

# Mass-Spectrometric Study on Ion-Molecule Reactions of $\text{CH}_5^+$ , $\text{C}_2\text{H}_5^+$ , and $\text{C}_3\text{H}_5^+$ with $\text{C}_9$ – $\text{C}_{19}$ Alkylbenzenes in an Ion Trap

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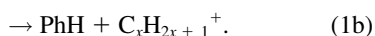
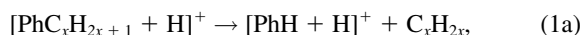
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Chemical ionization of alkylbenzenes ( $\text{PhC}_x\text{H}_{2x+1} = \text{M}$ ;  $x = 3$ – $13$ ) by the  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  ions has been studied under a reactant-ion selective mode of an ion-trap type of GC/MS. The dominant product ions for short-chain reagents ( $x < 7$ ) were  $[\text{M} + \text{H}]^+$ ,  $[\text{PhH} + \text{H}]^+$ , and  $\text{C}_x\text{H}_{2x+1}^+$  ions, produced through proton-transfer to benzene ring. On the other hand, the dominant product ions for long-chain reagents ( $x \geq 7$ ) were  $\text{C}_y\text{H}_{2y+1}^+$  ( $y < x$ ) and  $\text{PhC}_y\text{H}_{2y}^+$  ( $y \leq x$ ) ions. The former ions are produced through the attack of the reactant ions on the alkyl chain and/or the benzene ring, while the latter ones are exclusively formed through the attack of the reactant ions on the alkyl chain. Major formation processes of  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions in each reaction were discussed on the basis of observed distributions and calculated thermochemical data.

The gas phase ion-molecule reactions of alkylbenzenes in a methane atmosphere have been extensively studied since the first chemical ionization (CI) mass spectrometric measurements by Field et al.<sup>1–4</sup> They measured CI mass spectra of unbranched ( $\text{PhC}_x\text{H}_{2x+1} = \text{M}$ ;  $x = 0, 1, 5$ ) and branched alkylbenzenes at a medium  $\text{CH}_4$  pressure of 133 Pa, where dominant reactant ions were  $\text{CH}_5^+$  (48%),  $\text{C}_2\text{H}_5^+$  (40%), and  $\text{C}_3\text{H}_5^+$  (6%).<sup>1</sup> They observed abundant  $[\text{M} + \text{H}]^+$  ions, in most cases, as well as  $[\text{M} + \text{C}_2\text{H}_5]^+$  and  $[\text{M} + \text{C}_3\text{H}_5]^+$  adduct ions characteristic of the molecular weight. The major fragment ions could be explained by loss of  $\text{H}_2$  and/or small alkanes from  $[\text{M} + \text{H}]^+$ , olefin elimination from  $[\text{M} + \text{H}]^+$  and  $[\text{M} + \text{C}_2\text{H}_5]^+$  or, for larger alkyl substituents, formation of alkyl ions. The loss of  $\text{H}_2$  and small neutral alkanes has been shown to result from direct protonation of C–H or C–C bonds; the reactions are essentially hydride and alkanide ion abstraction reactions. After pioneering investigations by Field et al.,<sup>1–4</sup> more detailed studies have been carried out on CI mass spectra of  $\text{C}_8$ – $\text{C}_{11}$  alkylbenzenes.<sup>5–10</sup> It was found that major reaction channels for both  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  reactions are proton transfers to the benzene ring, leading to  $[\text{M} + \text{H}]^+$ . The  $[\text{M} + \text{H}]^+$  ion decomposes either by olefin elimination to form protonated benzene (1a) or by benzene elimination to form an alkyl ion (1b):



Isotopic labelling studies have shown that reaction (1a) involves non-random transfer of hydrogen from several different positions of the alkyl chain rather than specific hydrogen migration from a single position. There was substantial evidence that reactions (1a) and (1b) proceed through the intermediacy

of an ion/neutral complex consisting of  $\text{C}_x\text{H}_{2x+1}^+$  and PhH. Within this complex, the alkyl ions may undergo hydride shifts to form more stable alkyl ions.

All of previous medium-pressure  $\text{CH}_4$  CI mass studies on alkylbenzenes have been carried out without selecting reactant hydrocarbon ions.<sup>1–10</sup> Therefore, the reactivity of dominant  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  reactant ions for alkylbenzenes has not been determined. It is known that  $\text{C}_3\text{H}_5^+$  ion is involved as a minor reactant ion when  $\text{CH}_4$  is used as a CI gas. However, no information has been obtained on its reactivity for alkylbenzenes. To the best of our knowledge, no CI mass spectrometric study has been carried out for alkylbenzenes ( $\text{PhC}_x\text{H}_{2x+1}$ ) with a long alkyl chain ( $x > 5$ ).

Recently, the ion-trap detector (ITD), which can operate at much lower CI gas pressures than those in a conventional medium-pressure CI mass spectrometer, has been used as a new, more sensitive CI mass spectrometer.<sup>11–13</sup> Some comparative studies between medium-pressure CI using magnetic sector instruments and low-pressure CI in the ITD have been carried out.<sup>11–13</sup> In general, fragmentation increases and no adduct ions such as  $[\text{M} + \text{C}_2\text{H}_5]^+$  and  $[\text{M} + \text{C}_3\text{H}_5]^+$  are observed in the ITD. These facts were attributed to the lack of collisional stabilization of  $[\text{M} + \text{H}]^+$ ,  $[\text{M} + \text{C}_2\text{H}_5]^+$ , and  $[\text{M} + \text{C}_3\text{H}_5]^+$  ions due to secondary collisions with  $\text{CH}_4$  and He gases. The other reason for the higher fragmentation in the ion-trap experiments is higher kinetic energies of reactant ions.

We have recently studied  $\text{CH}_4$  CI mass spectra of *n*-paraffins ( $\text{C}_x\text{H}_{2x+2}$ ;  $x = 8$ – $18$ ) and 1-olefins ( $1\text{-C}_x\text{H}_{2x}$ ;  $x = 8$ – $18$ ) by the  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  ions using an ion-trap type of GC/MS.<sup>14,15</sup> In this study,  $\text{CH}_4$  CI mass spectra of a series of alkylbenzenes ( $\text{PhC}_x\text{H}_{2x+1}$ ;  $x = 3$ – $13$ ) by the  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  ions are measured under a reactant-ion selective mode of 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  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  for alkylbenzenes was discussed from the initial product-ion distributions and from thermochemical calculations of heats of reactions.

### Experimental

CI mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS under a reactant-ion selective mode. The CI  $\text{CH}_4$  gas was introduced directly in an ion-trap cell. The electron-impact ionization on  $\text{CH}_4$  provides primary  $\text{CH}_n^+$  ( $n = 2-4$ ) ions. One of the reactant  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  ions produced from the subsequent fast ion-molecule reactions of  $\text{CH}_n^+$  ( $n = 2-4$ ) with  $\text{CH}_4$  was selectively trapped as a reactant ion in an ion-trap cell. The maximum and average kinetic energies of the reactant ions in our apparatus were evaluated to be 10 and 4.2 eV (1 eV = 96.485 kJ mol<sup>-1</sup>) for  $\text{CH}_5^+$ , 6.0 and 2.4 eV for  $\text{C}_2\text{H}_5^+$ , and 4.3 and 1.7 eV for  $\text{C}_3\text{H}_5^+$ , respectively, using a pseudo-potential well method.<sup>14</sup> These energies are higher than that in the medium-pressure CI experiments, which was estimated to be less than 1 eV.<sup>16</sup> 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  $\text{CH}_4$  and He during their trapping time in the cell. The ion-trap cell was kept at  $\leq 170^\circ\text{C}$ . The reagents were diluted in hexane and injected into the GC with a high-purity carrier He gas. The partial pressures of  $\text{CH}_4$  and He and in an ion-trap cell were  $9 \times 10^{-3}$  and  $7 \times 10^{-3}$  Pa, 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 1000–10000 pg cm<sup>-3</sup> in order to reduce secondary ion-molecule reactions. It is known that the number of ions stored in the ion trap depends on the radio frequency voltage.<sup>17</sup> Thus, the CI mass spectra obtained in this study were calibrated against NIST standard data.<sup>18</sup>

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.<sup>1-4</sup> In the medium-pressure CI measurements, the typical  $\text{CH}_4$  gas pressure was 133 Pa and the residence time of reactant ions in the ionization-reaction chamber was about 10  $\mu\text{s}$ . Field<sup>4</sup> evaluated the total number of collisions of reactant ions with  $\text{CH}_4$  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  $\text{CH}_4$  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.

### Results and Discussion

**Contribution of Collisional Stabilization and Initial Product-Ion Distributions:** When CI mass spectra resulting from ion-molecule reactions of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  with alkylbenzenes ( $\text{PhC}_x\text{H}_{2x+1}$ ;  $x = 3-13$ ) were measured,  $[\text{M} + \text{H}]^+$ ,  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3-10$ ), and  $\text{PhC}_y\text{H}_{2y}^+$  ( $y = 1-13$ ) ions were observed. Here,  $x$  represents the number of carbons of alkyl groups in a reagent, while  $y$  stands for the number of carbons of fragment alkyl groups. In addition, the  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$  ion was observed in the  $\text{C}_2\text{H}_5^+$  reaction, and adduct  $[\text{M} + \text{C}_3\text{H}_5]^+$  ions were observed in the  $\text{C}_3\text{H}_5^+$  reaction. If the collisional stabilization takes part in the formation of product ions,

an excess energy will be partly relaxed by collisions with  $\text{CH}_4$  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.

For examples, Figs. 1 and 2 show product-ion distributions of  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3-10$ ) and  $\text{PhC}_y\text{H}_{2y}^+$  ( $y = 1-13$ ) in the reactions of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  with typical reagents ( $\text{PhC}_x\text{H}_{2x+1}$ ;  $x = 8$  and 13) at five different reaction times: 0.5, 2, 10, 20, and 40 ms. The  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3-10$ ) and  $\text{PhC}_y\text{H}_{2y}^+$  ( $y = 1-13$ ) distributions exhibit single peaks in most cases. It is clear from Figs. 1 and 2 that the  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  distributions depend on the reaction time in most cases, though the changes in the  $\text{PhC}_y\text{H}_{2y}^+$  distributions are smaller than those in the  $\text{C}_y\text{H}_{2y+1}^+$  ones. The decreases or increases in the product-ion distributions with increasing the reaction time are shown by arrows in Figs. 1 and 2. In all the six  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  reactions shown in Fig. 1, the branching ratios of  $\text{C}_y\text{H}_{2y+1}^+$  decrease with increasing the reaction time, except for the branching ratios of  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 9, 10$ ) in the  $\text{CH}_5^+/\text{PhC}_{13}\text{H}_{27}$  reaction, for which an inverse relation is observed. The branching ratios of  $\text{PhC}_y\text{H}_{2y}^+$  having small  $y$  values decrease, while those having large  $y$  values increase in many cases.

In addition to major  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions,  $[\text{M} + \text{H}]^+$ ,  $[\text{PhH} + \text{H}]^+$ ,  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$ ,  $[\text{M} + \text{C}_3\text{H}_5]^+$ , and  $[\text{M} + \text{C}_3\text{H}_5 - \text{C}_2\text{H}_4]^+$  ions were observed in many reactions. With increasing reaction time, the branching ratios of  $[\text{M} + \text{H}]^+$ ,  $[\text{M} + \text{C}_3\text{H}_5]^+$ , and  $[\text{M} + \text{C}_3\text{H}_5 - \text{C}_2\text{H}_4]^+$  ions increase, while those of  $[\text{PhH} + \text{H}]^+$  and  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$  either slightly decrease or are nearly constant. These findings indicate that collisional stabilization with  $\text{CH}_4$  and He participates in the formation of the former ions. We found here that collisional stabilization take part in most of all reactions. Thus, the initial product distributions were determined by extrapolating the dependence of branching ratios of product ions on the reaction time to zero reaction time. The results obtained are summarized in Tables 1–3. The uncertainties of the initial branching-ratios were estimated to be within  $\pm 8\%$ . Two major product ions are alkyl  $\text{C}_y\text{H}_{2y+1}^+$  ( $y \leq x$ ) and  $\text{PhC}_y\text{H}_{2y}^+$  ( $y \leq x$ ) ions. The dependence of their intensity distributions on the chain length  $x$  is shown below for the three reactions.

**Distribution of Alkyl  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3-10$ ;  $y \leq x$ ) Ions:** Figures 3(a)–3(i) show initial product-ion distributions of  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3-10$ ;  $y \leq x$ ) obtained for short ( $x = 3-5$ ), medium ( $x = 6-9$ ), and long ( $x = 10-13$ ) chain reagents. The  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3-10$ ) ions are observed in the  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  reactions; differences in the intensity distributions are relatively small among the three reactions. Figures 3(a)–3(i) show that the  $\text{C}_y\text{H}_{2y+1}^+$  distributions depend strongly on the chain length  $x$  for short reagents below  $x < 7$ , where the dominant alkyl ions are  $\text{C}_x\text{H}_{2x+1}^+$ . On the other hand, the distributions become similar for long-chain reagents  $x \geq 7$ , where the dominant alkyl ions are  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 4-6$ ). In the  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  reactions, the  $\text{C}_y\text{H}_{2y+1}^+$  distributions peak at  $y = 3-6$  for short ( $x = 3-6$ ) chain reagents, and at  $y = 4, 5$  for longer ( $x > 6$ ) chain reagents. In the  $\text{C}_3\text{H}_5^+$  reactions, the  $\text{C}_y\text{H}_{2y+1}^+$  distributions peak at  $y = 3, 4$  for short ( $x = 3-6$ )

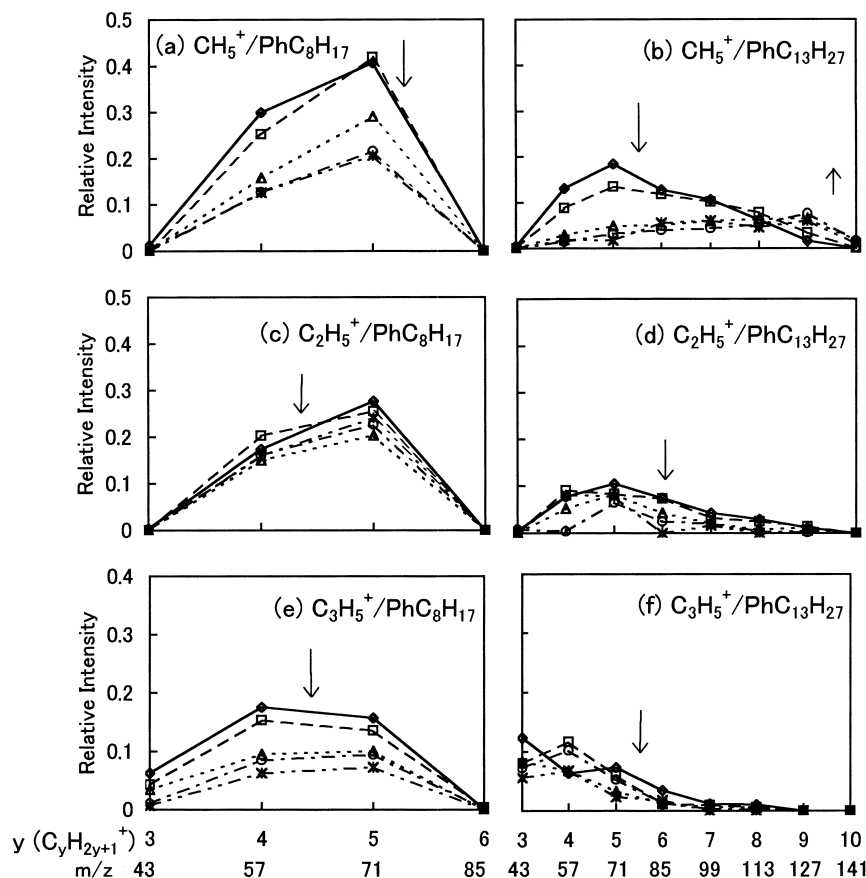


Fig. 1. Dependence of product-ion distributions of  $C_yH_{2y+1}^+$  ( $y = 3-10$ ) ion on the reaction time in the ion-molecule reactions of  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_3H_5^+$  with  $PhC_8H_{17}$  and  $PhC_{13}H_{27}$ . Reaction time  $\diamond$ : 0.5,  $\square$ : 2,  $\triangle$ : 10,  $\circ$ : 20, and  $\times$ : 40 ms. Relative intensities were branching ratios of each ion for total product ions. Arrows indicate an increase or a decrease in product-ion distribution with an increasing the reaction time. The line connecting the points in the graphs is the  $C_yH_{2y+1}^+$  formed from the same reaction time.

chain reagents and at  $y = 4, 5$  for medium ( $x = 7-9$ ) chain reagents, as in the cases of the  $CH_5^+$  and  $C_2H_5^+$  reactions. It should be noted that the  $C_yH_{2y+1}^+$  distributions in the  $C_3H_5^+$  reactions for long-chain reagents ( $x \geq 7$ ) shift to lower  $y$  values than those in the  $CH_5^+$  and  $C_2H_5^+$  reactions. This implies that the excess energies released in the  $C_3H_5^+$  reactions are larger than those in the  $CH_5^+$  and  $C_2H_5^+$  reactions for the formation of  $C_yH_{2y+1}^+$  from  $PhC_xH_{2x+1}$  ( $x \geq 7$ ).

**Distribution of  $PhC_yH_{2y}^+$  ( $y = 1-13; y \leq x$ ) Ions:** Figures 4(a)–4(i) show initial product-ion distributions of  $PhC_yH_{2y}^+$  ( $y = 1-13; y \leq x$ ) obtained for short ( $x = 3-5$ ), medium ( $x = 6-9$ ), and long ( $x = 10-13$ ) chain reagents. The  $PhC_yH_{2y}^+$  ( $y = 1-13$ ) ions are observed in the  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_3H_5^+$  reactions. Differences in the intensity distributions among the three reactions are larger than those observed for  $C_yH_{2y+1}^+$ . The  $PhC_xH_{2x}^+ = [M - H]^+$  ion peaks increase in the order of the  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_3H_5^+$  reactions. The  $PhC_yH_{2y}^+$  ( $y < x$ ) distributions depend on the chain length  $x$  for short-chain reagents  $x < 7$ , while they become similar for long-chain reagents  $x \geq 7$ . In the  $CH_5^+$  reactions, the  $PhC_yH_{2y}^+$  distributions peak at  $y = 1$  for  $x = 3-9$  reagents, and second peaks appear at  $y = 3$  for  $x = 10-13$  reagents. Although benzyl ion and tropylium ion are possible as  $PhC_yH_{2y}^+$  ( $y = 1$ ) ion, the latter ion is more stable than the former one by

0.52 eV.<sup>18</sup> Therefore, the  $C_7H_7^+$  ion observed here will be stable tropylium ion. In the  $C_2H_5^+$  reactions, the second peaks at  $y = 3$  or 4 become more pronounced for  $x = 6-13$  reagents. The  $PhC_yH_{2y}^+$  distributions in the  $C_3H_5^+$  reactions are similar to those in the  $C_2H_5^+$  reactions, except for the enhancement of the  $PhC_xH_{2x}^+$  peaks.

**Possible Mechanism and Energetics of Each Ion-Molecule Reaction:** In Schemes 1 and 2 are shown possible reaction pathways for the ion-molecule reactions of  $XH^+$  ( $X = CH_4$ ,  $C_2H_4$ , and  $C_3H_4$ ) with alkylbenzenes. Reactions (A-1) and (A-2), shown in Scheme 1, proceed through the attack of the reactant ions on the benzene ring, while reactions (B-1), (B-2), and (B-3), shown in Scheme 2, occur through the attack of the reactant ions on the alkyl chain. Protonation to benzene ring (A-1) gives three products:  $[M + H]^+$ ,  $C_xH_{2x+1}^+$  and  $[PhH + H]^+$ , while addition to benzene ring (A-2) provides  $[M + XH]^+$ ,  $[M + XH - C_2H_4]^+$ , and  $[PhH + XH]^+$  ions. Protonation either to C–H or C–C bond (B-1) leads to  $[M + H]^+$ ,  $[M - H]^+$ ,  $C_yH_{2y+1}^+$ , and  $PhC_yH_{2y}^+$ , while hydride-ion abstraction (B-2) gives the  $[M - H]^+$ ,  $C_yH_{2y+1}^+$ , and  $PhC_yH_{2y}^+$  ions. The  $PhC_zH_{2z}^-$  or  $C_zH_{2z+1}^-$  ion abstraction (B-3) provides  $C_yH_{2y+1}^+$  or  $PhC_yH_{2y}^+$  ions, respectively. In our previous study on the reactions of  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_3H_5^+$  reactions with *n*-paraffins,  $[M + H]^+$  ions could not be observed

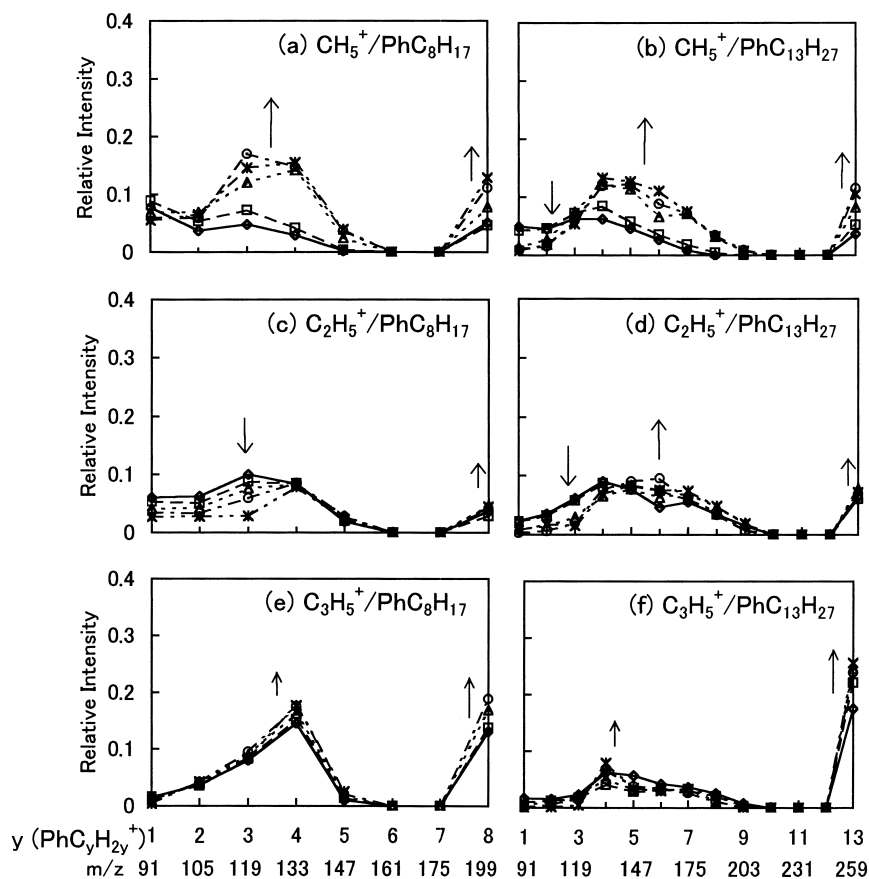


Fig. 2. Dependence of product-ion distributions of  $\text{PhC}_y\text{H}_{2y+1}^+$  ( $y = 1-13$ ) ion on the reaction time in the ion-molecule reactions of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  with  $\text{PhC}_8\text{H}_{17}$  and  $\text{PhC}_{13}\text{H}_{27}$ . Reaction time  $\diamond$ : 0.5,  $\square$ : 2,  $\triangle$ : 10,  $\circ$ : 20, and  $\times$ : 40 ms. Relative intensities were branching ratios of each ion for total product ions. Arrows indicate an increase or a decrease in product-ion distribution with an increasing the reaction time. The line connecting the points in the graphs is the  $\text{PhC}_y\text{H}_{2y+1}^+$  formed from the same reaction time.

Table 1. Branching Ratios of Each Product Channel in Reactions of  $\text{CH}_5^+$  with  $\text{PhC}_x\text{H}_{2x+1}$  [ $x = 3-13$ ]<sup>a)</sup>

| Reagents [ $x$ ( $\text{PhC}_x\text{H}_{2x+1}$ )]         | 3     | 4      | 5     | 6      | 7    | 8      | 9      | 10   | 11    | 12     | 13     |
|-----------------------------------------------------------|-------|--------|-------|--------|------|--------|--------|------|-------|--------|--------|
| Product ions                                              |       |        |       |        |      |        |        |      |       |        |        |
| Attack of the reactant on the benzene ring                |       |        |       |        |      |        |        |      |       |        |        |
| $[\text{M} + \text{H}]^+$                                 | 0.00  | 0.00   | 0.00  | 0.0057 | 0.00 | 0.00   | 0.00   | 0.00 | 0.00  | 0.0067 | 0.0080 |
| $\text{C}_x\text{H}_{2x+1}^+$                             | 0.86  | 0.88   | 0.74  | 0.57   | 0.00 | 0.00   | 0.00   | 0.00 | 0.00  | 0.00   | 0.00   |
| $\text{C}_6\text{H}_7^+$                                  | 0.13  | 0.038  | 0.00  | 0.00   | 0.00 | 0.00   | 0.00   | 0.00 | 0.00  | 0.00   | 0.00   |
| Attack of the reactant on the benzene ring or alkyl chain |       |        |       |        |      |        |        |      |       |        |        |
| $\text{C}_y\text{H}_{2y+1}^+$                             | 0.00  | 0.0063 | 0.19  | 0.31   | 0.87 | 0.87   | 0.86   | 0.85 | 0.84  | 0.80   | 0.75   |
| Attack of the reactant on alkyl chain                     |       |        |       |        |      |        |        |      |       |        |        |
| $\text{PhC}_x\text{H}_{2x}^+ = [\text{M} - \text{H}]^+$   | 0.00  | 0.00   | 0.00  | 0.00   | 0.00 | 0.0054 | 0.0058 | 0.00 | 0.018 | 0.0079 | 0.00   |
| $\text{PhC}_y\text{H}_{2y}^+$                             | 0.011 | 0.080  | 0.079 | 0.12   | 0.13 | 0.12   | 0.13   | 0.15 | 0.14  | 0.18   | 0.23   |

a) Uncertainties are within  $\pm 8\%$ .

due to complete decomposition of  $[\text{M} + \text{H}]^+$  into  $\text{C}_y\text{H}_{2y+1}^+$ .<sup>14</sup> It is therefore reasonable to assume that all  $[\text{M} + \text{H}]^+$  ions observed in this study are ring-protonated ions produced through reaction (A-1).

The heats of reactions of each process for the formation of dominant  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions were calculated using reported thermochemical data.<sup>18</sup> The results obtained are shown in Figs. 5(A)–5(F) for the case of  $x = 13$  reagent. Sim-

Table 2. Branching Ratios of Each Product Channel in Reactions of  $C_2H_5^+$  with  $PhC_xH_{2x+1}$  [ $x = 3-13$ ]<sup>a)</sup>

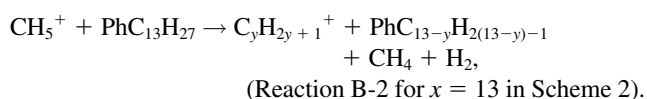
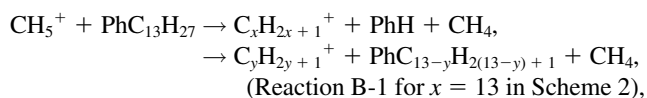
| Reagents [ $x(PhC_xH_{2x+1})$ ]                           | 3     | 4      | 5     | 6     | 7     | 8     | 9      | 10    | 11    | 12    | 13    |
|-----------------------------------------------------------|-------|--------|-------|-------|-------|-------|--------|-------|-------|-------|-------|
| Product ions                                              |       |        |       |       |       |       |        |       |       |       |       |
| Attack of the reactant on the benzene ring                |       |        |       |       |       |       |        |       |       |       |       |
| $[M + H]^+$                                               | 0.20  | 0.18   | 0.12  | 0.12  | 0.045 | 0.058 | 0.026  | 0.043 | 0.051 | 0.059 | 0.042 |
| $C_xH_{2x+1}^+$                                           | 0.28  | 0.42   | 0.40  | 0.34  | 0.022 | 0.00  | 0.00   | 0.00  | 0.00  | 0.00  | 0.00  |
| $C_6H_7^+$                                                | 0.065 | 0.011  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00   | 0.00  | 0.00  | 0.00  | 0.00  |
| Attack of the reactant on the benzene ring or alkyl chain |       |        |       |       |       |       |        |       |       |       |       |
| $C_yH_{2y+1}^+$                                           | 0.00  | 0.0053 | 0.15  | 0.23  | 0.55  | 0.48  | 0.48   | 0.49  | 0.49  | 0.44  | 0.43  |
| Attack of the reactant on alkyl chain                     |       |        |       |       |       |       |        |       |       |       |       |
| $PhC_xH_{2x}^+ = [M - H]^+$                               | 0.15  | 0.11   | 0.058 | 0.043 | 0.029 | 0.029 | 0.041  | 0.028 | 0.050 | 0.064 | 0.061 |
| $PhC_yH_{2y}^+$                                           | 0.056 | 0.12   | 0.16  | 0.21  | 0.30  | 0.39  | 0.43   | 0.43  | 0.40  | 0.43  | 0.46  |
| Addition to the benzene ring                              |       |        |       |       |       |       |        |       |       |       |       |
| $[PhC_2H_5 + H]^+$                                        | 0.17  | 0.13   | 0.061 | 0.032 | 0.020 | 0.015 | 0.0061 | 0.00  | 0.00  | 0.00  | 0.00  |

a) Uncertainties are within  $\pm 8\%$ .Table 3. Branching Ratios of Each Product Channel in Reactions of  $C_3H_5^+$  with  $PhC_xH_{2x+1}$  [ $x = 3-13$ ]<sup>a)</sup>

| Reagents [ $x(PhC_xH_{2x+1})$ ]                           | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10     | 11     | 12    | 13    |
|-----------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|--------|--------|-------|-------|
| Product ions                                              |       |       |       |       |       |       |       |        |        |       |       |
| Attack of the reactant on the benzene ring                |       |       |       |       |       |       |       |        |        |       |       |
| $[M + H]^+$                                               | 0.073 | 0.080 | 0.073 | 0.11  | 0.065 | 0.11  | 0.084 | 0.10   | 0.12   | 0.14  | 0.10  |
| $C_xH_{2x+1}^+$                                           | 0.56  | 0.39  | 0.22  | 0.16  | 0.00  | 0.00  | 0.00  | 0.00   | 0.00   | 0.00  | 0.00  |
| $C_6H_7^+$                                                | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00   | 0.00   | 0.00  | 0.00  |
| Attack of the reactant on the benzene ring or alkyl chain |       |       |       |       |       |       |       |        |        |       |       |
| $C_yH_{2y+1}^+$                                           | 0.00  | 0.022 | 0.37  | 0.44  | 0.61  | 0.50  | 0.50  | 0.48   | 0.59   | 0.41  | 0.37  |
| Attack of the reactant on alkyl chain                     |       |       |       |       |       |       |       |        |        |       |       |
| $PhC_xH_{2x}^+ = [M - H]^+$                               | 0.17  | 0.20  | 0.13  | 0.09  | 0.09  | 0.10  | 0.09  | 0.13   | 0.09   | 0.13  | 0.16  |
| $PhC_yH_{2y}^+$                                           | 0.020 | 0.11  | 0.087 | 0.11  | 0.18  | 0.27  | 0.30  | 0.28   | 0.13   | 0.23  | 0.29  |
| Addition to the benzene ring                              |       |       |       |       |       |       |       |        |        |       |       |
| $[M + C_3H_5]^+$                                          | 0.13  | 0.13  | 0.060 | 0.020 | 0.00  | 0.00  | 0.00  | 0.00   | 0.00   | 0.00  | 0.00  |
| $[M + C_3H_5 - C_2H_4]^+$                                 | 0.022 | 0.046 | 0.040 | 0.059 | 0.050 | 0.021 | 0.00  | 0.0055 | 0.0094 | 0.025 | 0.025 |

a) Uncertainties are within  $\pm 8\%$ .

ilar energy relationships are obtained for the reactions of other alkylbenzenes. For example,  $\Delta H^\circ$  values in Fig. 5(A) represent the heats of reaction of the following reactions, leading to various  $C_yH_{2y+1}^+$  ( $y \leq x$ ) ions:



There are three possible  $C_3H_5^+$  isomers, whose  $\Delta H^\circ$  values are 946, 969, and 1069 kJ mol<sup>-1</sup> for  $CH_2=CHCH_2^+$ ,  $CH_3C=CH_2^+$ , and protonated cyclopropene ion, respectively.<sup>18</sup> Since the most stable  $CH_2=CHCH_2^+$  isomer is a significant ion produced from  $CH_4$  CI gas,<sup>19</sup> all thermochemical calculations for  $C_3H_5^+$  are carried out using the above  $\Delta H^\circ$  value of  $CH_2=CHCH_2^+$ . The  $\Delta H^\circ$  values in Figs. 5(A)–5(F) are shown only for the formation of unstable  $-CH_2^+$  ( $= C_yH_{2y+1}^+$ ) and  $-CH=CH^+$  ( $= C_yH_{2y-1}^+$ ) ions, *n*-paraffins, and 1-olefins as ionic and neutral products, for the sake of clarity. However, more stable isomers having secondary and tertiary alkyl groups will also be formed. Since the  $\Delta H^\circ$  values of secondary and tertiary carbocations are lower than the value of primary ones by about 0.87 and 1.3

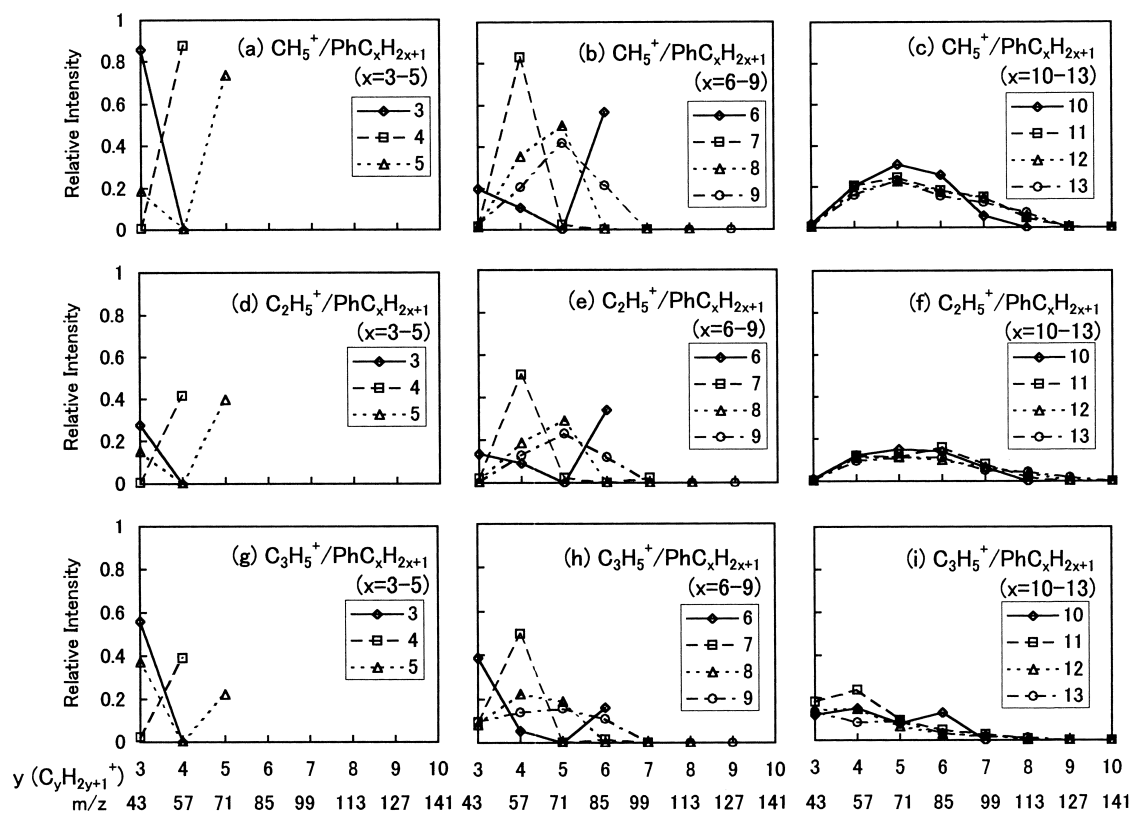


Fig. 3. Initial product-ion distributions of  $C_yH_{2y+1}^+$  ( $y = 3-10$ ) ion in the ion-molecule reactions of  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_3H_5^+$  with  $C_9$ - $C_{19}$  alkylbenzenes. (a), (d), (g)  $\diamond$ :  $PhC_3H_7$ ,  $\square$ :  $PhC_4H_9$ , and  $\triangle$ :  $PhC_5H_{11}$ , (b), (e), (h)  $\diamond$ :  $PhC_6H_{13}$ ,  $\square$ :  $PhC_7H_{15}$ ,  $\triangle$ :  $PhC_8H_{17}$ , and  $\circ$ :  $PhC_9H_{19}$ , (c), (f), (i)  $\diamond$ :  $PhC_{10}H_{21}$ ,  $\square$ :  $PhC_{11}H_{23}$ ,  $\triangle$ :  $PhC_{12}H_{25}$ , and  $\circ$ :  $PhC_{13}H_{27}$ . The largest  $C_yH_{2y+1}^+$  ions correspond to the  $C_xH_{2x+1}^+$  ions. The line connecting the points in the graphs is the alkyl  $C_yH_{2y+1}^+$  ( $y = 3-x$ ) ion formed from the same alkylbenzene.

eV, respectively,<sup>18</sup> many endoergic processes change to exothermic ones for the formation of large  $C_yH_{2y+1}^+$  and  $PhC_yH_{2y}^+$  ions via stabilization due to isomerization. The  $\Delta H^\circ$  values for proton transfer channels, (A-1) and (B-1), increase in the order of  $CH_5^+$ ,  $C_2H_5^+$ , and  $C_3H_5^+$  reactions due to increase in the proton affinity in the order of  $CH_4$  (PA = 5.7 eV),  $C_2H_4$  (7.1 eV) and  $C_3H_4$  (8.0 eV).<sup>18</sup> On the other hand, there are no significant differences in the  $\Delta H^\circ$  values among the hydride-ion abstraction (B-2) and  $PhC_zH_{2z}^-$  or  $C_zH_{2z+1}^-$  ion abstraction reactions (B-3). Although the  $C_yH_{2y+1}^+$  and  $PhC_yH_{2y}^+$  ions can competitively be produced through reactions (B-1), (B-2), and (B-3), the formation of the  $PhC_yH_{2y}^+$  ions is energetically more favorable than that of  $C_yH_{2y+1}^+$  ones on the basis of the energetics. It is clear from Figs. 5(A)–5(F) that the  $\Delta H^\circ$  values are essentially independent of chain length of fragment ions  $y$  for the formation of  $C_yH_{2y+1}^+$ , while they generally decrease with increasing  $y$  for the formation of  $PhC_yH_{2y}^+$  without taking isomerization into account.

In the  $CH_5^+$  reactions,  $[M + H]^+$ ,  $C_yH_{2y+1}^+$  ( $y \leq x$ ),  $[PhH + H]^+$ , and  $PhC_yH_{2y}^+$  ( $y \leq x$ ) ions are observed, as shown in Table 1. Among them,  $[M + H]^+$ ,  $C_xH_{2x+1}^+$ , and  $[PhH + H]^+$  are produced via proton transfer to benzene ring (A-1). The  $C_yH_{2y+1}^+$  ions can be formed via reactions (A-1), (B-1), and (B-2), while the  $PhC_yH_{2y}^+$  ions can be formed via reactions (B-1) and (B-2). It is clear from Fig. 5(A) and Fig. 5(D) that reaction (B-1) is exothermic, while reactions (A-1) and (B-2) are

endothermic in most cases. Thus, chain protonation transfer (B-1) is most favorable on the basis of thermochemical stability of the final products. It is shown that the formation of  $C_yH_{2y+1}^+$  ions in the  $CH_5^+$  reactions dominantly proceeds through proton-transfer to C–H or C–C alkyl chain for  $n$ -paraffins and proton-transfer to C=C bond and  $H^-$  abstraction from the alkyl portion for 1-olefins.<sup>14,15</sup> Since there are more C=C double bonds in alkylbenzenes than in 1-olefin, the probability of the attack of the reactant ions to a C=C bond in ring will become larger than that to alkyl chain. It is therefore highly likely that the dominant formation process of  $C_yH_{2y+1}^+$  from alkylbenzenes is (A-1). In reaction (A-1), the  $C_yH_{2y+1}^+$  ions are produced through the decomposition of  $C_xH_{2x+1}^+$  into  $C_yH_{2y+1}^+$  + olefins. Although the  $\Delta H^\circ$  values for the formation of the  $C_xH_{2x+1}^+$  +  $PhH$  are the same for reactions (A-1) and (B-1), those for the formation of  $C_yH_{2y+1}^+$  +  $PhH$  + olefin through reaction (A-1) are higher than those for the formation of  $C_yH_{2y+1}^+$  +  $PhC_{x-y}H_{2(x-y)+1}$  through reaction (B-1) by about 1 eV. The preferential formation of  $C_yH_{2y+1}^+$  through reaction (A-1), even though it is energetically less favorable than reaction (B-1), is explained by the stability of precursor ring-protonated ions being higher than that of chain protonated ones. We found that no  $C_xH_{2x+1}^+$  ions are formed for molecules  $x > 7$  and that major product alkyl ions are  $C_yH_{2y+1}^+$  ( $y = 4-6$ ). This indicates that significant stabilization of  $C_yH_{2y+1}^+$  occurs by isomerization before decomposition of  $C_xH_{2x+1}^+$ , as ob-

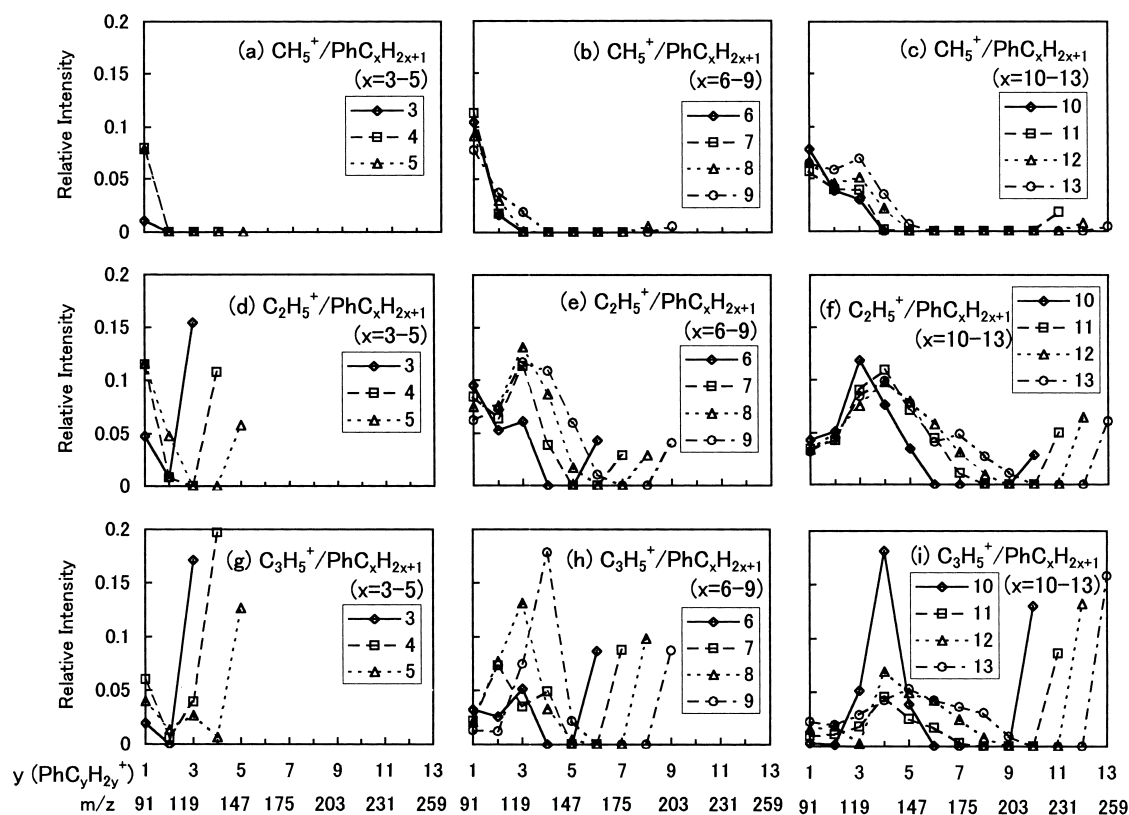


Fig. 4. Initial product-ion distributions of  $\text{PhC}_y\text{H}_{2y}^+$  ( $y = 1-13$ ) ion in the ion-molecule reactions of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  with  $\text{C}_9$ – $\text{C}_{19}$  alkylbenzenes. (a), (d), (g)  $\diamond$ :  $\text{PhC}_3\text{H}_7$ ,  $\square$ :  $\text{PhC}_4\text{H}_9$ , and  $\triangle$ :  $\text{PhC}_5\text{H}_{11}$ , (b), (e), (h)  $\diamond$ :  $\text{PhC}_6\text{H}_{13}$ ,  $\square$ :  $\text{PhC}_7\text{H}_{15}$ ,  $\triangle$ :  $\text{PhC}_8\text{H}_{17}$ , and  $\circ$ :  $\text{PhC}_9\text{H}_{19}$ , (c), (f), (i)  $\diamond$ :  $\text{PhC}_{10}\text{H}_{21}$ ,  $\square$ :  $\text{PhC}_{11}\text{H}_{23}$ ,  $\triangle$ :  $\text{PhC}_{12}\text{H}_{25}$ , and  $\circ$ :  $\text{PhC}_{13}\text{H}_{27}$ . The largest  $\text{PhC}_y\text{H}_{2y}^+$  ions correspond to the  $\text{PhC}_x\text{H}_{2x}^+$  ions. The line connecting the points in the graphs is the  $\text{PhC}_y\text{H}_{2y}^+$  ( $y = 1-13$ ) ion formed from same alkylbenzene.

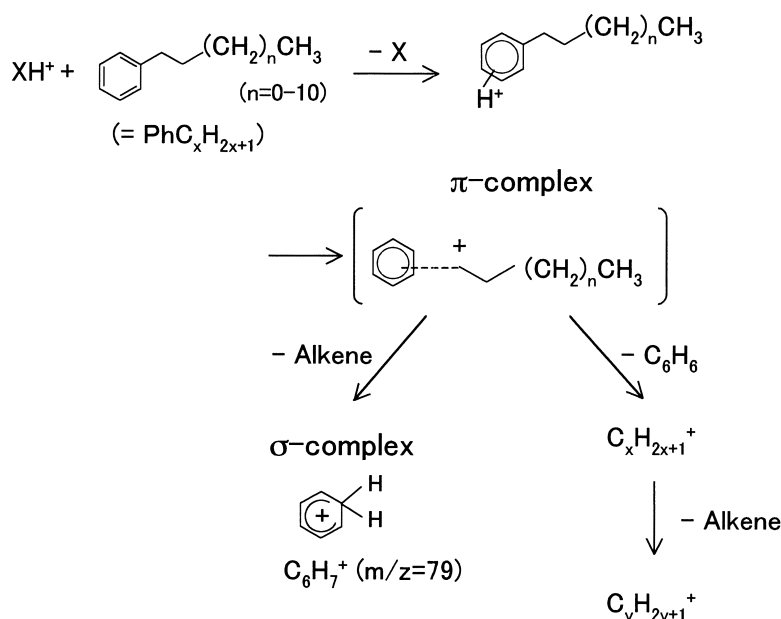
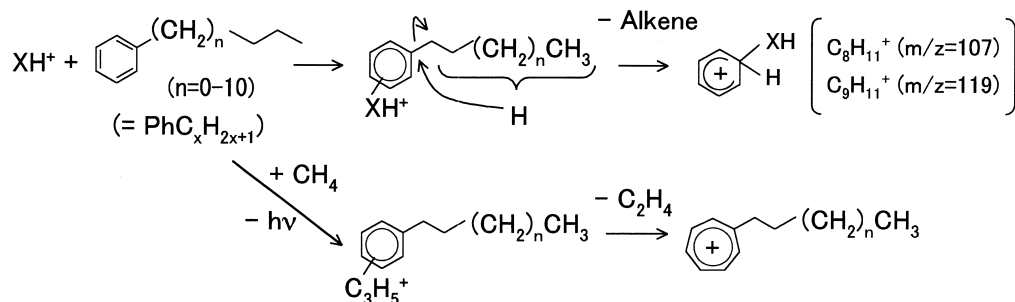
served by Harrison et al. for the formation of  $\text{C}_x\text{H}_{2x+1}^+$  in reaction (A-1).<sup>7,8</sup>

The branching ratios of  $\text{PhC}_x\text{H}_{2x}^+ = [\text{M} - \text{H}]^+$  increase greatly in the order of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  reactions, indicating that the fragmentation is suppressed in the same order due to a decrease in the excess energy. The  $\text{PhC}_x\text{H}_{2x}^+$  ions can be produced through (B-1) and (B-2) in the  $\text{CH}_5^+$  reactions, and through (B-1), (B-2), and (B-3) in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. Although no significant changes are found for the  $\Delta H^\circ$  values among reactions (B-2) and (B-3), such a tendency is found among the  $\Delta H^\circ$  values for reaction (B-1). It is therefore reasonable to assume that proton transfer to alkyl chain, followed by  $\text{H}_2$  loss (B-1), is dominantly responsible for the formation of  $\text{PhC}_x\text{H}_{2x}^+$  in the three reactions.

The  $\text{PhC}_y\text{H}_{2y}^+$  ( $x < y$ ) ions can also be produced through (B-1) and (B-2) in the  $\text{CH}_5^+$  reactions, and through (B-1), (B-2), and (B-3) reactions in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. The extent of fragmentation of  $\text{PhC}_y\text{H}_{2y}^+$  in the  $\text{CH}_5^+$  reactions is higher than the extents in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. This suggests that the  $\Delta H^\circ$  values for the formation of  $\text{PhC}_y\text{H}_{2y}^+$  in the  $\text{CH}_5^+$  reactions are much higher than those in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. Since the  $\Delta H^\circ$  values for the formation of  $\text{PhC}_y\text{H}_{2y}^+$  through hydride-ion abstraction (B-2) are similar among the three reactions, it can be excluded as a major process. On the other hand, the  $\Delta H^\circ$  values for the formation of  $\text{PhC}_y\text{H}_{2y}^+$  through (B-1) in the  $\text{CH}_5^+$  reactions are much lower than those through (B-1) and (B-3) in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  re-

actions. It is therefore concluded that (B-1) is responsible for the formation of  $\text{PhC}_y\text{H}_{2y}^+$  in the  $\text{CH}_5^+$  reactions, and (B-1) and/or (B-3) are responsible for the formation of  $\text{PhC}_y\text{H}_{2y}^+$  in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. The relative contribution of (B-1) and (B-3) in the latter reactions cannot be determined in the present study. The preferential formation of  $\text{C}_7\text{H}_7^+$  in the  $\text{CH}_5^+$  reactions indicates that stable tropylium ion is favorably produced when a sufficient excess energy is supplied to  $\text{PhC}_y\text{H}_{2y}^+$  ( $y \leq x$ ).

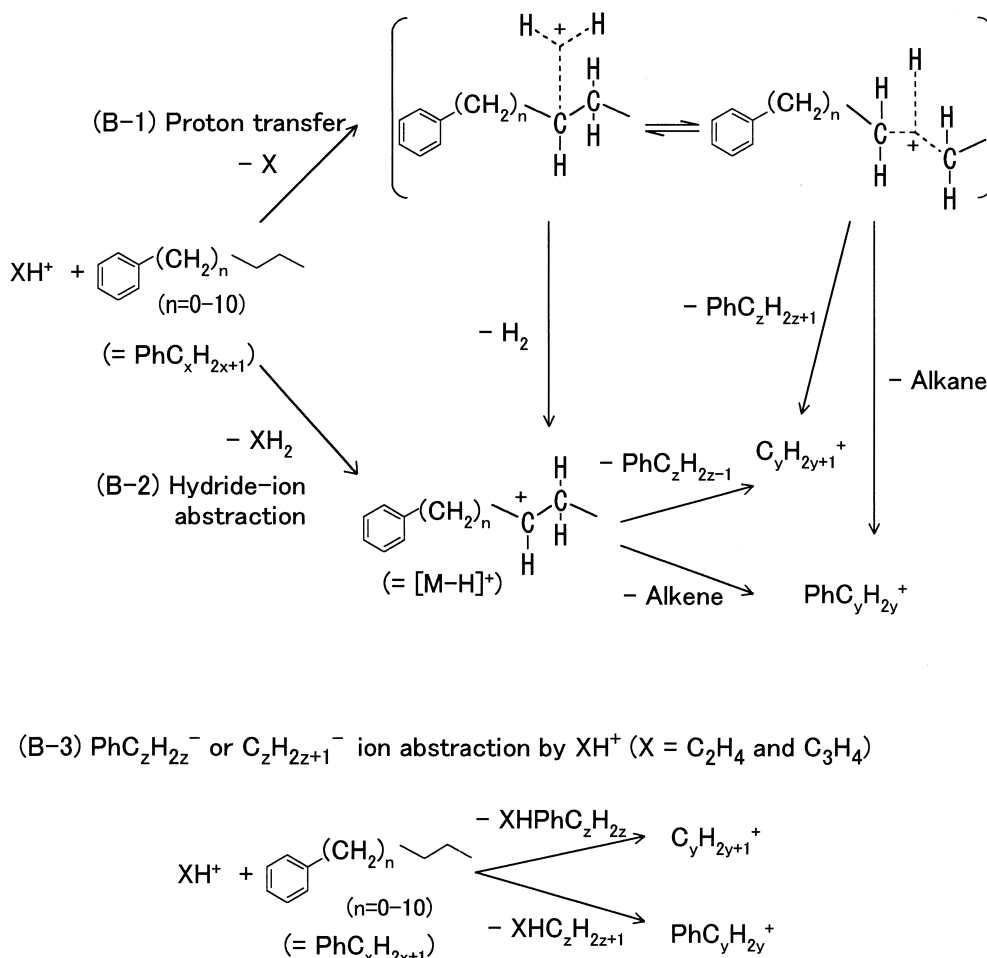
In the  $\text{C}_2\text{H}_5^+$  reactions, the  $[\text{M} + \text{H}]^+$ ,  $\text{C}_y\text{H}_{2y+1}^+$  ( $y \leq x$ ),  $[\text{PhH} + \text{H}]^+$ ,  $\text{PhC}_y\text{H}_{2y}^+$  ( $y \leq x$ ), and  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$  ions are observed, as shown in Table 2. Among them,  $[\text{M} + \text{H}]^+$ ,  $\text{C}_x\text{H}_{2x+1}^+$ , and  $[\text{PhH} + \text{H}]^+$  are produced via proton transfer to benzene ring (A-1). The  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$  ion is produced through addition of  $\text{C}_2\text{H}_5^+$  to the benzene ring (B-3). In addition to reactions (A-1), (B-1), and (B-2),  $\text{PhC}_z\text{H}_{2z}^-$  ion abstraction (B-3) is possible for the formation of  $\text{C}_y\text{H}_{2y+1}^+$  in the  $\text{C}_2\text{H}_5^+$  reactions. It is shown that the formation of the  $\text{C}_y\text{H}_{2y+1}^+$  ions in the  $\text{C}_2\text{H}_5^+$  reactions dominantly proceeds through via hydride-ion abstraction for *n*-paraffins and proton transfer to  $\text{C}=\text{C}$  bond in the reactions of  $\text{C}_2\text{H}_5^+$  with 1-olefins.<sup>14,15</sup> It is clear from Fig. 5(B) that  $\text{PhC}_z\text{H}_{2z}^-$  ion abstraction reactions (B-3) are more favorable than reactions (A-1), (B-1), and (B-2) on the basis of energetics. The  $\text{C}_y\text{H}_{2y+1}^+$  distributions in the  $\text{C}_2\text{H}_5^+$  reactions are similar to those in the  $\text{CH}_5^+$  reactions, indicating that excess energies released in  $\text{C}_y\text{H}_{2y+1}^+$  are similar to those in the  $\text{CH}_5^+$  reactions. There are no significant differ-

(A-1) Proton transfer to the benzene ring by  $XH^+$  ( $X = CH_4, C_2H_4, C_3H_4$ )(A-2) Addition to the benzene ring by  $XH^+$  ( $X = C_2H_4$  and  $C_3H_4$ )Scheme 1. Reaction scheme of the ion-molecule reactions of  $XH^+$  ( $X = CH_4, C_2H_4$ , and  $C_3H_4$ ) with alkylbenzenes for attack of the reactant ion on the benzene ring.

ences in the  $\Delta H^\circ$  values for the formation of  $C_yH_{2y+1}^+$  between (B-3) in the  $C_2H_5^+$  reactions and (B-1) in the  $CH_5^+$  reactions. It is therefore reasonable to assume that  $C_yH_{2y+1}^+$  ions are dominantly formed via  $PhC_zH_{2z}^-$  ion abstraction reactions (B-3) in the  $C_2H_5^+$  reactions.

In the  $C_3H_5^+$  reactions, the  $[M + H]^+$ ,  $C_yH_{2y+1}^+$  ( $y \leq x$ ),  $[PhH + H]^+$ ,  $PhC_yH_{2y}^+$  ( $y \leq x$ ),  $[M + C_3H_5]^+$ , and  $[M + C_3H_5 - C_2H_4]^+$  ions are observed, as shown in Table 3. There are no doubts that  $[M + H]^+$ ,  $C_xH_{2x+1}^+$ , and  $[PhH + H]^+$  are produced through reactions (A-1), while  $[M + C_3H_5]^+$  and  $[M + C_3H_5 - C_2H_4]^+$  are formed via reactions (A-2). Although the  $[PhC_3H_5 + H]^+$  ion can be formed through reaction (A-2), its  $m/z$  value (119) is identical with that of  $PhC_yH_{2y}^+$  ( $y = 3$ ). Therefore, it is difficult to distinguish whether  $m/z = 119$  peaks are  $[PhC_3H_5 + H]^+$  or  $PhC_3H_6^+$ . However, no significant enhancement of the  $m/z = 119$  peak was found in the  $C_3H_5^+$  reactions. Therefore,  $m/z = 119$  peaks observed in this study will be  $PhC_yH_{2y}^+$  ( $y = 3$ ).

Reactions (A-1), (B-1), (B-2), and (B-3) are possible for the formation of  $C_yH_{2y+1}^+$  ions in the  $C_3H_5^+$  reactions. It has been demonstrated that the formation of the  $C_yH_{2y+1}^+$  ions in the  $C_3H_5^+$  reactions dominantly proceeds through via alkanide ion abstraction and hydride-ion abstraction for  $n$ -paraffins and addition to C=C bond for 1-olefins.<sup>14,15</sup> It is clear from Fig. 5(C) that  $PhC_zH_{2z}^-$  ion abstraction reactions (B-3) are more favorable than reactions (A-1), (B-1), and (B-2). The  $\Delta H^\circ$  values for the formation of  $C_yH_{2y+1}^+$  from reaction (B-3) in the  $C_3H_5^+$  reactions are similar to those of (B-1) in the  $CH_5^+$  reactions, and there are no more low-energy reaction pathways leading to  $C_yH_{2y+1}^+$  in the  $C_3H_5^+$  reactions. The extents of fragmentation of  $C_yH_{2y+1}^+$  in the  $C_3H_5^+$  reactions are either higher or similar to those in the  $CH_5^+$  reactions, indicating that similar or higher excess energies are released in the  $C_3H_5^+$  reactions. It is therefore reasonable to assume that  $C_yH_{2y+1}^+$  ions are dominantly formed via lowest energy  $PhC_zH_{2z}^-$  ion abstraction reactions (B-3) in the  $C_3H_5^+$  reactions.



Scheme 2. Reaction scheme of the ion-molecule reactions of  $\text{XH}^+$  ( $\text{X} = \text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{H}_4$ ) with alkylbenzenes for attack of the reactant ion on the alkyl chain.

### Changes in Reaction Mechanism with the Chain Length:

In Figs. 6(a-1), 6(a-2), 6(a-3), 6(b-1), 6(b-2), and 6(b-3), we plot the dependence of branching ratios of major products on the alkyl chain  $x$  in  $\text{PhC}_x\text{H}_{2x+1}$  in the  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  reactions. Figures 6(a-1), 6(a-2), and 6(a-3) shows results for the three product ions,  $[\text{M} + \text{H}]^+$ ,  $\text{C}_x\text{H}_{2x+1}^+$ ,  $[\text{PhH} + \text{H}]^+$ , produced through the attack of the reactant ions on the benzene ring. Figures 6(b-1), 6(b-2), and 6(b-3) shows the results for  $\Sigma([\text{M} + \text{H}]^+)$ ,  $\text{C}_x\text{H}_{2x+1}^+$ ,  $[\text{PhH} + \text{H}]^+$  denoted by A,  $\Sigma\text{C}_y\text{H}_{2y+1}^+$  ( $y < x$ ) denoted by B, and  $\Sigma\text{PhC}_y\text{H}_{2y+1}^+$  ( $y \leq x$ ) denoted by C,  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$ , and  $\Sigma([\text{M} + \text{C}_3\text{H}_5]^+)$  and  $[\text{M} + \text{C}_3\text{H}_5 - \text{C}_2\text{H}_4]^+$ . In all the three reactions, dominant ions are the  $[\text{M} + \text{H}]^+$ ,  $\text{C}_x\text{H}_{2x+1}^+$ , and  $[\text{PhH} + \text{H}]^+$  ions, produced through reaction (A-1) for short-chain reagents ( $x < 7$ ). The branching ratios of  $[\text{M} + \text{H}]^+$  in the  $\text{CH}_5^+$  reactions are smaller than those in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. This indicates that ring-protonated  $[\text{M} + \text{H}]^+$  ions are decomposed into  $\text{C}_x\text{H}_{2x+1}^+$ , when sufficient excess energies are supplied to the precursor  $[\text{M} + \text{H}]^+$  ions in reaction (A-1). For long-chain reagents ( $x \geq 7$ ), major product ions are  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$ . Dominant  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions produced from  $x \geq 7$  reagents are  $y = 4-6$  fragment ions. The lack of  $\text{C}_x\text{H}_{2x+1}^+$  and high branching ratios of  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions for  $x \geq 7$  are

attributed to the fact that isomerization to secondary and tertiary alkyl groups occurs significantly for  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$ . Therefore, the  $\text{C}_x\text{H}_{2x+1}^+$  and  $\text{PhC}_x\text{H}_{2x}^+$  ions are decomposed into smaller stable  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions with a secondary or tertiary alkyl group, when they are produced. The low branching ratios of  $\text{C}_y\text{H}_{2y+1}^+$  for  $x < 7$  can be explained by the absence of or the low probability of such a low-energy decomposition channel for short alkyl  $\text{C}_x\text{H}_{2x+1}^+$  ions. Therefore, the  $\text{C}_x\text{H}_{2x+1}^+$  ions become dominant alkyl ions for  $x < 7$ .

The branching ratios of  $\text{C}_y\text{H}_{2y+1}^+$  in the  $\text{CH}_5^+$  reactions are larger than those in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  ones. One reason for this is higher excess energies of  $[\text{M} + \text{H}]^+$  and  $\text{C}_x\text{H}_{2x+1}^+$  ions in the  $\text{CH}_5^+$  reactions due to the highest acidity, which induces higher probability of fragmentation of these ions into smaller  $\text{C}_y\text{H}_{2y+1}^+$  ions. It should be noted that the  $[\text{M} + \text{H}]^+$  ions are observed in the  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  reactions for long-chain reagents ( $x > 7$ ) and that their branching ratios are nearly constant. Although the branching ratios of  $[\text{M} + \text{H}]^+$  ions, produced through the attack of the reactant ions on benzene ring, will decrease with increasing the chain length, they are essentially independent of  $x$ . One reason for this will be an effective occurrence of intramolecular proton transfer from chain proto-

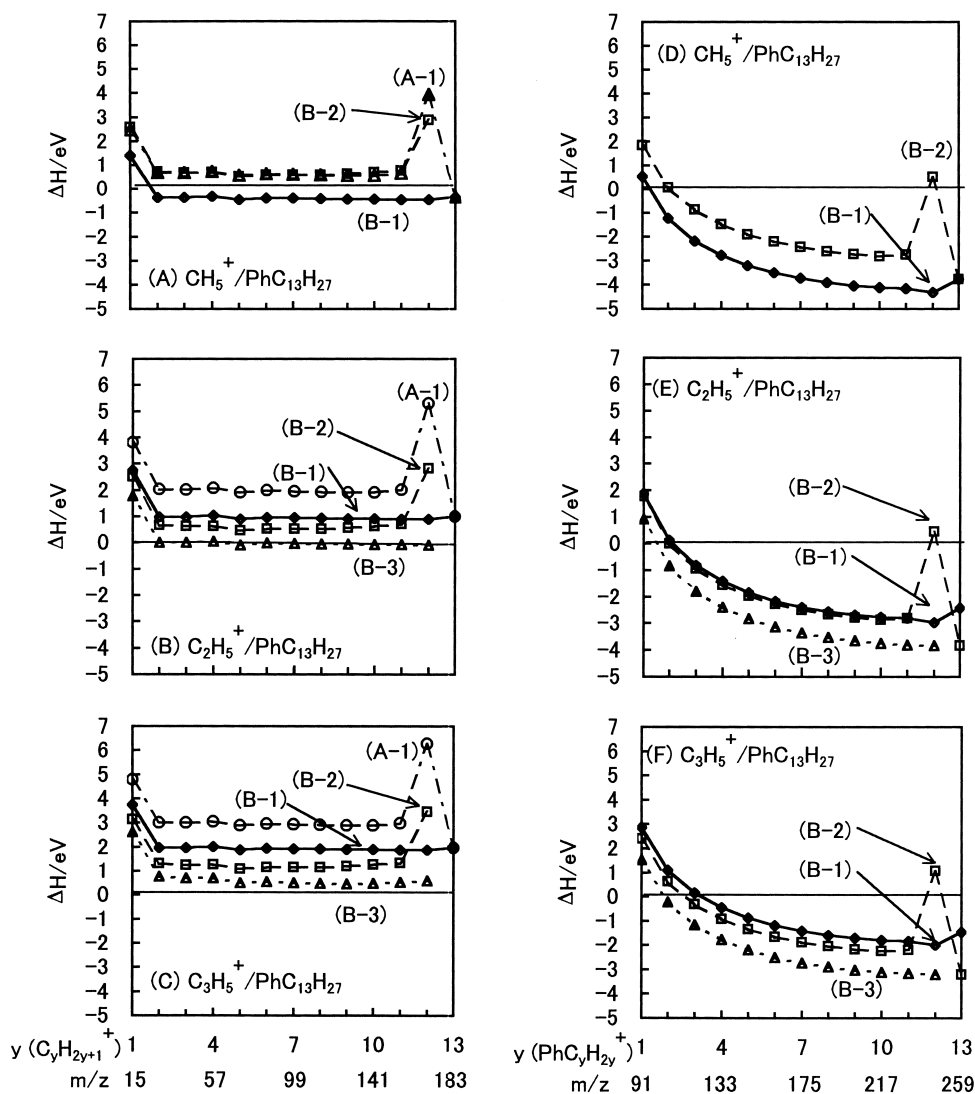


Fig. 5. Energy relations in the ion-molecule reactions of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  with  $\text{PhC}_{13}\text{H}_{27}$  leading to  $1\text{-C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$ .  $\diamond$ : (1a) Proton transfer,  $\square$ : (2a) hydride-ion abstraction,  $\triangle$ : (3a)  $\text{PhC}_x\text{H}_{2x-}$  ion abstraction. The largest  $\text{C}_y\text{H}_{2y+1}^+$  ions correspond to the  $\text{C}_x\text{H}_{2x+1}^+$  ions.  $\diamond$ : (1b) Proton transfer,  $\square$ : (2b) hydride-ion abstraction,  $\triangle$ : (3b)  $\text{C}_x\text{H}_{2x+1}^-$  ion abstraction. The largest  $\text{PhC}_y\text{H}_{2y}^+$  ions correspond to the  $\text{PhC}_x\text{H}_{2x}^+$  ions. The line connecting the points in the graphs is the  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  formed from the same reaction pathway.  $\Delta H^\circ$  values are shown in eV units ( $1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$ ).

nated ions to more stable ring ones, though this mechanism is not described in Scheme 2 for the sake of clarity.

**Concluding Remarks:** The gas-phase ion-molecule reactions of  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ , and  $\text{C}_3\text{H}_5^+$  with alkylbenzenes ( $\text{PhC}_x\text{H}_{2x+1}$ ;  $x = 3\text{--}13$ ) have been studied in an ion-trap type of GC/MS by separating each reactant ion. In all the reactions,  $\text{C}_y\text{H}_{2y+1}^+$  ( $y = 3\text{--}10$ ),  $\text{PhC}_y\text{H}_{2y}^+$  ( $y = 1\text{--}13$ ), and  $[\text{M} + \text{H}]^+$  ions were observed. In addition,  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$  ions were observed in the  $\text{C}_2\text{H}_5^+$  reactions, while adduct  $[\text{M} + \text{C}_3\text{H}_5]^+$  and  $[\text{M} + \text{C}_3\text{H}_5 - \text{C}_2\text{H}_4]^+$  ions were observed in the  $\text{C}_3\text{H}_5^+$  reactions. The dependence of the relative intensities of product ions on the reaction times indicated that collisional stabilization took part in the formation of some product ions. For short-chain reagents ( $x < 7$ ), dominant product ions were the  $[\text{PhH} + \text{H}]^+$ ,  $\text{C}_x\text{H}_{2x+1}^+$ , or  $[\text{PhH} + \text{H}]^+$  ions, produced by proton transfer to benzene ring. For long-chain reagents ( $x \geq 7$ ), the  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions were observed as major

products. On the basis of the product-ion distributions and the energetics, major reaction mechanisms for the formation of  $\text{C}_y\text{H}_{2y+1}^+$  and  $\text{PhC}_y\text{H}_{2y}^+$  ions are discussed. The dominant formation processes of  $\text{C}_y\text{H}_{2y+1}^+$  ions are proton transfer to benzene ring in the  $\text{CH}_5^+$  reactions, and  $\text{PhC}_x\text{H}_{2x-}$  ion abstraction in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. On the other hand, the processes of  $\text{PhC}_y\text{H}_{2y}^+$  ions are proton transfer to alkyl chain in the  $\text{CH}_5^+$  reactions, and proton transfer and/or  $\text{C}_x\text{H}_{2x-}$  ion abstraction in the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_5^+$  reactions. Further detailed experimental and theoretical studies are required to confirm the above prediction.

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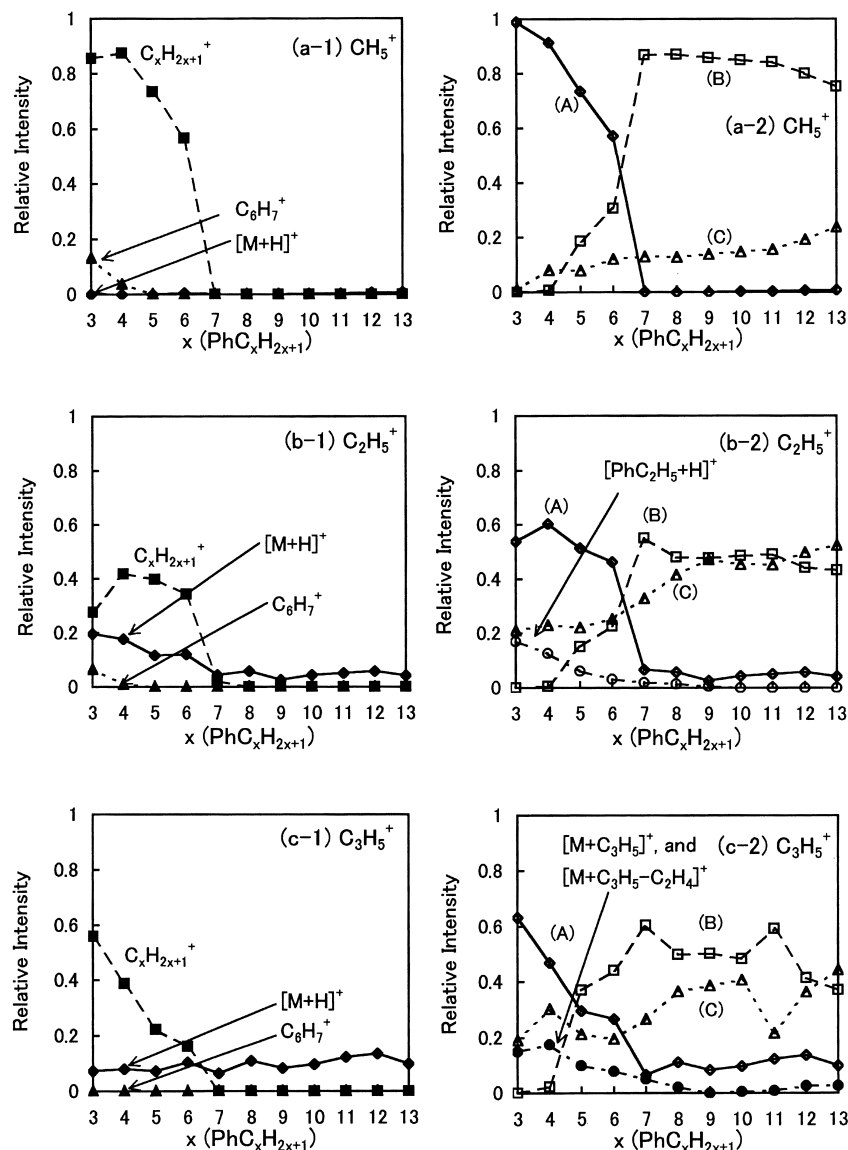


Fig. 6. Dependence of the branching ratios of product ions on the alkyl chain  $x$  in  $\text{PhC}_x\text{H}_{2x+1}$ . (a)  $\text{CH}_5^+$ , (b)  $\text{C}_2\text{H}_5^+$ , and (c)  $\text{C}_3\text{H}_5^+$ .

◆:  $[\text{M} + \text{H}]^+$ , ■:  $\text{C}_x\text{H}_{2x+1}^+$ , ▲:  $[\text{PhH} + \text{H}]^+$ , ◇: (A) =  $\Sigma([\text{M} + \text{H}]^+, \text{C}_x\text{H}_{2x+1}^+, \text{and } [\text{PhH} + \text{H}]^+)$ , □: (B) =  $\text{C}_y\text{H}_{2y+1}^+$  ( $y < x$ ), and △: (C) =  $\text{PhC}_y\text{H}_{2y+1}^+$  ( $y \leq x$ ). ○:  $[\text{PhC}_2\text{H}_5 + \text{H}]^+$ , ●:  $\Sigma([\text{M} + \text{C}_3\text{H}_5]^+ \text{ and } [\text{M} + \text{C}_3\text{H}_5 - \text{C}_2\text{H}_4]^+)$ .

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