# ESR Evidence for Localized Forms of C····C Ring-Opened Oxirane Radical Cations

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Localized forms of the C---C ring-opened oxirane and methyl-substituted oxirane radical cations have been detected by ESR spectroscopy following  $\gamma$ -irradiation of solid solutions of the parent compounds in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix. For oxirane, 1,2-dimethyloxirane, and tetramethyloxirane, the localized forms possess the RCH<sub>2</sub>, RCHMe, and the RCMe<sub>2</sub> radical centers, respectively. In the unsymmetrically substituted methyloxiranes, the radical center is localized at the oxirane carbon with the least number of methyl groups. The temperature needed to bring about the formation of the localized species increases with methyl substitution at the localized radical center, the oxirane and methyloxirane species being formed during irradiation at 77 K while the tetramethyloxirane species is produced subsequently from the delocalized planar form of the ring-opened cation at 105-110 K. In contrast, only the delocalized forms of the oxirane cations have been observed in CFCl<sub>3</sub>, CF<sub>3</sub>CCl<sub>3</sub>, and CCl4, even at much higher temperatures (145-215 K) close to the softening points of these matrices. The possible structures of the localized forms of the oxirane radical cations are discussed, the two most reasonable models being either an orthogonal structure with noninteracting radical and carbocation centers or a similar species in which the carbocation center is complexed with the solvent or combined with a chloride ion. Despite the lack of ESR and other evidence for some type of solvent halogen participation in the localized structure, the latter model cannot be ruled out at present.

#### Introduction

Recently, measurements of ESR<sup>1,2</sup> and electronic absorption<sup>3</sup> spectra have established that the radical cation produced radiolytically from ethylene oxide in certain halocarbon matrices at 77 K is the symmetrical  $(C_{2\nu})$  C···C ring-opened planar structure isoelectronic with the allyl radical. These results showing that the parent ethylene oxide cation ring opens with little or no activation energy are consistent with many earlier gas-phase studies<sup>4-10</sup> (see especially ref 10) and agree well with the results of high-level theoretical calculations.<sup>11-13</sup>

Another significant feature of the ab initio calculations<sup>11-13</sup> is that they predict a relatively small barrier between 1.911 and 6.712 kcal mol<sup>-1</sup> for methylene group rotation in the ring-opened oxirane cation, indicating that allylic resonance is much less important for linear  $CH_2OCH_2^+$  than it is for the allyl radical itself.<sup>11</sup> Moreover, the potential energy surface for the ring-opened ethylene oxide cation is also predicted to be very flat for asymmetric distortions resulting from slightly unequal C-O bond lengths.<sup>11,12</sup> These theoretical results clearly raise the possibility that rigid asymmetric structures may be attained for linear CH<sub>2</sub>OCH<sub>2</sub><sup>+</sup>. in the solid state at low temperatures, especially given the presence of solvent interactions<sup>14,15</sup> for this cation in some Freon matrices.<sup>1,2</sup>

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It was with considerable interest, therefore, that the parent cyclopropane and 1,1,2,2-tetramethylcyclopropane radical cations, which are stable at low temperatures, were recently observed to undergo ring opening in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix above 80 and 110 K, respectively, to give localized radical centers associated with twisted forms of the linear cations.<sup>16,17</sup> This monorotatory ring-opening reaction did not occur in other Freon matrices, even at higher temperatures, serving to emphasize the special properties of the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix in this connection.

In view of these findings, and as a natural extension of our previous oxirane studies,<sup>1,2</sup> we have studied the radical cations formed from several oxiranes in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix. The results show quite convincingly that this matrix strongly favors the formation of asymmetric C---C ring-opened structures. Even in cases where the ring-opened cation initially formed from a substituted oxirane possesses a delocalized structure, this only appears to reflect a local minimum in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix and the cation structure changes over irreversibly to the localized form on matrix annealing.

#### **Experimental Section**

Ethylene oxide (99.7%) from Matheson,  $(1,2^{-13}C_2)$  ethylene oxide (99%) from Cambridge Isotope Laboratories, Inc., and trans-2,3-epoxybutane (trans-1,2-dimethyloxirane) (96%) from Wiley Organics were used as received. Also studied were propylene oxide (99% from Aldrich) and isobutylene oxide (from Research Organic/Inorganic Chemicals, Inc.). The purity of the latter compound was checked by <sup>1</sup>H NMR, the spectrum consisting of two sharp peaks at 1.3 (6 H) and 2.55 ppm (2 H).

Tetramethyloxirane and trimethyloxirane were prepared by the epoxidation of 2,3-dimethyl-2-butene (Gold Label 99+% from Aldrich Chemical Co.) and 2-methyl-2-butene (99.9% from Wiley Organics), respectively, using the following procedure adapted from that of Hickinbottom and Hogg.<sup>18</sup> About 1 g of the olefin was added over ca. 30 min to an ice-cold solution containing a suitable excess (2.5 g) of 3-chloroperoxybenzoic acid in 50 mL of methylene chloride. After standing overnight in the refrigerator, the solution was filtered to remove the white precipitate of 3chlorobenzoic acid and then transferred on a vacuum line so as to leave behind any residual amounts of dissolved 3-chlorobenzoic acid and of the unused peroxy compound. The methylene chloride

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TABLE I: ESR Parameters<sup>a</sup> for C···C Ring-Opened Oxirane Radical Cations in the CFCl<sub>2</sub>CF<sub>2</sub>Cl Matrix

radical cation	form <sup>b</sup>	$T_{\rm f}^{c}/{ m K}$	T <sup>d</sup> /K	g	hyperfine couplings/G	
oxirane	1	77	90	2.0035	21 (2 H <sub>a</sub> )	
methyloxirane	1	77	90	2.0033	21 $(2 H_a)$	
cis-1,2-dimethyloxirane <sup>e</sup>	1	90	95	2.0033	22.5 (1 $H_{er}$ 3 $H_{e}$ )	
trans-1,2-dimethyloxirane	1	95	100	2.0038	23 $(1 H_{a}, 3 H_{b})^{\prime\prime}$	
trimethyloxirane	1	95	105	2.0033	22 (1 $H_{a}$ , 3 $H_{b}$ )	
tetramethyloxirane	d	77	95	2.0023	$15.1 (12 H_{\beta})$	
tetramethyloxirane	1	105-110	115	2.0026	21 (6 $H_{\beta}$ )	

<sup>a</sup> Measurements were made from the experimental spectra. <sup>b</sup> Localized (l) or delocalized (d). <sup>c</sup> Temperatures at which radical cation are formed in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix. <sup>d</sup> Temperatures at which ESR measurements were made. <sup>c</sup> The quintet spectrum from *cis*-1,2-dimethyloxirane was much better resolved than that from *trans*-1,2-dimethyloxirane shown in Figure 4.

TABLE II: ESR Parameters<sup>a</sup> for the Localized Oxirane Radical Cation in the CFCl<sub>2</sub>CF<sub>2</sub>CI Matrix at ca. 100 K

	nucleus	hyperfine tensor components/G			direction cosines			
radical cation		$A_1$	$A_2$	$A_3$	$l_x^b$	$l_y^b$	$l_z^b$	$g_{\rm iso}$
		-11.5			1	0	0	
+CH <sub>2</sub> OĊH <sub>2</sub>	${}^{1}H_{a}$		-24.5		0	1	0	2.0035
	•			-18.0	0	0	1	
		-11.5			-0.5	0.866	0	
	${}^{1}H_{b}$		-24.5		-0.866	-0.5	0	
	•			-18.0	0	0	1	
		+9.9°			1	0	0	
	<sup>13</sup> C		+9.9°		0	1	0	
				+95.7°	0	0	1	

<sup>a</sup> Determined by computer simulation (see text and Figures 1c and 2c) using a line width of 9.5 G. <sup>b</sup> The z axis is perpendicular to the CH<sub>2</sub> plane at the radical center while the x axis is taken along the C-H<sub>a</sub> bond. <sup>c</sup> The principal values of the <sup>13</sup>C hyperfine tensor yield  $A_{iso} = 38.5$  G and 2B = 57.2 G, the latter corresponding to a spin density of 0.8-0.9 in a <sup>13</sup>C 2p<sub>z</sub> orbital.

solvent was then distilled off at atmospheric pressure (bp 40–42 °C) and the oxirane product collected in a subsequent vacuum distillation. The <sup>1</sup>H NMR spectrum of the purified tetramethyloxirane in CH<sub>2</sub>Cl<sub>2</sub> showed a peak at 1.1 ppm (12 H) while the trimethyloxirane gave signals at 2.7 ppm (1 H, quartet) and 1.15–1.20 ppm (9 H), the latter consisting of overlapping peaks from the hydrogens of the three nonequivalent methyl groups.

The Freon solvents consisted of trichlorofluoromethane (Lot 10078 from PCR/SCM Specialty Chemicals), 1,1,1-trichlorotrifluoroethane (99% from Aldrich), and 1,1,2-trichlorotrifluoroethane (Lot 9709 from PCR/SCM Specialty Chemicals).

Details of sample preparation,  $\gamma$ -irradiation at 77 K, and subsequent low-temperature ESR measurements have been given previously.<sup>15</sup> Powder ESR patterns were simulated with a computer program<sup>19</sup> written by Dr. Paul H. Kasai (IBM Instruments, Inc.).

#### Results

As shown in Figure 1, the ESR spectra of the radical cations derived radiolytically from ethylene oxide (a) and propylene oxide (b) in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix are very similar and consist of broad 1:2:1 triplet patterns reminiscent of those obtained for RCH<sub>2</sub>. radicals in the solid state.<sup>19</sup> If the directly measured ESR parameters (Table I) are taken as a guide, the spectral patterns can be satisfactorily simulated (Figure 1c) in terms of an isotropic g tensor and an anisotropic hyperfine interaction with two hydrogens, the principal values and mutual orientations of the hyperfine coupling tensors (Table II) being characteristic of those for two  $\alpha$ -hydrogens in a carbon-centered  $\pi$  radical.<sup>19b</sup> The spectra retained their basic triplet character as decay occurred in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix from 95 to 110 K, but the anisotropic line shape was still evident and the center line did not intensify relative to the outer components. It appears, therefore, that the two  $\alpha$ -hydrogens do not undergo rapid positional interchange in this temperature range (80-120 K).

The triplet ESR spectrum (A(2 H) = ca. 20 G) observed here for the cation generated from ethylene oxide in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix contrasts with the quintet spectrum (A(4 H) = 16.2 G)previously reported for the cation generated from the same com-



Figure 1. First-derivative ESR spectra of radicals derived from ethylene oxide (a) and propylene oxide (b) by  $\gamma$ -irradiation (dose, 0.4 Mrad) of 1 mol % solutions in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix at 77 K. The lower spectrum (c) was simulated by using the ESR parameters given in Table II and a line width of 9.5 G.

pound in the CFCl<sub>3</sub> and CF<sub>3</sub>CCl<sub>3</sub> matrices.<sup>1</sup> Further evidence for this specific matrix effect comes from studies using 1,2-<sup>13</sup>C<sub>2</sub>-labeled ethylene oxide, and the pertinent ESR spectra are shown in Figure 2. Spectrum a of the species generated in the CFCl<sub>3</sub> matrix clearly consists of a <sup>1</sup>H quintet of strong central  $M_1(^{13}C) = 0$  lines together with anisotropically broadened  $M_1(^{13}C)$ = ±1 wing features of which only the parallel components are

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Figure 2. First-derivative ESR spectra of radicals derived from  $1,2^{-13}C_2$  labeled ethylene oxide by  $\gamma$ -irradiation (dose, 1.0 Mrad) at 77 K of 1 mol % solutions in CFCl<sub>3</sub> (a), CF<sub>3</sub>CCl<sub>3</sub> (b), and CFCl<sub>2</sub>CF<sub>2</sub>Cl (c, solid line). The spectra were recorded at 110, 140, and 90 K, respectively. The spectrum shown by the dashed line in (c) was simulated by using the ESR parameters in Table II and a line width of 9.5 G.

well resolved.<sup>2</sup> Similarly, spectrum b of the cation generated in  $CF_3CCl_3$  shows an intense central quintet although in this case the wing components are not resolved out of the broad spectral envelope. The selective broadening of the wing lines in these spectra (Figure 2, a and b) is characteristic of an anisotropic hyperfine interaction with two equivalent <sup>13</sup>C nuclei, the tensors having a common principal axis system so that the central components of the <sup>13</sup>C triplet remain sharp and show no <sup>13</sup>C hyperfine broadening. On the other hand, the spectrum (Figure 2c) of the cation generated in  $CFCl_2CF_2Cl$  shows no central feature and consists of an anisotropic doublet<sup>20</sup> from interaction with one <sup>13</sup>C nucleus.

Figure 2c also shows that it is possible to simulate the spectrum of the <sup>13</sup>C-labeled cation generated in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix by using the **g** and <sup>1</sup>H hyperfine tensors for the corresponding unlabeled species with additional <sup>13</sup>C(1) hyperfine parameters, and the results are given in Table II. Although the <sup>1</sup>H triplet structure is not well resolved in the experimental spectrum of the



Figure 3. First-derivative ESR spectra of radicals derived from tetramethyloxirane by  $\gamma$ -irradiation (dose, 0.4 Mrad) at 77 K of 1 mol % solutions in CFCl<sub>3</sub> (a) and CFCl<sub>2</sub>CF<sub>2</sub>Cl (b). Spectrum c is that of the radical which grows in when the  $\gamma$ -irradiated CFCl<sub>2</sub>CF<sub>2</sub>Cl solution is annealed to 115 K.

<sup>13</sup>C-labeled species, this lack of a well-defined substructure is also a feature of the simulated spectrum (Figure 2c) and therefore there is no inconsistency on this point. Thus, the ESR results provide clear evidence that the cation generated from ethylene oxide in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix differs from that produced in the CFCl<sub>3</sub> and CF<sub>3</sub>CCl<sub>3</sub> matrices and possesses a hyperfine structure resulting from interaction with only two <sup>1</sup>H nuclei and one <sup>13</sup>C nucleus in the molecule.

Corresponding studies on tetramethyloxirane revealed another facet of this matrix effect. Although in this case the structure of the cation formed initially in CFCl<sub>3</sub> and CFCl<sub>2</sub>CF<sub>2</sub>Cl at 77 K appears to be the same, the species in CFCl<sub>2</sub>CF<sub>2</sub>Cl sustains an irreversible structural change on subsequent annealing. These findings are illustrated by the results presented in Figure 3. Comparison of the ESR spectra a and b shows that each spectrum initially consists of a set of 13 lines with binomial line intensities and a hyperfine coupling, A(12 H), of 15.1 G, the only difference being the greater line widths associated with spectrum b of the CFCl<sub>2</sub>CF<sub>2</sub>Cl sample. However, while spectrum a of the CFCl<sub>3</sub> sample remains essentially unchanged up to the softening point (ca. 155 K) of the matrix, spectrum b undergoes an irreversible change above 105 K to give a 7-line pattern with a coupling A(6H) of 21 G, as shown in spectrum c recorded at 115 K.<sup>21</sup> This

<sup>(20)</sup> The appearance of this <sup>13</sup>C doublet is dominated by the parallel components  $(A_z)$  of the hyperfine tensor (Table II). The perpendicular features are not resolved, possibly owing to a lack of axial symmetry  $(A_x \neq A_y)$  resulting in a more uniform intensity distribution for the absorption envelope. Additional support for this <sup>13</sup>C radical cation assignment comes from annealing studies, the irreversible decay of the broad doublet envelope (Figure 2c) between 95 and 110 K in the CFCl<sub>2</sub>CF<sub>2</sub>CI matrix exactly paralleling the decay characteristics of the triplet spectrum from the radical cation of the <sup>12</sup>C compound (vide supra). Another doublet spectrum  $(a(^{19}F) = 68 \text{ G})$  assigned to a matrix radical becomes well resolved in this system at 110–130 K.

<sup>(21)</sup> The tetramethyloxirane radical cation undergoes a second irreversible spectral change in the  $CFCl_2CF_2Cl$  matrix between 120 and 140 K, the outermost components in the septet spectrum of the localized species apparently disappearing while shoulder features emerge on lines 3 and 5 of the original septet pattern. The nature of this transformation or perturbation is not clear at this time.



**Figure 4.** First-derivative ESR spectra of the radicals derived from *trans*-1,2-dimethyloxirane (a) and trimethyloxirane (b) by  $\gamma$ -irradiation (dose, 0.5 Mrad) at 77 K of 1 mol % solutions in CFCl<sub>2</sub>CF<sub>2</sub>Cl and subsequent annealing to the indicated temperatures. The stick diagram is a reconstruction of the spectra by assuming a hyperfine pattern from an anisotropically broadened doublet of 1:3:3:1 quartets.

change in the ESR spectrum is accompanied by the simultaneous loss of the reddish-purple color<sup>3</sup> associated with the planar delocalized form of the radical cation. The structural change is therefore particularly well documented here since the septet ESR spectrum of the product radical can readily be assigned to a localized RCMe<sub>2</sub>· structure analogous to the RCH<sub>2</sub>· structure produced from oxirane in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix (vide supra).

Similar transformations yielding a localized radical center were observed for the radical cations of *trans*-1,2-dimethyloxirane and trimethyloxirane in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix. In each case the initial ESR pattern begins to decay at ca. 95 K and goes over rapidly to a different spectrum above 100 K. The spectra of the radicals that grow in are shown in Figure 4, and although there are line-shape differences, each of the two patterns consists of five broad lines, as expected for hyperfine interaction with one methyl group and one anisotropic  $\alpha$ -hydrogen. Thus, in the ultimate form of the trimethyloxirane radical cation in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix, the radical is localized at RCHMe-, that is, at the oxirane carbon atom with the least number of methyl group substituents.<sup>22</sup> The ESR parameters for these localized radical cations are collected in Table I.

#### Discussion

The present work reveals a striking matrix effect on the ultimate structure of the radical cations derived from oxirane and some of its methyl-substituted derivatives in Freon matrices. Thus, while the radical cations derived from oxirane<sup>1,2</sup> and tetramethyloxirane<sup>23</sup> in both the CFCl<sub>3</sub> and CF<sub>3</sub>CCl<sub>3</sub> matrices have been shown to possess the delocalized allylic structure 1, we now find that these



oxirane cations adopt localized radical structures in the  $CFCl_2$ - $CF_2CI$  matrix. Since the simplest way in which the structure of these cations can be modified is by twisting one of the  $-CR_2$  (R = H or Me) groups about the C-O bond in a C···C ring-opened structure, the orthogonal structure 2 is a suitable model for the localized radical species. However, there is also the possibility of a strong solvent or chloride ion interaction at the carbocation center (vide infra).

Before considering the structure of these localized species in more detail, let us examine the relatively uninteresting possibility that the localized species are formed by deprotonation reactions, such reactions being commonly observed in the CFCl<sub>2</sub>CF<sub>2</sub>CI matrix.<sup>16,24</sup> That deprotonation is not a general explanation for the results reported here is indicated, however, by the fact that a localized species is formed from oxirane itself, which has no  $\beta$ -proton available for elimination at a carbocation center.<sup>24b</sup> Moreover, only one localized radical species appears to be formed from trimethyloxirane, whereas two different species might have been expected had proton loss occurred randomly from the three methyl groups in the delocalized species (1, R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = Me).

The only plausible alternative to structure 2, therefore, is a species wherein the carbocation end of the radical cation is either complexed or combined with a nucleophile. In the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix, the two most reasonable possibilities are a solvent or chloride ion interaction at the carbocation center of 2 giving either a chloronium ion CFCl<sub>2</sub>CF<sub>2</sub>Cl<sup>+</sup>CR<sub>3</sub>R<sub>4</sub>OCR<sub>1</sub>R<sub>2</sub> or C-Cl covalent bond, as in ClCR<sub>3</sub>R<sub>4</sub>OCR<sub>1</sub>R<sub>2</sub>. While we did not observe halogen splittings for any of the localized species, halogen bonding at the  $\gamma$  carbon of a radical center is not easily detected by solid-state ESR spectroscopy, and hence these halogen-containing structures cannot be excluded on the basis of negative ESR results. A similar problem was addressed recently in connection with the localized ring-opened forms of the cyclopropane<sup>16</sup> and tetramethylcyclopropane<sup>17</sup> radical cations,<sup>25,26</sup> no evidence again being found for halogen hyperfine coupling.<sup>25b</sup>

It is undoubtedly significant that the radical center observed in the asymmetrically substituted oxiranes is localized at the oxirane carbon with the least number of methyl groups, the other possible radical center being undetectable. This is indeed the

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<sup>(22) 1,1-</sup>Dimethyloxirane provides an exception to this rule. Instead of a 1:2:1 triplet as expected on the basis of the results for other methyl-substituted oxiranes, the spectrum of the derived cation in CFCl<sub>2</sub>CF<sub>2</sub>Cl consists of a septet (A(6 H) = 22.7 G) of doublets (A(1 H) or A(1 F) = 16.0 G), this pattern being well resolved at 104 K before signal decay sets in at a slightly higher temperature. At lower temperatures, the spectrum is anisotropically broadened, an effect probably resulting from the hyperfine coupling to the unique hydrogen or fluorine nucleus. Two structural assignments seem possible. First, the radical could be localized at RCMe2. instead of RCH2. following C...C ring opening, but then it would also be necessary to postulate that the additional doublet hyperfine interaction occurs to a fluorine nucleus in the solvent, a combination which at first sight appears unlikely. An alternative assignment is to the 2,2-dimethyl-substituted vinyl alcohol cation, Me<sub>2</sub>C= CHOH+, but this would require both a C-O ring opening and a hydrogen migration from carbon to oxygen. Interestingly, thermochemical measure ments (J. L. Holmes, J. K. Terlouw, and F. P. Lossing, J. Phys. Chem., 80, 2860 (1976)) and ab initio calculations (W. J. Bouma, J. K. MacLeod, and L. Radom, J. Am. Chem. Soc., 101, 5540(1979)) concur that the parent vinyl alcohol cation is the lowest energy isomer of the 11 possible  $C_2H_4O^+$  isomers.

<sup>(23)</sup> Experimental support for the delocalized planar C···C ring-opened structure for the tetramethyloxirane radical cation comes from studies in the  $CCl_3CF_3$  and  $CCl_4$  matrices showing that the 13-line spectrum undergoes the alternating line-width effect expected for the interchange of methyl groups between exo and endo positions on the ESR time scale (L. D. Snow and F. Williams, unpublished results).

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<sup>(26)</sup> In contrast to the results for the oxirane cations, the localized ringopened cyclopropane radical cations are produced from the ring-closed species and the planar delocalized forms are not observed.<sup>16,17</sup>

expected result if the process of localization occurs by the simultaneous development of radical and carbocation centers since hyperconjugative stabilization by a methyl group is generally considered to be more efficient at a carbocation than at a radical center.<sup>27</sup> On the other hand, a mixture of radical centers might be expected to follow from chloride ion attack, given the less discriminate character of the products resulting from nucleophilic reactions with asymmetric allylic carbonium ions.<sup>28</sup>

There is also a correlation between the temperature needed for the formation of the localized species and the extent of methyl substitution at the radical end of the molecule. Thus, the localized forms of the radical cations from ethylene and propylene oxides with the RCH<sub>2</sub> radical center are already produced at 77 K while the radical cations from 1,2-dimethyloxirane and trimethyloxirane with the RCHMe- radical center are generated between 95 and 105 K. Also, the RCMe2 center of the localized tetramethyloxirane cation requires an even higher temperature (105-110 K) for its formation. As a corollary, the strikingly different results for propylene oxide and 1,2-dimethyloxirane are difficult to rationalize on the basis of halogen attack since the complexed or substituted carbocation end of the radical cation would be virtually identical for these two molecules.

The lack of supporting evidence for a halogen interaction from considerations of ESR hyperfine patterns,<sup>29</sup> localized radical structure, and annealing studies refocuses attention on the orthogonal structure 2. If this model is correct, then the  $CFCl_2CF_2Cl$ matrix must impose this twisted structure on the radical cation<sup>30</sup> because the planar delocalized structure, at least for the parent

oxirane radical cation, is observed in CFCl<sub>3</sub>, CF<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, and  $SF_{6}^{1,2}$  In this event, the lower symmetry of the  $CFCl_2CF_2Cl$ molecule could be an important or even a decisive factor.

#### **Concluding Remarks**

In contrast to the delocalized forms of the C…C ring-opened oxirane radical cations found in other Freon-type matrices,<sup>1,2</sup> there is a remarkable preference for the formation of localized forms in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix, these species being produced irreversibly by irradiation at 77 K or on subsequent annealing to 110 K. The radical center in these species is always localized at the oxirane carbon with the least number of substituted methyl groups; increasing methyl substitution at this carbon raises the temperature needed for the formation of the localized radical cation.

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## Structures and Reactions of C<sub>2</sub>H<sub>4</sub> Adsorbed on Small Pt Clusters

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The authors have used NMR to determine the structure of  $C_2H_4$  adsorbed at room temperature on small Pt clusters supported on alumina. They observe an ethylidyne species (C-CH<sub>3</sub>), with a C-C bond length of  $1.49 \pm 0.02$  Å. The CH<sub>3</sub> groups rotate freely about the C-C direction at 77 K. Up to 390 K, the C-C bond length remains the same, suggesting the same surface species. C-C bond scission takes place above 390 K, and is complete at about 480 K, forming predominantly single carbon atoms with no hydrogen attached and a small amount of CH<sub>3</sub> species, in contrast with CH or CH<sub>2</sub> species proposed to form on Pt(111) surfaces.

Structures and reactions of simple molecules adsorbed on metal surfaces are of great importance in studying catalysis. There have been extensive studies of adsorption of simple molecules, such as  $C_2H_2$  and  $C_2H_4$ , on single crystal surfaces. The extent to which industrial catalysts containing small metal clusters of 10 to 100 Å in diameter may be thought of as composed of single crystal surfaces is not well-known. One might question whether the structure and reaction of adsorbed molecules on small metal

particles will be different from that on single crystal surfaces. In this Letter we report NMR studies of the molecular structure, of C-C bond rupture, and of the nature of the postrupture products of ethylene  $(C_2H_4)$  on Pt catalysts. We compare the results with single crystal studies.

The species formed from ethylene adsorbed at room temperature on Pt(111) surfaces have been of great interest. From earlier single crystal studies three species were proposed: CH-CH<sub>3</sub>,<sup>1</sup>CH-CH<sub>2</sub>,<sup>2</sup>

<sup>(27)</sup> A. G. Evans, Discuss. Faraday Soc., 10, 109 (1951).

<sup>(28)</sup> R. H. DeWolfe and W. G. Young, Chem. Rev., 56, 753 (1956).
(29) It is perhaps revealing that although the delocalized form of the ethylene oxide radical cation shows weak halogen hyperfine interactions in other matrices  $(CFCl_3, CF_3CCl_3)$ ,<sup>1,2</sup> the localized form is not produced in these cases, even on annealing to the softening point of the matrix. This suggests that the dominant factor in bringing about the transformation is a more specific interaction of the radical cation with the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix that stabilizes the localized form.

<sup>(30)</sup> A referee has invited us to comment on the direction of the temperature dependence of the structure observed in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix, asking why is there a change from a delocalized to a localized structure as the temperature is increased? First, one must say that the explanation would be trivial if chlorine attack were responsible for the transformation since either the release of chloride ion from the matrix radical anion or the formation of a chloronium ion could be expected to occur irreversibly at higher temperature. However, the correlations discussed in the text appear to offer little independent support for a mechanism based on chlorine intervention. Now, the question is, of course, much more interesting if the localized radical cations do indeed have orthogonal structures. If we assume this to be the case, the delocalized form of the tetramethyloxirane radical cation originally present in the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix below 105 K represents only a local energy minimum since it is converted irreversibly into the localized form above this temperature. This change is not observed in other matrices (CFCl<sub>3</sub>, CF<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, SF<sub>6</sub>) and recent high-level theoretical calculations<sup>11-13</sup> affirm that the planar delocalized form of the oxirane radical cation is more stable than the twisted form, although the estimates for the energy difference  $(1.9^{11} \text{ and } 6.7^{12} \text{ kcal mol}^{-1})$  are relatively small. We therefore surmise that the CFCl<sub>2</sub>CF<sub>2</sub>Cl matrix interaction inverts the ordering of the energy levels for these two structures, allowing the delocalized form of the cation to adjust to the more stable localized form on relaxation in this particular matrix