## ESR Study of Radical Cations from $\gamma$ -Irradiation of Bicyclo[3.1.0]hex-2-ene in Freon Matrices

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Key Words: Radical Cations; ESR Spectroscopy; Rearrangement; y-Radiolysis

**Abstract:** Bicyclo[3.1.0]hex-2-ene radical cation, generated by  $\gamma$ -irradiation of the parent compound in freon matrices at 77 K, undergoes ring opening to the 1,3-cyclohexadiene radical cation. In CF<sub>2</sub>CICFCI<sub>2</sub> matrix both radical cations also undergo deprotonation to the corresponding neutral radicals.

Radical cations of polycyclic hydrocarbons have attracted considerable attention in recent years because of their unique spectroscopic and chemical properties, in particular with respect to strain energies and rearrangemental behavior. Pursuing the investigation in this field<sup>1)</sup> we here report on the  $\gamma$ -radiolytic generation and characterization, by ESR spectroscopy, of the radical cations derived from the strained hydrocarbon bicyclo[3.1.0]hex-2-ene (1) in freon matrices<sup>2,3</sup>. Although the radical cation 2 of the parent compound 1 only could be tentatively identified by its ESR spectrum, indirect evidence has been obtained regarding its radiolytic generation at 77 K.

The ESR spectrum obtained after  $\gamma$ -irradiation of 1 in CFCI<sub>3</sub> matrix at 77 K was identified as due to the 1,3-cyclohexadiene radical cation (3)<sup>4</sup> (Fig. 1). This result strongly suggests that the primary radical cation (2) is unstable at 77 K and undergoes a facile electrocyclic ring opening followed by a 1,4-hydrogen shift. Such a rearrangement is expected to take place in a disrotatory mode and to be facilitated by electron delocalization as well as release of ring strain.





**Figure 1.** (A) ESR spectrum recorded at 153 K after  $\gamma$ -irradiation of 1 in CFCl<sub>3</sub> matrix at 77 K. (B) Computer simulation based on the hfs of the 1,3-cyclohexadiene radical cation (3)<sup>4</sup>): a(H-1,4) = 8 (2H), a(H-2,3) = 4 (2H), a(H-5,6) = 30 (2H) G.

The  $\gamma$ -irradiation of 1 in CF<sub>2</sub>CICFCl<sub>2</sub> matrix at 77 K yielded a complex, poorly resolved ESR spectrum (Fig. 2 A), where two major components can be recognized: a doublet feature of about 40 G line distance and a weak quintet structure of about 30 G hyperfine splitting (hfs). On prolonged storing at 77 K the "doublet" slowly disappeared, accompanied by the increase of the intensity of the quintet pattern (Fig. 2 B). The latter signal displays the characteristics of the 1,3-cyclohexadiene radical cation (3) with a linewidth somewhat broader than that observed in CFCl<sub>3</sub> matrix. On further warming, the spectrum acquires resolution and could be analyzed via computer simulation as arising from a superposition of the (neutral) cyclohexadienyl radical (4) and the bicyclo[3.1.0]hex-2-en-4-yl radical (5). These results can be rationalized in terms of the following sequence:  $\gamma$ -irradiation generates the radical cation 2 which at 77 K slowly decomposes both by ring opening to 3 and by deprotonation to the neutral radical 5.

Above 77 K 3 also undergoes deprotonation to give the cyclohexadienyl radical (4). The possibility that 4 is formed by ring opening of 5 can be disregarded with respect to the applied conditions, for this reaction could only be observed to occur with a sufficient rate in adamantane matrix at temperatures above 210 K<sup>5</sup>). Thus, the ring opening of 2 is associated with a somewhat lower activation barrier than the (symmetry-forbidden) opening of the corresponding neutral radical 5 ( $\Delta G^{\dagger} = 14.5$  kcal mol<sup>-1</sup>)<sup>5</sup>).



- Figure 2. (A) ESR spectrum recorded at 77 K after  $\gamma$ -irradiation of 1 in CF<sub>2</sub>ClCFCl<sub>2</sub> matrix.
  - (B) Spectrum from A after prolonged storing at 77 K.
  - (C) Spectrum from B after annealing at 130 K.
  - (D) Simulation of spectrum C as a 1:1 superposition of 4 and 5 using the hfs parameters as given in ref.<sup>5)</sup>.

The above results clearly demonstrate that the stability and chemical behaviour of radical cations 2 and 3, respectively, is strongly influenced by the nature of the matrix. Similar matrix effects have been reported before<sup>6</sup>, however, a convincing explanation of this phenomenon has not been yet given.

The structural and ESR properties of the bicyclo[3.1.0]hex-2-ene radical cation (2) were also explored by MNDO and INDO calculations (Table 1). The molecular geometry is predicted to be similar to that of the parent compound 1 except for a significant lengthening of the C-2-C-3 bond from 134 to 145 pm and of the C-1-C-5 bond from 152 to 160 pm. The latter change can be related to the observed ease of ring opening, since it reflects a weakening of the bond to be broken first in the rearrangement.

bond lengths [pm]	bond angles (°)	dihedral angles [°]
C1-C2 145	C5-C1-C2 105.8	C1-C2-C3-C5 -0.8
C2-C3 143	C1-C2-C3 110.5	C1-C5-C3-C4 179.6
C3-C4 151	C2-C3-C4 112.9	C2-C1-C5-C6 -116.3
C4-C5 154	C4-C5-C1 103.5	H1-C1-C5-H5 -9.9
C5-C1 160	C1-C6-C5 62.7	H1-C1-C5-C6 99.5
C6-C1 158	H4-C4-H4' 106.4	H5-C5-C1-C6 -109.4
C6-C5 150	H6-C6-H6' 111.6	H2-C2-C3-H3 -4.6

Table 1. Selected MINDU parameters of the Dicyclo[3.1.0]nex-2-ene radical cation	icyclo[3.1.0]hex-2-ene radical cation	bicyclo	of the	parameters	MNDO	Selected	1.	ible	T
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The optimized MNDO geometry was used as input for the INDO calculation to afford the following hfs: a(H-1) = 0.94, a(H-2) = -0.05, a(H-3) = 9.6,  $a(H-4_{eyn}) = 14.9$ ,  $a(H-4_{anti}) = 35.9$ , a(H-5) = 12,  $a(H-6_{eyn}) = 3.8$ ,  $a(H-6_{anti}) = 0.69$  G. Interestingly, a different magnetic interaction is predicted for the two hydrogen atoms at C-4. This implies that under conditions of poor resolution the ESR spectrum of the radical cation 2 may appear as a doublet, which indeed agrees with the experimental observation (Fig. 2A). According to the MNDO calculations the SOMO of radical cation 2 is delocalized over the entire molecule with the major contribution (ca. 65%) coming from the p-orbitals at C-2 and C-3. Such an electronic structure accounts for the large hfs of the hydrogens at C-4. However, their magnetic inequivalence cannot be explained in terms of different orientations of the two C-4-H bonds with respect to the singly-occupied orbital since the cyclopentene ring appears to be essentially planar. The ineqivalence more likely results from a through-space interaction of the *endo*-oriented hydrogen atom at C-6 of the cyclopropyl ring with the SOMO.

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(Received in UK 20 January 1992)