Structure and Reactions of Radicals
Derived from Cyclopentane, Cyclopentenes, and Cyclohexenes
in Low-Temperature Matrices. An ESR Study

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Z. Naturforsch. 46a, 993–1000 (1991); received August 14, 1991

The radical species derived from cyclopentane, cyclopentenes and cyclohexenes by 60Co γ-ray irradiation at 77 K in halocarbon matrices have been studied by ESR spectroscopy. The electronic and geometrical structures of the radical species are discussed on the basis of the experimental hyperfine coupling constants and semiempirical MO calculations. Exposure of the tetramethylsilane frozen solution containing cyclopentene to 60Co γ-rays produced specifically 3-cyclopenten-1-yl.

1. Introduction

Since the electron beam radiolysis study of neat cyclopentene by Fessenden et al. [1, 2], ESR studies on cyclopentene and cyclhexene radical cations in halocarbon matrices have been made by several investigations. Shida et al. reported on the structure and reaction of the cyclopentene radical cation in CC13F matrix [3]. Lund et al. studied the cyclopentene radical cation in CC13CF3 [4], finding a concentration-dependent reaction [4]. According to these studies [3, 4], the hyperfine coupling (hfc) constants of the two axial and two equatorial β-protons in the cyclopentene radical cation are dependent on the temperature, in contrast to those in the cyclohexene radical cation, and the cyclohexene radical cation is nonplanar in CC13F and CC13CF3 at low temperatures.

In the present paper, we report the electronic and geometrical structures and reactions of the radical species derived from cyclopentene and cyclhexene derivatives in low-temperature matrices. Exposure of the cyclopentene and cyclhexene derivatives to 60Co γ-rays in solid matrices resulted in interesting reactions. The geometries optimized by use of the single-point UHF-AM1 method under the constraint of specified symmetries G and the accompanying total energies will be referred to as the AM1-G geometries and energies, respectively. The geometries optimized by use of the Gaussian 88 program in UHF mode at the 4-31G level will be referred to as the G88 geometries. The hfc constants calculated for the AM1-G geometries by use of the UHF-INDO method will be referred to as the INDO-AM1-G hfc constants, while those calculated for the G88 geometries of selected species derived from cyclopentane, cyclopentenes and cyclhexenes by 60Co γ-rays in solid matrices resulted in interesting reactions. The geometries optimized by use of the single-point UHF-AM1 method under the constraint of specified symmetries G and the accompanying total energies will be referred to as the AM1-G geometries and energies, respectively. The geometries optimized by use of the Gaussian 88 program in UHF mode at the 4-31G level will be referred to as the G88 geometries.
Gaussian peak-to-peak line widths $\Delta H = 8.0 \text{ G (b) and 3.0 G (d).}$ The asterisks refer to the signals of the TMS radical and damaged cell.

Table 1. Theoretical ESR parameters.

<table>
<thead>
<tr>
<th>Radical species</th>
<th>Proton hfc constants/G $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentyl$^+$</td>
<td></td>
</tr>
<tr>
<td>(A) $C_2$ geometry ($\varphi = 25^\circ$)</td>
<td>-17.3 (z) 56.6 ($\beta$, ax) 29.5 ($\beta$, eq)</td>
</tr>
<tr>
<td>(B) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-53.3 (z) 45.9 ($\beta$, ax) 26.5 ($\beta$, eq)</td>
</tr>
<tr>
<td>3-Cyclopenten-1-yl$^-$</td>
<td></td>
</tr>
<tr>
<td>(A) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-17.7 (z) 50.3 ($\beta$, ax) 24.8 ($\beta$, eq)</td>
</tr>
<tr>
<td>(B) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-54.2 (z) 41.8 ($\beta$, ax) 24.3 ($\beta$, eq)</td>
</tr>
<tr>
<td>Cyclohexene$^-$</td>
<td></td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-7.0 (z) 53.5 ($\beta$, ax) 42.5 ($\beta$, eq)</td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>16.1 (y, ax) 6.5 (y, eq)</td>
</tr>
<tr>
<td>1-Methyl-1-cyclopentene$^+$</td>
<td></td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-8.6 (z) 50.5 ($\beta$, ax) 40.0 ($\beta$, eq)</td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>37.4 ($\beta_2$, ax) 29.9 ($\beta_2$, eq)</td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>8.7 (y, ax) 2.5 (y, eq) 14.0 (CH$_3$)</td>
</tr>
<tr>
<td>Cyclohexene$^+$</td>
<td></td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-5.1 (z) 55.4 ($\beta$, ax) 24.6 ($\beta$, eq)</td>
</tr>
<tr>
<td>1-Methyl-1-cyclohexene$^+$</td>
<td></td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>-8.7 (z) 52.8 ($\beta_3$, ax) 25.3 ($\beta_3$, eq)</td>
</tr>
<tr>
<td>(C) $C_2$ geometry ($\varphi = 30^\circ$)</td>
<td>36.9 ($\beta_6$, ax) 15.2 ($\beta_6$, eq) 15.7 (CH$_3$)</td>
</tr>
</tbody>
</table>

$^a$ 1 G = 0.1 mT. (A): INDO-AM1; (B): ab initio; (C) INDO. The protons are specified in parentheses. See the theoretical section and relevant inserts.

$^b$ The stated symmetry does not refer to the substituent.

dihedral or distortion angles, as the case may be, by use of the GSCF3 program in UHF mode at the 4-31G level will be referred to simply as the ab initio hfc constants. The hfc constants and total energies calculated by use of the UHF-INDO method for assumed, unoptimized geometries of symmetries G will be refered to as the INDO-G hfc constants and energies, respectively. Table 1 and the pertinent figures collect the hfc constants and total energies thus calculated. For comparison, Table 1 also lists the data for the cyclopentene and cyclohexene radical cations which were not studied experimentally in this work.

4. Results and Discussion

4.1. Cyclopentyl

Figure 1a shows the ESR spectrum of the radical species derived from cyclopentane in TMS at 77 K, which is the same as that of cyclopentyl in CCl$_2$FCClF$_2$ at 100 K, converted by deprotonation from the cyclopentane radical cation [10]; the radical species derived from cyclopentane in CCl$_2$FCClF$_2$ at 77 K is the
cyclopentane radical cation [10]. Figure 1b shows the spectrum simulated well with the hfc constants of cyclopentyl determined by Lund et al. [10] for α-protons, axial and equatorial β-protons, $a^{H\alpha}(1\,H) = 21.4\,G$ ($1\,G = 0.1\,mT$), $a^{H\alpha}(ax)(2\,H) = 46.9\,G$ and $a^{H\alpha}(eq)(2\,H) = 24.4\,G$. Thus, it is concluded that $^{60}$Co γ-ray irradiation of cyclopentane in TMS at 77 K gives rise to cyclopentyl. The cyclopentyl generated by electron beam radiolysis of neat cyclopentane gives the hfc constants of $a^{H\alpha}(1\,H) = 21.48\,G$ and $a^{H\alpha}(4\,H) = 35.16\,G$, the hfc constants for β-protons being dynamically averaged [1, 2].

Since we observed the triplet spectrum ascribable to $(\text{CH}_3)_4\text{SiCH}_2$ [11, 12], we propose the following reaction scheme for the formation of cyclopentyl in TMS:

$$\begin{align*}
(\text{CH}_3)_4\text{Si} + \gamma &\rightarrow (\text{CH}_3)_4\text{Si}^+ + e^{-}, \\
(\text{CH}_3)_4\text{Si}^+ + (\text{CH}_3)_3\text{Si} &\rightarrow (\text{CH}_3)_4\text{Si}^+H + (\text{CH}_3)_3\text{SiCH}_2,
\end{align*}$$

$$(\text{CH}_3)_3\text{SiCH}_2 + \text{SH} \rightarrow \text{S}^+ + (\text{CH}_3)_4\text{Si},$$
$$e^- + (\text{CH}_3)_4\text{Si}^+H \rightarrow (\text{CH}_3)_4\text{Si} + H^-,$$

where γ stands for γ-ray and SH is the solute.

Another possible reaction scheme is that the radical cation, $(\text{CH}_3)_4\text{Si}^+$, directly abstracts a proton from SH to yield S$^\cdot$.

The observation of the two distinct hfc constants for the four β-protons, $a^{H\beta}(ax)$ and $a^{H\beta}(eq)$, shows that the radical is rigid in TMS matrix at 77 K. This is also contrast to the case of the cyclopentane radical cation in CCl$_3$CF$_3$ matrix at 77 K, in which the carbon-ring inversion averages the hfc constants of the four protons on the carbon atoms C$_2$ and C$_5$ [13], where the carbon-carbon bonds C$_1$–C$_2$ and C$_1$–C$_5$ are elongated.

Figure 2a shows the INDO-AM1-Cs hfc constants for β-protons and AM1-Cs energy, as functions of the dihedral angle φ between the planes of the carbon atoms, C$_2$–C$_1$–C$_4$ and C$_2$–C$_3$–C$_4$–C$_5$; these hfc constants do not reproduce the experimental in magni-

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**Fig. 2.** The dihedral angle dependence of the INDO-AM1-Cs hfc constants (hfcc) for β-protons and AM1-Cs energy (a), and the distortion angle dependence of the INDO-AM1-C$_2$ hfc constants for the same protons and AM1-C$_2$ energy (b) of cyclopentyl. See also the theoretical section and the first and second inserts.
Fig. 3. The dihedral angle dependence of the INDO-AM1-C≤ hfc constants (hfcc) for β-protons and AM1-C≤ energy (a) and the distortion angle dependence of the INDO-AM1-C≤ hfc constants for the same protons and AM1-C≤ energy (b) of 3-cyclopenten-1-yl. See also the theoretical section and the third and fourth inserts.

According to Lund et al., cyclopentyl is likely to take C≤ symmetry rather than Cs [10].

The listed ab initio hfc constants also reproduce the experimental ones, except for the overestimated absolute value of $a^Hα$ as in the case of the methyl radical [14], indicating that cyclopentyl takes C≤ symmetry. According to Lund et al., cyclopentyl is likely to take C≤ symmetry rather than Cs [10].
4.2. 3-Cyclopenten-1-yl

Figure 1c shows the ESR spectrum of the radical species generated from cyclopentene in TMS at 77 K, which differs from that of the cyclopentene radical cation. According to Fessenden et al., cyclopentyl is formed from cyclopentene by addition of a hydrogen atom to α-position and cyclopentyl by hydrogen-atom elimination from β-position [1, 2]. However, the spectrum of Fig. 1c cannot be attributed to any of these radical species. It can be assigned to the 3-cyclopenten-1-yl interpreted to be formed by hydrogen atom elimination from γ-position; as Fig. 1d shows, the spectrum is simulated well with the hfc constants assumed for 3-cyclopenten-1-yl, \( a^{H1}(1H) = 20.7 \) G, \( a^{H2}(2H) = 46.3 \) G and \( a^{H5}(eq)(2H) = 24.7 \) G. The γ-proton hfc constants cannot be identified, as is seen from Fig. 1c and Table 1. The similarity of these experimental hfc constants to those of cyclopentyl supports the specific formation of 3-cyclopenten-1-yl in TMS by \(^{60}\)Co γ-ray irradiation, for which the mechanism will be investigated further in a forthcoming paper.

Figure 3a shows the INDO-AM1-C\(_5\) hfc constants for β-protons and AM1-C\(_5\) energy of 3-cyclopenten-1-yl, as functions of the dihedral angle \( \phi \); these hfc constants do not reproduce the experimental, similarly to the case of cyclopentyl. Figure 3b shows the INDO-AM1-C\(_2\) hfc constants for β-protons and AM1-C\(_2\) energy, as functions of the distortion angle \( \phi' \); these hfc constants agree well with the observed at around \( \phi' = 30^\circ \), although the total energy is not exactly minimal. Thus, Table 1 lists the theoretical hfc constants calculated for the C\(_2\) geometries of \( \phi' = 30^\circ \). The ab initio \( a^{H1} \) is larger in absolute value than the experimental, as in the preceding case of cyclopentyl. As for β-protons, the ab initio hfc constants also well reproduce the experimental. Thus, 3-cyclopenten-1-yl takes C\(_2\) symmetry, similarly to the case of cyclopentyl.

4.3. Cyclopentenyl

Figure 4a shows the ESR spectrum observed at 97 K of the radical species derived from cyclopentene in CCl\(_2\)FCCIF\(_2\). It differs from those of the cyclopentene radical cation in CCl\(_3\)F and CCl\(_3\)CF\(_3\) reported previously [3, 4], while it is the same as that observed at 155 K of the allylic radical in CCl\(_3\)F formed through cation-parent molecule reaction [3], and is also the same as that of cyclopentenyl [1, 2].

Figure 4b shows the spectrum simulated well with \( a^{H1, 2, 3, 4}(4H) = 23.4 \) G, \( a^{H5, 7}(2H) = 14.4 \) G and \( a^{H6}(1H) = 3.1 \) G. These hfc constants are similar to those of cyclopentenyl in CCl\(_3\)F [3], but a little different from those in neat cyclopentene, \( a^{H1, 2, 3, 4}(4H) = 19.75 \) G, \( a^{H5, 7}(2H) = 15.50 \) G and \( a^{H6}(1H) = 2.76 \) G [1, 2]. The discrepancies may be due to the difference in matrix.
Fig. 4. ESR spectra of cyclopentenyl observed in CCl$_2$FCCIF$_2$ at 97 K (a) and simulated (b). The simulation is as in Fig. 1, except for the width $\Delta H = 1.5$ G.

The INDO-AM1-C$_2$ hfc constants listed in Table 1 well reproduce the experimental, confirming the formation of cyclopentenyl.

In CCl$_2$FCCIF$_2$, the allylic radical is formed even at 77 K.

4.4. 1-Methyl-1-cyclopentene Radical Cation

Figure 5a shows the ESR spectrum of 1-methyl-1-cyclopentene radical cation in CCl$_3$CF$_3$ observed at 133 K. Figure 5b shows the spectrum simulated well with $a^H_{\alpha}(1\,H) = 11.8$ G, $a^C_{\alpha H}(3\,H) = 17.7$ G, $a^{H\beta}(2\,H) = 48.4$ G of $\beta$-protons nonadjacent to the methyl group, $a^{H\gamma}(2\,H) = 36.0$ G of $\beta$-protons adjacent to the methyl group, and $a^{H\beta}(2\,H) = 3.6$ G. The methyl group rotates freely as indicated by the methyl-proton isotropic four lines. The electronic structure is affected remarkably by the methyl group, as $a^{H\beta}$ is considerably different from $a^{H\gamma}$. The 1-methyl-1-cyclopentene radical cation exerts a rapid puckering motion at 133 K in the same manner as the cyclopentene radical cation, since the above values of $\beta$- and $\gamma$-protons are the averaged ones.

Table 1 collects the INDO-C$_s$ hfc constants of the cyclopentene and 1-methyl-1-cyclopentene radical cations calculated with the carbon skeleton of cyclopentene with C$_s$-symmetry [15] and the dihedral angle $\phi = 10^\circ$ of the cyclopentene radical cation [3]; these hfc constants are in good agreement with the observed, particularly those for $\beta$-protons nonadjacent to the methyl group being larger than those for $\beta$-protons adjacent. The 1-methyl-1-cyclopentene radical cation is concluded to take $\phi \geq 10^\circ$, showing little effect of the methyl group on the molecular structure.
4.5. 1-Methyl-1-cyclohexene Radical Cation

Figure 6a shows the ESR spectrum of the 1-methyl-1-cyclohexene radical cation in CC\textsubscript{13}CF\textsubscript{3} observed at 133 K. Figure 6b shows the spectrum simulated well with \( a^H_{\alpha}(1H) = 11.6 \text{ G}, \ a^H_{\beta}(3H) = 17.9 \text{ G}, \ a^H_{\beta\beta}(ax)(1H) = 38.7 \text{ G} \) and \( a^H_{\beta\beta}(eq)(1H) = 30.4 \text{ G} \) of axial and equatorial \( \beta \)-protons nonadjacent to the methyl group, and \( a^H_{\beta\beta}(ax)(1H) = 36.2 \text{ G} \) and \( a^H_{\beta\beta}(eq)(1H) = 24.5 \text{ G} \) of axial and equatorial \( \beta \)-protons adjacent to the methyl group. The hfc constants of the axial and equatorial \( \beta \)-protons are distinct in the 1-methyl-1-cyclohexene radical cation as in the cyclohexene radical cation [3, 4], indicating that the cyclohexene and 1-methyl-1-cyclohexene radical cations are rigid in structure even at 133 K. The methyl group rotation is free similarly to the case of the 1-methyl-1-cyclopentene radical cation. The hfc constants for \( \beta \)-protons nonadjacent to the methyl group are fairly larger than those for the other \( \beta \)-protons.

Figures 7a and b show the INDO-C\textsubscript{2} hfc constants of \( \beta \)-protons and INDO-C\textsubscript{2} energies of the cyclohexene and 1-methyl-1-cyclohexene radical cations, respectively, as functions of the distortion angle \( \phi' \) defined below, calculated by use of the half-chair carbon skeleton of cyclohexene with C\textsubscript{2}-symmetry [16].

The total energy is minimal at around \( \phi' = 30^\circ \), either for the cyclohexene or for the 1-methyl-1-cyclohexene radical cation. When \( \phi' = 25^\circ - 30^\circ \), the INDO-C\textsubscript{2} hfc constants of the cyclohexene radical cation are in
The distortion angle dependences of the INDO-C\textsubscript{2} hfc constants (hfcc) for \(\beta\)-protons and INDO-C\textsubscript{2} energies of the cyclohexene radical cation (a), and 1-methyl-1-cyclohexene radical cation (b). See the theoretical section and the seventh and eighth inserts.

Fig. 7. The distortion angle dependences of the INDO-C\textsubscript{2} hfc constants (hfcc) for \(\beta\)-protons and INDO-C\textsubscript{2} energies of the cyclohexene radical cation (a), and 1-methyl-1-cyclohexene radical cation (b). See the theoretical section and the seventh and eighth inserts.

Table 1 collects the INDO-C\textsubscript{2} hfc constants for the cyclohexene and 1-methyl-1-cyclohexene radical cations with \(\phi' = 30^\circ\), which are in good agreement with the observed for the former cation, but are in qualitative agreement for the latter. The observed hfc constants of \(\beta\)-protons nonadjacent to the methyl group are larger than those of the other \(\beta\)-protons, as the theory also predicts, reflecting the electron-donating nature of the methyl group.

The authors wish to thank Messrs. Hiroki Ujita and Tatsuya Miyamoto for their helpful assistance. All MO calculations were carried out on a Facom M-780/20 system at the Computer Center of Kyushu University.