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ESR STUDIES OF THE RING OPENING OF CYCLOPROPANE RADICAL CATIONS IN FREON MATRICES

XUE-ZHI QIN and FRANCON WILLIAMS*
Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, U.S.A.

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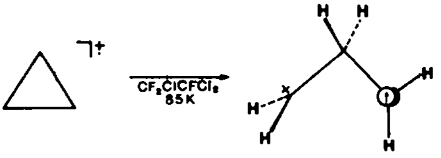
Abstract—The radical cations of cyclopropane and several of its methyl derivatives have been characterized by ESR spectroscopy following their generation by γ irradiation of dilute solutions of the parent compounds in Freon matrices at 77 K. In the $CFCl_3$, CF_3CCl_3, and CF_2ClCCl_3 matrices, only the ring-closed species is usually observed in the accessible temperature range up to *ca* 160 K. In the $CFCl_2CF_2Cl$ matrix, however, the ring-closed radical cations initially formed at 77 K undergo ring opening between 83 and 110 K, the more highly substituted radical cations requiring a higher temperature for this transformation. The ring-closed radical cations are $^2A_1$ species for C_{2v} symmetry, the most substituted cyclopropane C—C bond being elongated with the spin density largely confined to the basal carbons in a face-to-face (90°, 90°) structure. In the ring-opened radical cations, the radical center is localized on the most substituted carbon atom following the breaking of the weakened C—C bond of the ring-closed species. The radical conformations of the ring-opened species have been determined, the $RCH_2CH_2\cdot$ center produced from cyclopropane having a bisected conformation while the $RCH_2CMe_2\cdot$ center obtained from 1,1,2,2-tetramethylcyclopropane is eclipsed, as expected for the presence of α-methyl substituents at the radical site. The nature of the putative carbocation center in the ring-opened radical cations is discussed with reference to recent proposals that this center is strongly coordinated to an electrophile (Cl^- or RCl) thereby negating the requirement for an orthogonal structure. Consideration of the strong matrix dependence of the ring-opening reaction suggests a possible solvation effect, however, in which the $CFCl_2CF_2Cl$ matrix assists the twisting of one of the CR_1R_2 groups at the most substituted bond, leading to the rupture of this one-electron σ bond. A strong solvation effect also explains why ring-opening can occur in a suitable polar solvent despite theoretical calculations of unfavorable energetics for a similar gas-phase reaction. Experiments are also described on spiro[2.5]octane, the cyclopropane ring undergoing scission at the CH_2—CH_2 bond of this radical cation to give an $RCH_2\cdot$ radical center. This radical then undergoes a H-atom abstraction with a neutral spiro[2.5]octane molecule in the $CFCl_2CF_2Cl$ matrix at higher temperature to give the spiro[2.5]oct-6-yl radical.

INTRODUCTION

Recent ESR studies have provided clear evidence for the ring opening of oxirane and cyclopropane radical cations in certain Freon matrices at low temperatures.[1-6] For the parent and methyl-substituted oxiranes, only the C...C ring-opened forms (*vide infra*) of the radical cations have been detected at 77 K and higher temperature,[1-3] suggesting that their ring-closed precursors are unstable under these conditions. On the other hand, both the ring-closed and the ring-opened forms of the cyclopropane and 1,1,2,2-tetramethylcyclopropane radical cations have been observed and characterized by ESR spectroscopy.[4-6]

An intriguing feature of the cyclopropane studies[4-6] is that the ring opening has only been reported to occur in the $CFCl_2CF_2Cl$ matrix. In $CFCl_3$, for example, the ring-closed cyclopropane and 1,1,2,2-tetramethylcyclopropane radical cations are stable up to at least 140 and 160 K, respectively. These temperatures are close to the softening point of the $CFCl_3$ matrix and are well above the threshold values of 83 and 110 K for the ring opening of the cyclopropane and 1,1,2,2-tetramethylcyclopropane radical cations in the $CFCl_2CF_2Cl$ matrix.[4,5] Thus a specific solvent effect on the ring-opening reaction appears to be indicated. Similarly, it has been found that the localized forms of the C...C ring-opened oxirane radical cations are produced irreversibly in the $CFCl_2CF_2Cl$ matrix at or above 77 K whereas only the planar delocalized (edge-to-edge) forms of these radical cations are observed in the $CFCl_3$, CCl_4, and CF_3CCl_3 matrices over a wide temperature range.[3]

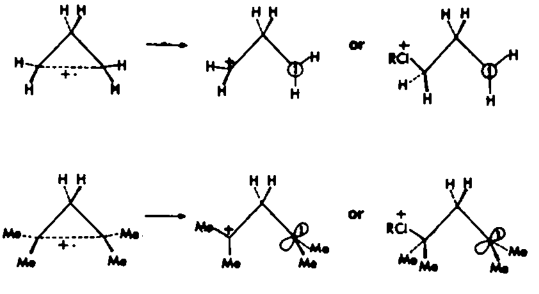
The precise structure of the ring-opened form of the cyclopropane radical cation produced in the $CFCl_2CF_2Cl$ matrix has aroused considerable interest.[7-9] Since the ESR results demonstrate clearly that the unpaired spin is localized on one of the terminal CH_2 groups in a bisected conformation at the radical center, we originally proposed the orthogonal structure shown in Scheme 1.[4] This structure can be achieved from the face-to-face ring-closed radical cation by a monorotatory ring opening such that the radical site becomes localized at the rotated CH_2 group. Of course a carbocation center is thereby generated at the other terminal CH_2 group leading to the formation of a distonic ion in which the charge and radical sites are separated.[10,11] A similar orthogonal species has also been proposed for the ring-opened form of the 1,1,2,2-tetramethylcyclopropane radical cation[5] but here the



Scheme 1.

ESR results show that the conformation at the radical center is eclipsed, as would be expected for two α-methyl substituents.[12] Thus, in this case, ring opening by a CMe_2 monorotation yields the carbocation rather than the radical site at the rotated group.

An alternative explanation for the ring-opened cyclopropane structures has been suggested by Symons.[7] He reasons that since a carbocation center in an orthogonal structure would represent a powerful electrophile, a relatively strong bonding of this center to one chlorine ligand of the $CFCl_2CF_2Cl$ solvent molecule should occur. In other words, he proposes that the carbocation center can be replaced by a chloronium ion in the ring-opened structure. These two alternative forms of the ring-opened cyclopropane radical cation are depicted below.



The ring opening of the cyclopropane radical cation has also been studied theoretically by two groups,[8,9] and their *ab initio* MO calculations concur in showing that the (0, 0) ring-opened planar form is at least 20 kcal mol^{-1} higher in energy than the (90, 90) ring-closed form while the (90, 0) orthogonal species lies at even higher energy and does not correspond to a minimum on the potential surface.[8] Thus, according to these calculations, ring opening is extremely unfavorable energetically, and this has led to further suggestions that the ring-opened species detected by ESR in the $CFCl_2CF_2Cl$ matrix is not the trimethylene radical cation but the product of nucleophilic attack by chloride ion[8] or by the solvent[9] at the carbocationic center.

Turning to the other experimental investigations of cyclopropane radical cations, Roth and Schilling have shown by elegant CIDNP studies[13] that the most substituted cyclopropane bond is either broken or weakened. Despite the elongation of this bond, however, the conformational integrity of the neutral molecule appears to be retained in a more-or-less (90, 90) ring-closed cation. Specifically, no evidence was found for the interconversion of *cis*- and *trans*-1,2-diphenylcyclopropane radical cations indicating that the (0, 0) and (90, 0) ring-opened structures are unaccessible on the relatively short timescale of these CIDNP experiments[13] and probably represent high-lying transition states in this system.[13c] On the other hand, it has been shown that a substituted cyclopropane ring undergoes rearrangement in the radical cations produced from strained bicyclic[13b] and polycyclic[14] compounds. Here the chemical evidence for the intermediacy of a ring-opened form is very strong, as it is for the observation of ring-opened products from the electrochemical oxidation of 1,1,2,2-tetramethylcyclopropane.[15]

In view of the interest generated in the problem, we have extended our earlier ESR work[3-6] to other methyl-substituted cyclopropanes and to spiro[2.5] octane. The primary goals of this study have been to establish the generality of the cyclopropane cation ring-opening reaction in the $CFCl_2CF_2Cl$ matrix, and to see if this reaction can also take place in other Freon solvents, at least for some particular cyclopropane derivatives. Although this work does not bring about a resolution of the problem regarding the nature of the ring-opened species in the $CFCl_2CF_2Cl$ matrix, the results obtained do offer some insight on this question and suggest further avenues by which additional information may be obtained.

EXPERIMENTAL

Cyclopropane (99%) was obtained from Matheson Gas Products, Morrow, GA. *cis*-1,2-Dimethylcyclopropane (99.9%), *trans*-1,2-dimethylcyclopropane (99%), 1,1,2-trimethylcyclopropane (99.5%), 1,1,2,2-tetramethylcyclopropane (99.9%) and spiro[2.5] octane (98%) were all obtained from Wiley Organics. The Freon solvents included trichlorofluoromethane (PCR and Aldrich), 1,1,1-trichlorotrifluoroethane (Aldrich), 1,1,2-trichlorotrifluoroethane (PCR and Aldrich), 1,2-dichlorotetrafluoroethane (Matheson), and 2,2-difluorotetrachloroethane (Aldrich). All compounds and solvents were used as received.

The cyclopropanes were dissolved in the Freons to a concentration of about 1.0 mol % and the solutions were then degassed on a vacuum line and sealed in Spectrosil or Suprasil quartz tubes. The samples were irradiated at 77 K in a ^{60}Co γ source for a dose of less than 0.5 Mrad. The ESR measurements at 80–160 K were carried out on a Bruker ER 200D SRC instrument equipped with a variable-temperature control device.

RESULTS

Cyclopropane

The transformation of the ring-closed cyclopropane radical cation[16] to the ring-opened form in the $CFCl_2CF_2Cl$ matrix has been described in our previous communications.[4,6] Figure 1(a) shows a well-resolved ESR spectrum of the ring-opened species at 105 K that clearly establishes the identity of the radical site as an $RCH_2CH_2\cdot$ species, the expected triplet-of-triplets pattern being well reproduced by the simulated spectrum (b) using isotropic couplings. Since it was already reported[6] that greater line broadening occurs for the center triplet, the present simulation included a larger linewidth parameter for these $M_I(2H_\beta) = 0$ components (Fig. 1). The resulting fit is very satisfactory except that the relative intensities of the outer pairs of lines in spectrum (a) deviate appreciably from a 1 : 2 ratio, presumably because of selective line broadening associated with residual α-hydrogen hyperfine anisotropy.

The unusual matrix effect noted earlier in this paper on the ring opening of the cyclopropane radical cation[4,6] led us to investigate the species generated from cyclopropane in the previously unexamined CF_2ClCF_2Cl matrix. The resulting ESR spectrum became partly resolved at 106 K (Fig. 2(a)) to reveal a set of sharp components that corresponds exactly to the hyperfine pattern of the ring-opened radical cation in the $CFCl_2CF_2Cl$ matrix (Fig. 2(b)). A comparison of the two spectra indicates that the main difference resides in the line intensities of this pattern relative to the broad background signal from matrix

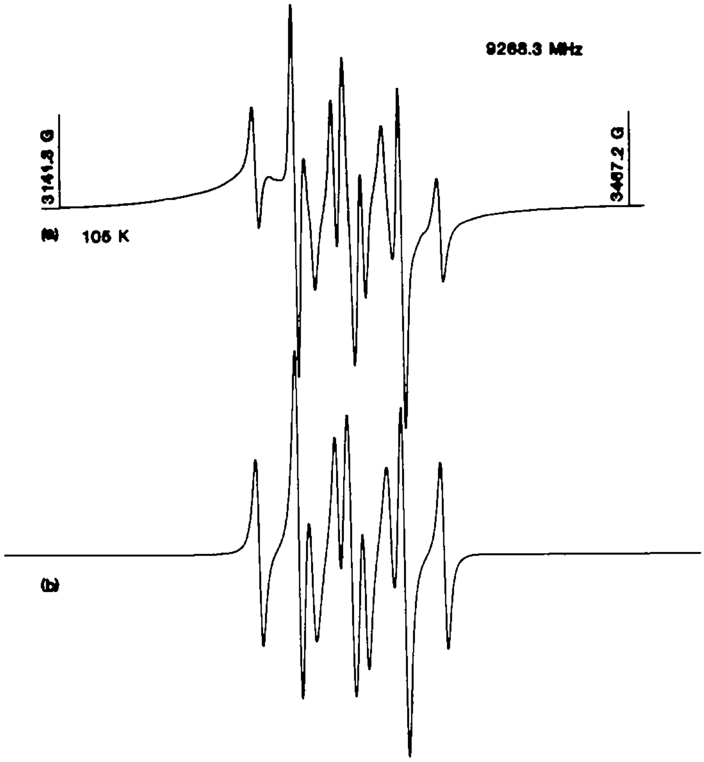


Fig. 1. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened form of the cyclopropane radical cation in $CFCl_2CF_2Cl$. Spectrum (b) was simulated by using $A(2H) = 22.4$ G, $A(1H) = 60.4$ G with 100% intensity and a Lorentzian linewidth of 3.2 G plus $A(2H) = 22.4$ G with 90% intensity and a Lorentzian linewidth of 4.5 G. This prescription was used to broaden lines 3, 5 and 7 for which $M_I(2H_\beta) = 0$ (see text and Ref. 6). The actual hyperfine couplings are given in Table 2.

radicals, suggesting perhaps that the radiation chemical yield of cyclopropane cations is smaller in the CF_2ClCF_2Cl matrix. It should be noted that the ring-opened cation was already present in the CF_2ClCF_2Cl matrix at 80 K after the γ irradiation at 77 K, and that its ESR signal did not increase on cycling the matrix to higher temperatures, in contrast to the results obtained in $CFCl_2CF_2Cl$.[4] Thus it appears that the cyclopropane radical cation undergoes ring opening below 80 K in the CF_2ClCF_2Cl matrix, as compared to 83 K in $CFCl_2CF_2Cl$.[4]

Spiro[2.5]*octane*

The ESR spectra of the radical cation generated from this compound in $CFCl_2CF_2Cl$ and $CFCl_3$ matrices, shown in Fig. 3, consist of identical 1 : 2 : 1 triplets with a 23 G coupling. This is strong evidence that the radical center is of the $RCH_2\cdot$ type with no β-hydrogen coupling. The ring opening of the radical cation between the unsubstituted carbons of the cyclopropane ring would be expected to give just such a center, whereas the other unsymmetrical mode of ring opening in the cyclopropane ring would generate either a tertiary alkyl radical or an $RCH_2CH_2\cdot$ species, both of which can be excluded by the ESR results. Incidentally, no evidence could be obtained for a quintet pattern from a ring-closed radical cation precursor in these systems despite careful studies down to 80 K.

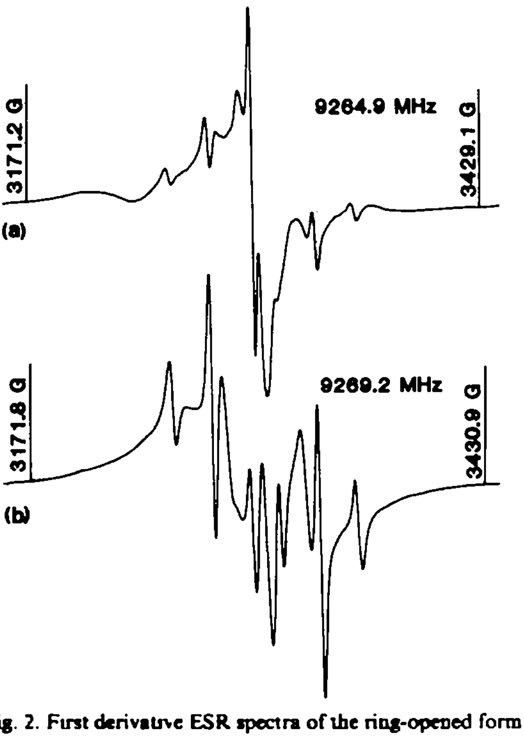


Fig. 2. First derivative ESR spectra of the ring-opened form of the radical cation of cyclopropane (a) in CF_2ClCF_2Cl at 106 K and (b) in $CFCl_2CF_2Cl$ at 109 K.

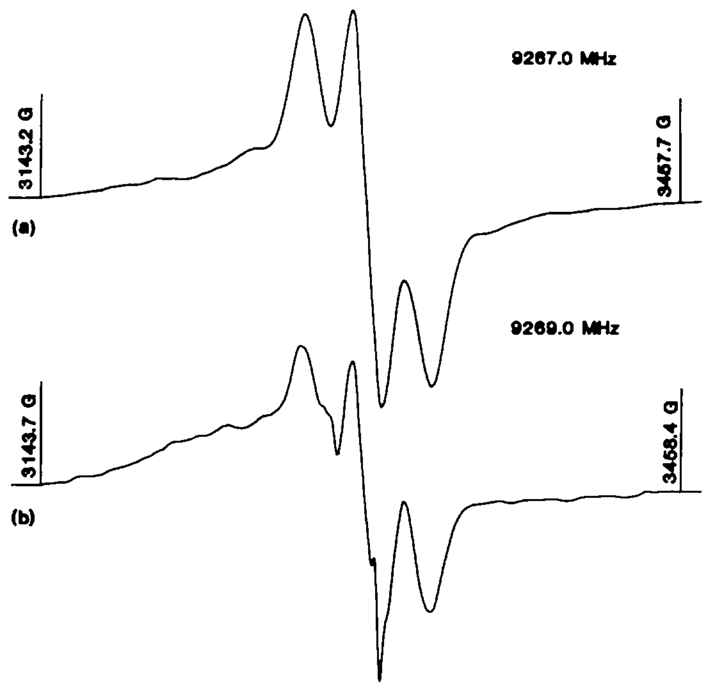


Fig. 3. First-derivative ESR spectra of the ring-opened form of the radical cation of spiro[2.5] octane (a) in $CFCl_2CF_2Cl$ at 95 K and (b) in $CFCl_3$ at 140 K.

An interesting secondary reaction was observed on annealing the γ-irradiated $CFCl_2CF_2Cl$ sample to about 112 K. At this temperature the triplet spectrum of the ring-opened radical cation decayed while the much wider spectrum shown in Fig. 4(a) grew simultaneously. The analysis of this spectrum into a triplet (A(2H) = 41.6 G) of doublets (A(1H) = 22.3 G) of triplets (A(2H) = 5.1 G) is confirmed by the simulation in Fig. 4(b), all the hyperfine structure being revealed in the experimental spectrum despite the considerable line broadening which is present. The hyperfine parameters are very similar to those reported for

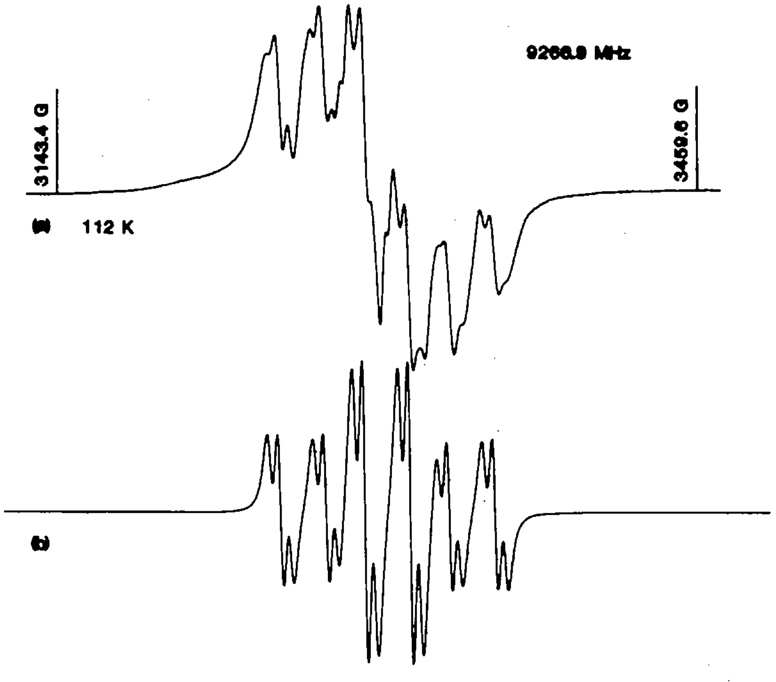


Fig. 4. (a) Observed and (b) computer simulated first-derivative ESR spectra of the spiro[2.5]oct-6-yl radical in $CFCl_2CF_2Cl$. The simulation used the ESR parameters $a(2H_\beta) = 41.6$ G, $a(2H_\beta) = 5.1$ G, $a(1H_\alpha) = 22.3$ G and a Lorentzian linewidth of 2.5 G.

cyclohexyl radicals[17,18] and there is little doubt that the secondary radical is formed by H-atom abstraction from the cyclohexane ring of the spiro[2.5]octane.

In contrast, the above reaction was not observed in the $CFCl_3$ matrix and the ring-opened radical cation simply decayed above 145 K. Since an intramolecular hydrogen abstraction would not be expected to show such a strong solvent dependence in the solid state, these results suggest that the reaction in $CFCl_2CF_2Cl$ takes place intermolecularly when the temperature exceeds that required for the onset of molecular diffusion. Stereochemical considerations (*vide infra*) also appear to favor an intermolecular hydrogen abstraction reaction.

The background absorption that is especially prominent in the ESR spectrum of the $CFCl_3$ solution (Fig. 3(b)) could be due to the formation of rearranged radicals. Possibilities include ring expansion to give cyclooctene radical cations but the characterization of these poorly defined signals must await further work.

cis- *and* trans-1,2-*Dimethylcyclopropanes*

The ring-closed radical cations of these isomers produced in $CFCl_3$ are stable up to the softening point (*ca* 155 K) of the matrix, whereas they both undergo irreversible ring opening in the $CFCl_2CF_2Cl$ matrix. These results are similar to those reported previously for 1,1,2,2-tetramethylcyclopropane,[5] the only difference being that the dimethylcyclopropane radical cations start to ring open at 95 instead of 110 K.

Thus, for each isomer, the low-temperature spectra taken before annealing were identical in the two matrices. However, the 150 K spectrum in $CFCl_3$ showed better resolution so we present the spectra of the ring-closed cations in $CFCl_3$ and those of the ring-opened cations in $CFCl_2CF_2Cl$; these are shown for the cations derived from the *cis* compound, together with their simulations, in Figs 5 and 6, while the corresponding spectra pertaining to the cations from the *trans* isomer are given in Figs 7 and 8.

In general, the simulations in Figs 5–8 provide excellent fits to the experimental spectra, and therefore the ESR parameters are considered to be quite reliable. These are summarized in Tables 1 and 2 for the ring-closed and ring-opened species, respectively. As expected, the hyperfine parameters of the ring-closed *cis*- and *trans*-dimethylcyclopropane radical cations are similar but not identical to each other. Similarly, the coupling constants for the three sets of equivalent hydrogens are in reasonable accord with the corresponding isotropic values for the ring-closed cyclopropane[16] and 1,1,2,2-tetramethylcyclopropane[5] radical cations, save for the fact that the β-methyl hydrogen couplings are about 6 G smaller (*ca* 15 G vs 21 G) in the tetramethylcyclopropane cation. This decrease in coupling with increasing methyl substitution at a carbon radical center is a well-known effect[17] attributable to a reduction in spin density at the α-carbon by methyl hyperconjunction.

Turning to the ring-opened forms of these 1,2-dimethylcyclopropane radical cations, the simulations made with the same set of parameters (Table 2) in Figs 6 and 8 show clearly that the basic hyperfine

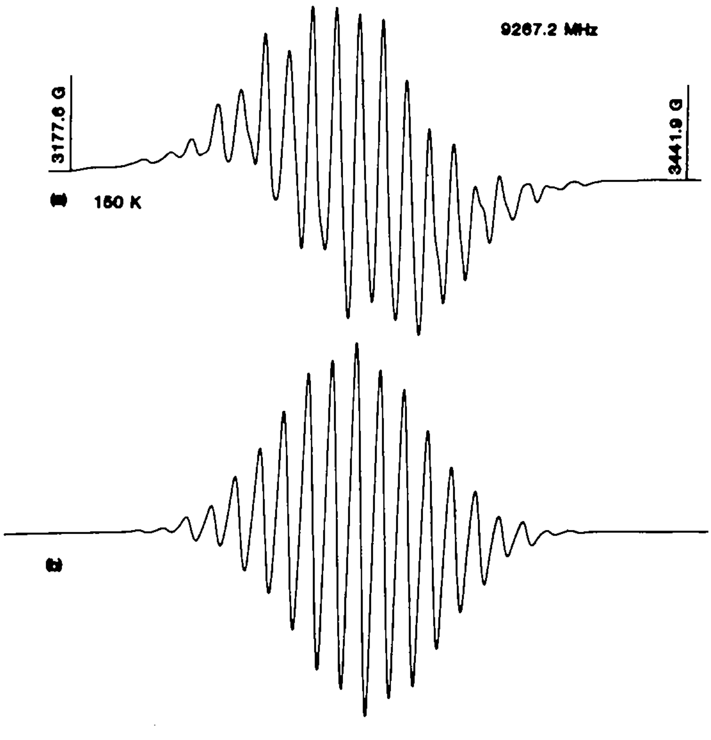


Fig. 5. (a) Observed and (b) computer simulated first-derivative ESR spectra of the ring-closed form of the radical cation of *cis*-1,2-dimethylcyclopropane in $CFCl_3$. Spectrum (b) was simulated by using the ESR parameters given in Table 1 and a Lorentzian linewidth of 3.5 G.

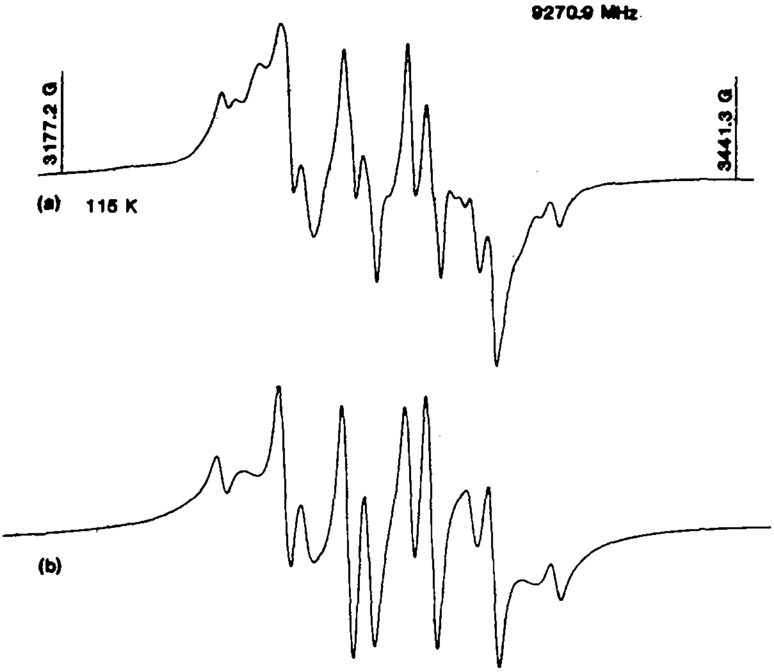


Fig. 6. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened form of the radical cation of *cis*-1,2-dimethylcyclopropane in $CFCl_2CF_2Cl$. Spectrum (b) was simulated by using the ESR parameters in Table 2 and a Lorentzian linewidth of 3.5 G. A broad background signal was added to spectrum (b).

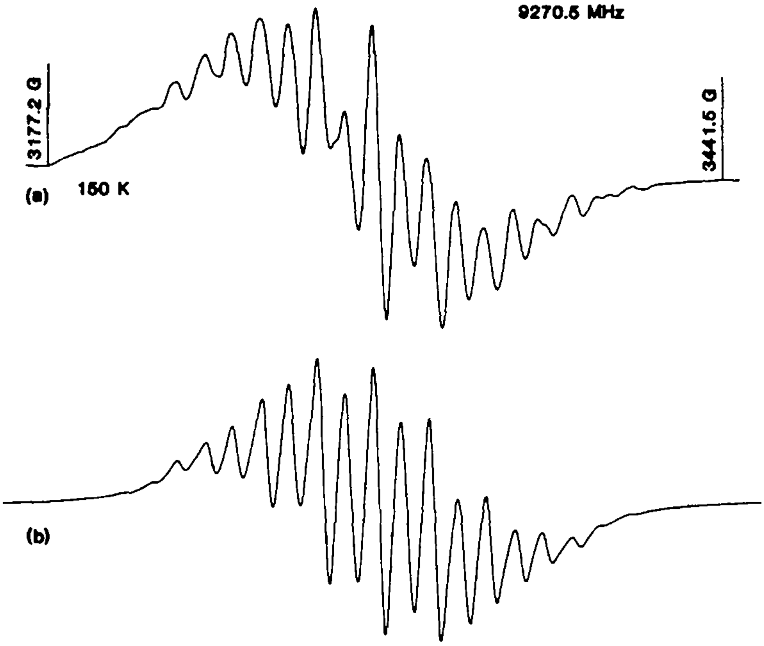


Fig. 7. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-closed form of the radical cation of *trans*-1,2-dimethylcyclopropane in $CFCl_3$. Spectrum (b) was simulated by using the ESR parameters in Table 1 and a Lorentzian linewidth of 3.5 G. A broad background signal was added to spectrum (b).

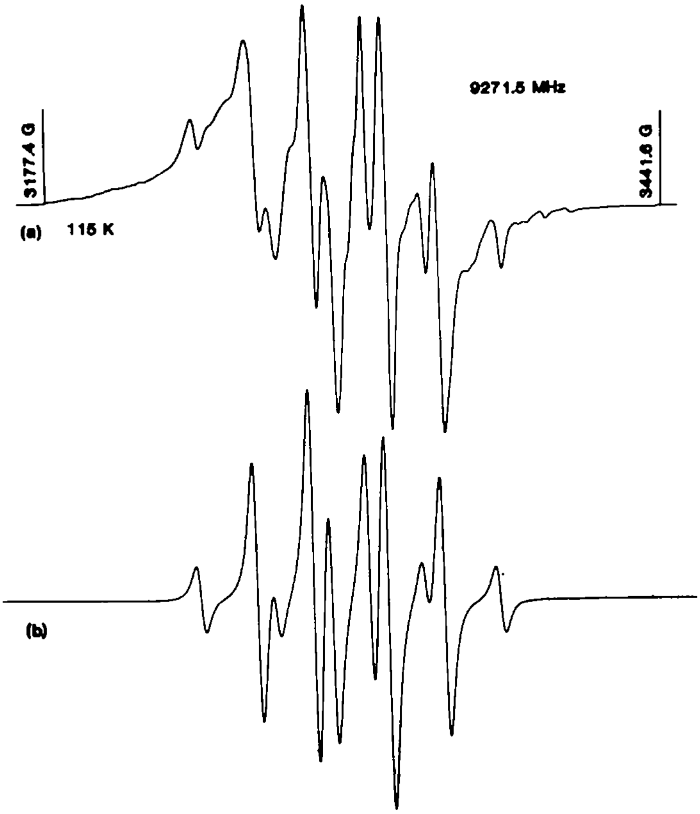
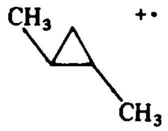
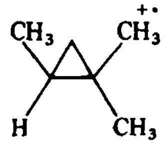
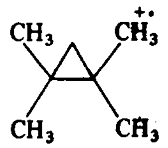


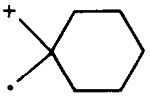
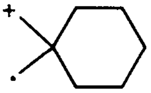
Fig. 8. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened form of the radical cation of *trans*-1,2-dimethylcyclopropane in $CFCl_2CF_2Cl$. Spectrum (b) was simulated by using the ESR parameters in Table 2 and a Lorentzian line width of 3.5 G.

Table 1. ESR parameters for the ring-closed forms of the radical cations of cyclopropane and its derivatives

Radical cation	Matrix	*T* (K)	Hyperfine couplings (G)	*g*
$c\text{-}C_3H_6^{+\cdot}$	$CFCl_2CF_2Cl$	80	unresolved	2.0042
	$CFCl_2CF_2Cl$	4.2	$a(4H_\alpha) = -12.5$,[a] $a(2H_\beta) = 21.0$[a]	2.0040
	$CFCl_3$	150	$a(2H_\alpha) = 10.4$, $a(2H_\beta) = 20.5$, $a(2CH_3) = 20.5$	2.0041
	$CFCl_3$	150	$a(2H_\alpha) = 11.9$, $a(2H_\beta) = 21.8$, $a(2CH_3) = 21.8$	2.0040
	$CFCl_3$	150	$a(1H_\alpha) = 9.8$, $a(2H_\beta) = 17.9$, $a(CH_3) = 14.5$, $a(2CH_3) = 20.6$	2.0040
	$CFCl_3$	145	$a(4CH_3) = 15.0$, $a(2H_\beta) = 18.7$	2.0033
	CF_2ClCCl_3	155	$a(4CH_3) = 15.0$, $a(2H_\beta) = 18.7$	2.0033

[a] Ref. 16.

Table 2. ESR parameters for the ring-opened forms of the radical cations of cyclopropane and its derivatives

Radical cation	Matrix	T (K)	Hyperfine couplings (G)	g
$+CH_2CH_2CH_2\cdot$	$CFCl_2CF_2Cl$	109	$a(2H_\alpha) = 22.4$, $a(2H_\beta) = 30.2$	2.0028
$+CH_2CH_2CH_2\cdot$	CF_2ClCF_2Cl	106	$a(2H_\alpha) = 22.4$, $a(2H_\beta) = 30.2$	2.0028
	$CFCl_2CF_2Cl$	95	$a(2H_\alpha) = 23.3$	2.0029
	$CFCl_3$	140	$a(2H_\alpha) = 23.3$	2.0029
$CH_3\overset{+}{C}HCH_2\dot{C}HCH_3$[a]	$CFCl_2CF_2Cl$	115	$a(1H_\alpha) = 24.7$, $a(1H_\beta) = 32.4$ or $a(2H_\beta) = 16.2$,[b] $a(CH_3) = 24.7$	2.0028
$CH_3\overset{+}{C}HCH_2\dot{C}(CH_3)_2$	$CFCl_2CF_2Cl$	115	$a(2H_\beta) = 11.8$, $a(2CH_3) = 23.6$	2.0029
$(CH_3)_2\overset{+}{C}CH_2\dot{C}(CH_3)_2$	$CFCl_2CF_2Cl$	117	$a(2H_\beta) = 11.7$, $a(2CH_3) = 23.3$	2.0029

[a] Formed from both *cis*- and *trans*-dimethylcyclopropane.
[b] See text.

patterns are identical in the experimental spectra of these species, the difference in gross appearance resulting from stronger background resonances in the spectrum derived from the *cis* isomer. Thus ring opening must occur in the same manner for both isomers. The large number of hydrogen couplings and the total width of the spectrum immediately rules out a $\cdot CH_2CH(CH_3)R$ radical center but this still leaves open two possibilities, namely $\cdot CH(CH_3)CH_2R$ for a symmetrical rupture of the cyclopropane ring between the two substituted carbons[5,13] in accordance with Roth and Schilling's rule,[13] or an unsymmetrical split to give $\cdot CH(CH_3)CH(CH_3)R$. There are a number of possible conformations and motional effects within these two radicals that could give rise to the observed spectra; these will be discussed later in this paper, as will the nature of the group represented by R.

1,1,2-*Trimethylcyclopropane*

The spectra of the ring-closed and ring-opened forms of this radical cation were obtained under the same conditions as those described for the corresponding species from the dimethylcyclopropanes, and are shown together with the simulated spectra in Figs 9 and 10, respectively. The hyperfine parameters for the ring-closed species are unexceptional given the data for the other methylcyclopropane cations, the only point of interest being the different couplings of 20.6 G for the *gem*-dimethyl hydrogens as compared to 14.5 G for the hydrogens from the other methyl group. While these results appear to indicate a slightly unsymmetrical spin distribution between the substituted α-carbons (*vide infra*), this imbalance is not reflected in the coupling of the α-hydrogen which has a normal value of 9.8 G.

The ring opening of the 1,1,2-trimethylcyclopropane radical cation in the $CFCl_2CF_2Cl$ matrix occurred at 100 K, in between the temperatures of 95 and 110 K required for the ring opening of the 1,2-dimethylcyclopropane and 1,1,2,2-tetramethylcyclopropane radical cations in this matrix.

Except for an alternating linewidth effect, the spectrum of the ring-opened 1,1,2-trimethylcyclopropane radical cation (Fig. 10) is almost exactly comparable to the spectrum of the corresponding species from 1,1,2,2-tetramethylcyclopropane,[5] essentially the same hyperfine parameters being obtained (Table 2). Therefore the radical center must also be of the $\cdot CMe_2CH_2R$ form[5] produced by fission of the most highly substituted C—C cyclopropane bond.[13] Although more pronounced, the line-broadening effect is similar to that reported for the ring-opened cyclopropane radical cation, and again probably originates from an out-of-phase modulation of the β-methylene hydrogen couplings.

It is also of interest to make a preliminary report here that the 1,1,2-trimethylcyclopropane radical cation undergoes a further transformation from the ring-opened form to a third radical species at 120–125 K in the $CFCl_2CF_2Cl$ matrix. The ESR spectrum of this product radical is better resolved at 138 K, and is shown in Fig. 11. Clearly this spectrum is quite different from that of the ring-opened species (Fig. 10), a tentative analysis suggesting doublet and quartet splittings of 50.6 G (1H) and 22.7 G (3H) with some additional unresolved fine structure in each line component. A spectrum with a quite similar overall hyperfine structure is also produced from the thermal decay of the ring-opened form of the *cis*-1,2-dimethylcyclopropane radical cation in the $CFCl_2CF_2Cl$ matrix. Further work is now in progress in an attempt to characterize these additional radical species.

1,1,2,2-*Tetramethylcyclopropane*

In addition to the work reported earlier,[5] we have generated the ring-closed radical cation in the CF_2ClCCl_3 matrix, the ESR parameters agreeing with those obtained for the species in $CFCl_3$ (Table 1).[5]

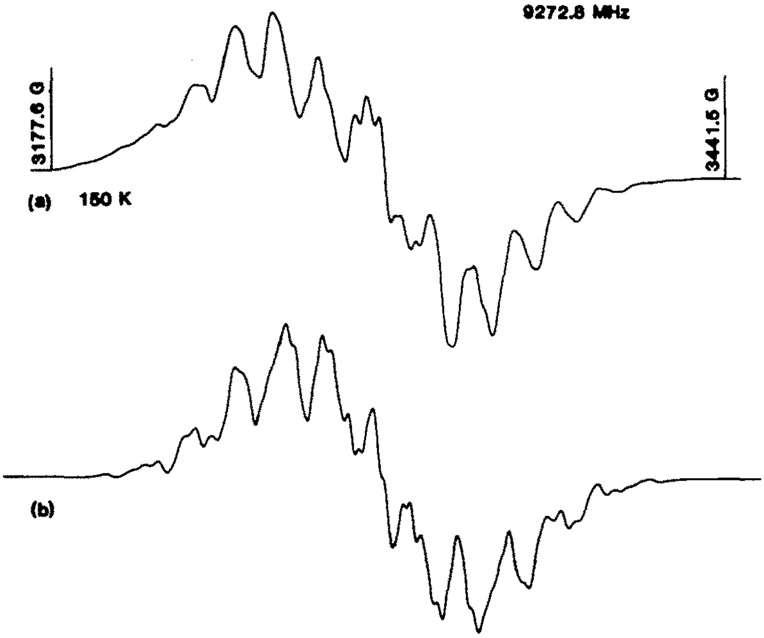


Fig. 9. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-closed form of the radical cation of 1,1,2-trimethylcyclopropane in $CFCl_3$. Spectrum (b) was simulated by using the ESR parameters in Table 1 and a Lorentzian linewidth of 3.5 G.

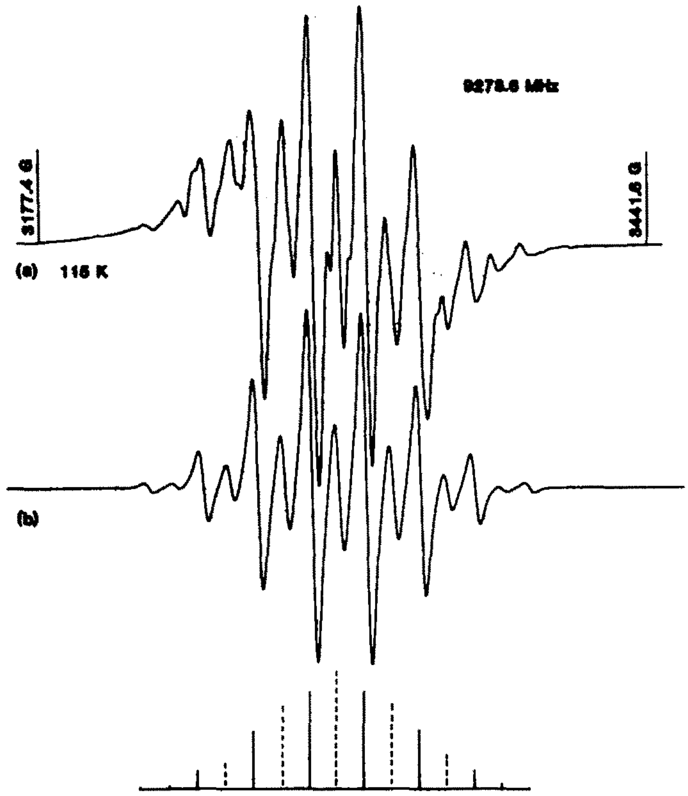


Fig. 10. (a) Observed and (b) computer-simulated first-derivative ESR spectra of the ring-opened form of the radical cation of 1,1,2-trimethylcyclopropane in $CFCl_2CF_2Cl$. Spectrum (a) shows an alternating line width effect as indicated by the stick diagram. Spectrum (b) was simulated by combining 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 has the effect of reducing the intensity of the center lines in the triplets resulting from the coupling to two equivalent methylene hydrogens in accordance with an out-of-phase modulation (see text).

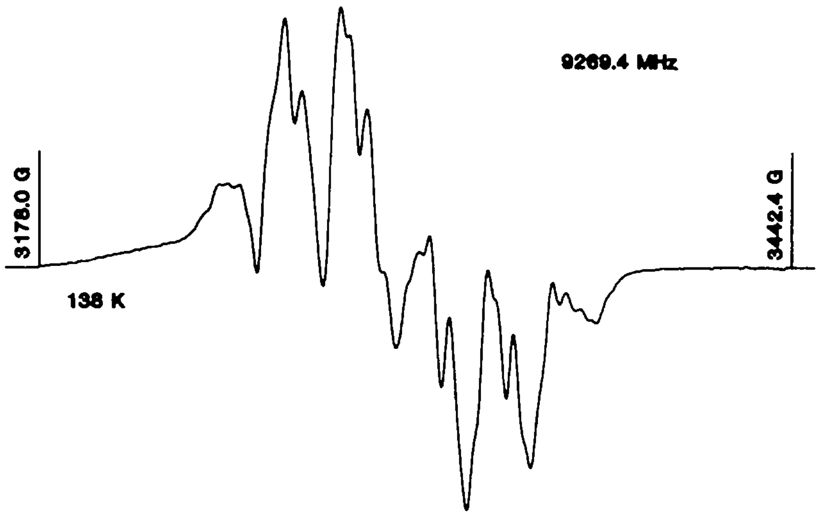


Fig. 11. First-derivative ESR spectrum of the radical produced from the ring-opened 1,1,2-trimethylcyclopropane radical cation at 125 K in the $CFCl_2CF_2Cl$ matrix and recorded at 138 K.

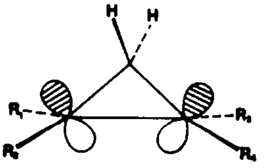
No evidence was obtained for ring opening in CF_2ClCCl_3 up to 160 K, at which temperature the ESR spectrum of the radical cation decayed. Incidentally, an intense signal which we assign to the isotropic spectrum of the matrix radical $CF_2ClCCl_2\cdot$ ($a(2F) = 13.6$ G and $a(2\ ^{35}Cl_x) = 4.5$ G) grew in independently at about the same temperature in the CF_2ClCCl_3 matrix, this sudden onset being highly reminiscent of the remarkable signal growth observed in γ-irradiated CF_3CCl_3 at *ca* 145 K and attributed to the $CF_3CCl_2\cdot$ radical.[19]

It is striking that the molecules ($CFCl_3$, CF_3CCl_3, and CF_2ClCCl_3) of each matrix in which the 1,1,2,2-tetramethylcyclopropane radical cation fails to undergo ring opening possess the CCl_3 group. Also this group is absent in $CFCl_2CF_2Cl$, the only matrix in which the reaction has hitherto been observed. However, more studies with other matrices are needed to establish empirical correlations of this type before they can be seriously considered.

DISCUSSION

Ring-closed cyclopropane radical cations

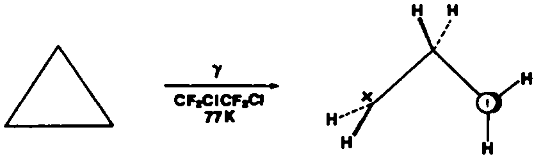
The electronic structure of the radical cations derived from cyclopropane and its derivatives in their ground states has usually been discussed in terms of the SOMO shown below.[8,9,13,16] This a_1 orbital in C_{2v} symmetry is bonding between two carbon atoms of the cyclopropane ring so that this bond becomes weakened and elongated in the radical cation.[8] Iwasaki *et al.*[16] have shown by ESR studies at 4 K that the cyclopropane radical cation does indeed distort in this way to a C_{2v} structure with most of the spin density located on the basal carbon atoms. Moreover, Roth and Schilling's CIDNP studies[13] have established that in the radical cations of methyl-substituted cyclopropanes, the weakened bond is always the most highly substituted C—C bond in the ring.



Our ESR results in Table 1 are in complete accord with the above principles. Thus, the four methyl groups are equivalent in the 1,1,2,2-tetramethylcyclopropane radical cation, and despite the lower symmetry of the *cis*- and *trans*-1,2-dimethylcyclopropane radical cations, the methyl groups and the methine hydrogens are equivalent in pairs at this level of spectral resolution. The results for the unsymmetrical 1,1,2-trimethylcyclopropane radical cation are also consistent with spin densities situated mainly at the most substituted ring carbons, as shown by the large couplings to the hydrogens of all three methyl groups. Finally, it is noteworthy that the g factors for these ring-closed radical cations are significantly higher than the free-spin value of 2.0023.

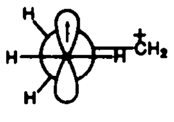
Ring-opened cyclopropane radical cations

The structure of these cations is of considerable interest given that high-level theoretical calculations deny the existence of these species,[8,9] at least in the gas phase! First, it is interesting to note that the ring-opened cyclopropane cation has now been generated in the CF_2ClCF_2Cl matrix as well as in $CFCl_2CF_2Cl$ (Figs 1 and 2). However, this finding does not allow a choice to be made between the various proposed structures.[6-9] The basic problem is that the ESR results only pertain to the radical center in these species, and offer little or no guidance regarding a possible bonding situation at the putative carbocat-



ionic site.[6] Accordingly, the arguments about the latter[6–9] have been based on speculation and secondary considerations which are difficult to evaluate. We will return to this important question, however, after discussing (a) the conformations at the radical sites of the ring-opened species, and (b) the ring opening of the spiro[2.5]octane radical cation.

In addition to establishing the radical site labelled as C_α, the ESR parameters in Table 2 provide information from the β-hydrogen couplings as to the conformation about the C_α—C_β bond in the ring-opened structure. The results obtained for the radical cations derived from cyclopropane, 1,1,2,2-tetramethylcyclopropane, and 1,1,2-trimethylcyclopropane are unambiguous and establish the conformations as 1–3, respectively. Moreover, the fact that 1 assumes the bisected form whereas 2 and 3 are eclipsed exactly parallels the findings for alkyl radicals having the same C_α—C_β end groups.[12,17,20]



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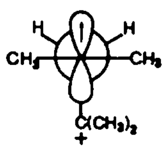

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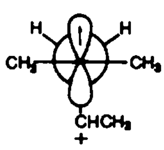

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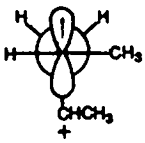
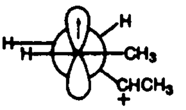
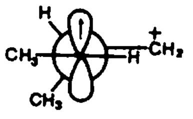


4a

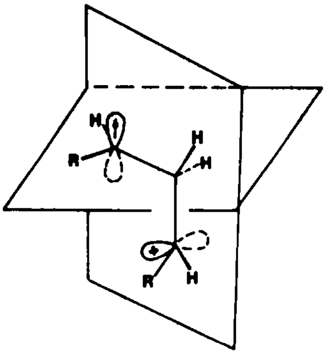


4b



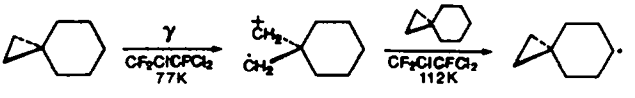
5

The conformation of the ring-opened radical cation formed from the 1,2-dimethylcyclopropanes is not as clearcut, however. In this case the ESR results are ambiguous because the spectra (Figs 6 and 8) are consistent either with one large β-hydrogen coupling of 32.4 G or with two nearly equivalent couplings of 16.2 G that undergo an out-of-phase modulation resulting in an apparent doublet splitting of 32.4 G instead of a 16.2 G triplet. This latter possibility would be consistent with the eclipsed conformation 4a following the breakage of the most substituted C—C bond. The other possibility of a large coupling to a single β-hydrogen is accommodated by either of the two conformations 4b or 5. These are taken as representative of the several conformations yielding an $H_\alpha C_\alpha C_\beta H_\beta$ dihedral angle of 60°. Conformation 4b, again resulting from ring opening at the CHMe—CHMe bond, is shown next in greater detail to illustrate the orthogonality of the carbon $2p_z$ orbitals at the carbocation and radical sites. It can be seen that the two planes perpendicular to these orbitals intersect at the β-carbon, each plane also containing one (H_{β_1} or H_{β_2}) of the methylene hydrogens at this carbon.



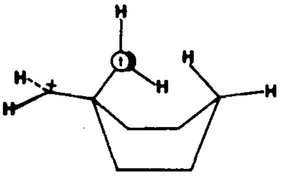
Since these $C_\alpha C_\beta H_{\beta_1}$ and $C_\gamma C_\beta H_{\beta_2}$ planes are necessarily perpendicular to each other at the tetrahedral β-carbon, it follows that the symmetry (z) axes of the carbon 2p orbitals normal to these planes are also orthogonal to each other. Conformation 5 is also consistent with the ESR data but this requires ring opening to occur at the CH_2—CHMe bond, a process which is much less likely given that the spin distribution in the ring-closed forms of the 1,2-dimethylcyclopropane radical cation is in agreement with Roth and Schilling's generalization.[13] In summary, then, the conformation of the ring-opened 1,2-dimethylcyclopropane radical cations appears to be either 4a or 4b; a choice between these two possibilities might be possible if ESR studies could be carried out at temperatures considerably higher than those attainable in the present work.

Turning to the ring-opened form of the spiro [2.5]octane radical cation, we have already seen that the ESR results strongly support a CH_2—CH_2 bond scission in the cyclopropane ring, as depicted in the scheme shown below. The conformation at the $RCH_2\cdot$ radical site, however, cannot be determined because of the absence of β-hydrogen couplings in this case. Nevertheless, it is of interest to consider the radical conformation relative to the cyclohexane ring because of the secondary H-atom abstraction reaction leading to the formation of a cyclohexyl radical (Fig.



Scheme 2.

4). If this reaction were to occur intramolecularly, the boat conformations **6** and **7** would seem to be demanded, but these are almost certainly of higher energy than the alternative chair conformations **8** and **9**. Thus, stereochemical considerations should favor an intermolecular reaction if diffusion is possible in the matrix. Since the reaction occurs in the $CFCl_2CF_2Cl$ matrix at 112 K but not in $CFCl_3$ up to 160 K, the results are indeed consistent with a process of intermolecular diffusion in $CFCl_2CF_2Cl$ at about 110 K. Strong support for such radical cation–molecule reactions in $CFCl_2CF_2Cl$ comes from the observation of the secondary radical produced from the ring-opened cyclopentene oxide radical cation **10** at 100 K.[21] Instead of the radical being **11** as would be the case for a simple deprotonation reaction, the radical formed is **12** and clearly this can only occur by H-atom abstraction from a neutral cyclopentene oxide molecule. Similarly, the secondary radical formed from the ring-opened cyclohexene oxide radical cation **13** is **15** and not **14**,[21] although in this case it is not clear from the ESR results whether **13** is delocalized or not. It is also interesting to note that these hydrogen abstraction reactions are all regiospecific with respect to the cyclohexane and cyclopentane ring systems, the favored site(s) for H-atom abstraction being farthest removed from the 3-membered ring.



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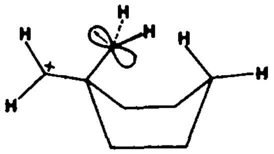

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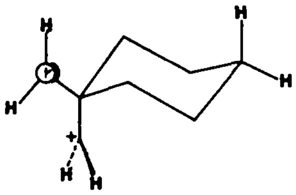

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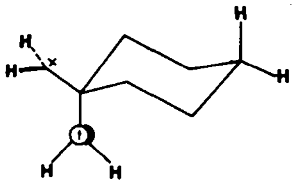

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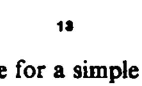

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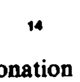

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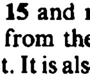
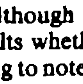
12



13



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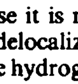

15

Matrix effect on ring opening of cyclopropane radical cations

The new results presented here for the radical cations of *cis*- and *trans*-1,2-dimethylcyclopropane, and of 1,1,2-trimethylcyclopropane, accord with the previous observations[4-6] that ring opening occurs readily in $CFCl_2CF_2Cl$ but not in $CFCl_3$ and CF_3CCl_3, even at much higher temperatures. However, the present study has uncovered an exception to this rule insofar as the ring-opened form of the spiro[2.5]octane radical cation is generated directly in both $CFCl_2CF_2Cl$ and $CFCl_3$ by γ irradiation at 77 K. Moreover, the cyclopropane radical cation has now been shown to undergo ring opening in the CF_2ClCF_2Cl matrix as well as in $CFCl_2CF_2Cl$. While these new observations dispel the notion that the ring opening of cyclopropane radical cations occurs uniquely in $CFCl_2CF_2Cl$, it is nevertheless true to say that the radical cation of every cyclopropane derivative hitherto examined undergoes ring opening in this matrix. Thus the results certainly indicate that the $CFCl_2CF_2Cl$ matrix allows the ring-opening reaction to occur with particular ease in comparison with matrices of other halocarbons, especially those containing the CCl_3 group.

A special role of the $CF_2ClCFCl_2$ matrix in stabilizing the localized forms of ring-opened radical cations is also indicated by previous studies on oxirane derivatives.[3] Whereas only the delocalized forms of the C…C ring-opened oxirane and methyl-substituted oxirane radical cations are observed in $CFCl_3$, CF_3CCl_3, and CCl_4,[1-3] the localized forms are produced in $CFCl_2CF_2Cl$ either directly on γ irradiation at 77 K or by an irreversible change from the delocalized forms of these cations at higher temperatures.[3] Thus it appears that in the $CFCl_2CF_2Cl$ matrix, there is a remarkable preference for the localized ring-opened oxirane radical cations just as there is for the corresponding ring-opened cyclopropane cations described in the present study.

In connection with matrix effects, it is also of interest to draw a simple analogy between the ring opening of cyclopropane radical cations as described here and the twisting of olefin radical cations from planarity.[22-24] In each case the process involves the rotation of a CR_2 group that, in the limit of a 90° twist, results in the complete breaking of a one-electron σ (cyclopropane) or π (olefin) 2p—2p bond between two carbon atoms. Recent work[22-24] has shown that olefin radical cations do in fact adopt twisted structures with large twist angles in many cases. The point of interest here is that the twist angle seems to be matrix dependent as evidenced by significant variations in the hyperfine coupling constants for species such as the propylene radical cation in different solvents.[23,24] We conclude that the matrix can play a very significant role in monorotatory processes which lead to the partial or complete breaking of a one-electron bond.

Nature of the carbocationic center in ring-opened species

As discussed in the Introduction, the results of *ab initio* MO calculations on the cyclopropane radical cation do not lend support to an orthogonal ring-opened form of this cation, a (90, 0) structure being predicted to be metastable with respect to the ring-closed (90, 90) face-to-face structure.[8,9] It has been emphasized, however, that this prediction applies only to the gas phase,[9] since the difficult problem of possible solvent interactions was not considered in the calculations.[8,9] Our experimental results, on the other hand, provide clear evidence that specific matrix interactions are of critical importance to ring opening, as summarized in the previous section. Therefore, there is no underlying conflict between theory and experiment on this question.

In order to explain the stability of the ring-opened structure, it has been suggested that the carbocation center is strongly bonded to a suitable nucleophile which could be either the chloride ion,[8] produced as a result of dissociative electron attachment to the matrix,[25] or a solvent molecule.[7,9] We had previously considered these possibilities but failed to obtain direct ESR evidence for halogen bonding at the γ carbon.[6]

The present work sheds some additional light on this question. We find it significant that the cyclopropane ring of the spiro[2.5]octane radical cation opens in the unencumbered CH_2—CH_2 position on generation of this species in the $CFCl_3$ matrix at 77 K. This result stands in sharp contrast to the observation of only the ring-closed radical cations from other cyclopropanes in this matrix at temperatures up to 150–160 K. Were the ring-opening reaction to be initiated by the release of chloride ion in the matrix, no such difference would be expected.

Another approach to the problem is suggested by recent work on the bicyclic oxiranes, cyclopentene oxide and cyclohexene oxide.[21] We find that the delocalized form of the cyclopentene oxide radical cation **10** produced in the $CFCl_2CF_2Cl$ matrix persists until 100 K, at which point it undergoes the H-atom abstraction reaction to form **12**, as mentioned earlier. In contrast, the linear radical cations formed from the monocyclic methyl-substituted oxiranes change from their delocalized to localized forms in this matrix below about 100 K.[3] This difference is surprising if localization occurs as a result of nucleophilic attack by either a chloride ion or a solvent molecule on the delocalized radical cation. On the other hand, the results are understandable if localization of the radical cation requires a twisting at one carbon center relative to the other, because this process would be opposed by the greater rigidity of a ring system.

Applying the same general idea to cyclopropane derivatives, it should be of interest to study the radical cation of bicyclo[3.1.0]hexane. Assuming that the cyclopropane ring opens symmetrically between the bridgehead carbons, a localized form of the radical cation would be expected by nucleophilic attack. In the absence of such an attack, the initial radical cation product of the C—C bond fission would presumably be a (0, 0) delocalized species which should easily rearrange to the cyclohexene radical cation by a 1,2-hydride shift. Any such rearrangement of a localized species resulting from nucleophilic attack would, of course, be blocked by a chloride ion substitution or chloronium ion formation at the carbocation center. Thus, in this case, the identification of the product radical could perhaps serve to distinguish nucleophilic attack from a solvent-assisted ring opening and rearrangement of the radical cation. An actual example of this distinction is provided by the work of Toriyama and co-workers†[26] who observed the ring opening of the cyclobutane radical cation to the but-1-ene radical cation rather than the species $R\overset{+}{C}l(CH_2)_3CH_2\cdot$ which would have resulted from a nucleophilic solvent attack.

In line with the previous discussion, we should like to draw a clear conceptual distinction between the case of strong nucleophilic coordination to the carbocation center, as with chloride ion[8] or a single chlorine ligand of a solvent molecule,[7] and a general solvation effect involving probably more than one solvent molecule. We emphasize that the former case involves a replacement of the carbocation by a covalent C—Cl bond in a neutral molecule or a chloronium ion, whereas the latter does not imply a loss of the carbocation function. Considering the fact that the ring opening is strongly matrix dependent (*vide supra*) among several chlorine-containing solvents, it seems reasonable to invoke a solvent rather than a chlorine atom ligand effect.

Assuming an appreciable solvent interaction at the carbocation center, the requirement that the carbocation and radical centers be orthogonal to each other in the localized species no longer applies rigorously because the asymmetry induced by this solvation effect will likely render the spin distribution insensitive to twist angle. The way in which a polar solvent may modify the potential energy surface for ring opening is shown schematically in Fig. 12, the driving force being the greater solvation energy of the carbocation in the localized than in the ring-closed species. The exoergic nature of this process suggests that the transition state may involve only a small twist angle and therefore a relatively small energy barrier. In other words, a strong specific solvation effect can in principle overcome the difficulties associated with the high energy of the isolated (90, 0) ring-opened species. Finally, in terms of a solvation effect, the specific effectiveness of $CFCl_2CF_2Cl$ in facilitating the ring-opening process could well be due to the greater

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† Toriyama *et al.*[26a] have recently suggested that the ESR spectrum (Figs 1 and 2) attributed by us to the trimethylene radical cation could also be due to the n-propyl radical formed by intermolecular hydride-ion transfer from cyclopropane to a ring-closed cyclopropane radical cation. However, they also add that our interpretation in terms of $\cdot CH_2CH_2CH_2^+$ "is quite attractive and probably correct".

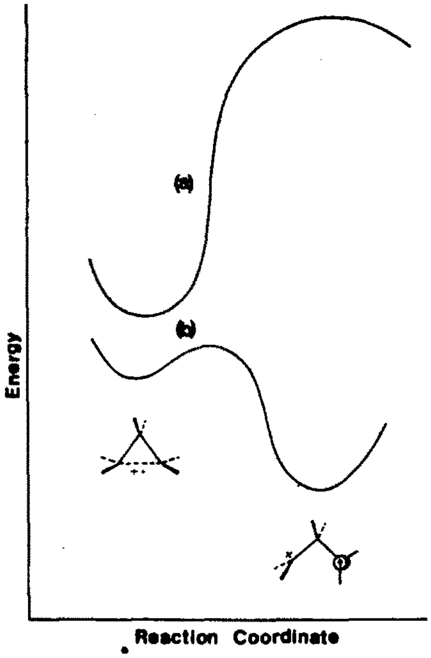

Fig. 12. Schematic potential energy diagram for the ring opening of the cyclopropane radical cation (a) in the gas phase, and (b) in a polar solvent. The twist angle in the solvated ring-opened species may differ from 90° (see text).

plasticity of this matrix in the temperature range of interest.

Acknowledgements—We thank Dr L. D. Snow for helpful discussions concerning the relation of the present work to his studies on oxirane compounds. We also thank Dr D. D. M. Wayner and Professor W. T. Borden for sending us preprints of their manuscripts (Refs 8 and 9) and for useful comments on this work. The final manuscript also incorporated helpful suggestions from one of the referees and Dr H. D. Roth. This research has been supported by the Division of Chemical Sciences, U.S. Department of Energy (Report No. DOE/ER/02968-161).

REFERENCES

[1] L. D. Snow, J. T. Wang and F. Williams, *Chem. Phys. Lett.* **100**, 193 (1983).
[2] X.-Z. Qin, L. D. Snow and F. Williams, *J. Am. Chem. Soc.* **107**, 3366 (1985).
[3] X.-Z. Qin, L. D. Snow and F. Williams, *J. Phys. Chem.* **89**, 3602 (1985).
[4] X.-Z. Qin and F. Williams, *Chem. Phys. Lett.* **112**, 79 (1984).
[5] X.-Z. Qin, L. D. Snow and F. Williams, *J. Am. Chem. Soc.* **106**, 7640 (1984).
[6] X.-Z. Qin, L. D. Snow and F. Williams, *Chem. Phys. Lett.* **117**, 383 (1985).
[7] M. C. R. Symons, *Chem. Phys. Lett.* **117**, 381 (1985).
[8a] D. D. M. Wayner, R. J. Boyd and D. R. Arnold, *Can. J. Chem.* **61**, 2310 (1983); [b] D. D. M. Wayner, R. J. Boyd and D. R. Arnold, *Ibid.* **63**, 3283 (1985).
[9] D. A. Hrovat, P. Du and W. T. Borden, private communication.
[10] B. F. Yates, W. J. Bouma and L. Radon, *J. Am. Chem. Soc.* **106**, 5805 (1984).
[11] T. M. Sack, R. L. Cerny and M. L. Gross, *J. Am. Chem. Soc.* **107**, 4562 (1985).
[12] K. S. Chen, D. Y. H. Tang, L. K. Montgomery and J. K. Kochi, *J. Am. Chem. Soc.* **96**, 2201 (1974).
[13a] H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.* **105**, 6805 (1983); [b] H. D. Roth and M. L. M. Schilling, *Can. J. Chem.* **61**, 1027 (1983); [c] H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.* **103**, 7210 (1981).
[14] P. G. Gassman and B. A. Hay, *J. Am. Chem. Soc.* **107**, 4075 (1985), and refs therein.
[15] T. Shono and Y. Matsumura, *Bull. Chem. Soc. Japan* **48**, 2861 (1975).
[16a] M. Iwasaki, K. Toriyama and K. Nunome, *J. Chem. Soc., Chem Commun.* 202 (1983); [b] M. Iwasaki, K. Toriyama and K. Nunome, *Faraday Discuss. Chem. Soc.* **78**, 19 (1984).
[17] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **39**, 2147 (1963).
[18] C. Roberts and J. C. Walton, *J. Chem. Soc., Perkin Trans* **2**, 841 (1985).
[19] B. W. Walther and F. Williams, *J. Chem. Phys.* **79**, 3167 (1983).
[20a] D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.* **94**, 6485 (1972); [b] K. S. Chen, D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.* **95**, 7036 (1973); [c] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.* **93**, 846 (1971).
[21] X.-Z. Qin, L. D. Snow and F. Williams, unpublished results.
[22] M. Kira, H. Nakazawa and H. Sakurai, *J. Am. Chem. Soc.* **105**, 6983 (1983).
[23] K. Toriyama, K. Nunome and M. Iwasaki, *Chem. Phys. Lett.* **107**, 86 (1984).
[24] M. Shiotani, Y. Nagata and J. Sohma, *J. Phys. Chem.* **88**, 4078 (1984).
[25] A. Hasegawa, M. Shiotani and F. Williams, *Faraday Discuss. Chem. Soc.* **63**, 157 (1977).
[26a] K. Toriyama, K. Nunome, M. Iwasaki, K. Ushida and T. Shida, 48th Annual Meeting Chem. Soc. Japan, p. 3 (1983); *Chem. Phys. Lett.* **122**, 118 (1985); [b] M. Iwasaki and K. Toriyama, *Faraday Discuss. Chem. Soc.* **78**, 89 (1984).

Note added in proof

Since this contribution was submitted, a paper by Gross and co-workers[27] has appeared describing mass-spectrometric studies of the ring opening of gas-phase cyclopropane radical cations. These authors conclude that ring opening to the trimethylene radical cation is consistent with their results, and that this process is entirely analogous to the structural change of cyclopropane radical cations in condensed phases. Also Ushida, Shida and Walton[28] have recently reported that the radical cation of bicyclo[2.1.0]pentane rearranges to the cyclopentene radical cation in the $CFCl_3$ matrix, even at 4 K. Their result argues against a mechanism of cyclopropane ring opening brought about through nucleophilic attack either by chloride ion or by a solvent molecule. As discussed in the last section of our paper, such a mechanism applied to a substituted cyclopropane ring in a bicyclic system would not lead to a rearranged radical cation isomer. Instead, the incipient carbocationic center of the ring-opened intermediate would be expected to combine with the nucleophile to produce a chloro-substituted cycloalkyl radical rather than undergo a hydride ion shift to give the cycloalkene radical cation.

[27] T. M. Sack, D. L. Miller and M. L. Gross, *J. Am. Chem. Soc.* **107**, 6795 (1985).
[28] K. Ushida, T. Shida and J. C. Walton, *J. Am. Chem. Soc.* **108**, 2805 (1986).