Isomer effect on ionization processes in collisions of 6-MeV/amu bare ions with C$_3$H$_6$ molecules

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Abstract. Gross and partial ionization cross sections for C$_3$H$_6$ isomers, propene and cyclopropane, have been measured under impact of 6 MeV/amu fully stripped ions with charge state $q=1, 2, 6, 10, \text{and } 18$. The gross ionization cross sections have been found to depend weakly on the projectile charge $q$ compared with the $q^2$ dependence, especially for highly-charged projectiles. The cross sections for cyclopropane have been found to be slightly larger than those for propene in all projectiles studied. The most prominent product was parent C$_3$H$_6^+$ ions in cyclopropane, whereas C$_3$H$_5^+$ ion dominated C$_3$H$_6^+$ ion in propene, indicating an isomer effect on fragmentation processes. Mechanisms relevant to the production of fragmented ions are also discussed.

1. Introduction
Collision processes involving hydrocarbon molecules are known to be important in a number of applications such as material, plasma, astrochemical, and medical sciences. We have been studying ionization of small hydrocarbons in 6-MeV/amu fully stripped-ion impact through measurements of absolute cross sections and relative intensities of individual secondary ions. For hydrocarbons, as the number of carbon atoms increases, the number of isomers tends to increase. It has been recognized that isomers show apparent differences in various physical and chemical properties. In the present study, the target was chosen to be C$_3$H$_6$ isomers, cyclopropane (denoted by (CH$_2$)$_3$) and propene C$_3$H$_6$, to study the effect of molecular structure on the ionization and fragmentation processes under energetic heavy ion impact.

2. Experimental method
The experiment was carried out using the 6-MeV/amu-H$^+$, -He$^{2+}$, -C$_6^+$, -Ne$^{10+}$, and -Ar$^{18+}$ projectiles provided by the Heavy Ion Medical Accelerator in Chiba (HIMAC) of the National Institute of Radiological Sciences (NIRS). The absolute values of gross ionization cross sections were measured using the parallel-plate-condenser method, detail of which was described in a previous paper [1]. The systematic uncertainties in the gross ionization cross section were estimated to be 8.7%, and the statistical error was within 1.2%. The mass/charge spectra of secondary ions were measured using a double-focusing sector magnet [2].

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3. Results and discussion

3.1 Ionization cross section

The measured gross ionization cross sections are listed in table 1. To illustrate how the cross sections depend on the projectile charge $q$, they were plotted as a function of $q$ in figure 1.

|           | H$^+$ | He$^{2+}$ | C$^{6+}$ | Ne$^{10+}$ | Ar$^{18+}$ |
|-----------|-------|-----------|----------|------------|------------|
| C$_3$H$_6$ | 0.956 | 3.77      | 30.2     | 71.3       | 179        |
| (CH$_2$)$_3$ | 0.993 | 3.88      | 31.1     | 72.7       | 183        |

As can be seen, the cross sections for H$^+$ and He$^{2+}$ projectiles are well on a line showing $q^2$ dependence, indicating validity of the perturbation treatment such as first Born approximation for light projectiles. On the other hand, in higher charge projectiles such as Ne$^{10+}$ and Ar$^{18+}$, the cross sections are considerably smaller than those predicted by the $q^2$ dependence. This causes that the cross sections for these molecules are about 40% smaller than the prediction from $q^2$ dependence under Ar$^{18+}$ impact, indicating failure of the first Born approximation for high charge projectiles even in the present collision energy of 6 MeV/amu.

![Cross section graph](image)

**Figure 1.** Projectile charge $q$ dependence of gross ionization cross sections for propene C$_3$H$_6$ and cyclopropane (CH$_2$)$_3$.

In table 1 we can also note that the cross sections of cyclopropane are 2-3% larger than those of propene for all projectiles studied here. On the contrary, the electron impact experiments for C$_3$H$_6$ isomers showed that the cross sections of propene were larger than those of cyclopropane by 2-4% in the energy range between 10 and 3000 eV [3]. The cause of such differences might be explained by the deviation from the first Born approximation. For impact of fast projectiles, perturbation theory is valid, and the cross section for a specified process can be written as a Born series,

$$
\sigma = a_1(V_p)q^2 + a_2(V_p)q^3 + a_3(V_p)q^4 + \ldots \ldots ,
$$

where $q$ is the projectile charge and $V_p$ the projectile velocity. At very high velocity, the cross section is given to high accuracy by the first term. It is proportional to $q^2$ and independent of projectile mass and sign ($\pm$) of charge as well. The second term might be responsible for the difference between ion
and electron impact.

3.2 Mass/charge spectra of recoil ions
Mass/charge spectra of recoiled ions were measured under He$^{2+}$, C$^{6+}$, and Ar$^{18+}$ collisions. Figure 2 shows the recoil ion spectra for propene and cyclopropane in Ar$^{18+}$ ion impact. It should be noted that the most prominent peak is the parent molecular (CH$_2$)$_3$ ion in cyclopropane, whereas C$_3$H$_6^+$ ion predominates C$_3$H$_5^+$ in propene, indicating an isomer effect in fragmentation. Doubly charged molecular ions such as C$_3$H$_6^{2+}$, C$_3$H$_5^{2+}$, C$_3$H$_4^{2+}$ and C$_3$H$_3^{2+}$ are found to be appreciably produced in these molecules. The apparent peak shift appearing in the left panel is mainly due to a hysteresis of the analyzing magnet used in the present experiment.

![Figure 2](image.png)

**Figure 2.** Mass/charge spectra for (CH$_2$)$_3$ and C$_3$H$_6$ molecules in Ar$^{18+}$ impact

3.3 Partial ionization cross sections
From the measured ionization cross sections and relative intensities of recoil ions, we can calculate partial ionization cross sections for individual ion species. The obtained partial cross sections for (CH$_2$)$_3$ target are plotted as a function of charge $q$ in figure 3.

![Figure 3](image.png)

**Figure 3.** Partial ionization cross sections for cyclopropane as a function of projectile charge $q
The charge dependence of cross sections could be divided tentatively into two groups. As shown in the left panel of figure 3, one consists of parent (CH$_2$)$_3^+$ ion and fragmented C$_3$H$_5^+$, C$_3$H$_5^+$, C$_3$H$_6^+$, and C$_2$H$_7^+$ ions, charge dependence of which is quite similar to the gross ionization cross sections and slightly weak compared with the $q^2$ dependence, indicating that they are mainly produced through distant collisions. Moreover, the intensity ratios of fragmented ions to parent (CH$_2$)$_3^+$ ion were independent of $q$ within experimental error. This result suggests that these fragments are mainly produced through two-step processes as described by the quasiequilibrium theory (QET) by Rosenstock [4]: An excited state molecular (CH$_2$)$_3^*$ ion is first produced in the ion impact, and this ion then fragments statistically with a fragmentation pattern which depend only on the internal energy of the excited (CH$_2$)$_3^*$ ion.

As the right panel of figure 3 shows, in highly fragmented ions such as C$_3$H$_5^+$, C$_3$H$_7^+$, C$_5$H$_7^+$, CH$_3$+ and so on, cross sections show charge dependence steeper than $q^2$, indicating that intimate collisions might take part in their production. In addition, the intensity ratios of these ions to parent (CH$_2$)$_3^+$ ion were found to change considerably with projectile charge $q$. In production of such highly fragmented ions, multiple ionization, which would yield immediate dissociation of molecular ion, might contribute to considerable extent. Multiply charged C$_2^{2+}$ and C$_3^{+}$ ions were also detected with remarkable cross sections of $10^{-17} \sim 10^{-18}$ cm$^2$ in the Ar$^{18+}$ impact. Quite similar results have also been obtained in propene molecule.

4. Summary

Gross ionization cross sections for C$_3$H$_6$ and (CH$_2$)$_3$ molecule in collision of 6-MeV/amu-H$^+$, -He$^{2+}$, -C$^{6+}$, -Ne$^{10+}$, and -Ar$^{18+}$ ions were found to depend weakly on the projectile charge $q$ compared with the $q^2$ dependence predicted by the first Born approximation. The cross sections for cyclopropane in ring shape was found to be slightly larger than those for propene, in contrast to the electron impact ionization, in which cross sections were reported to be larger in propene. These results might indicate the failure of the first Born approximation for high charge projectiles even in the present collision energy. The mass/charge spectra of recoil ions showed that the most prominent product was fragmented C$_3$H$_5^+$ ion in propene target, while C$_3$H$_6^+$ ion dominated C$_3$H$_5^+$ in cyclopropane, indicating an isomer effect in fragmentation. Deviation from quasiequilibrium theory was observed in production of highly fragmented ions.

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