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Isomerization of 4-Vinylcyclohexene Radical Cation: A Tandem Mass Spectrometry Study

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Isomerizations are often invoked to rationalize complex decomposition pathways in which no direct mechanism is apparent. This is particularly true for dissociation of unsaturated hydrocarbon radical cations that may exist in isomeric forms, the relative importance of which depends on the structure of the precursor, the barrier for isomerization, and internal energy.[1] Detailed investigations of the isomerization of hydrocarbon radical cations, however, are challenging, and the results are often not entirely convincing.

The potential energy surface of the C_8H_{12} radical cation has been investigated by mass spectrometry,[2] theoretical calculations,[3] and ESR.[4] The reaction of 1,3-butadiene radical cation with 1,3-butadiene neutral, which was studied by using high-pressure chemical ionization[2] and *ab initio* calculations,[3] proceeds through an acyclic intermediate to form the 4-vinylcyclohexene ion, **1**. Investigation by matrix-isolation ESR has shown that **1** surprisingly undergoes isomerization to the bicyclo[3.2.1]oct-2-ene ion, **3**[4] (Scheme 1).

Here we demonstrate the occurrence of this isomerization in the gas phase by use of tandem (MS/MS) sector[5] and Fourier transform (FT) mass spectrometries. The sector instrument utilized conventional MS/MS techniques for isomer differentiation.[6] The FT mass spectrometer, however, incorporated a new methodology, recently demonstrated in our laboratory,[7] that allows for switching between the Penning trapping mode,[8] which typically operates at low pressure ($<10^{-6}$ Torr; 1 Torr = 133.3 Pa), and the Paul trapping mode,[9] which is called the rf-only-mode event and is well-suited for high pressure ($\sim 10^{-3}$ Torr). This methodology constitutes a powerful new approach for the study of gas-phase ion chemistry.

The radical cations of 4-vinylcyclohexene (IE = 8.93 eV)[10] or bicyclo[3.2.1]oct-2-ene (approximately 14 kcal/mol more stable than that of 4-vinylcyclohexene[4]) were formed, in separate trials, in a chemical ionization (CI) source by electron ionization (EI). The radical cations were then studied by obtaining their collisionally activated decomposition (CAD) spectra. The CAD spectra are similar,[11] indicating that the isomerization has occurred.

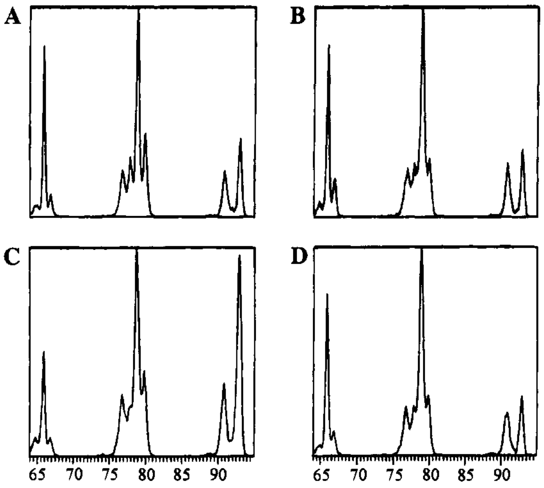
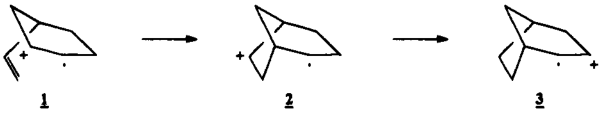


Figure 1. CAD spectra of the 4-vinylcyclohexene radical cation, **1**, without (A) and with (C) CS_2 addition, and of the bicyclo[3.2.1]-2-octene radical cation, **3**, without (B) and with (D) CS_2 addition. The data were taken with the tandem sector mass spectrometer.

Scheme 1



The C_8H_{12} radical cations were then ionized in the presence of a CS_2 bath gas (~300 mTorr). The CAD spectra for the two isomers are distinctive; the abundance ratio of the *m/z* 93 to the *m/z* 66 ions is particularly informative. For **1**, the abundance ratio changes from 0.5 (13.7/27.0)[12] with no bath gas (see Figure 1A) to 1.8 (27.8/15.4) with CS_2 addition (see Figure 1C), whereas the abundance ratio for **3** remains constant at 0.4 (10.5/28.5, without CS_2; 9.7/27.5, with CS_2) (see Figure 1B,D). The CS_2 acts as a low-energy charge-exchange reagent (IE of CS_2 = 10.06 eV)[10] and as a collisional stabilization gas to produce a narrow distribution of low-energy ions compared to those formed by EI.[13]

To study the isomerization further, an FT mass spectrometer operating in the two trapping modes mentioned above was utilized to form, via collisional stabilization in the rf-only-mode event, low-energy ions as well as to select and store ions for extended periods of time. In separate experiments, the C_8H_{12} ions were produced from their respective neutrals by charge exchange with preformed toluene radical cations for a period of 10 s. During this time, the rf-only-mode event, accompanied by a high-pressure ($\sim 5 \times 10^{-4}$ Torr) pulse of helium, was implemented to provide collisional stabilization of the radical cations. The C_8H_{12} radical cations were isolated by ejection of all other ions, and excited via their cyclotron mode[14] to collide with residual helium, and the resulting products were analyzed.

The two C_8H_{12} radical cations fragment similarly as those in the sector mass spectrometer. Again, the ratio of abundances for ions of *m/z* 93 to *m/z* 66 is the distinguishing feature. For **1**, the abundance ratio is 2.0 (14.0/7.0)[11] whereas **3** undergoes

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(11) The CAD spectra of 4-vinylcyclohexene agree with those reported in ref 2 and rule out interconversion of the 4-vinylcyclohexene with 13 other C_8H_{12} isomers.

(12) The normalized peak heights are given in parentheses so that the composition of isomeric structures of the ions can be calculated according to Bass and Bowers: Bass, L. M.; Bowers, M. T. *Org. Mass Spectrom.* **1982**, *17*, 229. Differences in the peak ratios are used for the qualitative arguments made here.

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(14) Ion excitation at an amplitude less than that used for ejection was used to increase the internal energy of the ions in the cyclotron motion by a radio-frequency burst. For a review of ion manipulation of FTMS, see: Jacoby, C. B.; Holliman, C. L.; Gross, M. L. *Mass Spectrometry in the Biological Sciences: A Tutorial;* Gross, M. L., Ed.; Kluwer Academic Publishers: Dordrecht, 1993; p 93.

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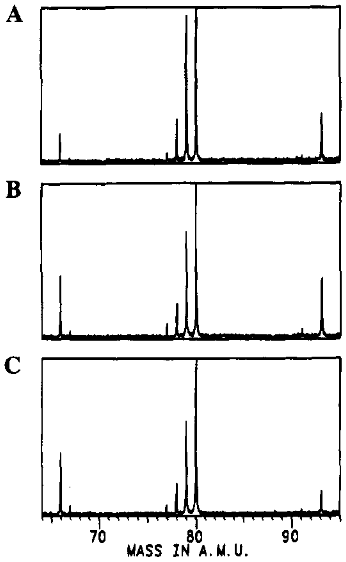


Figure 2. CAD spectra of 4-vinylcyclohexene radical cations at low (A), at mid (B), and at high excitation (C). The degree of ion excitation is directly proportional to the amount of internal energy added to the ions. The data were taken with the FT mass spectrometer.

fragmentation to produce a ratio of 0.1 (2.0/25.0). The difference is largely determined by the ability of **1** to undergo loss of $^{\bullet}CH_3$ more readily than **3**, and by the ability of **3** to lose C_3H_6 more readily than **1**. These differences are indicative of a more homogeneous population of C_8H_{12} ions owing to the greater number of and the less energetic collisions occurring in the FT compared to those in the sector mass spectrometer.[15] The differences can also be attributed to the lower excitation energy, which cannot be measured accurately, for the FT mass spectrometer.

The mechanism for "cooling" the 4-vinylcyclohexene ion during the rf-only-mode event is not yet well understood. In particular, there are two factors that affect whether the CAD spectrum of **1** is observed when generated from its neutral precursor. First, the equilibrium pressure of the helium during the rf-only-mode event must be below 1×10^{-3} Torr. Normally, the momentum-loss collisions during the high-pressure pulse serve to reduce internal energy and to compensate for any heating effects due to the rf field. At higher He pressures ($>1 \times 10^{-3}$ Torr), however, the cooling collisions are less efficient and scattering losses take place,[16] indicating that higher energy collisions are occurring. Second, the number of ions present during, but not necessarily after,[17] the rf-only-mode event must be high (~1 000 000). In this case, high ion numbers produce space-charge effects and may shift the Mathieu stability parameters,[18] which govern ion motion in an electric field. These position shifts are known to affect the ion temperature in the Paul ion trap[14] and possibly in the FT mass spectrometer during the rf-only-mode event. Further investigations are required to determine whether low He pressure and high ion number are essential to produce "cooler" ions.

An experiment was then designed to examine the possibility of promoting, in a controlled way, the isomerization of **1** to **3**,

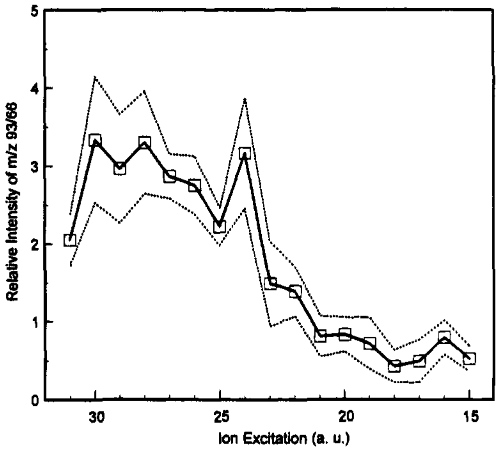
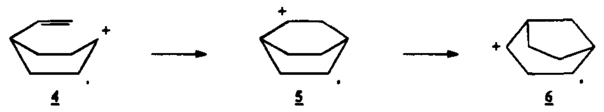


Figure 3. Relative abundance ratios of the *m/z* 93 to the *m/z* 66 ions for 4-vinylcyclohexene as a function of increasing ion excitation. The solid line represents the average of six consecutive ion-excitation scans. The dotted lines represent the standard deviation of those scans. The data were taken with the FT mass spectrometer.

Scheme 2



which is more stable.[4] In separate experiments, the internal energy contents of the ions were increased, by way of ion excitation, during the rf-only-mode event and in the presence of high-pressure helium. After the rf-only-mode event, a CAD spectrum was again obtained for each isomer. The abundance ratio of *m/z* 93 to *m/z* 66 is constant, 0.5, for **1** and **3**. The change in the abundance ratio for **1** (without excitation, 2.0; with 0.5) is evidence that the isomerization to **3** is occurring.

The ability to excite ions during the rf-only-mode event offers a unique way of controlling isomerization of the 4-vinylcyclohexene radical cation. This is demonstrated by varying the amplitude of the ion excitation for **1** (see Figures 2 and 3). At low excitation power, the abundance ratio of the *m/z* 93 to the *m/z* 66 ions is 1.7. As the ion excitation is increased, the abundance ratio decreases, indicating a change in the structure of **1**. A gradual increase, however, is observed (left portion of Figure 3) and may point to the sampling of an intermediate structure, such as **2**, in going from **1** to **3**. This hypothesis cannot be tested because a stable neutral precursor for **2** does not exist. A parallel experiment was performed for **3**, and the abundance ratio remained from 0.5 to 0.1 for a range of excitation powers.

Both the sector and the FT mass spectrometer results reflect those obtained in the matrix-isolation ESR investigation. That is, **1** isomerizes to **3** at high internal energy, but is stable at low internal energy.[4] Two mechanisms explain this rearrangement (Schemes 1 and 2).[4] The second mechanism is questionable because the most stable olefin radical cation formed from **5** is that of bicyclo[2.2.2]-2-octene, which gives different ESR and CAD spectra than those of **1** or **3**.[4] The CAD spectrum of bicyclo[2.2.2]-2-octene radical cation indicates that the retro-Diels–Alder loss of ethylene is more facile than that from **1** or **3**.

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[15] The number of collisions, estimated by using the Langevin collision model, of the C_8H_{12} radical cations is approximately 100 with CS_2 in the sector and approximately 50 000 with He in the FT mass spectrometer.

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[17] A suspended trapping event, which decreased the ion number after the rf-only-mode event but before detection, was used to determine if the number of ions affected detectability. For a description of suspended trappings, see: Hogan, J. D.; Laude, D. A., Jr. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 431.

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