

Mass-Spectrometric Study on Ion-Molecule Reactions of CH_5^+ , C_2H_5^+ , and C_3H_5^+ with $\text{C}_8\sim\text{C}_{18}$ 1-Alkynes in an Ion Trap

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Chemical ionization of 1-alkynes ($\text{C}_x\text{H}_{2x-2}$; $x = 8\sim 18$) by the CH_5^+ , C_2H_5^+ , and C_3H_5^+ ions has been studied under a reactant-ion selective mode of an ion-trap type of GC/MS. Although no peaks corresponding to $[\text{MW} + \text{H}]^+$, $[\text{MW} - \text{H}]^+$, $[\text{MW} + \text{C}_2\text{H}_5]^+$, $[\text{MW} + \text{C}_3\text{H}_5]^+$ ions were detected, fragment alkenyl $\text{C}_y\text{H}_{2y-1}^+$ ($y \geq 4$) and alkynyl $\text{C}_y\text{H}_{2y-3}^+$ ($y \geq 4$) ions were observed. Their initial product-ion distributions were determined by extrapolating the dependence of relative intensities of $\text{C}_y\text{H}_{2y-1}^+$ and $\text{C}_y\text{H}_{2y-3}^+$ ions on the reaction time to zero reaction time. In the CH_5^+ , C_2H_5^+ , and C_3H_5^+ reactions, the initial $\text{C}_y\text{H}_{2y-1}^+$ ion distributions had peak at $y = 4$ and decrease with increasing y , whereas the initial $\text{C}_y\text{H}_{2y-3}^+$ ion distributions gave broad peaks in the $y = 5\sim 10$ range. On the basis of observed initial distributions and calculated thermochemical data, reaction mechanisms for the formation of alkenyl $\text{C}_y\text{H}_{2y-1}^+$ and alkynyl $\text{C}_y\text{H}_{2y-3}^+$ ions were discussed. In almost all reactions, total intensities of $\text{C}_y\text{H}_{2y-1}^+$ ions were larger than those of $\text{C}_y\text{H}_{2y-3}^+$ ions, indicating that proton transfer reactions are more favorable than hydride-ion abstraction reactions.

Key words: Chemical ionization, Hydrocarbon ions, 1-Alkynes, Alkenyl ions, Alkynyl ions, Ion trap type GC/MS, Collisional stabilization

1. Introduction

The gas phase ion-molecule reactions in a methane atmosphere have been studied for many reagent molecules since the first chemical ionization (CI) mass spectrometric measurements by Field *et al.*¹⁻⁵⁾ about 60 years ago. Now CH_4 CI mass spectrometry has been established as a standard soft-ionization method for the determination of molecular weight (MW) and molecular structure of reagent molecules. Field measured CH_4 CI mass spectra at a medium CH_4 pressure of 1 Torr (= 133.33 Pa), where dominant reactant ions were CH_5^+ (48%), C_2H_5^+ (40%), and C_3H_5^+ (6%).⁶⁾ In their CH_4 CI experiments, these reactant hydrocarbon ions have not been

selected, because the most important information on $[\text{MW} + \text{H}]^+$ can be easily obtained from proton transfer reactions between a mixture of these hydrocarbon ions and reagent molecules without selecting hydrocarbon ions.

Low-pressure chemical ionization in ion trap mass spectrometry is a new powerful tool for the study on the reactivity of each reactant ion.⁷⁾ By using a reactant-ion selective CI mode of an ion-trap type of GC/MS, we have made a systematic mass spectrometric study on ion-molecule reactions of CH_5^+ , C_2H_5^+ and C_3H_5^+ ions with many organic molecules such as monosubstituted benzenes, and $\text{C}_8\sim\text{C}_{18}$ *n*-paraffins 1-olefins, and alcohols.⁸⁻²¹⁾ 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),²²⁾ more excess energies are released in the CH_5^+ reactions. In a general way, CH_5^+ ions exclusively induce proton transfer and dissociative proton transfer; this can be explained by the instability of the $[\text{M} + \text{CH}_5]^+$ adduct ion. The formation of $[\text{M} + \text{C}_2\text{H}_5]^+$ and $[\text{M} + \text{C}_3\text{H}_5]^+$ adduct ions in the C_2H_5^+ and C_3H_5^+

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reactions is assumed to result from radiative association.

In our previous study on $C_8\sim C_{18}$ *n*-paraffins (C_xH_{2x+2}),¹⁵⁾ major product ions were parent alkyl ($MW - 1, = C_xH_{2x+1}^+$) ions and fragment alkyl $C_yH_{2y+1}^+$ ($y = 3 \sim x-3$) ions. In this work, symbol x represents the total number of carbons in reagent hydrocarbons, while symbol y stands for the total number of carbons in fragment alkyl, alkenyl, and alkynyl ions. Major product ions from 1-olefins (C_xH_{2x}) with a $C=C$ double bond were fragment alkyl $C_yH_{2y+1}^+$ ($y = 3\sim x$) and alkenyl $C_yH_{2y-1}^+$ ($y = 3\sim x$) ions.¹⁶⁾

For 1-alkynes with a $C\equiv C$ triple bond, CH_4 CI mass study has been carried out by Field²³⁾ on C_6 and C_8 1-alkynes at a medium CH_4 pressure of 1 Torr. The spectra consisted of alkenyl $C_yH_{2y-1}^+$ ($y = 4\sim x$) and alkynyl $C_yH_{2y-3}^+$ ($y = 4\sim x$) ions. Since the reactant hydrocarbon ions have not been separated in their CI study, the reactivity of each hydrocarbon ion has not been determined.

In this study, CH_4 CI mass spectra of a series of 1-alkynes (C_xH_{2x-2} : $x = 8\sim 18$) by the CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ ions are measured by using an ion-trap type of GC/MS under a reactant-ion selective mode. The dependence of product-ion distributions on the reaction time was measured in order to examine the effects of collisional stabilization. The reactivity of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ for $C_8\sim C_{18}$ 1-alkynes was discussed from the initial product-ion distributions and thermochemical data for each reaction. The results obtained were compared with our previous results for 1-olefins.¹⁶⁾

2. Experimental

CI mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS under a reactant-ion selective mode. The CI CH_4 gas was introduced directly in a trap cell. The electron-impact ionization on CH_4 provides primary CH_n^+ ($n = 2\sim 4$) ions. One of the reactant CH_n^+ , $C_2H_5^+$, and $C_3H_5^+$ ions produced from the subsequent fast ion-molecule reactions of CH_n^+ ($n = 2\sim 4$) with CH_4 was selectively trapped as a reactant ion in an ion-trap cell. The time for storing a reactant ion was kept at a constant time of 5 ms. If reactant ions in vibrationally excited levels are formed, they will be thermalized by collisions with CH_4 and He during their trapping time in the cell. The ion-trap cell was kept at ≤ 170 °C. The reagents purchased from Tokyo Chemical Industry Co., Ltd. were diluted in hexane, which has a much shorter retention time than those of 1-alkynes,

and injected into the GC with a high-purity carrier He gas. The partial pressures of CH_4 and He and in an ion-trap cell were 7×10^{-5} and 5×10^{-5} Torr, respectively. The reaction time corresponding to the residence time in the ion-trap was varied from 0.5 to 40 ms. The mass spectra were measured at low reagent concentrations of about $1000\sim 10000$ pg cm^{-3} in order to reduce secondary ion-molecule reactions.

The operating conditions in the ion-trap cell used in this work were significantly different from those of the conventional medium-pressure CI mass spectrometer developed by Field *et al.*¹⁻⁶⁾ In the medium-pressure CI measurements, the typical CH_4 gas pressure was 1 Torr and the residence time of reactant ions in the ionization-reaction chamber was about 10 μs . Field⁴⁾ evaluated the total number of collisions of reactant ions with CH_4 during this residence time to be about 200. In the present low-pressure CI measurements, the total number of collisions of a product ion with CH_4 was estimated to be about 1~100 times within the reaction time of 0.5~40 ms from a simple gas-kinetic hard-sphere collision model. CI mass spectra were measured under the conditions, where concentrations of reactant ions were much higher than those of product ions. Therefore, it was difficult to determine rate constants from plots of a decay of a reactant ion against the reaction time or the concentration of a reagent.

3. Results and discussion

3.1 CI mass spectrum and effects of collisional stabilization

For example, Fig. 1 shows mass spectrum obtained from the $C_2H_5^+/1-C_{15}H_{28}$ reaction,

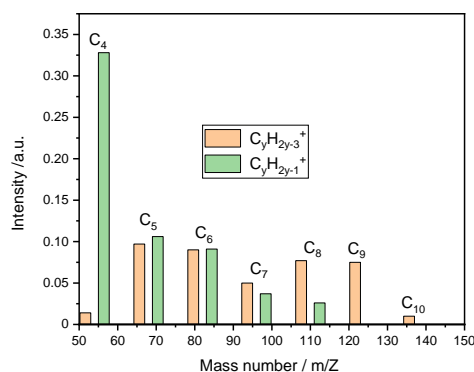
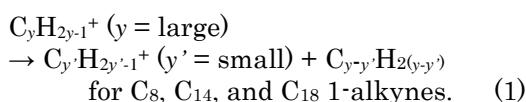


Fig. 1. CI mass spectrum obtained from the $C_2H_5^+/1-C_{15}H_{28}$ reaction.

where alkenyl $C_yH_{2y-1}^+$ ($y = 4\sim 8$) and alkynyl $C_yH_{2y-3}^+$ ($y = 4\sim 10$) ions are observed. For the $C_yH_{2y-1}^+$ ions, C_4 peak is strongest and then the intensity rapidly decreases with increasing the mass number. On the other hand, a broad intensity distribution is observed for the $C_yH_{2y-3}^+$ ions in the $C_5\sim C_9$ region. When CI mass spectra resulting from ion-molecule reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with 1-alkynes (C_xH_{2x-2} ; $x = 8\sim 18$) were observed, similar alkenyl $C_yH_{2y-1}^+$ ($y \geq 4$) and alkynyl $C_yH_{2y-3}^+$ ($y \geq 4$) ions were observed in all cases. No peaks corresponding to $[MW + H]^+$, $[MW - H]^+$, $[MW + C_2H_5]^+$, $[MW + C_3H_5]^+$ ions are detected, indicating that it is difficult to determine MW values of 1-alkynes using CH_4 CI mass spectrometry at low pressures.

If the collisional stabilization takes part in the formation of product ions, excess energy released in the reaction is partly relaxed by collisions with CH_4 and He gases. Therefore, fragmentation will be suppressed in CI mass spectra obtained at long reaction times. In order to examine the contribution of collisional stabilization in our CI conditions, the dependence of product-ion distributions on the reaction time was measured. As typical results for short, medium, and long carbon chain 1-alkynes used in this work, Figs. 2A and 2B show product-ion distributions of $C_yH_{2y-1}^+$ ($y = 4\sim x$) and $C_yH_{2y-3}^+$ ($y = 4\sim x$) in the reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with C_8 , C_{14} , and C_{18} 1-alkynes at five different reaction times: 0.5, 2, 10, 20, and 40 ms, respectively. The decreases or increases in the product-ion distributions with increasing the reaction time are shown by arrows in Figs. 2A and 2B. In many cases, the product-ion distributions of small $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ ions decrease, while those of large ones increase with increasing the reaction time. These results suggest that large ions are often stabilized by collisions with CH_4 and He gases in our conditions. Without collisional stabilization at short reaction times, secondary fragmentation from large $C_yH_{2y-1}^+$ ions to small $C_{y'}H_{2y'-1}^+$ ions occurs.



The initial product-ion distributions were determined by extrapolating the dependence of relative intensities of $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ ions on the reaction time to zero reaction time, as is shown for the case of the $CH_5^+/1\cdot C_{16}H_{30}$

reaction in Figs. 3A and 3B. The uncertainties of the initial branching-ratios were estimated to be within $\pm 8\%$ in most cases.

3.2 Initial Distributions of alkenyl $C_yH_{2y-1}^+$ and alkynyl $C_yH_{2y-3}^+$ ions

Figures 4A(a)-(i) show initial product-ion distributions of alkenyl $C_yH_{2y-1}^+$ ($y = 4\sim x$) ions obtained for short ($x = 8\sim 11$), medium ($x = 12\sim 14$), and long ($x = 15\sim 18$) carbon chain reagents. In all the reactions, no long chain $C_yH_{2y-1}^+$ alkenyl ions ($y > 10$) are formed. In the CH_5^+ reactions, the intensity distributions of $C_yH_{2y-1}^+$ ions peak at $y = 4$ and then rapidly decrease with increasing y in all cases except for $C_{10}\sim C_{14}$ reagents, for which second peaks are observed at $y = 7$ and/or $y = 10$. In the $C_2H_5^+$ reactions, the intensity distributions of $C_yH_{2y-1}^+$ ions also peak at $y = 4$ and then decrease with increasing y in most cases. Small second peaks of $C_yH_{2y-1}^+$ are found at $y = 6$ for $C_{12}\sim C_{18}$ reagents. A difference between the CH_5^+ and $C_2H_5^+$ reactions is that the distributions of long chain $C_yH_{2y-1}^+$ ions above $y = 6$ decrease with increasing y in the cases of $C_2H_5^+$ reactions. In the $C_3H_5^+$ reaction, the intensity distributions of $C_yH_{2y-1}^+$ ions also give peak at $y = 4$ and they decrease with increasing y in all cases except the case of C_{10} reagent, where a broad distribution within $y = 5\sim 9$ is observed.

Figures 4B(a)-(i) show initial product-ion distributions of alkynyl $C_yH_{2y-3}^+$ ($y = 4\sim x$) ions obtained for short ($x = 8\sim 11$), medium ($x = 12\sim 14$), and long ($x = 15\sim 18$) chain reagents. The distributions of large $C_yH_{2y-3}^+$ ($y = 13\sim x$) ions are zero in the reactions of $C_{12}\sim C_{18}$ 1-alkynes. The $C_yH_{2y-3}^+$ ($y = 4\sim x$) ions are distributed in a wide y range. In the CH_5^+ reactions, for short and medium chain $C_8\sim C_{14}$ reagents, the $C_yH_{2y-3}^+$ distributions have broad peaks at $y = 5\sim 10$, whereas for long-chain $C_{15}\sim C_{18}$ reagents, they have broad peaks at $y = 5\sim 12$. In the $C_2H_5^+$ reactions, the distributions of $C_yH_{2y-3}^+$ have peaks at $y = 6$ and weak second peaks are found at $y = 8$ or 9 in many cases. In the $C_3H_5^+$ reactions, broad $C_yH_{2y-3}^+$ distributions are observed in the $y = 5\sim 11$ range.

It should be noted that, as a whole, the initial distributions of $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ ions from $C_8\sim C_{18}$ 1-alkynes are similar in the three MH⁺ ($M = CH_4$, C_2H_4 , and C_3H_4) reactions. The $C_yH_{2y-1}^+$ ion distributions have peaks at $y = 4$ and decrease with increasing y . On the other hand, the initial distributions of $C_yH_{2y-3}^+$ ions have broad peaks in the $y = 5\sim 10$ range. It is noteworthy that these distributions are similar

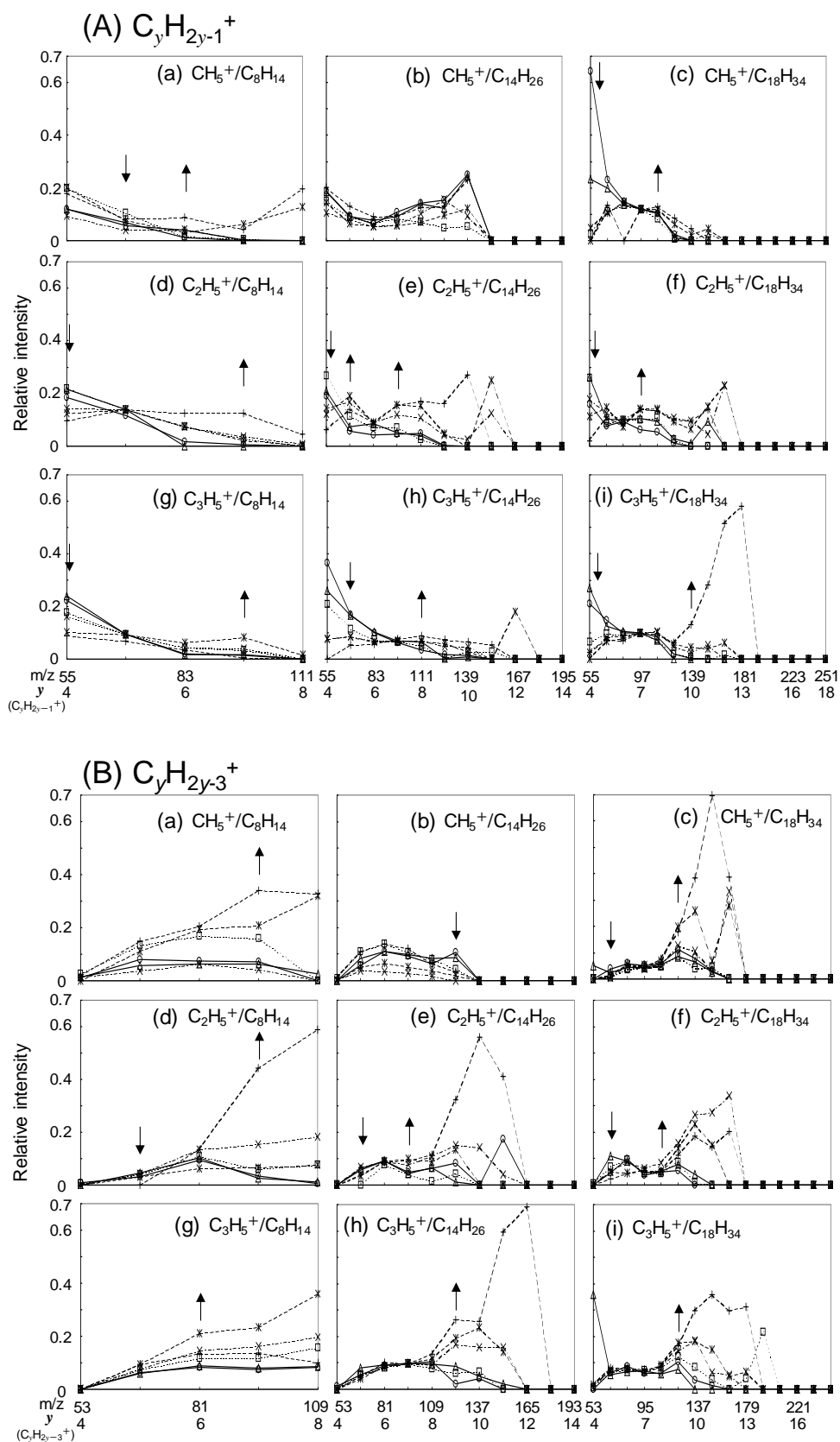


Fig. 2. Production-ion distributions of (A) alkenyl $C_yH_{2y-1}^+$ ($y = 4 \sim x$) ions and (B) alkynyl $C_yH_{2y-3}^+$ ($y = 4 \sim x$) ions in the reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with C_8 , C_{14} , and C_{18} 1-alkynes at five different reaction times: \circ 0.5, \square 2, \times 10, $*$ 20, and $+$ 40 ms.

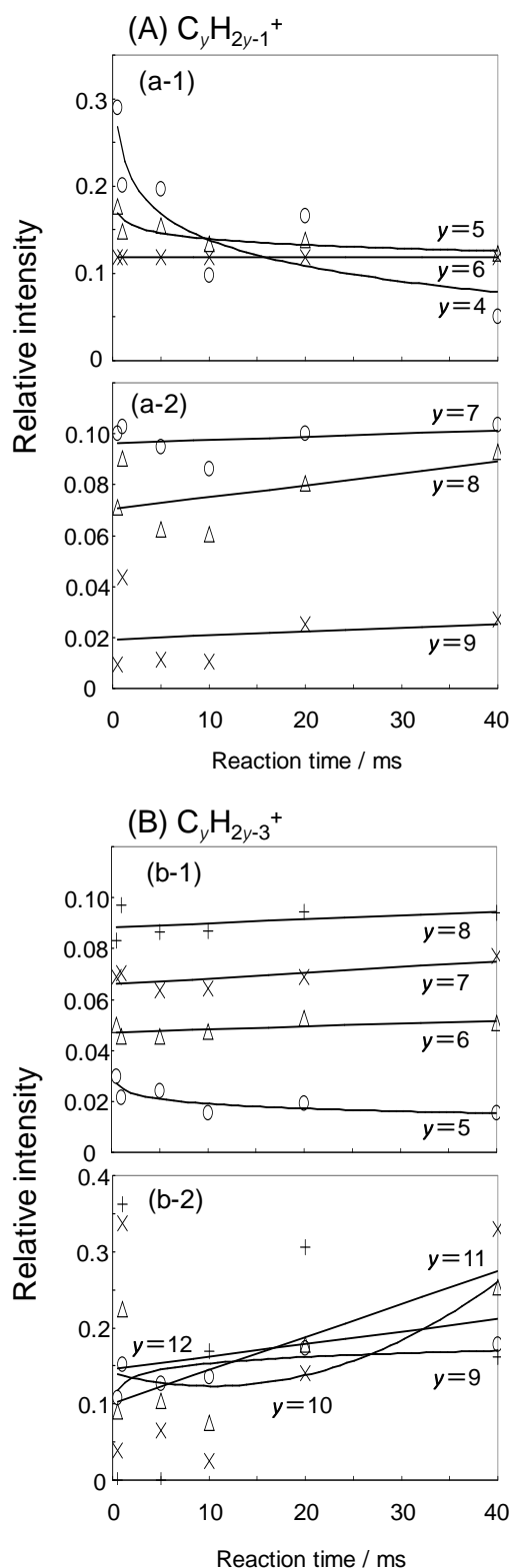
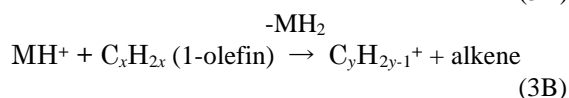
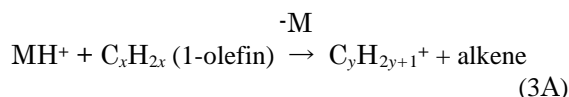
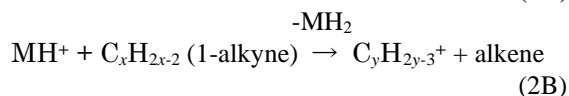
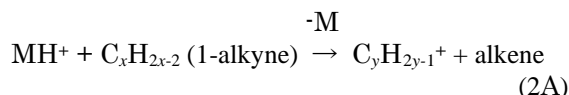


Fig. 3. Dependence of product-ion distributions of (A) alkenyl $C_yH_{2y-1}^+$ ($y = 4\sim 9$) ions and (B) alkynyl $C_yH_{2y-3}^+$ ($y = 5\sim 12$) ions on the reaction time in the $CH_5^+/C_{16}H_{30}$ reaction.

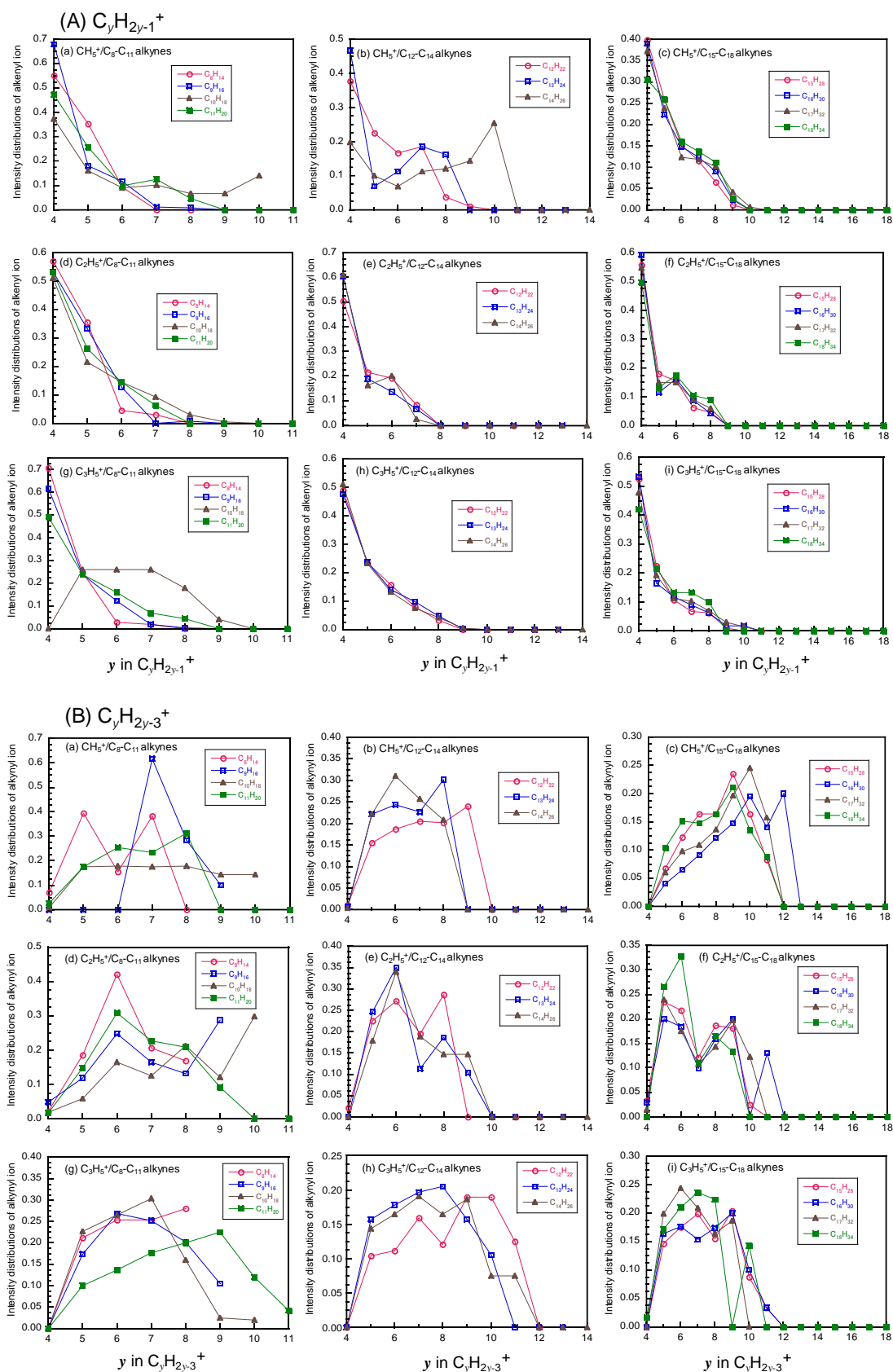
to those of alkyl $C_yH_{2y+1}^+$ and alkenyl $C_yH_{2y-1}^+$ ions from $C_8\sim C_{18}$ 1-olefins.¹⁶⁾ In the MH^+ ($M = CH_4, C_2H_4,$ and C_3H_4) reactions with $C_8\sim C_{18}$ 1-alkynes (C_xH_{2x-2}) and 1-olefins (C_xH_{2x}), protonation followed by alkene elimination gives $C_yH_{2y-1}^+$ and $C_yH_{2y+1}^+$ ions through processes (2A) and (3A), whereas H^- abstraction followed by alkene elimination provide $C_yH_{2y-3}^+$ and $C_yH_{2y-1}^+$ ions through processes (2B) and (3B), respectively.



It should be noted that similar initial product-ion distributions are observed between $C_yH_{2y-1}^+$ in (2A) and $C_yH_{2y+1}^+$ in (3A) and between $C_yH_{2y-3}^+$ in (2B) and $C_yH_{2y-1}^+$ in (3B). These results imply that the favorable product ions formed by protonation and hydride-ion abstraction reactions are similar in the CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ reactions with $C_8\sim C_{18}$ 1-alkynes and 1-olefins, even though the total number of H atoms in product ions and reagent hydrocarbons is different by two due to presence of a C=C or C≡C bond.

3.3 Branching ratios of alkenyl and alkynyl ions in the MH^+ ($M = CH_4, C_2H_4,$ and C_3H_4) reactions

In Figs. 5a-5c we plot the branching ratios of all the $C_yH_{2y-1}^+$ ($y = 4\sim x$) and $C_yH_{2y-3}^+$ ($y = 4\sim x$) ions formed from $C_8\sim C_{18}$ 1-alkynes. In most of all reactions, $\Sigma C_yH_{2y-1}^+$ ($y = 4\sim x$) values are larger than those of $\Sigma C_yH_{2y-3}^+$ values. On the basis of this finding, protonation products are more favorable than hydride-ion abstraction products in the MH^+ ($M = CH_4, C_2H_4,$ and C_3H_4) reactions with $C_8\sim C_{18}$ 1-alkynes. In the CH_5^+ and $C_3H_5^+$ reactions, $\Sigma C_yH_{2y-1}^+$ values increase, while $\Sigma C_yH_{2y-3}^+$ values decrease with increasing carbon chain length x . On the other hand, the $\Sigma C_yH_{2y-1}^+$ and $\Sigma C_yH_{2y-3}^+$ values are independent of x in the $C_2H_5^+$ reactions. Results show that reaction mechanisms for the formation of



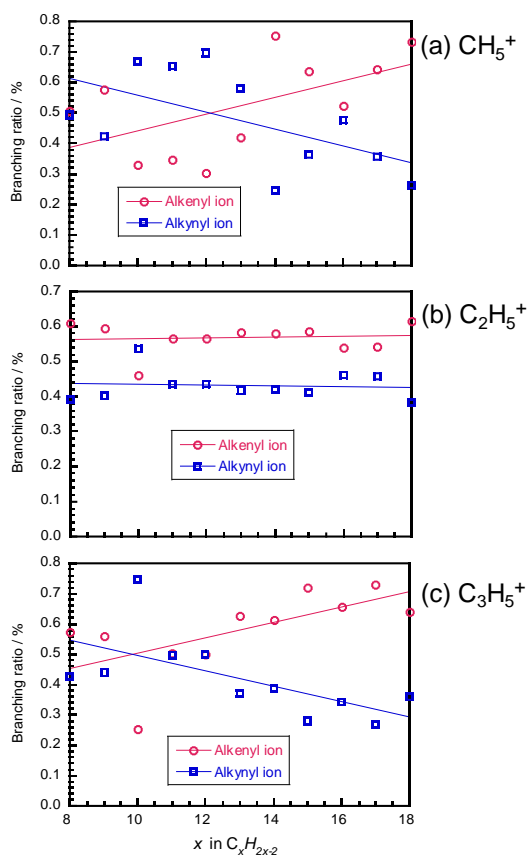


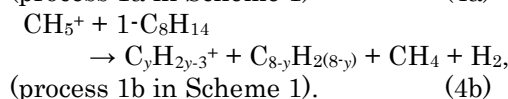
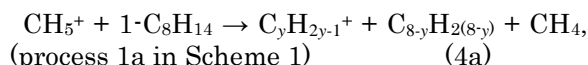
Fig. 5. The dependence of total alkenyl ($\Sigma C_y H_{2y-1}^+$) and alkynyl ($\Sigma C_y H_{2y-3}^+$) ion intensities on the reagent carbon chain length x in the reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with $C_8 \sim C_{18}$ 1-alkynes.

alkenyl and/or alkynyl ions in the $C_2H_5^+$ reaction are different from those in the CH_5^+ and $C_3H_5^+$ reactions.

3.4 Energetics and formation mechanisms of alkenyl and alkynyl ions from the ion-molecule reactions of MH^+ ($M = CH_4, C_2H_4,$ and C_3H_4) ions with 1-alkynes

Scheme 1 shows possible formation processes of alkenyl $C_y H_{2y-1}^+$ and alkynyl $C_y H_{2y-3}^+$ ions from the MH^+ ($M = CH_4, C_2H_4,$ and C_3H_4) reactions with 1-alkynes. Alkenyl $C_y H_{2y-1}^+$ ions can be formed via proton transfer to an alkynyl (1a) and adduct-ion formation (4a). On the other hand, alkynyl $C_y H_{2y-3}^+$ ions are produced via proton transfer to an alkyl group followed by loss of H_2 (1b), hydride-ion abstraction (2), alkanide-ion ($C_{x-y}H_{2(x-y)+1}^-$) abstraction (3), and adduct-ion formation (4b). The rearrangement shown in Scheme 1 represents hydride and alkyl shifts leading to more stable isomers (e.g. primary \rightarrow secondary \rightarrow tertiary ions).

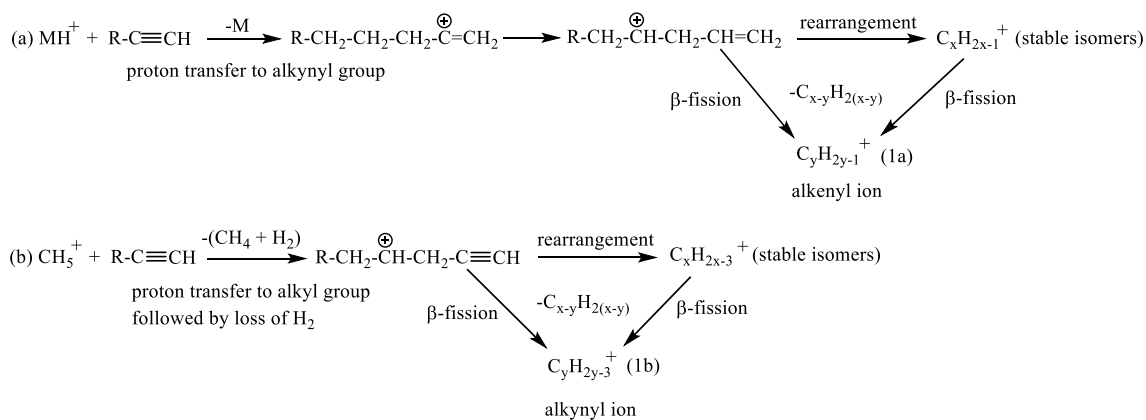
The energetics for the formation of $C_y H_{2y-1}^+$ and $C_y H_{2y-3}^+$ from (1a), (1b), (2), (4a) and (4b) was calculated using reported thermochemical data.²²⁾ The ΔH° values obtained are shown in Figs. 6A and 6B for the cases of $C_8, C_{14},$ and C_{18} reagents. Similar energy relationships are obtained for the reactions of other 1-alkynes. For example, ΔH° values in Figs. 6A (a) and 6B (a) represent the heats of reaction of the following $CH_5^+/1-C_8H_{16}$ reactions leading to various $C_y H_{2y-1}^+$ and $C_y H_{2y-3}^+$ ions:



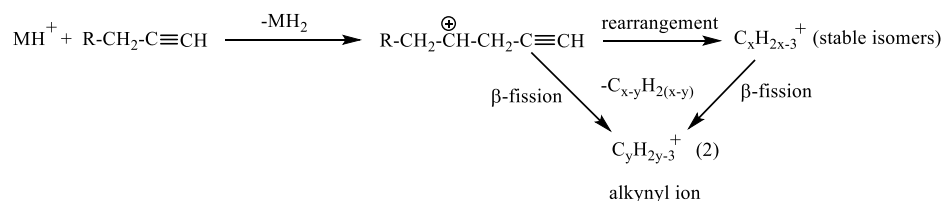
There are three possible $C_3H_5^+$ isomers, whose ΔH° values are 946, 969, and 1069 kJ mol^{-1} for $CH_2=CHCH_2^+$, $CH_3C=CH_2^+$, and protonated cyclopropene ion, respectively.²²⁾ Since the most stable $CH_2=CHCH_2^+$ isomer is a significant ion produced from CH_4 CI gas,²⁾ all thermochemical calculations for $C_3H_5^+$ are carried out using the above ΔH° value of $CH_2=CHCH_2^+$.

It is clear from Figs. 6A and 6B that the ΔH° values for the formation of alkenyl $C_y H_{2y-1}^+$ ions and alkynyl $C_y H_{2y-3}^+$ ions decrease with increasing the product-ion chain length y , except for the highly endoergic processes at $y = x-1, x+1,$ or $x+2$, where unstable CH_2 radicals are formed as a neutral byproduct. The ΔH° values for the formation of $C_y H_{2y-1}^+$ from protonation process (1a) given in Figs. 6A increase in the order of $CH_5^+, C_2H_5^+,$ and $C_3H_5^+$ reactions due to an increase in the proton affinity (PA) in the order of CH_4 (PA = 543.5 kJ mol^{-1}), C_2H_4 (680.5 kJ mol^{-1}), and C_3H_4 (775.3 kJ mol^{-1}).²²⁾ Therefore, the formation of $C_y H_{2y-1}^+$ ($y = 4$) ions slightly endoergic in the $C_2H_5^+$, and $C_3H_5^+$ reactions. These ΔH° values are calculated for the formation of primary ions. Actually, an intramolecular rearrangement leading to more stable secondary ($s-C_y H_{2y-1}^+$) and tertiary ($t-C_y H_{2y-1}^+$) ions occurs. Since ΔH° values of secondary and tertiary carbocations are lower than that of primary ones by 0.87 and 1.3 eV, respectively,²⁾ such endoergic processes can also occur energetically. The formation of $C_y H_{2y-1}^+$ from $C_2H_5^+$ addition (4a) is energetically more favorable than that from proton transfer (1a) by about 1 eV, and they are exoergic for $y = 4 \sim x-2$. There are no significant differences in the ΔH° values for the formation

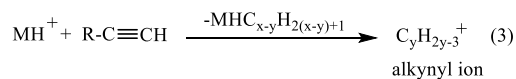
(1) Proton transfer by MH^+ ($M = CH_4, C_2H_4, C_3H_4$) by loss of alkene or H_2 + alkene



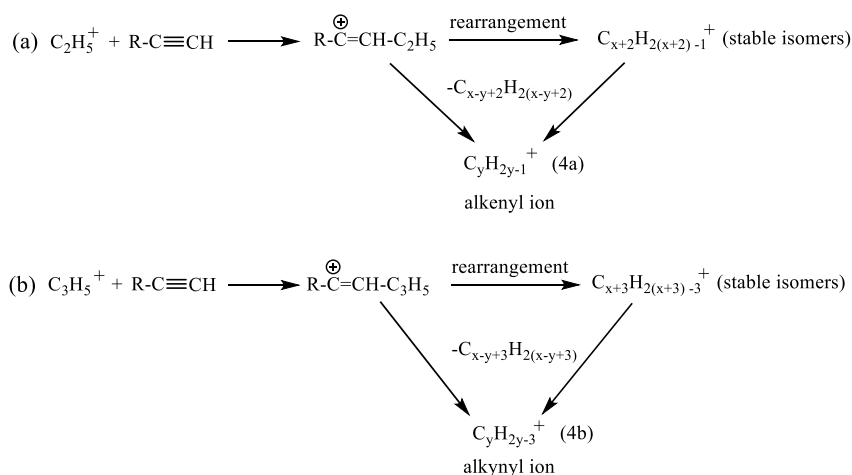
(2) H^- abstraction by MH^+ ($M = C_2H_4, C_3H_4$) by loss of alkyne



(3) Alkanide-ion abstraction by MH^+ ($M = C_2H_4, C_3H_4$)



(4) Adduct-ion formation by MH^+ ($M = C_2H_4, C_3H_4$)



Scheme 1. Possible reaction mechanisms for the formation of alkenyl $C_yH_{2y-1}^+$ and alkynyl $C_yH_{2y-3}^+$ ions in the reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with C_8 ~ C_{18} 1-alkynes.

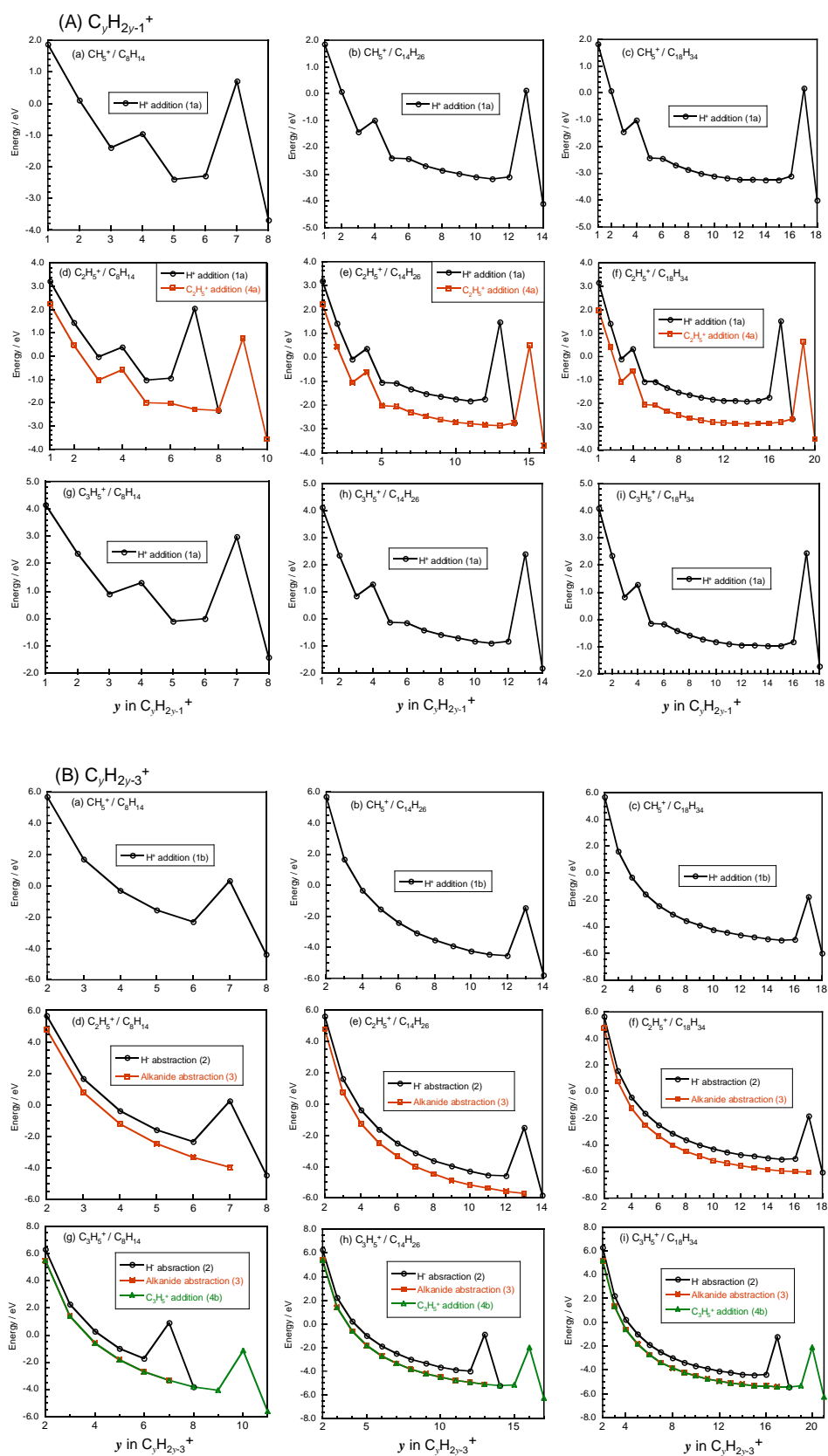


Fig. 6. The ΔH° values obtained for the formation of (A) alkenyl $C_yH_{2y-1}^+$ ions and (B) alkynyl $C_yH_{2y-3}^+$ ions from processes (1a), (1b), (2), (4a) and (4b) in Scheme 1.

of $C_yH_{2y-3}^+$ ions from H^- abstraction (2) in the CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ reactions, and the formation of $C_yH_{2y-3}^+$ ($y = 4 \sim x-2$) ions are energetically possible without occurrence of intramolecular rearrangement. The formation of $C_yH_{2y-3}^+$ ions from alkanide-ion abstraction (3) and $C_2H_5^+$ and $C_3H_5^+$ addition (4b) are energetically more favorable than that from H^- abstraction (2) by 0.84~0.86 eV.

$C_yH_{2y-1}^+$ ions are formed via proton transfer reaction (1a) in the CH_5^+ and $C_3H_5^+$ reactions, whereas they can be formed not only via proton transfer reaction (1a) but also via $C_2H_5^+$ addition (4a) in the $C_2H_5^+$ reactions. The $\Sigma C_yH_{2y-1}^+$ and $\Sigma C_yH_{2y-3}^+$ values increase and decrease with increasing the chain length in the CH_5^+ and $C_3H_5^+$ reactions. In general, the probability of collisions of a reactant ion with an alkyl group increases, whereas that with a $C\equiv C$ group decreases with increasing the carbon chain length of reagent (x). It may therefore be reasonable to assume that major active sites for the formation of $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ are the alkyl chain and the $C\equiv C$ triple bond, respectively. This prediction is inconsistent with the major reaction mechanisms for the formation of alkenyl and alkynyl ions, assuming that the alkenyl and alkynyl ions are dominantly formed through proton transfer (1) and H^- abstraction (1b) in Scheme 1, respectively.

According to ICR studies on the CH_5^+/n -paraffins reactions using deuterium, alkyl $C_yH_{2y+1}^+$ ions are formed by the attack of H^+ on a C-H or C-C bond of the alkane leading to extremely unstable carbonium ions; the subsequent decomposition by loss of H_2 or smaller alkane molecules yields $C_xH_{2x+1}^+$ and various fragment alkyl $C_yH_{2y+1}^+$ ions, respectively.²⁴⁻²⁷ On the basis of above facts, the attack of H^+ on an alkyl part of 1-alkyne leading finally to $C_yH_{2y-1}^+$ by loss of alkene from $C_xH_{2x-1}^+$ may also occur in the CH_5^+ /1-alkynes reactions studied here. If such proton transfer reactions to alkyl group take part in the formation of $C_yH_{2y-1}^+$ ions, the increase in the $\Sigma C_yH_{2y-1}^+$ values with increasing reagent chain length in the CH_5^+ and $C_3H_5^+$ reactions can be explained. This process is not described in Scheme 1 for the sake of clarity.

In the $C_2H_5^+$ reactions, the $\Sigma C_yH_{2y-1}^+$ and $\Sigma C_yH_{2y-3}^+$ values are constant. This may be due to the occurrence of attach of $C_2H_5^+$ not only on an alkyl chain ((1a) in Scheme 1) but also on a $C\equiv C$ triple bond ((4a) in Scheme 1) for the formation of $C_yH_{2y-1}^+$.

$C_yH_{2y-3}^+$ ions can be formed via proton

transfer followed by loss of H_2 (1b) in the CH_5^+ reaction. They can be formed via H^- abstraction (2) and alkanide-ion abstraction (3) in the $C_2H_5^+$ reactions, whereas in addition to the above two processes, $C_3H_5^+$ addition process (4b) can contribute to the formation of $C_yH_{2y-3}^+$ ions in the $C_3H_5^+$ reactions. The decrease in $\Sigma C_yH_{2y-3}^+$ values with increasing the chain length in the $C_3H_5^+$ reaction may arise from the contribution of $C_3H_5^+$ addition process (4b) because the probability of attach of $C_3H_5^+$ to a $C\equiv C$ triple bond decreases with increasing chain length.

4. Summary and Conclusion

The gas-phase ion-molecule reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with 1-alkynes (C_xH_{2x-2} ; $x = 8\sim 18$) have been studied in an ion-trap type of GC/MS by separating each reactant ion. Although no peaks corresponding to $[MW + H]^+$, $[MW - H]^+$, $[MW + C_2H_5]^+$, $[MW + C_3H_5]^+$ ions are detected, fragment alkenyl $C_yH_{2y-1}^+$ and alkynyl $C_yH_{2y-3}^+$ ions were observed. The dependence of the relative intensities of $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ ions on the reaction times indicated that collisional stabilization took part in the formation of some product ions. As a whole, no significant differences were observed in the initial product-ion distributions of $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ ions for the three reactant hydrocarbon ions. The $C_yH_{2y-1}^+$ distributions peaked at the lowest C_4 ion and decreased with increasing y . On the other hand, the $C_yH_{2y-3}^+$ distributions gave broad distributions in the $y = 5\sim 10$ range. The $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ distributions were similar to the $C_yH_{2y+1}^+$ and C_yH_{2y-1} ones produced from 1-olefins, respectively.¹⁶ These results suggest that product ions formed from protonation ($+H^+$) and hydride abstraction ($-H^-$) gave similar distributions between two unsaturated aliphatic hydrocarbons (1-alkynes and 1-olefins). The total alkenyl-ion intensities were larger than those of total alkynyl-ion ones, indicating that protonation processes are more favorable than H^- abstraction processes in the MH^+ ($M = CH_4, C_2H_4, \text{ and } C_3H_4$) reactions with 1-alkynes. The total alkenyl and alkynyl ion intensities increased and decreased with increasing the reagent chain-length in the CH_5^+ and $C_3H_5^+$ reactions, while they were independent of the chain length in the $C_2H_5^+$ reactions. These results suggested that major active sites for the formation of $C_yH_{2y-1}^+$ and $C_yH_{2y-3}^+$ in the CH_5^+ and $C_3H_5^+$ reactions are an alkyl chain and a $C\equiv C$ triple bond, respectively.

The attack of CH_5^+ and C_3H_5^+ ions on alkyl parts may contribute to the formation of $\text{C}_y\text{H}_{2y-1}^+$ ions, though further detailed experimental studies using deuterium are necessary to confirm this prediction. The different dependence in the C_2H_5^+ reactions may be due to the contribution of adduct-ion production process for the formation of $\text{C}_y\text{H}_{2y-1}^+$ ions. The present results provide new information on the reactivity of hydrocarbon ions for 1-alkynes; they are important in understanding organic reactions by carbocations.

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