Electron ionization of 1,3-cyclohexadiene and 1,4-cyclohexadiene

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ABSTRACT

Electron ionization of the two cyclohexadiene isomers has been found to produce similar ion populations with comparable total cross sections. The total cross sections for 1,3-cyclohexadiene and 1,4-cyclohexadiene were measured to be at maxima of 1.42×10^{-15} and 1.41×10^{-15} cm^2, respectively, at 80 eV. Results show that the major product ions are the four largest ions, $C_6H_{5-8}^+$, with combined intensities contributing more than three quarters of the ion populations. Minor product ions include $C_5H_{3,5}^+$, $C_4H_{2-6}^+$, $C_3H_{2,3,5}^+$ and $C_2H_3^+$. The branching ratios for the major product ions from the two isomers match each other well at low energies near thresholds but differ slightly at elevated energies; while the branching ratios for the minor ions are approximately identical between the two isomers within error limits.

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1. Introduction

Benzene is an important precursor to soot production in hydrocarbon flames [1] and the mechanism of benzene formation during fuel combustion processes has become an active subject of research. It has been reported that benzene is formed exclusively from fuel dehydrogenation via cyclohexene and cyclohexadiene intermediates in cyclohexane flames [1,2]. In experiments on methane flames doped with cyclic hydrocarbon gases including cyclohexane, cyclohexene, and cyclohexadienes, it is found that cyclohexadienes mostly dehydrogenate to benzene, while cyclohexane and cyclohexene mostly decompose to C2, C3 and C4 hydrocarbons [3]. Ionic mechanisms of soot production in flames have been investigated [4,5]. In a systematic study of positive ion population in hydrocarbon flames by means of mass spectrometry, cyclohexadienylium and monocyclic aromatic ions have been identified [5]. It is therefore of great interest to study to kinetics for the formation of hydrocarbon ions via electron ionization of the cyclohexadienes. In this paper, results of our recent measurements on the electron energy dependences of the total electron ionization cross sections of 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD), along with the branching ratios of the product ions, will be presented. The comparison of the two cyclohexadiene isomers in their ionization cross sections is also of interest in basic research because they have different double bond positions: one isomer has

a conjugated π system while the other has double bonds that are separated by an sp^3 carbon.

2. Experimental

All of the experiments were performed using a modified FTMS equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and a 2 T superconducting magnet [6]. 1,3-CHD (97%, Sigma-Aldrich) or 1,4-CHD (>97%, Sigma-Aldrich) was mixed with Ar (99.999%, Matheson) in a pressure ratio of ~1:1 to a total pressure of ~20 Torr, as determined by capacitance manometry. The mixture was then admitted through a precision leak valve (Varian variable leak valve) into the FTMS system. Ions were formed by electron impact in the trapping cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiated the cell with a few hundred picocoulombs of electrons at a varying energy within the range of 10–200 eV, with a spectral width of ±0.6 eV. The motions of the product ions were constrained radially by the superconducting magnetic field and axially by an electrostatic potential applied to the faces of the cubic trapping cell that were perpendicular to the magnetic field. Ions of all mass-to-charge ratios, in a range of 10–500 amu, were simultaneously and coherently excited into cyclotron orbits by applying a stored waveform inverse Fourier transform (SWIFT) [7–9] to two opposing trap faces that were parallel to the magnetic field. Following cyclotron excitation, the image currents induced on the two remaining faces of the trap were amplified, digitized and Fourier analyzed to yield a mass spectrum. In this study, the intensity ratios of the ions from 1,3-CHD or 1,4-CHD to Ar$^+$ gave cross sections relative to those for
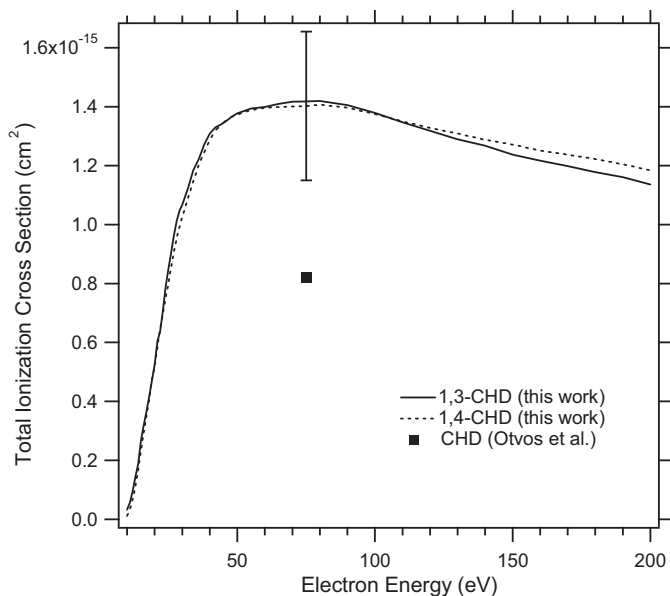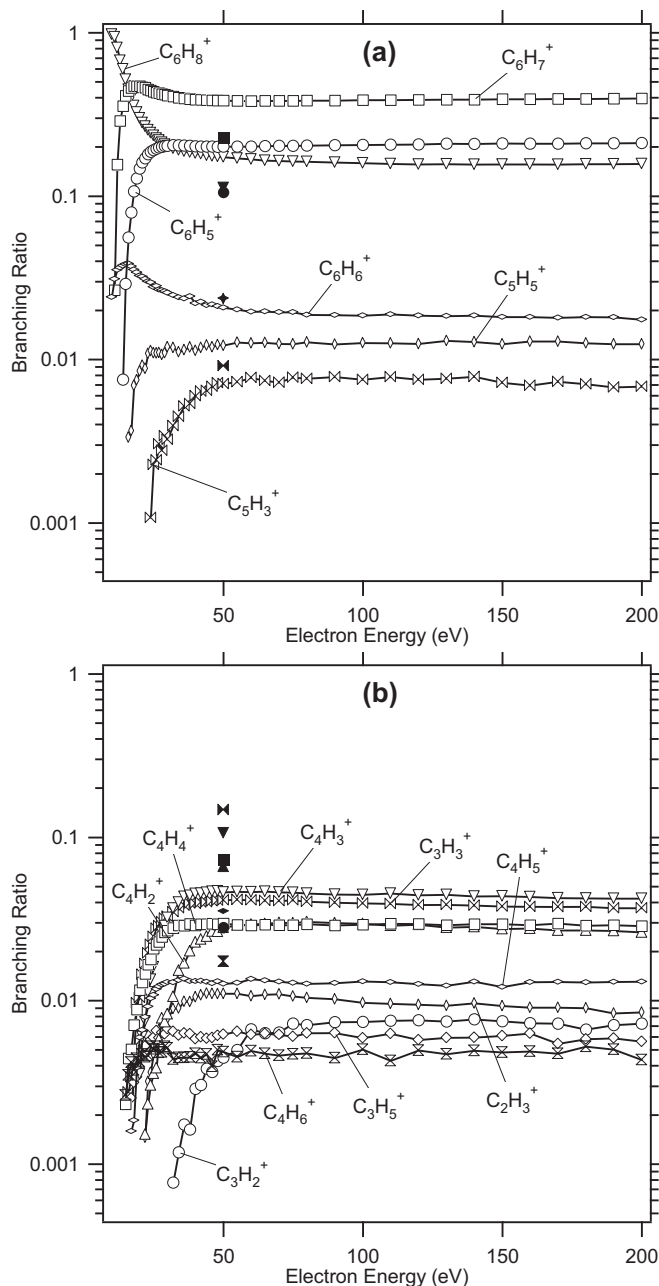
Fig. 1. Total electron ionization cross sections of 1,3-CHD (solid line) and 1,4-CHD (dashed line) measured by this work and by Otvos and Stevenson [11] (filled squares).

Fig. 2. Branching ratios of product ions from electron ionization of 1,3-CHD that have partial cross sections greater than 5×10^{-18} cm^2 at 50 eV electron energy, measured by this work (lines and open symbols). For visual clarity data are presented in plots (a) for C$_6$ and C$_5$ ions and (b) for C$_4$, C$_3$ and C$_2$ ions, with the same scale for easy comparison of the amplitudes for different ionization channels. Also shown are branching ratios derived from relative abundances of product ions reported by Franklin and Carroll [16] (filled symbols).

electron ionization of Ar [10], since the pressure ratio of 1,3-CHD or 1,4-CHD to Ar was known. Due to the limits of electronic parameters used in the current FTMS system, H$^+$ is not detectable in our experiments.

3. Results and discussion

Figs. 1–3 present the results of our measurements on the total ionization cross sections and the product branching ratios. The findings show that electron ionization of either 1,3-CHD or 1,4-CHD produce similar ion populations, with the four largest product ions, C$_6$H$_{5-8}$$^+$, being the most dominant ions. Combined together, these four ions contribute more than 75% of the ion product population throughout the energy range studied, 10–200 eV. Other noticeable product ions include C$_5$H$_{3,5}$$^+$, C$_4H_{2-6}$$^+$, C$_3H_{2,3,5}$$^+$ and C$_2$H$_3$$^+$, which have partial cross sections greater than 5×10^{-18} cm^2 at 50 eV electron energy. The total cross sections of 1,3-CHD and 1,4-CHD are shown in Fig. 1, displaying maxima of 1.42×10^{-15} and 1.41×10^{-15} cm^2, respectively, at 80 eV. The two cyclohexadienes have rather similar electron energy dependences of total cross sections, with slight differences only at energies above 120 eV. Also shown in Fig. 1 is a total cross section value at 75 eV reported by Otvos and Stevenson [11] for cyclohexadiene (no particular isomer was specified). Considering that the Ar cross section used for calibration in the present work is different than Otvos and Stevenson reported, their value of the cyclohexadiene cross section has been recalibrated against the Ar cross section used here. The uncertainty in our cross section data from the FTMS experiments is estimated to be ±18% [12], with an example error bar displayed in Fig. 1 for 1,4-CHD at 75 eV. Our total cross sections for both 1,3-CHD and 1,4-CHD are significantly greater, beyond the uncertainty limits, than the value reported by Otvos and Stevenson.

The branching ratios of the product ions mentioned above are shown in Figs. 2 and 3. The first fragment ions emerging as the electron energy increases from thresholds are C$_6$H$_7$$^+$ and C$_6$H$_6$$^+$, followed by C$_6H_5$$^+$, all formed by loss of H and/or H$_2$ from the parent ion, C$_6$H$_8$$^+$. At higher energies, fragment ions resulting from the loss of hydrocarbon moiety of the parent ion appear, among which are C$_5$H$_5$$^+$, C$_4H_4$$^+$, C$_4H_3$$^+$ and C$_3$H$_3$$^+$, all with relatively significant branching ratios. It is interesting to compare the branching ratios of

1,3-CHD and 1,4-CHD. The uncertainty of the branching ratios to be compared between the isomers is expected to be ±4% for major ions [12] and to be increasingly greater for minor ions with decreasing intensities. We find that the light fragment ions, i.e., C$_5$H$_5$$^+$ and lighter ones, have similar branching ratios from the two isomers over the electron energy range. For the heavy ions, C$_6$H$_{5-8}$$^+$ (which are also the most abundant ions), branching ratios from the two isomers are similar only at low electron energies near the thresholds, but differ slightly to a noticeable extent at elevated electron energies. The comparison is shown in Fig. 4 for certain selected ions. One can see that among the heavy ions, only C$_6$H$_7$$^+$ has greater intensity from 1,3-CHD than from 1,4-CHD, and the other ions have a