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ELECTRON SPIN RESONANCE STUDIES OF HETEROCYCLOPROPANE RADICAL
CATIONS GENERATED RADIOLYTICALLY IN FREON MATRICES

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Dedicated to the memory of my father

Han Chuan Qin

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ABSTRACT

Several heterocyclopropane radical cations radiolytically generated in Freon matrices were studied by electron spin resonance spectroscopy. The results show: (a) The radical cations of cyclopropane and its derivatives are ring-closed with $^2A_1$ structures in CF_3Cl between 80 and 160 K and in $CF_2ClCFCl_2$ at low temperatures. On annealing in $CF_2ClCFCl_2$, however, these ring-closed cations all undergo ring opening irreversibly to form localized structures. The ring-opened cyclopropane radical cation further rearranges to the propene cation by U.V. irradiation, while the ring-opened trimethylcyclopropane cation further rearranges to the 4-methyl-2-pentene cation either by U.V. irradiation or by annealing. The possible mechanisms of ring-opening were discussed. (b) Both the ring-opened delocalized planar structure ($^2A_2$) and the localized structure of the oxirane radical cation were observed in SF_6 at low temperatures from studies of oxirane, 1,2- D_2 -oxirane, and the 1,2- ^{13}C oxirane radical cations. On annealing to above the phase transition at 95 K, the delocalized form is changed to the localized form irreversibly. (c) The aziridine radical cation in CF_3Cl possesses the ring-opened planar structure with spin mostly on two carbons. (d) The monomer radical cation of thiirane in CF_3Cl is the ring-closed $^2B_1(\pi)$ state with most of the spin on the sulfur atom. The dimer radical cation of thiirane with a $\sigma^2\sigma^{1*}$ bond is produced in $CF_2ClCFCl_2$ and CF_3CCL_3 and on annealing it dissociates with the extrusion of an ethylene molecule. (e) The cyclopropylamine radical cation readily ring opens to form $\cdot CH_2CH_2CH=NH_2^+$, which does not rearrange to the nitrogen-centered radical cation $CH_3CH_2CH=NH^{+\cdot}$; in contrast, the corresponding ring-opened neutral radical is $CH_3CH_2CH=N\cdot$ rather than $\cdot CH_2CH_2CH=NH$. Cyclobutylamine behaves similarly, the results again showing a remarkable reactivity difference between the radical cation and the neutral radical. In addition, the present studies report that the radical cation center of 1,1-dimethylallene radical cation is localized on the dimethyl-substituted side of the molecule. Ion-molecule reactions were studied in the $CF_2ClCFCl_2$ matrix for radical cations of spiro[2.5]octane, cyclopentene oxide, exo-epoxynorbornane, tetramethylethylene, and dimethyl sulfide. The results show the possible importance of hydrogen-abstraction

processes in some of the ion-molecule reactions.

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CHAPTER I

INTRODUCTION

A. Radical Cations

This dissertation reports some novel small-ring radical cations and related species. These cations were generated by employing the Freon technique described later, and examined by using electron spin resonance spectroscopy. The investigations reported here demonstrate a remarkable matrix influence on the structures and the chemistry of these radical cations.

Radical cations are recognized as important chemical entities in many areas today. Their physics and chemistry have been under rapid development over the past decade.^{1,2} The interested readers are referred to the literature quoted in references 1 and 2 for details.

By definition, radical cations are intermediates with both a positive charge and an unpaired electron in the same molecule. They can be generated by removing one electron from their parent molecules. The ease of this process is controlled by the energy of the highest occupied molecular orbital (HOMO) of the parent molecule. This energy can be calculated by quantum mechanical methods, or experimentally determined by measuring the gas-phase ionization potential (IP) or solution phase oxidation potential (E_1^0) of the molecule.

Radical cations can be produced experimentally by many techniques such as radiolysis, electrochemical oxidation of neutral molecules or reduction of dipositive cations, photoionization, and photoinduced electron transfer.¹ New methods have been under development in the past decade. One of the significant findings is the discovery of the Freon technique which makes possible systematic studies of many highly reactive organic radical cations (See Sections B and C).

Radical cations can be detected and characterized by many methods including quantitative electrochemistry, optical spectroscopy, and magnetic resonance. They are complementary to each other. In this

work, electron spin resonance (ESR) spectroscopy has been employed mainly since it can provide detailed structural information on the radical cations (see Section D).

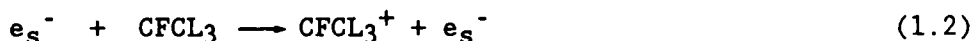
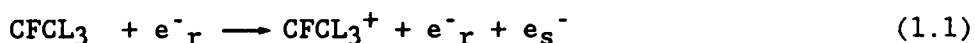
B. Freon Technique

It has been well established that very reactive, short-lived intermediates can be stabilized by preparing them in a rigid medium. This method of matrix isolation was first used by Lewis and Lipkin in 1942,³ and subsequently developed in many different directions by several researchers.⁴ In 1966 Hamill and Shida found that aromatic radical cations could be generated and stabilized by γ -irradiation of their solutions in certain chloroalkane matrices, as demonstrated by optical studies of these cations.⁵ Two years later, Grimison and Simpson similarly generated and studied radical cations of heteroaromatic compounds by using a Freon matrix.⁶ However, the combination of this technique with the use of ESR spectroscopy to characterize radical cations did not come until 1979 when Shida and Kato published their pyridine radical cation study in CFCl_3 .⁷ A variety of novel organic and inorganic radical cations have been produced and studied by this technique over the past decade.²

In the work described in this dissertation, the radical cations were all produced and studied by this technique. The substrate is first dissolved in a Freon solvent to make a 0.1 to 2.0 mole% solution. After the sample is degassed, it is frozen in liquid nitrogen temperature, and exposed to γ -irradiation for a suitable time. After the irradiation, the sample is transferred at low temperature to the ESR instrument for examination.

The mechanism of radical cation formation in this process has not been fully elucidated but the overall process is well understood. Since photons of the order of 1 MeV, such as γ -rays, interact with matter mostly by the Compton effect, many fast electrons (e^-) are produced in the Freon by Compton scattering.⁸ These energetic electrons ionize Freon molecules to form the corresponding Freon cations together

with the secondary electrons (e_s^-), some of which also possess enough energy to ionize or excite Freon molecules in their path. Such repeated ionizations take place along the track of the primary fast electron, and many Freon cations are thereby produced. These cations are mobile via positive charge transfer, and finally can reach and react with substrate molecules (S) to produce substrate radical cations (S^+) provided that the IP of the substrate is less than that of the Freon, which is true for most organic substrates.⁹ These processes are summarized in the following reactions:



Reaction (1.5), describing the electron-scavenging property of the Freon molecules,¹⁰ is also very important, since it prevents the otherwise free, and therefore highly mobile electrons from recombining with the substrate cations of interest. A dilute solution of the parent molecule and low temperatures are desired since many substrate radical cations are very reactive in ion-molecule reactions with their parent molecules. By using a low concentration of the substrate and low temperatures, radical cations can be isolated by the inert Freon molecules so that they have a relatively long lifetime suitable for carrying out ESR or other measurements.

In addition, this technique possesses these advantages for ESR studies: (a) The ESR signals from the matrix radicals, such as CFCL_3^- and CFCL_2 , do not interfere with those from the substrate radicals, since the spectra of the former are anisotropically broadened to a considerable extent at low temperatures; (b) Freons have relatively high softening points allowing the substrate radical cations to be studied over a fairly large temperature range; and (c) ESR spectra of organic radical cations in these matrices are often well resolved and possess little anisotropy, especially at higher temperatures due to the

possibility for the rotational or translational motion of the cations in these solid matrices.

However, like many other techniques, this technique also has its drawbacks. The most serious limitation is the solubility problem. If molecules of interest do not dissolve in Freons, they cannot be studied by this technique. Unfortunately this is the case for many polar molecules. Despite this and some other drawbacks, the Freon technique has been used very successfully to study a variety of radical cations in the 1980s as mentioned above.²

C. Variable-Matrix Studies

As a result of studies on many Freons and many substrate-Freon systems, it is becoming increasingly clear that Freons can be divided into two groups in terms of their suitability for studying specific reactions of radical cations. One group includes CFCl_3 (F-11), CF_3CCl_3 (F-113U) and $\text{CF}_2\text{ClCCl}_3$, all having the $-\text{CCl}_3$ group. By using these rigid Freons as matrices, only primary radical cations and products of their unimolecular reactions (for example, intramolecular rearrangement) have been reported at low concentrations. The other group includes $\text{CF}_2\text{ClCFCl}_2$ (F-113S), $\text{CF}_2\text{ClCF}_2\text{Cl}$ and $\text{CFCl}_2\text{CFCl}_2$. By using these Freons as matrices, primary radical cations can also often be detected at low temperatures, but on subsequent annealing, secondary reactions occur. These ion-molecule reactions can take place by diffusion of the ion, or diffusion of the molecule, which can be monitored by ESR if one or more products are paramagnetic. Ion-molecule reactions can also be studied in CFCl_3 or other first-group Freons by increasing the substrate concentration. However, the mechanism of the ion-molecule reactions is no longer diffusion-controlled since the reaction occurs in the aggregates during γ -irradiation. Therefore, the neutral radical products from the ion-molecule reactions are observed at very low temperatures. In this case, the conversion of the primary radical cations into the neutral radicals cannot be followed as clearly as it can using the second group of Freons.

SF_6 does not belong to the Freon series but it has also been used successfully to generate radical cations¹¹ with the advantage of its very high IP (15.69 eV).¹² SF_6 can be compared with the second group of Freons since it was found that below the phase-transition temperature (94.5 K) of this matrix, the primary radical cation is usually stable, but above 94.5 K, ion-molecule reactions can take place. In this high-temperature phase one can also usually detect the SF_6^+ and SF_5 radical species.¹¹ Although there seems to be no report about corresponding phase-transition temperatures for the Freon solvents, it may be inferred that there exists a phase transition temperature for each of the second-group Freons. Below that temperature, the radical cations can be stabilized in the matrices, but above that temperature, the matrix becomes elastic to allow the diffusion of ions or molecules. Since the ion-molecule reactions usually take place above 105 K in $\text{CF}_2\text{ClCFCl}_2$ (F-113U), above 135 K in $\text{CFCl}_2\text{CFCl}_2$, and above 85 K in $\text{CF}_2\text{ClCF}_2\text{Cl}$, these may be considered as the phase-transition temperatures for these matrices from the present studies. These temperatures are significant since radical cations can undergo many competing reactions which have different activation energy barriers. Therefore, the different phase transition temperatures of the Freons may be used to study the competing ion-molecule reactions.

By using two groups of Freons for a particular substrate, considerable information about the radical species derived from the substrate can be obtained, including information about the structure of the radical cation, its unimolecular reactions, and its ion-molecule reactions. This can give an overall picture of the radical cation under investigation. This overall picture is helpful in the structural assignment of the radical cation because the structure of the radical cation is often closely related with its subsequent reactions. Furthermore, the resolution of the ESR spectra of the radical cations are different from matrix to matrix. The poor resolution and the distorted intensity of the spectrum which are frequently encountered in solid-state ESR studies may lead to the wrong assignment of the radical cation under investigation. By using several matrices for the investigation, one can hope to avoid the possible errors resulting from

a study limited to one matrix.

In order to emphasize the importance of employing two groups of Freon matrices, it is called a variable-matrix study in this dissertation. The overall success of much of the work in this dissertation can be attributed to the use of this approach.

D. Basic Concepts of ESR Analysis

Electron spin resonance (ESR) is a branch of spectroscopy used to study paramagnetic species. The fundamentals of ESR theory are well established,¹³ and will not be repeated in detail in this dissertation. It should be pointed out that this dissertation is not concerned with ESR theory itself but only uses the principles of ESR spectroscopy to solve the radical cation problems. Moreover, the ESR principles are used mainly in an empirical way. That is, the assignments are made mainly by comparing the ESR data with those of well-established radical species in the literature. The spin-density calculations on radical species by theoretical methods such as AM1, INDO are complementary methods.

By definition, paramagnetic species possess an unpaired electron or electrons. A free electron or an unpaired electron in molecules behaves like a tiny magnet. Under the applied magnetic field, electrons orient themselves either parallel ($m_s = -1/2$) or antiparallel ($m_s = +1/2$) to the field (H). These two alignments have slightly different energy. According to the Boltzmann distribution law, the lower energy level ($m_s = -1/2$) has slightly more population than the higher level ($m_s = +1/2$). The transition from the $m_s = -1/2$ level to the $m_s = +1/2$ level can be induced by applying the energy in the form of radiofrequency electromagnetic radiation to the system. Such a transition is the basis of ESR spectroscopy.

The resonance equation for a free electron is well-known:

$$E = h\nu = g\beta H \quad (1.6)$$

where h , ν , and β are Planck's constant, microwave frequency, and the electron Bohr magneton, respectively, and g is a parameter governing the position of the resonance absorption. For a free electron, $g = 2.0023$.

In molecules, the unpaired electron also interacts with the magnetic nuclei present. Under the applied magnetic field, the total interaction of the electron in the molecule with one magnetic nucleus should be described by the Hamiltonian:

$$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} - g_n \beta_n \mathbf{I} \cdot \mathbf{H} + h \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} \quad (1.7)$$

where the symbols $\mathbf{S}$ and $\mathbf{I}$ are the electronic and nuclear spin vectors; g_n is the Lande factor for the nucleus, and β and β_n are the Bohr and nuclear magnetons, respectively. $\mathbf{A}$ will be discussed later.

The second term in this equation refers to the nuclear Zeeman effect. Since the energy of this interaction is much smaller than that of the electron Zeeman effect described by the first term, and cancels in obtaining the first-order ESR transition energy, it is usually neglected. However, it can be important in considering higher-order effects in ESR spectra.^{13e}

The g -value for an unpaired electron in molecules may deviate from the value of 2.0023 stemming from the spin-orbital coupling. In general, g is anisotropic since the spin angular momentum of the electron and the orbital angular momentum of the electron are vector quantities. Thereby g is expressed as a tensor in the first term of this equation. The first term can also be represented with matrices as:

$$[S_x S_y S_z] \begin{bmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{bmatrix} \begin{bmatrix} H_x \\ H_y \\ H_z \end{bmatrix} \quad (1.8)$$

The matrix elements of the g -tensor, taking g_{zx} for example, means the contribution to g along the z -axis when the field is applied

along the x-axis. The diagonal elements are called principal g-values which are characteristic quantities along the principal axes of a radical species.

Although $\mathbf{g} \cdot \mathbf{H}$ is a vector quantity, it can be related to the scalar quantity of the transition energy by:

$$(\Delta E)^2 = \beta^2 (\mathbf{H} \cdot \mathbf{g}) \cdot (\mathbf{H} \cdot \mathbf{g}) = \beta^2 \mathbf{H} \cdot \mathbf{g}^2 \cdot \mathbf{H} \quad (1.9)$$

Turning back to equation (1.7), the third term refers to the magnetic hyperfine coupling (abbreviated as hfc from now on) interaction. This interaction usually gives the most useful information for a paramagnetic species. The operator A is also tensorial in nature, the components of which can be decomposed into isotropic ($\underline{a}$) and anisotropic parts ($\underline{A}$). There always exists a coordinate system, in which the A-tensor is diagonal and can be written as:

$$\mathbf{A} = \begin{bmatrix} A_x & & \\ & A_y & \\ & & A_z \end{bmatrix} = \begin{bmatrix} A_x + a & & \\ & A_y + a & \\ & & A_z + a \end{bmatrix} \quad (1.10)$$

These isotropic (a) and anisotropic (A_x, A_y, A_z) hyperfine components are directly related to the electronic configuration of the paramagnetic species, which can be described by the well known equations:^{13f}

$$a = (8\pi/3)g\beta\beta_n g_n \langle \Psi(0) \rangle^2 \quad (1.11)$$

$$A_{ii} = g\beta g_n \beta_n \langle (3i^2 - r^2)/r^3 \rangle, \quad i = x, y, z \quad (1.12)$$

where the angular brackets of equation (1.12) denote an expectation value over the electron wavefunction:

$$\langle A \rangle = \iiint \Psi^*(x, y, z) A \Psi(x, y, z) dx dy dz \quad (1.13)$$

It is then clear in terms of these relations that the isotropic a originates from the Fermi contact interaction, where $\langle \Psi(0) \rangle^2$ is the probability of finding the unpaired electron in contact with the nucleus giving rise to the a . This term requires that the orbital containing the unpaired electron has some s character. On the other hand, the anisotropic couplings originate from the interaction between electron and nuclear dipoles. In the equation (1.12) r is the distance between the nucleus and an electron.

One case often seen in anisotropic spectra analysis, especially in this work, is where $A_{xx} = A_{yy} \neq A_{zz}$, or in other words, the radical species possesses axial symmetry. In this case the anisotropic term of the tensor becomes:

$$\begin{bmatrix} -B & 0 & 0 \\ 0 & -B & 0 \\ 0 & 0 & +2B \end{bmatrix} \quad (1.14)$$

where B is the abbreviation of the term $(2/5)g\beta g_n \beta_n \langle 1/r^3 \rangle$ and is called the anisotropic hyperfine coupling constant. The equation (1.14) can be derived from equation (1.12) for the case of a p orbital on a central atom. In addition, the following formalisms are generally used:

$$A_{\perp} = A_{xx} = A_{yy} \text{ and } A_{\parallel} = A_{zz} \quad (1.15)$$

and correspondingly:

$$g_{\perp} = g_{xx} = g_{yy} \text{ and } g_{\parallel} = g_{zz} \quad (1.16)$$

The relation between the isotropic and anisotropic hfcs is:

$$A_{iso} = 1/3 (A_{xx} + A_{yy} + A_{zz}) = 1/3 (A_{\parallel} + 2A_{\perp}) \quad (1.17)$$

$$B = 1/3 (A_{\parallel} - A_{\perp}) \quad (1.18)$$

while the relation between the isotropic g and the anisotropic g values is:

$$g_{iso} = 1/3 (g_{xx} + g_{yy} + g_{zz}) = 1/3 (g_{||} + 2g_{\perp}) \quad (1.19)$$

According to ESR theory, A_{iso} is directly proportional to the s -spin density on that magnetic nucleus. Similarly, the anisotropic B parameter is directly proportional to the p -spin density by the simple relations:

$$\rho_s = A_{iso}/A_0 \quad (1.20)$$

$$\rho_p = B/B_0 \quad (1.21)$$

where the values of A_0 and B_0 means the hyperfine coupling constants for unit spin in an s or p orbital, respectively. Some books^{13c} list these values.

In summary, the equations (20) and (21) allow the spin-density distribution to be obtained from experimental results, and therefore the nature of the SOMO (semi-occupied orbital) of that species can be deduced.

The ESR spectra encountered in this dissertation are mostly powder spectra of the radical species in the solid state. These spectra differ from those of the radicals in the liquid phase where the radicals can tumble freely so that the anisotropic interactions are averaged to zero to give isotropic spectra. In the powder spectra, the g and hyperfine tensors should usually be considered since the radical species do not freely tumble. The presence of hyperfine and g anisotropy can be readily recognized by the overall appearance of the ESR spectrum. If g anisotropy is present, the spectrum loses its center of symmetry because the hyperfine patterns center around their respective g values. For large differences in g_x , g_y , and g_z , three separate sets of lines can be observed as in the case of the radical cation of dimethyl sulfide in this dissertation. In other cases such as the thiirane and thietane radical cations, two sets of lines were observed because the molecule is rotating around the z -axis;

consequently the g_z becomes $g_{||}$ while g_x and g_y are averaged to $g_{\perp}$. In all these cases, there is no inversion about the spectral center (H_0). In other words, a highly symmetric spectrum having a center of inversion is indicative of little g anisotropy.

In the absence of g anisotropy, however, there is still the possibility of hyperfine anisotropy. For example, in the radical cation of azetidine, g anisotropy is small, but the hyperfine tensor of the nitrogen interaction was observed to be large and axially symmetric. In the azetidine radical cation, the spin is mainly in the p -orbital of nitrogen, so the two principal hfc values perpendicular to the orbital are identical, which is 9.5 G, while the principal hfc value parallel to the symmetry axis of the p -orbital is 38.2 G. In some other cases, a small amount of hyperfine anisotropy may be recognized by a progressive broadening of the resonance lines as the M_I value increases. This situation is frequently encountered in solid state ESR spectra. Since these spectra appear as the average of all possible orientations for a powder sample, the spread in hyperfine anisotropy can range from its maximum value ($A_{\max}$) to the minimum value ($A_{\min}$) containing all possible intermediate values. One example of this kind is represented by the $\cdot\text{CH}_2\text{R}$ radical, where the hyperfine anisotropy of the two α protons smears the two outer lines of the triplet more than the center line. However, in order for the center line of the triplet to be invariant of the changes in hyperfine coupling for a constant g factor, the principal axes of the two proton hyperfine tensors would have to coincide, which is not the case here.

Nevertheless, as mentioned in describing the Freon technique, the Freon matrices sometimes approximate to solid rotator types of matrices, and therefore many spectra obtained by using this technique possess little anisotropy, and can be treated as isotropic spectra. This is especially true at the higher temperatures with the Freon matrices. Most of the spectra in this work are treated as isotropic, emphasis being on the analysis of spectra at the highest temperature attainable in a given matrix so as to diminish the amount of possible residual anisotropy present.

CHAPTER II

EXPERIMENTAL

A. Sample Making and ESR Measurement

1. Sample Making

All ESR samples for this work were prepared in a concentration range of 0.5 - 1.0 mole %, and degassed thoroughly on a vacuum line. One or two liquid nitrogen traps were always used on the vacuum line to prevent any back diffusion of gases from the pump oil and to prevent any toxic material from entering the work area. The vacuum line was checked and cleaned regularly. The ESR tubes used in this work are all made of Spectrosil or Suprasil quartz. A graded-seal was used to fuse the quartz to Pyrex glass so that the ESR tube could be attached to ground glass joints and operated on the vacuum line. Before reuse the tubes were always annealed under vacuum until a reddish glow of the quartz was observed to remove any residual quartz signal. For the most of the substrates in this work which are transferable under vacuum, a small amount of the substrate (typically between 3-5 mm Hg) was collected in an ESR tube jointed to the vacuum line and degassed with three or two freeze-pump-thaw cycles. In a separated vessel jointed to the vacuum line, the Freon solvent was degassed in a similar way before mixing with the substrate. After the substrate and the Freon solvent were both degassed, about 300-450 mm Hg of the Freon solvent was transferred to the ESR tube containing the substrate. Then the ESR tube was freezed with liquid nitrogen and sealed by fusion of the Pyrex glass attachment. After the tube was allowed to come to room temperature, it was inverted several times to assure uniform mixing. For some of the substrates which are non-transferable under vacuum, the sample preparation steps were similar but the substrate was directly dropped into the ESR tube.

2. γ -Irradiation

After the sample was made, it was cooled in a liquid-nitrogen dewar, and the dewar put into a γ -source for irradiation. The source is an Atomic Energy of Canada Ltd. Gammacell 200 ^{60}Co source. It had a certified dose rate of 0.463 Mrad/h when it was reloaded on 14 September, 1971. The half life of ^{60}Co is 5.29 years. During the period of this work, the dose rate ranged from 0.096 Mrad/h to 0.065 Mrad/h. Hence for a typical irradiation time of 4.5 hours, the total dose received by the samples was about 0.3-0.45 Mrad.

3. ESR Measurement

The sample was immediately subjected to ESR measurements after γ -irradiation. The ESR instrument used in this work is a 1982 Bruker ER 200-D SRC spectrometer equipped with an rectangular cavity, a gaussmeter and a variable-temperature unit.

The sample was placed in the precooled ESR cavity, the microwave bridge tuned, and the measurements were carried out between 80 and 180 K depending on the softening points of the Freon solvents used. In a typical experiment, the spectra were recorded between the low and high temperature extremes. If spectral changes were observed, the temperature was cycled to document the reversibility of the changes so that a distinction between reactions and conformational changes could be made since only the latter was reversible. The ESR instrument can be operated at various power settings. Since different radical species possess different power saturation behavior, it was important to adjust the power to get the best signal-to-noise ratio for the spectra. An attenuation of 15-25 dB was found the best for studying organic compounds in this work. The low-temperature (< 77 K) technique was described by L.D. Snow.¹⁴

The cavity of the ESR instrument has removable front panels suitable for photolysis studies. For visible-light studies, a 1000 W tungsten lamp was used. For UV-light studies, a high pressure mercury arc lamp was used. Suitable filters were used to select the wavelength of the incident light, these filters being the Corning Glass Works Products. The light was focused into the cavity with an 8'' diameter

lens having a focal length of about 1 meter. The sample was rotated in all directions every few minutes during photobleaching experiment. This is because Freon solutions are not very transparent at low temperatures.

4. Computer Simulation

The Bruker instrument used an IBM EPRSRC.015 software package written for the Aspect 2000 Computer. All isotropic spectrum simulations were performed by using this cabability. The simulations for anisotropic spectrum used the programs from Dr. Paul H Kasai and a DEC-10 Computer.

5. Product Analysis

Product analysis was performed by gas chromatography and NMR. Gas chromatography is a Perkin-Elmer Model 800 instrument with a flame ionization detector. The column (Cat. No. 8408-PC from Alltech Associates Inc.) consists of a 6' x 0.125'' O. D. x 0.085'' I. D. stainless steel coil packed with 10% Carbowax 20 M on 80/100 Chromosorb W-HP. NMR instruments used are a Varian 60 MHz model and a 200 MHz NMC-1280 model from the Nicolet Magnetics Corporation.

6. Computer Calculation

Computer calculations were performed by using the AM1¹⁵ program. This was kindly supplied by Prof. Nelsen. This program package is a general-purpose semi-empirical molecular orbital package. The semi-empirical Hamiltonians MNDO, MINDO/3, and AM1 are implemented. The calculations were all carried out by using a VAX computer.

B. Chemicals and Suppliers

The chemicals used in this work are listed in Table I. The purity of these chemicals was verified by NMR or gas chromatography. All of them were used as received.

Besides these purchased chemicals, aziridine was made in this

TABLE I

CHEMICALS USED AND SUPPLIERS

Suppliers	Compounds
Aldrich Chemical Company, Inc.	trichlorofluoromethane 1,1,1-trichlorotrifluoroethane 1,1,2-trichlorotrifluoroethane 1,2,2,2-tetrachlorodifluoroethane tetramethylethylene dimethyl sulfide Thietane Thiirane Cyclopropylamine Cyclobutylamine Cyclopentene oxide exo-2,3-epoxynorbornane 2-Aminoethyl hydrogen sulfate
Wiley Organics	<u>cis</u> -2,3-epoxybutane <u>trans</u> -2,3-epoxybutane 1,1,2,2-tetramethylcyclopropane 1,1,2-trimethylcyclopropane cis-1,2-dimethylcyclopropane trans-1,2-dimethylcyclopropane spiro[2.5]octane tetramethylallene 2-Methyl-2-pentene <u>trans</u> -4-methyl-2-pentene <u>cis</u> -4-methyl-2-pentene
Fluka Chemical Corp.	Azetidine Thiirane
Cambridge Isotope Laboratories, Inc.	1,2- ¹³ C-ethylene oxide
Matheson Gas Product	Ethylene oxide Sulfur hexafluoride Allene Cyclopropane Ethylene trichlorofluoromethane

Table I (CONTINUED)

Supplier	Compounds
Merck, Sharpe & Dohme	Ethylene-1,2-d ₂ -oxide(mixture of cis and trans) Cyclopropane-d ₆
PCR/SCM Specialty Chemicals	trichlorofluoromethane 1,1,1-trichlorotrifluoroethane 1,1,2-trichlorotrifluoroethane
Sigma Chemical Company	Cyclopropylamine
Tokyo Chemical Industry Co.	2,4-dimethyl-2,3-pentadiene

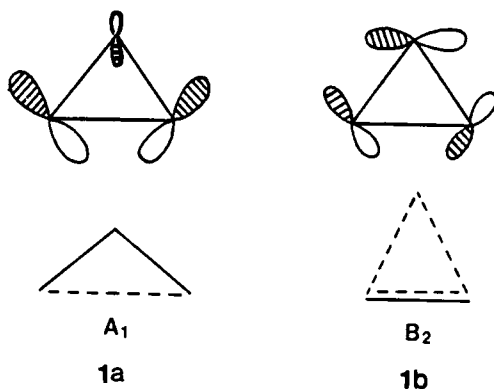
laboratory by the reaction of 2-aminoethyl hydrogen sulfate with sodium hydroxide^{16a}. The collected fraction boiling at 55-60° C showed a single peak at 1.6 ppm. The N-H proton signal was undetected by ¹H NMR.^{16b} Aziridine-N-d was made by stirring 0.2 g of aziridine with a 2-g solution of 10% KOD in D₂O.

CHAPTER III

CYCLOPROPANE RADICAL CATIONS

A. Introduction

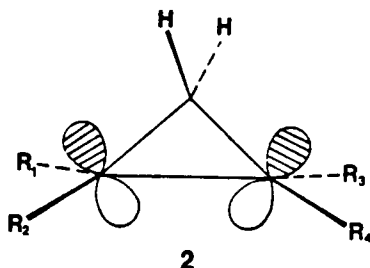
The structure of the cyclopropane radical cation may be evaluated by considering the nature of the highest occupied molecular orbitals (HOMOs) of cyclopropane, which can be described by the Walsh model.¹⁷ One of this degenerate pair, the symmetrical orbital 1a, is bonding between two carbon atoms and antibonding between one of them and the third carbon. Ejecting an electron from it results in a trimethylene radical cation with an elongated one-electron carbon-carbon bond ($^2A_1$). The antisymmetrical orbital 1b, on the other hand, is antibonding between two carbons and bonding between one of them and the third carbon. Accordingly, loss of an electron from it produces a radical cation which can be viewed as a π complex between ethylene and a methylene cation ($^2B_2$).



In other words, the HOMOs of cyclopropane are degenerate $3e'$ orbitals of the D_{3h} group, while its radical cation undergoes symmetry reduction from D_{3h} to C_{2v} expected from the Jahn-Teller active e' ring deformation vibration.¹⁸ However, it was found that the semi-occupied orbital (SOMO) of this cation depended on how it was generated. For instance, in the gas phase, the lowest transition in the photoelectron spectrum of cyclopropane was proposed to arise from the b_2 orbital.¹⁹ On the other hand, in the condensed phase, as shown by Iwasaki and

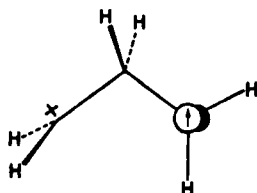
co-workers, the cyclopropane radical cation was distorted from an equilateral to an obtuse triangle with the unpaired electron in the a_1 orbital²⁰ at low temperatures.

In agreement with Iwasaki's work, it is found in this Chapter that the ring-closed radical cations of cyclopropane and its methyl-substituted derivatives radiolytically generated in Freons all possess $^2A_1$ structures with a one electron C-C bond. The new finding for cyclopropane derivatives is that the one-electron bond is located at the most substituted side as illustrated by 2 except in the spiro[2.5]octane case which will be reported in Chapter IX. That the unpaired electron is located at the most substituted side of the cyclopropane derivative radical cations was first proposed by Roth and Schilling in their CIDNP studies of phenyl-substituted cyclopropane radical cations.²¹



Another important finding of this work is the ring-opening of the cyclopropane radical cations. It was found that the ring opening only occurred in certain matrices such as F-113U, CF_2ClCF_2Cl , and $CFCl_2CFCl_2$; but not in F-11 and F-113S even to the softening points of those matrices. The structure of the ring-opened form of the cyclopropane radical cation can be described by 3, a distonic ion,²² in which the unpaired electron is localized on one of the terminal CH_2 groups in a bisected conformation at the radical center, while the other terminal CH_2 is a carbocation center. Note that the radical and cation sites are orthogonal to each other, thereby preventing unpaired-electron delocalization. This structure was proposed originally in this lab²³, and can be achieved by the monorotation of one CH_2 group of the ring-closed radical cation 2. The formation of the ring-opened cation was attributed to special matrix effects since it is

matrix-dependent.



3

However, this proposal was disputed by Symons,²⁴ and by theoretical calculations.²⁵ According to Symons, a carbocation center in 3 is a powerful electrophile, a relatively strong bonding of this center to one chlorine of the matrix should certainly occur. On the other hand, ab initio MO calculations showed that 3, or the (90,0) orthogonal species, did not correspond to a minimum on the potential surface, and therefore it cannot exist as a stable intermediate. The alternative structures proposed were those resulting from nucleophilic attack by chloride ion or by the matrix molecule at the carbocation center.

In this Chapter, the results of the ring-opening studies of the radical cations of cyclopropane and its derivatives are presented in detail. The possible mechanisms for the ring-opening processes are further discussed based on these results.

B. Results

1. Cyclopropane Radical Cation

Figure 1 shows the cyclopropane radical cation in F-113U, which is a broad single line (a total width of about 100 G) with poorly defined substructures. This spectrum is essentially the same as that described by Iwasaki and co-workers for the ring-closed cyclopropane radical cation.²⁰ Hence the spectrum is also assigned to the ring-closed cyclopropane radical cation.

On annealing to 84 K for 5 minutes, the spectrum Figure 1 was converted irreversibly to a new spectrum. The new spectrum was not well resolved at 84 K but became resolved above 108 K as shown in Figure 2a.

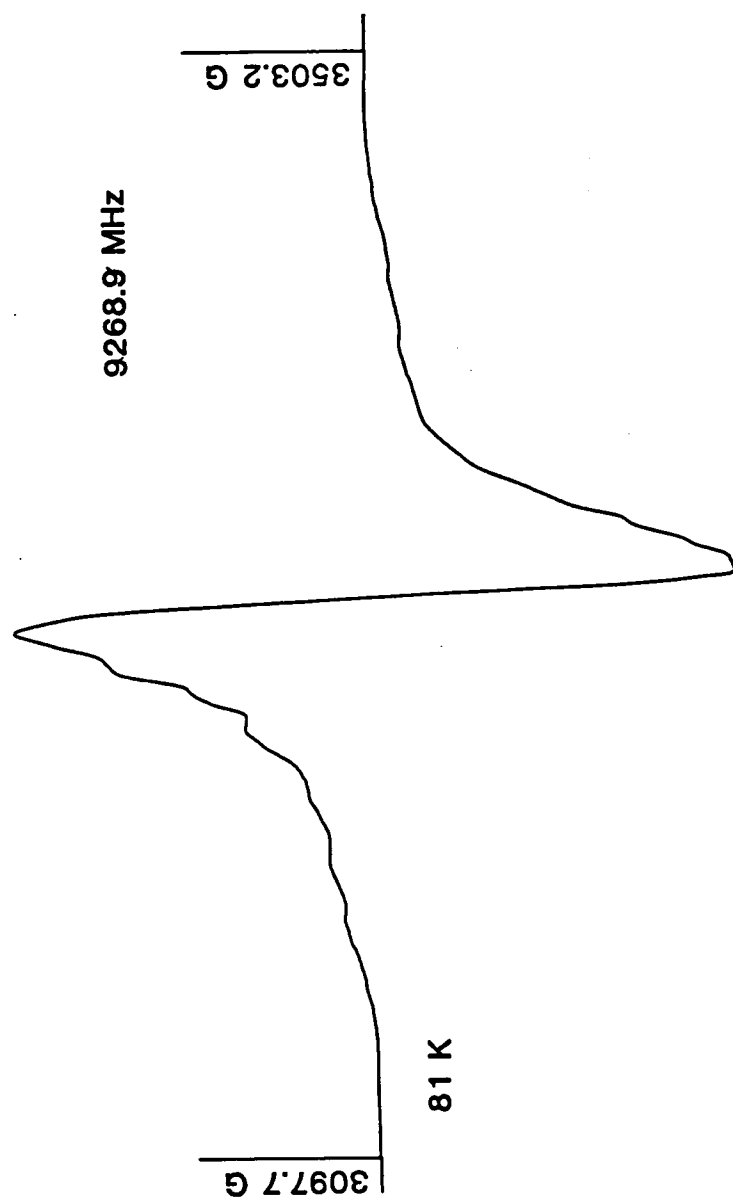


Figure 1. First-derivative ESR spectrum of the ring-closed radical cation of cyclopropane in F-113U.

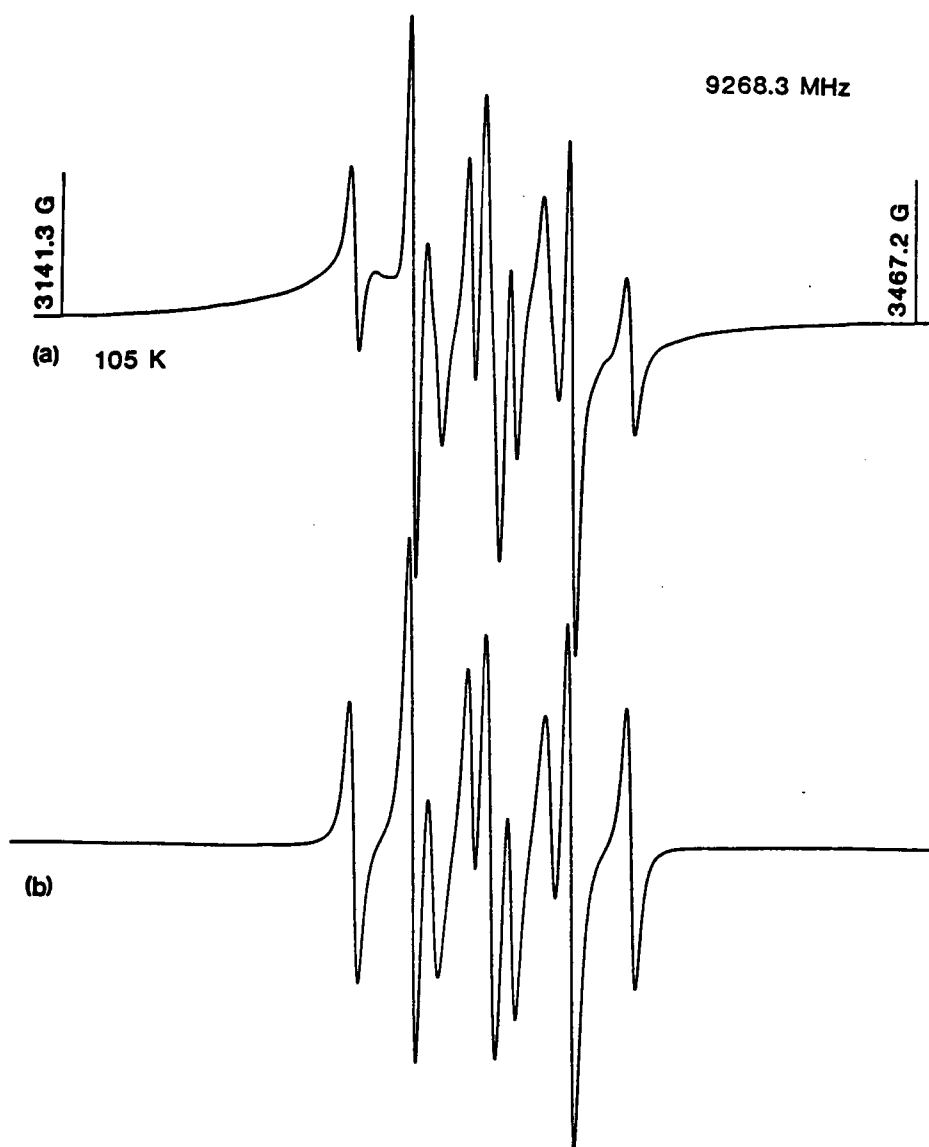
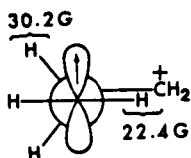


Figure 2. First-derivative ESR spectra of the ring-opened radical cation of cyclopropane in F-113U: (a) experimental, and (b) simulation by using $a(2H) = 22.4$ G, $a(1H) = 60.4$ G with 100% intensity and a Lorentzian linewidth of 3.2 G plus $a(2H) = 22.4$ G with 90 % intensity and a Lorentzian linewidth of 4.5 G. This has the effect to broaden lines 3, 5, and 7 for which $M_I(2H_\beta) = 0$.

This spectrum is easily analyzed as a triplet (30.2 G) of triplets (22.4 G). The 22.4 G triplet is ascribed to two α -protons, while the 30.2 G triplet is ascribable to two β -protons provided that the conformation at the radical center is bisected as shown in below.



3

According to the McConnell and Heller $B\cos^2\theta$ rule for the β -proton hfcs,²⁶ the B value is calculated to be 40.3 G, from the β -coupling of 30.2 G and the dihedral angle of 30° for the bisected conformation.

The B-value as well as the hfcs of this new radical is in accord with those reported for the n-propyl and other $\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$ radicals, which are also known to possess the bisected conformation at their radical centers.²⁷ Clearly, 3 can only be formed by the ring-opening of the cyclopropane ring.

The ESR spectrum of the cyclopropane- d_6 radical cation in the same matrix was also studied. This is also a single-line spectrum, but with a total width narrower by about a factor of 3.25 than that for the cyclopropane radical cation, as expected by the ratio of H over D magnetic moment. Above 92 K, this single line-spectrum changed irreversibly to a new spectrum, which can be satisfactorily simulated by $A(2D_\beta) = 4.64$ G and $A(2D_\alpha) = 3.44$ G which can be calculated by dividing the corresponding hfcs derived from the ring-opened form of the cyclopropane radical cation by 6.514. These facts prove the ring-opening proposal firmly.

As indicated in the introduction of this Chapter, the ring-opened radical cation can be formed by the monorotation of one CH_2 group through 90° in the ring-closed cation, the unpaired electron occupying the $2p_z$ orbital in the rotated CH_2 group while the unrotated CH_2 becomes a carbocation center, as described by 3. However, the orthogonality of the structure 3 will not be strictly obeyed if the

ring-opening arises from a strong solvent or other interaction with the carbocation center. On further warming to 115 K, the ring-opened cyclopropane radical cation decayed, while a large doublet (61 G) due to the matrix radical $\cdot\text{CF}_2\text{CLCF}_2\text{CL}$ grew in, which decayed at 130 K. No further change of the ring-opened cation was observed on annealing.

On the other hand, if the sample was illuminated with U.V. light at 100 K for about half an hour before annealing, a new radical species rather than the matrix radical grew in when the ring-opened form disappeared. The ESR spectrum of this third radical is shown in Figure 3a. This spectrum was recorded at 125 K since it was better resolved. Interestingly it resembles that of the propene radical cation in the F-11 matrix,²⁸ except for the much stronger background signals in the present spectrum. Consequently, the simulation shown in Figure 3b using the known parameters for the propene cation in F-11²⁸ fits the third radical spectrum very well. A control experiment, namely, the illumination of cyclopropane in F-113U at 100 K for half an hour by U.V. light did not give the propene cation. Therefore, the propene radical cation must have been produced from the rearrangement of the ring-opened form of the cyclopropane radical cation. Unfortunately, the propene cation cannot be directly produced from propene and warmed up to above 100 K in F-113U to make a direct comparison. This is because the cation undergoes an ion-molecule reaction to form allyl radical in γ -irradiated propene-F-113U system.

The ring-opening of the cyclopropane radical cation was also observed in the $\text{CF}_2\text{CLCF}_2\text{CL}$ and $\text{CF}_2\text{CL}_2\text{CF}_2\text{CL}_2$ matrices. The temperature required for the ring-opening were 80 K and 120 K in these two matrices, respectively. The observed ring-closed and ring-opened forms of the cyclopropane radical cations were the same as those observed in F-113U. The ESR parameters for the ring-closed and ring-opened forms of cyclopropane radical cations in these matrices are collected in Table II and III, respectively.

2. Tetramethylcyclopropane Radical Cation

The 1,1,2,2-tetramethylcyclopropane radical cation (TMCP^+) was studied in several matrices. In F-11 and F-113S, only the ring-closed

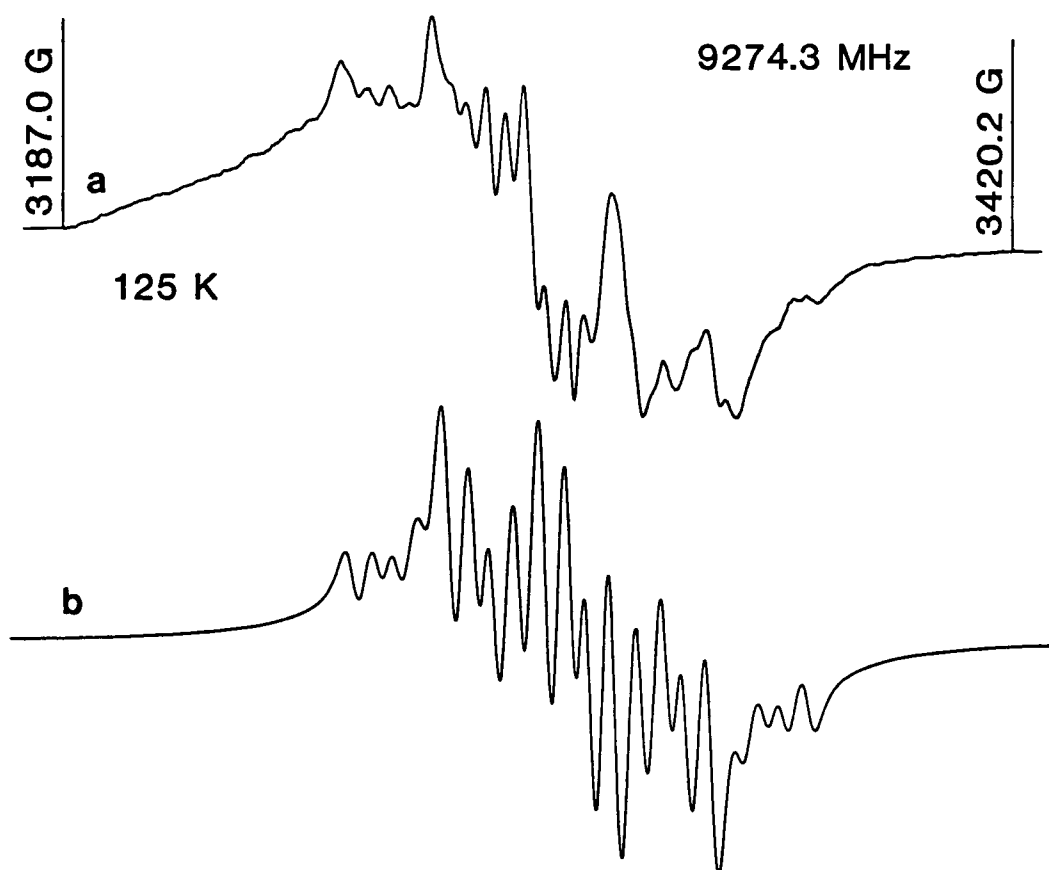


Figure 3. First-derivative ESR spectra of propene radical cation produced from the ring-opened cyclopropane radical cation in F-113U by U.V. illumination at 100 K: (a) experimental, and (b) simulation by using ESR parameters: $a(\text{CH}) = 6.0$ G, $a(\text{CH}_2) = 23.5$ G, and $a(\text{Me}) = 23.5$ G, and a Lorentzian linewidth of 2.5 G (see text).

TABLE II

ESR PARAMETERS FOR THE RING-CLOSED FORMS OF THE RADICAL
CATIONS OF CYCLOPROPANE AND ITS DERIVATIVES

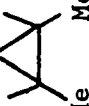
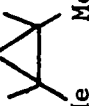
Radical Cations	Matrix	T/K	Hyperfine Couplings/G	g
$\underline{\text{C}}\text{-C}_3\text{H}_6^{+\cdot}$	F-113U	80	unresolved	2.0042
Me  $\text{Me}^{+\cdot}$	F-11	150	10.4 (2H_α), 20.5 (2H_β), 20.5 (2Me)	2.0041
Me  $\text{Me}^{+\cdot}$	F-11	150	11.9 (2H_α), 21.8 (2H_β), 21.8 (2Me)	2.0040
Me  $\text{Me}^{+\cdot}$	F-11	150	9.8 (1H_α), 17.9 (2H_β), 14.5 (Me), 20.6 (2Me)	2.0040
Me  $\text{Me}^{+\cdot}$	F-11	145	15.0 (4Me), 18.7 (2H_β)	2.0033
Me  $\text{Me}^{+\cdot}$	F-113U	90	15.0 (4Me), 18.7 (2H_β)	2.0033
Me  $\text{Me}^{+\cdot}$	F-113S	130	15.0 (4Me), 18.7 (2H_β)	2.0033

TABLE III

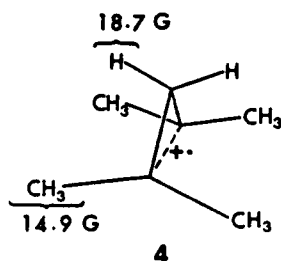
ESR PARAMETERS FOR THE RING-OPENED FORMS OF THE RADICAL
CATIONS OF CYCLOPROPANE AND ITS DERIVATIVES

Radical Cations	Matrix	T/K	Hyperfine Couplings/G	g
+CH ₂ CH ₂ $\dot{\text{C}}\text{H}_2$	F-113U	109	22.4 (2H _α), 30.2 (2H _β)	2.0028
	CF ₂ CLCF ₂ CL	80	22.4 (2H _α), 30.2 (2H _β)	2.0028
	CFCL ₂ CF ₂ CL	120	22.4 (2H _α), 30.2 (2H _β)	2.0028
⁺ MeCHCH ₂ $\dot{\text{C}}\text{HMe}^a$	F-113U	115	24.7 (1H _α), 32.4 (1H _β)	2.0028
			24.7 (Me)	
			or 24.7 (1H _α), 16.2 (2H _β) 24.7 (Me)	
⁺ MeCHCH ₂ $\dot{\text{C}}(\text{Me})_2$	F-113U	115	11.8 (2H _α), 23.6 (2Me)	2.0029
(Me) ₂ $\dot{\text{C}}\text{CH}_2\dot{\text{C}}(\text{Me})_2$	F-113U	117	11.7 (2H _α), 23.3 (2Me)	2.0029

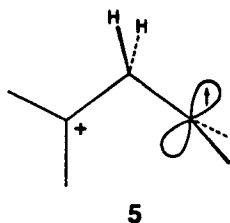
^aformed from both cis- and trans-1,2-dimethylcyclopropane.

form of TMCP^+ was observed. In F-113U and $\text{CFCL}_2\text{CFCL}_2$, both the ring-closed and ring-opened forms of TMCP^+ were observed.

Shown in Figure 4a is the ESR spectrum of the TMCP radical cation in F-113U at low temperature. It consists of 15 almost evenly spaced lines with a distorted triplet fine structure on 11 of them. The correct model for the spectrum is the ring-closed TMCP radical cation 4, which will produce a pattern with a 13-line binomial set of lines from the interaction of four methyl groups further split into slightly larger triplets from the interaction of the two methylene protons. The excellent fit of the simulation shown in Figure 4b by using $a(2\text{H}) = 18.7 \text{ G}$ and $a(12\text{H}) = 14.9 \text{ G}$ confirms this analysis. The ESR spectra observed in F-11 and F-113S are essentially the same as that of Figure 4a (Table II). They all can be assigned to the ring-closed TCMP radical cation with an elongated C..C bond depicted by 4.



On annealing to 110 K in F-113U, the ring-closed TCMP^+ decayed, while a new radical species grew in irreversibly. The ESR spectrum of this new species is shown in Figure 5a. The spectrum consists of 15 evenly spaced lines but the intensity ratios do not correspond to a binomial distribution of 14 protons. By analog with the ring-opening of the cyclopropane radical cation, this new spectrum is attributed to the ring-opened TCMP cation 5, since the localized form 5 should couple with six protons (two methyl groups) and two methylene protons to give a septet of triplets pattern. This pattern should consist of 15 non-binomial lines if the triplet hfc is just twice that of the septet.



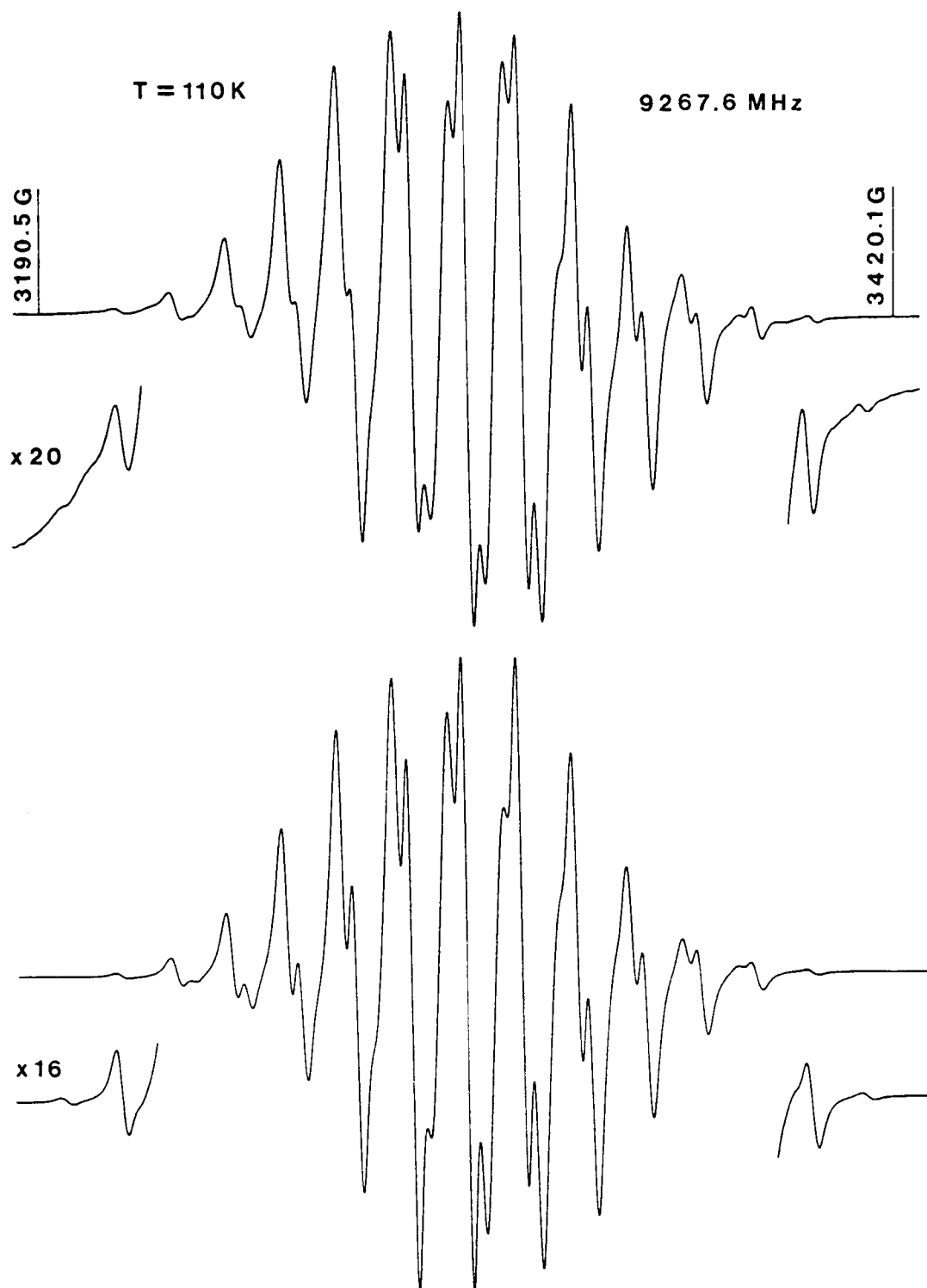


Figure 4. First-derivative ESR spectra of the ring-closed radical cation of tetramethylcyclopropane in F-113U: (a) experimental, and (b) simulation by using ESR parameters in TABLE II and a Lorentzian linewidth of 3.5 G.

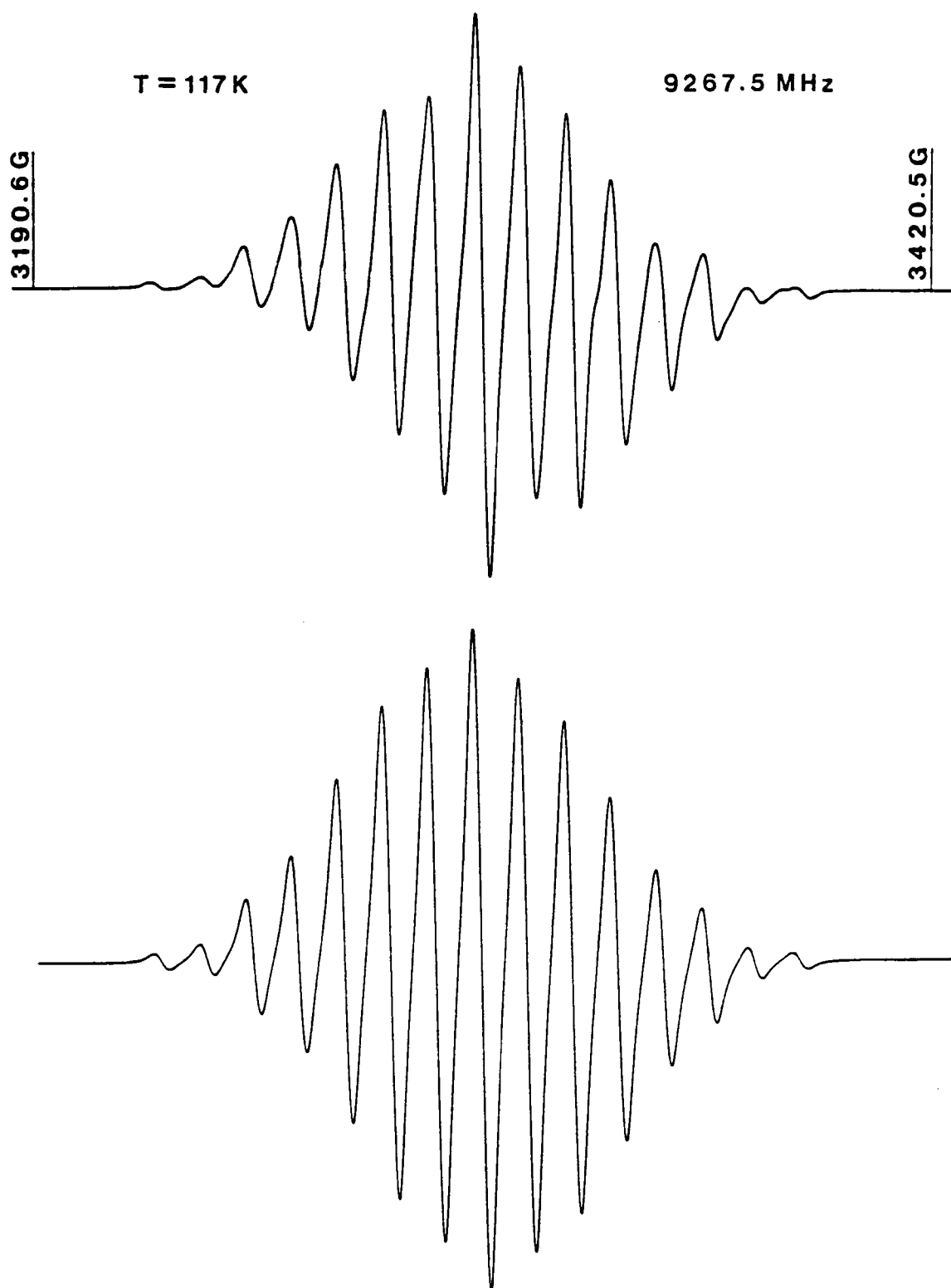
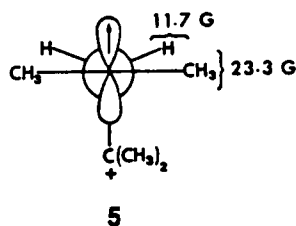


Figure 5. First-derivative ESR spectra of the ring-opened radical cation of tetramethylcyclopropane in F-113U: (a) experimental, and (b) simulation by using ESR parameters in TABLE III and a Lorentzian linewidth of 3.5 G.

The simulation shown in Figure 5b based on $a(2H) = 23.3$ G and $a(6H) = 11.7$ G fits the experimental spectrum very well, verifying this analysis.

The parameters of the second species are virtually the same as those of the $CCL_3CH_2\dot{C}Me_2$ radical ($a(6H) = 23.52$ G and $a(2H) = 11.61$ G)^{27b}, which possesses the eclipsed conformation at the radical center. The similarity of ESR parameters in both cases may be ascribed to the similar electronegativities of the $-CCL_3$ group and the $+C(Me)_2$ group. Therefore, the conformation of the ring-opened TMCP cation at the radical center is now eclipsed as shown below, instead of bisected as in the cyclopropane case.



Using the B-value of 40.3 G derived from the ring-opened cyclopropane radical cation and the dihedral angle of 60° for the eclipsed conformation, the calculated two methylene proton hfc is 10.1 G, in reasonable agreement with the observed hfc. It follows that the ring opening of the TMCP occurred by the monorotation of $-CMe_2$ group such that the unpaired electron is in the unrotated $-CMe_2$ group, and the carbocation is located at the rotated group. It should keep in mind, however, that the orthogonality of the structure 5 should not be obeyed because of the strong solvent interaction at the carbocation center.

The other possible species which might correspond to the spectrum is $CH_2=C(Me)CH_2\dot{C}Me_2$. This could be formed via ring-opening followed by proton loss from the methyl group at the carbocation center in 5. However, this can be ruled out by its different ESR parameters (vide infra). The possible species 2,4-dimethyl-2-pentene radical cation which could be formed from 5 by a 1,2-hydride shift can also be ruled out because the hfc's of the CMe_2 group in the similar radical cations such as trimethylethylene, tetramethylethylene, and isobutene

are never higher than 17.2 G.^{28,29} 5 underwent a further change either by thermal annealing or by U.V. irradiation. Figure 6a shows the ESR spectrum of the third radical species generated by U.V. irradiation of 5 for half an hour at 100 K, and then warmed up to 130 K. The same spectrum was obtained on annealing 5 to 135 K. But the signal intensity of the third radical was less in the latter case. This new spectrum can be simulated based on a model of the tetramethylallyl radical which can be formed by proton loss from the methylene protons of the ring-opened radical cation. Although the ESR parameters are not known for this radical, the best simulation for the spectrum of Figure 6a shown in Figure 6b gives $a(2\text{Me}) = 14.5 \text{ G}$, $a(2\text{Me}) = 10.1 \text{ G}$ and $a(1\text{H}) = 3.0 \text{ G}$, all of which are certainly reasonable for allyl radicals. The 14.5 G and 10.1 G couplings can be assigned to exo and endo methyl protons, respectively, the difference of 4.4 G being just as expected for the exo and endo methyl couplings.³⁰ The hfc of 3.0 G is reasonably assigned to the central proton. The other support for the tetramethylallyl radical assignment is the g-value of 2.0026, which is in the correct region for allyl radicals.³⁰ The other route to form tetramethylallyl radical from 5 might be by hydrogen abstraction from the methylene position of the neutral TMCP molecule by the TMCP cation followed by the breakage of the $(\text{Me})_2\text{C}-\text{C}(\text{Me})_2$ bond of the neutral molecule. However this seems less possible because the transformation could also be induced by U.V. light at much lower temperatures.

The other chemically possible species for the third radical is $(\text{CH}_3)_2\text{CH}-\text{CH}=\dot{\text{C}}(\text{CH}_3)_2$ produced by a 1,2-hydride shift from 5. The expected ESR pattern for it should be a doublet (1H) of doublets (1H) of quartets (Me) of quartets (Me). However, no reasonable ESR parameters for this species could be found to simulate the experimental spectrum.

The TMCP radical cations were also studied in the $\text{CFCl}_2\text{CFCl}_2$ matrix. The ring-closed form of the TMCP cation was stable between 80 K and 135 K. Above 135 K, ring-opening occurred. The ESR spectra of the ring-opened form observed in this matrix are the same as those observed in F-113U (Table III). On further warming to 150 K, the ring-opened form 5 in $\text{CFCl}_2\text{CFCl}_2$ changed to a new species irreversibly. However, it

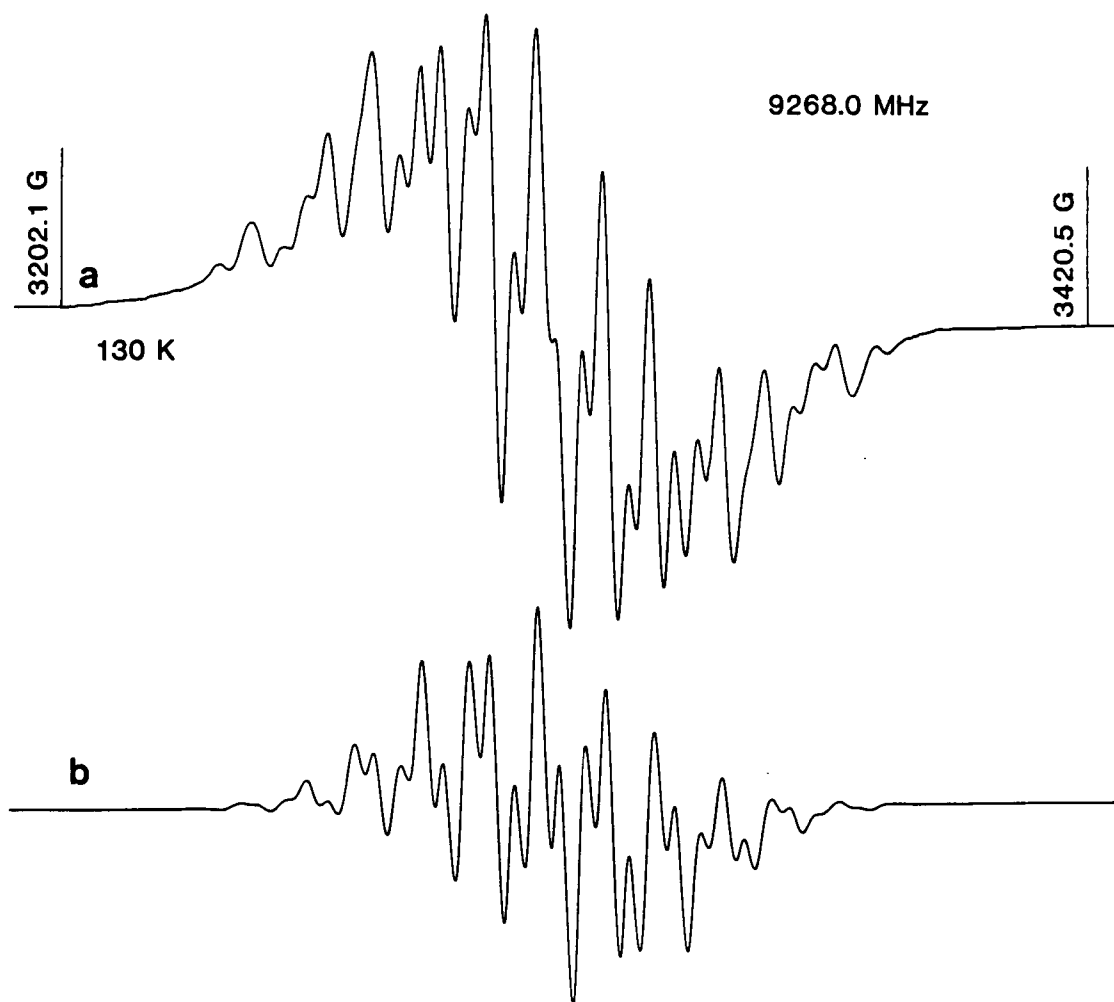
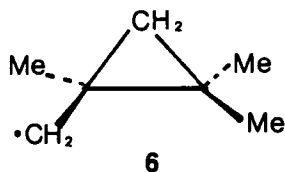


Figure 6. First-derivative ESR spectra of tetramethylallyl radical produced from the ring-opened radical cation of tetramethylcyclopropane in F-113U: (a) experimental, and (b) simulation by using ESR parameters: $a(2\text{Me}) = 14.5$ G, $a(2\text{Me}) = 10.1$ G, $a(1\text{H}) = 3.0$ G (see text) and a Lorentzian linewidth of 3.0 G.

was not the tetramethylallyl radical in this case. As shown in Figure 7a, the ESR spectrum of the third radical in this case is a septet of large doublets of small doublets. The ESR parameters obtained are: $a(2\text{Me}) = 24.1 \text{ G}$, $a(1\text{H}) = 14.8 \text{ G}$, $a(1\text{H}) = 7.4 \text{ G}$, and $g = 2.0034$. These parameters agree with those for the radical $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$.^{27c} In fact, the hfcs for the two methyl groups in this new species are close to those of 5, and the hfcs for the two nonequivalent β -protons of this radical only requires that the H C C H dihedral angle of 5 be rotated a few degrees after the $\text{C}(\text{Me})_2$ group of 5 is replaced by the $\text{CH}_2=\text{C}(\text{Me})$ group of this secondary radical. This neutral radical $\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\dot{\text{C}}(\text{Me})_2$ decayed gradually above 165 K in this matrix. The fact that two different neutral radicals were produced from the ring-opened TMCP radical cation may also be accounted for by a mechanism which does not involve proton transfer in the latter case. Thus the radical $\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\dot{\text{C}}(\text{Me})_2$ may be produced not only by proton loss from 5 but by hydrogen atom abstraction from a TMCP molecule by 5 followed by the ring-opening of the radical 6.



It appears possible that in some cases like this, the different phase-transition temperatures of the matrices can cause radical cations to undergo different reactions.

3. Trimethylcyclopropane Radical Cation

Like tetramethylcyclopropane, both ring-closed and ring-opened forms of the trimethylcyclopropane radical cation were observed in F-113U, while only the ring-closed form was observed in the F-11 and F-113S matrices.

Due to its unsymmetrical structure, the ring-closed form of the trimethylcyclopropane radical cation gives ESR spectra which are more complex than those of TMCP cations. The best spectrum of the ring-closed form was found in F-11, which is shown in Figure 8a. The

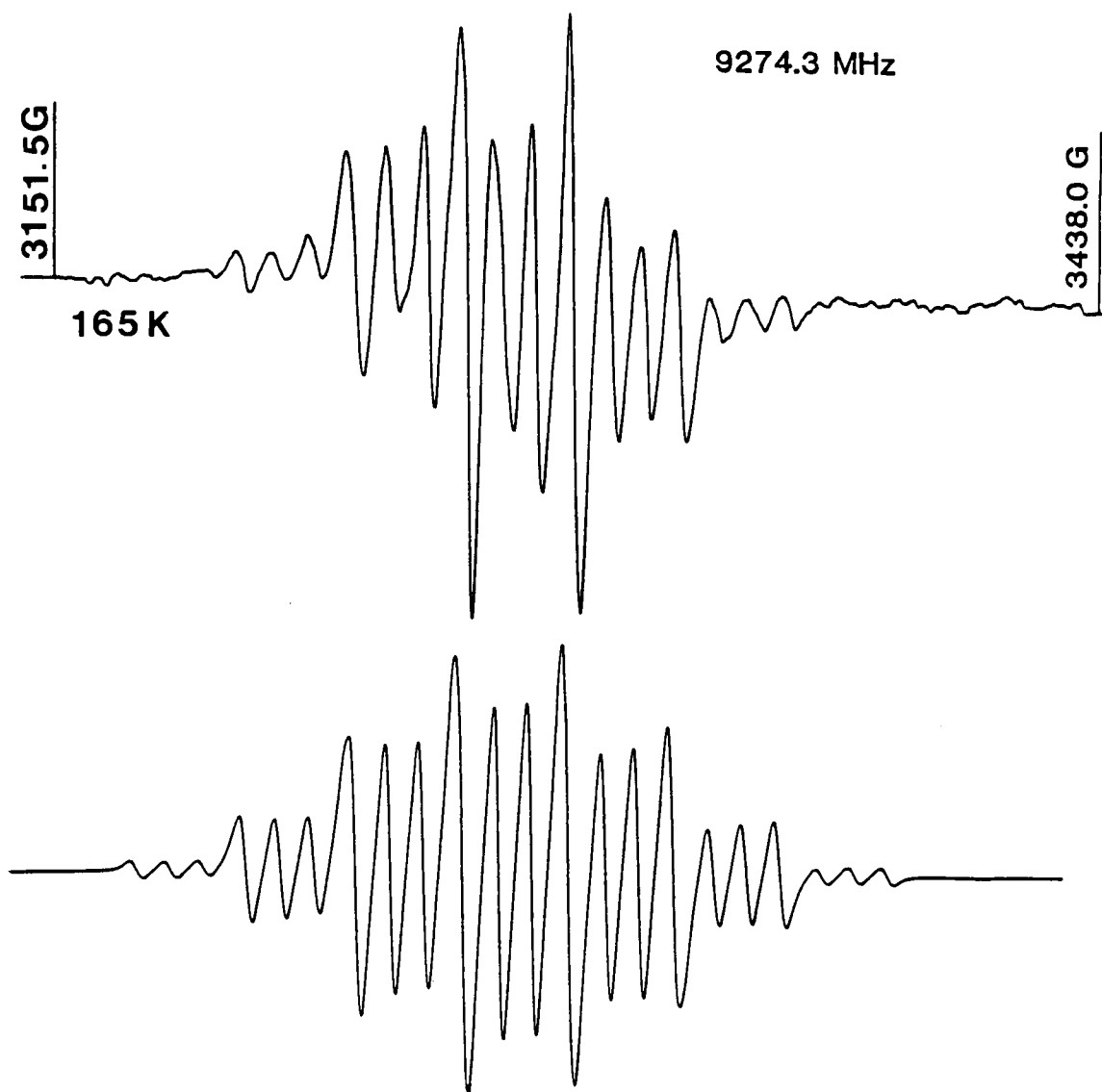


Figure 7. First-derivative ESR spectra of $\text{CH}_2\text{-C}(\text{Me})\text{CH}_2\dot{\text{C}}(\text{Me})_2$ in $\text{CFCL}_2\text{CFCL}_2$: (a) experimental, and (b) simulation by using $a(2\text{Me}) = 24.1$ G, $a(1\text{H}) = 14.8$ G, $a(1\text{H}) = 7.4$ G (see text) and a Lorentzian linewidth of 3.0 G.

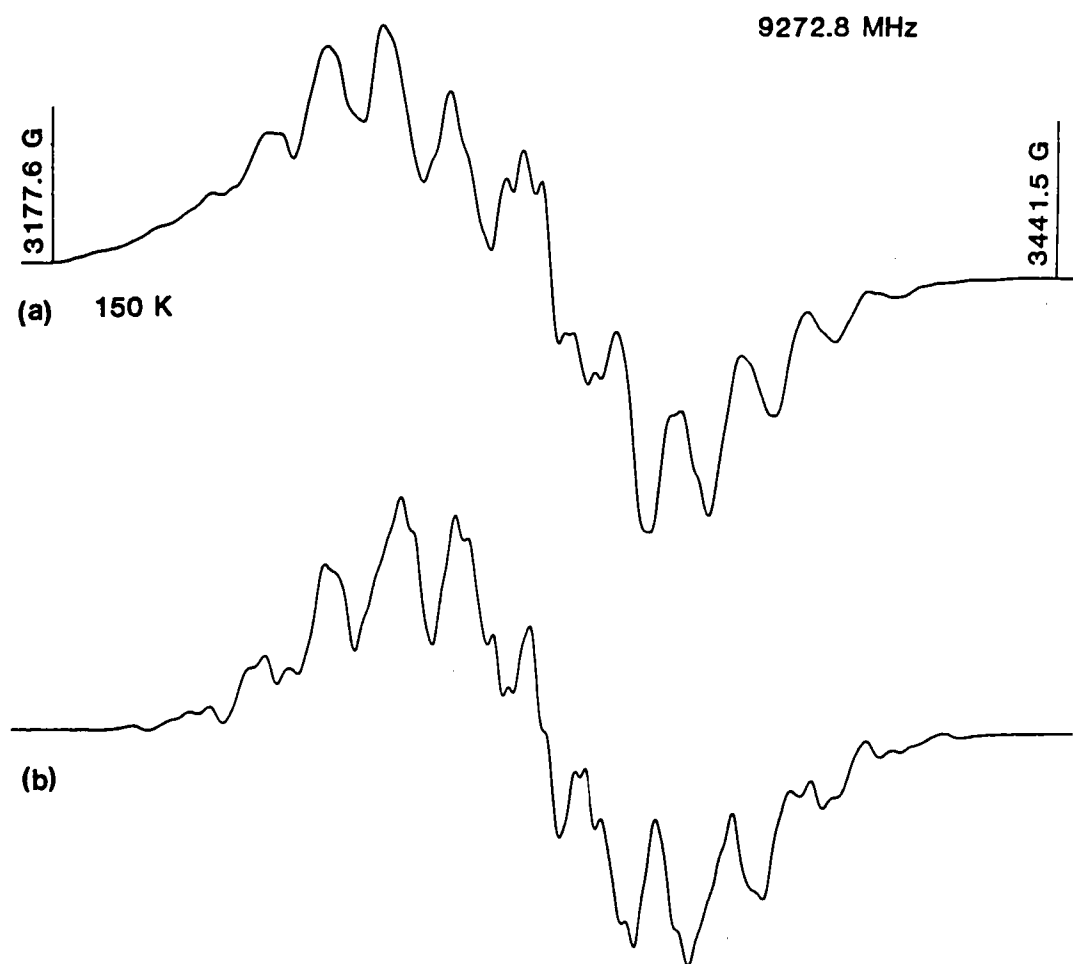
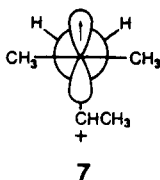


Figure 8. First-derivative ESR spectra of the ring-closed radical cation of trimethylcyclopropane in F-11: (a) experimental, and (b) simulation by using ESR parameters in TABLE II (p 26) and a Lorentzian linewidth of 3.5 G. A broad background signal was added to spectrum (b).

ESR parameters of this spectrum are collected in Table II (p 26). By using these parameters, the simulation shown in Figure 8b fits the experimental spectrum very well. Clearly, these parameters are in the same region as those of other methylcyclopropane radical cations (Table II (p 26)). However, it is noteworthy that the couplings of the gem-dimethyl protons (20.6 G) are larger than those for the other methyl group (14.5 G) in this species indicating that the spin is not evenly distributed in the unsymmetrical structure.

The ring-closed form of the trimethylcyclopropane radical cation in F-113U was only observed at low temperatures, and its ESR spectrum is not well resolved. A better-resolved spectrum cannot be obtained since, on annealing to 100 K, the ring-closed form of this radical cation underwent an irreversible ring-opening process. A typical ESR spectrum of the ring-opened form of this cation is given in Figure 9a. Noticeably, this spectrum in Figure 9a is almost comparable to that in Figure 6a showing the spectrum for the ring-opened form of the TMCP cation, except for the alternating linewidth effect indicated by the stick diagram in the former spectrum. Indeed, the ESR parameters derived from the simulation shown in Figure 9b are found to be the same as those of the ring-opened form of the TMCP cation (Table II (p 26)). Therefore, the radical center of the ring-opened form of the trimethylcyclopropane cation must be of the type $\cdot\text{C}(\text{Me})_2\text{CH}_2\text{R}$ generated by ring cleavage at the most substituted carbon-carbon bond. This is expected since the spin density in the ring-closed form was mostly located at the most substituted bond, especially at the carbon of the gem-dimethyl group, as noted earlier. Hence, on ring-opening, the spin remains on the $\text{C}(\text{Me})_2$ group leaving the other side to become a carbocation center by rotation. The alternating linewidth effect can be readily attributed to the out-of-phase modulation of the methylene proton couplings in this structure.



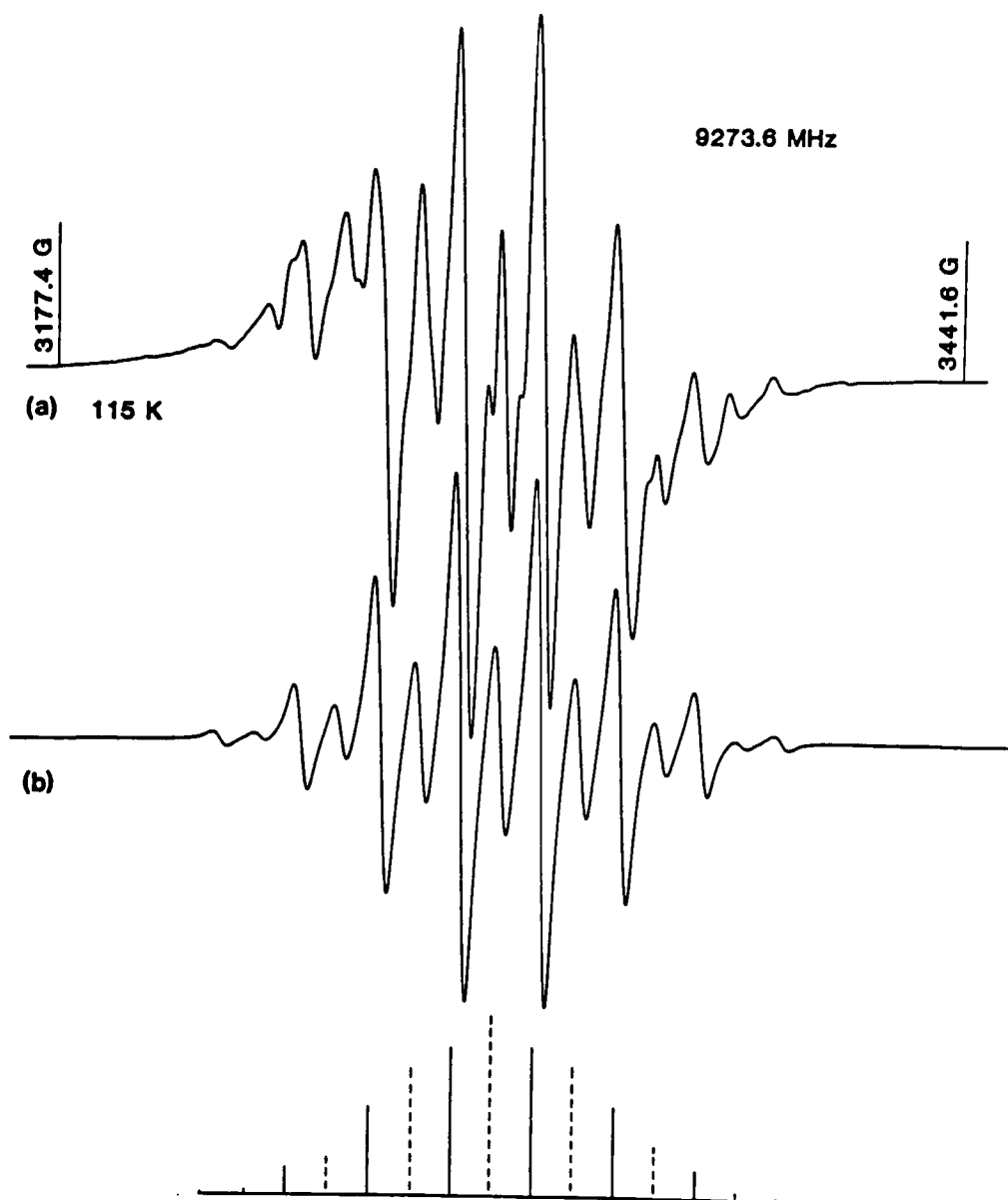


Figure 9. First-derivative ESR spectra of the ring-opened radical cation of trimethylcyclopropane in F-113U: (a) experimental, and (b) simulation by combining equal weights of an $a(6H) = 23.6$ G, $a(2H) = 11.8$ G pattern with an $a(6H) = 23.6$ G, $a(1H) = 23.6$ G pattern using a Lorentzian linewidth of 3.5 G. This reduces the intensity of the center lines in the triplets resulting from the interaction of two equivalent methylene protons in accordance with an out-of-phase modulation (see text).

On warming the sample to 135 K, the ring-opened form of the trimethylcyclopropane cation changed irreversibly to a third radical species, which can also be produced by U.V. irradiation of the ring-opened form **7** at much lower temperature (90 K). The ESR spectrum of the third radical is given in Figure 10a. This spectrum consists of a large doublet of quartets with some additional, although not well resolved, fine structures on each of the line components. In terms of this analysis, the simulation using $a(1H) = 48.6$ G, $a(3H) = 22.6$ G, $a(1H) = 9.6$ G, $a(1H) = 4.4$ G, and $g = 2.0029$ shown in Figure 10b best matches the experimental spectrum. Accordingly, the third radical can be tentatively assigned to the olefin cation $CH(Me)^{\pm}CH-CH(Me)_2$ produced by a 1,2-hydride shift of the ring-opened form **7**. A large doublet of 62 G for the α -proton of the similar olefin cation $(Me)_2C^{\pm}CH(Me)$ has been pointed out by Iwasaki and co-workers.²⁸ In addition, the coupling of the methyl group in the present case is also close to the 21 G of the methyl coupling in their olefin cation.²⁸ For the other hfc's, the 9.6 G coupling is assignable to the olefinic proton of the $-CHCH(Me)_2$ group, while the smallest hfc of 4.0 G is ascribed to the $-CH(Me)_2$ proton which may be nearly in the nodal plane. The structure of this olefin cation can then be described as twisted with the spin largely located at the $CH(Me)$ side. In trying to check the assignment, the olefin $CH(Me)^{\pm}CHCH(Me)_2$ was studied in F-113U directly. However, the low-temperature spectra of the radical species produced from the olefin only showed a broad envelope of lines with undefined structures. On warming to 105 K, unfortunately, ion-molecule reactions took place to produce neutral radicals. Therefore, a direct comparison of well-resolved spectra for this olefin cation from two sources cannot be made. Nonetheless, it should be stressed that even though the radical cation $CH(Me)^{\pm}CHCH(Me)_2$ could not be made directly from the olefin at 135 K, the twisting of the olefin cation might well be different when generated from two different sources since the twist angle of olefin cations is very sensitive to the conditions under which the cation was generated.³¹ The subtle environment of the cation may alter the twist angle of the cation and influence the spin distribution greatly. And hence the ESR parameters might well be different between the present

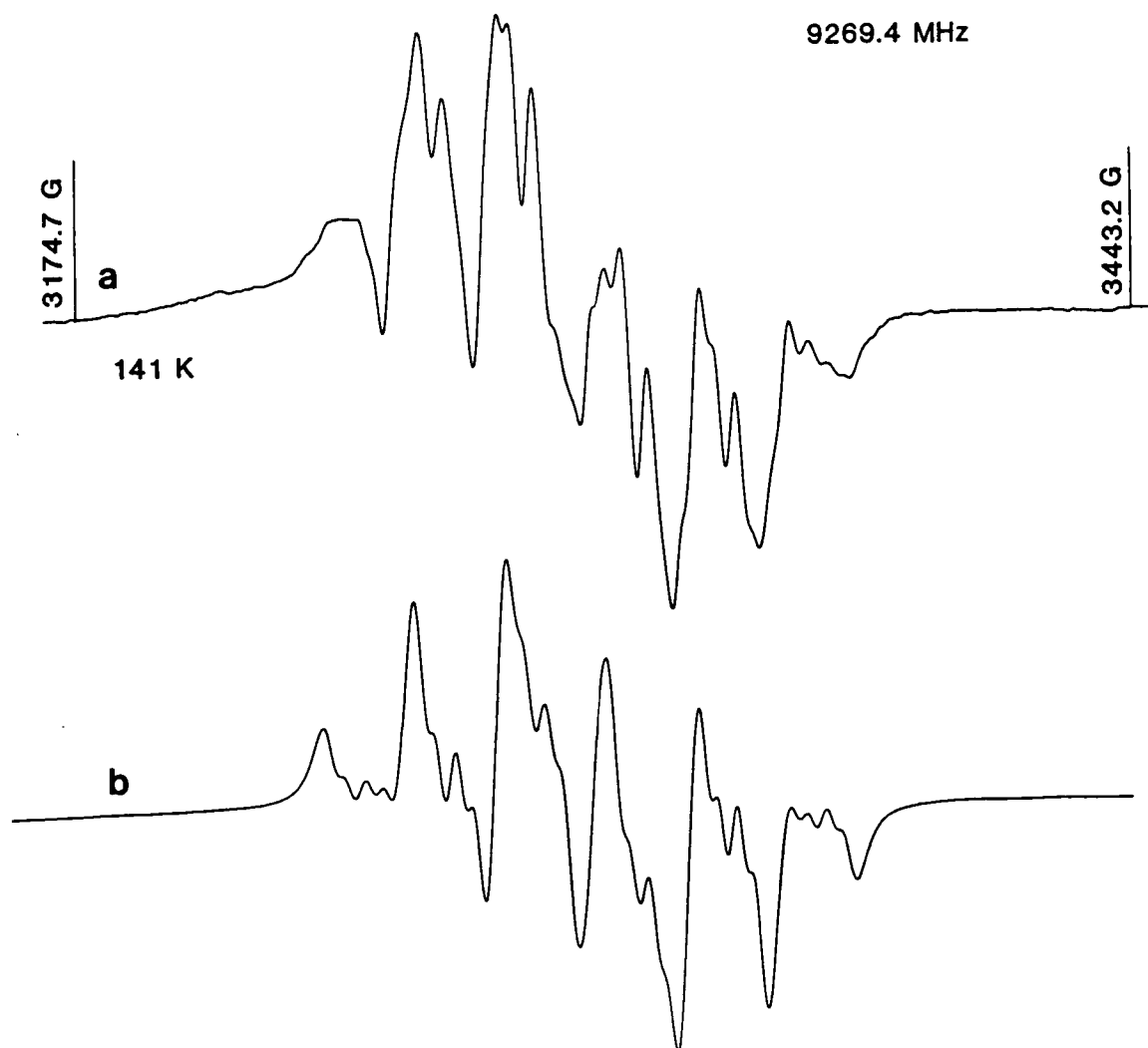


Figure 10. First-derivative ESR spectra of the $\text{CH}(\text{Me})^{\dot{+}}=\text{CHCH}(\text{Me})_2$ radical cation produced from the ring-opened radical cation of trimethylcyclopropane in F-113U: (a) experimental, and (b) simulation by using $a(1\text{H}) = 48.6$ G, $a(3\text{H}) = 22.6$ G, $a(1\text{H}) = 9.6$ G, $a(1\text{H}) = 4.4$ G, and a Lorentzian linewidth of 3.5 G.

case and the $\text{CH}(\text{Me})^{\dot{+}}\text{CH}-\text{CH}(\text{Me})_2$ directly generated from the parent molecule in the same matrix. Lastly, it should be mentioned that the simulations of the third radical based on the allyl type of radicals all failed leaving the olefin cation as the only candidate so far.

4. Cis- and Trans-1,2-Dimethylcyclopropane Radical Cation

Cis- and trans-1,2-dimethylcyclopropane radical cations were also studied in F-11, F-11U and F-113S matrices. Like the last cases, the ring-closed forms of the cis- and trans-1,2-dimethylcyclopropane radical cations gave the best resolved ESR spectra in F-11. Accordingly, shown in Figure 11a and 11b are the ESR spectra of the ring-closed form of the cis-isomer with its simulation, and shown in Figure 12a and 12b are the ESR spectra of the ring-closed form of the trans-isomer with its simulation, the experimental spectra referring to the F-11 matrix. Clearly, the simulation in Figure 11b matches 11a while the simulation in Figure 12b matches 12a quite well, giving reasonable ESR parameters for these two species listed in Table II (p 26).

In terms of their similar ESR parameters, it appears that the different methyl group conformations in cis and trans ring-closed species only causes a small difference to their hyperfine coupling constants. The SOMO of these two species are considered to be of the same type as those of the corresponding cyclopropane, trimethylcyclopropane, and tetramethylcyclopropane species, namely, the $^2\text{A}_1$ structure. The spin is located at the $(\text{Me})\text{CH}-\text{CH}(\text{Me})$ bond since the spectra show couplings from two methyl groups rather than from one methyl group which would be expected if the spin were located in the C-C bond on the less substituted side of the ring. The ESR parameters of these two species are clearly in the same region as those of the radical cations of cyclopropane, trimethylcyclopropane, and tetramethylcyclopropane (Table II (p 26)). However, the methyl hfcs for the dimethyl cations are about 6 G larger than those of the tetramethyl cations. This is not surprising, however, because it is well documented that methyl substitution at a carbon radical has the effect of reducing the spin density at that carbon by hyperconjugation, so that the more

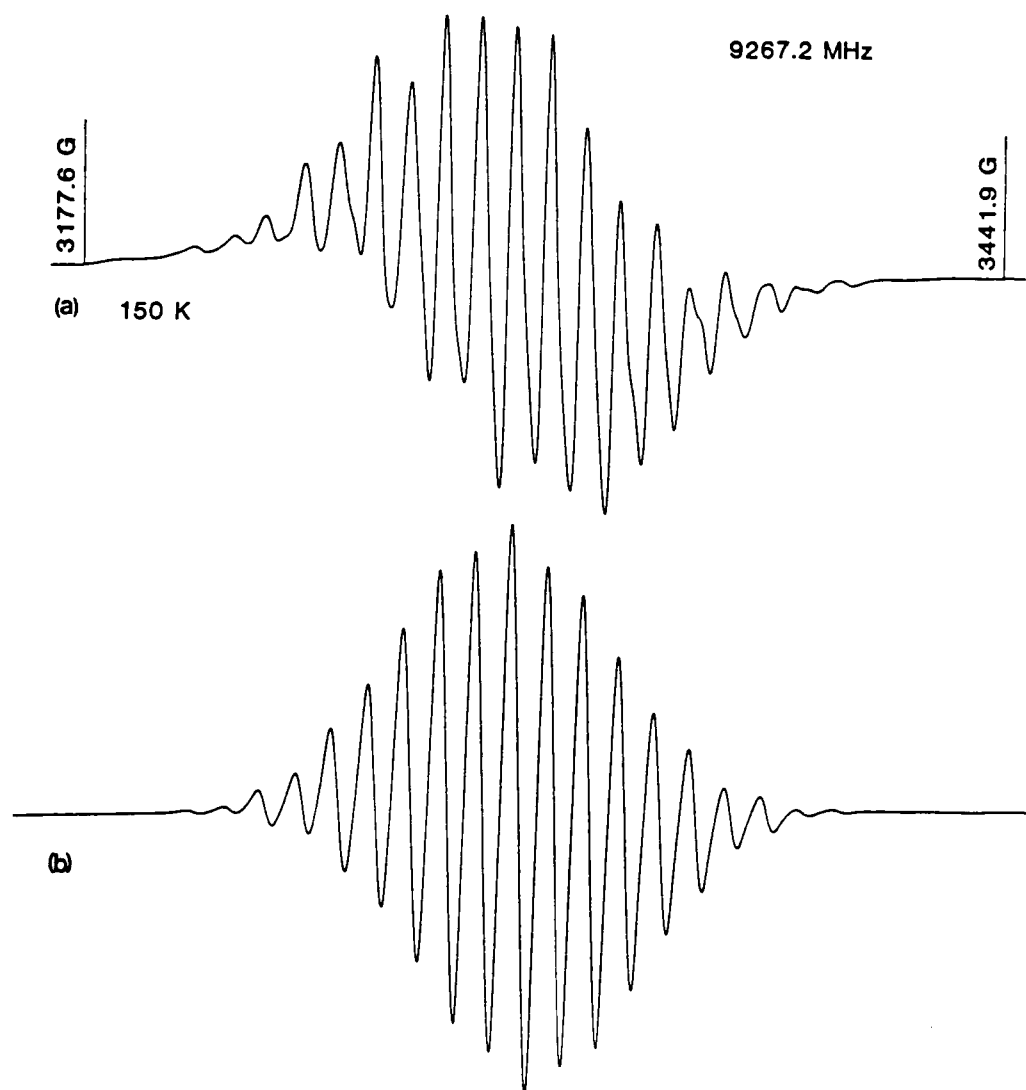


Figure 11. First-derivative ESR spectra of the ring-closed radical cation of 1,2-cis-dimethylcyclopropane in F-11: (a) experimental, and (b) simulation by using ESR parameters in TABLE II (p 26) and a Lorentzian linewidth of 3.5 G.

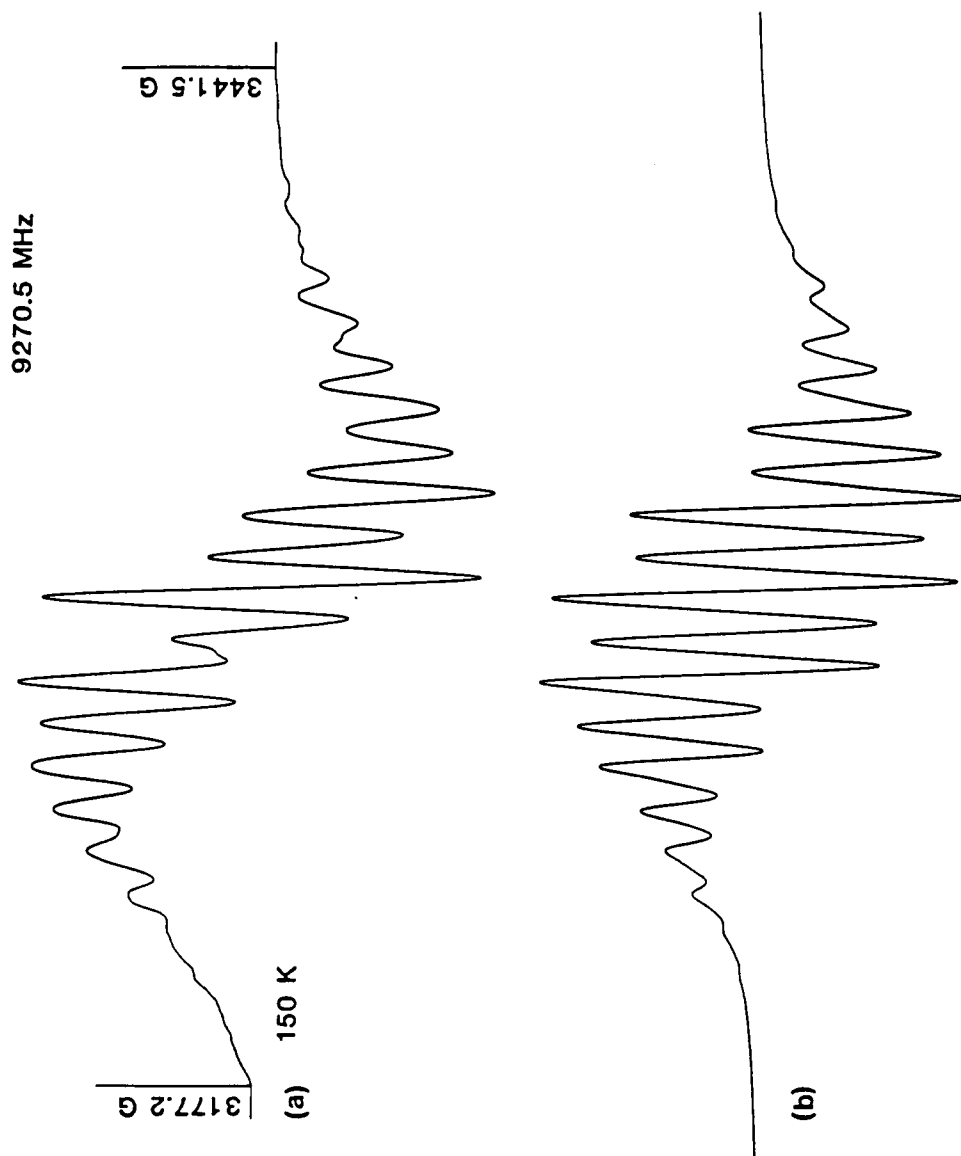
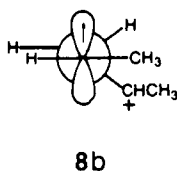
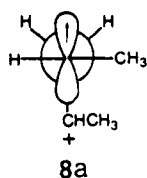


Figure 12. First-derivative ESR spectra of the ring-closed radical cation of 1,2-trans-dimethylcyclopropane in F-11: (a) experimental, and (b) simulation by using ESR parameters in TABLE II (p 26) and a Lorentzian linewidth of 3.5 G.

substitution which has occurred, the more reduction should be expected.²⁷ Hence, it can be concluded that every methyl substituted cyclopropane radical cation possesses the a_1 SOMO with the spin localized in the C-C bond representing the most substituted side.

The ring-closed forms of cis- and trans- dimethylcyclopropane radical cations were only stable in F-113U up to 95 K. Above 95 K, these species were converted to their corresponding ring-opened species irreversibly. The temperature for the ring-opening in these cases is 5 K lower than that for the ring opening of the trimethylcyclopropane species and 15 K lower than that for the ring-opening of the TMCP species. Such a temperature effect may give a hint regarding the ring-opening mechanism of these species, as will be discussed in the next section. Turning now to the ESR spectra of the ring-opened species, Figure 13a and 13b show the ESR spectrum of the ring-opened form of the cis-isomer and its simulation, while Figure 14a and 14b show the ring-opened form of the trans-isomer and its simulation, respectively. Clearly the simulations in Figure 13b and 14b fit the experimental spectra of Figure 13a and 14a satisfactorily, giving reliable, identical ESR parameters to the ring-opened species from cis and trans-compounds (Table III (p 27)). Although the background signals in the cis spectrum are much stronger, this does not alter the analysis. It follows that ring opening of these two species brought about the same localized structure for both cis and trans isomers. Although the ESR data of the cis and trans isomers have immediately ruled out the unsymmetrical ring-cleavage product with a $\cdot\text{CH}_2\text{CH}(\text{Me})\text{R}$ radical center in these two cases because this radical center does not have as many protons as required by the simulations, the ESR data still leave open two possible choices. One is a symmetrical ring cleavage product with a $\cdot\text{CH}(\text{Me})\text{CH}_2\text{R}$ radical center which can interpret the observed ESR spectra by either of the two conformations 8a or 8b.



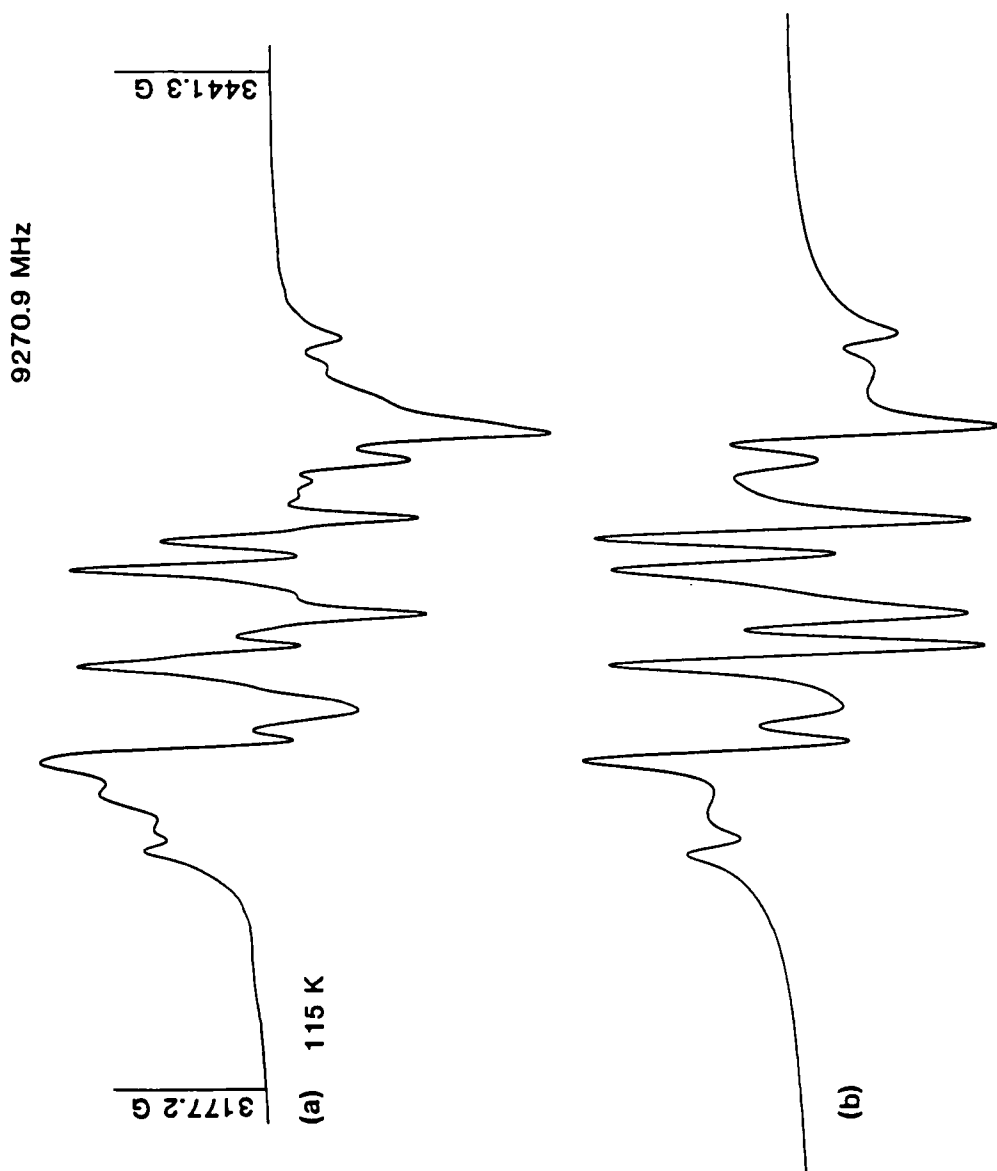


Figure 13. First-derivative ESR spectra of the ring-opened radical cation of 1,2-cis-dimethylcyclopropane in F-113U: (a) experimental, and (b) simulation by using ESR parameters in TABLE III (p 27) and a Lorentzian linewidth of 3.5 G.

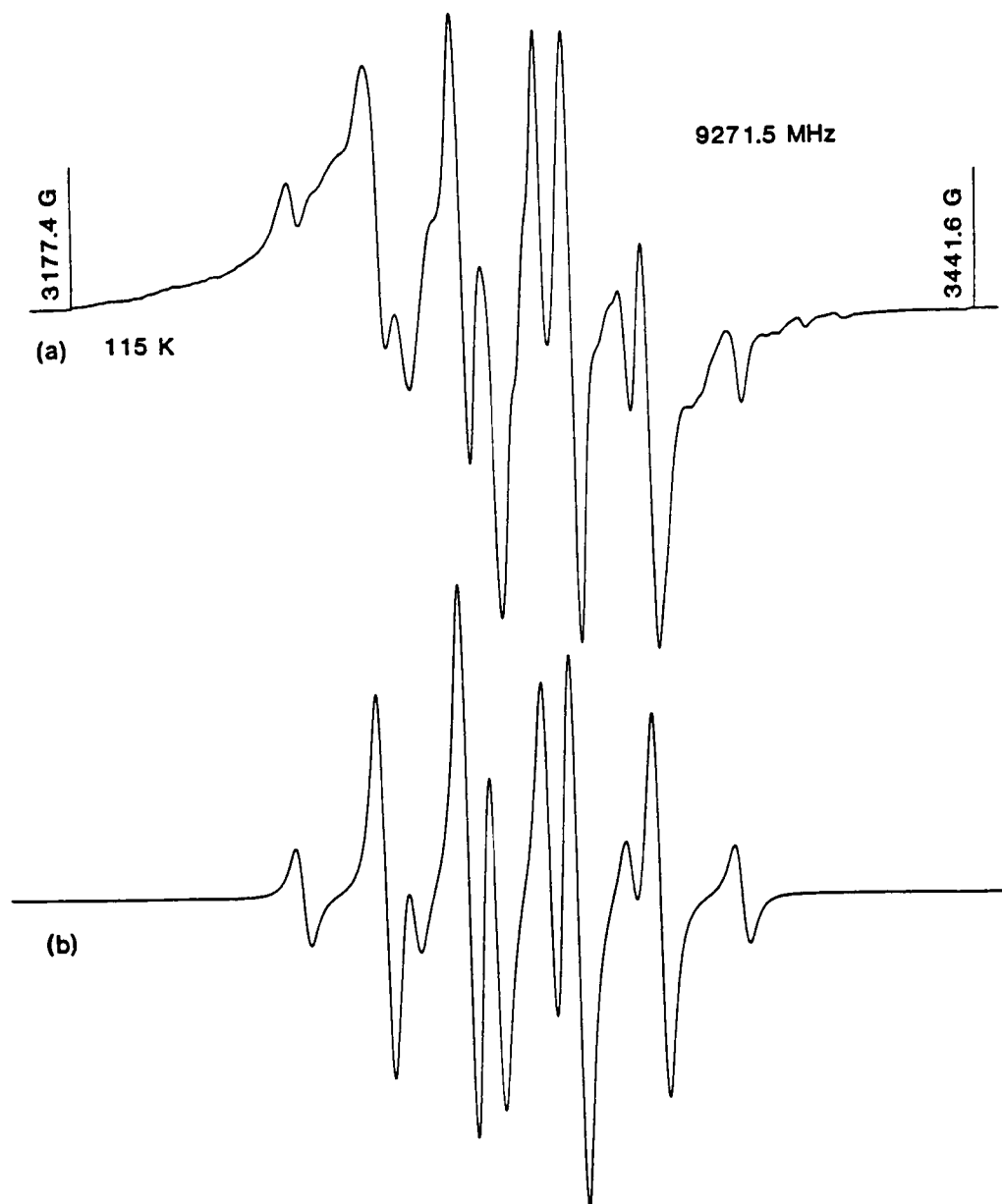


Figure 14. First-derivative ESR spectra of the ring-opened radical cation of 1,2-trans-dimethylcyclopropane in F-113U: (a) experimental, and (b) simulation by using ESR parameters in TABLE III (p 27) and a Lorentzian linewidth of 3.5 G.

The spectrum of 8a should consist of two nearly equivalent proton hfcs of 16.2 G that undergo an out-of-phase modulation giving rise to an apparent doublet splitting of 32.4 G. While the structure 8b also possesses two β -protons, one is in the nodal plane and the other has a dihedral angle of 30° with respect to the p-orbital containing the unpaired electron, so its spectrum should then consist of a large doublet of 32.4 G. The other choice is an unsymmetrical ring cleavage product with the $\cdot\text{CH}(\text{Me})\text{CH}(\text{Me})\text{R}$ radical center which can also account for the observed ESR spectra by one large β -proton hfc of 32.4 G. The ESR parameters in the available temperature range cannot distinguish between these choices. However, from the chemical point of view, since the ring-closed forms of the dimethylcyclopropane radical cations have been demonstrated to have the spin localized at the bond between the methyl substituted carbons, the unsymmetrical ring-cleavage seems unlikely. It is then concluded that the ring-opened form of the dimethylcyclopropane radical cation is generated by symmetrical ring-cleavage and has the structure represented either by 8a or by 8b.

On further annealing to above 135 K, the ring-opened form of the cis-isomer decayed, accompanied by a growth of a new radical species. This new radical species can also be produced by U.V. irradiation of the ring-opened form of the cis-isomer at 100 K for 15 minutes. This new spectrum (Figure 15) is similar in its main pattern to that of the third radical species derived from the trimethylcyclopropane ring-opened species. This may imply that the third radical in the present case is the $\text{CH}(\text{Me})^+\text{CH}=\text{CH}_2(\text{Me})$ radical cation produced by a 1,2-hydride or a 1,2-hydrogen shift in the ring-opened form of the cis-isomer. This olefin cation is similar to the radical cation $\text{CH}(\text{Me})^+\text{CH}=\text{CH}(\text{Me})_2$ derived from the trimethylcyclopropane ring-opened cation except that one Me group in the isopropyl moiety has been replaced by one hydrogen in the present case. Therefore they should give similar ESR spectra if the spin is localized mostly at the $\text{CH}(\text{Me})$ side of the olefin group, as mentioned earlier. However, a full analysis has not been obtained because of the complexity of the spectrum.

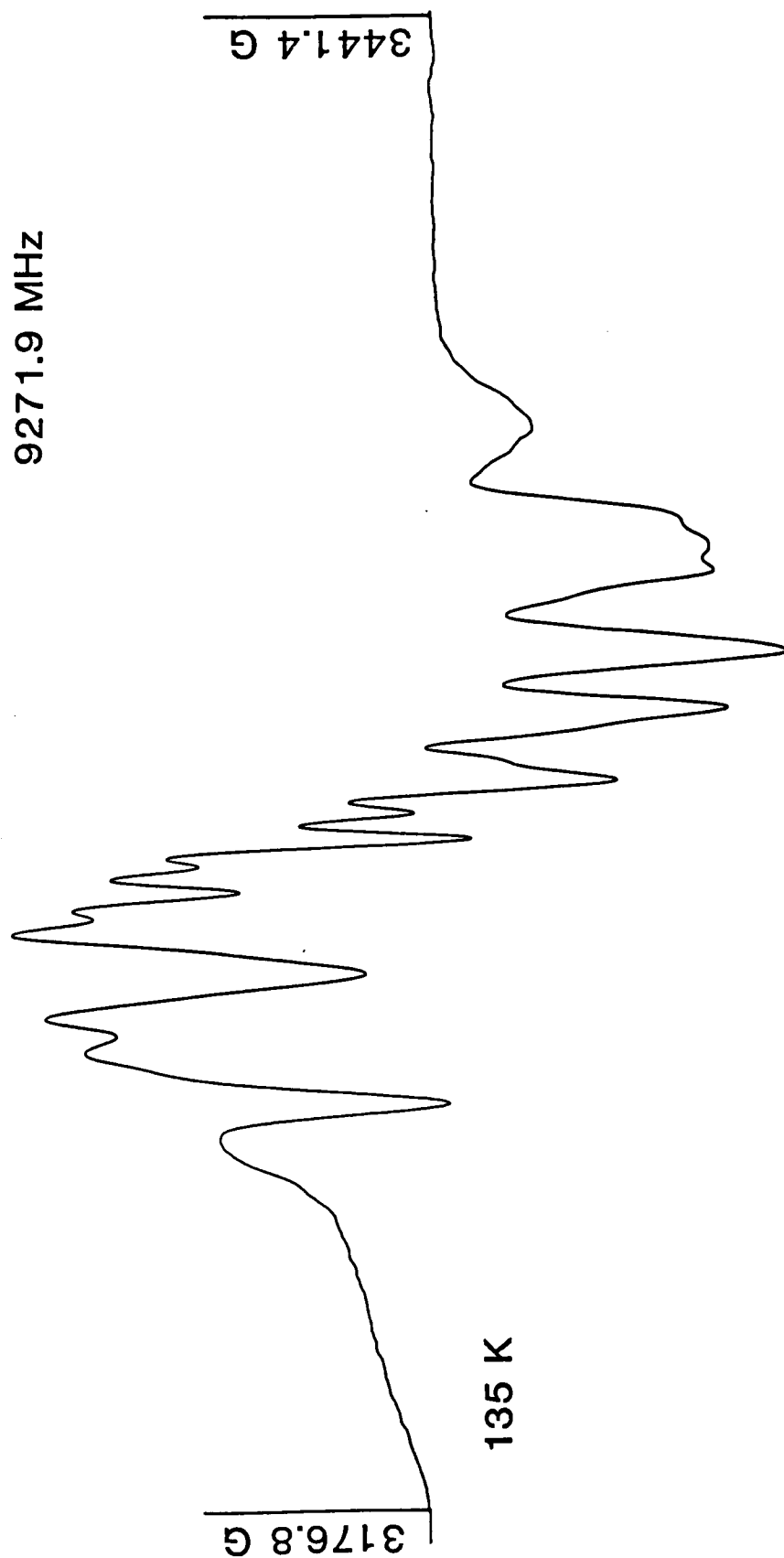


Figure 15. First-derivative ESR spectrum of the third radical generated from the ring-opened radical cation of cis-1,2-dimethylcyclopropane in F-113U.

C. Discussion

1. The Ring-Closed Forms of the Cyclopropane Radical Cations

Although there are two degenerate HOMO orbitals for cyclopropane in D_{3h} symmetry, the radical cation of cyclopropane was found to have a $^2A_1$ state in C_{2v} symmetry, corresponding to a Jahn-Teller distortion. Thus, Iwasaki and co-workers²⁰ showed that the ring-closed $^2A_1$ structure of the cyclopropane radical cation in F-113U at 4 K exhibits a 3 x 5 line spectrum with hfc's of 21.0 G (2H) and -12.5 G (4H), which gives a total width of 92 G. The spectrum shown in Figure 1 in the present study has a total width of about 100 G indicating that this broad line-spectrum is an unresolved triplet (21.0 G) of quintets (12.5 G). Careful examination of this spectrum reveals three peaks at low field side and three at high field side belonging to the triplet-of-quintets pattern, the space between these peaks being about 12 to 13 G in agreement with the quintet hfc reported by Iwasaki *et al.* The assignment of the $^2A_1$ structure of the cyclopropane radical cation in F-113U at low temperatures is thereby confirmed.

Iwasaki and co-workers reported also that the 100 G spectrum of the cyclopropane cation underwent a sudden coalescence of the outer lines to a single line over a narrow temperature range on annealing in F-11. This was attributed to the onset of a dynamical process involving site-jumping between three possible $^2A_1$ structures of the cyclopropane molecule.²⁰ This coalescence was not detected in F-113U because on annealing, the ring-opening occurred irreversibly. Interestingly, this coalescence was also observed in SF_6 at 95 K during the present study and as in F-11, this rapid exchange effect was not followed by ring-opening. Instead, an ion-molecule reaction occurred in SF_6 with the formation of the cyclopropyl radical as previously reported by Iwasaki *et al.*²⁰ The failure to undergo ring opening may be directly related to the exchange effect. Although speculative, it could be argued that ring-opening requires the spin to localize at one C-C bond for a longer time than that required for the ring-opening, a condition which is not met when coalescence occurs.

Undoubtedly, all the methyl substituted cyclopropane radical

cations possess the $^2A_1$ type of structure. But for these species, another question arises. Since the methyl substitution destroys the D_{3h} symmetry of the parent cyclopropane, the spin can localize at either the most substituted side or one of the less substituted sides of the ring. The spin, according to the above results, is in fact localized at the most substituted side. This rule was first pointed out by Roth and Schilling in their CIDNP study of the phenyl-substituted cyclopropane radical cations,²¹ while the present studies demonstrate that it is also applicable to the methyl-substituted cyclopropanes. The reason may be that the phenyl or methyl groups are electron-donating groups which can stabilize the positive charge of the ring-closed species better.

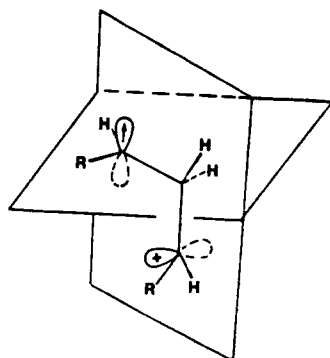
2. The Ring-Opened Cyclopropane Radical Cations

The ring-opened cyclopropane radical cations are, in fact, distonic species in which the radical center is separated from the carbocation center. The ring-opening was found in F-113U, $CFCl_2CFCl_2$, and CF_2ClCF_2Cl matrices, but not in F-11, CF_2ClCCL_3 , and F-113S matrices. It is noteworthy that the matrices in which the ring-opening did not occur has the CCL_3 group while the matrices in which the ring-opening occurred has the $CFCl_2$ or CF_2Cl group, although this finding gives no guide about the structures of the ring-opened cations.

Based on the ESR results, the conformations of the ring-opened cations at the radical side have been established unambiguously. As described in the results section, the ring-opened radical cations derived from cyclopropane, 1,1,2,2-tetramethylcyclopropane, and 1,1,2-trimethylcyclopropane possess the conformations described by 3, 5, and 7, respectively. The structure 3 has the bisected form, whereas 5 and 7 have the eclipsed form. As would be expected, these conformations are in accord with those for alkyl radicals having the same $C_\alpha-C_\beta$ end groups²⁷. Unfortunately, the ESR data do not provide information about a possible bonding situation at the carbocation site, and the nature of this site has been the subject of speculation. Among them, the simplest explanation is that of an orthogonal structure in which the p-orbital of the carbocation is perpendicular to the p-orbital of the radical. This kind of structure makes the through-space as well the through-bond

interaction between these two orbitals impossible, and therefore it accounts for the localized radical which is observed. However, this structure was strongly disputed by *ab initio* calculations.²⁵ Nonetheless, these calculations did not consider the strong solvent effect in the condensed phase, and to this extent are not directly applicable to the present study. Moreover, evidence for the trimethylene radical cation has been obtained even in the gas phase. Specifically, a species derived from the activation of the cyclopropane cation was found to react differently from the propene cation in ion-molecule reactions.³² The results of the theoretical calculations should be taken into consideration but the possible existence of a trimethylene radical cation under certain conditions cannot be excluded absolutely by these calculations.

While the possible orthogonal structures for the ring-opened cyclopropane, trimethylcyclopropane, and tetramethylcyclopropane species are easily defined on the basis of the known conformation at the radical center, such structure is not so obvious for one of the dimethyl species. As described in the results, the preferred cations are either 8a or 8b. The conformation of 8a is again eclipsed, in which the orthogonal structure is easily achieved. The orthogonality of the carbon $2p_z$ orbitals at the carbocation and radical sites of 8b, however, is not so apparent. But it can also be achieved by the following structure. Here it can be seen that the two planes normal to these orbitals intersect at the β -carbon, each plane also containing one β -proton of the methylene group. Since these $C_\alpha C_\beta H_\beta$ and $C'_\alpha C'_\beta H_\beta$ planes are orthogonal to each other at the tetrahedral-carbon, it is then clear that the carbon $2p$ orbitals perpendicular to these planes are also perpendicular to each other.

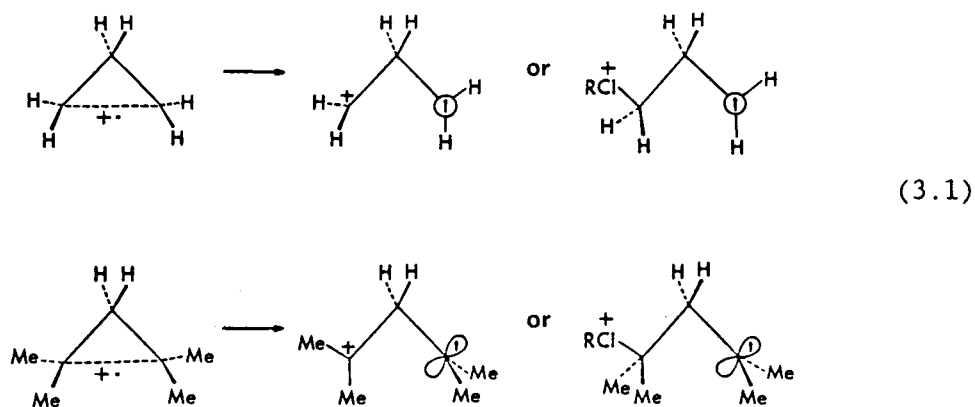


Although every ring-opened radical cation derived from cyclopropane and its derivatives can adopt an orthogonal structure, it has been stressed that these structures do not have to be strictly obeyed if the ring opening is accompanied by a strong solvation effect or other strong interaction at the carbocation center. These effects may be implied by the fact that the ring opening only occurs in certain matrices.

3. The Mechanism for the Ring-Opening Process

While the ring-opening itself is unequivocal, and this is the main contribution of the present work, neither the nature of the putative carbocation site in these ring-opened isomers, nor the mechanism for the ring-opening is clear due to the limited information available. Four mechanisms will be discussed in this section. They are: (1) the nucleophilic attack mechanism; (2) the hydride-ion transfer mechanism; (3) the ion-molecule reaction mechanism; and (4) the solvation mechanism.

The nucleophilic attack mechanism described by equation (3.1) indicates that the localized ring-opened radical cations of cyclopropane and its derivatives are stabilized by the bonding between the carbocation center of these species and a suitable nucleophile which can be either the chloride ion produced from the dissociative electron attachment of the Freon radical anion, or a solvent molecule RCL. The former was suggested by Arnold *et al* and Borden,²⁵ while the latter was proposed by Symons,²⁴ as mentioned in the Introduction.



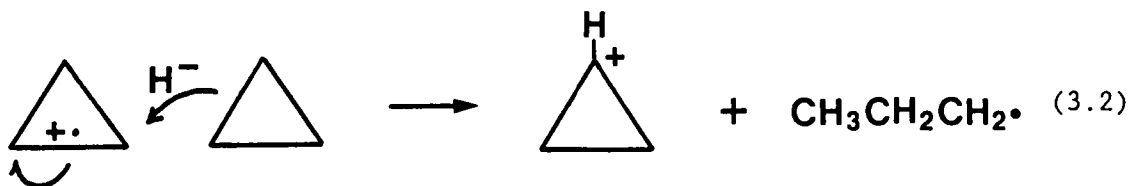
However, no ESR evidence for $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CL}$ or $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CL}^+\text{CFCLCF}_2\text{CL}$ was obtained. It is known that the ESR spectrum of the $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CL}$ radical displays a special alternating linewidth effect owing to the in-phase modulation of β -proton hfcs between 123 K and 173 K.³³ This effect arises from a conformational change produced by a 180 degree rotation of the γ -CL in the nodal plane about the bond. A chloronium ion might be expected to behave similarly. In the present study, the localized ring-opened cyclopropane radical cation in F-113U was carefully examined from 120 K to 140 K by using both the rapid scan capabilities of the spectrometer and a computer to record the ESR spectra during its fast decay, and no such alternating linewidth effect was observed. In $\text{CFCL}_2\text{CFCL}_2$, the ring-opened cyclopropane cation can be studied up to 160 K, but still no such linewidth effect was observed. The only observed effect, as pointed in the Figure caption of Figure 2, is a slight inequivalence of the β -protons as revealed by the broadening of the three $M_I = 0$ components of the β -protons. This effect is readily explained by a slow torsional oscillation about the $\text{C}_\alpha\text{-C}_\beta$ bond, and these out-of-phase modulation effects are quite different from the in-phase effect observed for the $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CL}$ radical.

Another explanation for out-of-phase modulation effects is a rotation about $\text{C}_\beta\text{-C}_\gamma$ bond where the γ substituted CL or RCL^+ moves above and below the nodal plane to confer nonequivalence on the β proton. This type of effect has been proposed to explain similar effects in the ESR spectra of 3-fluoropropyl^{33a} and n-butyl radical³⁴ showing out-of-phase modulation to give line broadening of $M_I = 0$ components of β -protons. However, for this mechanism to occur for a chloronium ion, the movement of a bulky group would be required which seems unlikely. Also, this mechanism does not apply to the 3-chloropropyl radical as already mentioned.

In addition, the experiments show that the ring opening occurred only in F-113U but not in F-11. If this were caused by the chloride ion or Freon molecule attack, this attack should be easier in F-11 as pointed by Iwasaki and co-workers,³⁵ in contrast with the observation.

The lack of evidence for the chloride attack led Nunome,

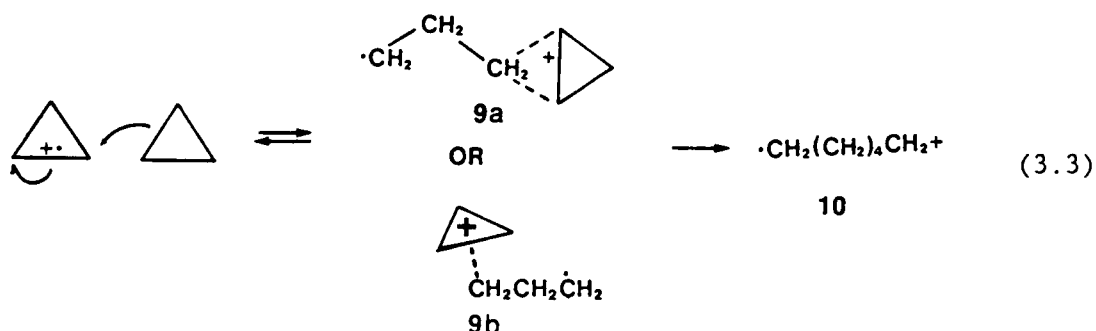
Toriyama and Iwasaki to propose that the spectrum comes from a propyl radical formed by a hydride transfer mechanism.³⁵ This involves an ion-molecule reaction mechanism which is written as:



In this mechanism, the propyl radical is formed by hydride transfer from a neutral cyclopropane molecule to the cyclopropane cation followed by ring-opening. The ESR parameters assigned to the ring-opened cyclopropane radical cation are very close to those of the propyl radical consistent with this mechanism. It was found that in the gas phase, ion-molecule reactions by hydride ion transfer often take place to alkene radical cations from neutral alkanes to form alkyl radicals. Since cyclopropane has both alkane and alkene character, it is possible that it can also undergo such a reaction. The problem with this explanation is its failure to explain the formation of a third radical. Like the chloride attack mechanism, the carbocation character of the localized forms is also lost in this mechanism. As a consequence, it cannot explain the secondary changes after the ring-opening has occurred in F-113U. These changes can be summarized as follows: (a) the conversion of the ring-opened cyclopropane cation to propene cation by U.V. irradiation; (b) the conversion of the ring-opened cis-1,2-dimethylcyclopropane cation to a third radical species either by U.V. irradiation or by thermal annealing; (c) the conversion of the ring-opened trimethylcyclopropane cation to 4-methyl-1-pentene cation either by U.V. irradiation or by thermal annealing; and (d) the formation of tetramethylallyl radical from the ring-opened tetramethylcyclopropane cation by U.V. irradiation or thermal annealing. All these changes are consistent with active carbocation centers in these ring-opened radical cations whereas such changes would not be expected for the radicals postulated by the other two mechanisms. Furthermore, Ushida, Shida and Walton³⁶ have recently reported that the radical cation of bicyclo[2.1.0]pentane undergoes

ring-opening by the breakage of the cyclopropane bond, followed by a rearrangement to form the cyclopentene radical cation in F-11, even at 4 K. Their result also argues against the above mechanisms, since if the carbocationic center of the ring-opened radical cation of their molecule had been attacked by hydride ion, chloride ion, or the $\text{CF}_2\text{CLCFCL}_2$ group, the rearrangement should not have been observed.

Turning now to consider the remaining two mechanisms, an ion-molecule addition reaction mechanism has been discussed privately in connection with the formation of the localized oxirane radical cations.³⁷ The formation of the localized cyclopropane cation can be interpreted in a similar way:



This is, of course, a bimolecular reaction mechanism. First, the radical cation of cyclopropane approaches the cyclopropane molecule by mutual diffusion, and then the σ -complex, analogous to protonated cyclopropane depicted as 9a,³⁸ or the π -complex depicted as 9b, may be formed as an intermediate. Legon and Millen have recently shown that cyclopropane is the best nucleophile among ethyne, ethene and cyclopropane.³⁹ These intermediates may be stable or may undergo ring-opening to form the $\cdot\text{CH}_2(\text{CH}_2)_4\text{CH}_2^+$ distonic ion 10. Either 9a, 9b, or 10 can account for the triplet of triplets spectrum observed. This mechanism implies that the ring-opening of the cyclopropane cation is actually caused by the attack of the parent molecule. This mechanism is certainly very attractive in the sense that all these localized forms of cyclopropanes were produced in the temperature range in which the ion-molecule reactions can take place by diffusion, implying that the formation of the localized form results from some kind of ion-molecule

reaction. The formation of the σ -complex 9a is understandable on the basis of the Walsh model of cyclopropane. According to this model, the p-orbitals of three carbons lie in the plane of cyclopropane ring. These filled p orbitals can interact with a proton or carbocation to form the corresponding intermediates.⁴⁰ As a result, when the methyl substitution increases the steric effect, the σ -complex will become more difficult to form, which accounts for the higher temperatures observed for the ring-opening of the methyl-substituted cyclopropanes.

In addition, this mechanism can be viewed as modified S_N2 reaction, in which the neutral molecule behaves as the nucleophile which attacks the radical cation while the radical produced by the bond break corresponds to the leaving group. Interestingly, according to this mechanism, the attack of the neutral molecule cannot occur at the less sterically hindered side of the radical cations since, for example, in the tetramethylcyclopropane, the attack at the methylene position would produce the $(Me)_2\dot{C}C(Me)_2-R^+$ radical center which is not observed. This may be explained by the fact that the spin is localized at the most substituted bond of the ring-closed TMCP radical cation, and the attack takes place where the spin and charge are concentrated. This mechanism is also not in conflict with the observations of the secondary changes of the ring-opened cations mentioned earlier since the σ -complex 9a or the π -complex 9b do not have strong bonding between the carbocation center of the ring-opened radical cation and the cyclopropane neutral molecule. Thus it is reasonable to assume these complexes can be dissociated either by U.V. irradiation or by thermal annealing, allowing the ring-opened cation to undergo further reactions. On the other hand, one would not expect species such as 10 to yield secondary radicals on photobleaching or annealing with the same number of carbons as the original cyclopropane.

The solvation mechanism was originally proposed in this laboratory.²³ As mentioned earlier, the matrices with $CFCl_2$ or CF_2Cl groups seem to have some special role in facilitating the bond breakage and stabilizing the localized radical cations which is in sharp contrast with the matrices containing the CCL_3 group. This is also supported by other experiments. For example, the thermal dissociation

of $t\text{-BuSnMe}_3$ to the tert-butyl radical at 110-120 K was only observed in F-113U but not in F-11 and F-113S matrices.⁴¹

That the matrix can play an important role in determining the structures of radical cations has also been demonstrated by studies of the twisting of olefin radical cations, which is solvent-dependent as exemplified by the change of hfcs of the propene cation in different matrices.³¹ The similarity between the olefins and cyclopropanes is that the olefin cations possess a one-electron $\pi(2p_z-2p_z)$ bond between two carbons, while cyclopropane cations possess a one electron σ -bond between two carbons. If solvent can assist the partial breaking of the π -bond leading to olefin cation twisting, the solvent is likely to assist the breaking of the one electron-bond of cyclopropanes leading to formation of the localized cyclopropane cations.

It has thus been proposed that a polar Freon solvent can alter the potential energy surface for the process of ring-opening of cyclopropane cations. Since the positive charge in the localized forms of these cations is more concentrated than in the ring-closed forms, the solvation energy should be much greater in the former cases, and as a consequence this gives the driving force to the ring-opening. Moreover, since the ring-opening process is exoergic, the transition state should resemble the ring-closed form and only involve a small twist angle, and accordingly, the ring-opening only requires a relatively small energy barrier as described by Figure 16. The solvation mechanism can account for the secondary changes mentioned above satisfactorily, since the active carbocationic centers in cyclopropane radical cations still exist.

It should be stressed that the dipole moments as well as the polarizability of the Freon molecules are little different among the F-11, F-113U and others. The quite different behavior of the matrices to stabilize the localized forms, therefore, indicates that while the polar property or the polarizability property of the Freon molecules may be a necessary condition for the formation of the localized isomers, it is not sufficient. Whether or not the matrices can play a specific role depends on whether they are rigid or elastic. It can be concluded that the deformability of the matrices is therefore the most

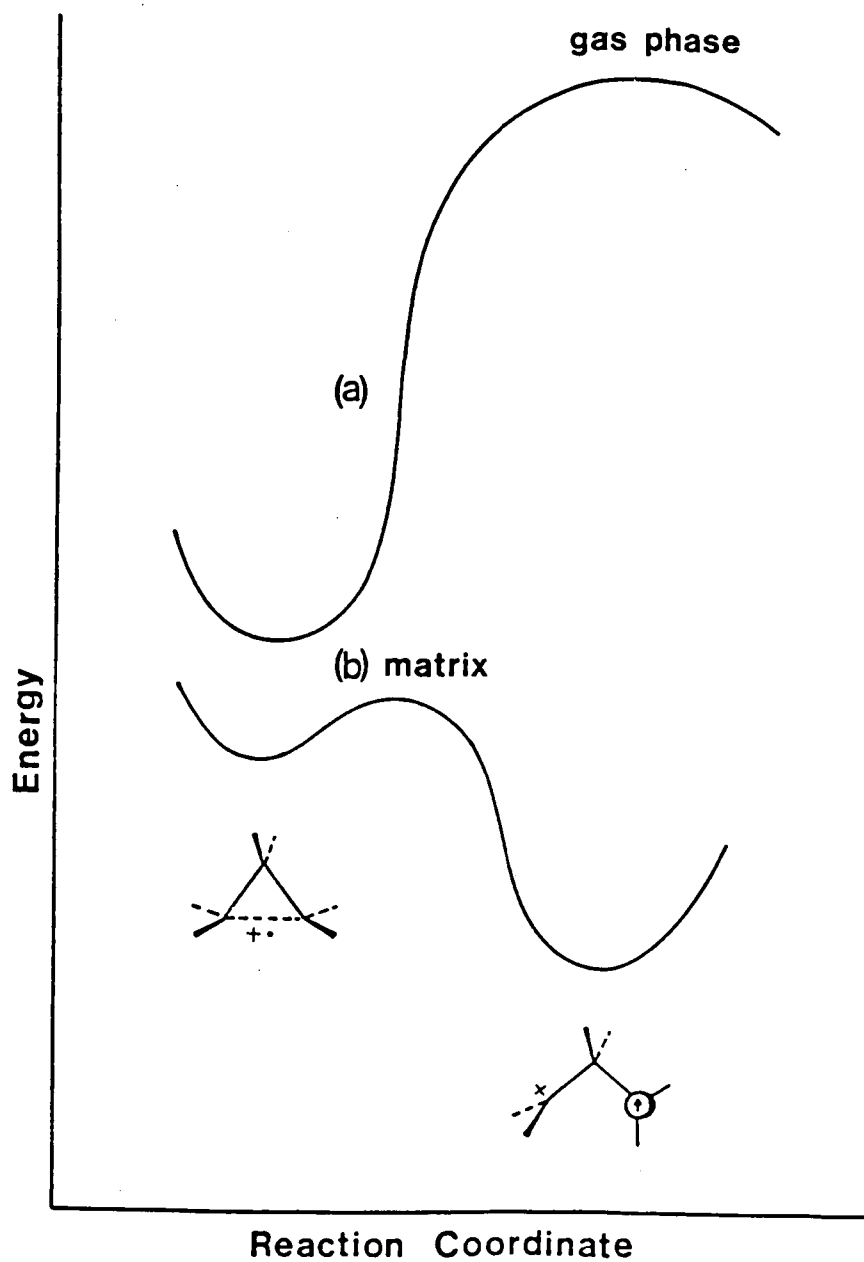


Figure 16. Energy diagram of the ring-opening process of cyclopropane radical cation in the gas phase and in the matrix.

important property in influencing the radical cation chemistry in these matrices. The ion-molecule reaction mechanism and the solvation mechanism depend on this elastic property of the F-113U matrix, since it affects translational and rotational mobility.

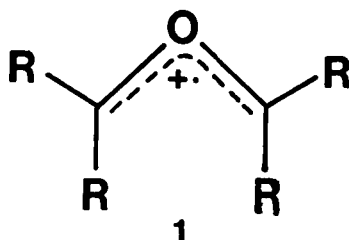
In summary, the ring-opening of the radical cations of cyclopropane and its derivatives can be explained by four general mechanisms so far. From the present evidence, the ion-molecule reaction mechanism and the solvation mechanism are the better choices to account for the ring-opening of these radical cations. But no decisive evidence has been obtained to choose any one of them. Moreover, all the ring-opening may be caused by only one mechanism but it is also possible that one mechanism plays the key role in one case while the other mechanisms play the key role in other cases. New approaches may be necessary to solve these problems.

CHAPTER IV

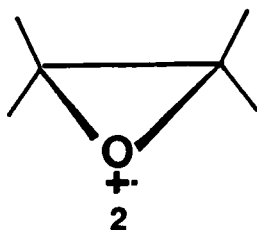
OXIRANE RADICAL CATIONS

A. Introduction

It was proposed in a report from this laboratory that the oxirane radical cation produced from the γ -irradiation of oxirane in F-11 at 77 K is the C...C ring opened isomer 1 possessing a planar structure of C_{2v} symmetry.⁴²



This assignment is largely based on the measured hfc ($A(4H) = 16.2 + 0.2$ G), since the expected β -hfc for a ring-closed B_1 oxirane cation 2 should be much larger, the value for the oxetane cation being 65 G.³⁵ However, comparison of the results for the ring-closed thiirane and thietane cations,⁴³ as well as AM1 calculations on oxirane and oxetane cations,⁴³ have led to a revised estimate of 36 G for the expected β -hfc of a $^2B_1$ oxirane cation.

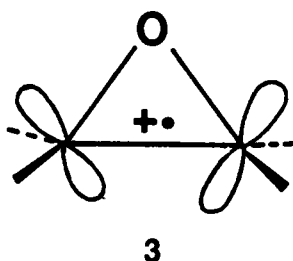


This assignment was confirmed by the anisotropic ^{13}C study of the cation in the same matrix, the derived ESR data ($A(^{13}C) = 57.2$ G, $A(^{13}C) = 9.0$ G, $A_{iso} = 25.1$ G, and $2B = 32.7$ G) being consistent with the π -allylic structure 1, giving a $2p(\pi)$ population of 0.42.⁴⁴

The finding of the ring opening of the oxirane cation in F-11 is consistent with mass spectrometric studies in the gas phase,⁴⁵ and is supported by optical studies of the radical cations of oxirane

derivatives.⁴⁶ Moreover, it accords well with numerous theoretical studies which predict a low barrier to the ring opening of the oxirane cation.⁴⁷

On the other hand, Symons and Wren did not consider ring opening in their original report and suggested the alternative $^2A_1$ ring-closed structure 3 for the oxirane cation in F-11 to explain the low 16.2 G (4H) hfc that was obtained.⁴⁸

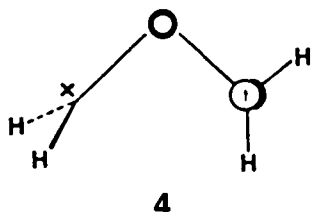


Although the evidence for the ring-opening of oxirane is very strong, they still insisted on the $^2A_1$ assignment in a recent paper in which they judged the ring-opening by a visual examination of the colors.⁴⁹ Their argument is that intense red-violet colors are to be expected for all ring-opened structures, and hence oxirane cation in F-11 is ring closed since it is not strongly colored. On the other hand, they argued that the oxirane cation in SF_6 is ring opened because they claimed to observe an intense orange-red color.

In this Chapter the oxirane radical cation is further studied in SF_6 in detail. The results are compared with those obtained in F-11. It should be stressed that visual examination of the color is a useful qualitative guide, but is certainly not a decisive criterion for ring opening. Although the color of the oxirane cation in F-11 is too weak to be seen clearly by eye, while its color in SF_6 is a brownish yellow in our experience, the doubly labeled ^{13}C oxirane cation gave similar ESR features with similar ESR parameters in both matrices, indicating the existence of the same ring-opened structure 1 rather than different structures of the oxirane cation in these two matrices.

In addition, this Chapter reports the observation of the ring-opened localized form of the oxirane cation 4 at low temperatures in SF_6 , which was not reported in the former studies. This is a

significant finding since the localized form has only been found previously in the F-113U matrix.⁵⁰ The new results reported here sheds more light on the mechanism of generation of the localized form.



Another interesting problem concerning the oxirane cations is the direction of its ring-opening. Snow examined this problem in his dissertation by studying the cations derived from cis- and trans-1,2-dimethyloxirane. Accordingly, Snow reported the results of the study of these two cations in F-11 and suggested the disrotatory process for the ring-opening⁵¹ based on the comparison of different low and high temperature spectra from each of the cations. The identical high-temperature spectra from both cations were assigned to the ring-opened cation in which the two methyl groups were both at the *exo* positions. Since the low-temperature spectrum from the *cis*-compound, even though complicated by the matrix interaction, was similar to the high-temperature spectrum, it was also assigned to the *exo-exo* ring-opened cation. While the low-temperature spectrum from the *trans*-compound was quite different from the high-temperature spectrum, it was assigned to the *exo-endo* ring-opened isomer. This analysis, therefore, indicated a disrotatory process for the ring-opening. However, since the low-temperature spectra are complicated by the matrix interaction in F-11, he could not analyze the low-temperature spectra, and hence the evidence he presented is not strong. It has been found in the course of the present work that the CF₂CLCCL₃ and the F-11 matrices give similar results in general except that the substrate radical cation spectra are not obscured by matrix interaction in the former. Both cis- and trans-1,2-dimethyloxirane cations have therefore been studied in this matrix in the present Chapter. Interestingly, low and high-temperature spectra, although showing no matrix-interaction, were also found to be different in this matrix for each of the cations derived from the *cis*-

and trans-isomers. A carefully examination of the spectra reveals more information about the ring-opening process, but no support for a disrotatory process of ring-opening was obtained.

B. Results

1. Oxirane Radical Cation in SF₆

Figure 17a shows the ESR spectrum of the oxirane cation in SF₆ at 82 K. It can be interpreted as arising from two species as described by the stick diagram. The quintet pattern ($A(4H) = 16.2$ G) is attributed to 1 while the triplet ($A(2H) = 23.1$ G) is assigned to the ring-opened localized form 4, since the expected ESR patterns are a quintet for 1 and a triplet for 4, respectively. No hyperfine substructure from the matrix interaction such as that observed in F-11 was detected.

On annealing to 95 K, 1 decayed with the increase of the intensity of the triplet belonging to 4. This was confirmed by the cooled-down spectrum shown in Figure 17b. Although the spectrometer gain was reduced by a factor of 0.4, the signal amplitude of the triplet is still comparable to that recorded in Figure 17a. The linewidth of the triplet became significantly narrower above 95 K, as can be seen from the comparison of the spectrum in Figure 18a recorded at 94 K with that in Figure 18b recorded at 100 K. This effect implies a greater motion of 4 in SF₆ above 95 K, the phase transition temperature of the SF₆ matrix. It was found that 4 decayed above 120 K.

The radical cation of 1,2-D₂-oxirane behaves similarly. Its ESR spectrum at 81 K is given in Figure 19a. The spectrum arises from the corresponding D-substituted ring-opened planar form 1 and the localized form 4. As illustrated by the stick diagram, the former becomes a triplet ($A(2H) = 16.2$ G) while the latter becomes a doublet ($A(1H) = 23.2$ G). As expected, in both cases the hfcs from the deuterium atoms are not resolved at low temperatures.

Upon annealing to 95 K, the decay of the triplet pattern of 1 was accompanied by the growth of the doublet pattern of 4 in keeping

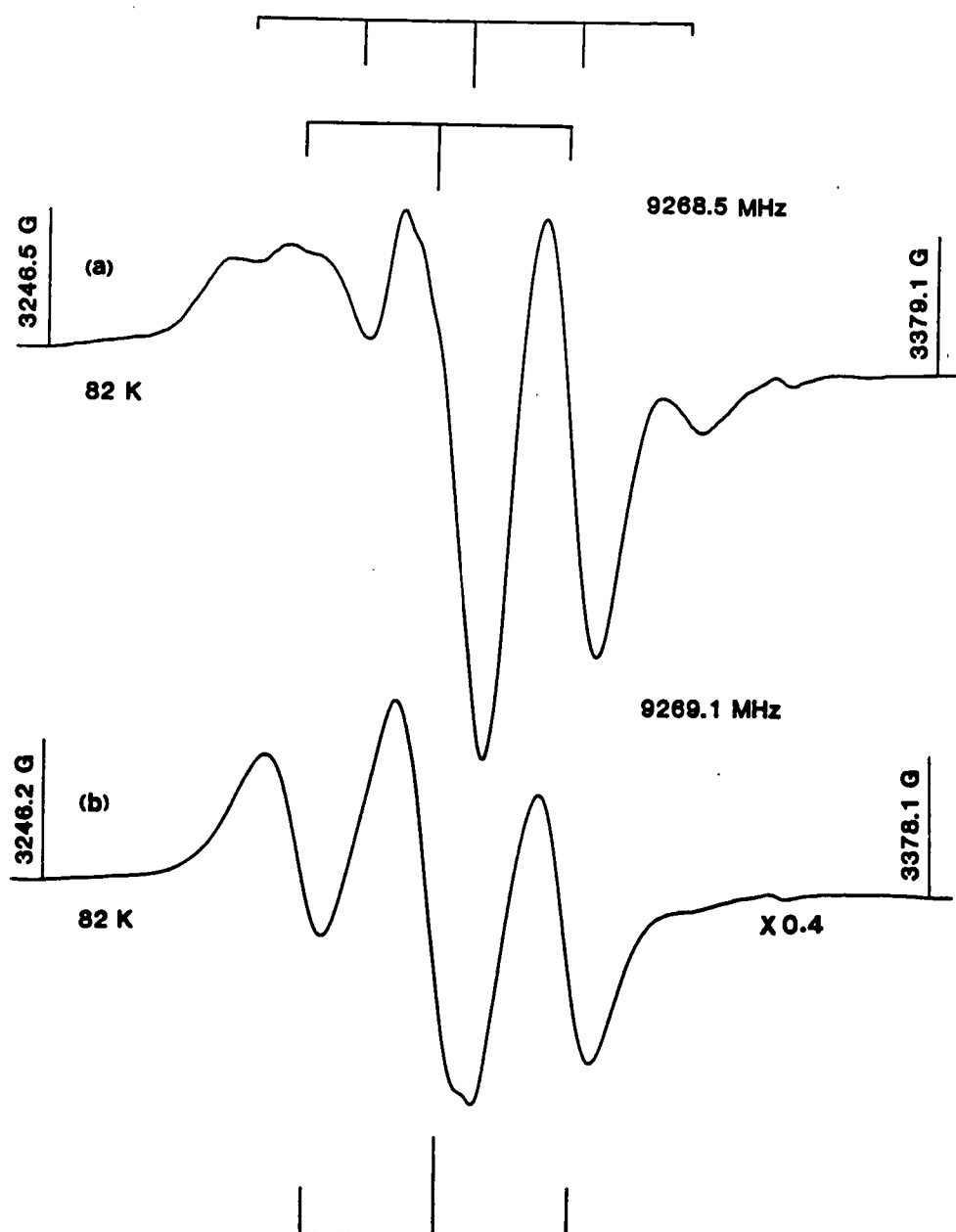


Figure 17. First-derivative ESR spectra of the ring-opened planar and ring-opened localized forms of the oxirane radical cation in SF_6 : (a) originally produced 82 K spectrum, and (b) the recooled 82 K spectrum after annealing the sample to 95 K. The spectrometer gain for (b) was reduced to 40% of that used to record (a).

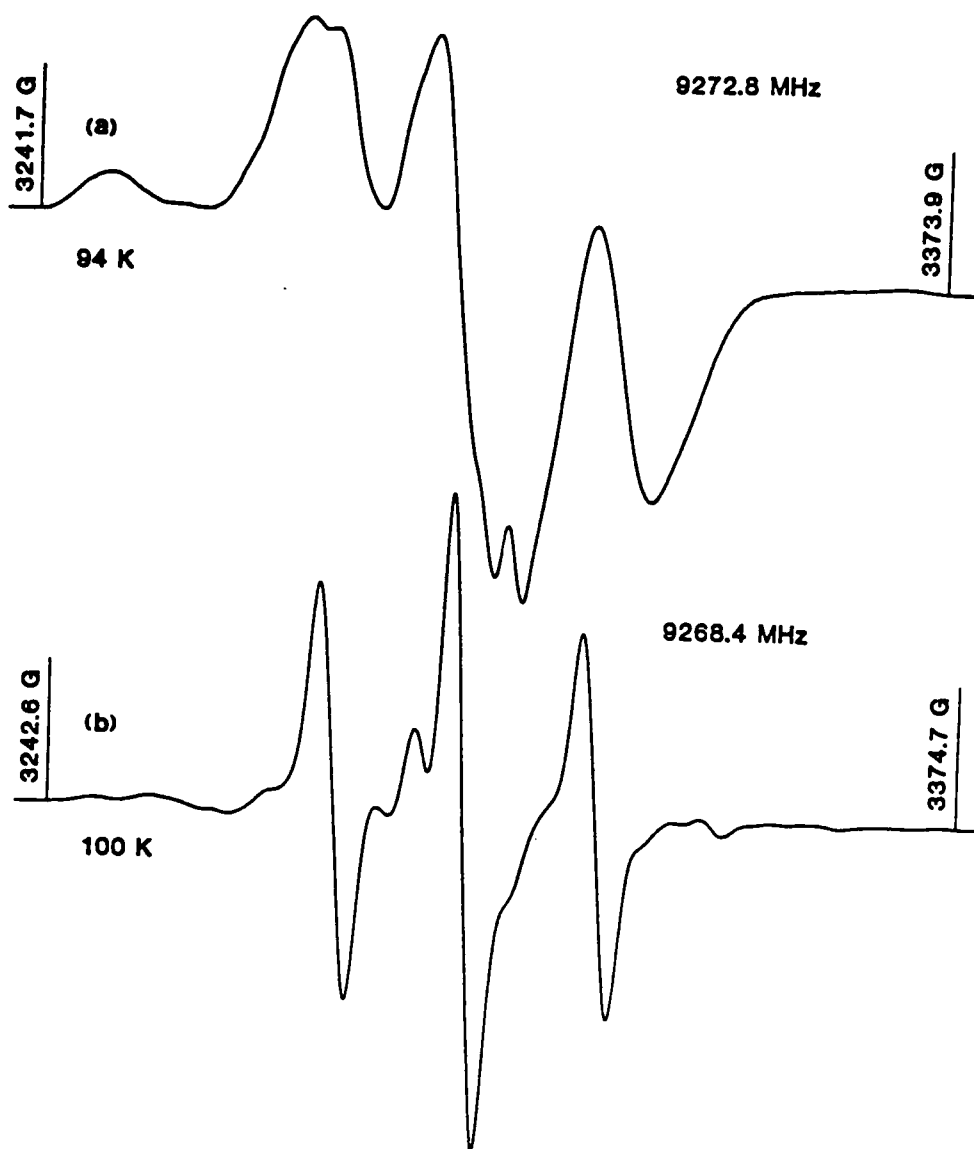


Figure 18. First-derivative ESR spectra of the localized form of the oxirane radical cation at two temperatures in SF_6 .

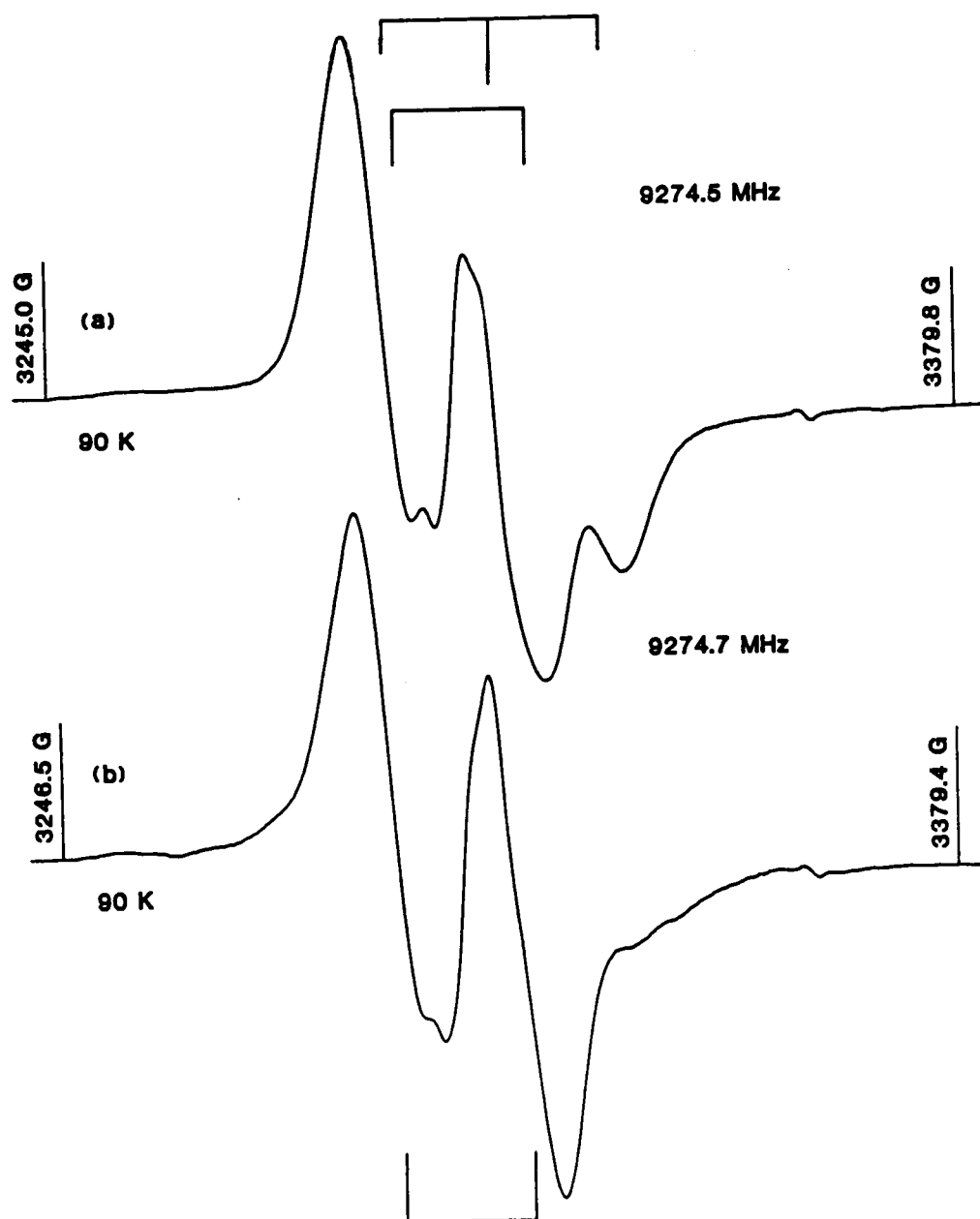


Figure 19. First-derivative ESR spectra of the ring-opened planar and ring-opened localized forms of the 1,2-D₂-oxirane radical cation in SF₆: (a) originally produced 90 K spectrum, and (b) recooled 90 K spectrum after annealing the sample to 95 K.

with the results for the nondeuterated oxirane. This can be clearly seen by the comparison of the intensity of the doublet in Figure 19a with that of the cooled-down spectrum shown in Figure 19b. The apparent doublet in Figure 19a is contributed by the intensity from both 1 and 4. When 1 decayed, the doublet signal intensity should therefore have decreased if 1 had not been converted to 4. However, the intensity of the doublet in Figure 19b is at least as strong as that in Figure 19a, indicating the efficient conversion of 1 to 4.

Above 120 K, as the signal from the doublet decayed, the linewidth became so sharp that the coupling from one D of the localized form 4 was resolved out. This is indicated by the lower stick diagram of Figure 20b, where the D coupling is found to be 3.5 G, in keeping with the expected value of 3.5 G calculated by dividing the corresponding proton hfc 23.2 G of the localized form 4 by 6.514. The higher stick diagram indicates the growth of the SF₅ radical in this matrix above 95 K.

These results nicely establish that (a) there are two species produced from the γ -irradiation of oxirane in this matrix from the beginning (77 K), one being the planar form 1, while the other being the localized form 4; and (b) the planar form is converted irreversibly to the localized form on annealing.

According to these results, it is expected that for the ¹³C-labeled oxirane cations in this matrix, there should also exist corresponding planar and localized forms from the beginning. Turning to the results, Figure 21a shows the ESR spectrum of the 1,2-¹³C labeled oxirane cation at 81 K in SF₆. As indicated by the stick diagram, the spectrum can be reconstructed in terms of an anisotropic triplet (57.2G) of quintets. The triplet splitting is larger than the proton hfc and can be readily assigned to the parallel features of the interaction from two equivalent ¹³C nuclei in the molecule. For the ring-opened planar species, the anisotropic hyperfine tensors of these two ¹³C nuclei should have a common principal axis system so as to give an anisotropic triplet with an intense central component. This triplet is further split into quintets (16.2 G) from the interaction with the four protons in the molecule. These results are similar to those found

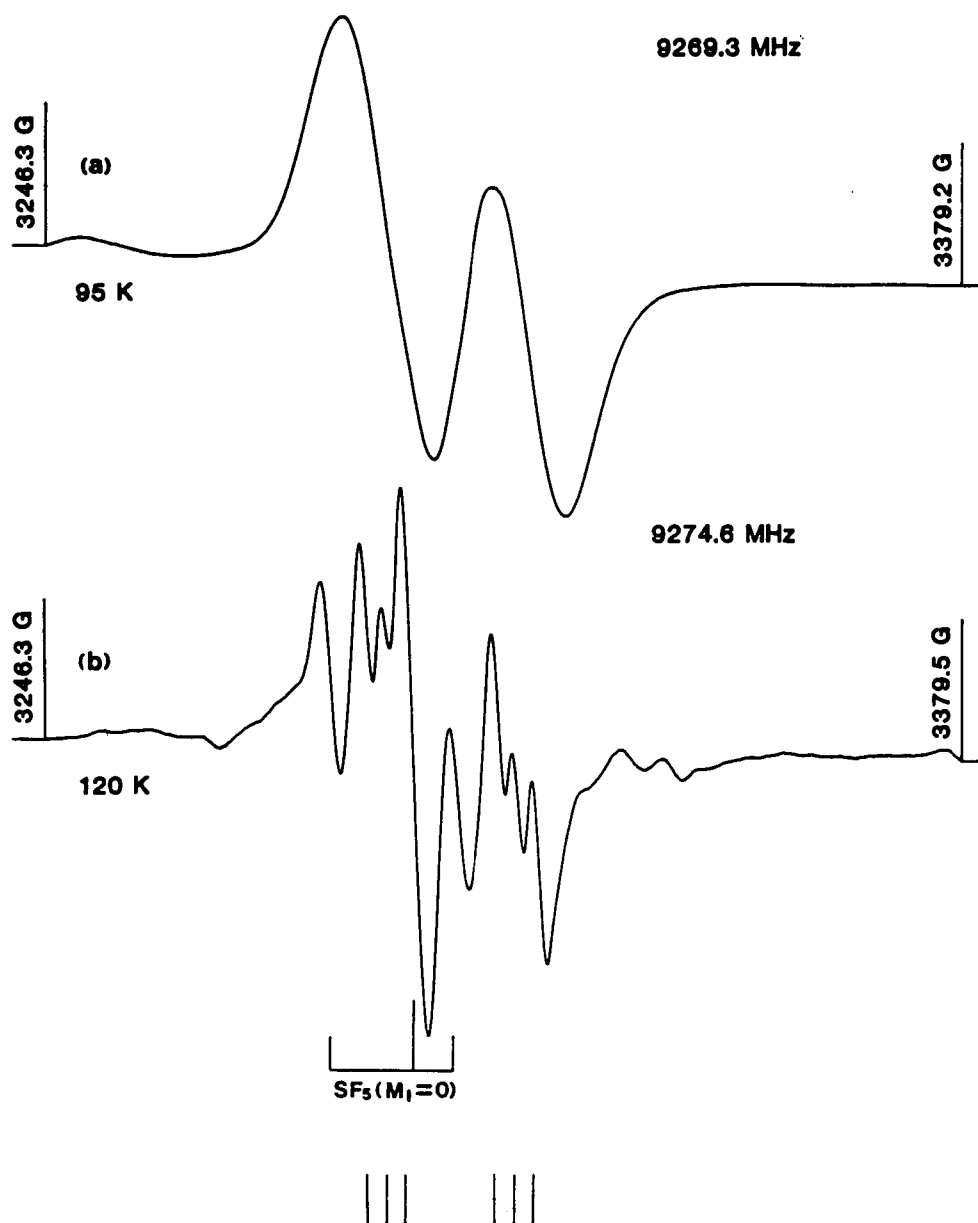


Figure 20. First-derivative ESR spectra of the localized form of the 1,2-D₂-substituted oxirane radical cation in two different temperatures in SF₆.

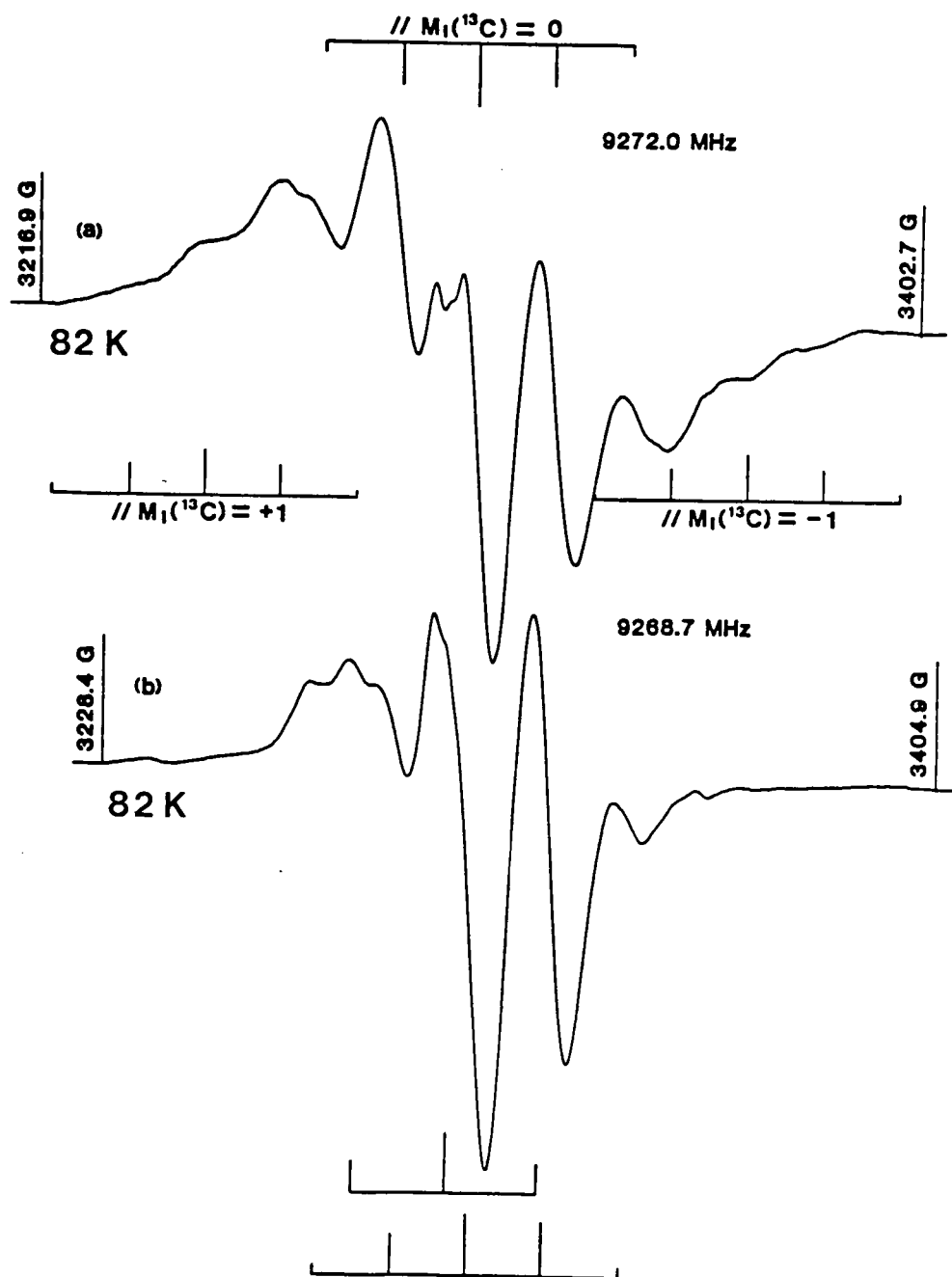


Figure 21. (a) First-derivative ESR spectrum of the ring-opened planar and the localized forms of the doubly C-13 labelled oxirane radical cation, and (b) the corresponding spectrum of the C-12 oxirane radical cation. These cations were radiolytically produced in SF_6 for a dose of 0.3 Mrad. The spectrometer gain of (a) is 8.0×10^4 , and that of (b) is 6.3×10^4 .

the F-11 matrix and assigned to the planar ring-opened structure,⁴⁴ the central quintet ($M_I = 0$ component of the triplet from the interaction of two ^{13}C nuclei) in this matrix being as intense as that in F-11, except for some distortion produced perhaps by signals from the localized species in the present spectrum. This fact establishes that the same ring-opened planar form of the oxirane radical cation was generated in these two matrices. The spectral differences in the two matrices are that (a) the $M_I = \pm 1$ components of the triplet in SF_6 are generally much broader than those in F-11, (b) no matrix interaction such as that in F-11 was observed in the present spectrum, and (c) the corresponding perpendicular features of the triplet from the interaction of two ^{13}C nuclei cannot even be tentatively identified in SF_6 because of the overlapping of the signals of the planar form with that of the localized form (vide infra). But these differences do not alter the above statement. To further verify the ^{13}C triplet assignment, the ^{13}C spectrum is compared with the ^{12}C spectrum shown in Figure 21b where the $M_I = \pm 1$ components of the triplet are clearly missing. Therefore, the above analysis is confirmed.

In contrast, the 23.1 G triplet from the localized form 4 that can be clearly seen in Figure 21b, the spectrum from the unlabeled oxirane, is not well defined in Figure 21a, the spectrum from the ^{13}C oxirane. The triplet (23.1 G) belonging to the localized form is lost in the ^{13}C spectrum. Actually, this is just what is expected. The reason is that the additional anisotropic hyperfine tensor for the single ^{13}C nucleus of the localized form greatly broadens the spectrum, as has been demonstrated previously for this localized form in $\text{CF}_2\text{CLCFCL}_2$. Hence the missing triplet (23.1 G) of the localized form in the ^{13}C case actually confirms the existence of the localized species identified from the ^{12}C spectrum. Moreover, this study further proved that the strong center quintet features observed in the ^{13}C case is indicative of the ring-opened planar form of the oxirane radical cation.

Upon annealing to phase transition of 95 K, the planar form decayed leaving a very complicated spectrum probably resulting from a mixture of the matrix radicals and the localized form. No attempt was

made to fully analyze those spectra. As a result, the conversion of the planar form into the localized form could not be followed for the ^{13}C oxirane radical cation. Nevertheless, this conversion is already clear from the studies of the oxirane cation and the 1,2- D_2 -oxirane cation in SF_6 , as mentioned earlier.

2. Cis- and Trans-1,2-Dimethyloxirane Cation in $\text{CF}_2\text{ClCCL}_3$

The ESR spectrum of the cis-1,2-dimethyloxirane radical cation in $\text{CF}_2\text{ClCCL}_3$ at 81 K is shown in Figure 22a. It consists of a 9-line or 7-line pattern with a hfc of 18.7 G and g-value of 2.0022. No matrix interaction causing fine substructures in the spectrum was observed. Upon warming to 95 K, this 9-line or 7-line pattern changed irreversibly to a much broader 9-line pattern shown in Figure 22b. The ESR parameters for the new spectrum are: $a(8\text{H}) = 16.4$ G and g-value of 2.0023. On cooling down the sample, this broad 9-line pattern was reversibly converted to a broad 8-line spectrum as was also found in F-11 by Snow⁵¹ and by Symons *et al.*⁴⁹ In fact, they assigned this broad 8-9 line pattern to the ring-opened planar radical cation of cis-dimethyloxirane.

The ESR spectrum derived from the radical cation of the trans-1,2-dimethyloxirane is given by Figure 23a. It consists of the same sharp 9-line or 7-line pattern as in the cis species since the hfc of 18.7 G and the g-value of 2.0022 are the same although the appearance of the spectra are somewhat different. Furthermore, this sharp 9-line or 7-line pattern was also converted to the same broad 9-line pattern with $a(8\text{H}) = 16.4$ G and g-value of 2.0023 (Figure 23b) upon warming up the sample to 95 K. This broad 9-line pattern also changed reversibly to an 8-line spectrum on cooling which is shown in Figure 23c. Clearly, the spectrum of the radical cation derived from trans-1,2-dimethyloxirane that is characterized by the broad 8-9 line patterns can be assigned to the same ring-opened cation as that produced from the cis-1,2-dimethyloxirane.

Turning to the structure of these ring-opened cations characterized by the 8-9 line pattern, since the hfcs from 8 protons (two α -protons and 6 methyl protons) are nearly identical, the

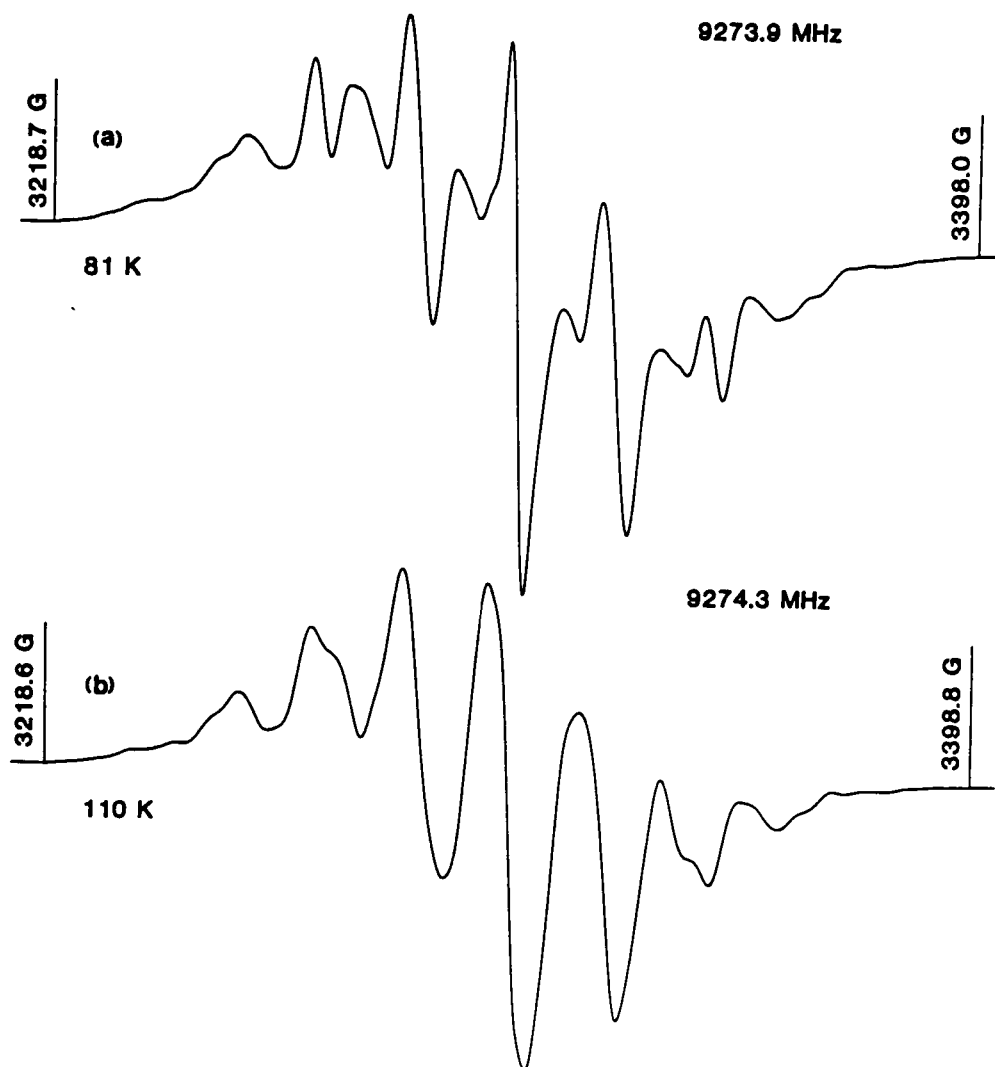


Figure 22. (a) First-derivative ESR spectrum of the radical species produced by γ -irradiation of the cis-1,2-dimethyloxirane in $\text{CF}_2\text{ClCCL}_3$, and (b) the first-derivative ESR spectrum of the ring-opened cis-1,2-dimethyloxirane radical cation in $\text{CF}_2\text{ClCCL}_3$.

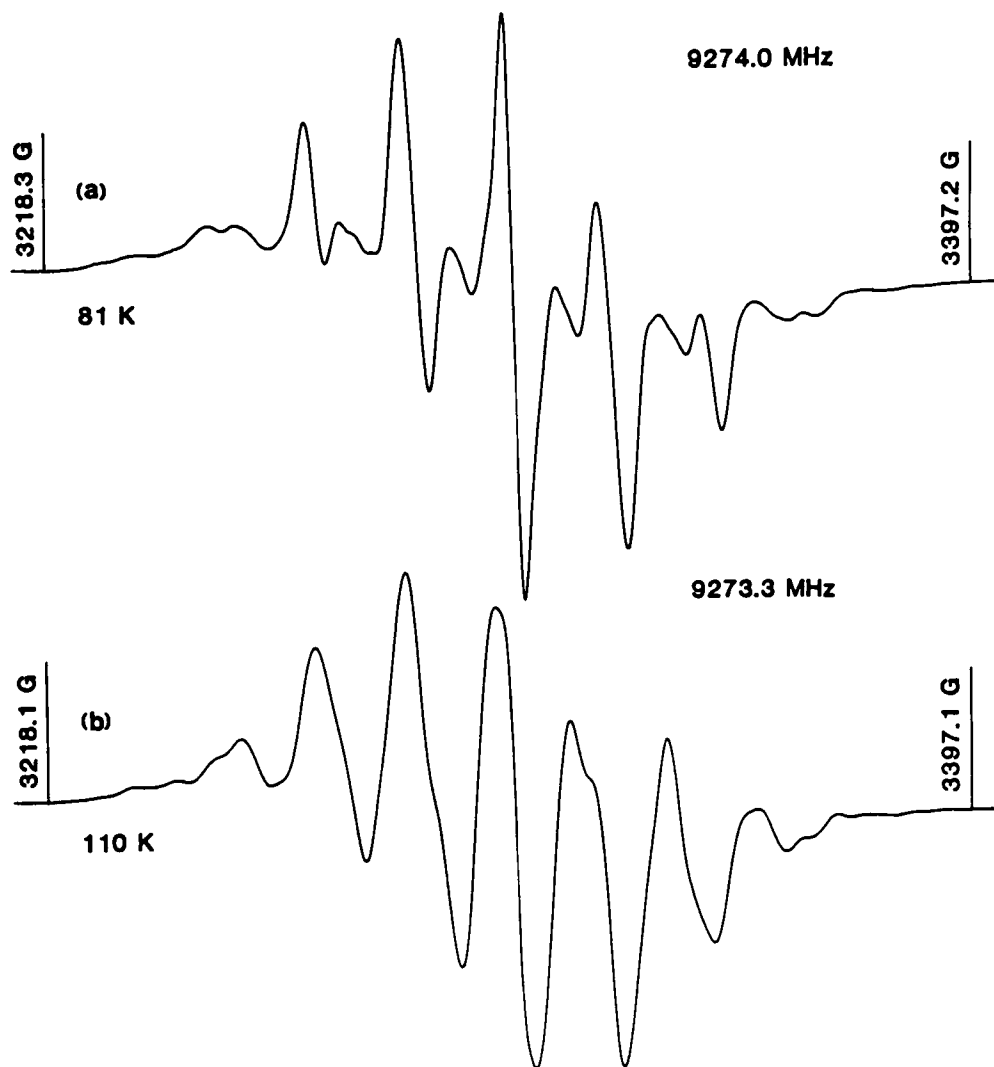


Figure 23. (a) First-derivative ESR spectrum of the radical species produced by γ -irradiation of the trans-1,2-dimethyloxirane in $\text{CF}_2\text{ClCCl}_3$, and (b) the first-derivative ESR spectrum of the ring-opened trans-1,2-dimethyloxirane radical cation in $\text{CF}_2\text{ClCCl}_3$.

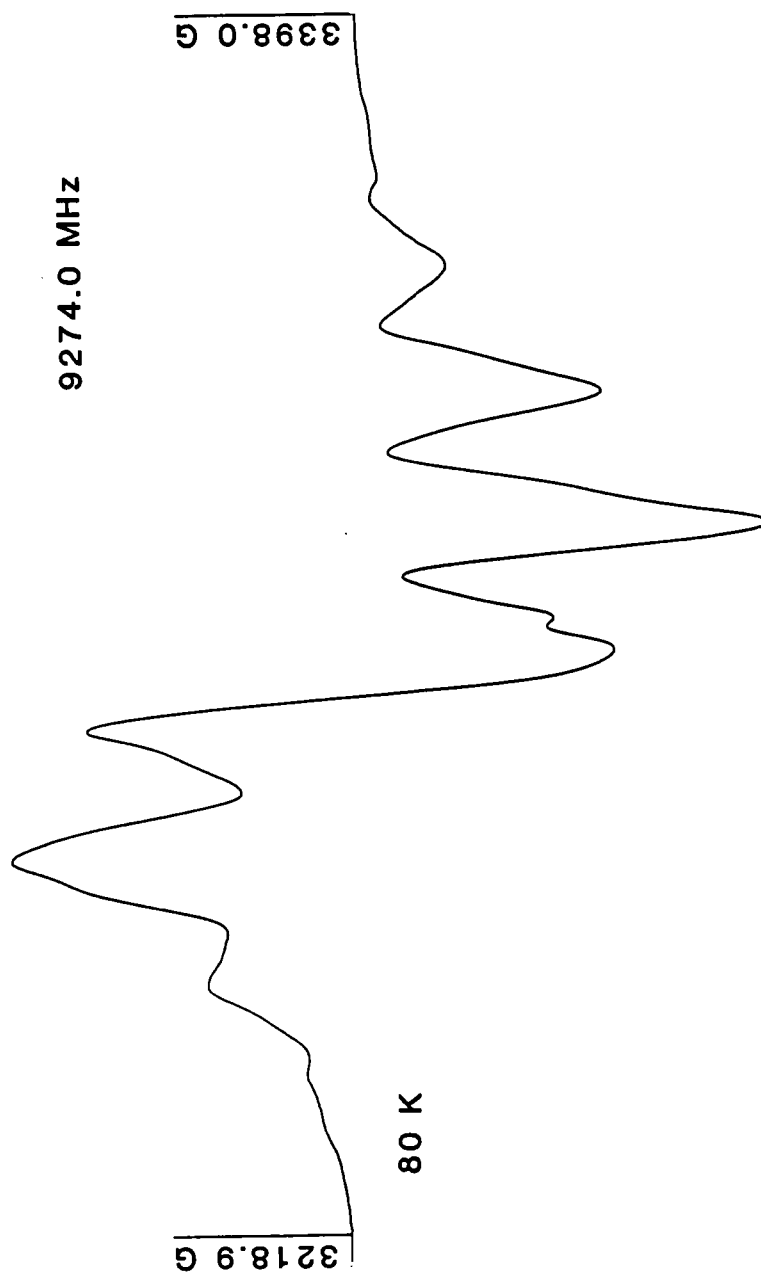


Figure 23. (c) First-derivative ESR spectrum of the radical cation derived from trans-1,2-dimethyloxirane at 80 K after annealing the sample to 95 K in $\text{CF}_2\text{ClCCl}_3$.

conformation of these cations that is likely to be the most stable is the one in which the two methyl groups are both in the exo-exo positions. The ESR assignment is consistent with a study of the 1,2-dimethylallyl radical,⁵² where the hfc difference between α -protons and the methyl groups is smallest for the exo-exo conformation as compared to any exo-endo combination of the methyl and proton arrangement. The other argument for the exo-exo conformation is the fact that the high temperature ring-opened radical cations have the same conformation from both cis- and trans-isomers on the basis of ESR parameters. It is hard to think that they can both ring open to, for example, the exo-endo conformation, since this requires that cis-isomer ring opens in a disrotatory manner while the trans-isomer ring opens in a conrotatory manner which are contradictory. On the other hand, that both cis and trans isomers become the most stable form (the exo-exo conformation) on warming is understandable because the energy barrier for the rotation around the C-O bond in the ring-opened planar oxirane cations is quite small.⁴⁷

The remaining problem is the assignment of the original sharp 9-line or 7-line spectrum, which will be discussed in next section.

The ESR parameters for the oxirane radical cation in SF₆ and for the cis- and trans-1,2-dimethyloxirane radical cations in CF₂ClCCL₃ are collected in Table IV.

C. Discussion

1. The Ring-Opening of the Oxirane Cation in SF₆

ESR spectra of the parent oxirane radical cation produced in SF₆ have been reported by Symons⁴⁹ for the ¹²C compound and by Snow⁵¹ for the ¹³C compound. However, neither groups showed that there are two cation species produced at 77 K. The present study has demonstrated this aspect clearly. One species is the ring-opened planar form 1. Unlike the F-11 results, there is agreement that the oxirane radical cation possesses the ring-opened planar form in SF₆.^{49,51} The evidence for this assignment comes from the strong central features of its ¹³C

TABLE IV

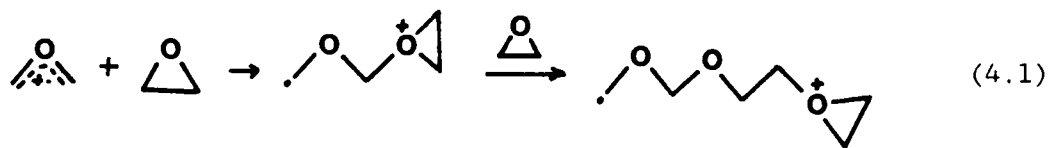
ESR PARAMETERS FOR THE RING-OPENED PLANAR AND RING-OPENED LOCALIZED
FORMS OF THE OXIRANE RADICAL CATION IN SF₆ MATRIX

Radical Cations	T/K	Hyperfine Couplings/G	g
CH ₂ OCH ₂ ⁺	82	16.2 (4H _α)	2.0025
CHDOCHD ⁺	82	16.2 (2H _α)	2.0025
¹³ CH ₂ O ¹³ CH ₂ ⁺	82	A (2 ¹³ C) = 57.2 G, a (4H _α) = 16.2 G	2.0024
+CH ₂ OĊH ₂	82	23.2 (2H _α)	2.0027
+CHDOĊHD	82	23.2 (1H _α)	2.0027
+CHDOĊHD	95	23.2 (1H _α), 3.5 (1D _α)	2.0027
+ ¹³ CH ₂ O ¹³ ĊH ₂	82	unidentified	

spectrum just as in the other Freons, as well as from appearance of the yellow color of the cation in SF_6 . The central feature is the $M_I(^{13}\text{C}) = 0$ component of the triplet arising from the two equivalent ^{13}C nuclei in the molecule. The existence of the sharp, strong central features requires that the hyperfine tensors of the two C-13 nuclei have common principal axes. This requirement is met, and is only met by the structure 1 since the p-orbitals of 1 are parallel to each other. This strong central feature will be totally lost for other structures of the oxirane cation, such as 2 and 3.^{44,50} From a tentative analysis, it was found that the anisotropic ^{13}C hfc's of the planar ring-opened oxirane cation in CCL_4 reported at 140 K appear to be different from the parameters found in F-11, but consistent with the isotropic values in these two matrices being the same.⁴⁴ This difference probably reflects greater motional averaging in the CCL_4 matrix. In SF_6 , the $M_I(^{13}\text{C}) = \pm 1$ components are much broader than those in F-11 probably due to the motional effect of the cation in this matrix. Hence, the isotropic hfc cannot be determined accurately, since the perpendicular features of the ^{13}C triplet could not be identified. Upon warming 1 decayed irreversibly so that a better-resolved spectrum for 1 could not be obtained. Nonetheless, the same strong center features observed in F-11 and the similar parallel hfc (57.2 G) obtained in the two matrices have established that the oxirane cation is the ring-opened planar form in F-11 as well as in SF_6 . It is noteworthy that whereas the ESR spectra of the ring-opened planar oxirane cation in F-11 display a weak interaction with the matrix, the ESR spectra of the ring-opened planar oxirane cation do not show such an interaction in SF_6 . The interaction of the matrix in the former case, although weak, may alter the optical nature of the ring-opened cation, therefore, and cause a slight different optical absorption in the two matrices. This is consistent with the study of the tetramethyloxirane radical cation which does not show a matrix interaction with F-11 molecule nor with SF_6 .⁵¹ Consequently it has the same reddish purple color in both matrices. It can then be concluded that color is not a good criterion for judging the ring-opening of the oxirane radical cation, because the color of the cations may be influenced by other factors.

The other species, namely the localized form 4, is also present initially at 77 K in SF₆. This is significant since this localized form has only previously been reported in F-113U.⁵⁰ This cation 4 is drawn as an orthogonal structure because this is a simplest way to look at it. However, there is also the possibility of a strong solvent or halogen anion interaction at the carbocation center as discussed in the case of cyclopropanes. In F-113U such interaction would give either a chloronium ion CFCL₂CF₂CL⁺CH₂OCH₂ or C-CL covalent bond. In a published paper,⁵⁰ this possibility has been carefully considered for the localized forms of the radical cation of oxirane and its derivatives on the basis of ESR hyperfine patterns, localized radical structures, and annealing studies. No supporting evidence for such interactions was obtained. In SF₆, there is no chlorine in the matrix. In this case the solvent or halogen anion interaction should bring about the formation of F₅SF⁺CH₂OCH₂ or a C-F covalent bond. However, although the linewidth of the ESR signals from the localized form became very sharp above 95 K, especially in the D-substituted localized form, where the D hfc was observed, no fluorine hfc was seen. Therefore even though the present study cannot exclude this kind of interaction completely, it does not lend any support for it. Interestingly, although the planar oxirane cation shows weak halogen hfcs in F-11 and F-113S, it does not change to the localized form even at their softening points. But in SF₆ and F-113U, although there is no such weak interaction observed for the planar form,⁵⁰ it changes to the localized form readily. It can then be concluded that such solvent or halogen anion interaction has no significant influence on the localized form formation.

The other possible explanation which was considered in the case of ring-opened cyclopropane cation³⁷ is the ion-molecule mechanism which accounts for the generation of the localized form by the following reactions:



In this sequence, the neutral oxirane molecule attacks the planar radical cation 1 by diffusion which causes the radical site of 1 to localize at one CH₂ site, while the positive charge is transferred from the cation 1 to the oxygen of the neutral molecule to give 5. This is followed by the C-O bond fission of 5 by the second oxirane molecule attack. This process can continue for many molecules. Therefore this sequence is actually a cationic polymerization process. Certainly this explanation is very reasonable on the basis of the fact that ion-molecule reactions are general in F-113U above 105 K and in SF₆ above 95 K, but not in F-11 and F-113S. The same situation has been discussed in the localized cyclopropane radical case (see Chapter III). The difficulty of this explanation is that Snow has demonstrated that cyclopentene oxide and cyclohexene oxide radical cations do not form the localized species in the F-113U matrix.⁵¹ In the present work it is further found that the cyclopentene oxide ring-opened radical cation actually undergoes an ion-molecule reaction to form the neutral radical in F-113U (Chapter IX). These findings do not favor the above interpretation because the cationic polymerization should proceed more easily for these species.⁵³

The other possible explanation for the formation of the localized oxirane cation is a specific solvation effect of the F-113U matrix as discussed for the cyclopropane radical cations. The driving force is the stronger solvation for the localized form than for the delocalized planar form, since the positive charge is more concentrated in the former radical. The energy release from the stronger solvation for the localized form can easily overcome the energy difference between these two forms which was reported to be only about 1.9^{47f} or 6.7^{47d} kcal mol⁻¹. The effectiveness of such a solvent effect may be due to the elastic property of the F-113U and SF₆ matrices, which is presumed to be absent in the F-11 matrix. This explains why the localized form was not observed in F-11 matrix. That the radical cations of cyclopentene oxide and cyclohexene oxide do not form the localized species can be accounted for by the fact that the twisting to form the localized form in these rings is much more difficult than in the open chain species, and therefore, in these cases the ion-molecule

reactions can compete with the generation of the localized form.

Just as in the cyclopropane case, no decisive evidence has been obtained to choose one of the above explanations. All these interpretations can explain some facts, but fail to explain some other facts. Therefore, while the formation of the localized species has been demonstrated experimentally, the clear interpretation of the formation mechanism still needs more work by different approaches and possibly by using other experimental methods in conjunction with ESR spectroscopy.

2. Cis- and Trans-1,2-Dimethyloxirane Cations in $\text{CF}_2\text{ClCCL}_3$

The broad 8, 9-line spectrum has been assigned to the exo-exo ring-opened form of the dimethyloxirane cation as mentioned above. The broad 9-line spectrum was observed above 95 K. Therefore the two $\text{CH}(\text{Me})$ groups may be able to rotate about the C-O bond to average the hfc's of the two α - protons and the six methyl protons. While the broad 8-line pattern may be considered as the spectrum for the fixed exo-exo conformer, since it was observed at low temperatures. Since the change of the sharp 9-line or 7-line pattern to the broad 8, 9-line pattern is irreversible; and these ESR patterns possess different hfc's and different line shapes, the sharp 9-line or 7-line pattern cannot be assigned to the exo-exo ring-opened form again. Careful examination of the low temperature spectra in Figure 22a (p 72) and in Figure 23a (p 73) reveals broad humps between the sharp 9-line or 7-line patterns, which are attributable to the 8-line pattern since these humps are at the right position of the broad 8-line pattern that becomes the main pattern in the recooled spectrum shown in Figure 23c (p 74). This fact further demonstrates that the sharp 9- or 7-line pattern is not the exo-exo ring-opened dimethyloxirane cation.

However, the assignment of the sharp 9- or 7-line pattern is still not clear. One of the possible assignments is the ring-closed $^2\text{A}_1$ form. The magnitude of the α -proton hfc for the ring-closed form is unknown. Therefore no direct comparison could be made. But the B value of 36.7 G for β -protons is known from the study of the 9,10-octatin oxide radical cation,⁵⁵ which is a well-established ring-closed cation. In terms of this value the hfc for a freely rotating methyl proton of

the ring-closed oxirane cation is calculated to be 18.8 G, in good agreement with the experimental value of 18.7 G. Although this gives support to the ring-closed form assignment, the expected g-shift of the ring-closed form was not observed in the 1,2-dimethyloxirane cases. Moreover, the parent oxirane radical cation, the tetramethyloxirane radical cation and cyclopentene oxide cation all have been unequivocally assigned to the ring-opened planar forms,⁵¹ it is very hard to think that the dimethyloxirane radical cations should be ring-closed under the similar conditions. AM1 calculations show that the ring-closed forms of these cations are 60 kcalmol⁻¹ higher in energy than the ring-opened planar form, therefore, the ring-closed form assignment seems less possible.

Another possible assignment of the sharp 9- or 7-line pattern is the endo-endo ring-opened cation of the dimethyloxirane. The reasoning is that in the low-temperature Freon matrix, many rigid Freon molecules are around the dimethyloxirane molecule. When the radical cation of the dimethyloxirane undergoes ring opening to form the exo-exo conformer, it has to push away these surrounding rigid Freon molecules, while it is empty in the inside of the dimethyloxirane, therefore the methyl groups likely rotate toward the inside to form the endo-endo conformer even though this conformer is higher in energy than the exo-exo conformer. The endo-endo conformer is converted to the exo-exo conformer irreversibly on annealing which can account for the observed spectral changes. More information is needed to clarify these points.

CHAPTER V

AZIRIDINE AND AZETIDINE RADICAL CATIONS

A. Introduction

Aziridine and azetidine are the nitrogen-containing heterocyclic compounds analogous to cyclopropane and cyclobutane, respectively. The radical cation studies of compounds in this class are not as extensive as those for the corresponding oxygen-containing compounds. For example, compared to the work on oxirane, the work on the radical cation of aziridine is very much limited. However, many nitrogen-containing compounds are involved in biological processes. Aziridine, for instance, is found to be a very important material in biological studies.⁵⁴ Therefore, the investigation of some nitrogen-containing radical cations from small ring compounds should be significant.

As demonstrated in the preceding Chapters, suitable matrices can be chosen to study different aspects of structure and chemistry of the radical cations derived from oxiranes and cyclopropanes. In this Chapter, this variable-matrix approach is also applied to study the aziridine and azetidine radical cations. It was found that the aziridine radical cation in F-11 at 77 K is a C...C ring-opened planar isomer, while the azetidine radical cation is a nitrogen-centered ring-closed isomer. These results correspond to those found for their oxygen counterpart species (oxirane and oxetane radical cations) in the same matrix. However, the aziridine radical cation does not become the localized isomer on annealing in F-113U in contrast to the oxirane cation. Instead, it undergoes an ion-molecule reaction with its parent molecule to produce the 1-aziridinyl radical. The azetidine radical cation behaves similarly to form the 1-azetidiny radical.

The aziridine radical cation had been studied in the gas phase by Holmes *et al*⁵⁵ before the present work. However, they were unable to determine whether the aziridine radical cation is ring-closed or ring-opened on the basis of their mass-spectrometric study. The detection of the ring-opened aziridine radical cation in this work is

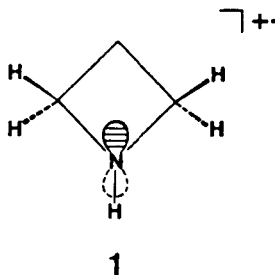
therefore of particular interest.

B. Results and Discussion

1. Azetidine Radical Cation

The ESR spectrum of the azetidine radical cation in F-11 is shown in Figure 24. As indicated by the stick diagram for the center sharp lines, it comprises mainly a binomial quintet (54.2 G) of doublets (22.6 G) pattern. The quintet belongs to the interaction from the four protons adjacent to the nitrogen. The doublet is ascribed to the N-H proton interaction. The humps between the main features arise from ^{14}N interaction. Unfortunately, because of the overlapping in this region, no clear analysis can be obtained from these humps. To avoid the overlapping problem, the approach is to examine the outermost peaks. Indeed, this examination reveals some broad doublet features on both wings. These features are assigned to the parallel and perpendicular $M_I = \pm 1$ components of the ^{14}N interaction as indicated by the stick diagram on both wings. The assignment is based on: (a) the spacing of the parallel and perpendicular doublets on both wings are equal to that of the main pattern indicating that the hyperfine couplings are nearly isotropic; and (b) the parallel and perpendicular features of the ^{14}N interaction are temperature-dependent, as shown by two sets of values at 90 K and 140 K in Table V, but the isotropic ^{14}N hfc remains unchanged.

The ESR parameters for the azetidine radical cation are clearly indicative of a ring-closed nitrogen-centered structure 1.



The isotropic ^{14}N hfc obtained as well as the hfc from the N-H proton is very similar to those of the nitrogen-centered dimethylamine

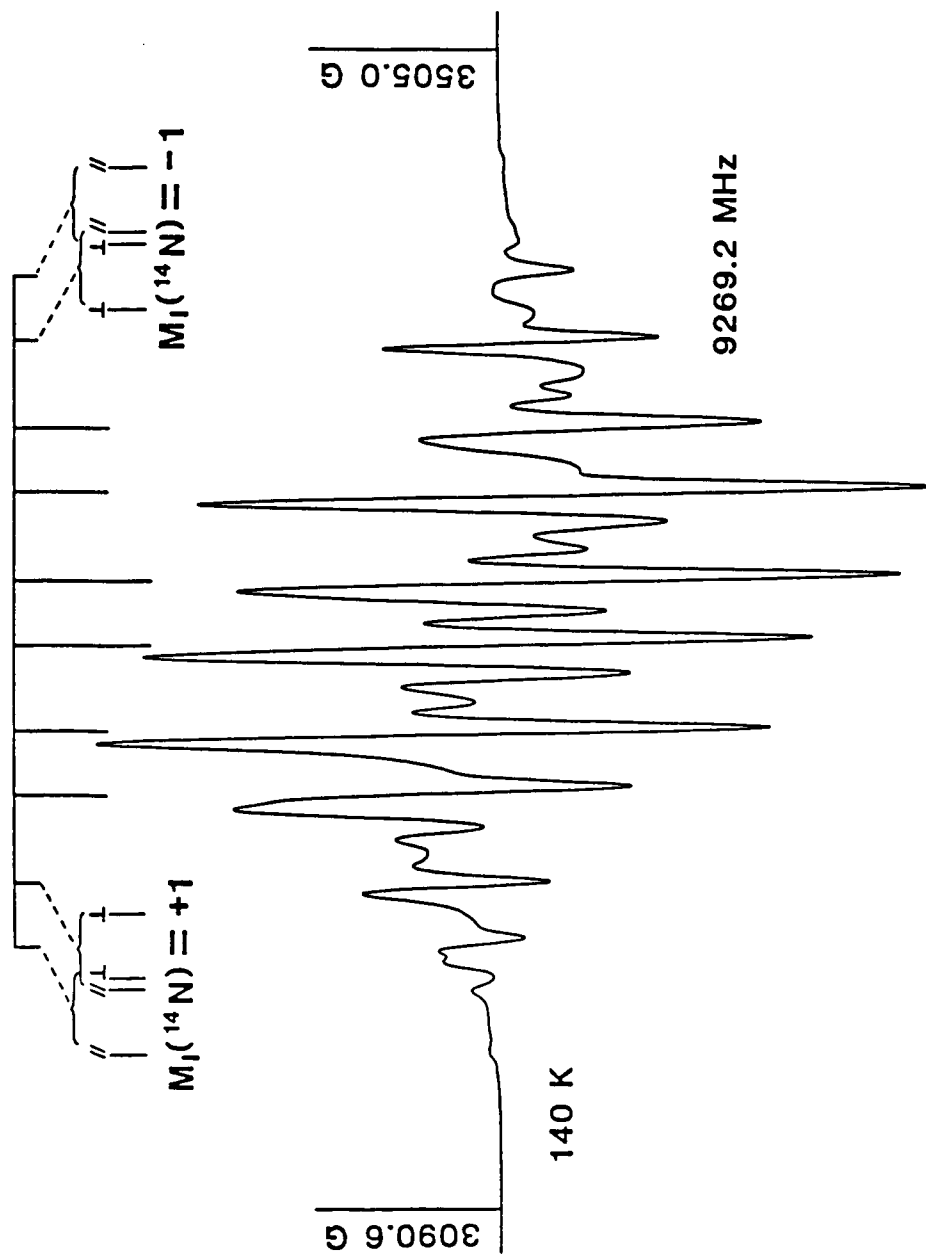
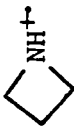


Figure 24. First-derivative ESR spectrum of the ring-closed azetidine radical cation in F-11. The stick diagram reconstructs the spectrum by a binomial quintet (4H) of doublets (1H) pattern at center and the outermost parallel and perpendicular $M_I = \pm 1$ components of a ^{14}N hyperfine interaction at both sides.

TABLE V

ESR PARAMETERS FOR THE RADICAL CATIONS OF AZIRIDINE
AND AZETIDINE AND RELATED SPECIES

Radical Cations	Matrix	T/K	Hyperfine Couplings/G	g
	F-11	140	22.6 (N-H), 54.2 (4H β) A $_{\text{H}}$ (^{14}N) = 38.2 G, A $_{\text{L}}$ (^{14}N) = 9.5 G, A $_{\text{iso}}$ = 19.1 G	2.0038
		90	22.6 (N-H), 54.2 (4H β), A $_{\text{H}}$ (^{14}N) = 41.4 G, A $_{\text{L}}$ (^{14}N) = 8.0 G, A $_{\text{iso}}$ = 19.1 G	2.0037
CH ₂ NHCH ₂ ⁺	F-11	150	16.1 (4H β), 4.3 (N-H), 7.7 (^{14}N), 2.7 (1F)	2.0026
CH ₂ NDCH ₂ ⁺	F-11	150	16.1 (4H β), 0.66 (N-D), 7.7 (^{14}N), 2.7 (1F)	2.0026
CH ₂ OCH ₂ ⁺	F-11	145	16.3	2.0022
CH ₂ =CH- $\dot{\text{C}}\text{H}_2$	MeCH=CH ₂	143	14.8 (2H $_{\text{exo}}$), 13.9 (2H $_{\text{endo}}$), 4.1 (C-H)	2.0026

cation.⁵⁶ Moreover, in terms of the $B\cos^2\theta$ relation for the β -proton hfc's and the $a(6H_\beta) = 34.3$ G from the dimethylamine cation, the hfc from the interaction of four protons in the ring is calculated to be 51.45 G which is close to the observed value of 54.2 G. Interestingly, the hfc's of the four β -protons in the four-membered heterocyclic compounds have the tendency: 65.5 G (oxetane) > 54.2 G (azetidine) > 31.4 G (thietane).

2. Aziridine Radical Cation

The ESR spectrum of the aziridine radical cation in F-11 is shown in Figure 25. The total width of the spectrum is 87 G, only about 0.28 that of the azetidine radical cation (ca. 316 G). If the aziridine cation was the nitrogen centered ring-closed structure, the total width of its spectrum were expected to be about 152 G according to two assumptions: (a) the ratio of β -couplings of the ring-closed aziridine cation over the ring-closed azetidine cation is assumed to be 0.52 derived from the sulfur-centered thiirane and thietane cations (see Chapter V); and (b) the N-H coupling of aziridine cation is assumed to be 22.6 G which is not changed from azetidine to aziridine, only the β -couplings being changed as the ring size is changed. The much narrower total width (87 G compared with 152 G) thus clearly excludes the nitrogen-centered ring-closed structure assignment.

The analysis of the spectrum of the aziridine-N-h radical cation is not straightforward. In order to simplify the spectrum, aziridine-N-d was made. The ESR spectrum of the deuterated radical cation in F-11 is shown in Figure 26. This spectrum is recognized as a quintet (16.1 G) of 1:1:1 triplets (7.7 G) with the quintet spacing about twice the triplet spacing. The quintet is obviously due to the interaction from four β -protons while the 1:1:1 triplet is attributed to the ^{14}N interaction. The total spectral width difference between the radical cations of N-h and N-d species is about 5 G that is the indicative of the coupling of the N-H proton. Based on this information, the spectrum for the aziridine-N-h radical cation was best simulated by $A(4H) = 16.1$ G, $A_{\text{N-H}} = 4.3$ G, $A(^{14}\text{N}) = 7.7$ G, and $a(1F) = 2.7$ G. The additional doublet of 2.7 G is used to fit the substructures on each component of

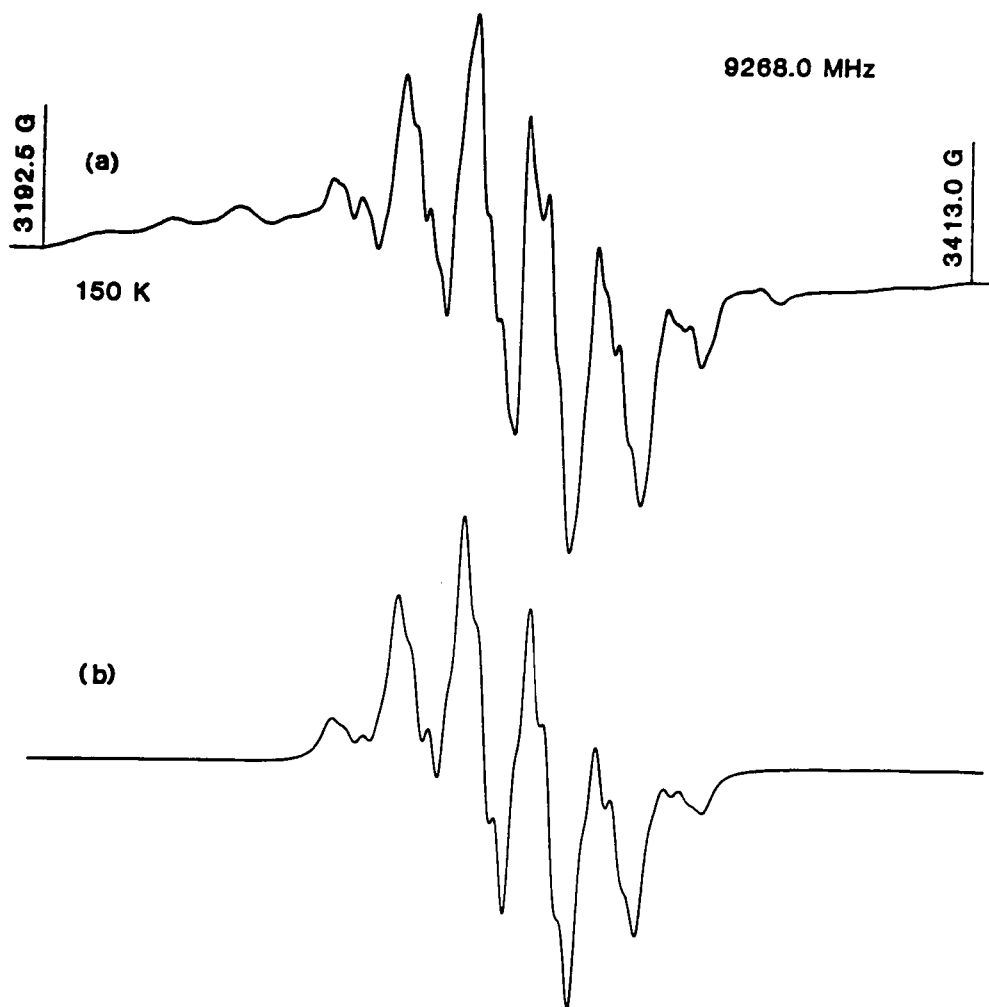


Figure 25. First-derivative ESR spectra of the aziridine radical cation in F-11: (a) experimental, and (b) simulation by using ESR parameters in TABLE V and a Lorentzian linewidth of 3.0 G.

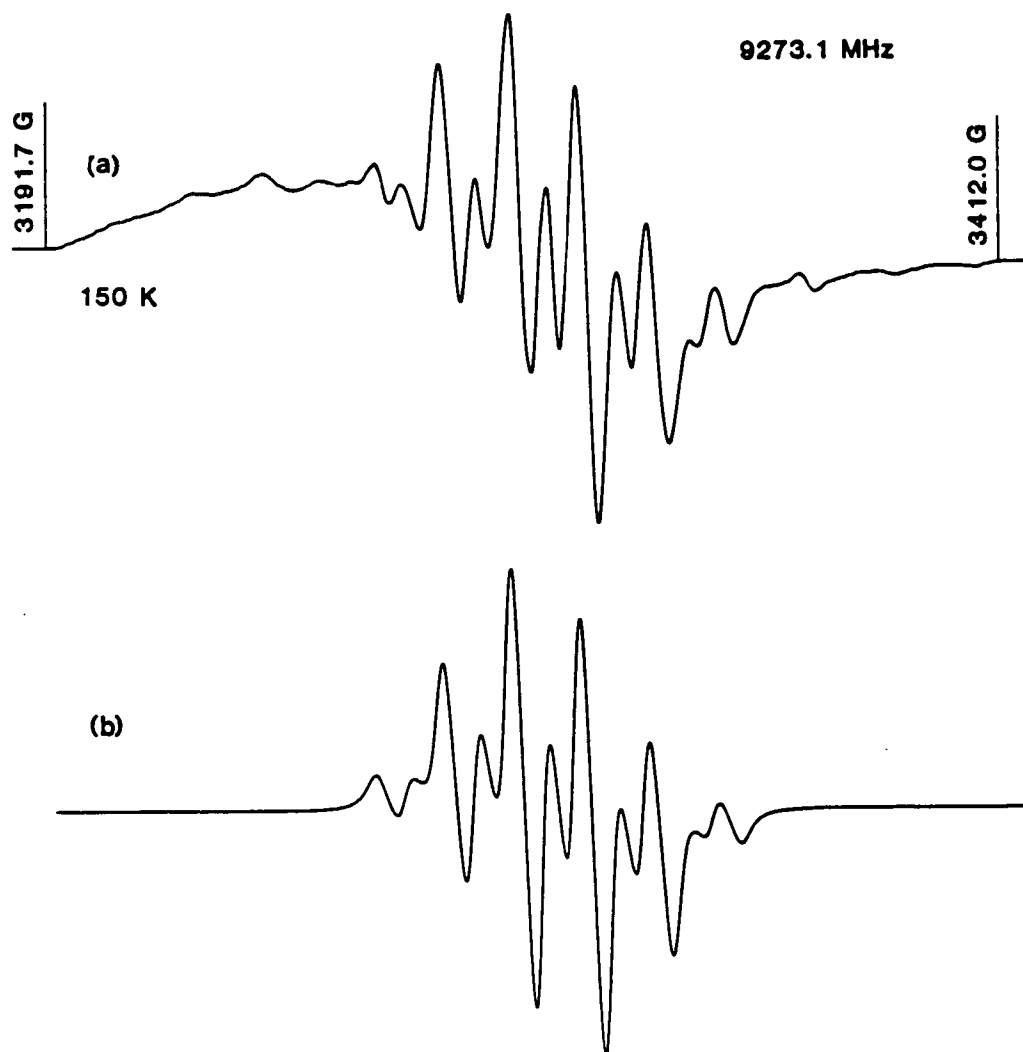
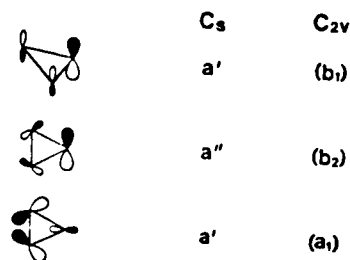


Figure 26. First-derivative ESR spectra of the aziridine-N-D radical cation in F-11: (a) experimental, and (b) simulation by using ESR parameters in TABLE V and a Lorentzian linewidth of 3.0 G.

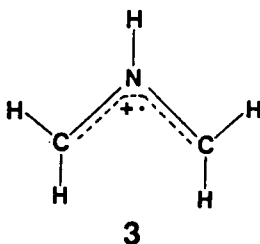
the main six-line pattern. This hfc might arise from the interaction of fluorine of the matrix, or the chlorine of the matrix. Such a matrix interaction was also observed in the oxirane cation-F-11 system.⁵⁰ After satisfactorily simulating the N-h species, the next step is to simulate the N-d species by replacing 4.3 G of the N-H coupling by 0.66 G of the N-D coupling and maintaining all other couplings. The simulation shown in Figure 26b fits the experimental spectrum very well which then confirms the analysis. The other way to simulate the N-h spectrum is to use the sets of couplings: $A_{\text{exo}}(2\text{H}) = 17.2$ G, $A_{\text{endo}}(2\text{H}) = 14.0$ G, $A_{\text{N-H}}(1\text{H}) = 4.3$ G, and $A(^{14}\text{N}) = 7.7$ G. The excellent fit to the N-h spectrum can be obtained without using the additional 2.7 G coupling. However, the corresponding simulation for the N-d spectrum does not fit very well. Therefore this possibility is ruled out. Clearly the obtained ESR parameters further argue against the assignment of the ring-closed aziridine cation, since this nitrogen-centered radical cation should give much larger proton and nitrogen couplings as those of the ring-closed azetidine cation mentioned earlier. That the ring-closed aziridine cation must be the nitrogen-centered radical cation is demonstrated by the photoelectron spectroscopy study,^{57,58} which showed that the highest three molecular orbitals of aziridine are a' , a'' and a' in structure 2.



2

Clearly, the nitrogen-centered ring-closed radical cation is the ground state a' in which the spin is mostly at nitrogen. Only the excited a' state analogous to the $^2A_1$ state of the ring-closed oxirane cation could give more suitable spin distribution in a ring-closed cation to fit the ESR data, but this is ruled out readily by the unfavorable energetics.

As mentioned in the introduction, mass spectral study did not distinguish between the ring-opened and ring-closed cations.⁵⁵ On the other hand, theoretical calculations have long predicted that the planar ring-opened aziridine radical cation is $26.5 \text{ kcal mol}^{-1}$ more stable than the ring-closed cation.⁵⁹ The observed spectrum in F-11 is then assigned to the ring-opened planar radical cation 3 in terms of the ESR data and the theoretical calculations.



This structure is isoelectronic with the ring-opened oxirane cation as well as the allyl radical. The g -values and the proton hfcs for these radicals are collected in Table V for comparison. Clearly, they are very similar indicating that they possess similar structures. The isotropic ^{14}N coupling of 7.7 G for the aziridine cation is also reasonable since the most spin in 3 is placed on the two carbons. Unfortunately, the ^{13}C coupling for the 2-carbon of the allyl radical is not available to make a direct comparison.

3. Ion-Molecule Reactions

One of the suitable matrices to study ion-molecule reactions is F-113U. The low temperature spectra obtained from azetidine are found to be similar to that observed in F-11 matrix, indicating that the same radical cation was produced. On annealing to 100 K, however, some irreversible change occurred. The original radical cation decayed accompanied by two observations: (a) its ESR spectrum became better resolved; and (b) some strong, new signals grew in. The change was complete after several minutes giving a new anisotropic spectrum. This spectrum became well resolved at 115 K which is shown in Figure 27a. As can be seen, it consists of a quintet (38.4 G) of 1:1:1 triplets ($a(^{14}\text{N}) = 13.6 \text{ G}$) that are identical to those reported for the 1-azetidiny radical in the liquid phase.⁶⁰ Therefore, the above

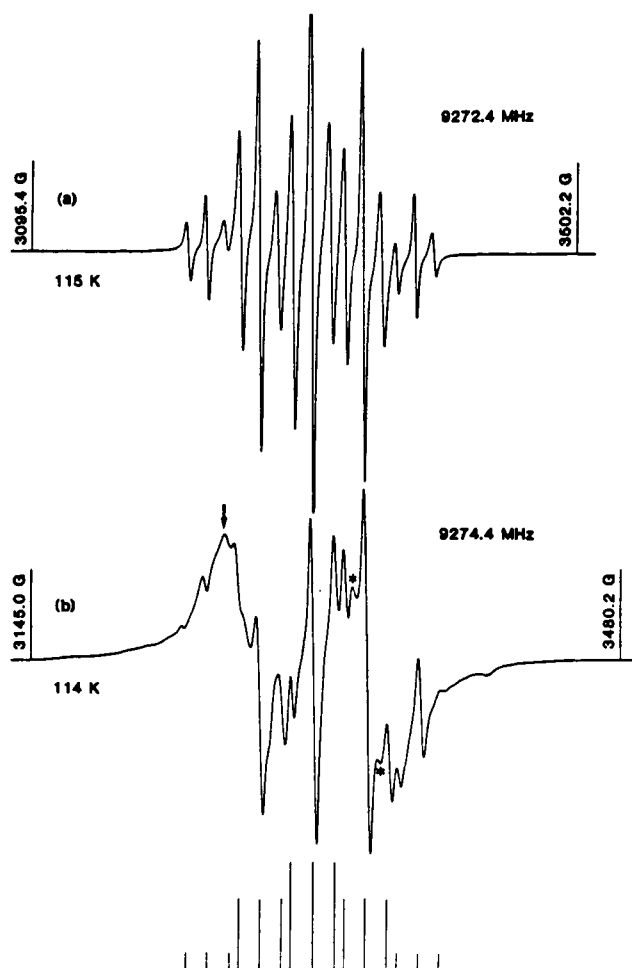


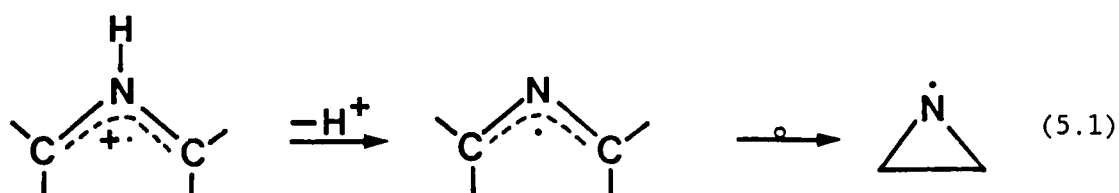
Figure 27. (a) First-derivative ESR spectrum of the 1-azetidiny radical in F-113U, and (b) First-derivative ESR spectrum of the 1-aziridinyl radical in F-113U, the stick diagram in b indicates the components belonging to the 1-aziridinyl radical while the * indicates the unidentified species and the arrow indicates the matrix signal.

results described that the ring-closed azetidinium radical cation reacted with its parent molecule to form 1-aziridinyl radical around 100 K.

The aziridine radical cation, on the other hand, was not even detected at 80 K. The neutral 1-aziridinyl radical was produced from the beginning. This is probably owing to the easier aggregation of the smaller aziridine molecules. Therefore the ion-molecule reaction took place during the irradiation process within the aggregates rather than on annealing by the diffusion of the cations or molecules. The low temperature spectra of this radical are anisotropic which only show a quintet from the interaction of the four β -protons (the $M_I(^{14}\text{N}) = 0$ components). The other $M_I(^{14}\text{N}) = \pm 1$ components are too broad to be seen. On warming up to 115 K, although some matrix radical signals grew up to distort the spectrum, the $M_I(^{14}\text{N}) = \pm 1$ components became partly resolved as shown in Figure 27b. This spectrum can be clearly analyzed as a quintet (30.3 G) of 1:1:1 triplets ($a(^{14}\text{N}) = 12.4$ G). These parameters are almost the same as those reported for the 1-aziridinyl radical in solution.⁶⁰ Therefore, the radical can be assigned to the 1-aziridinyl radical unambiguously.

As will be discussed in detail in Chapter IX, the ion-molecule reactions can be described as either proton loss or hydrogen atom transfer. The ion-molecule reaction of the azetidinium radical cation with its parent molecule gives the same radical product from these two pathways; therefore, no distinction can be made from the present study between these two choices. The situation for aziridinyl radical generation is somewhat complicated. Since the radical cation of aziridine is the ring-opened planar isomer, if it donates a proton to its parent molecule, the formed neutral radical should be CH_2NCH_2 . This is an interesting species because it has never been described in the literature. Unfortunately this species was also not detected in the present study on annealing; the only species observed is the 1-aziridinyl radical which indicates that the CH_2NCH_2 is not stable under the condition it was produced, instead it underwent ring closure immediately after its formation. This finding is also interesting in comparison with the results from the cyclopropylamine radical cation studies (Chapter VII) where it will be shown that in the neutral

radical case the spin tends to stay on the nitrogen whereas in the radical cation case the spin tends to stay on carbons. Similarly in the present case if it is the radical cation, the aziridine cation becomes the ring-opened planar form rendering the spin mainly on the two carbons, whereas if it is the neutral radical CH_2NCH_2 the spin tends to move to nitrogen by the ring-closure to form aziridiny radical as shown by the following equation:



However aziridine radical cation can also abstracts a hydrogen from the neutral aziridine molecule to form the 1-aziridiny radical. In this latter case no CH_2NCH_2 is formed as the intermediate. This latter possibility cannot be ruled out by the information from the present study.

CHAPTER VI

THIIRANE AND THIETANE RADICAL CATIONS

A. Introduction

In this Chapter, the radical cations of the three- and four-membered sulfur-containing rings, thiirane and thietane, were studied in detail. The two main important findings of these studies are: (a) the radical cation of thiirane, as well as that of thietane, was found to be ring-closed, in contrast to the cases of the oxirane and aziridine cations. This finding gives an opportunity to describe the extent of hyperconjugation as a function of ring size in heterocycloalkanes; and (b) ethylene molecule was found to be excluded via the dissociation of the thiirane dimer radical cation. This novel ion-molecule reaction was only reported in the gas phase,⁶¹ but has not been reported in the solid state before. In addition, the results in this Chapter disprove, or further disprove two literature errors: (a) the hfc due to the interaction of four protons of the thiirane radical cation was incorrectly shown to be 31.0 G⁶² instead of the correct value of 16.1 G reported here; and (b) the five-line pattern observed after γ -irradiation of ethylene in F-113U was incorrectly assigned to the ethylene radical cation.⁶³ This error was first pointed out by Fujisawa *et al.*,⁶⁴ but the present work provides clearer evidence to argue against the assignment.

B. Results and Discussion

1. Thietane Monomer Radical Cations

Thietane monomer radical cation was observed in F-11 from 80 K to 160 K. A typical example of its ESR spectra is shown in Figure 28. As indicated by the stick diagram, this spectrum consists of two binomial quintet patterns, one related with $g_{\perp} = 2.027$ at low field,

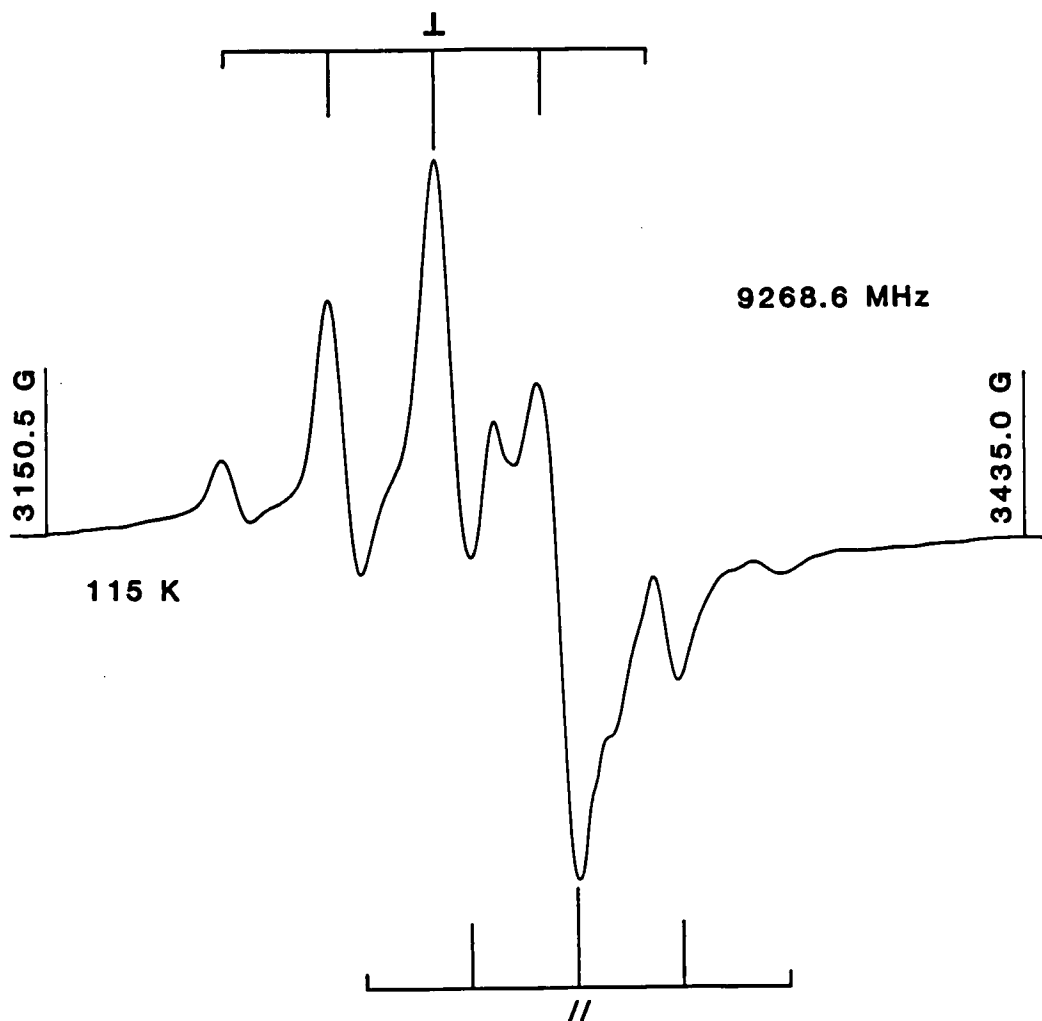
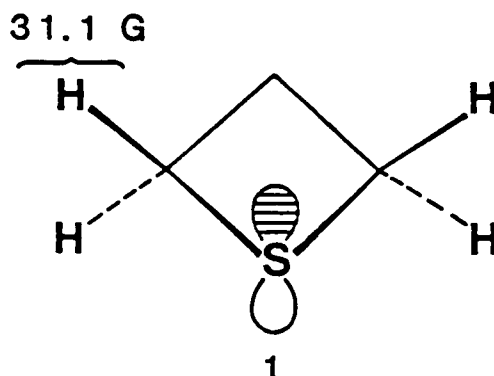


Figure 28. First-derivative ESR spectrum of the monomer thietane radical cation in F-11. The stick diagram reconstructs the parallel and perpendicular features of this cation.

and the other with $g_{\parallel} = 2.008$ at high field. The β -hfc ($A(4H) = 31.1$ G) is nearly isotropic. The spectrum is then confidently assigned to the ring-closed thietane monomer radical cation 1 on the basis of the following considerations: (1) the g -tensor of this cation is similar to that of the ring-closed oxetane cation ($g_{\perp} = 2.0046$ and $g_{\parallel} = 2.0135$);⁴² and (2) by using the $B\cos^2\theta$ -relationship for the β -hfcs, the calculated β -hfc for the ring-closed structure 1 is 30.6 G by taking the hfc of 20.4 G of the dimethyl sulfide cation⁶⁵ as reference which is in good agreement with the observed value. The corresponding calculation of the β -hfcs is also applicable to the ring-closed oxetane cation - dimethylether cation pair.⁴² However, the β -hfcs in the thietane and dimethyl sulfide cations are lower than those in the oxetane and dimethyl ether cations^{42,65} by a factor of 0.47, respectively. This is attributable to the poorer overlap of the s -orbitals of the β -protons of these two species with the more diffuse sulfur orbitals.



2. Thietane dimer Radical Cations

The thietane dimer radical cation was detected in both F-113S and F-113U matrices. In these matrices, however, the monomer cation has not been detected.

The ESR spectrum of the thietane dimer cation in F-113S at 120 K is shown in Figure 29a. The lower temperature spectra are not as well resolved as this spectrum. Above 120 K, the spectra remained little changed up to 145 K. Except some distortions at high field, the 120 K spectrum comprises a binomial nonet pattern ($A(8H) = 8.7$ G) just expected for the dimer cation as indicated by the stick diagram.

The assignment is further confirmed by comparisons of the hfc

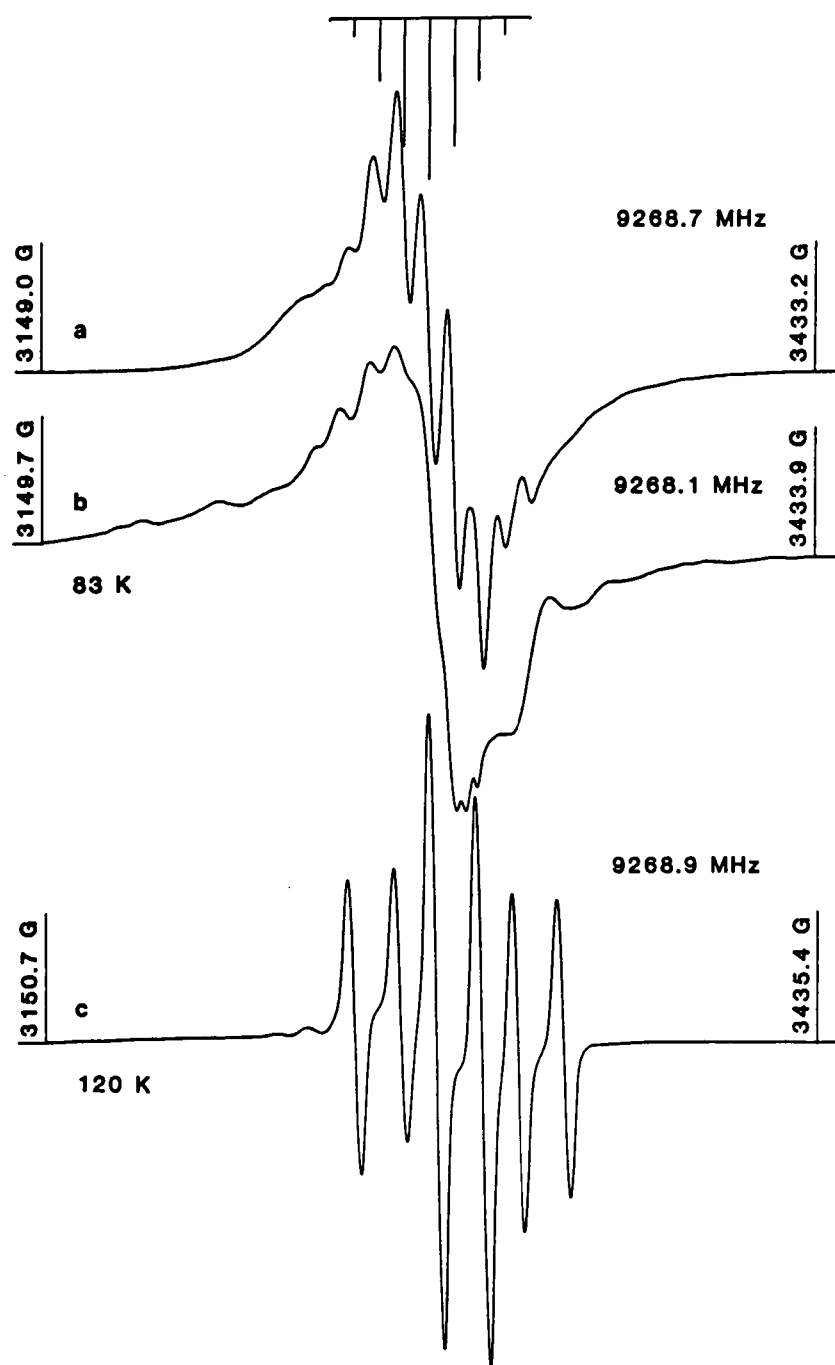


Figure 29. First-derivative ESR spectra of the thietane dimer radical cation in F-113S (a), and in F-113U (b), and its reaction product thietane-2-yl radical in F-113U (c).

and the average g value of this pattern with the known parameters for the dimer cation of dimethyl sulfide.^{66,67} First, the average g -values of these two species are very similar (2.012 for thietane dimer and 2.010 for dimethyl sulfide dimer); and secondly, the ratio of the hfc to the β -protons for the thietane dimer ($A(8H) = 8.7$ G) over that for the dimethyl sulfide dimer ($A(12H) = 6.3$ G) is about 1.5, which is about the same as that found for their corresponding monomer species (31.1 G/ 20.4 G = 1.5).

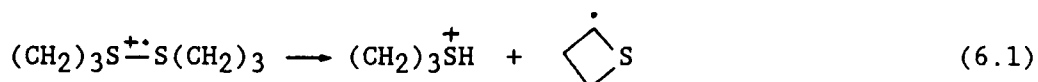
The low temperature spectrum of the dimer radical cation in F-113U is shown in Figure 29b. Although this spectrum is not as well resolved as Figure 29a for the dimer cation in F-113S, they can match very well. The g values obtained from two spectra are also the same. Therefore there is little doubt that the dimer cation was also produced in F-113U at low temperatures. The better resolved spectrum for the dimer species could not be obtained in F-113U, since above 105 K, the thietane dimer cation decayed, accompanied by the growth of the carbon-centered 2-thietanyl radical shown in Figure 29c. The assignment of this radical is clear-cut in terms of a triplet (29.5 G) of doublets (16.4 G) pattern of its spectrum with a g -value of 2.0043. Ion-molecule reactions can sometimes be detected in F-113S above 145 K. But this matrix has two disadvantages: (a) the matrix radical CF_3CCL_2 grows strongly above 145 K,⁶⁸ which often obscures the observation of the product radicals; and (b) the matrix becomes softened above 145 K so that radicals produced from the ion-molecule reactions decay too fast to be detected. However, the 2-thietanyl radical was detected after the decay of the dimer cation in F-113S since it is quite stable and its spectrum is wider than the matrix-radical spectrum.

3. The Structure of the Thietane Dimer Cation and its Dissociation

The determination of the dimer cation structure is again based on the comparison of the thietane dimer cation with the dimethyl sulfide dimer radical cation. The latter was shown to possess the σ^* antibonding SOMO made up of the two p -orbitals of sulfur atoms from the studies in solutions⁶⁶ as well as in Freons.⁶⁵ The thietane dimer cation is considered to also possess the similar σ^* SOMO on the basis

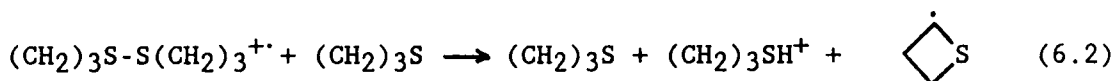
of (a) the ratio of the β -proton hfcs for the thietane monomer and dimer species is about three rather than two. This ratio of three was described to be associated with a σ^* SOMO of the dimers in the studies on Me_2S dimer cation.⁶⁵ In contrast, the corresponding ratio associated with a σ SOMO of the dimer cation like Me_6Ge_2 was shown only to be 1.1,⁶⁵ and (b) the average g-value of the thietane dimer cation is 2.012, reasonably close to the isotropic value of 2.010 for the $(\text{Me}_2\text{S})_2^+$ species in solutions.⁶⁶ The isotropic g-value around 2.010 is indicative of the σ^* radicals.^{65,66}

The observation that the 2-thietanyl radical grew in while the thietane dimer cation decayed above 105 K in F-113U can be explained by the decomposition of the dimer cation:



This decomposition can also account for the similar growth of the 2-thietanyl radical in the F-113S matrix above 145K. In more detail, the reaction (6.1) can be understood by the mechanism of either hydrogen atom or proton transfer in which the hydrogen atom is moved from a thietane molecule to a cation or a proton is transferred from a cation to a thietane molecule. These processes can occur simultaneously during the dissociation of the dimer cation, or occur stepwisely after the dissociation of the dimer cation. Such ion-molecule reactions are also involved in the dissociation process of the dimethyl sulfide dimer cation and other systems in which the dimer cations were not observed (see Chapter IX). The dimer cation may be considered as the intermediate in the process of the ion-molecule reaction between thietane and thietane monomer cation in the present case. However, the large temperature difference (ca. 40 K) for the dimer-cation dissociation in F-113U and in F-113S seems to argue against the self-dissociation of the dimer cation. Considering that the dimer cation always dissociates in the temperature range where the diffusion-controlled ion-molecule reactions can occur, it is not impossible that the dimer cation dissociation was actually assisted by the attack of the neutral molecules. In other words, the 2-thietanyl

radical may be formed by the ion-molecule reactions between the thietane dimer cation and the thietane molecule as written below:



4. Thiirane Monomer and Dimer Radical Cations

Thiirane monomer and dimer cations were both studied in F-11. Shown in Figure 30 are the ESR spectra of the radical species generated from the thiirane-F-11 system. The spectrum b at 90 K is composed of two groups of overlapping signals. As indicated by the stick diagrams, the features at low field ($g_{\perp} = 2.028$) consist of a quintet pattern (16.1 G), whereas the feature at higher field ($g = 2.012$) consists of a nonet pattern (5.8 G) with narrower linewidth. The low field features are attributed to the perpendicular signals of the thiirane monomer cation. The parallel features of the monomer cation are obscured by the overlap with the central nonet pattern except the two outermost highfield peaks pointed out by the arrows on the right. In terms of these two peaks, $g_{\parallel} = 2.008$ for the monomer cation was obtained. The central nonet pattern apparently does not belong to the monomer cation which is ascribable to the thiirane dimer cation, since the nonet indicates the interaction from eight protons expected for the dimer cation. The ratio of 3.1 of the hfcs for the monomer and dimer cations is similar to the ratio of 3.1 for the corresponding cations from thietane or from dimethyl sulfide,^{65,66} which confirms the assignment. On annealing to 100 K, the perpendicular features of the monomer cations revealed some substructure as illustrated in spectrum 30a recorded at 120 K. This substructure is owing to the weak F-11 matrix interaction which has been reported in other cases before.⁴² At above both monomer and dimer cations decayed irreversibly, with the monomer cation decaying more rapidly. In F-11 no new ESR signals were observed after the disappearing of these species.

Thiirane cations were also studied in F-113U and F-113S

in the former matrix, the low temperature spectrum shown in Figure 31 is mainly a broad signal with not-well resolved

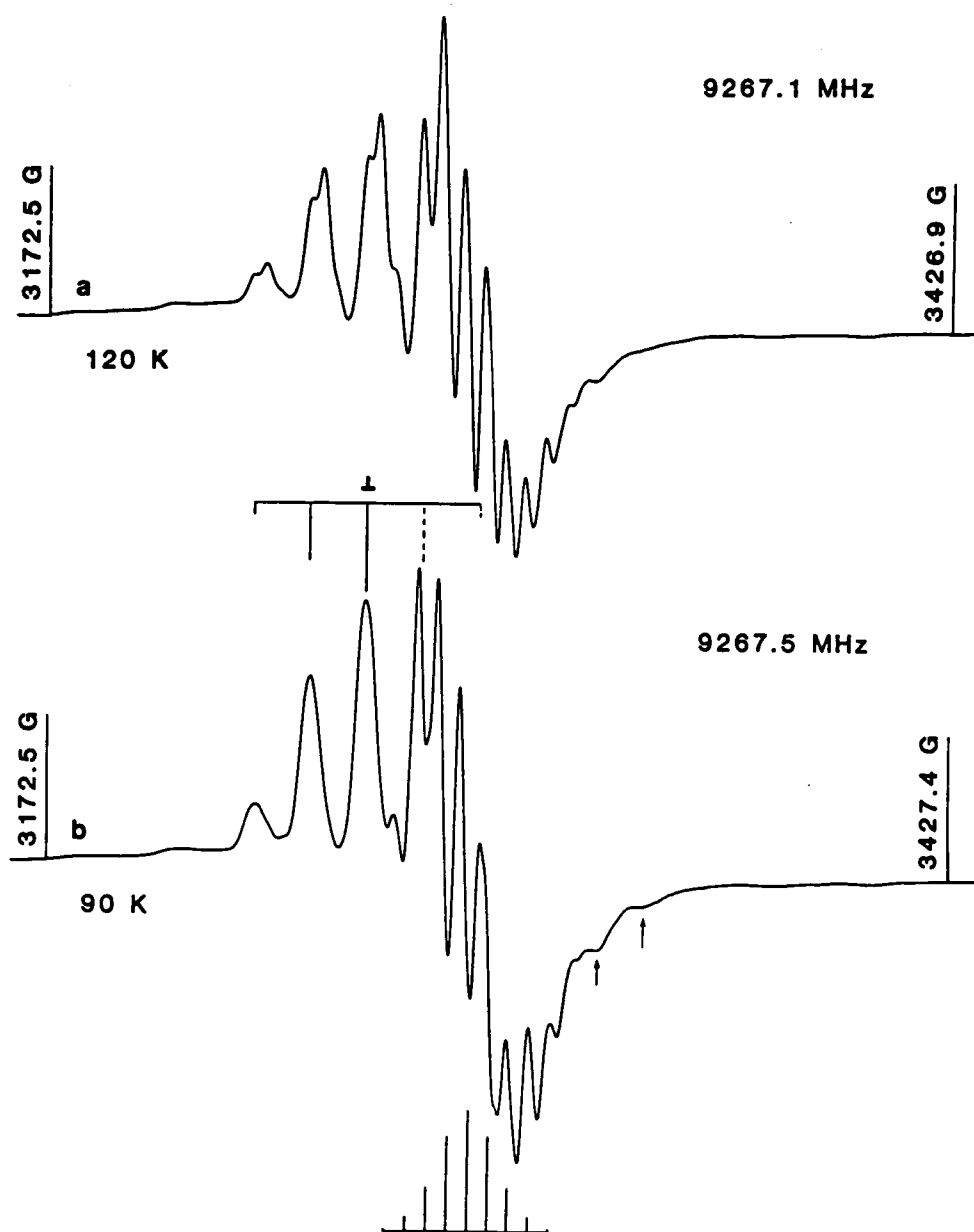
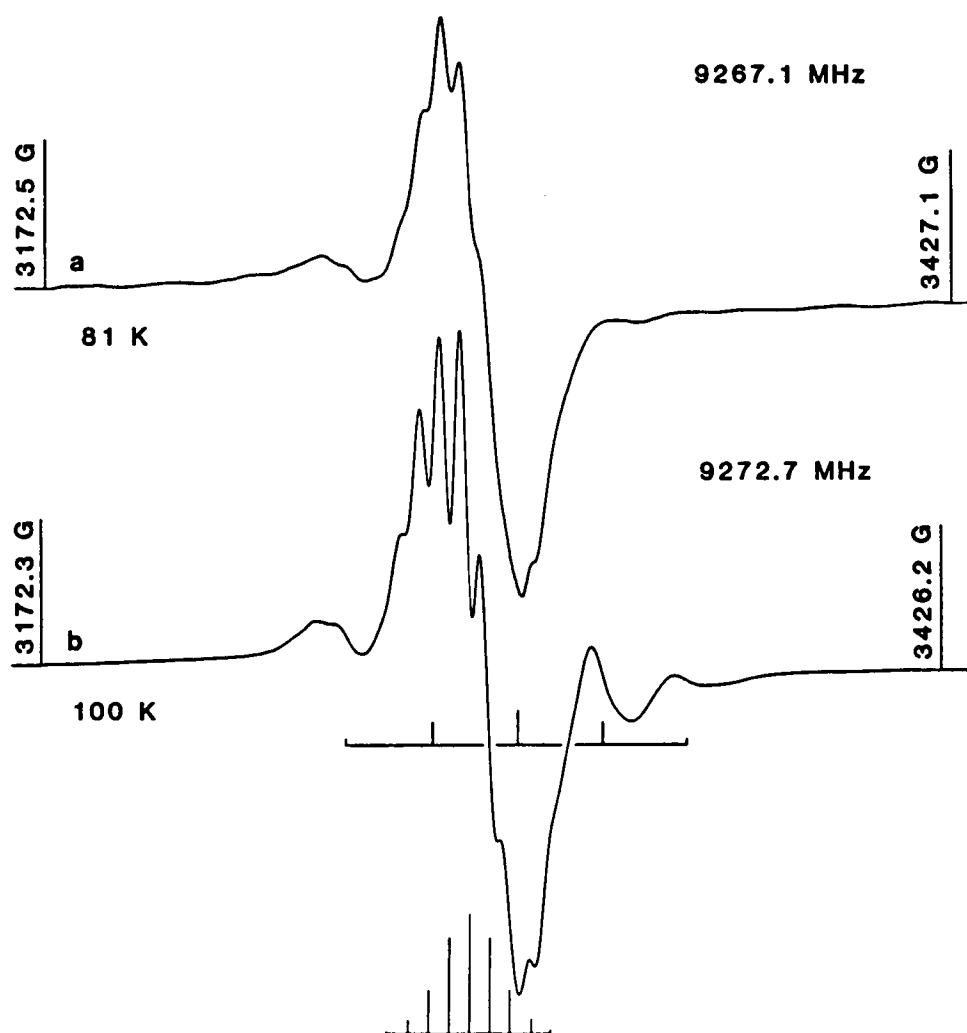


Figure 30. First-derivative ESR spectra of the thiirane monomer and dimer radical cations in F-11. The upper stick diagram in b illustrate the perpendicular features of the monomer cation while the two peaks pointed out by the two arrows on the right are the outermost peaks of the parallel features. The lower stick diagram in b shows the hyperfine components of the dimer cation.



Figuer 31. First-derivative ESR spectra of the thiirane dimer radical cation in F-113U. The quintet stick diagram in b describes the neutral radical $\text{CF}_2\text{CLCFCLCH}_2\dot{\text{C}}\text{H}_2$ that grows in at the temperature indicated.

substructures from the dimer cation. There is no indication of the presence of the monomer cation. This observation parallels that of the thietane cations in the same matrix. On warming up, the dimer cation spectrum became better resolved showing the expected nonet pattern but started to decay at about 100 K. Interestingly, as indicated by the upper stick diagram of Figure 31b, a new species grew in simultaneously. The ESR spectrum of the new species consists of a broad quintet (ca. 23 G) with a g-value of 2.0023. It is assigned to the neutral radical $\text{CF}_2\text{CLCFCLCH}_2\dot{\text{C}}\text{H}_2$ (vide infra).

In F-113S the thiirane dimer cation is also the only species detected, the ESR spectrum of which is shown in Figure 32. The spectrum consists of a nonet pattern with hfcs of 5.7 G and g-value of 2.012, as expected. The dimer cation persisted until the softening point of the matrix at 145 K. After that, its ESR signals decayed. However, it was surprisingly accompanied with the growth of a new, sharp quintet feature ($A(4\text{H}) = 23$ G and $g = 2.0023$). Even more surprisingly, the growth of the $\text{CF}_3\dot{\text{C}}\text{CL}_2$ radical which is always observed at this temperature range⁶⁸ was not observed this time. This is attributed to its addition to the produced ethylene and will be discussed later.

Turning now to the structures of the thiirane monomer and dimer cations, as discussed above, the ESR parameters for the ring-closed thietane monomer cation are usual because the hfcs of 31.1 G can be derived from the known parameters for the acyclic dimethyl sulfide species by the $\cos^2\theta$ -relationship. On the other hand, the β -proton hfcs of 16.1 G for the thiirane cation are unusual since they are a factor of 0.57 smaller than those for the thietane cation and cannot be derived from the $\cos^2\theta$ -relationship from the hfcs of dimethyl sulfide monomer cation. This decreased hyperconjugation effect in the three-membered ring is in fact predicted from the MNDO calculations by Glidewell.⁶⁹ He reported the calculated 1s spin densities of 0.016 and 0.027 for the four β -protons of the sulfur-centered ring-closed thiirane and thietane monomer radical cations giving a ratio of 0.59 in accord with the present experimental results. Therefore, the thiirane is considered to be a ring-closed sulfur-centered cation with the SOMO depicted by 2.

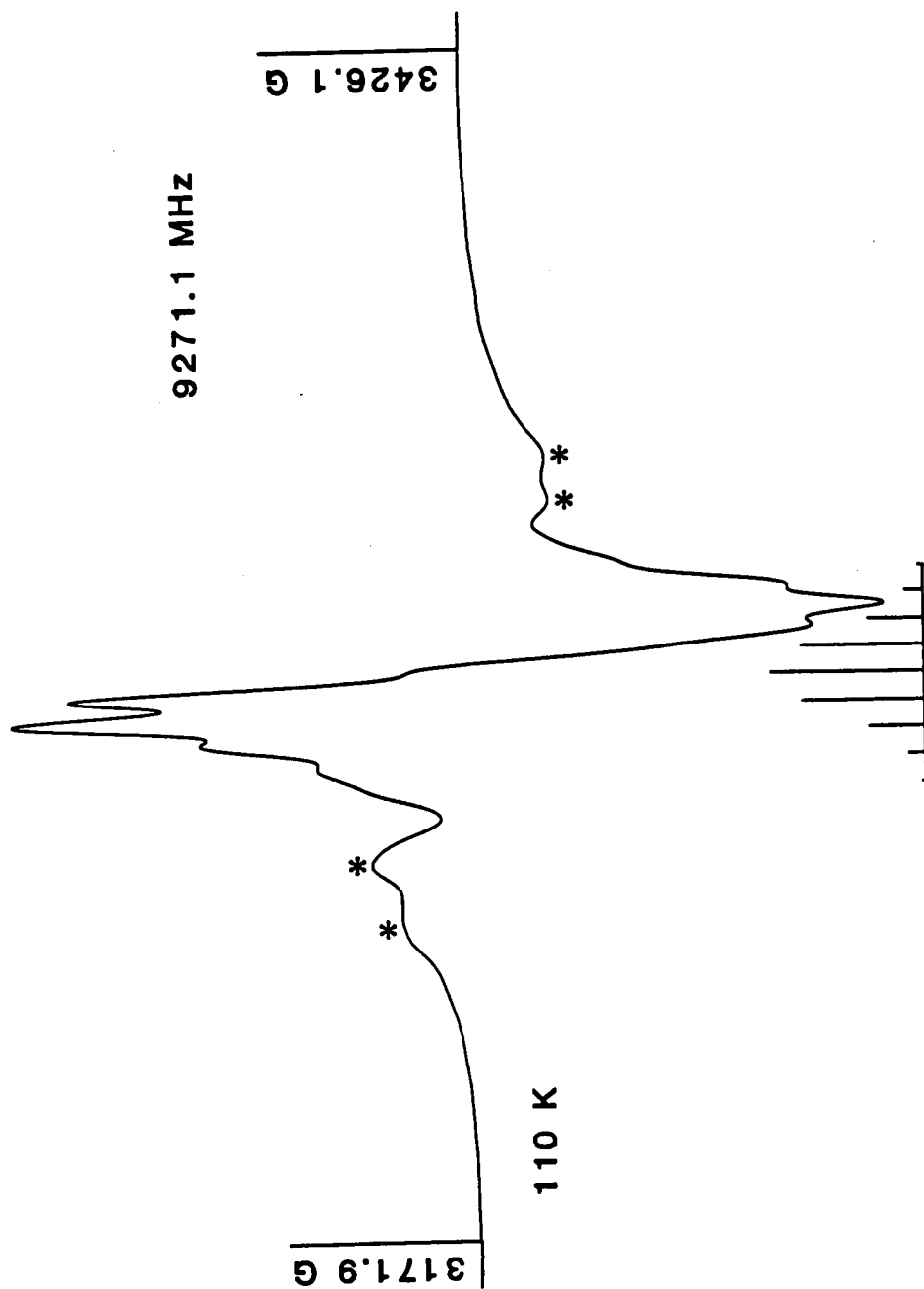
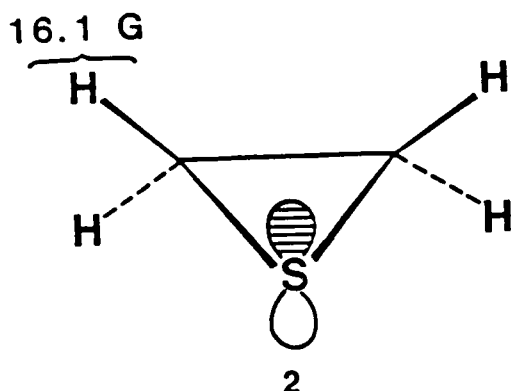


Figure 32. First-derivative ESR spectrum of the thiirane dimer radical cation in F-113S. The asterisks show the unidentified species signals.



Further strong support for this assignment comes from the study of the g -tensor. This becomes more important in this assignment, since the ring-proton hfcs of the ring-closed radical cations of the three-membered heterocycles have never been reported. Both oxirane and aziridine radical cations are ring-opened isomers as already described. As a result, there is no direct comparison which can be made in terms of the hyperfine coupling constants. It is found that the apparent g -tensors for the thiirane and thietane cations are almost identical. Each is axially symmetric with $g_{||} = 2.008$ and $g_{\perp} = 2.028$. This similarity indicates strongly that they possess very similar structures. In other words, if the thiirane cation were a planar C...C ring-opened isomer similar to the ring-opened oxirane cation where the spin is mainly localized on the two carbons, it should show a much lower and less anisotropic g -value (g -value of the oxirane cation is 2.0024).⁴² However, the fact is that the g -tensor of thiirane cation as well as the thietane cation is quite close to those for the ring-closed oxetane cation as mentioned above.⁴² Hence it can be concluded independently from the g -tensor study that the thiirane cation is ring-closed with the unpaired electron on the sulfur.

The ring-closed thiirane cation assignment is further supported by the corresponding study of propylene sulfide cation in F-11. As shown in Figure 33, the perpendicular features of the propylene cation in F-11 is clear, which can be satisfactorily simulated by a doublet (17.2 G) of triplets (12.5 G) from the interaction of three ring protons. Undoubtly it is a ring-closed cation with spin on sulfur atom, because it does not show the interaction from the methyl protons as is expected for a ring-opened structure. Besides, the g for this cation

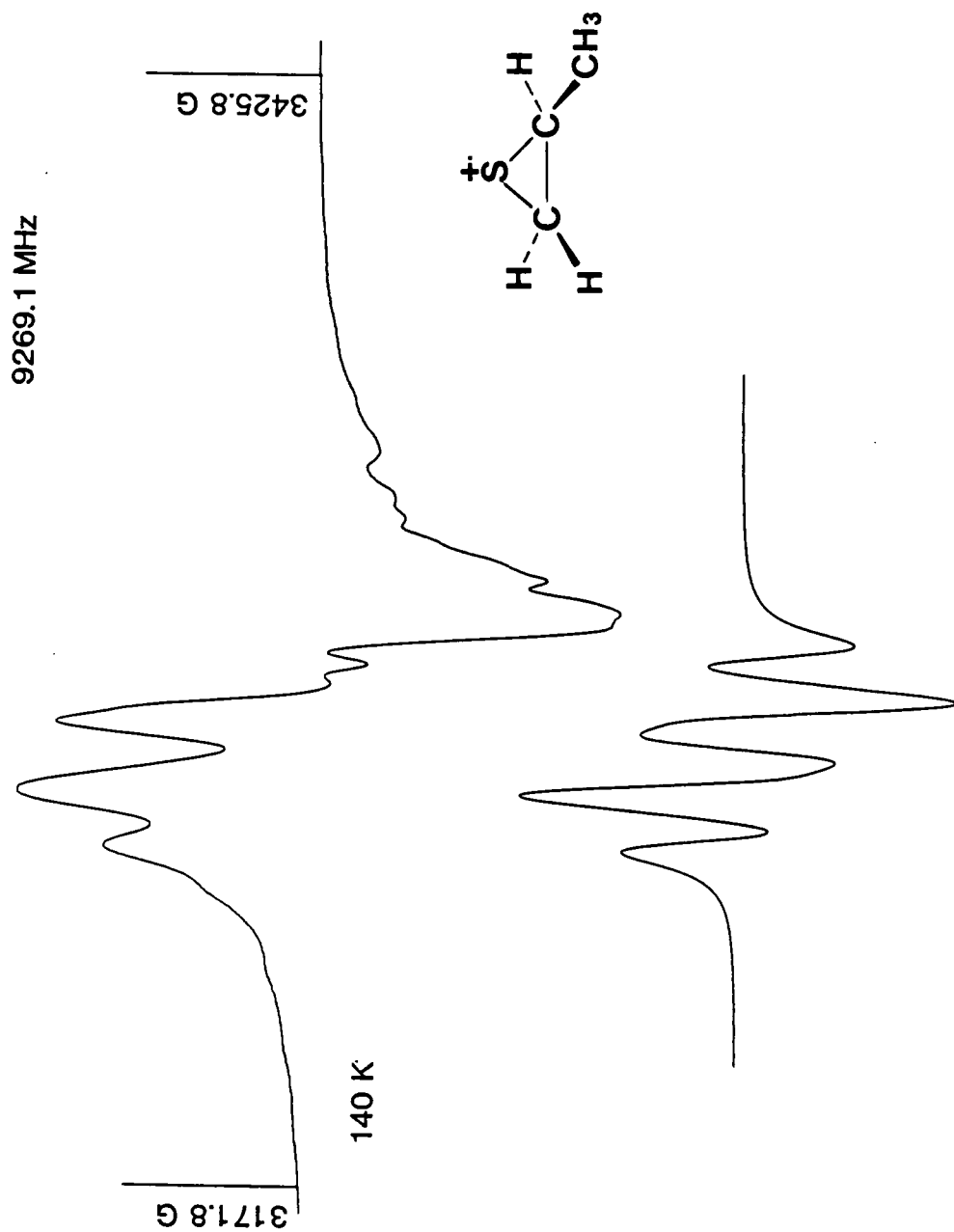
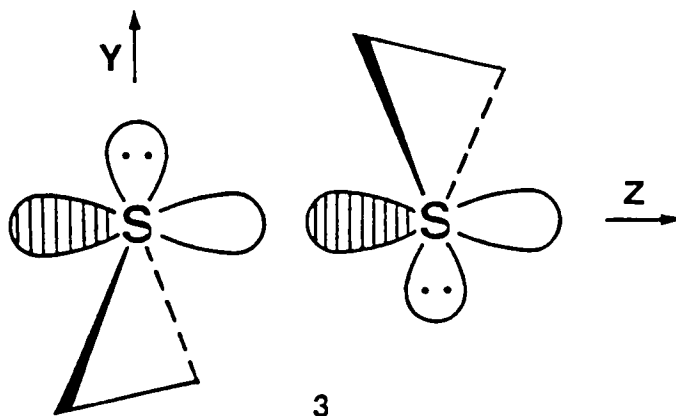


Figure 33. Observed (upper) and simulated (lower) first-derivative ESR spectra of the monomer radical cation of propylene sulfide in F-11. The lower spectrum simulated the perpendicular features of the propylene sulfide cation.

is 2.0028, i.e. the same as that of the thiirane cation.

The other support for the ring-closed thiirane monomer cation assignment is the observation of the thiirane dimer cation and the recognition of the $\sigma^2\sigma^*$ structure of the thiirane dimer cation 3 shown below:



The dimer assignment is supported by two aspects: (a) the hfcs ratio of 2.8 for the thiirane monomer-dimer cations pair is close to the ratio of 3.1-3.2 for the σ^* dimer cations of Me_2S , Me_2Se and thietane, and differs from the ratio of 1.1 for the σ dimer radical cations, and (b) the g-factor of 2.012 is in the right range for the σ^* radicals.

5. Effect of Ring Size on Hyperconjugation in Heterocycloalkanes

The hyperfine data for the thiirane, thietane and dimethyl sulfide cations are summarized in Table VI. It has already been stressed that the β -proton hfcs are quite different in thietane and thiirane cations. The significance is that the β -proton hfcs in π radicals is thought to be a reliable measure of the hyperconjugation of these protons. Hence the present study can give a quantitative description of the extent of hyperconjugation as a function of ring size. This description is not obtainable for the first-row heterocycloalkane radical cations because the $^2\text{B}_1$ and $^2\text{A}_1$ states of the oxirane and aziridine cations are unstable and undergo C...C ring-opening to give allylic structures.

According to the hfcs, the hyperconjugation effect in the four-membered heterocycles is usual. In other words, such effect is similar to that in acyclic hetero-compounds. In contrast, the hfc in

TABLE VI

ESR PARAMETERS FOR RADICAL CATIONS FROM THIIRANE,
THIETANE AND DIMETHYL SULFIDE

Radical Cations	Matrix	T/K	Hyperfine Couplings/G	$g_{\parallel}$	$g_{\perp}$	g_{av}
	F-11	90	16.1 (4H)	2.008	2.028	2.021
	F-11	90	31.1 (4H)	2.008	2.027	2.021
$\text{Me}_2\text{S}^{+\cdot}$	F-11	124	20.4 (6H)			2.0137
	F-11	90	5.8 (8H)			2.012
	F-113S	120	5.7 (8H)			2.012
	F-113U	95	9.4 (8H)			2.012
	F-113S	110	8.7 (8H)			2.012
$\text{Me}_2\text{S}^{+\cdot}\text{SMe}_2$	F-113S	120	6.5 (12H)			2.010
	H_2O	295	6.8 (12H)			2.0103
	$\underline{\text{C}}-\text{C}_3\text{H}_6$	158	6.3 (12H)			2.0102

the thiirane cation is reduced 57% which indicates the large reduction in hyperconjugation in forming the three-membered ring system. This decreased hyperconjugation effect is very striking. As mentioned earlier such an effect has been predicted by the Glidewell's calculation which shows that the 1s spin densities for the four protons in the thiirane and thietane are 0.016 and 0.027, respectively.⁶⁹ Accordingly the hfcs of 16 and 27 G can be derived by using the proposed scale factor of ca. 1000 G for the conversion of proton spin density into hyperfine coupling for the sulfur-centered radicals.⁶⁹ These results are certainly not far away from the present experimental results. It is noteworthy that AM1 calculations by Nelsen⁷⁰ on the theoretical ring-closed $^2B_1$ cation of oxirane and the oxetane cation predict β -proton hfcs of 35.9 and 61.5 G. The ratio of these calculated hfcs is 0.58, almost the same as 0.57 for the corresponding sulfur heterocycles.

The decreased hyperconjugation effect of the three-membered rings also accords with the work of Mollere and Houk⁵⁷ on the photoelectron spectroscopy of heterocycloalkanes. They found that the lowest ionization potentials for heterocyclopropanes are always larger than those for the corresponding four-membered rings or acyclic compounds. They interpreted this in terms of differences in hyperconjugative interaction by arguing that the b_1 orbital in the heterocyclopropanes is destabilized less than in the four-membered rings or acyclic systems. This effect is attributed to the more bonding character of the symmetric combination of (CH_2) orbitals in the strained cyclopropane ring which decreases the interaction with the highest b_1 orbital on the heteroatom. In other words, there is a smaller admixture of the CH_2 group orbital into the b_1 orbital for the heterocyclopropanes than for the heterocyclobutanes. Clearly this is precisely illustrated by the present ESR studies.

Finally, it should be mentioned that the reduced hyperconjugation effect still remains in the thiirane dimer radical cation as judged by the ratio of 0.61 derived from the hfcs of thiirane and thietane dimer radical cations (5.8 G for the thiirane dimer cation and 9.4 for the thietane dimer cation).

6. Ethylene Molecule Extrusion from Thiirane Dimer Radical Cation

Another important result of this work is the finding of ethylene molecule extrusion from the thiirane dimer radical cation.

As mentioned earlier, a new species grew in at about 100 K in F-113U matrix when the thiirane dimer cation decayed. The ESR spectrum of this new species shown in Figure 34b consists of a broad quintet pattern with hfcs of 23 G and a g-value of 2.0033. On warming to 115 K, this quintet pattern became a better resolved spectrum shown in Figure 34a, which was reversibly converted to the 100 K quintet pattern on cooling, establishing that they arise from the same species. Figure 34a can be analyzed as a doublet (27.3 G) of quartets (22.1 G). The additional lines between this main pattern especially on both wings are attributable to the residual α -proton hyperfine anisotropy. The spacing of 11.2 G calculated from both the first two and the last two lines of the spectrum is typical of such anisotropy. Surprisingly, the spectra as well as the parameters are in fact similar to those reported for the ethylene radical cation at 105 K in the same matrix.⁶³

To make a direct comparison, Figure 35 gives the ESR spectra obtained in ethylene-F-113U system at 110 K and 105 K. As can be seen, the 105 K spectrum comprising a quintet envelop pattern is similar to the spectrum obtained from thiirane at 100 K. Furthermore, the 110 K spectrum for the ethylene system is very similar to the spectrum observed for thiirane system at 115 K in every detail despite that the former spectrum is not as well resolved. On further warming up the ethylene solution, unfortunately, some additional lines appeared in its ESR spectrum irreversibly. The comparison at higher temperatures is, therefore, not possible. However, the spectra shown in Figure 34 and 35 are so similar that there is little doubt that similar radicals are generated above 100 K from these two totally different systems.

As also described above, after the thiirane dimer cation was decayed in F-113S above 140 K, a sharp quintet pattern appeared which is now shown in Figure 36a. The spectrum is remarkably similar to that obtained from the ethylene-F-113S system at 140 K.⁶⁴ Figure 36b gives the ESR spectrum derived from the latter system for a direct comparison. These two spectra comprise mainly a well resolved, sharp

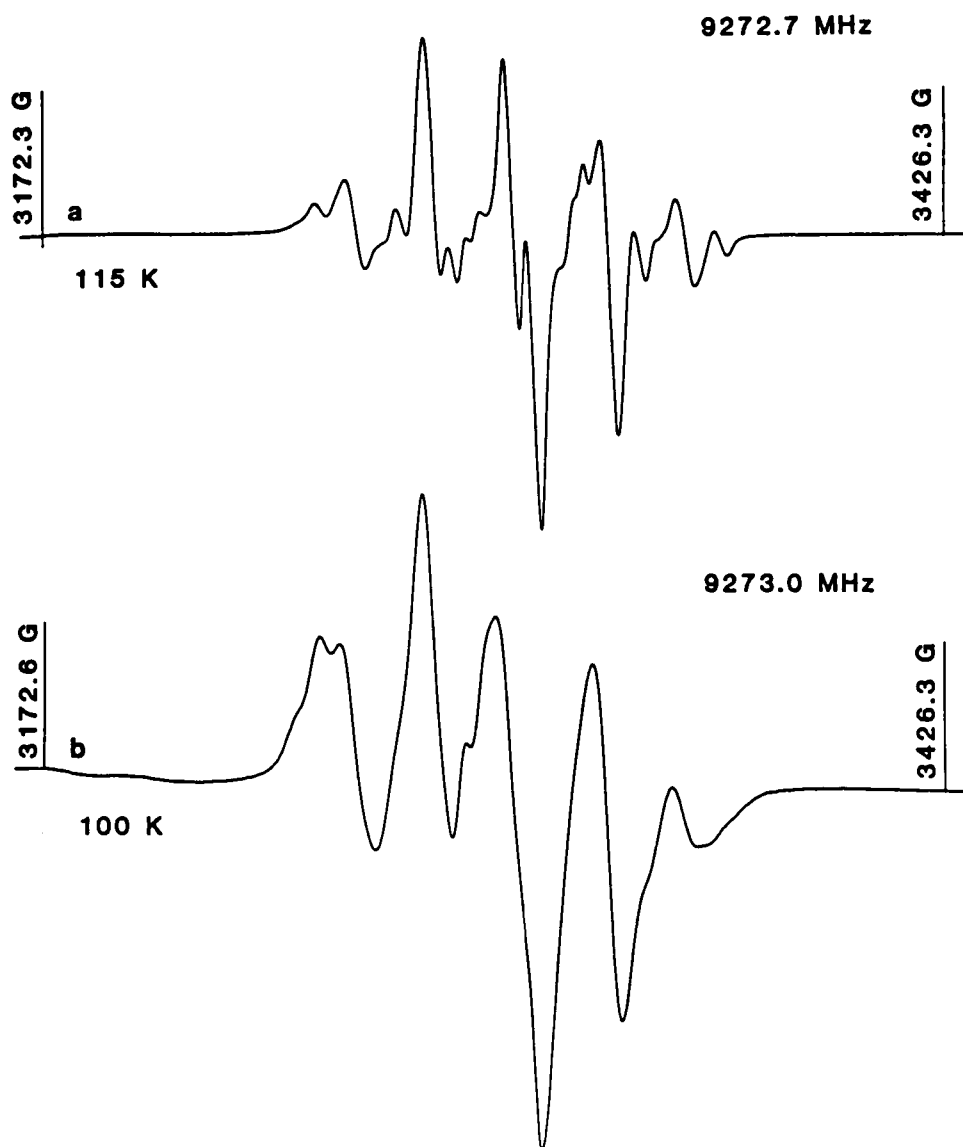


Figure 34. First-derivative ESR spectra attributed to the $\text{CF}_2\text{CLCFCLCH}_2\dot{\text{C}}\text{H}_2$ radical produced in F-113U by γ -irradiation of a 1 mol% solution of thirane at 77 K: (a) recorded at 115 K, and (b) recorded after cooling the sample again to 100 K.

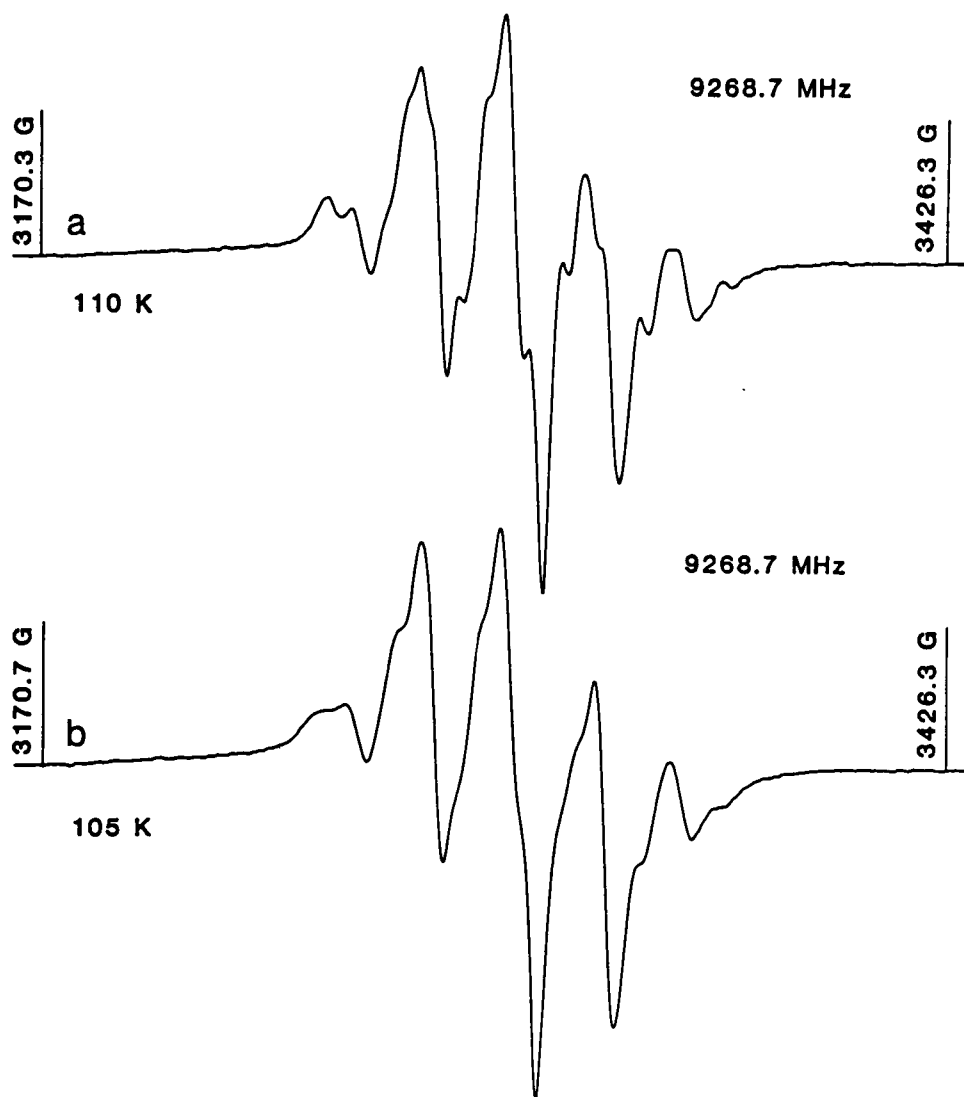


Figure 35. First-derivative ESR spectra attributed to the $\text{CF}_2\text{CLCFCLCH}_2\text{CH}_2$ radical produced in F-113U by γ -irradiation of a 1 mol% solution of ethylene at 77 K: (a) recorded at 110 K, and (b) recorded after cooling the sample again to 105 K.

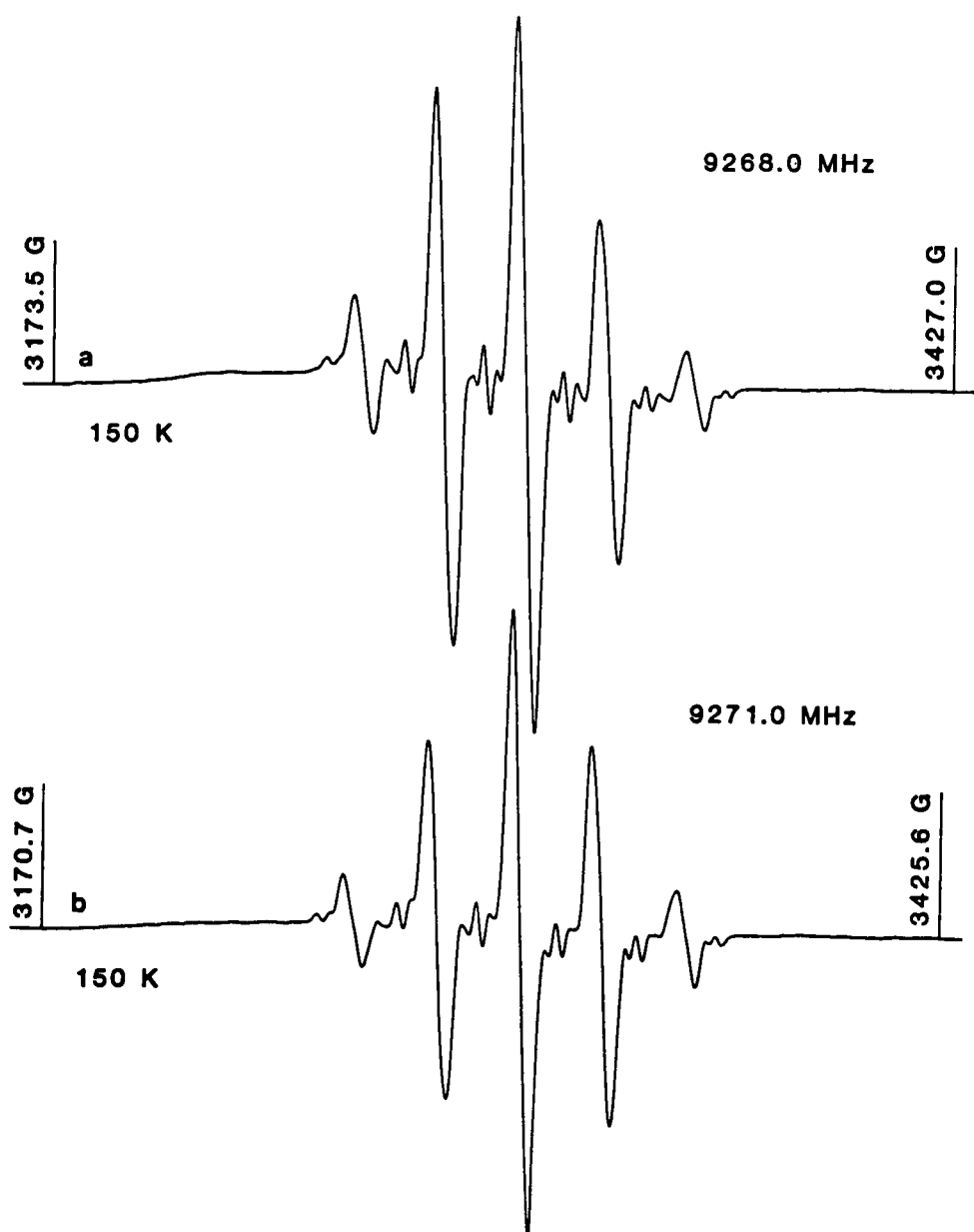
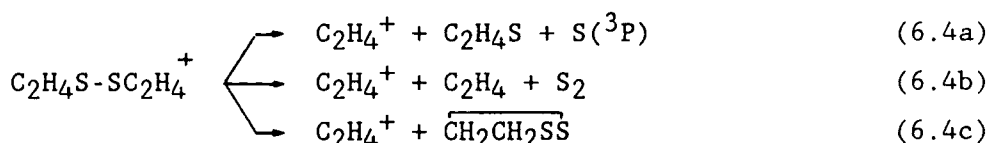


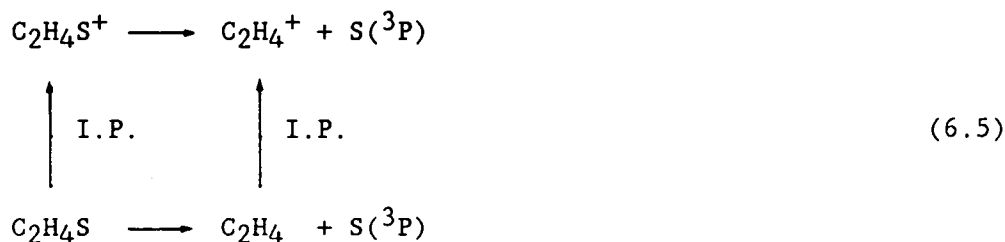
Figure 36. First-derivative ESR spectra attributed to the $\text{CF}_3\text{CCL}_2\text{CH}_2\dot{\text{C}}\text{H}_2$ radical produced by γ -irradiation of a 1 mol% thiirane (a) and a 1 mol% ethylene solution (b) in F-113S at 77 K and then annealed to 150 K.

quintet (23.7 G) with some small additional features between the main pattern. Undoubtedly, the main pattern as well as the additional features match very well between these two spectra. Moreover, after the two samples had been cooled down from 150 K to 100 K, they can also match very well as shown in Figure 37a and 37b. The match over such a large temperature range can only be explained by that the same secondary radical species was generated above 145 K in F-113S from these two different systems.

The remaining problem is how to explain these facts. Two possibilities should be considered. The first possibility is that the secondary radical in each case is $C_2H_4^+$ which accounts for the broad quintet pattern in F-113U as well as the sharp quintet pattern in F-113S. In fact this was proposed by Shiotani and co-workers⁶³ on the basis of their study of γ -irradiation of the ethylene-F-113U system and observation of the broad quintet ESR signals. This is reasonable since the quintet pattern is the expected pattern for the ethylene cation. However, if this cation were also produced from the thiirane dimer cation, it has to be produced indirectly by the dissociation of the monomer cation (pathway (6.3)) or by the dissociation of the dimer cation (pathway (6.4)) as shown below:



The energetics of pathway (6.3) can be judged by a simple thermochemical calculation:



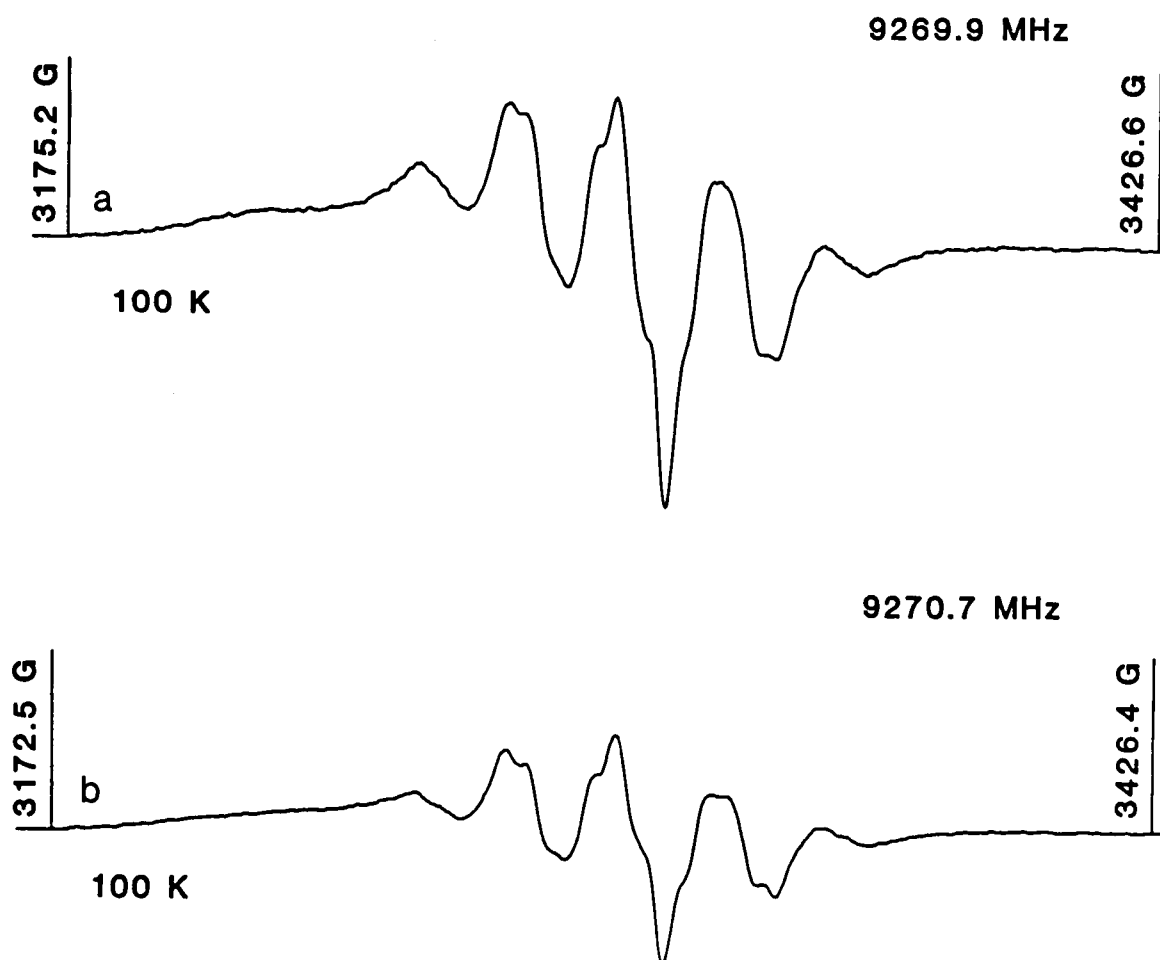


Figure 37. First-derivative ESR spectra attributed to the $\text{CF}_3\text{CCL}_2\text{CH}_2\dot{\text{C}}\text{H}_2$ radical produced by γ -irradiation of 1 mol% thiirane (a) and 1 mol% ethylene solution (b) in F-113S at 77 K, annealed to 150 K, and then cooled to 100 K.

By using the calculated energy (1.54 eV) for the dissociation of neutral C_2H_4S to C_2H_4 and $S(^3P)$,⁷¹ ionization potential of C_2H_4 (10.52 eV), and ionization potential energy of C_2H_4S (9.05 eV),⁷² the reaction (6.3) is found to be endothermic by 3.01 eV, or 67 kcalmol⁻¹. Similarly pathway (6.4a) can be excluded since it is even more endothermic than pathway (6.3) by adding more enthalpy for the dimer cation formation. Moreover, the low S-S bond energy (1.45 eV) indicates that pathways (6.4b) and (6.4c) should also be highly endothermic, and cannot easily take place at low temperatures in matrices.

Another strong argument against the $C_2H_4^+$ assignment is the inconsistency in the fact that $C_2H_4^+$ was produced at 145 K in F-113S or at 105 K in F-113U irrespective of whether ethylene or thiirane is initially present in the Freons, since it is difficult to understand that it was produced at 145 K or 105 K rather than 77 K directly from ethylene. In fact, the assignment of the ethylene cation in the ethylene-F-113S system has already been questioned by Fujisawa *et al.*⁶⁴ As they argued in terms of their ESR results that (a) the ethylene cation was unstable at 77 K, thereby, the 1-butene cation was actually formed initially by an ion-molecule reaction of the ethylene cation with its parent molecule, and (b) the broad five-line pattern observed at 105 K is attributed to the propagating radicals $\cdot CH_2(CH_2)_nCH_2^+$ which can be produced by the successive addition of ethylene to the 1-butene cation. The present study is in favor of this general idea of the secondary radical formation but the nature of the secondary radical is believed not the propagating radicals (*vide infra*).

An alternative interpretation, taking the results in F-113S as an example, is that the prior species to the formation of the same secondary radical with the five-line ESR pattern is ethylene itself rather than the ethylene cation, which can be put in directly or produced indirectly from thiirane cation. Above 145 K, ethylene molecule reacts with some radical to form the radical with general form of $RCH_2\dot{C}H_2$ to account for the observed ESR spectra. This is consistent with the observation that ion-molecule reactions can sometimes occur above 145 K in the F-113S matrix as mentioned earlier.

The other possible secondary radical in the thiirane case is

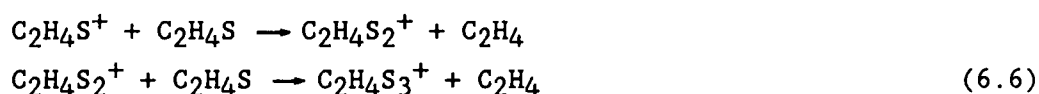
RSCH₂CH₂, but this kind of radical lacks ESR evidence since the β -proton hfcs of such radicals were found to be consistently smaller (ca. 13 to 17 G)^{33b} than those for the observed secondary radical. This rules out this choice, and also rules out the possibilities of an accidental spectral coincidence between radicals of RSCH₂CH₂ formed from thiirane and the RCH₂CH₂ radical produced in ethylene system.

Although Fujisawa et al correctly suggested that the secondary radical has the general form RCH₂CH₂·, it seems that the propagating radical is not ·CH₂(CH₂)_nCH₂⁺ as they suggested, since the α - and β -proton hfcs should not be virtually identical in the well-resolved spectrum of these propagating radicals. Neither the high temperature nor the low temperature spectra of n-butyl through n-decyl radicals show any such equivalence.⁷³ Therefore this kind of propagating radical has no ESR support.

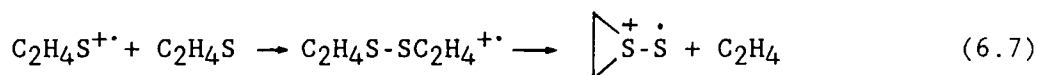
The clue to the structure is that the CF₃CCl₂· radical was not observed at 145 K when the secondary radical grew in both in the thiirane and ethylene solutions, which is rather unusual. It is thus suggested that this radical is added to the ethylene molecule by the diffusion of the ethylene to produce CF₃CCl₂CH₂CH₂· which accounts for the five-line pattern. The similar radical CCl₃CH₂CH₂· possesses equal alpha and beta proton hfcs (both are 22.3 G) and a g-value of 2.00366 close to the parameters of the observed secondary radical,⁷⁴ which lends ESR support to this assignment. Similarly the secondary radical in F-113U can be thought to be the CF₂ClCFClCH₂CH₂· by the addition of the matrix radical such as CF₂ClCFCl· to ethylene. This argument is supported by the fact that the oxygen molecule can diffuse to add to the matrix radical resulting in the formation of RO₂ radicals in CF₂ClCFCl₂, the g-tensor for RO₂ being found to be very similar to the values reported for CF₃O₂ and CCl₃O₂.⁷⁵ The ethylene molecule has the same or smaller size than oxygen, it may also be able to diffuse like oxygen in the matrix to approach the matrix radical above 145 K in F-113S or above 100 K in F-113U. The assumption of the ethylene extrusion is further supported by product analysis. This was done in the pure thiirane liquid phase expecting that the product yields originating from ion-molecule reactions would be maximized in the pure liquid. It

was found that ethylene was always detected after the exposure of liquid thiirane samples at room temperature to γ -irradiation for doses of a few Mrad, while unirradiated samples showed no response.

After having established unequivocally the ethylene molecule extrusion by experiment. The mechanism for such extrusion should come into consideration. In the literature, the generation of ethylene from thiirane has been studied in the gas phase by an ICR mass spectrometer.⁶¹ Their results can be written as the successive ion-molecule reactions:



and so on, the sulfur atom being transferred to the thiirane cation from the thiirane molecule accompanied with the ethylene extrusion in each step. The reactions become slower and slower when the Number of the S atoms increases in the cation. However, those results do not give detailed mechanistic information about the processes. The contribution of the present study is that it establishes that the ethylene molecule extrusion proceeds through the dissociation of the thiirane dimer cation as written by reaction (6.7) on the basis of the fact that ethylene was only produced after the decay of the dimer. This gives a clue to its mechanism.



However, Reaction (6.7) can still be interpreted by two mechanisms, one is concerted while the other is stepwise. The concerted mechanism has been described by an MO correlation diagram.⁴³ There are three species involved in the reaction (6.7). The σ^* structure of the dimer cation has already been discussed. The structure of the disulfide product $\text{C}_2\text{H}_4\text{S}^+-\dot{\text{S}}$ is described by the interaction of a ground-state $3p$ sulfur atom with the monomer radical cation, as shown in Figure 38. The two p_z orbitals interact with each other by using one p_z electron from sulfur atom and one unpaired electron from the monomer cation to form

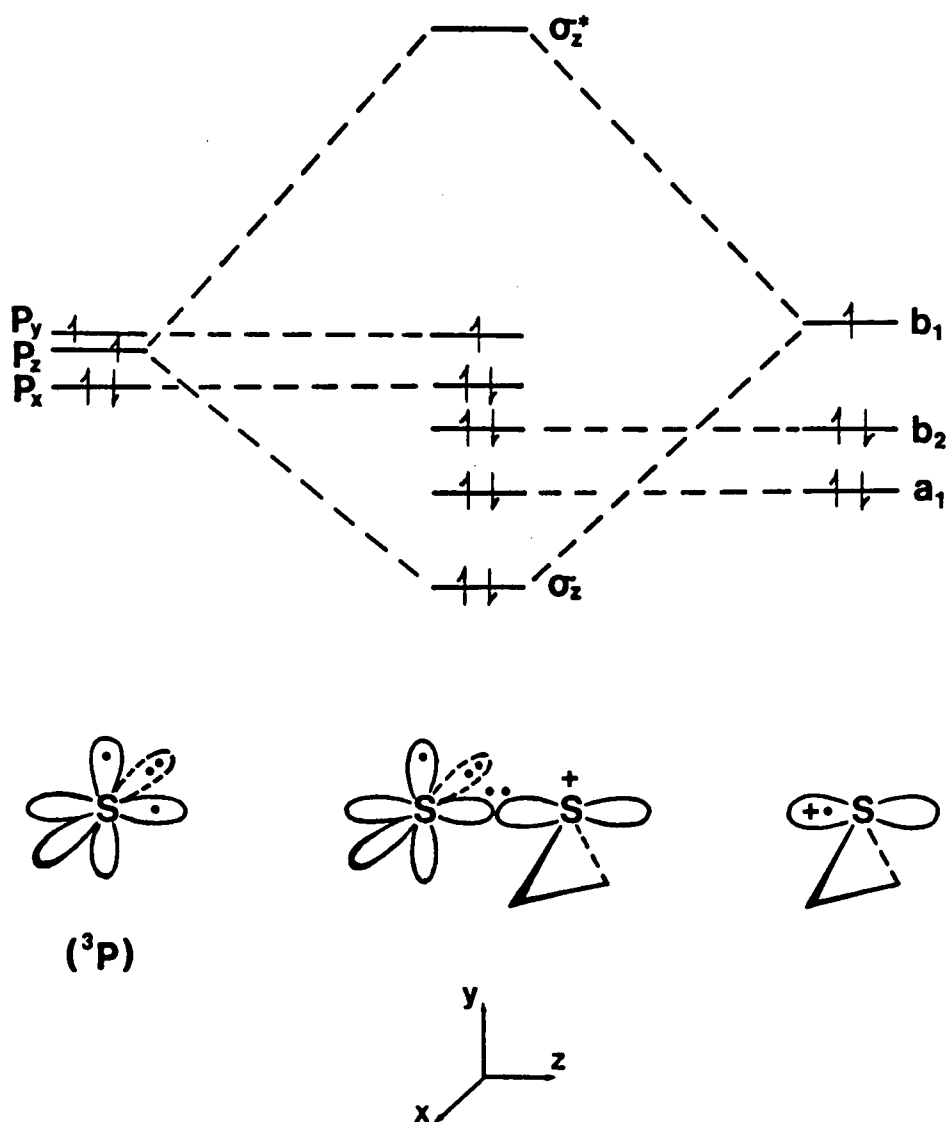


Figure 38. A qualitative MO energy-level diagram showing the radical formation by the addition of a sulfur atom in the ^3P state to the thiirane monomer cation.

the σ_z S-S bond, leaving the p_y electron to stay in the sulfur atom. Therefore, the nature of the radical center in this disulfur species is the same as that of the monomer cation or a monosulfide radical ($RS^\bullet$), since the SOMO is still a sulfur 3p orbital. It should be pointed out that the representations of b_1 , b_2 , and a_1 for the molecular orbitals of thiirane⁷⁶ are referenced to the usual coordinate system for molecules of C_{2v} symmetry with the C_2 axis along the z direction and the CSC ring in the yz plane, therefore, the p_x , p_y , p_z sulfur atomic orbitals used in Figure 38 and 39 should possess b_2 , a_1 , and b_1 symmetry, respectively, when transformed to the same coordinate system. The third species is ethylene. Its orbitals are well known which are shown in Figure 39.

After examining the MO pictures of the each species involved. The ethylene extrusion from the dimer cation can be described by Figure 39. which shows that during the extrusion the two electrons of the a_1 thiirane orbital transfer into the newly formed ethylene π orbital and the b_2 electron pair goes into the p_x orbital of the non-ring sulfur atom. Thus the correlation between the filled MO's comprising the two C-S bonds in one of the thiirane moieties and the ground-state orbital in the reaction products is very good. However, the σ_z^* SOMO in the dimer cation does not correlate directly with the p_y SOMO of π symmetry in the disulfide radical product. But, since the electron moves from the high energy σ_z^* antibonding orbital to the much lower bonding p_y orbital, the symmetry restriction at the non-ring sulfur atom should be relaxed to allow the process to occur. The energy releasing in this process gives the driving force for the extrusion.

The other mechanism, the stepwise mechanism, states that the ethylene extrusion starts from one S-CH₂ bond breakage in one of the thiirane moieties of the dimer cation such that:



The support for it comes from the study of the dissociation of the dimer radical cation of dimethyl sulfide by Asmus.⁷⁷ He found that the dimer cation of dimethyl sulfide can eliminate a Me radical to form

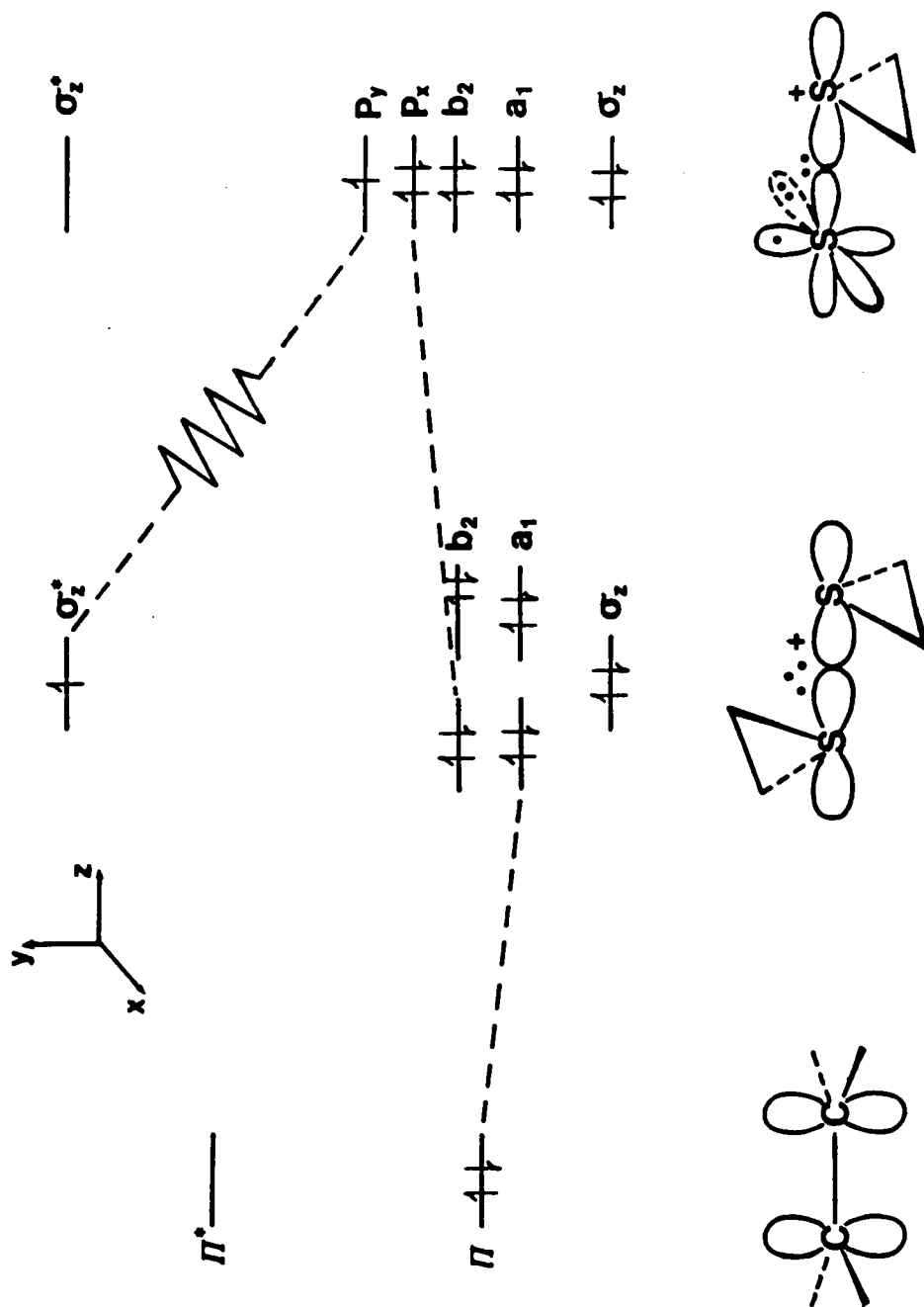
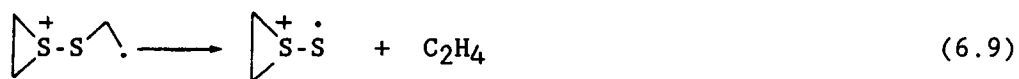


Figure 39. A qualitative MO correlation diagram describing the dissociation of the thirane dimer radical cation to the radical and an ethylene molecule.

Me_2SSMe^+ easily. Similarly, the thiirane dimer cation might as well undergo such homolytic S-C bond cleavage at first, then it extrudes the ethylene molecule by another S-C bond breakage as written below:



This stepwise mechanism gives the same final product of ethylene and disulfide cation. The present study does not provide enough information to distinguish between those two mechanisms.

CHAPTER VII

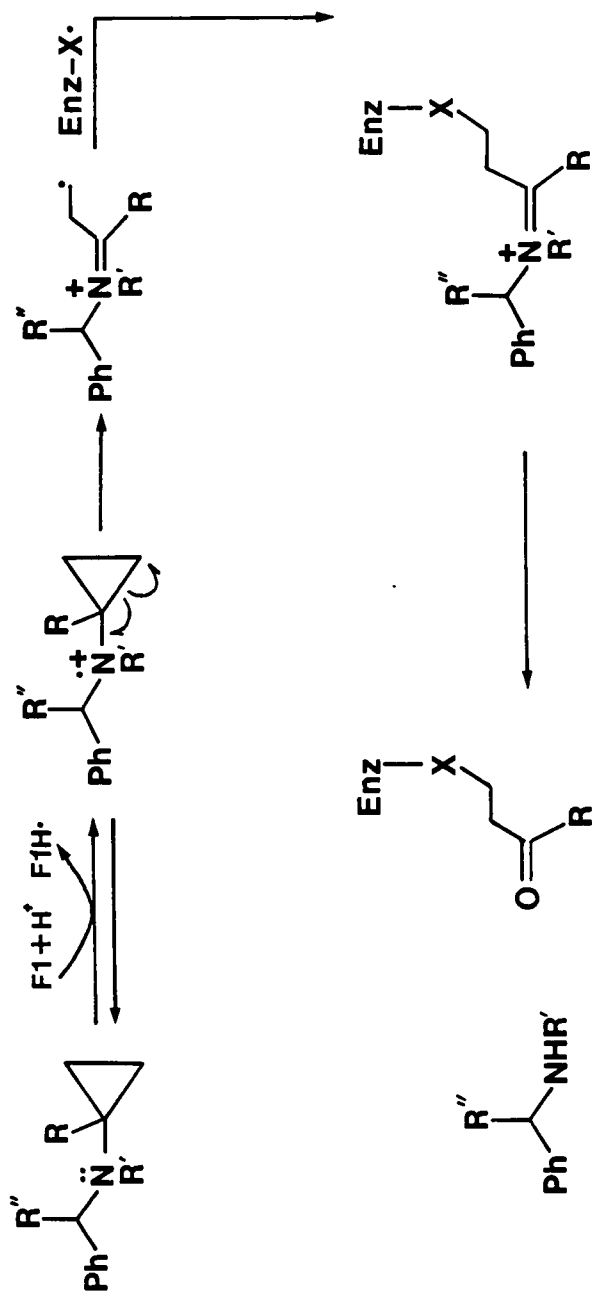
CYCLOBUTYLAMINE AND CYCLOPROPYLAMINE RADICAL CATIONS

A. Introduction

The other part of this work that involves nitrogen-containing compounds is concerned with studies of the radical cations of cyclobutylamine and cyclopropylamine. Part of this work can also be considered to be an extension of Chapter III for the substituted cyclopropane radical cations.

Cyclobutylamine and cyclopropylamine are known to inhibit some enzymes such as monoamine oxidase and P450.⁷⁸ Taking cyclopropylamine as an example, a mechanism for the inhibition was proposed by Silverman⁷⁹ as shown in Figure 40. The key steps are the ring-opening of the aminium radical cation formed by the oxidation of cyclopropylamine by enzyme to the carbon-centered radical which subsequently attacks the active site of the enzyme, leading to its inactivation. This proposal was based on the biochemical product analysis.

In the present study this important problem was approached by ESR and variable-matrix studies of the radical cations of cyclobutylamine and cyclopropylamine. It was hoped that direct studies of the radical cations would give more information about the inhibition mechanism. Indeed, it is found that the cyclobutylamine radical cation undergoes facile ring opening to form the carbon-centered radical cation $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$, which does not convert to its isomer $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{NH}^+$. On the other hand, the corresponding ring-opened neutral species generated from cyclobutylamine is the nitrogen-centered radical $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\dot{\text{N}}$ rather than $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{NH}$. These results, therefore, strongly support Silverman's proposal since only the ring-opened form of the radical cation gives a carbon-centered radical. This finding fits the observation that the inhibitor is bound to the enzyme through carbon rather than nitrogen. Parallel results were found



F1 represents the flavin cofactor, $\text{Enz-X}\cdot$ is an enzyme-bound radical,

$\text{R}=\text{H}$ or $\cdot\text{H}$, $\text{R}'=\text{H}$ or CH_3 , $\text{R}''=\text{H}$ or CH_3

Silverman, R.B.

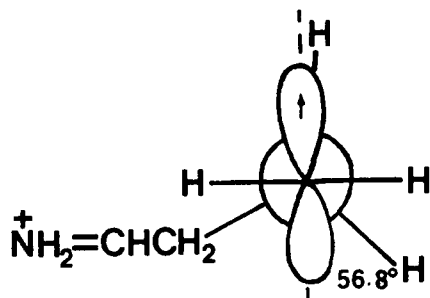
Figure 40. A mechanism for the inhibition of enzymes by cyclopropylamine proposed by Silverman (see text).

in the study of the cyclopropylamine radical cation in Freon matrices which therefore also support the above mechanism.

B. Results

1. The Radical Cations of Cyclobutylamine and Cyclopropylamine in F-113S

F-11 and F-113S are both suitable matrices for studying primary radical cations. As an example, the ESR spectrum of the cyclobutylamine radical cation in F-113S is shown in Figure 41a. It can be interpreted as a doublet (52.5 G) of doublets (15.8 G) of triplets (19.9 G). The simulation shown in Figure 41b by using these parameters matches the experimental spectrum quite well. The triplet (19.9 G) is due to the interaction from two α -protons, and the two different doublets are due to the interaction from two different β -protons. Therefore the spectrum is assigned to the ring-opened radical cation $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$ **2** which is a distonic species. The conformation at the radical center can be described by the following Newman projection:



The B-value calculated by use of the $B\cos^2\theta$ relationship from this project is 52.6 G. Since the β -proton hfcs of this cation differ significantly from those for neutral $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{NR}$ radicals⁸⁰ (Table VII), the radical cation assignment is confirmed. The facile ring-opening of this cation is certainly assisted by the formation of the protonated imine group that stabilizes the carbocationic center in **2**. On annealing **2** persists until 145K, the softening point of the matrix, without converting to **3**.

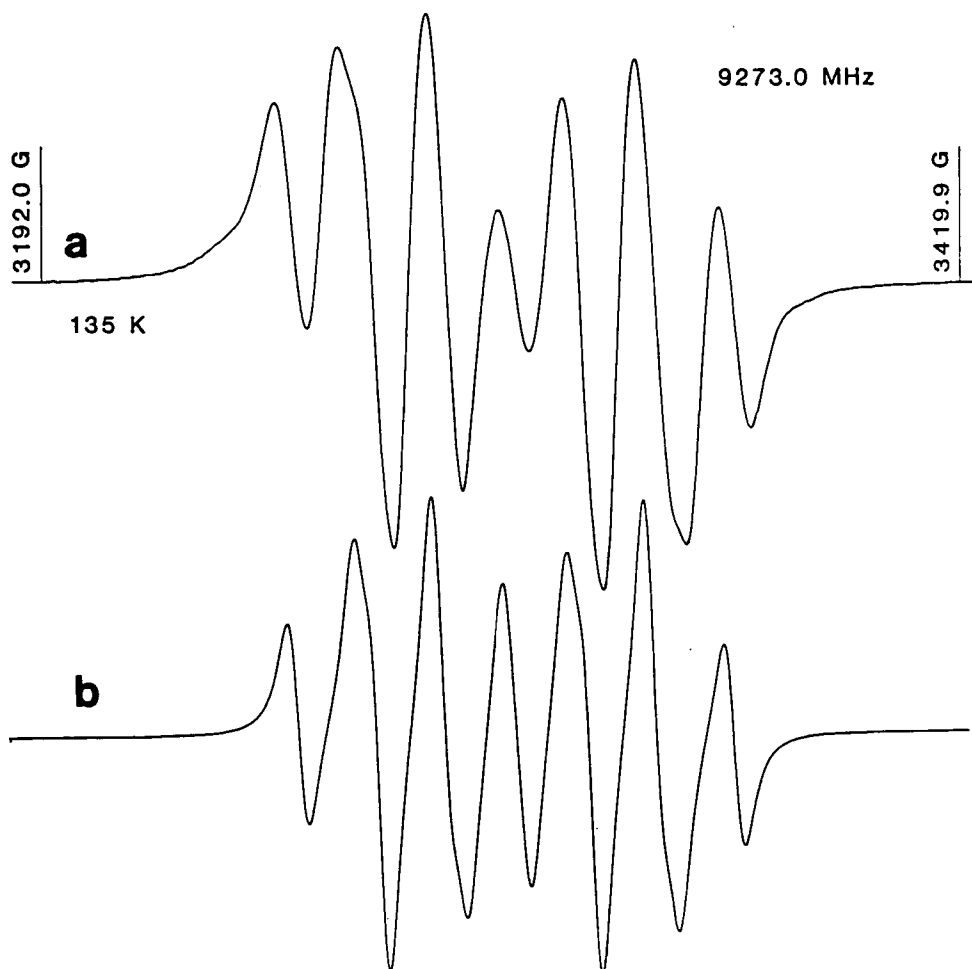


Figure 41. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened cyclobutylamine radical cation in F-113S. The simulation uses the ESR parameters in TABLE VII and a Lorentzian linewidth of 3.5 G.

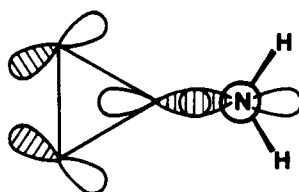
TABLE VII

ESR PARAMETERS OF CYCLOBUTYLAMINE AND CYCLOPROPYLAMINE RADICAL CATIONS
AND RELATED RADICAL SPECIES

Radical Cations or Radicals	Matrix	T/K	Hyperfine Couplings/G	g
$\dot{\text{C}}\text{H}_2(\text{CH}_2)_2\text{CH}=\text{NH}_2^+$	F-113S	135	19.9 (2H_α), 15.8 (1H_β), 52.5 (1H_β)	2.0029
$\dot{\text{C}}\text{H}_2(\text{CH}_2)_2\text{CH}=\text{NR}^*$	$\underline{\text{c}}\text{-C}_3\text{H}_6$	270	21.8 (2H_α), 28.1 (2H_β)	2.0025
$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{NH}_2^+$	F-113S	84	22.6 (2H_α), 17.0 (2H_β)	2.0029
$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{NR}^*$	$\underline{\text{c}}\text{-C}_3\text{H}_6$	135	22.1 (2H_α), 29.2 (2H_β)	2.0027
$\text{Me}(\text{CH}_2)_2\text{CH}=\dot{\text{N}}$	F-113U	125	80.9 (1H), 9.8 (^{14}N), 1.5 (1H_γ), 6.4 (1H_γ)	2.0029
$\text{MeCH}_2\text{CH}=\dot{\text{N}}$	F-113U	125	80.5 (1H), 9.7 (^{14}N), 3.0 (2H_γ)	2.0029
$\text{MeCH}_2\text{CH}=\dot{\text{N}}^{**}$	$\underline{\text{c}}\text{-C}_3\text{H}_6$	223	79.5 (1H), 9.6 (1N), 2.76 (2H), 0.45 (3H)	2.0028

* ref. 80. ** ref. 82.

Figure 42a shows the ESR spectrum of the radical cation of cyclopropylamine in F-113S. It consists of a triplet (22.6 G) of triplets (17.0 G) pattern. The larger triplet is attributed to two α -protons. The smaller triplet, therefore, is due to the interaction of two equivalent β -protons. These parameters differ from those for the neutral $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NR}$ radical⁸⁰ (Table VII) and hence the spectrum is assigned to the ring-opened radical cation $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$ (2'). The formation of this cation can be explained by considering the HOMO of the cyclopropylamine⁸¹ shown below.



The removal of one electron from cyclopropylamine to form the radical cation causes the weakening of the C-C bonds. That the bond breaks at the C-CN H_2 site is ascribed to the formation of the protonated imine group that stabilizes the carbocationic center in this structure. This ring-opened structure 2' persisted until 145 K without converting to 3'. These results can be summarized by Figure 43.

2. The Secondary Radicals Generated from Cyclobutylamine and Cyclopropylamine Radical Cations in F-113U

As has already been shown, neutral secondary radicals can be generated in F-113U above 105 K by deprotonation of the radical cations or hydrogen transfer from the neutral molecule to the radical cation. After having studied the behavior of the radical cations of cyclopropylamine and cyclobutylamine, it was of interest to study their conjugate bases, and this has been done by using F-113U as a matrix.

The ring-opened radical cation of cyclobutylamine was observed in F-113U at low temperatures. However, unlike in F-113S in which the radical cation persisted until 145 K, it changed irreversibly to the butan-1-iminyl radical at 105 K in this matrix. The ESR spectrum of the butan-1-iminyl radical was anisotropic at 105 K but became isotropic at

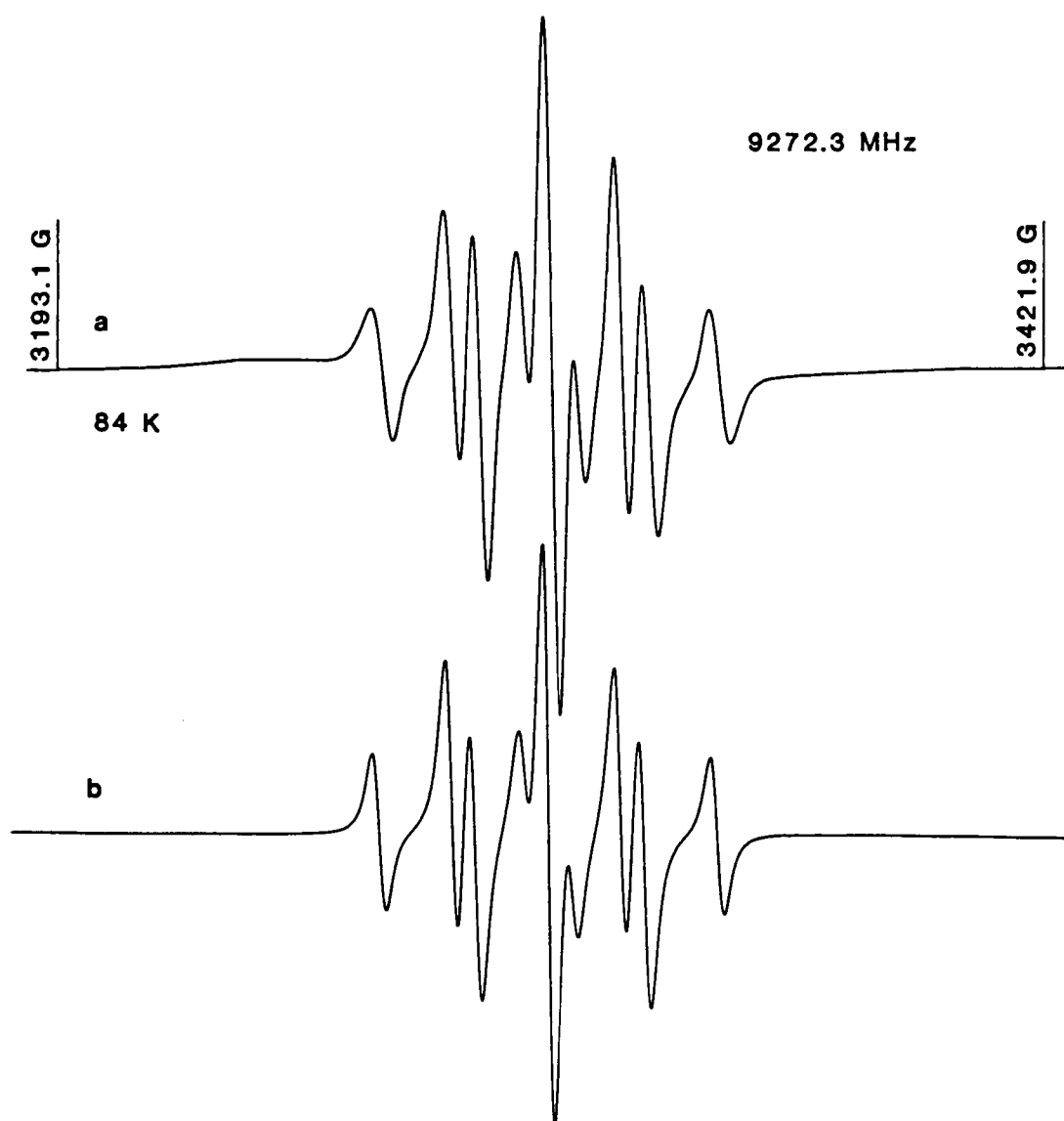
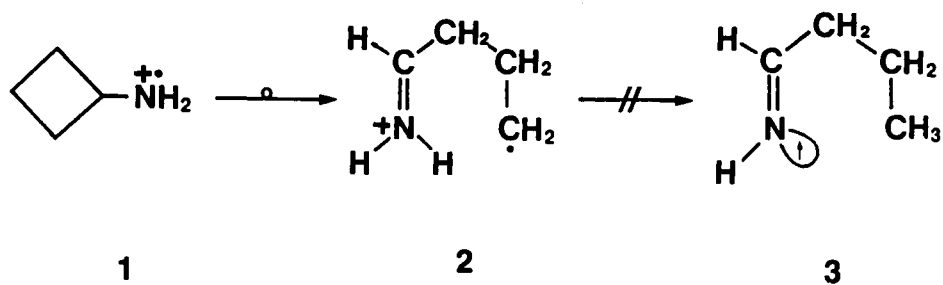


Figure 42. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened cyclopropylamine radical cation in F-113S. The simulation uses the ESR parameters in TABLE VII and a Lorentzian linewidth of 3.5 G.

a



b

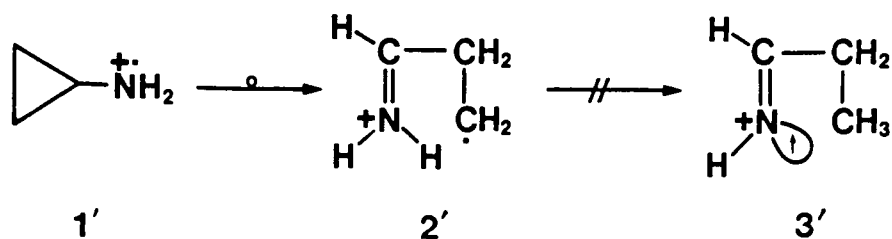


Figure 43. Schemes showing that the ring-opened cyclobutylamine and cyclopropylamine radical cations are not converted into the nitrogen-centered radicals.

125 K, as shown in Figure 44a. The spectrum can be readily analyzed as a large doublet ($a(1H) = 80.9$ G) of triplets ($a(^{14}N) = 9.8$ G). These couplings are in the range of this class of radicals⁸² (Table VII). The proton hfcs of the $-\underline{CH}_2-C=N$ group are not resolved, and they should be quite small. The observation of the butan-1-iminyl radical is rather surprising since the anticipated radical is $\cdot CH_2CH_2CH_2CH=NH$ 5. As described in Figure 45a, 5 may be formed by deprotonation (route a); or it may be formed by route b followed by route c. In this latter case the radical cation 2 abstracts hydrogen from its parent molecule to give the aminyl radical 4 by route b, and then 4 undergoes fast ring opening to give 5 by route c.⁸⁰ The fact of not seeing 5 clearly indicates that 5 was not stable under the condition whereby it was produced, and it is proposed that it underwent intramolecular hydrogen transfer to form 6 as illustrated in Figure 45a. This intramolecular hydrogen transfer has a six-membered ring transition state.

The corresponding study was carried out for cyclopropylamine in F-113U. The ring-opened radical cation was observed at low temperatures. It was converted irreversibly to the propan-1-iminyl radical above 105 K⁸² (Table VII and Figure 46a). The results as illustrated in Figure 45b are parallel to those reported for cyclobutylamine. The expected neutral radical $\cdot CH_2CH_2CH=NH$ (5') was not stable under these conditions after it was generated, and it underwent intramolecular hydrogen transfer to form $CH_3CH_2CH=N\cdot$ radical 6'. In this case, however, the transition state is a five-membered ring system.

C. Discussion

The above results are significant in two respects. First, it should be stressed that the thermal ring-opening of the cyclobutylamine radical cation is the only such reaction discovered among the four-membered ring radical cations. For example, the cyclobutane radical cation does not ring-open in the dark.⁸³ Also, oxetane, azetidine as well as the thietane radical cations are ring-closed as described in the preceding Chapters. Compared with their three-membered

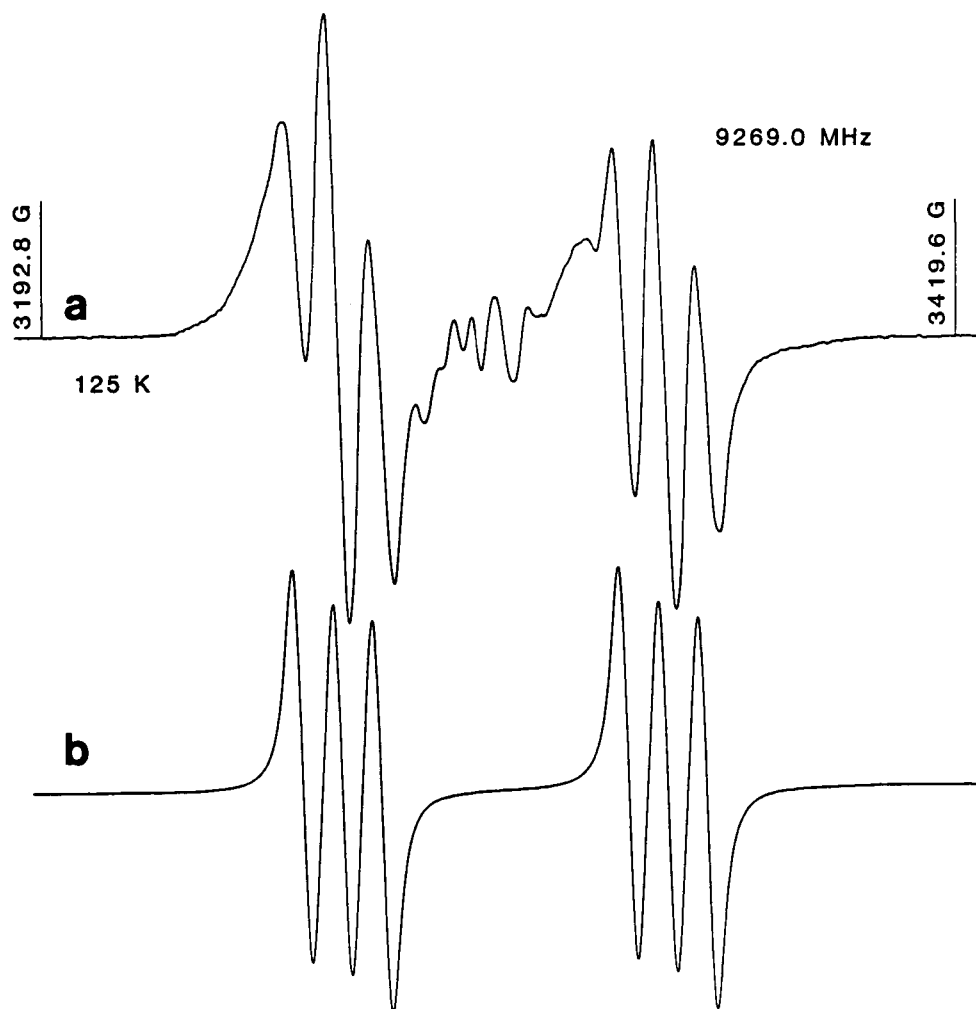


Figure 44. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\dot{\text{N}}$ radical in F-113U. The simulation uses the ESR parameters listed in TABLE VII and a Lorentzian linewidth of 3.0 G.

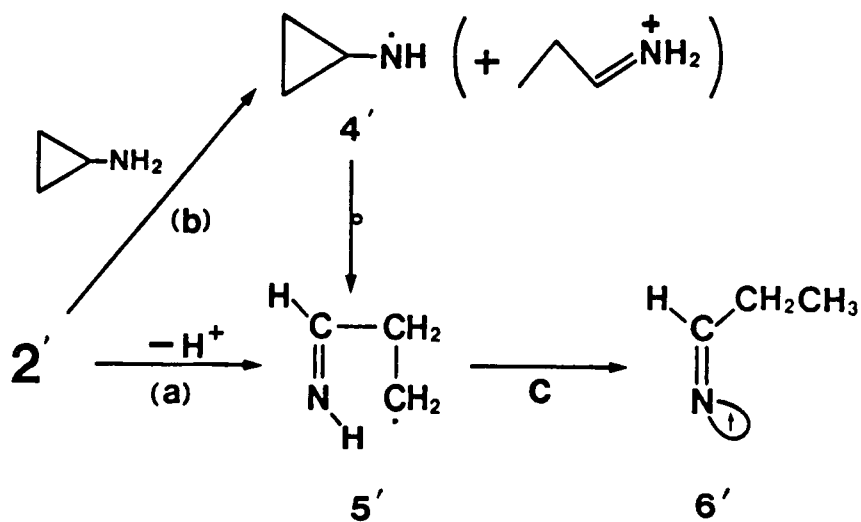
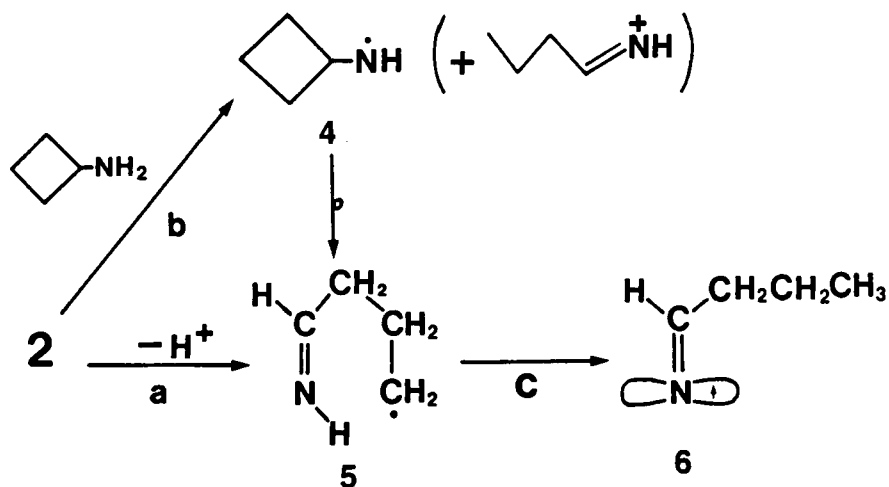


Figure 45. Schemes showing the formation of the $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CH}=\text{NH}$ and $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{NH}$ radicals and their relation with the $\text{MeCH}_2\text{CH}_2\text{CH}=\dot{\text{N}}$ and $\text{MeCH}_2\text{CH}=\dot{\text{N}}$ radicals, respectively.

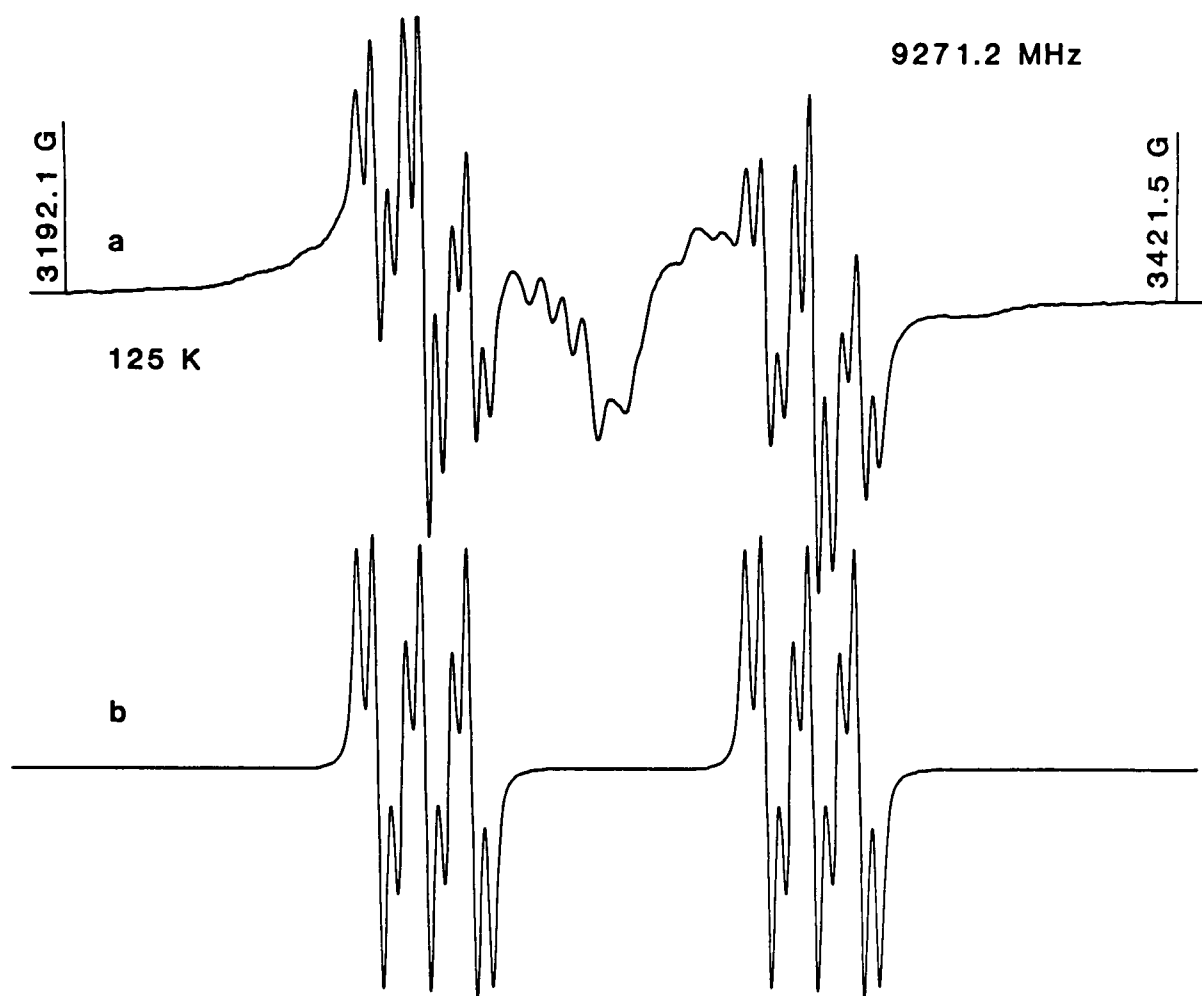
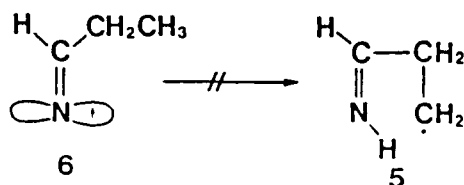
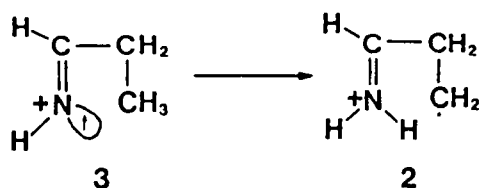


Figure 46. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the $\text{MeCH}_2\text{CH}-\dot{\text{N}}$ radical in F-113U. The simulation uses the ESR parameters listed in TABLE VII (p 127) and a Lorentzian linewidth of 2.5 G.

counterparts, four-membered ring cations do not seem to have enough driving force to undergo ring-opening. However, as described in this Chapter, the cyclobutylamine cation can undergo ring-opening just as easily as the cyclopropylamine cation. The driving force for this unusual behavior is obviously ascribable to the -NH_2 group which can stabilize the cationic center produced in the ring-opened cation 2 or 2' by forming the protonated imine group. It is noteworthy that these cations are distonic species. Therefore the present studies illustrate a way of forming these distonic species. Secondly, the results here established a remarkable reactivity difference between the radical cation 2 and the neutral radical 5, and also between the radical cation 2' and the neutral radical 5', over a wide temperature range. The ring-opened and carbon-centered radical cations 2 and 2' do not transform to the nitrogen-centered radical cations 3 and 3' whereas the carbon-centered neutral radicals 5 and 5' isomerize to the nitrogen-centered radical 6 and 6' readily. These relations can be related to the reverse processes in the well-known Hofmann-Löffler reaction.⁸⁴ As shown below, for the hypothetical Hofmann-Löffler reaction of the nitrogen-centered radical cation similar to 3 or 3', it isomerizes to produce a carbon-centered radical cation 2 or 2'. On the other hand, if the neutral nitrogen-centered radical similar to 6 or 6' is formed, it does not transform to the carbon-centered radical 5 or 5'.

HOFMANN-LÖFFLER REACTION (HYPOTHETICAL)



Thus the present work has uncovered the other side of the Hofmann-Löffler reaction. Clearly, combining information from the two systems indicates a thermodynamic basis for the reactivity difference.⁸⁵ In other words, the more stable species for radical cations are of type 2 (2') compared with 3 (3') while for neutral radicals they are of type 6 (6') compared with 5 (5'). This reactivity difference is clearly the reason which allows the cyclobutylamine radical cation 2 or cyclopropylamine radical cation 2' to play such an important role in enzyme inhibition.

The conclusion about the energetic difference between the radical cations and radicals is also supported by some recent *ab initio* calculations by Radom,⁸⁶ who found that the energy of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{NH}_2^+$ lies considerably lower than that of $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}^+$, while the energy of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{NH}$ lies higher than that of $\text{CH}_3\text{CH}_2\text{CH}=\dot{\text{N}}$.

Finally, the reactivity difference discussed above can well be understood by the prediction on the basis of the general argument that in hydrogen abstraction processes a stronger N-H bond will be formed for a nitrogen-centered radical cation than for its counterpart neutral radical.⁸⁷ It follows that the reverse process of hydrogen shift from nitrogen to carbon in the neutral radical should be easier than in the radical cation, as clearly demonstrated by the present work.

CHAPTER VIII

ALLENE RADICAL CATIONS

A. Introduction

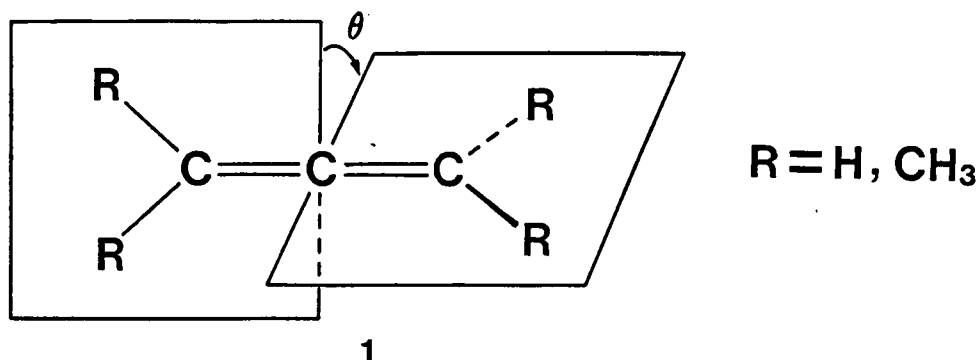
The allene radical cation has been studied experimentally by mass spectrometric,^{88,89} and electrochemical methods,⁹⁰ and by photoelectron⁹¹ and ESR⁹² spectroscopic techniques. An ab initio calculation⁹³ on the allene radical cation predicted a distortion from the D_{2d} symmetry of the parent molecule to D_2 symmetry in the radical cation with a skew angle of 45 - 52, in accord with the experimental results. However, no ESR studies of the radical cations of the methyl-substituted allenes have been reported. Moreover, the condensed phase chemistry of allene radical cations is not well documented. Recently, Mariano and co-workers reported that 2-phenyl-1-pyrrolinium perchlorate can easily photooxidize allene,⁹⁴ and that the generated radical cation-radical pair can undergo radical coupling, nucleophilic addition, or deprotonation. However, the exact reaction path was uncertain.

In the present work, the ESR studies have been expanded from the radical cation of allene to include those of 1,1-dimethylallene and tetramethylallene. The results show that as expected, the radical cations of allene and tetramethylallene are Jahn-Teller active species, while the radical cation of 1,1-dimethylallene is not a Jahn-Teller active species, its radical cation center being localized on the dimethyl-substituted side of the molecule. In the F-113U matrix, ion-molecule reactions between allene and the allene radical cation as well as between 1,1-dimethylallene and its radical cation have been found to produce allenyl-type neutral radicals, while tetramethylallene, with no α -protons, undergoes an unique reaction to form an allyl-type radical.

B. Results

1. Allene

Figure 47 shows the ESR spectrum of the allene radical cation in F-11. It has been previously reported by Takemura and Shida.⁹² However, they did not point out that this cation decayed above 130 K in this matrix. As they suggested, the allene radical cation can be represented by structure 1, which is called a "linear-45°-twisted" structure.



The ESR spectrum of the allene radical cation in F-113U is shown in Figure 48. The main quintet pattern with a hfc of 13.0 G and g-value of 2.0026 is essentially the same as that obtained in F-11, except that the residual anisotropic coupling of 1.0 G in Figure 47 is not resolved in this matrix. The resolution of the spectra in this matrix at low temperatures is usually not as good as that in F-11. Above 95 K, the cation decayed. It was accompanied by the growth of a new radical species, which gave the new ESR spectrum shown in Figure 49. This spectrum is not a 1:3:3:1 pattern since the spacings between the lines are not equal. Nor is it a doublet of doublets since the intensity of these lines are not right for such pattern. Considering that ion-molecule reactions generally occur in this matrix above 105 K, the new radical may be assigned to the allenyl radical formed by deprotonation or hydrogen abstraction during the reaction of the allene radical cation with its parent molecule. The spectrum of the allenyl radical is expected to be a doublet of triplets as indicated by the stick diagram. However the two components represented by $M_I(H_\alpha) = -1/2$, $M_I(2H) = -1$ and $M_I(H_\alpha) = +1/2$, $M_I(2H) = +1$ are largely obscured. This spectrum for the allenyl radical was also obtained by Volman and

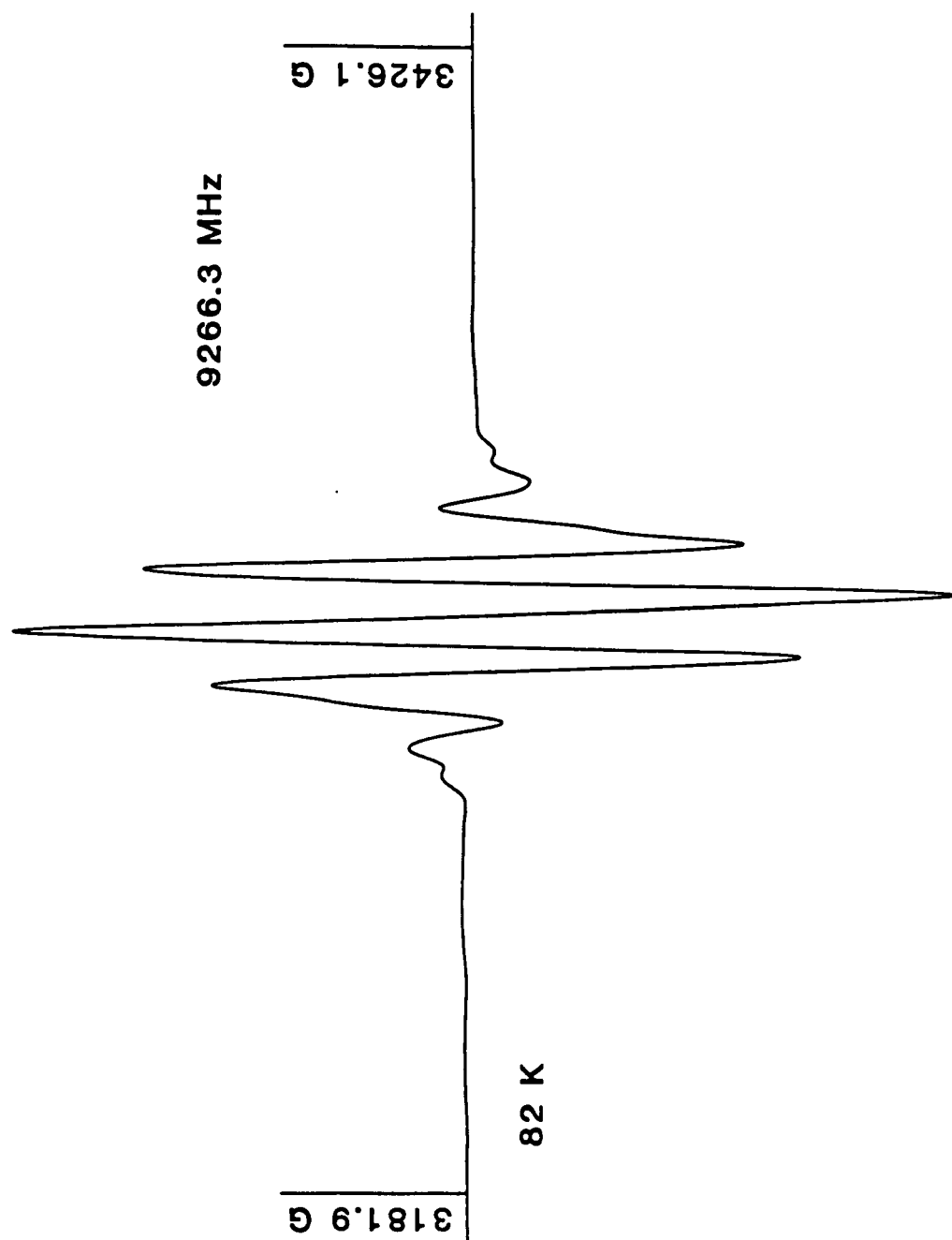


Figure 47 . First-derivative ESR spectrum of the allene radical cation in F-11.

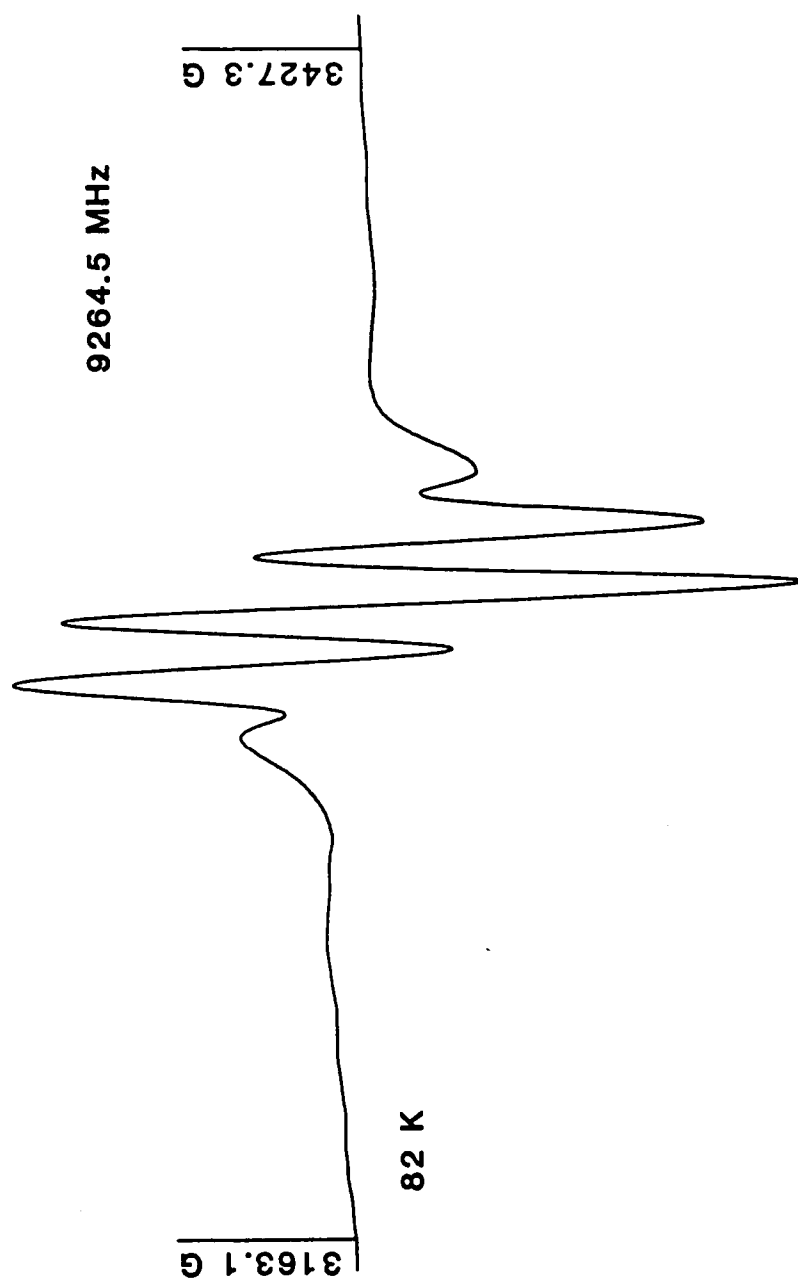


Figure 48. First-derivative ESR spectrum of the allene radical cation in F-113U.

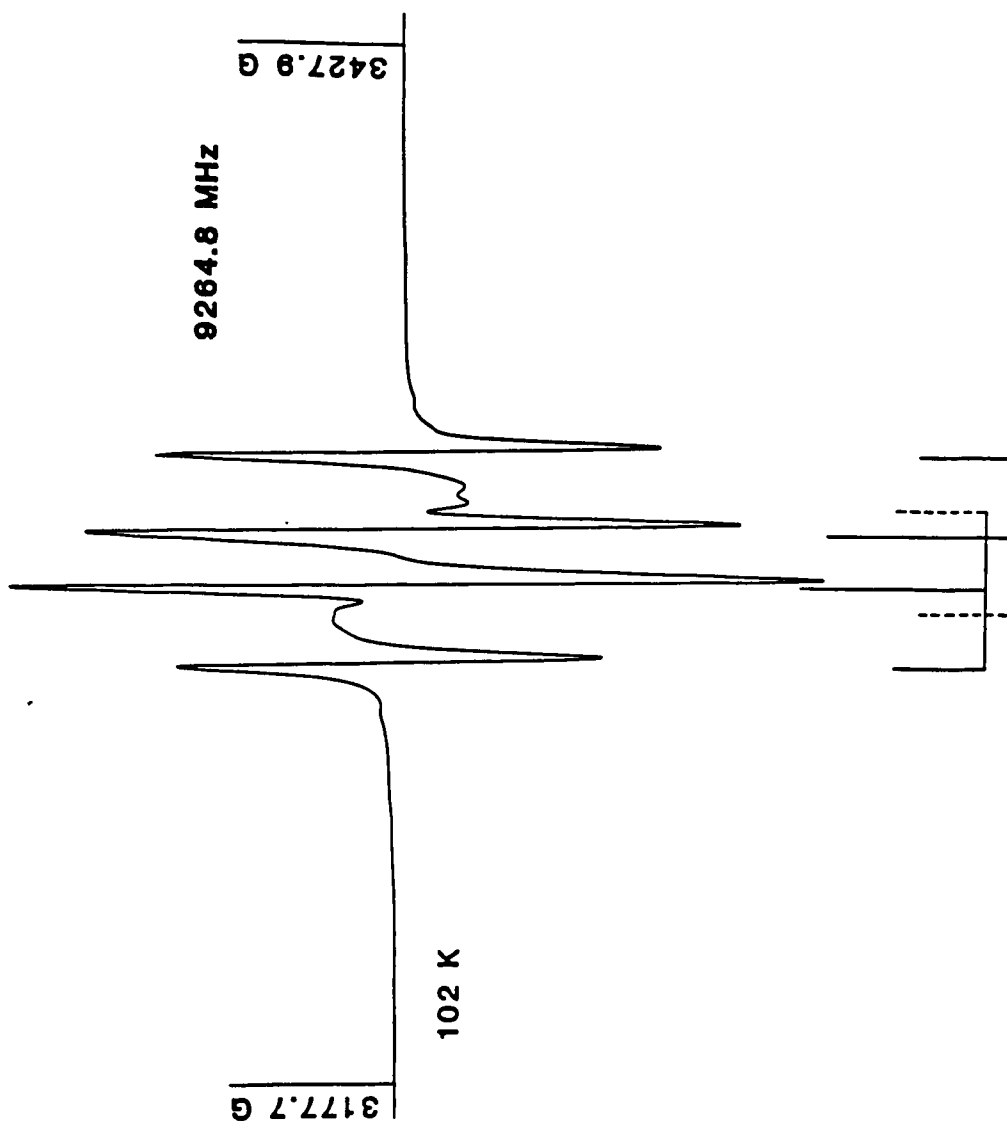
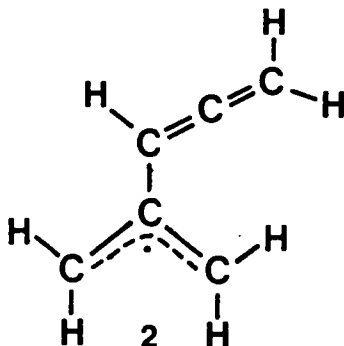


Figure 49. First-derivative ESR spectrum of the allenyl radical in F-113U.

co-workers,⁹⁵ and therefore is characteristic despite the unusual form of the pattern, the allenyl radical being generated by ultraviolet-irradiation of allene at 77 K in their case. The hfcs obtained in the present study agree very well with the known values for the allenyl radical.^{95,22a} Therefore, the assignment is confident.

Further warming of the allene sample in this matrix to 105 K led a second change. The allenyl radical was irreversibly converted to a third radical species as shown by the ESR spectrum in Figure 50. This spectrum consists of a new quintet pattern with a hfc of 14.0 G and a g-value of 2.0026. The new radical can be easily assigned to the allyl radical 2 formed by the addition of the allenyl radical to the central carbon of the neutral allene molecule. Radical addition to allene is a well-documented reaction.⁹⁶



2. 1,1-Dimethylallene

Figure 51a gives the ESR spectrum of the 1,1-dimethylallene radical cation in F-11. The spectrum is readily analyzed into a septet ($a(6H) = 13$ G) of triplets ($a(2H) = 10$ G) (Table VIII) and is easily assigned to the 1,1-dimethylallene radical cation since the hfcs account for all the protons in this molecule. This radical cation persisted until the softening point of the matrix at 160 K.

The low-temperature spectrum obtained by γ -irradiation of 1,1-dimethylallene in F-113U is essentially the same as that observed in F-11 but is not as well resolved. This situation is similar to that for the allene radical cation in these two matrices. On warming up the sample in F-113U to 100 K, the spectrum became very well resolved showing a clear septet of triplets, but some other spectral change also occurred in the same temperature range. This irreversible change

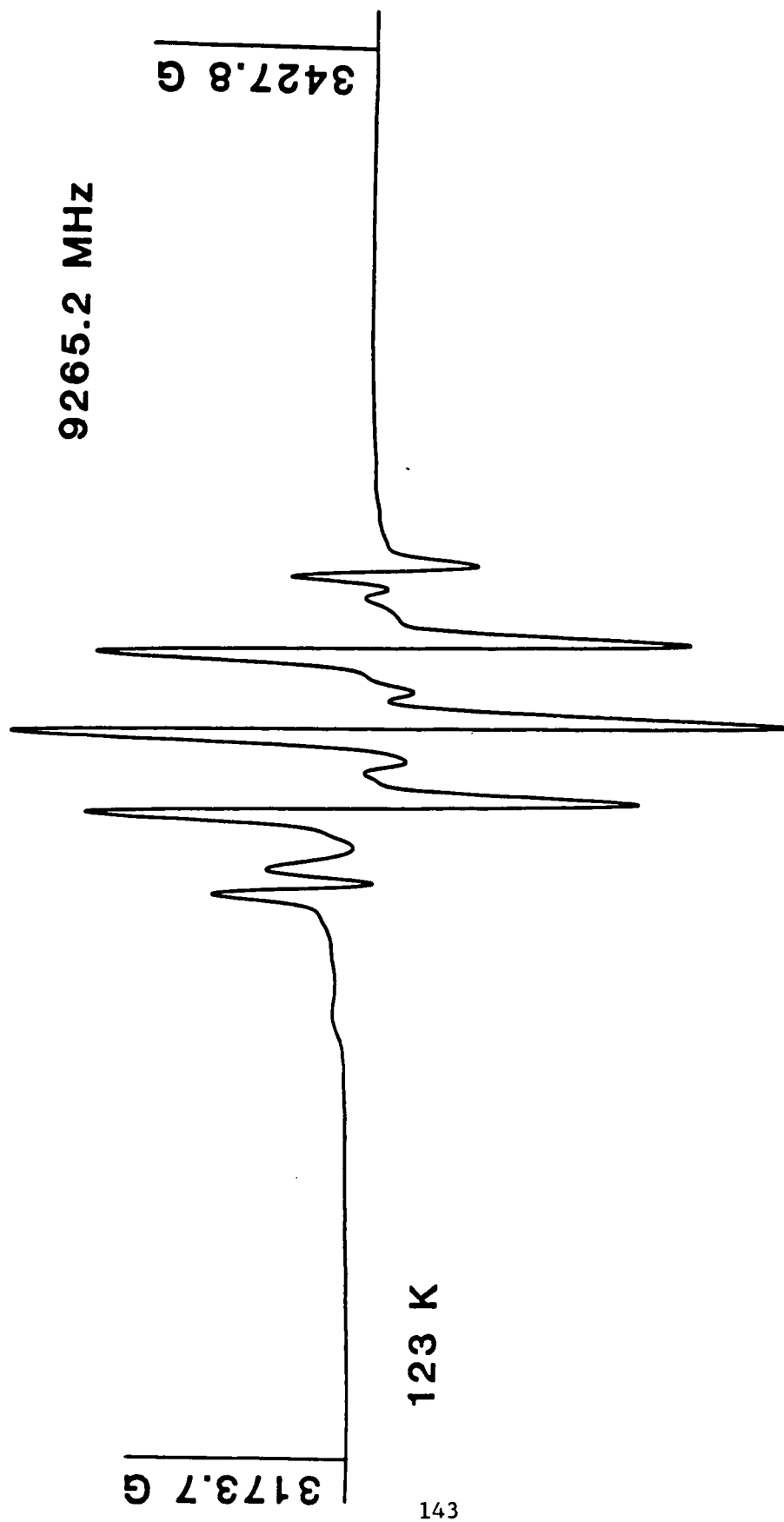


Figure 50. First-derivative ESR spectrum of the allyl radical $\text{CH}_2\text{C(R)CH}_2$ in F-113U.

TABLE VIII

ESR PARAMETERS FOR THE RADICAL CATIONS OF ALLENE,
DIMETHYLALLENE, AND TETRAMETHYLALLENE
AND RELATED RADICALS

Radical Cations or Radicals	Matrix	T/K	Hyperfine Couplings/G	g
$\text{CH}_2=\text{C}=\text{CH}_2^{+\cdot}$	F-113U	80	13.0 (4H)	2.0029
$\text{Me}_2\text{C}=\text{C}=\text{CH}_2^{+\cdot}$	F-11	87	34.4 (2H), 14.6 (6H)	2.0029
	F-113U	100	34.4 (2H), 14.6 (6H)	2.0028
$\text{Me}_2\text{C}=\text{C}=\text{CMe}_2^{+\cdot}$	F-11	88	8.1 (12H)	2.0028
	F-113U	110	8.1 (12H)	2.0028
$\text{Me}_2\text{C}=\text{C}=\dot{\text{C}}\text{H}$	F-113U	105	11.4 (1H), 17.6 (6H)	2.0026
$\text{CH}_2=\text{C}=\dot{\text{C}}\text{H}$	F-113U	105	12.6 (1H), 18.9 (2H)	2.0026

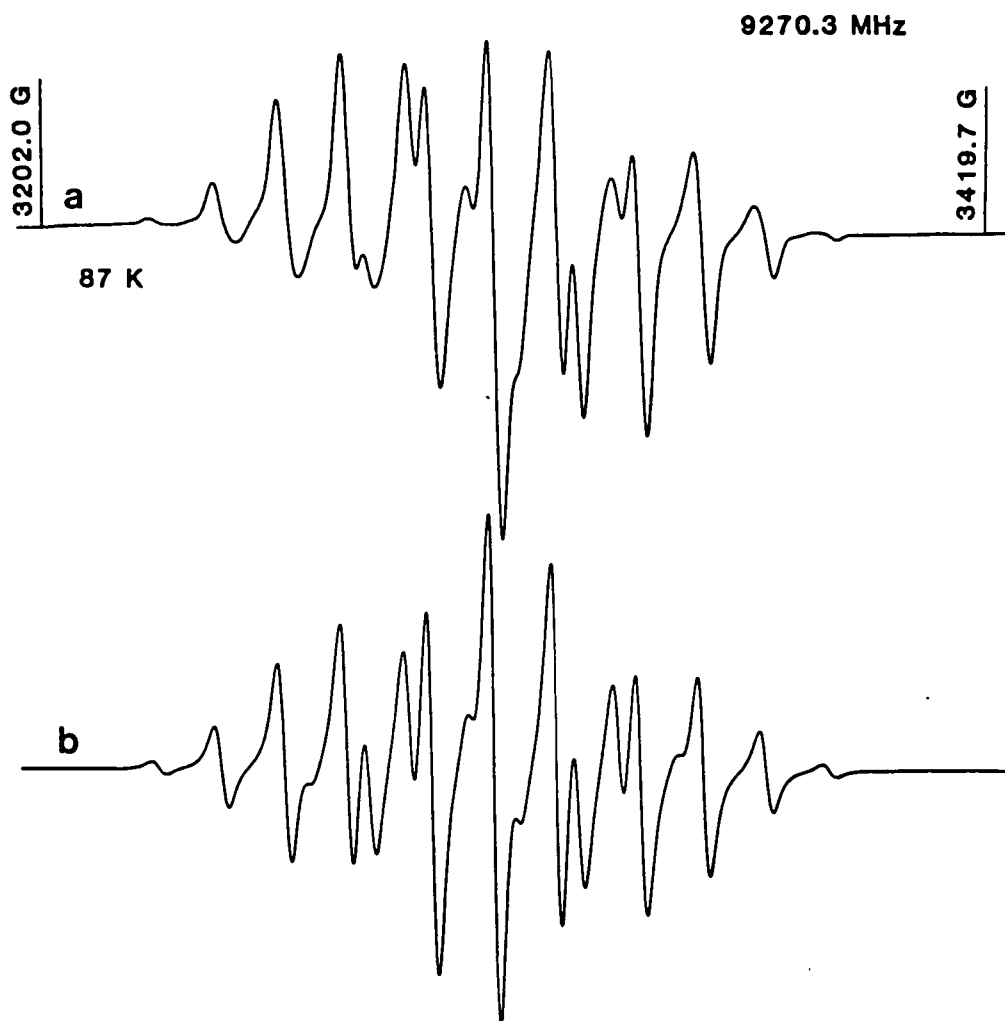


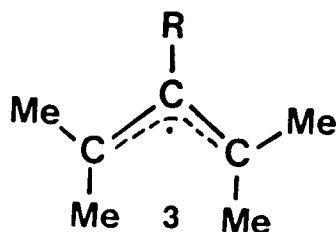
Figure 51. (a) Observed and (b) computer-simulated ESR spectra of the 1,1-dimethylallene radical cation in F-11. The simulation uses the ESR parameters listed in TABLE VIII and a Lorentzian linewidth of 3.5 G.

finally brought about the formation of the 3-methyl-1,2-butadienyl radical with hfcs of $a(6H) = 17.6$ G, $a(1H) = 11.4$ G, and a g-value of 2.0027 as shown by the spectrum in Figure 52, these ESR parameters for this radical being in agreement with those previously reported.⁹⁷ This radical decayed above 125 K without producing a third radical, in contrast with the allene case.

3. Tetramethylallene

The ESR spectrum of the tetramethylallene radical cation in F-11 is shown in Figure 53a. The spectrum consists of a binomial 13-line pattern ($a(12 H) = 8.1$ G). Hence the unpaired electron is delocalized over the entire molecule. This cation can be represented by a linear- θ° -twisted structure (structure 1 where $R = Me$). The twisted angle was calculated by the AM1 method as 45° .

The tetramethylallene radical cation was also observed in F-113U at low temperatures. One typical ESR spectrum of the cation is shown in Figure 53b, which gives the same ESR parameters as those obtained from Figure 53a in F-11. This radical cation persisted to well above 110 K. Although ion-molecule reactions occurred in this temperature range in the allene and 1,1-dimethylallene cases, in this case such reactions seemed not to occur. A spectral change was only observed on further warming up the sample to 125 K. The ESR spectrum of the new radical is shown in the upper spectrum of Figure 54. This spectrum does not fit the known 2,4-dimethyl-2,3-pentadiene-1-yl⁹⁸ radical, which might be produced by deprotonation of the radical cation or by hydrogen abstraction from the neutral molecule by the radical cation. The only satisfactory simulation of this spectrum was obtained by using the ESR parameters: $a(6H) = 11.6$ G and $a(6H) = 15.8$ G shown in the bottom of Figure 54. The average value for these two sets of methyl group hfcs (13.7 G) is very reasonable for the allyl-type radical depicted by 3.



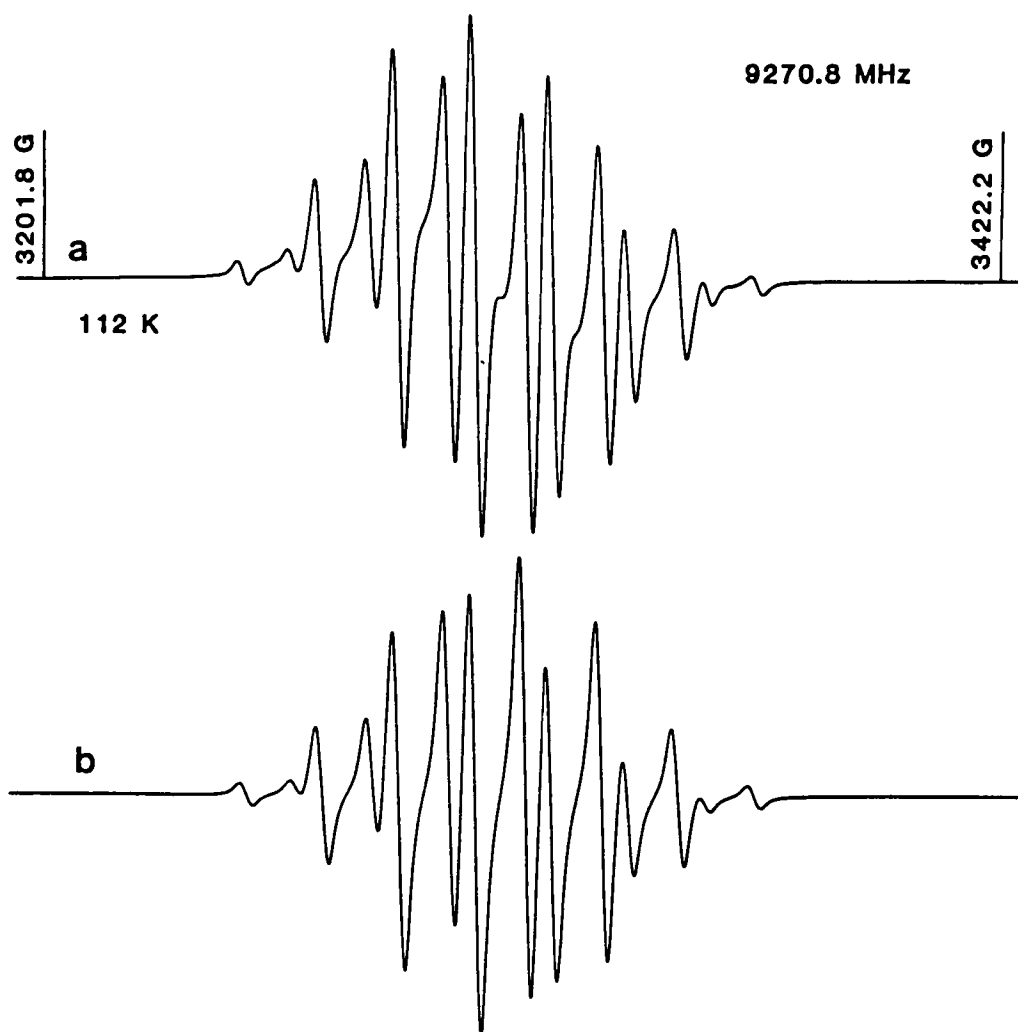


Figure 52. (a) Observed and (b) computer-simulated ESR spectra of the $\dot{\text{C}}\text{H}-\text{C}-\text{C}(\text{Me})_2$ radical in F-113U. The simulation uses the ESR parameter listed in TABLE VIII and a Lorentzian linewidth of 3.5 G.

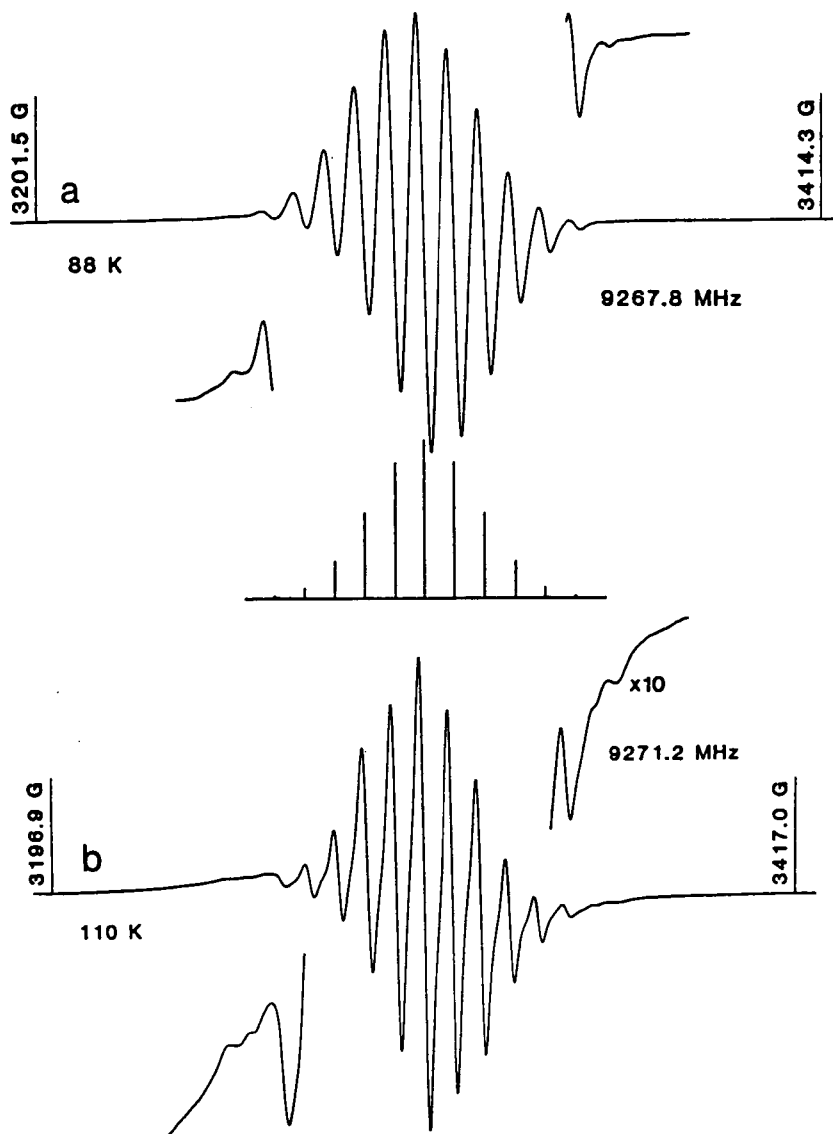


Figure 53. First-derivative ESR spectra of tetramethylallene radical cation in (a) F-11 and (b) F-113U.

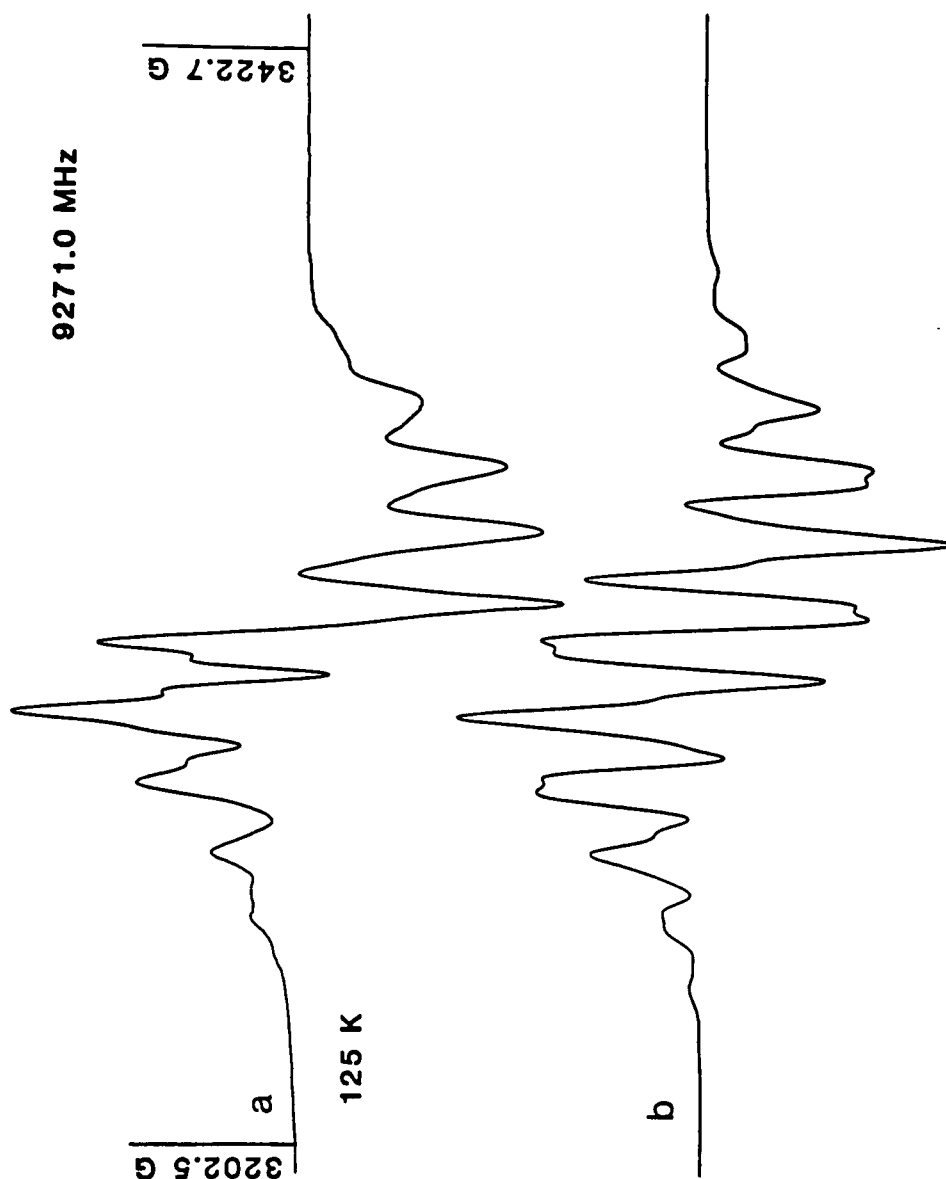


Figure 54 . (a) Observed and (b) computer-simulated first-derivative ESR spectra of the tetramethylallyl radical with the center H replaced by R group in F-113U (see text). The simulation uses the ESR parameters listed in TABLE VIII and a Lorentzian linewidth of 3.5G.

The central R group may have several possibilities. For instance, it may be the 2,4-dimethyl-2,3-pentadiene-1-yl group, by analogy with the allene case where the allenyl radical added to its parent molecule in this temperature range. Similarly, in the present case, if the 2,4-dimethyl-2,3-pentadiene-1-yl radical were to be formed by the ion-molecule reaction at this temperature, it might immediately add to tetramethylallene to form 3. The other choice of R is CL^- , which could attack the tetramethylallene radical cation to form 3. Nucleophilic attack on the central carbon of the allene radical cation is a well documented reaction.⁹⁹ However, since this kind of attack was not detected in the 1,1-dimethylallene case, it seems less likely.

C. Discussion

1. The Jahn-Teller Distortion of the Radical Cation of Allene and Tetramethylallene

The allene radical has been carefully studied by different techniques as mentioned earlier. It can be described by a linear- θ° -twisted structure. The twist angle was determined by semi-empirical or ab initio quantum calculations, and different values obtained depending on the methods used. Thus MINDO/2 predicted a 52° twisted angle,⁹⁴ while MNDO-UHF, SCF-UHF using STO-3G and higher level(4-31 G)⁹⁰ methods predicted 45° twist angle. All the calculations show that when one of the electrons in a degenerate π -orbital of the allene molecule is removed, the resulting odd electron can be delocalized into the other π -orbital, leading to a deviation from the orthogonality of these two π -orbitals in the neutral molecule. All these calculations also predict that the allene radical cation has high positive-charge density at the central carbon atom and large odd-electron density at the terminal carbons. Using the AM1 method to calculate the structure of the allene radical cation in the present study, a twist angle of 43° was found. The large spin density at terminal carbons and the high positive-charge density at the central carbon were also in agreement with the other calculations. Moreover, the calculated hfcs for the four

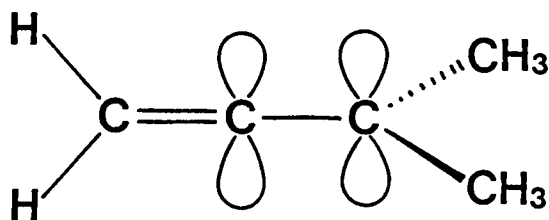
equivalent protons is 13.5 G by AM1 calculation, in reasonable agreement with the experimental result (13.0 G).

The structure of the tetramethylallene radical cation is not known in the literature, to the best of the author's knowledge. It is, however, expected to be also a Jahn-Teller active species since its parent molecule has degenerate π -orbitals. The hfc of 8.1 G for the protons from all four methyl groups in this species confirms this expectation. The AM1 calculation for this cation shows that it is best represented by a linear θ° -twisted structure with a twist angle of 45° . However, the spin density for this species is predicted to be slightly larger on the central carbon than in the case of allene radical cation. The difference may be explained by assuming that the methyl groups stabilize positive charge more than the odd-electron density, causing more positive charge than spin density to reside at the two terminal carbons. Since the AM1 calculation predicts the allene radical cation structure in agreement with the higher-level methods indicated above, it is reasonable to think that the calculations for the tetramethylallene radical cation should also give reasonable results. In fact, comparison of the observed hfc of 8.1 G with a value of 24 G for unit spin density suggests that only about 2/3 of the total spin density is in the terminal carbons.

2. The Structure of the 1,1-Dimethylallene Radical Cation

The two π orbitals in this molecule are no longer degenerate. As a result, there is no Jahn-Teller effect anticipated in this case. This point was also demonstrated by the photoelectron spectroscopic studies, showing that the HOMO of this molecule is the π orbital at the methyl-substituted side.¹⁰⁰ It follows that the electron will be removed from this orbital to form the corresponding radical cation. The ESR result in the present study giving a 14.6 G hfc for the protons from the two methyl groups establishes this prediction. Had the electron been removed from the unsubstituted side, the methyl-group protons would be in γ -positions, and the long-range hfc for them should be much smaller (ca. 6 G or less). But the result is understandable if the SOMO of the cation is localized at the methyl-substituted side since the observed

methyl proton hfc is quite close to that of 1,1-dimethylethene radical cation ($a(\text{Me}) = 16.5 \text{ G}$),^{23b} as would be expected. Interestingly, the two allenyl protons displays an even larger hfc ($a(2\text{H}) = 34.4 \text{ G}$). This suggests that the two π orbitals in this cation are still normal to each other as shown below, because if this cation is also twisted, the electron should be delocalized into two π -orbitals as in the former two cases, causing both the methyl hfcs and the two methylene proton hfcs to decline.



That the two allenyl β -protons are in the same plane of the SOMO π -orbital is strongly supported by comparison with the formaldehyde radical cation in which the two formaldehyde protons are in the plane of the oxygen p-orbital with the odd electron, the hfc for these two protons having the large value of 133 G .¹⁰¹ This similarity accounts for the larger-than-expected hfc of 34.2 G in the present case. Other examples of this class of radical cations with large β -proton couplings include H_2CN ($A = 87 \text{ G}$)¹⁰² and H_2BO ($A = 133 \text{ G}$).¹⁰³ The present study adds another interesting example to this class with no heteroatoms in the molecule. It is reasonable that the hfcs for these β -protons in the present case are less than half the corresponding values in the other cases, since the spin density at the central carbon is expected to be less than 0.5.

3. Ion-molecule Reactions

The isomerization of the allene radical cation to cyclic cations reported frequently in mass-spectrometric studies^{88,89} was not observed in this low-temperature study in Freons. Except for radical addition process, the only chemistry found is the ion-molecule reaction between the allene radical cation and its parent molecule to form the allenyl

radical. This can happen by either (a) the transfer of an allenyl hydrogen from an allene molecule to an allene radical cation by a free radical process; or (b) by deprotonation of a proton from an allene radical cation to an allene molecule. Such reactions are very common in certain matrices (see Chapter IX). The interesting finding in this study is that if the molecule has allenyl hydrogens such as allene and 1,1-dimethylallene, the ion-molecule reaction occurred around 105 K, the normal temperature range in which ion-molecule reactions can be observed in the relevant matrices. But for tetramethylallene molecule which has no allenyl hydrogen, the apparent ion-molecule reaction occurred at 15 K higher, indicating that proton loss or hydrogen abstraction is more difficult from the methyl position than from the olefinic position. This selectivity may be useful for the synthesis involving these radical cations.

CHAPTER IX

ION-MOLECULE REACTIONS OF RADICAL CATIONS

A. Introduction

It has been mentioned in the Introduction of this dissertation that for substrates whose ionization potentials are less than that of the Freon, the corresponding radical cations are formed after exposure to γ -rays in the Freon. Primary radical cations can be obtained in general, as is clearly seen in the above Chapters. However in certain matrices such as F-113U, the ESR spectra of the primary radical cations can only be observed at low temperatures (ca. 80 K to 100 K), since on annealing to above 105 K, ion-molecule reactions always take place. Many such reactions have been observed by using the Freon technique.²⁰ In the preceding Chapters, some of these reactions have also been described. In this Chapter, one very important and general ion-molecule reaction in which radical cations react with their parent molecules to form neutral radicals and carbocations, will be reported in detail for spiro[2.5]octane, cyclopentene oxide, exo-epoxynorbornane, tetramethylethylene and dimethylsulfide. Two mechanisms may be involved in these reactions. One is deprotonation written as:



where a proton is transferred from the radical cation to the neutral molecule. The other is hydrogen atom transfer, written as:



where the hydrogen atom is donated from the neutral molecule to the radical cation.

Iwasaki and co-workers have studied the reactions of alkane radical cations in F-113U and SF₆ systematically.^{20b} They concluded that alkane radical cations undergo deprotonation to form neutral

radicals, the general rule being that the bond breakage takes place where the spin density is the highest. In the course of the present work on radical cations in F-113U, however, it was found that their conclusion is not always applicable. In some cases, ion-molecule reactions take place where the C-H bond does not break at the highest spin-located bond of the radical cation. These reactions are better understood as hydrogen abstraction processes.

B. Results

1. Spiro[2.5]octane

Between 80 and 100 K, the ESR spectrum of this radical cation in F-113U shown in Figure 55a with a g -value of 2.0023 is a 23.0 G triplet (Table IX) due to only two α -protons. It is easily assigned to the ring-opened radical cation 1 formed by bond breakage at the unsubstituted carbons of the cyclopropane ring.

The bond breakage between the other carbons of either the cyclopropane ring or cyclohexane ring should give either a tertiary alkyl radical or an $\text{RCH}_2\dot{\text{C}}\text{H}_2$ radical, which can be ruled out by the ESR datum ($a(2\text{H}) = 23.0 \text{ G}$). A ring-closed radical cation should give a quintet pattern if the spin is in the cyclopropane ring; or it should give a much wider spectrum if the spin is in the cyclohexane ring;^{20b} both of these possibilities can also be ruled out by the ESR datum ($a(2\text{H}) = 23.0 \text{ G}$).

Upon warming to 112 K, the triplet spectrum was converted irreversibly to a new, much wider spectrum shown in Figure 55b. This new spectrum can be readily analyzed as a triplet (41.6 G) of doublets (22.3 G) of triplets (5.1 G) (Table X). The simulation shown in Figure 55c in terms of this analysis fits Figure 55b very well although the experimental spectrum has some additional background signals. These parameters are found to be very close to those reported for the cyclohexyl radical,^{104,27b} and accordingly it can be attributed to the spiro[2.5]oct-6-yl radical. The results can be illustrated by the following equations:

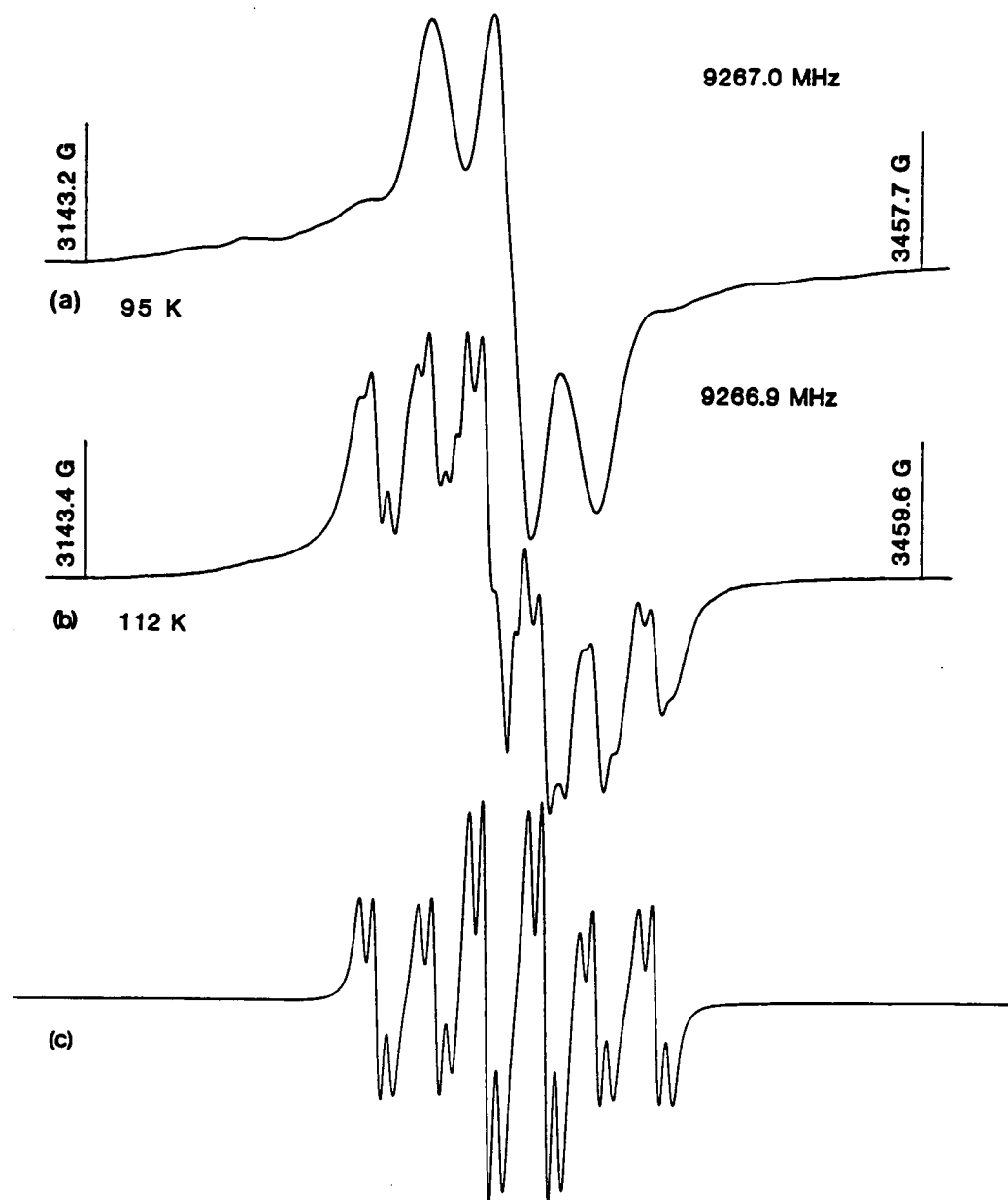


Figure 55. (a) First-derivative ESR spectrum of the radical cation radiolytically generated from spiro[2.5]octane in F-113U, (b) first-derivative ESR spectrum of the spiro[2.5]oct-6-yl radical, and (c) simulation of the spiro[2.5]oct-6-yl radical spectrum. The simulation uses the ESR parameters in TABLE X and a Lorentzian linewidth of 3.0 G.

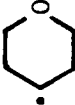
TABLE IX

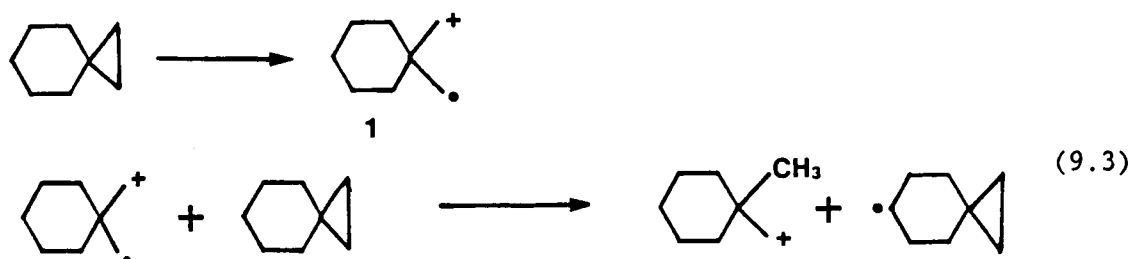
ESR PARAMETERS FOR THE RADICAL CATIONS IN THE ION-MOLECULE REACTIONS

Radical Cation	Matrix	T/K	Hyperfine Couplings/G	g
	F-113U	80	23.0 (2H)	2.0023
	F-113U	81	15.5 (2H _α), 9.1 (2H _β), 31.0 (2H _β)	2.0024
	F-113U	105	15.8 (2H _α), 8.2 (2H _β)	2.0023
(Me) ₂ C=C(Me) ₂ ⁺	F-113U	90	16.5 (12H)	2.0029
[(Me) ₂ C=C(Me) ₂] ₂ ⁺	F-113U	110	7.8 (24H)	2.0029
MeSMe ⁺	F-113U	81	20.4 (6H)	g _x = 2.032 g _y = 2.017 g _z = 2.002
(MeSMe) ₂ ⁺	F-113U	100	6.5 (12H)	2.010

TABLE X

ESR PARAMETERS FOR THE NEUTRAL RADICALS IN THE ION-MOLECULE REACTIONS

Radical	Matrix	T/K	Hyperfine Couplings/G	g
	F-113U	112	2.0 (1H _α), 26.6 (2H _β), 40.1 (2H _β)	2.0025
	F-113U	115	22.0 (1H _α), 26.6 (2H _β), 40.1 (2H _β)	2.0028
	F-113U	130	21.0 (1H _α), 26.2 (1H _β), 35.8 (1H _β), 3.7 (2H)	2.0024
•CH ₂ C(Me)=C(Me) ₂	F-113U	125	16.0 (3H _{exo}), 12.7 (3H _{endo}), 13.5 (2H), 3.3 (3H)	2.0029
•CH ₂ SMe	F-113U	120	16.7 (2H _α), 3.3 (3H _γ)	2.0048



2. Cyclopentene Oxide

The radical cation of this compound in F-11 has been carefully studied and its spectrum was convincingly assigned to the ring-opened planar form of the radical cation by Snow.⁵¹ The spectrum shown in Figure 56b for the radical cation of this compound observed in F-113U at 81 K is essentially the same as that in F-11. The ESR parameters obtained are collected in Table IX. The stick diagram reconstructs the spectrum by using these parameters, incorporating the out-of-phase α -proton modulation effect which was reported in F-11. Therefore, there is little doubt that the same ring-opened form of the cyclopentene oxide radical cation 2 was detected in F-113U at low temperatures.

By raising the temperature in F-11 to 160 K, the fast-limit spectrum of the ring-opened form of the cyclopentene oxide cation could be approached, where the alternating-linewidth effect due the two α -protons becomes less pronounced. A similar spectrum could also be observed in SF₆ at lower temperatures, as shown in Figure 56a. However, on annealing in F-113U to 105 K, the ring-opened form irreversibly decayed, giving rise to a new radical species. The ESR spectrum of the new radical is shown in Figure 57a. It consists of a triplet (40.1 G) of triplets (26.6 G) of doublets (22.0 G) from the best simulation shown in Figure 57b. The two sets of triplets can be easily attributed to two axial and two equatorial β -protons, while the magnitude of the doublet is typical of one α -proton hfc. The species responsible for the new spectrum is thus the symmetric carbon-centered radical 3. Another radical species which could be formed from the rearrangement of the ring-opened form of the cyclopentene oxide cation is 4. However, this

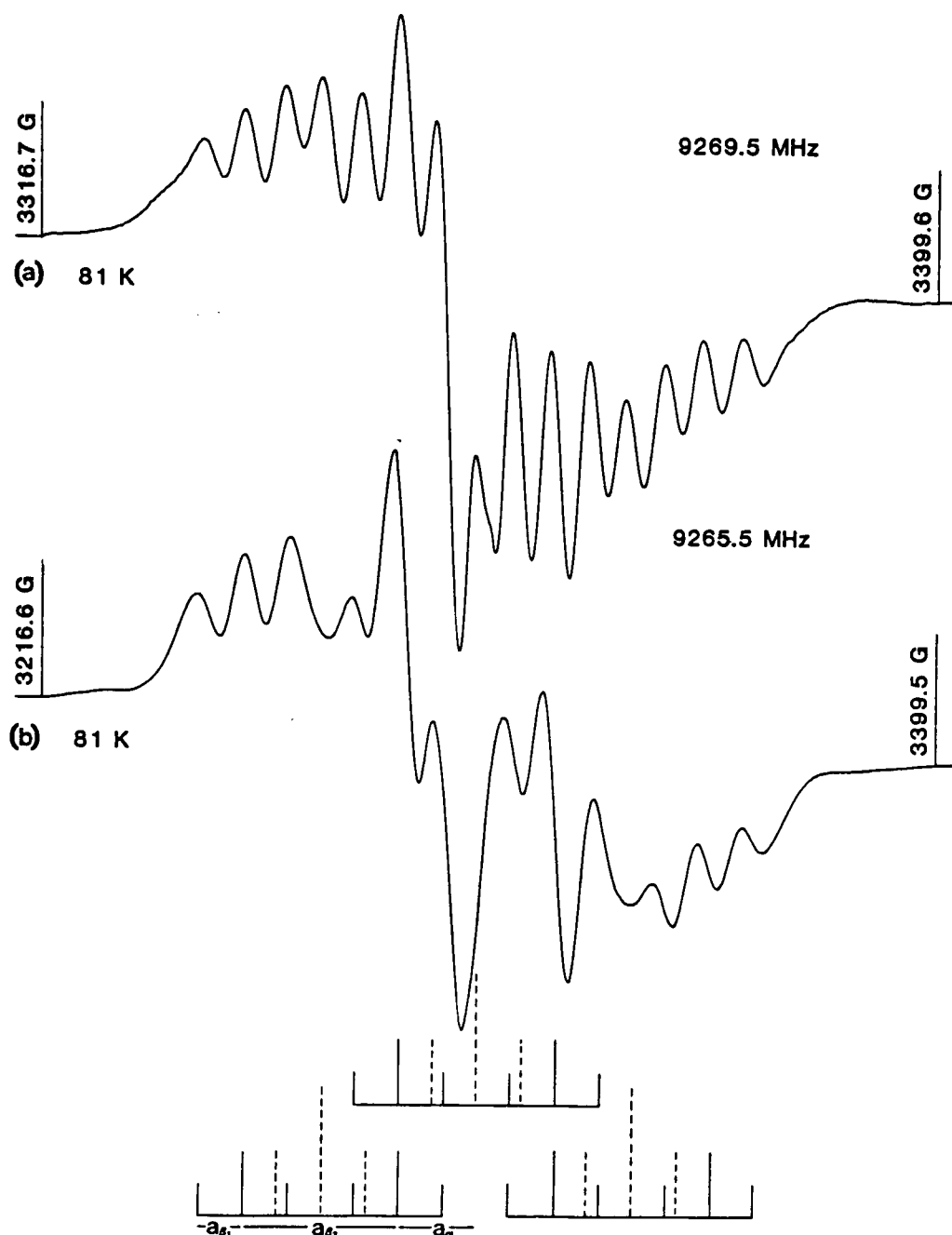


Figure 56. (a) First-derivative ESR spectrum of the ring-opened cyclopentene oxide radical cation in SF_6 , and (b) first-derivative ESR spectrum of the ring-opened cyclopentene oxide radical cation in F-113U , the stick diagram reconstructs the spectrum by using the ESR parameters for α , β_1 , and β_2 protons listed in TABLE IX, the dashed-lines indicating the alternating linewidth effect due to the α -proton out-of phase modulation.

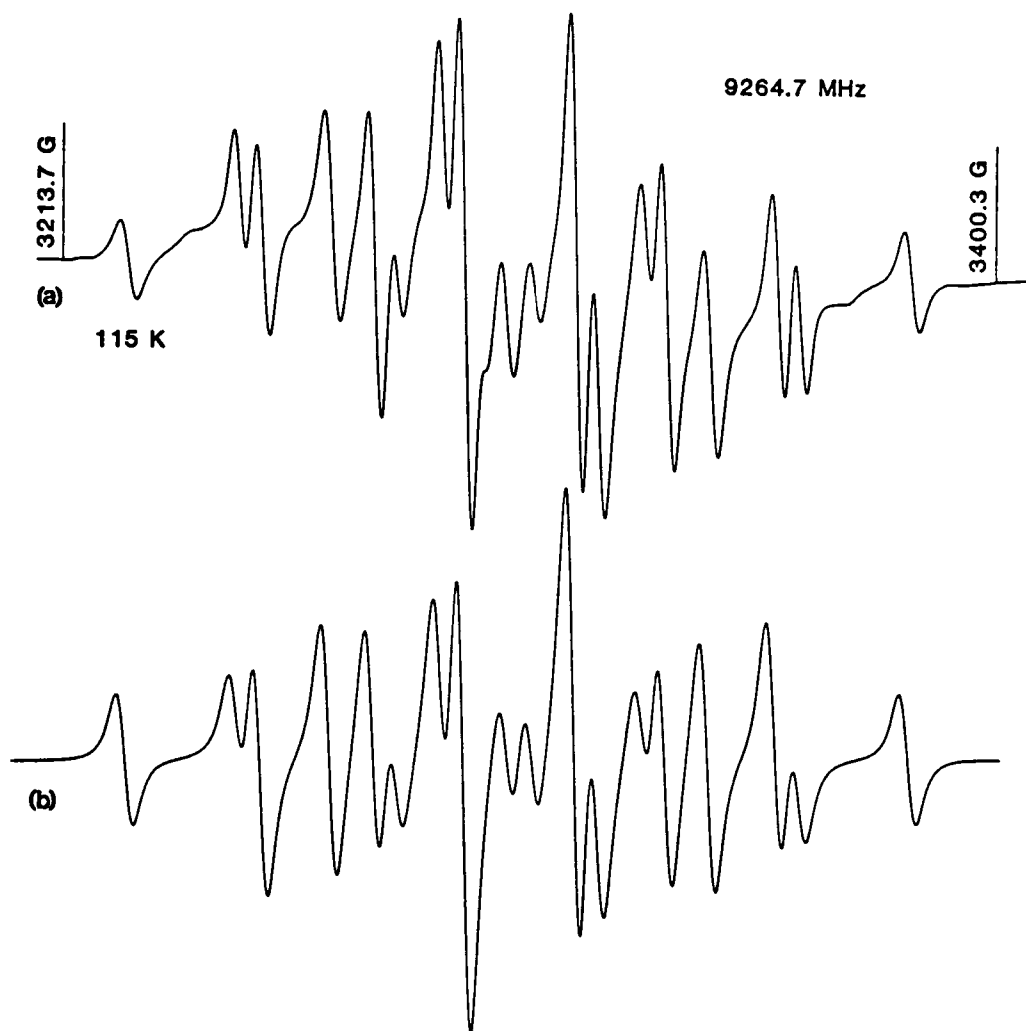
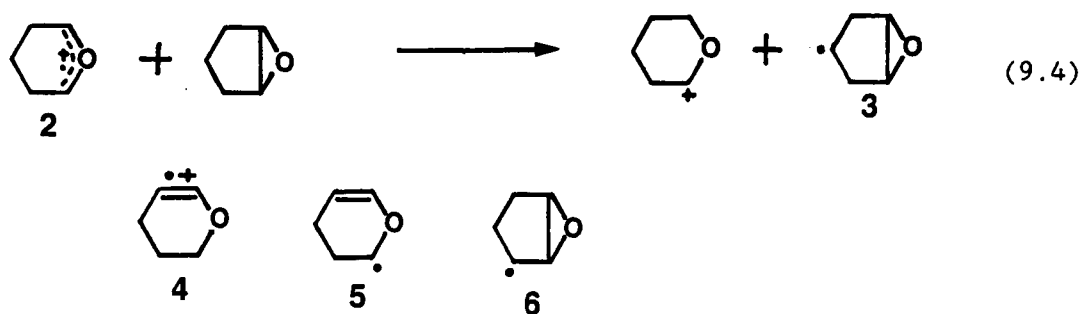


Figure 57. (a) Observed and (b) computer-simulated cyclopentene oxide 4-yl radical in F-113U. The simulation uses the ESR parameters listed in TABLE X and a Lorentzian linewidth of 3.5 G.

radical does not have two sets of two equivalent β -protons, and hence can be ruled out. Similarly, the radical 5 which could be formed by proton loss from 2 can also be ruled out for the same reason. The other possible radical which can be formed from the ion-molecule reaction is the cyclopentene oxide-3-yl radical 6. It can also be excluded owing to its lack of two sets of two equivalent protons.

It is noteworthy that the average β -proton hfc in this new radical is 33.4 G, which is significantly larger than the average β -proton hfc of 24 G for the cyclopentyl radical.¹⁰⁵ The above results can be summarized as:



3. Exo-Epoxybornane

The radical cation of this molecule in F-11 was studied in detail by Snow.⁵¹ The ESR spectrum of the radical cation of this compound in F-113U shown in Figure 58a is similar to that reported by him. By using the ESR parameters derived from the spectrum in F-11, an excellent simulation for the experimental spectrum (Figure 58a) was obtained as shown in Figure 58b. The alternating-linewidth effect due to the two α -protons was not considered in the simulation, although this effect was observed at low temperatures in the F-11 spectrum. Despite this difference, it is clear that the same ring-opened planar form of the exo-epoxybornane radical cation 7 was produced in F-113U as in F-11.

On annealing the sample in F-113U, an irreversible change took place. The originally formed radical cation was lost, and a new secondary radical grew in simultaneously. The ESR spectrum of the new species is given in Figure 59a. This new spectrum can be best simulated by: $a(H_\alpha) = 21.0$ G, $a(1H_\beta) = 26.2$ G, $a(1H_\beta) = 35.8$ G, and $a(2H) = 3.7$

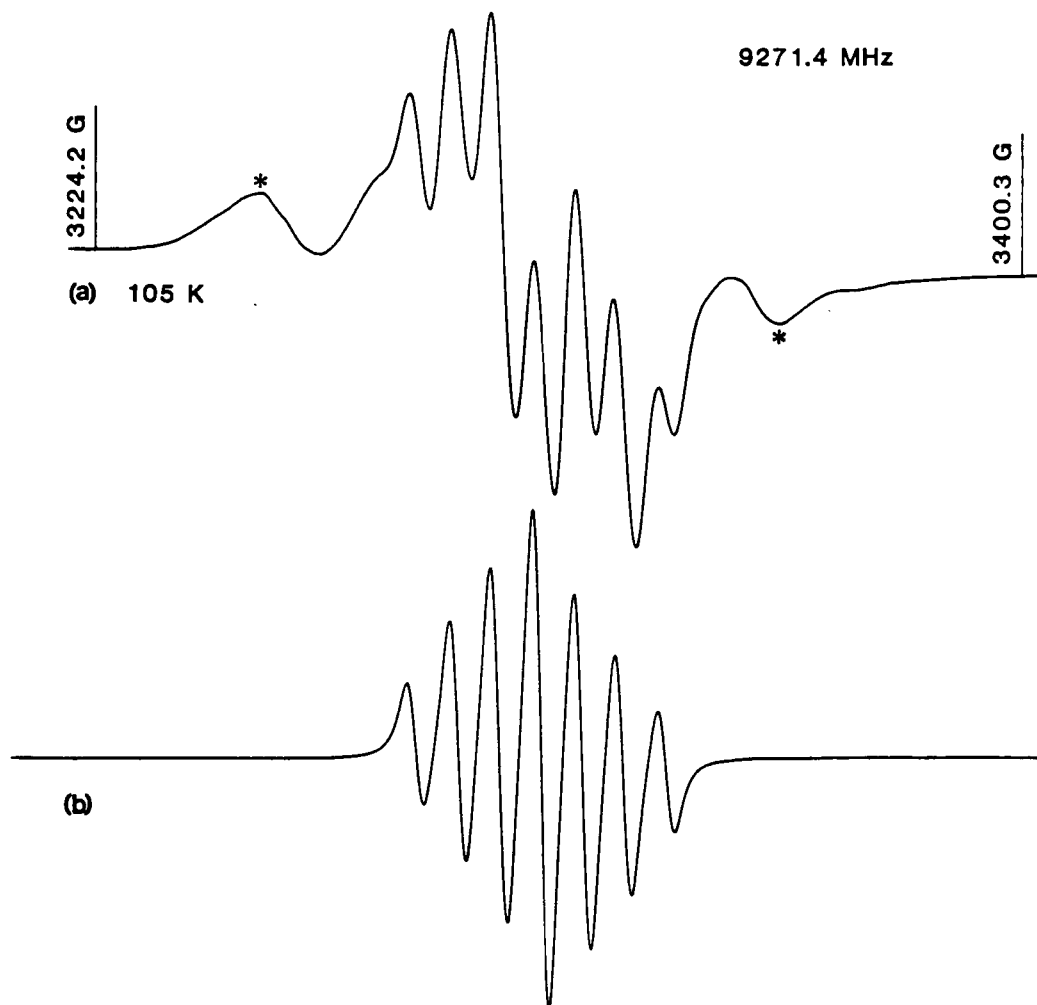


Figure 58. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened exo-epoxynorbornane radical cation in F-113U. The simulation uses the ESR parameters in TABLE IX (p 157) and a Lorentzian linewidth of 3.5 G. The asterisks in (a) indicates the signals of the matrix radical.

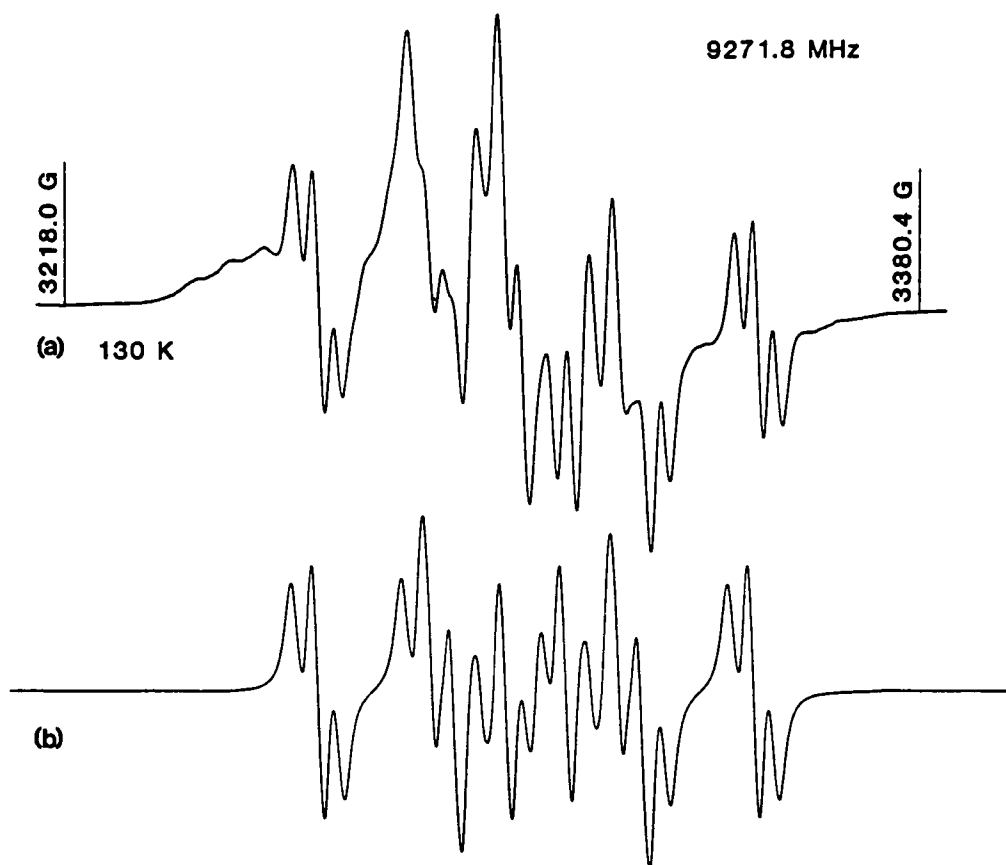
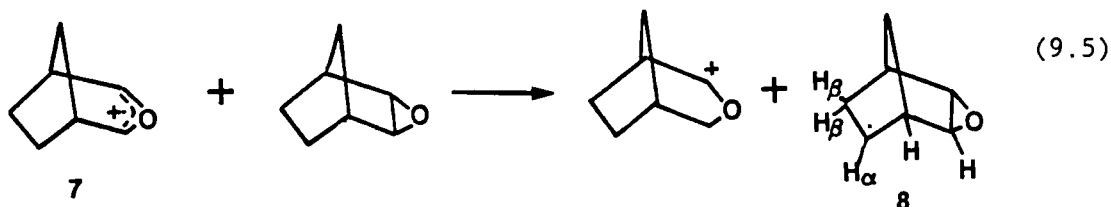


Figure 59. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the 5-exo-epoxynorbornyl radical in F-113U. The simulation uses the ESR parameters in TABLE X (p 158) and a Lorentzian linewidth of 3.5 G.

G. Since these parameters are very similar to those of the 2-norbornyl radical,¹⁰⁶ the spectrum can be assigned to the 5-exo-epoxynorbornyl radical 8. Other radical species which can be generated from the ion-molecule reactions in this system do not have similar ESR parameters, and can be excluded. The results can be described by:



4. Tetramethylethylene

The ESR spectrum of the initially formed monomer radical cation of this compound in F-113U is shown in Figure 60a. It consists of a binomial 13-line pattern with a hfc of 16.5 G in agreement with that reported by Ichikawa et al.¹⁰⁷ On annealing to 105 K, some additional lines grew in between each line of the 13-line pattern. This change was completed at 110 K, giving a new spectrum shown in Figure 60b. The spacing of the new spectrum is nearly half of that of the monomer radical cation, and can be attributed to the dimer radical cation of tetramethylethylene. The hfc of 7.8 G is very close to that reported by Ichikawa et al.¹⁰⁷ Although the ESR spectrum of the dimer cation consists of 25 lines, only the most intense 19 lines can be clearly identified. This is because the intensity of the weaker lines in both wings drops very fast in terms of the binomial distribution formula when the number of lines is 25. On further warming up the sample to 125 K, a second change occurred, and the dimer radical cation decayed while a third radical species grew in. As shown in Figure 61a, the ESR spectrum of the third radical is mainly a nonet with fine structures alternating from an apparent quintet on odd components to an apparent quartet on even components. Just such a pattern can be simulated in terms of the allylic $\cdot\text{CH}_2\text{C}(\text{Me})\text{C}=\text{C}(\text{Me})_2$ radical. The essential clue is that the difference between the hfcs of the exo and endo methyl protons is nearly equal to the hfc of the central proton. The best simulation shown in Figure 61b gives $a(\text{Me}_{\text{exo}}) = 16.05 \text{ G}$, $a(\text{Me}_{\text{endo}}) = 12.75 \text{ G}$, $a(\text{H})$

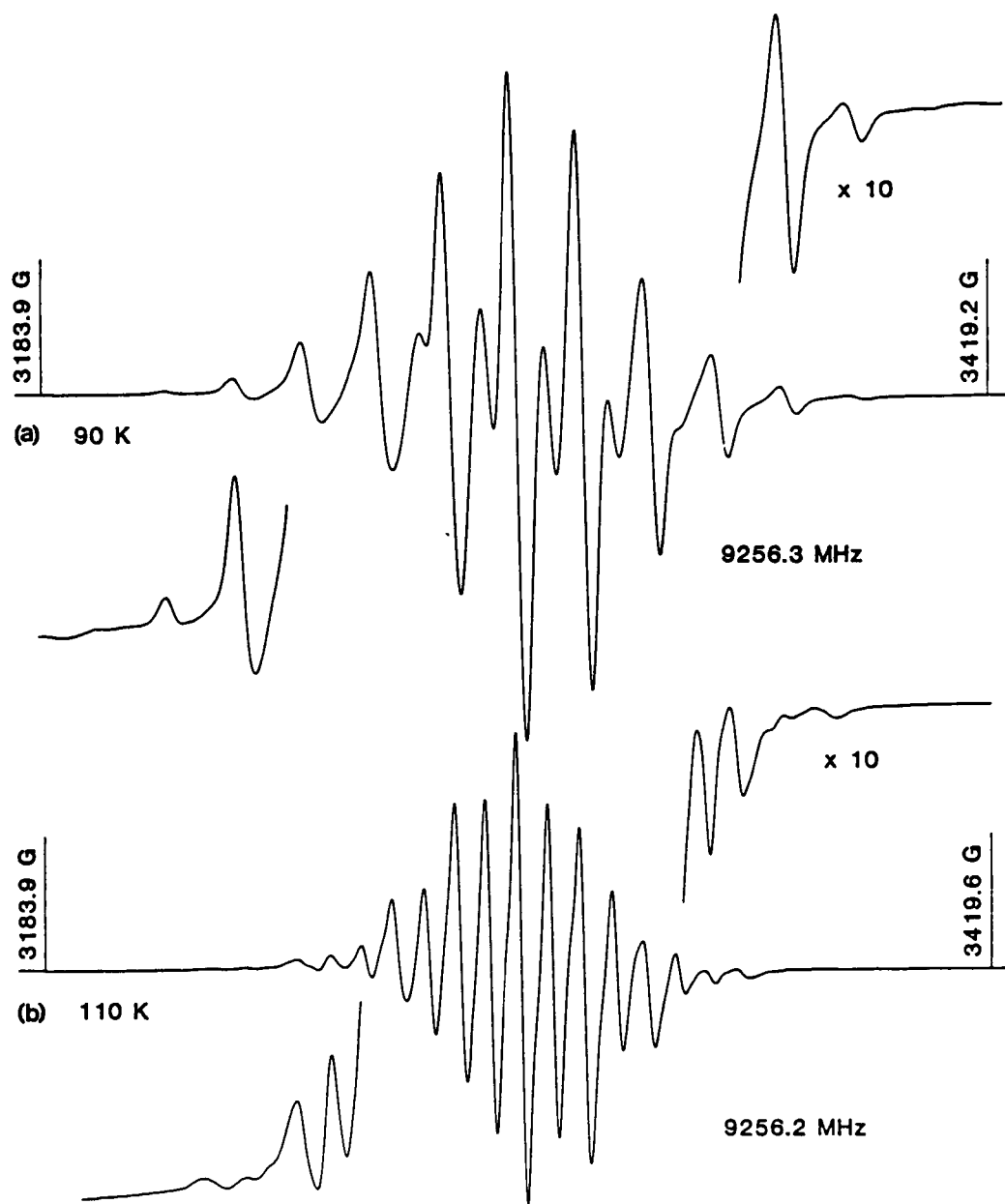


Figure 60. (a) First-derivative ESR spectrum of the monomer tetramethylethylene radical cation in F-113U, and (b) first-derivative ESR spectrum of the dimer tetramethylethylene radical cation in F-113U.

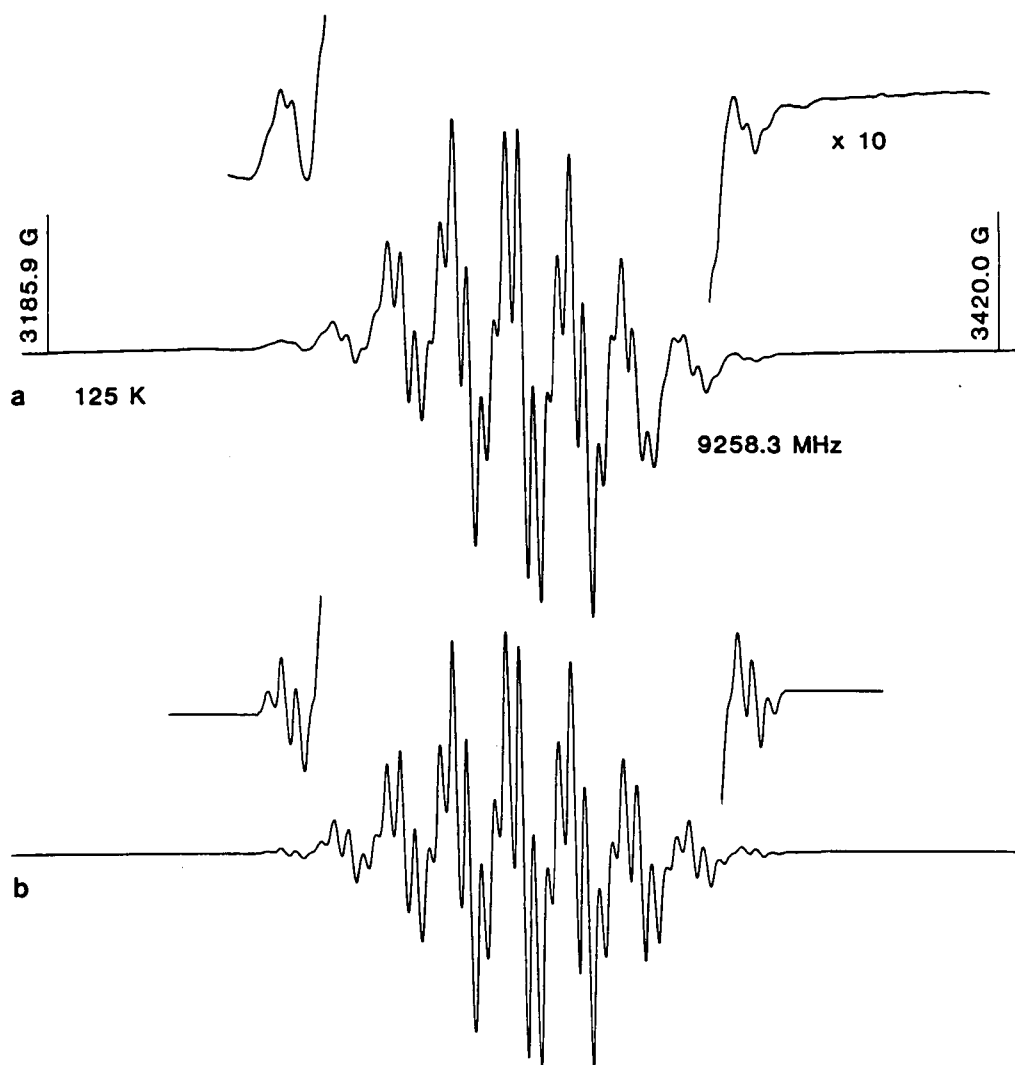
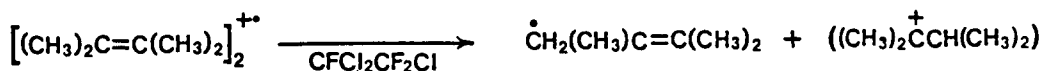


Figure 61. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the $\dot{\text{C}}\text{H}_2\text{C}(\text{Me})=\text{C}(\text{Me})_2$ radical in F-113U. The simulation uses the ESR parameters in TABLE X (p 158) and a Lorentzian linewidth of 2.5 G.

$a = 3.3$ G, and $a(2H) = 13.3$ G. These parameters are certainly reasonable for the trimethyl-substituted allyl radical. These results can be described as:



5. Dimethyl Sulfide

The low-temperature spectrum shown in Figure 62a is due to a mixture of monomer and dimer radical cations of dimethyl sulfide in F-11. The features due to the monomer cation are obscured in the center and on the high-field side by the much stronger signals of the dimer cation. According to the clearest four lines on the low-field side, the hfc of 20.4 G and g_x -value of 2.032 can be abstracted with confidence, which are in accord with the corresponding parameters reported by Bonazzola *et al.*¹⁰⁸ With the aid of their analysis of the other two g 's: $g_y = 2.0017$ and $g_z = 2.002$, together with the fact that the hyperfine anisotropy of the monomer cation is small, the stick diagram in Figure 62a was reconstructed.

On annealing to 100 K, the monomer cation features disappeared, leaving only the features arising from the dimer radical cation shown in Figure 62b. Because the signals of the monomer cation are very weak and are overlapped with the dimer cation, it is not clear whether or not the features of the dimer grew larger when the monomer cation decayed.

The ESR parameters for the dimer cation are $a(12 H) = 6.5$ G and $g = 2.010$. The ratio of the hfcs for the monomer-dimer cations pair here is 3.1 which is indicative of the σ^* structure for the dimer cation as pointed out in the studies of the thiirane and thietane dimer radicals in Chapter VI. The g -value is also within the diagnostic range of the σ^* dimer cation.

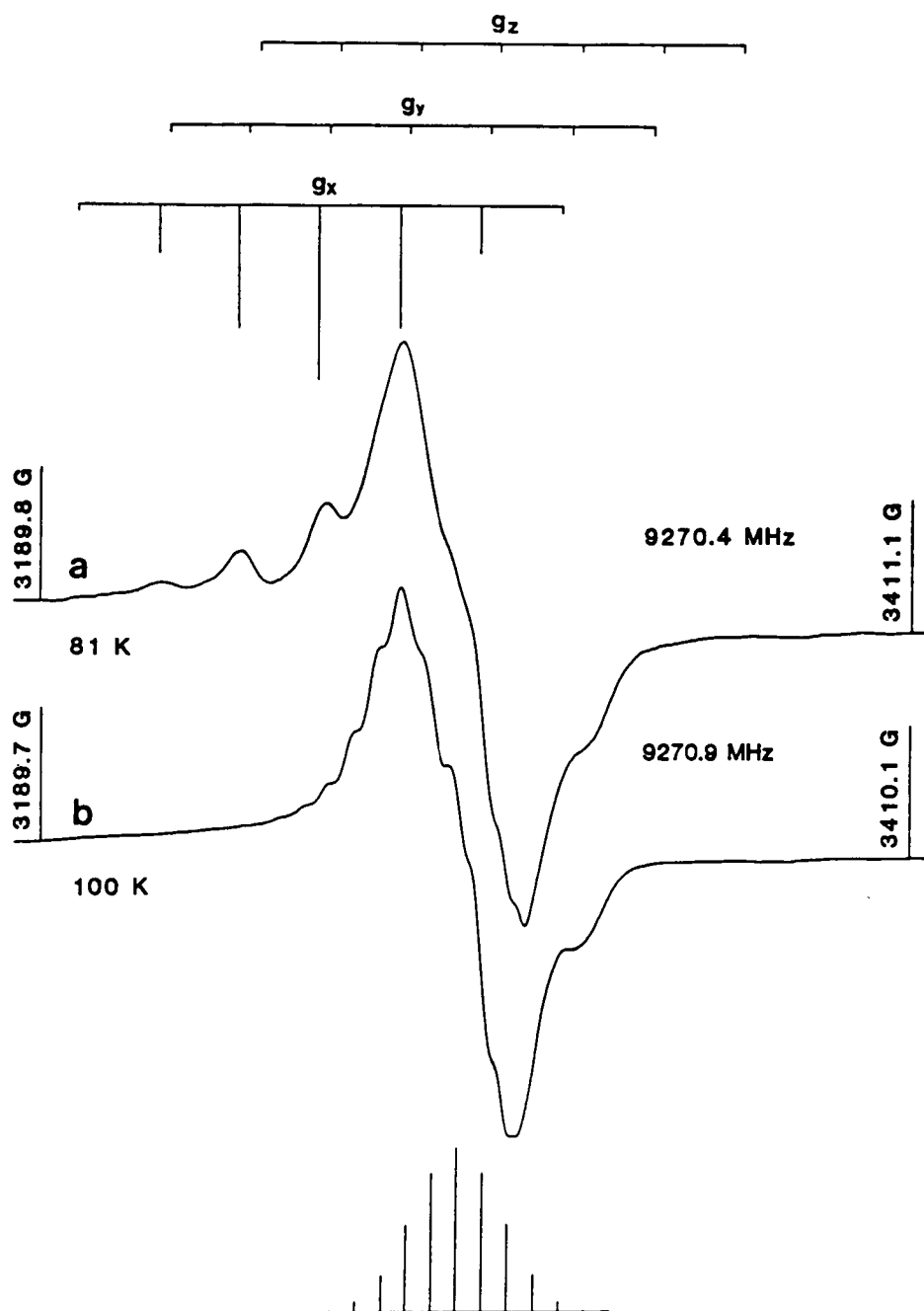
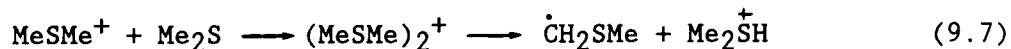


Figure 62. (a) First-derivative ESR spectrum of the monomer and dimer radical cations of dimethyl sulfide in F-113U. The upper stick diagrams describe the three g -components of the monomer cation (see text). (b) First-derivative ESR spectrum of the dimer radical cation of dimethyl sulfide in F-113U.

On further annealing to 110 K, the dimer cation irreversibly decayed while a new radical species grew in. The ESR spectrum of this new species is shown in Figure 63a. It is best simulated by the parameters of $a(2H) = 16.7$ G, $a(3H) = 3.3$ G, and can be ascribed to the neutral radical CH_2SCH_3 from the dissociation of the dimer cation.¹⁰⁹



All the ESR parameters for the radical cations in this section are listed in Table IX (p 157). All the ESR parameters for the neutral radicals are listed in Table X (p 158).

C. Discussion

1. Deprotonation or Hydrogen Abstraction

As indicated in the introduction of this Chapter, radical cations can possibly undergo either deprotonation or hydrogen abstraction reactions. In terms of this idea, the above reactions can be divided into two groups, the first group includes reactions (9.6) and (9.7) which can be explained by either mechanism. The second group includes reactions (9.3), (9.4) and (9.5) which cannot be explained by the deprotonation mechanism but can only be interpreted by the hydrogen atom abstraction mechanism. Obviously, the latter group is more interesting. First, it appears that in all these latter cases, the C-H bond breakage takes place at the bond where the spin density is not the highest in the radical cation as judged by the coupling constant at that position. This fact is in contrast to Iwasaki's rule for the deprotonation mentioned earlier. Taking spiro[2.5]octane radical cation as an example, the spin is localized at the CH_2 terminal of the cyclopropane ring, but the formation of the spiro[2.5]oct-6-yl radical requires that the C-H bond breaks at the 4-position of the cyclohexane ring having nearly no spin density. Therefore it seems more interesting to consider that the neutral radical is formed by hydrogen-atom transfer from the neutral molecule to the radical cation. And clearly

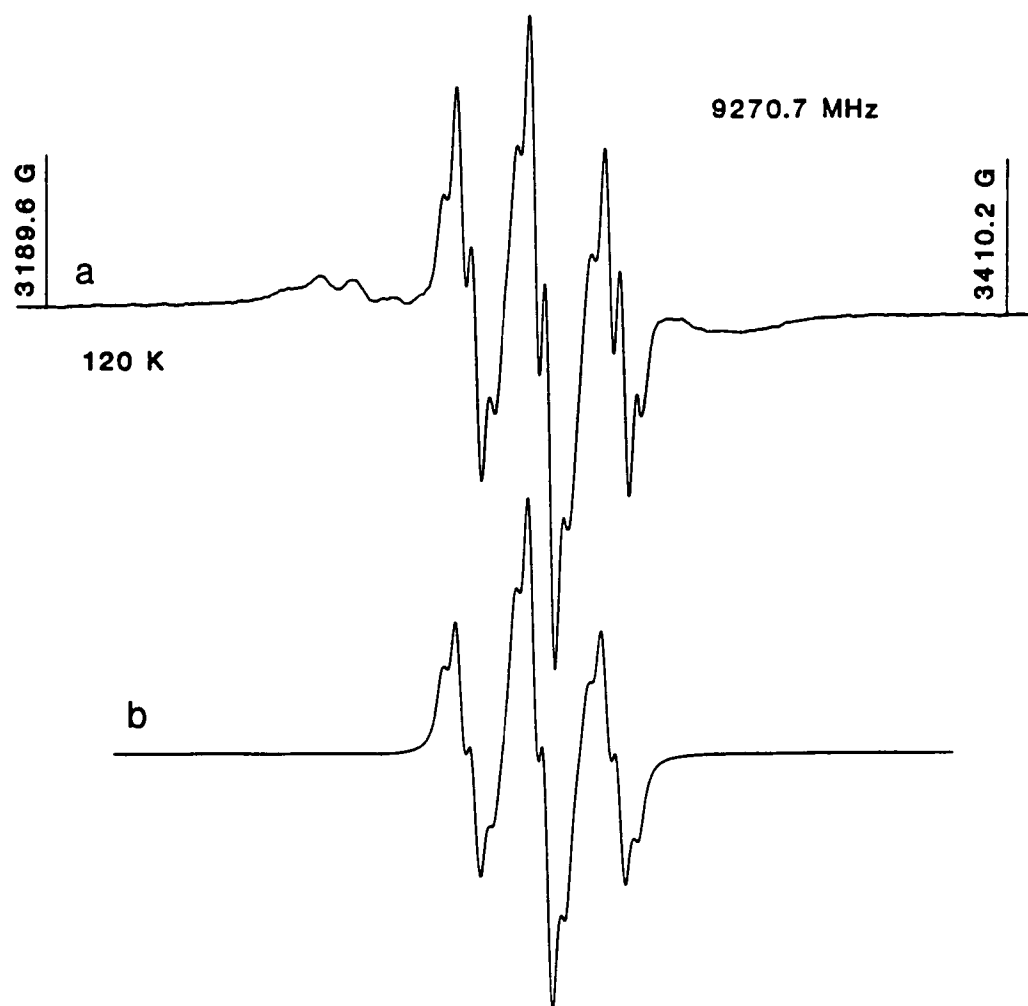
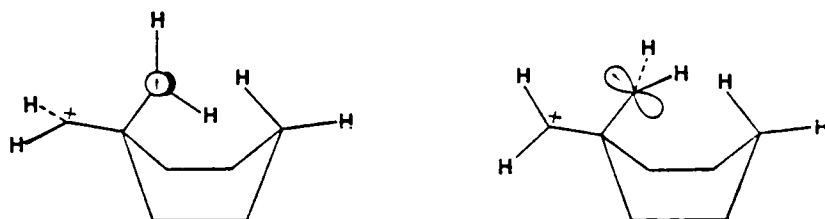


Figure 63. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the $\dot{\text{C}}\text{H}_2\text{SMe}$ radical in F-113U. The simulation uses the ESR parameters in TABLE X (p 158) and a Lorentzian linewidth of 3.0 G.

the 4-position of the cyclohexane ring is more open than other positions in the molecule, so that it is easier to be attacked by cations. One should perhaps argue that the secondary radical in this case is formed by intramolecular hydrogen abstraction. But such an intramolecular hydrogen abstraction is unlikely because (a) it requires a boat transition state as drawn below, which is unlikely;



and (b) the secondary radical was only observed in F-113U but not in F-11. If the abstraction were an unimolecular reaction, it should also occur in F-11.

Secondly, the argument against deprotonation for the second group is that the deprotonation of the ring-opened radical cations in the latter group cannot give rise to the observed neutral radicals at all. Taking the cyclopentene oxide ring-opened cation as an example, deprotonation should give 2,3-dihydropyran-2-yl radical rather than the observed cyclopentene oxide-4-yl radical which can only be produced by the bimolecular hydrogen abstraction process.

2. Unimolecular or Bimolecular Reaction

It is generally agreed that the observable reactions are bimolecular ion-molecule processes. This is because these reactions are concentration-dependent. As indicated earlier, no ion-molecule reactions can be observed in the dilute F-11 systems. But if the substrate concentration is increased to 10% or more, the neutral radicals from the ion-molecule reactions can often be detected as pointed out by Shida and co-workers.¹¹⁰ This can be explained by the formation of cluster of neutral molecules in the matrix at high concentrations. Hence the radical cation when produced can react with the adjacent molecules in the clusters. However, it should be stressed that even in the very dilute substrate-F-113U systems, the ion-molecule

reactions can always be detected above 105 K. This actually implies that the substrate molecule or its radical cation can diffuse in the matrix in the temperature range of above 105 K, since there is less cluster formation at very low concentrations. The relative absence of cluster formation in the dilute F-113U matrix is also indicated by the usual observation of the primary radical cations in this matrix at low temperatures. It seems that this matrix may undergo some kind of phase transition at around 105 K such that the structure of the matrix becomes looser. The matrix might form some big holes or cavities to allow molecular diffusion, or the molecules of the matrix become more elastic allowing the substrate or its radical cation to push and go through them. Based on this assumption, the Freon matrices can be divided into rigid (such as F-11) and elastic (such as F-113U) groups as discussed in the first Chapter.

Although ion-molecule reactions are by nature bimolecular, the evidence is not always clear from a study of the overall reactions. This question is not expected to be answered fully here, but certainly the present work sheds more light on it. Thus, as described in the results, in reactions (9.6) and (9.7) the radical cations first react with the parent molecules to form dimer radical cations. Significantly, the neutral radicals are only produced after the decomposition of the dimer cations. Therefore, the dimer cations may be viewed as the stable intermediate complexes of these two ion-molecule reactions, which provides further support for the bimolecular reaction mechanism.

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