures

Table IV. EPR parameters as a function of temperature for 5-methylcyclohexenyl radical.

Temperature °K	$a^H_{1,3}$	a^H_2	$a^H_{4,6}$	$a^H_{4',6'}$	a^H_5	$a^H_{4,6} + a^H_{4',6'}$	Lifetime, τ, sec
216	14.5	3.5	26.98	7.85	0.99	34.98	6.0×10^{-6}
254	14.5	3.53	26.92	7.90	0.99	34.82	2.0×10^{-6}
274	14.5	3.52	26.85	7.85	0.99	34.70	6.5×10^{-7}
284	14.4	3.62	26.69	7.90	0.99	34.59	3.0×10^{-7}
293	14.4	3.62	26.69	7.90	1.00	34.59	2.0×10^{-7}
302	14.4	3.62	26.65	8.00	1.00	34.65	1.0×10^{-7}
310	14.35	3.62	26.65	8.00	1.00	34.55	8.0×10^{-8}
322	14.35	3.62	26.65	8.00	1.00	34.55	6.3×10^{-8}

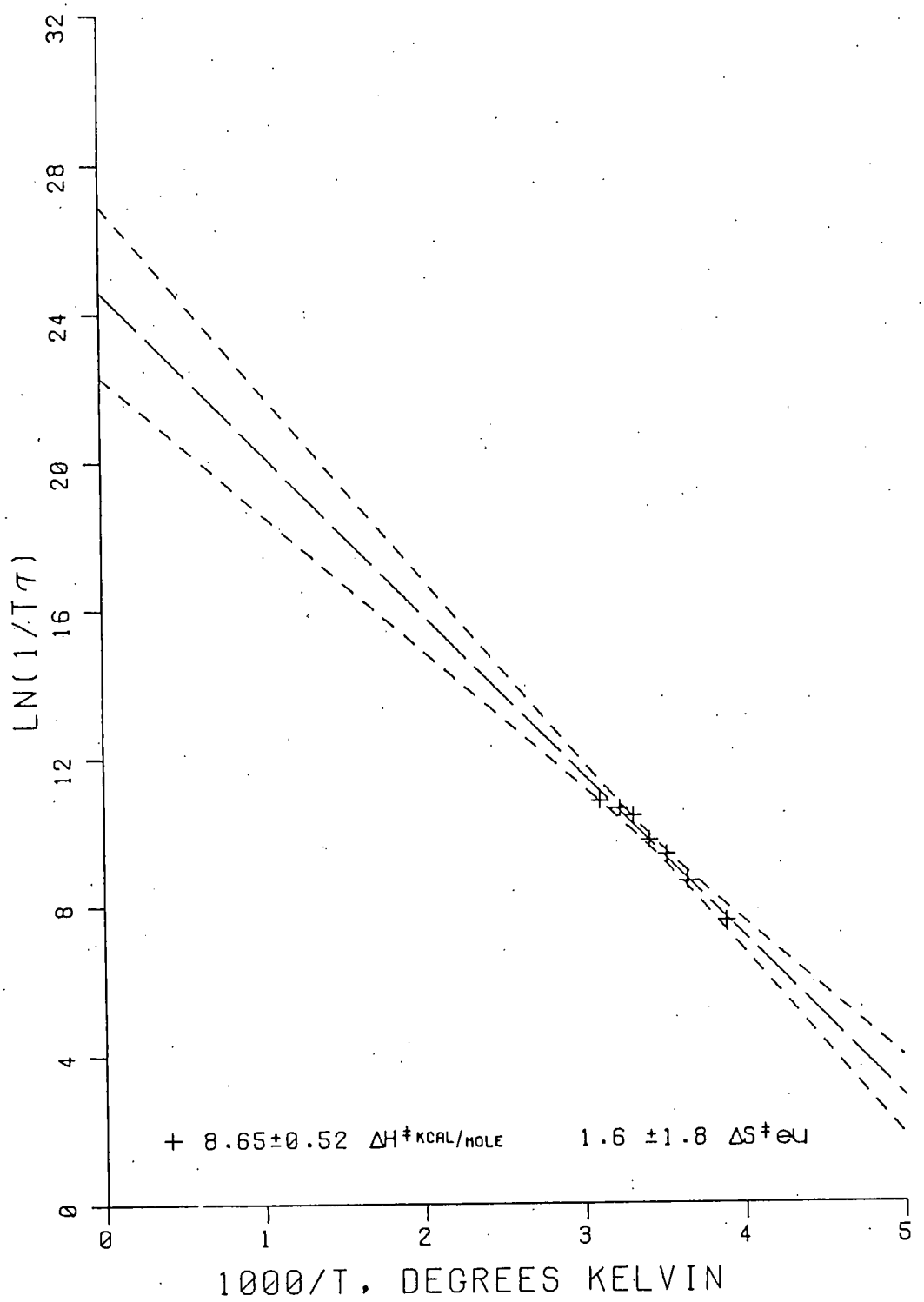


Figure 15 - Eyring plot for 5-methylcyclohexenyl radical

IV. DISCUSSION

Table V lists the activation parameters for the cyclohexenyl radical and some of its alkyl derivatives as determined in this work.

It is observed that the values of $\Delta H^{\neq}$ are the same within the experimental error for the cyclohexenyl and 1-methylcyclohexenyl radicals, and that substitution in the 5 position with methyl groups substantially increases $\Delta H^{\neq}$. The entropies of activation are essentially zero within experimental error for all radicals except 5,5 dimethylcyclohexenyl, which exhibits a large positive $\Delta S^{\neq}$.

As noted earlier, the conformational energy differences in all cases examined in this work are negligible.

Table VI indicates the range of activation parameters exhibited by selected six-membered ring systems. For cyclohexene, $\Delta H^{\neq}$ is about 10 kcal/mole.[11] Introduction of one sp^2 center into the ring, either by a small π system (cyclohexanone)[12] or by a radical (cyclohexyl)[6], appears to reduce $\Delta H^{\neq}$ by about one-half. Additional sp^2 centers, as in cyclohexene[13] and the cyclohexanonyl[7] radical, appear to have substantially less effect upon the activation enthalpy.

It is believed[14] that the chair-to-chair interconversion process in cyclohexane involves a "half-chair" transition state in which four of the ring atoms are in one plane and for which the energy barrier is $\sim$ 10 kcal/mole. The reaction pathway also includes a skew-boat or twist conformation which lies between the

Table V. Activation paramters for cyclohexenyl radical and some of its alkyl derivatives

Radical	$\Delta H^{\neq}$, kcal/mole	$\Delta S^{\neq}$, e.u.	$\Delta G^{\neq}_{298}$, kcal/mole
Cyclohexenyl	6.81 ± 0.58	-0.04 ± 2.40	6.82 ± 0.91
1-Methylcyclohexenyl	7.30 ± 1.09	2.16 ± 5.17	6.60 ± 1.98
5-Methylcyclohexenyl	8.65 ± 0.52	1.63 ± 1.78	8.16 ± 0.74
5,5-Dimethylcyclohexenyl	11.75 ± 0.46	8.80 ± 1.70	9.12 ± 0.73

Table VI. Activation parameters for selected six-membered ring systems.

Molecule	$\Delta H^{\neq}$, kcal/mole	$\Delta S^{\neq}$, e.u.	$\Delta G^{\neq}$, kcal/mole
Cyclohexane[11]	9 to 11	+3 to -7	10 to 11 (206° K)
Cyclohexanone[12]	---	---	4.2 (90° K)
Cyclohexyl[6]	4.9	---	---
Cyclohexene[13]	5.3	1.3	5.2 (109° K)
Cyclohexanonyl[7]	3.7	-2.3	4.38 (298° K)

two equivalent half-chair conformations at ~ 5.5 kcal/mole above the two chairs. The reduction in $\Delta H^{\neq}$ which occurs on introducing a single sp^2 center into the cyclohexene ring presumably reflects the fact that the resulting molecule or radical is partially planar in character, thereby reducing the amount of energy necessary to reach the half-chair conformation.

Unlike species containing zero or one sp^2 centers, six-membered rings containing two sp^2 centers are believed to exist in half-chair conformations. There are several possible pathways for their interconversion, but the most reasonable one involves a "true" boat transition state.[15] Consequently, a comparison of the activation parameters for cyclohexane and cyclohexene is not particularly meaningful in the present context since the interconversion process involves stable conformers and transition states of significantly different structures.

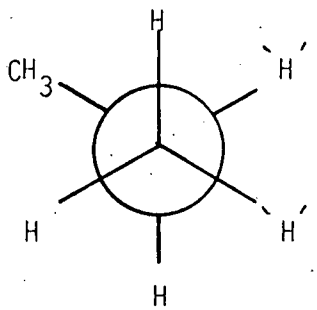
From a consideration of models, the most probable path for interconversion in six-membered rings containing three sp^2 centers such as the cyclohexenyl radical is via a "planar" transition state, i.e., one in which all carbon atoms of the ring are coplanar. In such a structure, the bond angle strain is considerable, and there are several eclipsing interactions between the substituents in the 4, 5, and 6 positions. These repulsive effects may account for the increase in the enthalpy of activation observed on going from cyclohexene to the cyclohexenyl radical since the true boat conformation of the former is almost certainly of lower energy than the planar form of the latter and the stable conformers of the two species more nearly equal in energy. However, such a comparison may not be particularly meaningful for

for the same reasons as noted above.

We can attribute the 6.8 - 7.0 kcal/mole activation enthalpy for the cyclohexenyl and 1-methyl cyclohexenyl radical interconversions of the type II $\rightleftarrows$ III to a combination of factors; angle strain, torsional strain, and non-bonded interactions. If we hold a model of the cyclohexenyl radical and sight along the C_4 - C_5 (or C_5 - C_6) bond, we see that the two pairs of methylene hydrogens (H_4, $H_{4'}$ and H_5, $H_{5'}$, or H_5, $H_{5'}$ and H_6, $H_{6'}$) and the attached carbon atoms (C_3 and C_6, or C_4 and C_1) have the same relative locations as the six hydrogen atoms in the staggered conformation of ethane. In a planar transition state, these same atoms have the same relative locations as the six hydrogen atoms in the eclipsed conformation of ethane. If we treat the attached carbon atoms of the cyclohexenyl radical as hydrogen atoms, then the activation enthalpy for the process II $\rightleftarrows$ III should be of the order of twice the rotational barrier in ethane since there two such eclipsing interactions, or 6 kcal/mole.[16] This is in reasonable agreement with the observed value of 6.8 - 7.0 kcal/mole: the additional $\sim$1.0 kcal/mole may be due to the additional contributions of angle strain and the non-bonded interactions of the attached carbon atoms which, of course, are not present in ethane.

The substitution of one or both C_5 hydrogens with methyl groups introduces an additional factor, namely the crowding together of atoms or groups at distances less than their van der Waals radii. This is called van der Waals or steric strain. We can estimate the magnitude of this effect by considering the possible conformations of n-propane and isobutane.

n-propane



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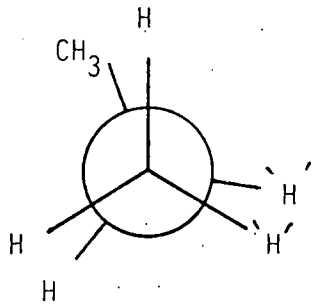

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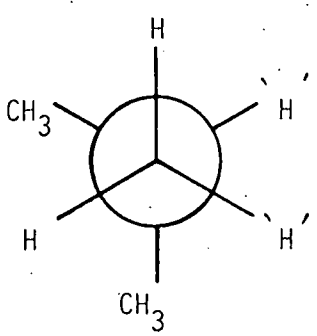
iso-butane



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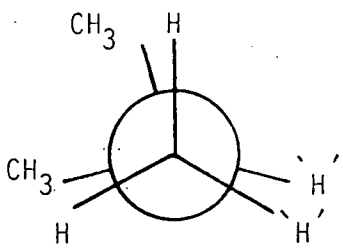

eclipsed

In these molecules, one or two H - H eclipsing interactions are replaced by one or two H - CH_3 eclipsing interactions. Since the rotational barriers in n-propane and isobutane are 3.3 and 3.9 kcal/mole, respectively,[16] we can estimate the activation enthalpies for the 5-methylcyclohexenyl and 5,5-dimethylcyclohexenyl radicals to be 6.6 and 7.8 kcal/mole, respectively. Again, these estimates are too low, by $\sim$ 2 and $\sim$ 4 kcal/mole, respectively. The explanation for these discrepancies is not clear.

Results reported in Table V for cyclohexenyl radical and its 1-methyl and 5-methyl derivatives show near zero entropies of activation with relatively large uncertainty margins. This lack of precision is most likely attributable to the measurement of rate constants over a rather small temperature interval[17] and the proper selection of experimental lifetimes (or k) in the absence of exchange. Values of $\Delta S^{\neq}$ near zero are most often observed for six-membered ring systems, but negative values have been reported for several substituted derivatives of cyclohexene.[18]

The large positive value of $\Delta S^{\neq}$ for the 5,5-dimethylcyclohexenyl radical would appear to be inconsistent with a planar transition state since the number of low-frequency vibrational modes available to the molecule in this form is significantly reduced. Further study of this problem is obviously required.

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