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**GAS-PHASE ION-MOLECULE REACTIONS IN  
SELECTED CYCLOHEXANES (PREPRINT)**

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## Gas-Phase Ion-Molecule Reactions in Selected Cyclohexanes

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### Abstract

Ion-molecule reactions of cyclohexane, methylcyclohexane and ethylcyclohexane with hydrocarbon cations derived from these cyclohexanes, respectively, have been studied. These ion-molecule reactions take place via various channels including charge transfer,  $H^+$  transfer,  $H_2^+$  transfer,  $H_3^+$  transfer, hydrocarbon anion transfer, and association with concerted fragmentation. Among these channels,  $H^+$  transfer is the most prevalent, and for many of the reacting ions, it is the exclusive channel. Most of the reactions proceed in a direct mode, except for the reactions of  $C_4H_5^+$  or  $C_4H_7^+$  with cyclohexane, which in certain channels proceed via the formation of a long-lived collision complex. Some general trends in the reaction rates are observed: smaller reactant ions tend to exhibit faster reaction rates, and odd-electron ions react faster than the even-electron ions. For certain reactant ions, there is evidence of the existence of multiple structural isomers that have different reactivities.

## 1. Introduction

The study of ion-molecule reactions in hydrocarbons is one of the more important topics in plasma research today, in particular in the field of combustion and ignition. Plasma assisted ignition and combustion have been of great interest in recent years [1]. Because the charged particles play a key role in the plasma processes, the kinetics of the formation and reactions of the charged particles are one of the crucial data sets required for the modeling of discharge plasmas. We have previously measured cross sections of the electron ionization of cycloalkanes including cyclohexane ( $C_6H_{12}$ ), methylcyclohexane ( $C_7H_{14}$ ) and ethylcyclohexane ( $C_8H_{16}$ ) [2,3]. These cycloalkanes are a significant component of many practical fuels [4], and  $C_6H_{12}$  and  $C_7H_{14}$  have been chosen as representative cycloalkanes in several proposed surrogate mixtures for jet fuels [5-11]. In this paper, we present our recent study on gas-phase reactions of  $C_6H_{12}$  and  $C_8H_{16}$  with selected hydrocarbon ions derived from these two cyclohexanes, respectively, as a result of electron ionization. Combined with the results of our previous study on the ion chemistries in  $C_7H_{14}$  [2], the general trends in the reaction kinetics and the reaction channels will be discussed.

## 2. Experimental

All of the experiments were performed using a modified Extrel Fourier transform mass spectrometry (FTMS) equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and a  $\sim 2$  T superconducting magnet [12]. Cyclohexane ( $\geq 99.7\%$ , Sigma-Aldrich) and Ethylcyclohexane (99+%, Aldrich) were separately mixed with Ar (99.999%, Matheson) in a pressure ratio of  $\sim 1:50$  to a total pressure of  $\sim 500$  Torr, as determined by capacitance manometry. In experiments requiring isotopic reactions, a mixture of cyclohexane, cyclohexane- $d_{12}$  (99.6 atom% D, Aldrich) and Ar with the pressure ratio of  $\sim 1:1:50$  was made. The mixture was then admitted through a precision leak valve (Varian variable leak valve) into the FTMS system. The hydrocarbon ions were formed by electron impact on  $C_6H_{12}$  or  $C_7H_{14}$  in the trapping cell at a total pressure in the  $10^{-5}$  Torr range. The motions of the ions were constrained radially by the superconducting magnetic field and axially by an electrostatic potential (trapping potential) applied to the trap faces that were perpendicular to the magnetic field. Each reactant ion to be studied was isolated from other ions by Stored Waveform Inverse Fourier Transform

(SWIFT) [13-15] applied to two opposing trap faces which were parallel to the magnetic field, to eject the other ions out of the trapping cell, followed by a cooling period in which the ion underwent multiple collisions with Ar for a certain length of time, typically 500 ms. SWIFT was used again to select the reactant ion from those that were formed during the cooling period, followed by a programmed reaction time selectable typically from 0 to 4000 ms. The pressure of Ar and the length of the cooling period were adjusted so that at the end of the cooling period there were still sufficient reactant ions to study and their reaction showed a single-exponential decay to the end of the reaction time at which only a few percent of the reactant ions were left over; in some cases non-single-exponential decay is observed even after an extended cooling period, which is considered to be due to the existence of multiple isomers of the reactant ion that have different reactivities, as will be discussed in the next section. At the end of the reaction time, ions of all mass-to-charge ratios in a range of 10 to 500 amu, were coherently excited into cyclotron orbits using SWIFT. The image currents induced on two remaining faces of the trap were amplified, digitized and Fourier analyzed to yield a mass spectrum.

With the high Ar partial pressure,  $\text{Ar}^+$  would become overpopulated during electron ionization, resulting in a significant space charge effect. To eliminate this effect, an rf waveform with the appropriate single-frequency for  $\text{Ar}^+$  cyclotron resonance was applied during the electron beam event to continuously and selectively eject  $\text{Ar}^+$  out of the trapping cell.

### 3. Results and Discussion

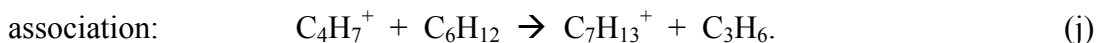
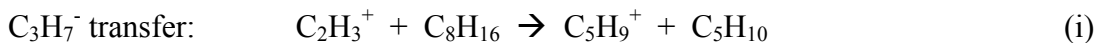
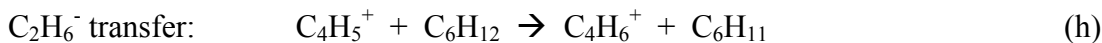
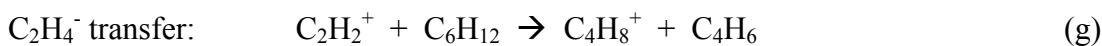
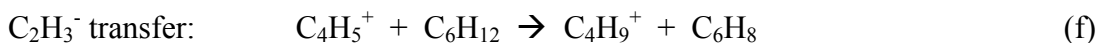
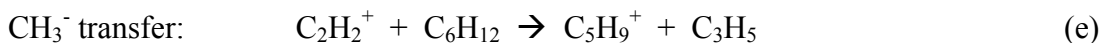
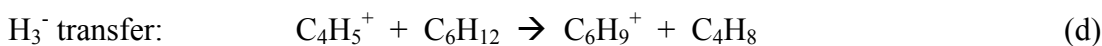
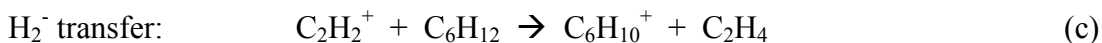
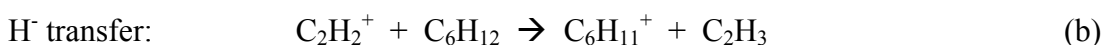
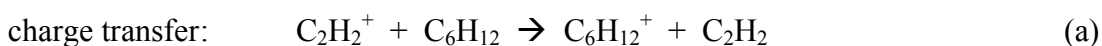
Results of this effort have been tabulated for selected hydrocarbon cations reacting with their parent gas molecules,  $\text{C}_6\text{H}_{12}$  and  $\text{C}_8\text{H}_{16}$ , shown in table 1. Also included in the table are results from our previous study [2] on the hydrocarbon ions reacting with  $\text{C}_7\text{H}_{14}$ . The primary data shown in table 1 are relative reaction rates along with the branching ratios for the various channels for ion-molecule reactions. The various reactant ions are displayed as rows in the table and each intersect three columns representing reactions with the three neutral cyclohexane parents. It should be noted that for each reactant ion, the isomer structure may differ across the row, as the reactant ion is derived from a different parent (the neutral cyclohexane with which it reacts) in each case. For example, the isomeric structure of  $\text{C}_4\text{H}_7^+$  in the reaction with  $\text{C}_6\text{H}_{12}$  may be different than in the  $\text{C}_4\text{H}_7^+$  reaction with  $\text{C}_7\text{H}_{14}$ . Prior to their reactions, as mentioned in the previous section, reactant ions undergo collisional cooling for typically 500 ms under Ar

**Table 1.** Reactions of cyclohexanes with selected derived hydrocarbon ion. The relative reaction rate constants (bold) are scaled to the fastest neutral rate constant. The branching ratios shown in parenthesis, in %, are for (a) charge transfer, (b) H transfer, (c) H<sub>2</sub><sup>-</sup> transfer, (d) H<sub>3</sub><sup>-</sup> transfer, (e) CH<sub>3</sub><sup>-</sup> transfer, (f) C<sub>2</sub>H<sub>3</sub><sup>-</sup> transfer, (g) C<sub>2</sub>H<sub>4</sub><sup>-</sup> transfer, (h) C<sub>2</sub>H<sub>6</sub><sup>-</sup> transfer, (i) C<sub>3</sub>H<sub>7</sub><sup>-</sup> transfer, (j) association reaction, and (k) dissociative H or H<sub>2</sub><sup>-</sup> transfer.

| Ionic Reactant                              | Neutral Reactant  |   |   |
|---|---|---|---|
|   | C <sub>6</sub> H <sub>12</sub>  | C <sub>7</sub> H <sub>14</sub> <sup>**</sup>  | C <sub>8</sub> H <sub>16</sub>  |
| C <sub>2</sub> H <sub>2</sub> <sup>+</sup>  | <b>1.00</b> g(41) e(30) a(14) b(13) c(2)  | ---   | ---   |
| C <sub>2</sub> H <sub>3</sub> <sup>+</sup>  | <b>0.92</b> b(100)  | <b>0.75</b> b(100)  | <b>1.00</b> b(50) i(50)   |
| C <sub>2</sub> H <sub>4</sub> <sup>+</sup>  | <b>1.00</b> a(67) b(33)   | <b>1.00</b> a(50) b(45) e(5)  | ---   |
| C <sub>2</sub> H <sub>5</sub> <sup>+</sup>  | <b>0.88</b> b(100)  | <b>0.63</b> b(100)  | <b>0.88</b> b(55) i(45)   |
| C <sub>3</sub> H <sub>3</sub> <sup>+</sup>  | No reaction   | No reaction   | No reaction   |
| C <sub>3</sub> H <sub>5</sub> <sup>+</sup>  | <b>0.53</b> b(100)  | <b>0.29</b> b(100)  | <b>0.65</b> b(87) i(13)   |
| C <sub>3</sub> H <sub>6</sub> <sup>+</sup>  | <b>0.69</b> c(64) b(36)   | <b>0.57</b> <sup>*</sup> b(69) c(31);<br><b>0.94</b> <sup>*</sup> a(46) c(38) k(16) | <b>0.84</b> b(46) a(26) i(15) h(13)   |
| C <sub>3</sub> H <sub>7</sub> <sup>+</sup>  | <b>0.54</b> b(100)  | ---   | <b>0.18</b> <sup>*</sup> b(100);<br><b>0.045</b> <sup>*</sup> b(100)                  |
| C <sub>4</sub> H <sub>3</sub> <sup>+</sup>  | <b>0.43</b> b(100)  | ---   | ---   |
| C <sub>4</sub> H <sub>5</sub> <sup>+</sup>  | <b>0.24</b> <sup>*</sup> b(48) j(26) d(26);<br><b>0.00</b> <sup>*</sup>                         | No reaction   | <b>0.44</b> <sup>*</sup> b(70) i(30)<br><b>0.00</b> <sup>*</sup>                      |
| C <sub>4</sub> H <sub>6</sub> <sup>+</sup>  | <b>0.30</b> <sup>*</sup> b(78) c(22);<br><b>0.012</b> <sup>*</sup> c(100)                       | <b>0.25</b> b(74) c(26)   | <b>0.46</b> <sup>*</sup> b(55) i(20) a(13) c(12);<br><b>0.031</b> <sup>*</sup> i(100) |
| C <sub>4</sub> H <sub>7</sub> <sup>+</sup>  | <b>0.14</b> b(66) j(15) f(12) d(7)  | <b>0.22</b> b(100)  | <b>0.34</b> b(91) e(9)  |
| C <sub>4</sub> H <sub>8</sub> <sup>+</sup>  | <b>0.17</b> <sup>*</sup> b(100)<br><b>0.019</b> <sup>*</sup> c(100)<br><b>0.00</b> <sup>*</sup> | <b>0.18</b> <sup>*</sup> c(100);<br><b>0.052</b> <sup>*</sup> b(100)                | <b>0.23</b> <sup>*</sup> b(41) c(35) a(16) i(8);<br><b>0.00</b> <sup>*</sup>          |
| C <sub>5</sub> H <sub>7</sub> <sup>+</sup>  | No reaction   | No reaction   | No reaction   |
| C <sub>5</sub> H <sub>8</sub> <sup>+</sup>  | No reaction   | <b>0.024</b> c(100)   | ---   |
| C <sub>5</sub> H <sub>9</sub> <sup>+</sup>  | No reaction   | <b>0.016</b> b(100)   | <b>0.020</b> <sup>*</sup> b(100)<br><b>0.00</b> <sup>*</sup>                          |
| C <sub>5</sub> H <sub>10</sub> <sup>+</sup> | ---   | <b>0.0054</b> c(100)  | ---   |
| C <sub>6</sub> H <sub>10</sub> <sup>+</sup> | No reaction   | <b>0.0052</b> c(100)  | <b>0.040</b> <sup>*</sup> b(100)<br><b>0.00</b> <sup>*</sup>                          |
| C <sub>6</sub> H <sub>11</sub> <sup>+</sup> | No reaction   | <b>0.088</b> b(100)   | <b>0.15</b> <sup>*</sup> b(100)<br><b>0.00</b> <sup>*</sup>                           |

<sup>\*</sup> There are two or more isomers of the reactant ion that have different reaction rates (see the text). <sup>\*\*</sup> Data from previous study [2].

pressure of  $\sim 10^{-5}$  Torr and are therefore expected to be thermalized externally and internally. The small possibility of long-lived excited states, though, cannot be excluded. Reactant ions with more than one reaction rate constant listed in table 1 are ions that have multiple isomers with different measurable reactivities, which will be discussed in detail later in this section. For these multiple isomer entries, the branching ratios are also listed. The rate constants are relative and normalized to the fastest rate constant of each neutral parent hydrocarbon; no comparison of rate constants of reactions with different neutral hydrocarbons has been made. The branching ratios are shown in parentheses for different reaction channels as listed in the table's caption and illustrated by the following equations as examples,



Explanation for the dissociative  $\text{H}^-$  or  $\text{H}_2^-$  transfer observed in reactions of  $\text{C}_7\text{H}_{14}$  can be found in our previous paper [2].

It can be seen from table 1 that there are some general trends in the reaction rates: the smaller the reactant ion is, the faster the reaction takes place, and odd-electron ions ( $\text{C}_x\text{H}_{2y}^+$ ) react faster than the even-electron ions ( $\text{C}_x\text{H}_{2y+1}^+$ ).  $\text{H}^-$  transfer is the most commonly observed channel in reactions of all three cyclohexanes. While  $\text{C}_3\text{H}_7^-$  transfer is rather common in reactions with  $\text{C}_8\text{H}_{16}$ , it is not observed in reactions with  $\text{C}_6\text{H}_{12}$  or  $\text{C}_7\text{H}_{14}$ .  $\text{H}_3^-$  transfer and association reaction are observed only in the reactions of  $\text{C}_6\text{H}_{12}$  with  $\text{C}_4\text{H}_5^+$  and  $\text{C}_4\text{H}_7^+$ , respectively.

The relative rate constants in table 1 are obtained from fitting the time-dependent ion intensities using a reaction model of a single-component reactant ion or multi-component reactant ions. The former is seen to have a single-exponential decay of the reactant ion, which

usually indicates that there is only one isomer in the reactant ion population or, if there is more than one, their reactivities are similar. The latter, indicated in table 1 by multiple rate constants listed, is seen to have a non-single-exponential decay of the reactant ion. Given the likelihood of the reactant ion being thermalized, the non-single-exponential decay is most likely caused by the existence of two or more isomers that have different reactivities. Table 1 shows that as reactant ions get bigger, they are more likely to have non-single-exponential decay, probably reflecting the fact that they are more likely to have multiple structural isomers. Among the reactions in the table,  $C_4H_8^+$  reacting with  $C_6H_{12}$  appears to be unique because it has 3 reaction rate constants and therefore is worth of detailed discussion. The reaction time dependency of the intensities of  $C_4H_8^+$  and its product ions are shown in figure 1. After its initial decay, the reactant ion intensity levels off at  $\sim 1500$  ms, suggesting that at least one isomer is unreactive toward  $C_6H_{12}$ . The reactive isomers produce  $C_6H_{11}^+$  and  $C_6H_{10}^+$  via  $H^-$  and  $H_2^-$  transfer, respectively, with branching ratios varying as a functions of the reaction time, suggesting that there are at least two isomers that react at different rates and give different yields of  $C_6H_{11}^+$  and  $C_6H_{10}^+$ . Six isomers of  $C_4H_8^+$  are listed in table 2 along with the enthalpies of reaction for their  $H^-$  or  $H_2^-$  transfer, calculated based on the thermochemical data from the literature [16] and the assumed neutral product structures shown in the table. The data show that for the four open-chain structures,  $H_2^-$  transfer but not  $H^-$  transfer is thermochemically allowed, while for the two cyclic structures, both channels are thermochemically possible. In a study on reactions of  $C_6H_{12}$  with selected hydrocarbon ions including  $C_4H_8^+$  derived from  $C_6H_{12}$ , Abramson and Futrell found that the major product ions were  $C_6H_{11}^+$  and  $C_6H_{10}^+$  and proposed that the reactant ion  $C_4H_8^+$  have more than one isomeric species [17]. In a similar study by Lias and Ausloos [18], the authors suggested that  $C_4H_8^+$  consist of 1- $C_4H_8^+$ , i- $C_4H_8^+$  and 2- $C_4H_8^+$ , and they found that 2- $C_4H_8^+$  reacted extremely slowly with  $C_6H_{12}$ , even though its  $H_2^-$  transfer with  $C_6H_{12}$  is energetically allowed. Based on the above discussion, we proposed the following reaction kinetic model for the curve fitting in figure 1:



**Table 2.** Enthalpies of reaction ( $\Delta H_{\text{rxn}}$ , in kJ/mol) for H transfer and  $\text{H}_2^-$  transfers between  $\text{C}_6\text{H}_{12}$  and different isomers of  $\text{C}_4\text{H}_8^+$ .

| Isomeric structure<br>of $\text{C}_4\text{H}_8^+$   | H <sup>+</sup> transfer forming $\text{C}_6\text{H}_{11}^+$ |                         | $\text{H}_2^-$ transfer forming $\text{C}_6\text{H}_{10}^+$ |                         |
|---|---|-------------------------|---|-------------------------|
|   | Neutral product   | $\Delta H_{\text{rxn}}$ | Neutral product   | $\Delta H_{\text{rxn}}$ |
| $[\text{CH}_2=\text{CHCH}_2\text{CH}_3]^+$          | $\text{CH}_3\text{CHCH}_2\text{CH}_3$                       | 3.3                     | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$              | -68.8                   |
| $[(\text{Z})-\text{CH}_3\text{CH}=\text{CHCH}_3]^+$ | $\text{CH}_3\text{CHCH}_2\text{CH}_3$                       | 56.3                    | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$              | -15.8                   |
| $[(\text{E})-\text{CH}_3\text{CH}=\text{CHCH}_3]^+$ | $\text{CH}_3\text{CHCH}_2\text{CH}_3$                       | 61.3                    | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$              | -10.8                   |
| $[\text{CH}_2=\text{C}(\text{CH}_3)_2]^+$           | $(\text{CH}_3)_3\text{C}$                                   | 28.3                    | $(\text{CH}_3)_3\text{CH}$                                  | -26.8                   |
| $[\text{c}-\text{C}_4\text{H}_8]^+$                 | $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$              | -54.7                   | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$              | -129.8                  |
| $[(\text{c}-\text{C}_3\text{H}_5)\text{CH}_3]^+$    | $\text{CH}_3\text{CHCH}_2\text{CH}_3$                       | -10.7                   | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$              | -82.8                   |

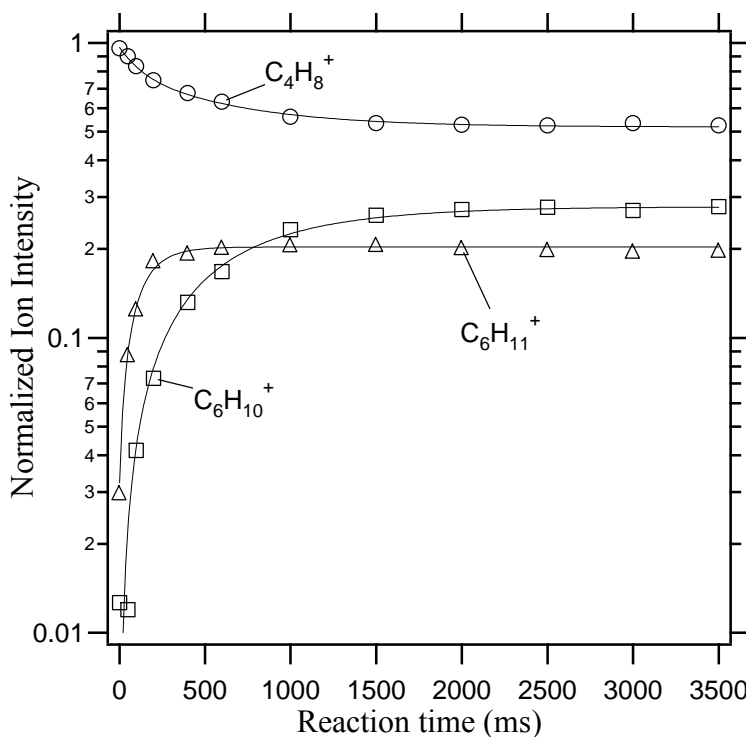


Figure 1. Semilogarithmic plot for the reaction of  $\text{C}_4\text{H}_8^+$  with  $\text{C}_6\text{H}_{12}$ . Symbols are experimental data, while lines are the fit of the kinetic model described in the text.

$C_4H_8^+$ (i) represents either or both isomers  $[c-C_4H_8]^+$  and  $[(c-C_3H_5)CH_3]^+$ , while  $C_4H_8^+$ (ii) represents either or both isomers  $[CH_2=CHCH_2CH_3]^+$  and  $[CH_2=C(CH_3)_2]^+$ , and  $C_4H_8^+$ (iii) represents either or both isomers  $[(Z)-CH_3CH=CHCH_3]^+$  and  $[(E)-CH_3CH=CHCH_3]^+$ . Please note that  $C_4H_8^+$ (iii) is unreactive, even though its  $H_2^-$  transfer is exothermic (table 2), as mentioned above. The fitting yields satisfactory results, shown in figure 1, with rate constants and branching ratios given in table 1 (the fitting yields the branching ratio of reaction 2 virtually zero). The non-single-exponential decay of  $C_4H_8^+$  in figure 1 can be alternatively explained by the possibility of long-lived excited states of  $C_4H_8^+$  that are sufficiently energetic to undergo endothermic reactions. Given that the reactant ions have undergone collisional cooling and that the thermochemical data in table 2 support the possibility of isomers with different reactivities, we believe the above multi-isomer reaction model is the better explanation.

Different types of reaction channels are listed in table 1 for the purpose of identifying the neutral products. An  $H^-$  transfer, for example, differs from a dissociative charge transfer in their neutral products:

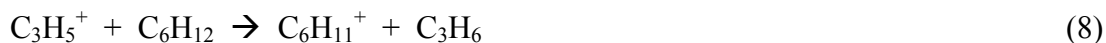


In detailed mechanisms, however, one may find that  $H^-$  transfer reaction is not as simple as the name refers but rather, for example, involves initial charge transfer followed by rapid H transfer to form an intermediate that subsequently dissociates into its component fragments:



such as in the case of  $OD^+$  ( $X^3\Sigma^-$ ) reacting with propyne studied by Liu *et al* [19]. Reaction 7 is, nonetheless, labeled as  $H^-$  transfer here because the multiple steps occur intramolecularly, yielding the net result as of  $H^-$  transfer.

Reaction channels are assigned to the formation of each product ions based on the isotope reaction results, and by other arguments mainly on the thermochemical ground as discussed in the following subsections. We have studied the isotopic reactions in  $C_6H_{12}$  and  $C_7H_{14}$ , but not in  $C_8H_{16}$ . However, certain reaction channels are common in  $C_6H_{12}$  and  $C_7H_{14}$ , and therefore are assumed in the case of  $C_8H_{16}$ . With exceptions only in the cases of  $C_4H_5^+$  and  $C_4H_7^+$  reacting with  $C_6H_{12}$ , the results for the isotopic reactions are in agreement with the assigned reaction channels. For example, shown in figure 2, when  $C_3H_5^+$  reacts with a mixture of  $C_6H_{12}/C_6D_{12}$ ,



no product ion containing a mixture of H and D atoms is detected. This isotope distribution supports the H<sup>+</sup> transfer mechanism and excludes some other reaction mechanisms such as dissociative proton transfer that has been observed in the reaction of CH<sub>5</sub><sup>+</sup> with hexane, with certain label retention in the product ions [20].

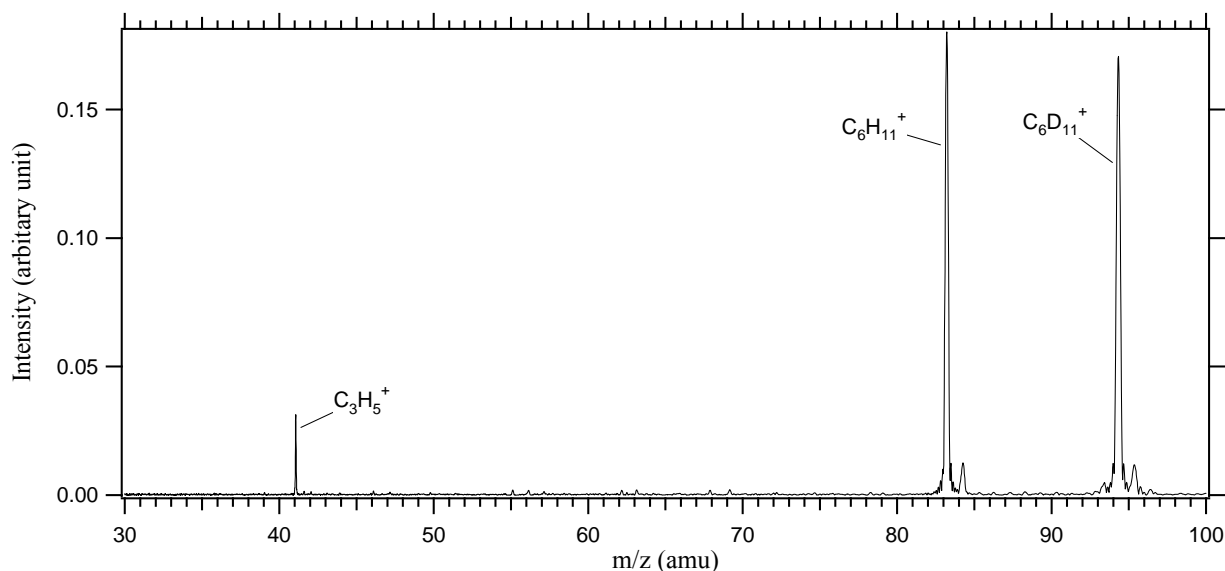
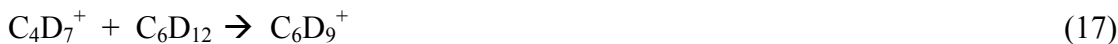


Figure 2. Mass spectrum of the reaction of C<sub>3</sub>H<sub>5</sub><sup>+</sup> with C<sub>6</sub>H<sub>12</sub>/C<sub>6</sub>D<sub>12</sub>.

The reaction of C<sub>4</sub>H<sub>7</sub><sup>+</sup> with C<sub>6</sub>H<sub>12</sub> appears to be a special case, with significant H scrambling indicated by the isotope distribution in product ions shown in figure 3. The reaction with no isotope reagent, shown in figure 3a, yields product ions through the following channels:



Equations 20-23 are, respectively, H<sup>+</sup> transfer, association reaction with concerted fragmentation, C<sub>2</sub>H<sub>3</sub><sup>-</sup> transfer, and H<sub>3</sub><sup>-</sup> transfer. When C<sub>4</sub>D<sub>7</sub><sup>+</sup> is used as the reactant ion to react with a mixture of C<sub>6</sub>H<sub>12</sub>/C<sub>6</sub>D<sub>12</sub>, as shown in figure 3b, the product ions contain more isotope peaks compared to figure 3a, ascribed to the following reaction equations (neutral products are not shown):



and



The existence of the isotope patterns such as  $\text{C}_6\text{H}_a\text{D}_{11-a}^+$  indicates that these reactions proceed via the formation of a long-lived collision complex  $[\text{C}_4\text{H}_7\text{-C}_6\text{H}_{12}]^+$  so that extensive H scrambling occurs before its dissociation into the final products. The groups of symbols in figure 3b are isotope patterns calculated based on the assumption of complete H scrambling, the statistical H/D combination of 7 D atoms and 12 H atoms originally from the ionic and neutral reactants. It can be seen that while  $\text{C}_4\text{H}_c\text{D}_{9-c}^+$  formed by  $\text{C}_2\text{H}_3^-$  transfer and  $\text{C}_6\text{H}_d\text{D}_{9-d}^+$  formed by  $\text{H}_3^-$  transfer are approximately statistical,  $\text{C}_7\text{H}_b\text{D}_{13-b}^+$  formed by association channel somewhat deviates from the complete H scrambling, favoring the product ion carrying statistically more H atoms from the neutral reactant. Note that in the mass spectrum,  $\text{C}_4\text{H}_c\text{D}_{9-c}^+$  overlaps with the reactant ion  $\text{C}_4\text{D}_7^+$  and  $\text{C}_6\text{H}_d\text{D}_{9-d}^+$  partially overlaps with  $\text{C}_6\text{H}_a\text{D}_{11-a}^+$ . The  $\text{H}^-$  transfer channel appears to have bi-distribution patterns: one approaches statistical or full H scrambling,  $\text{C}_6\text{H}_a\text{D}_{11-a}^+$ , while the other totally lacks H scrambling,  $\text{C}_6\text{H}_{11}^+$ . The isotope distribution features stated above are confirmed by the results of  $\text{C}_4\text{H}_7^+$  reacting with  $\text{C}_6\text{H}_{12}/\text{C}_6\text{D}_{12}$ , shown in figure 3c where the peaks of ions containing mixtures of the H/D atoms are compared to the calculated isotope patterns based on the statistical H/D combination of 7 H atoms and 12 D atoms from the reactants. The bi-distribution patterns for the  $\text{H}^-$  transfer channel appear to suggest the coexistence of two reaction mechanisms: the formation of an ion-molecule complex with a lifetime sufficiently long for a series of rearrangements leading to the extensive H/D exchange, and direct  $\text{H}^-$  transfer proceeding via large impact parameter collisions, favoring no H/D shuffling. Direct  $\text{H}^-$  transfer vs.  $\text{H}^-$  transfer via long-lived complex formation have been discussed in a study by Roithova *et al* on selected hydrocarbon dications reacting with methane [21]. In our current study, the coexistence of two reaction mechanisms may be explained by the possibility of two or more

structural isomers of the reactant ion  $C_4H_7^+$  that favor mechanisms of large impact parameter collisions and formation of ion-molecule complex, respectively.

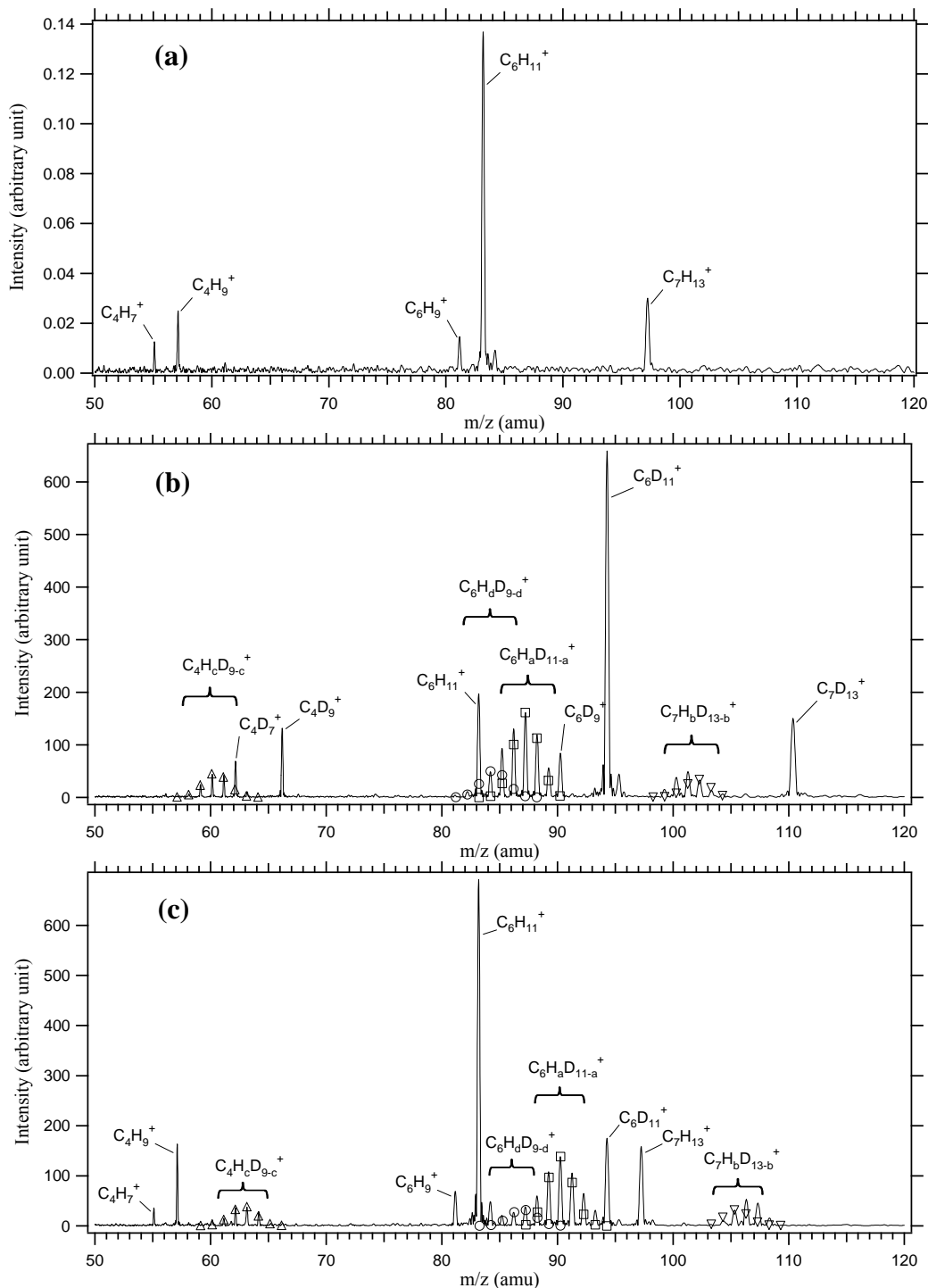


Figure 3. Mass spectra of reactions of (a)  $C_4H_7^+$  with  $C_6H_{12}$ , (b)  $C_4D_7^+$  with  $C_6H_{12}/C_6D_{12}$ , and (c)  $C_4H_7^+$  with  $C_6H_{12}/C_6D_{12}$ . Symbols in (b) and (c) are the isotope patterns calculated based on the assumption of complete H scrambling in the product ions (see the text).

The results of the isotopic reactions of  $C_4H_5^+$  with  $C_6H_{12}$  show that the  $H_3^-$  transfer channel yielding  $C_6H_9^+$  has extensive H scrambling, and  $H^-$  transfer and association channels yielding  $C_6H_{11}^+$  and  $C_7H_{11}^+$ , respectively, have no significant H scrambling.

In the following subsections we will present short discussions on all reaction channels listed in table 1, except dissociative  $H^-$  or  $H_2^-$  transfer that occurs only in the reaction of  $C_3H_6^+$  with  $C_7H_{14}$  and is discussed in reference [2]. Thermochemical data utilized to evaluate the exothermicity of reactions are from the work of Lias et. al [16] unless otherwise stated.

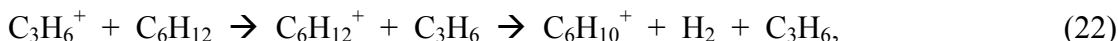
### 3.1 Charge transfer and $H^-$ transfer

Charge transfer and  $H^-$  transfer are two common reaction channels in table 1. In our previous paper on  $C_7H_{14}$ , we recognized a general relationship between the reactivities and the enthalpies of reaction for the charge transfer and hydride transfer involving  $C_7H_{14}$ : all reactions that are exothermic are observed and those reactions that are not observed are all endothermic [2]. In the current study on  $C_6H_{12}$  and  $C_8H_{16}$ , the same relationship also exists as far as the available thermochemical data are concerned. The ionization energies (IE) of  $C_6H_{12}$  and  $C_8H_{16}$  are  $9.86 \pm 0.03$  and  $9.54$  eV, respectively. For reactant ions listed in table 1, charge transfer occurs when their IEs are greater compared to the two cyclohexanes, and vice versa, except  $C_4H_3^+$  and  $C_6H_{11}^+$  which have no IE data available, and  $C_3H_6^+$ ,  $C_4H_6^+$ ,  $C_4H_8^+$ ,  $C_5H_8^+$  and  $C_6H_{10}^+$  that have some isomers with higher IEs and other isomers with lower IEs compared to the two cyclohexanes, which will be discussed in the following paragraph. Thermochemical data for  $H^-$  transfer in  $C_8H_{16}$  are not available. For  $H^-$  transfer in  $C_6H_{12}$ , the reactions are exothermic for reactant ions smaller than  $C_5H_8^+$  and are all observed to occur, with certain complications occurring for ions having possible isomers, including  $C_4H_5^+$ ,  $C_4H_6^+$  and  $C_4H_8^+$ . The situation is complicated by the fact that, for some isomers, the  $H^-$  transfer is exothermic, while for others, it is endothermic, and the experimental results can indeed be explained well by the multi-isomer kinetic model such as the one for  $C_4H_8^+$  discussed above in equations 11-14.  $C_5H_8^+$  and larger reactant ions do not undergo  $H^-$  transfer with  $C_6H_{12}$  and indeed this channel is endothermic at least for certain isomers. In summary, there exists the general occurrence of the charge transfer and hydride transfer between hydrocarbon cations and cyclohexanes, provided that they are energetically allowed; these two types of reactions are non-specific.

$C_3H_6^+$  has two isomers: chain and cyclic structures, with IE =  $9.73 \pm 0.02$  and 9.86 eV, respectively. The lack of charge transfer between  $C_3H_6^+$  and  $C_6H_{12}$  may suggest that only the chain isomer exists in the  $C_3H_6^+$  population derived from  $C_6H_{12}$ , since otherwise the cyclic isomer would have likely shown evidence of charge transfer. Among 7 isomers of  $C_4H_6^+$  listed in references [16, 22, 23], 1-butyne cation is the only one with IE greater than 9.86 eV [22, 23] and is therefore not expected to be in the  $C_4H_6^+$  population derived from  $C_6H_{12}$ , since no charge transfer is observed between  $C_4H_6^+$  and  $C_6H_{12}$ . With similar thermochemical arguments we propose that in  $C_4H_8^+$  there is no cyclobutane isomer and in  $C_5H_8^+$  there is no 1-pentyne or 3-methyl-1-butyne isomers, when either are derived from  $C_6H_{12}$ . Also noteworthy is that  $C_6H_{10}^+$ , which has not demonstrated charge transfer to any of the cyclohexanes, has 40 different isomers as listed in reference [16], and only a few of them have IE greater than 9.54 eV.

### 3.2 $H_2^-$ transfer

$H_2^-$  transfer to form  $[M-2H]^+$ , where M represents the parent molecule of the cyclohexanes, is also a common channel in table 1. It occurs only in the reactant ions that have an even number of H atoms, or in the odd-electron ions ( $C_xH_{2y}^+$ ). Possible alternative channels to form  $[M-2H]^+$  include dissociative charge or  $H^-$  transfer, but these are endothermic for certain reactant ions and thus less likely. For example, the following dissociative charge transfer,



is endothermic by 42.9 and 31 kJ/mol for the chain and cyclic isomers of  $C_3H_6^+$ , respectively, and the following dissociative  $H^-$  transfer,



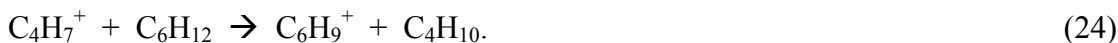
is endothermic by 334.0 and 195.7 kJ/mol for the chain and cyclic  $C_3H_6^+$ , respectively. For other reaction systems such as  $C_2H_2^+$  with  $C_6H_{12}$  the dissociative charge transfer is exothermic. However, since  $[M-2H]^+$  are common products for many odd-electron reactant ions, it is reasonable to argue that they are formed by the same channel, which should be  $H_2^-$  transfer.

It is noted that not all  $H_2^-$  transfers that are exothermic necessarily occur. For example,  $H_2^-$  transfer between  $C_2H_4^+$  and  $C_6H_{12}$  is exothermic by 118.2 kJ/mol but is not observed. In literature it has been reported that  $C_2H_4^+$  does not undergo  $H_2^-$  transfer with cyclobutane even though it is energetically allowed [24]. This may suggest that factors other than the

exothermicity of the reaction are important in determining the probability of a  $\text{H}_2^-$  transfer to occur.

### 3.3 $\text{H}_3^-$ transfer

$[\text{M-3H}]^+$  is observed only in the reactions of  $\text{C}_6\text{H}_{12}$  with  $\text{C}_4\text{H}_7^+$  and  $\text{C}_4\text{H}_5^+$ , respectively, which, in both cases, is considered most likely to be formed by  $\text{H}_3^-$  transfer, as shown below for the reaction of  $\text{C}_4\text{H}_7^+$ , for example:



A possible alternative channel to produce  $\text{C}_6\text{H}_9^+$  is via dissociative  $\text{H}^-$  transfer:



For all 6 isomers of reactant ion  $\text{C}_4\text{H}_7^+$  listed in reference [16], with exception of  $[\text{CH}_2=\text{CHCH}_2\text{CH}_2]^+$ , reaction 25 is endothermic, however. Moreover, the product ion  $\text{C}_6\text{H}_9^+$  has a different isotope distribution than its presumed intermediate precursor  $\text{C}_6\text{H}_{11}^+$ , when isotopic reagents are used: while the former approaches purely statistical distribution, the latter has bi-distribution patterns, as mentioned earlier. Therefore reaction 25 is less likely to occur. Another alternative channel to produce  $\text{C}_6\text{H}_9^+$ , via dissociative  $\text{H}_2^-$  transfer:



can be ruled out by the fact that reaction 26 is endothermic for all isomers of  $\text{C}_4\text{H}_7^+$  listed in reference [16].

For reactant ion  $\text{C}_4\text{H}_5^+$ , the dissociative  $\text{H}^-$  or  $\text{H}_2^-$  transfer can be similarly excluded on the thermochemical grounds, as far as the available thermochemical data are concerned.

$[\text{M-3H}]^+$  has been observed by Hunt *et al* as the product ion from the reaction of  $\text{NO}^+$  with saturated hydrocarbons[25]. These authors postulated that a long-lived collision complex was formed, followed by intramolecular triple hydrogen transfers and the subsequent dissociation of the complex to produce  $[\text{M-3H}]^+$ . If  $\text{H}_3^-$  transfer in our current study proceeds through a similar course of intramolecular triple hydrogen transfer, it will explain why  $[\text{M-3H}]^+$  is observed only in the reaction of  $\text{C}_6\text{H}_{12}$  with  $\text{C}_4\text{H}_5^+$  or  $\text{C}_4\text{H}_7^+$ : only these two reactions appear to have a long-lived collision complex mechanism as mentioned earlier, facilitating the multistep H transfers.

### 3.4 Hydrocarbon anion ( $C_mH_n^-$ ) transfer

Product ion  $C_5H_9^+$  is commonly observed in the reactions of  $C_8H_{16}$  with small hydrocarbon ions, considered to be a result of  $C_3H_7^-$  transfer. The analogy product ion of  $C_3H_7^-$  transfer is not observed in reactions with  $C_6H_{12}$  or  $C_7H_{14}$ , however.  $C_5H_9^+$  can be possibly formed by other channels such as  $C_3H_6$  transfer in the reaction of  $C_8H_{16}$  with  $C_2H_3^+$ ,  $CH_3$  transfer in the reaction of  $C_8H_{16}$  with  $C_4H_6^+$ , etc. However, the fact that  $C_5H_9^+$  is a common product for many different reactant ions implies a common reaction channel, which should be  $C_3H_7^-$  transfer. Other alternative channels such as dissociative charge transfer, which can also be deemed as a common channel for different reactant ions, can be examined on thermochemical grounds. Enthalpies of reaction have been calculated here for small reactant ions ranging from  $C_2H_3^+$  to  $C_3H_6^+$ . The available thermochemical data indicate that  $C_3H_7^-$  transfers are all exothermic or near thermoneutral regardless of the isomers if there are any, while dissociative charge and  $H_2^-$  transfer are, in general, endothermic, and dissociative  $H^-$  transfer is also endothermic for certain ions, such as both chain and cyclic structures of  $C_3H_6^+$ . For larger reactant ions, using thermochemical data is hindered by the fact that there are many structural isomers for each reactant or product ions, with  $C_3H_7^-$  transfer being exothermic for some and endothermic for others, and by the fact that there is often a lack of the thermochemical data for species involved. Nonetheless, if we assume that  $C_5H_9^+$  as the common product is created by the same reaction mechanism for small and large reactant ions, the mechanism should be  $C_3H_7^-$  transfer.

$CH_3^-$  transfers are observed from reactions of  $C_2H_2^+$  with  $C_6H_{12}$ ,  $C_2H_4^+$  with  $C_7H_{14}$ , and  $C_4H_7^+$  with  $C_8H_{16}$ . They are all energetically allowed, regardless of the isomers of the reactant ions. Possible alternative channels include dissociative charge,  $H^-$  or  $H_2^-$  transfer, but they are all endothermic except for the dissociative charge transfer between  $C_2H_2^+$  and  $C_6H_{12}$  when certain isomers of the product ion  $C_5H_9^+$  are concerned.

Other hydrocarbon anion transfers listed in table 1 are not common; there is only one occurrence of each in the table. For the reaction of  $C_2H_2^+$  with  $C_6H_{12}$  producing  $C_4H_8^+$ , we propose the  $C_2H_4^-$  transfer, which is exothermic regardless of the isomers of the products. The alternative channels, dissociative  $H^-$  transfer that is endothermic for all possible isomers, and charge or  $H_2^-$  transfer that are endothermic for some of the isomers, are therefore less favored. The similar discussion can be applied to the reaction of  $C_3H_6^+$  with  $C_8H_{16}$  producing  $C_6H_{10}^+$  that we consider to be  $C_2H_6^-$  transfer. For the reaction of  $C_4H_7^+$  with  $C_6H_{12}$  producing  $C_4H_9^+$ , we

propose a  $C_2H_3^-$  transfer because it is exothermic at least for some isomers while the alternative channels of charge,  $H^-$  or  $H_2^-$  transfer are all endothermic regardless of the isomers. The reaction of  $C_4H_7^+$  with  $C_6H_{12}$  needs to be given special consideration, however, because of its distinguishing isotope distribution in the product ion, which cannot rule out the possibility of  $H_2$  transfer from  $C_6H_{12}$  to  $C_4H_7^+$  to produce  $C_4H_9^+$ .  $H_2$  transfer from certain hydrocarbon cations to certain hydrocarbon neutrals have been proposed by Abramson *et al* [26] and Ausloos *et al* [27] respectively, to explain the observed product ions in their experiments. As mentioned earlier, the reaction of  $C_4H_7^+$  with  $C_6H_{12}$  producing  $C_4H_9^+$  is believed to be via the formation of a long-lived ion-neutral complex. The subsequent dissociation of the complex to form the products can take place in different ways that can be effectively envisioned as  $C_2H_3^-$  transfer,  $H_2$  transfer or other transfers. To properly address this issue, a more in depth investigation using isotope reagents including  $^{13}C$  compounds is needed. Since  $C_2H_3^-$  transfer,  $H_2$  transfer or other transfers result in the same neutral product (the same molecular formula), we simply label the reaction channel as  $C_2H_3^-$  transfer.

### 3.5 Association

Association with concerted fragmentation is observed only in the reactions of  $C_4H_7^+$  or  $C_4H_5^+$  with  $C_6H_{12}$ , proceeding through the formation of a long-lived collision complex as evidenced by the H scrambling in the product ions mentioned earlier:



Reaction 27 is exothermic for many combinations of isomers of  $C_4H_7^+$ ,  $C_7H_{13}^+$  and  $C_3H_6$ . The product  $C_7H_{11}^+$  in reaction 28 has data of heat of formation available only for one isomer, which is a multiple-ring cyclic structure [16]. Assuming this structure for  $C_7H_{11}^+$ , we find reaction 28 to be exothermic for all combinations of isomers of  $C_4H_5^+$  and  $C_3H_6$  listed in reference 16.

## 4. Summary

We have studied gas-phase ion-molecule reactions of selected hydrocarbon cations derived from  $C_6H_{12}$ ,  $C_7H_{14}$  and  $C_8H_{16}$ , respectively, with their parent molecules. Some general trends in the reaction rates are observed: smaller reactant ions tend to exhibit faster reaction rates, and odd-electron ions react faster than the even-electron ions. Reaction channels include

charge transfer, H<sup>-</sup> transfer, H<sub>2</sub><sup>-</sup> transfer, H<sub>3</sub><sup>-</sup> transfer, hydrocarbon anion transfer, and association with concerted fragmentation, which are assigned to each observed product ions based on the isotopic reaction results, the thermochemical data to evaluate the enthalpies of reaction, and other arguments. The assignment of the channels is for the purpose of identifying the neutral products, which are not directly detected; the actual reaction mechanisms may be more complicated than the names of the reaction channels imply. Among these channels, H<sup>-</sup> transfer is the most important, and to many reacting ions, it is the exclusive channel.

Kinetic data of certain reactions show non-single-exponential decay of the reactant ion, which is ascribed to the existence of multiple isomers of the reactant ion that have different reactivities. In some cases, one (or more) isomer is unreactive while others are reacted away, which is consistent with the thermochemical data indicating the exothermicities for the different isomers.

Results of isotopic reactions of the hydrocarbon ions with C<sub>6</sub>H<sub>12</sub> and C<sub>7</sub>H<sub>14</sub> suggest that all reactions take place in a direct mode, except the reactions of C<sub>4</sub>H<sub>5</sub><sup>+</sup> or C<sub>4</sub>H<sub>7</sub><sup>+</sup> with C<sub>6</sub>H<sub>12</sub>. Certain channels in the reactions of C<sub>4</sub>H<sub>5</sub><sup>+</sup> or C<sub>4</sub>H<sub>7</sub><sup>+</sup> with C<sub>6</sub>H<sub>12</sub> proceed via the formation of a long-lived ion-molecule complex, in which significant rearrangement occurs, yielding final products exhibiting H scrambling behavior.

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