# Chemical Ionization of 1-Olefins ($C_{15}$–$C_{18}$) by $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ in an Ion-Trap Type of Mass Spectrometer

Masaharu Tsuji,* Yuki Tanaka,[†] Takeshi Arikawa,[†] and Yukio Nishimura
*Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816-8580*
[†]*Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580*

(Received April 13, 2000; CL-000352)

Chemical ionization of 1-olefins (1-$C_xH_{2x}$: x = 15–18) by the $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ ions has been studied using an ion-trap type of GC/MS under a reactant-ion-selected mode. In all the reactions, $C_yH_{2y+1}^+$ (y = 3–x) alkyl and $C_yH_{2y-1}^+$ (y = 3–x) alkenyl ions were observed with maximum intensities at y = 3–5 for $C_yH_{2y+1}^+$ and at y=7 or 8 for $C_yH_{2y-1}^+$.

---

Chemical ionization (CI) mass spectra in a methane atmosphere provide valuable information on the reactivity of carbocations in the gas phase. Field[1] measured $CH_4$ CI mass spectra of 1-olefins (1-$C_xH_{2x}$: x = 6–10, 12, 16, 20) at a $CH_4$ pressure of 1 Torr (= 133 Pa), where dominant reactant ions were $CH_5^+$ (48%), $C_2H_5^+$ (40%), and $C_3H_5^+$ (6%). He has found that straight-chain 1-olefins undergo extensive fragmentation to produce the spectra consisting of series of $C_yH_{2y+1}^+$ (y = 3–x) alkyl and $C_yH_{2y-1}^+$ (y = 4–x) alkenyl ions. He has reported that the attack of the reactant ions on the olefin molecules occurs predominantly at the double bonds. Since CI mass spectra of 1-olefins were measured without selecting each reactant ion, the relative contribution of the major $CH_5^+$ (48%) and $C_2H_5^+$ (40%) ions to the formation of alkyl and alkenyl ions was not studied.

This study is the first measurements of $CH_4$ CI mass spectra of 1-olefins (1-$C_xH_{2x}$: x = 15–18) by selecting reactant $CH_5^+$, $C_2H_5^+$, or $C_3H_5^+$ ion in an ion-trap type of GC/MS. The dependence of product–ion distributions on the reaction time was measured in order to examine the effects of collisional stabilization. The reactivity of $C_nH_5^+$ (n = 1–3) for 1-$C_xH_{2x}$ (x = 15–18) was discussed from the product–ion distributions.

$CH_4$ CI mass spectra were obtained using a Hitachi M7200 GC/MS under a reactant-ion-selected mode. The partial pressures of CI source $CH_4$ gas and carrier He gas in the ion-trap cell were $7 \times 10^{-5}$ and $5 \times 10^{-5}$ Torr, respectively. The time for storing a selected reactant ion was 5 ms and the reaction time between the reactant ion and 1-$C_xH_{2x}$ was varied in the 0.2–50 ms region. The total number of collisions of a product ion with $CH_4$ and He was about 0.5–120 times during these reaction times. These values were smaller than 200 times in the medium-pressure CI experiments of Field[1] during a residence time of $10^{-5}$ s at a $CH_4$ gas pressure of 1 Torr.

CI mass spectra of 1-$C_xH_{2x}$ (x = 15–18) by the $C_nH_5^+$ (n = 1–3) ions consisted of $C_yH_{2y+1}^+$ (y = 3–x) alkyl and $C_yH_{2y-1}^+$ (y = 3–x) alkenyl ions. This result indicates that all the three reactant ions participate in the formation of alkyl and alkenyl ions. The intensity distributions of $C_yH_{2y+1}^+$ and $C_yH_{2y-1}^+$ depended on the reaction time. The maximum of the product distributions of alkyl and alkenyl ions shifted to low *m/z* value with decreasing the reaction time, though the peak shifts were small below 2 ms for the alkenyl ions. On the basis of this finding, we conclude that collisional stabilization takes part in the formation of alkyl and alkenyl ions at long reaction times. The initial branching ratios of each product ion were determined by extrapolating the intensity distributions to zero reaction time.

Figures 1(a)–1(f) show the initial branching ratios of $C_yH_{2y+1}^+$ and $C_yH_{2y-1}^+$ (y ≤ x) ions in the reactions of $C_nH_5^+$ (n = 1–3) with $C_xH_{2x}$ (x = 15–18). The intensity distributions of $C_yH_{2y+1}^+$ and $C_yH_{2y-1}^+$ are essentially independent of $C_x$ in the x = 15–18 range. In the $CH_5^+$ reactions, the $C_yH_{2y+1}^+$ distribution peaks at y = 5, and rapidly decreases with increasing *m/z*. The $C_yH_{2y-1}^+$ distribution is narrower than the $C_yH_{2y+1}^+$ one, having a sharp peak at y = 7. In the $C_2H_5^+$ reactions, the $C_yH_{2y+1}^+$ distribution peaks at y = 4, decreases more slowly than that in the $CH_5^+$ reactions with increasing *m/z*, and increases again for the largest $C_xH_{2x+1}^+$ ion. The $C_yH_{2y-1}^+$ distribution is bimodal with peaks at y = 4 and 7. The $C_yH_{2y+1}^+$ distribution in the $C_3H_5^+$ reactions is similar to that in the $C_2H_5^+$ reactions, except for a small shift of the peak position from y = 4 to 3. The $C_yH_{2y-1}^+$ distribution in the $C_3H_5^+$ reactions is also similar to that in the $C_2H_5^+$ reactions, though the second peak at y = 3 or 4 is more pronounced.

Field[1] measured $CH_4$ CI mass spectrum of 1-$C_{16}H_{32}$ without separating the reactant ions. The intensity distributions of $C_yH_{2y+1}^+$ and $C_yH_{2y-1}^+$ in his spectra were similar to those observed here in the $C_2H_5^+$/1-$C_{16}H_{32}$ reactions, except for the appearance of a relatively strong $C_{16}H_{31}^+$ peak and the lack of the second $C_yH_{2y-1}^+$ peak at y = 3 or 4. It is therefore reasonable to assume that responsible reactant ion for the formation of product ions was $C_2H_5^+$ in his CI measurement.

The maximum and average kinetic energies of reactant ions in our apparatus were evaluated to be 10 and 4.2 eV for $CH_5^+$, 6.0 and 2.4 eV for $C_2H_5^+$, and 4.3 and 1.7 eV for $C_3H_5^+$, respectively, using a pseudo-potential well method.[2] These energies are higher than those in the medium-pressure CI experiments of Field,[1] which were estimated to be less than 1 eV.[3] The extent of fragmentation in the $C_2H_5^+$/1-$C_{16}H_{32}$ reaction is slightly higher than that observed by Field.[1] This is explained by the higher kinetic energies and the lack of collisional stabilization at short reaction times in our experiments.

The following general tendencies are obtained from Figures 1(a)–1(f). The largest $C_xH_{2x+1}^+$ alkyl ions, produced by protonation of parent $C_xH_{2x}$ molecules, are observed in all the three reactions, and their branching ratios in the $C_2H_5^+$ and $C_3H_5^+$ reactions are larger than those in the $CH_5^+$ ones. The peak of the $C_yH_{2y+1}^+$ distribution shifts from y = 5 to 3 as the reactant ion changes from $CH_5^+$ to $C_3H_5^+$. The branching ratios of large $C_yH_{2y+1}^+$ (y ≥ 9) ions in the $CH_5^+$ reactions are smaller than those in the $C_2H_5^+$ and $C_3H_5^+$ ones. The branching ratios of the largest $C_xH_{2x-1}^+$ alkenyl ions are either zero or very small in all the three reactions. The most favorable alkenyl ion was $C_7H_{13}^+$ in almost all the reactions.

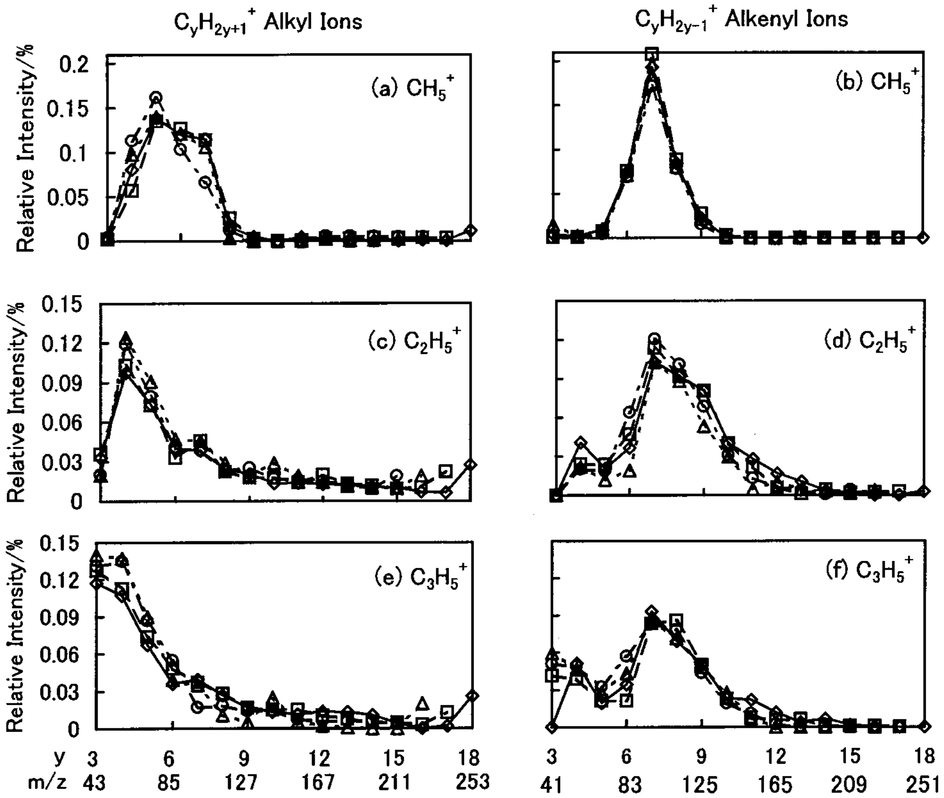

**Figure 1.** Intensity distributions of $C_yH_{2y+1}^+$ and $C_yH_{2y-1}^+$ in the $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ reactions. ◇:$C_{18}H_{36}$, □:$C_{17}H_{34}$, △:$C_{16}H_{32}$, ○:$C_{15}H_{30}$.

A second peak at y = 3 or 4 appears in the $C_2H_5^+$ and $C_3H_5^+$ reactions, and it is more prominent in the $C_3H_5^+$ reactions. The branching ratios of large $C_yH_{2y-1}^+$ ($y \geq 9$) ions in the $CH_5^+$ reactions are smaller than those in the $C_2H_5^+$ and $C_3H_5^+$ ones.

The $\Sigma\ I(C_yH_{2y+1}^+)/\Sigma\ I(C_yH_{2y-1}^+)$ ratios for $y \leq x$ in the $CH_5^+$, $C_2H_5^+$, or $C_3H_5^+$ reactions, which were essentially independent of $C_x$ (x = 15–18), were determined to be 1.3 ± 0.1, 1.1 ± 0.3, and 1.3 ± 0.1, respectively. This shows that reaction pathways leading to alkyl ions are slightly more favorable than those leading to alkenyl ions in all the three reactions.

Various reaction mechanisms leading to alkyl and alkenyl ions have been proposed.[1] The alkyl ions are expected to be produced through the proton transfer followed by $C_{x-y}H_{2(x-y)}$ elimination in the $C_nH_5^+$ (n = 1–3) reactions:

$$C_nH_5^+ + C_xH_{2x} \xrightarrow{-C_nH_4} C_xH_{2x+1}^+ \rightarrow C_yH_{2y+1}^+ + C_{x-y}H_{2(x-y)} \qquad (1)$$

On the other hand, possible formation processes of alkenyl ions are proton transfer followed by $H_2$ and $C_{x-y}H_{2(x-y)}$ elimination in the $CH_5^+$ reactions and abstraction of a hydride or alkide ion from olefins in the $C_nH_5^+$ (n = 2, 3) reactions:

$$CH_5^+ + C_xH_{2x} \xrightarrow{-CH_4} C_xH_{2x+1}^+ \rightarrow C_xH_{2x-1}^+ + H_2 \qquad (2a)$$

$$C_xH_{2x-1}^+ \rightarrow C_yH_{2y-1}^+ + C_{x-y}H_{2(x-y)} \qquad (2b)$$

$$C_nH_5^+ + C_xH_{2x} \xrightarrow{-C_nH_6} C_xH_{2x-1}^+ \rightarrow C_yH_{2y-1}^+ + C_{x-y}H_{2(x-y)} \qquad (3)$$

$$C_nH_5^+ + C_xH_{2x} \rightarrow C_yH_{2y-1}^+ + C_{n+x-y}H_{2(x-y+3)} \qquad (4)$$

The most favorable alkyl and alkenyl ions are nearly the same for x = 15–18, indicating that the dissociation of carbon chain occurs with the highest probability at the same position from the terminal. Since the proton affinity of $CH_4$ (5.7 eV) is smaller than those of $C_2H_4$ (7.1 eV) and $C_3H_4$ (8.0 eV),[4] more excess energies are released in the $CH_5^+$ reactions. This will be a major reason for the small branching ratios of large alkyl and alkenyl ions ($y \geq 9$) in the $CH_5^+$ reactions. Although the formation process of alkenyl ions in the $CH_5^+$ reactions is different from those in the $C_2H_5^+$ and $C_3H_5^+$ ones, the $\Sigma\ I(C_yH_{2y+1}^+)/\Sigma\ I(C_yH_{2y-1}^+)$ ratios were found to be similar among the three reactions. Further studies, including energy calculations of various reaction pathways, are in progress in order to explain this finding.

## References

1 F. H. Field, *J. Am. Chem. Soc.*, **90**, 5649 (1968).

2 J. F. J. Todd, R. M. Waldren, and R. F. Bonner, *Int. J. Mass Spectrom. Ion Phys.*, **34**, 17 (1980).

3 C. Chang, G. G. Meisels, and J. A. Taylor, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 411 (1973).

4 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data*, **17**, Suppl. 1 (1988).