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Initial Product-Ion Distributions in Ion-Molecule Reactions of CH$_5^+$, C$_2$H$_5^+$, and C$_3$H$_5^+$ with Anilines, Nitrobenzene, and Benzonitrile

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The gas-phase ion-molecule reactions of CH$_5^+$, C$_2$H$_5^+$, and C$_3$H$_5^+$ with five monosubstituted benzenes (M) carrying a nitrogen atom in the substituent [PhX: X = NH$_2$, NHCH$_3$, N(NCH$_2$)$_2$, NO$_2$, CN] have been reinvestigated under a reagent-ion selective mode of an ion-trap type of GC/MS. The dependence of product-ion distributions on the reaction time indicated that collisional stabilization takes part in the formation of all adduct (M + C$_n$H$_m$)$_n^+$ and (M + C$_n$H$_m$)$_n^+$ ions. It was found that radiative association also participates in the formation of adduct (PhNH$_2$ + C$_n$H$_m$)$_n^+$ and (PhCN + C$_n$H$_m$)$_n^+$ ions. 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 reaction mechanism was discussed based on initial product-ion distributions and heats of formation of each reaction pathway.

1. Introduction

We have recently made a systematic mass-spectrometric study on ion-molecule reactions of such typical hydrocarbon ions as CH$_5^+$, C$_2$H$_5^+$, and C$_3$H$_5^+$ with monosubstituted benzenes using an ion-trap type of GC/MS. In a previous paper, results for PhX [X = NH$_2$, NHCH$_3$, N(NCH$_2$)$_2$, NO$_2$, CN] have been reported. The reaction mechanism of these monosubstituted benzenes carrying a nitrogen atom in the substituent for the hydrocarbon ions was discussed based on product-ion distributions and semi-empirical PM3 calculations of potential energies of intermediates and products. We discussed reaction mechanism on the basis of product-ion distributions measured at a constant reaction time of 20 ms, assuming that the effects of secondary collisions were insignificant. However, we have recently noticed that this assumption is incorrect, because total number of collisions of a product ion with chemical ionization (CI) CH$_4$ gas is estimated to be about 50 times at 20 ms on the basis of a simple hard sphere gas kinetic model. Therefore, collisional stabilization may participate in the formation of product ions. In the present study, we have reinvestigated the ion-molecule reactions of CH$_5^+$, C$_2$H$_5^+$, and C$_3$H$_5^+$ with PhX [X = NH$_2$, NHCH$_3$, N(NCH$_2$)$_2$, NO$_2$, CN]. The dependence of product-ion distributions on the reaction time is measured in order to examine the contribution of collisional stabilization to the formation of product ions. The initial product-ion distributions are estimated by extrapolating the dependence of branching ratios of product ions on the reaction time to zero reaction time. The reaction mechanism is discussed based on initial product-ion distributions and heats of reactions of each reaction pathway calculated in the previous study.

2. Experimental

CH$_3$Cl mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS in a reactant-ion selective mode. The electron-impact ionization on CH$_3$Cl provides primary CH$_3^+$ (m = 2-4) ions, and the subsequent fast ion-molecule reactions yield the secondary CH$_7^+$, C$_2$H$_5^+$, and C$_3$H$_5^+$ ions:

\[
\begin{align*}
\text{CH}_3^+ + \text{CH}_4 &\rightarrow \text{CH}_5^+ + \text{CH}_3, \\
\text{CH}_5^+ + \text{CH}_4 &\rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2, \\
\text{CH}_7^+ + \text{CH}_4 &\rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2 + \text{H}_2.
\end{align*}
\]

Since further reactions of CH$_5^+$, C$_2$H$_5^+$, and C$_3$H$_5^+$ with CH$_4$ are very slow, these ions become dominant reactant ions in the CH$_3$Cl experiments. The reactant CH$_5^+$, C$_2$H$_5^+$, or C$_3$H$_5^+$ ion thus formed was selectively trapped in the ion trap. The maximum and average kinetic energies of the reactant ions in our apparatus were evaluated to be 10 and 4.2 eV for CH$_3^+$, 6.0 and 2.4 eV for C$_2$H$_5^+$, and 4.3 and 1.7 eV for C$_3$H$_5^+$, respectively, using a pseudo-potential well method. These energies are higher than that in the medium-pressure CI experiments, which was estimated to be less than 1 eV. The time for storing a reactant ion was 5 ms. The reaction time was varied from 1 to 100 ms. The ion-trap cell was kept at ≤170°C. The reagents were diluted in hexane and injected into the GC with a high-purity carrier He gas. The partial pressures of He and CH$_4$ in an ion-trap cell were estimated to be 5×10$^{-5}$ and 7×10$^{-5}$ Torr, respectively. The mass spectra were measured at low reagent concentrations of about 1,000-10,000 pg cm$^{-3}$ in order to remove secondary ion-molecule reactions with reagent molecules. 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
Reactions of RH\(^+\) with N-Containing Benzene Derivatives

Table 1. Initial Product-Ion Distributions in the Reactions of CH\(_2\)\(^+\), C\(_2\)H\(_2\)\(^+\), and C\(_3\)H\(_2\)\(^+\) with PhX (X=NH\(_3\), NHCH\(_3\), Ni(CH\(_3\))\(_2\), and CN\(^-\)) \(^{ab}\)

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Ionization potential (eV) (^{c})</th>
<th>PhNH(_2)</th>
<th>PhNHCH(_3)</th>
<th>PhNICH(_2)</th>
<th>PhNO(_2)</th>
<th>PhCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant</td>
<td>Ion</td>
<td>CH(_2)(^+)</td>
<td>C(_2)H(_2)(^+)</td>
<td>C(_3)H(_2)(^+)</td>
<td>CH(_2)(^+)</td>
<td>C(_2)H(_2)(^+)</td>
</tr>
<tr>
<td>Product ions</td>
<td>M(^+)</td>
<td>26(–) 45(–)</td>
<td>41(–) 59(–)</td>
<td>20(0) 58(–) 69(0)</td>
<td>100 100 92(+)</td>
<td>100 100 66(–)</td>
</tr>
<tr>
<td>(M+H(^+)) (^{d})</td>
<td>73.3</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
</tr>
<tr>
<td>(M+C(_2)H(_2))(^+) (^{d})</td>
<td>71.2</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
</tr>
<tr>
<td>(M+C(_3)H(_2)−C(_2)H(_2))(^+) (^{d})</td>
<td>9.86</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
</tr>
<tr>
<td>(M−O(^−)) (^{d})</td>
<td>9.62</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
<td>0(+) 0(+)</td>
</tr>
</tbody>
</table>

\(^{a}\) Uncertainties are ±7%.

\(^{b}\) Symbols, +, –, and 0 in brackets denote its branching ratio increases, decreases, or is unchanged with increasing the reaction time, respectively.

\(^{c}\) Reference 10.

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 Summary of mass spectrometric data

The observed product ions, their reaction-time dependence, and initial product-ion distributions in each reaction are summarized in Table 1. The branching ratios of product ions either increase, decrease, or are essentially unchanged with increasing the reaction time. They are represented by +, −, and 0, respectively, in brackets in Table 1. The initial product-ion distributions were estimated by extrapolating the dependence of branching ratios of product ions on the reaction time to zero reaction time. The uncertainties of the branching ratios were estimated to be within ±7%.

3.2 Anilines

Possible reaction pathways for anilines are proton transfer (PT), association, and charge transfer (CT), as shown in Scheme 1. Collisional stabilization and radiative association can participate in the association reactions. They are shown using such symbols as +CH\(_3\) and −H\(_2\)CO, respectively, in Scheme 1. Since ionization potentials of anilines, shown in Table 1, are lower than the recombination energies of C\(_2\)H\(_2\) (8.13 eV) and C\(_3\)H\(_2\) (8.13 eV for CH\(_2\)CH\(_2\)H\(_2\)), CT channels (1e) are energetically open. In the CH\(_2\)\(^+\) reactions, only PT channel is found for PhNH\(_2\) and PhNHCH\(_3\), while CT channel as well as PT one is observed for PhNICH\(_2\). On the basis of known thermochemical data, \(^{10}\) PhNICH\(_2\)\(^+\) in the CH\(_2\)\(^+\)/PhNICH\(_2\) reaction is expected to be produced through the following processes, though the relative importance between (R 4a) and (R 4b) cannot be determined in the present study:

\[
\text{CH}_2^+ + \text{PhNICH}_2 \rightarrow \text{PhNICH}_2^+ + \text{H}_2 + 0.74 \text{ eV}, \quad (\text{R} \ 4\text{a})
\]

\[
\text{CH}_2^+ + \text{PhNICH}_2 \rightarrow \text{PhNICH}_2^+ + \text{CH}_3 + \text{H} + 0.76 \text{ eV}, \quad (\text{R} \ 4\text{b})
\]

In the reactions of CH\(_2\)\(^+\) and C\(_2\)H\(_2\)\(^+\) with all the three anilines, PT (1a), association (1b), and CT (1c) channels are observed. In general, the proton-donating ability (acidity) of hydrocarbon ions decreases with increasing the dissociation energy of RH\(^+\) \cdot R \rightarrow II \(^+\), which is denoted as \(D_0(R-H\(^+\)).\) Since the \(D_0(R-H\(^+\))\) value increases in the order of CH\(_2\)\(^+\) (5.7 eV), C\(_2\)H\(_2\)\(^+\) (7.1 eV), and C\(_3\)H\(_2\)\(^+\) (7.83 eV for CH\(_2\)=CHCH\(_2\)), the acidity of hydrocarbon ions decreases in the same order. The M\(^+\)/ (M+H\(^+\)) ratios are shown in Table 1. With decreasing the acidity of the reactant hydrocarbon ion, the M\(^+\)/(M+H\(^+\)) ratio increases from 0 to 1.05 for PhNH\(_2\), from 0 to 1.44 for PhNICH\(_2\), and from 0.25 to 2.23 for PhN-
(CH₃)₂. It also increases from 0 to 0.25 for CH₄⁺, from 0.35 to 1.38 for C₃H₅⁺, and from 1.05 to 2.23 for C₅H₇⁺ with decreasing the ionization potential of anilines, probably because more CT product channels are open for molecules with low ionization potentials and/or PT channel is suppressed with increasing the bulkiness of substituent (NR'R²⁺).

It is known that three-body collisional association and two-body radiative association can participate in the formation of adduct ions. In radiative association, adduct ions are stabilized by radiating infrared emissions. A typical rate of infrared emission would be 100 photons s⁻¹, whereas the total collision numbers in this study are estimated to be 9–340 times during reaction times of 1–100 ms, corresponding to the collision rate of 2.400 collisions s⁻¹. Therefore, not only radiative association (−hv) but also collisional association (+CH₄) may participate in the formation of (M+C₂H₅)⁺ and (M+C₅H₇)⁺ under our operating conditions. In general, the formation rate of adduct ions (M+RH)⁺ by an ion-molecule reaction of RH⁺ with M is given by

$$\frac{df}{dt}[(M+RH)⁺] = k_f[RH⁺][M] + k_o[RH⁺][TM][CH₄].$$

(R-5)

where k_f and k_o are rate coefficients of radiative association and collisional association, respectively. If the dependence of product-ion distributions on the CH₄ pressure can be measured, the relative contribution of the two association processes can be determined. The reactant ions were not generated at low CH₄ pressures below 4×10⁻⁵ Torr, because secondary ion-molecule reactions (R-1)–(R-3b) did not take place efficiently. On the other hand, the upper limit of CH₄ pressure was restricted by the upper limit of stable operation of a turbomolecular pump (3×10⁻⁴ Torr). Since the variable range of the CH₄ pressure was quite narrow in our experiments, the relative contribution of the two association processes could not be determined from the dependence of product-ion distributions on the CH₄ pressure. The effect of three-body collisions can be examined by changing the reaction (residence) time of ions in the ion trap because the number of collisions with the third-body CH₄ molecule increases with increasing the reaction time. Thus, the dependence of product-ion distributions on the reaction time was measured in order to determine the relative contribution of the two association processes. The collision-free initial product-ion distributions, given in Table 1, were estimated by extrapolating the dependence of branching ratios of product ions on the reaction time to zero reaction time. Figures 1–3 show the results obtained.

Fig. 1. Dependence of branching ratios of product ions on the reaction time in the (a) C₅H₇⁺/PhNH₂ and (b) C₅H₇⁺/PhNH₃ reactions.

Fig. 2. Dependence of branching ratios of product ions on the reaction time in the (a) C₅H₇⁺/PhNHCH₃ and (b) C₅H₇⁺/PhNHCH₃ reactions.
for PhNH₃, PhNH₂CH₃, and PhN(CH₃)₂, respectively, where more than two ions are produced. It should be noted that the branching ratios of (M+CH₃H)⁺, (M+C₃H₃)⁺, and (M+C₆H₆-C₃H₃)⁺ ions decrease with decreasing the reaction time. This suggests that collisional stabilization plays a significant role in the non-dissociative and dissociative association leading to (M+C₂H₅)⁺, (M+C₃H₃)⁺, and (M+C₆H₆-C₃H₃)⁺. The branching ratios of (M+C₂H₆)⁺ for all the three anilines and (M+C₅H₅)⁺ for PhNH₂CH₃ and PhN(CH₃)₂ become zero at zero reaction time, indicating that they are exclusively formed via collisional stabilization. These adduct ions are observed at a low total (CH₄+He) pressure of 1.2×10⁻⁴ Torr. Therefore, we have previously concluded that initial adduct ions and their dissociation products are formed by radiative association in all the reactions of C₂H₅ and C₆H₆ with anilines. However, the present results for anilines indicate that this conclusion was incorrect. Although the branching ratios of (PhNH₂+CH₃H)⁺ and (PhNH₂+C₆H₆-C₃H₃)⁺ also decrease with decreasing the reaction time, they do not drop to zero at zero reaction time. This shows that not only collisional stabilization but also radiative association takes part in the formation of (PhNH₂+C₃H₃)⁺. The relative contribution of the latter process increases with decreasing the reaction time.

The (PhNR'R'''+H)⁺ ions can be formed through a PT to the lone-pair electrons of the N-atom or to the benzene ring, as shown in Scheme 1. The electron-donating effect of the NR'R'' group will enhance the formation of Wheland-type ring adduct ions, while a high reactivity of the lone-pair electrons on the nitrogen atom will yield N-protonated ions preferentially. It is likely that protonation is governed thermodynamically because there will be little barrier in the protonation processes. In our previous paper,³⁰ we reported energies of reactants and various products obtained using known thermochemical data and calculated PM3 data. Assuming that the protonation is controlled thermodynamically, the most stable N-protonated ions will be more favorable products. However, a possibility of preferential protonation to a ring cannot be excluded, because the energy differences between N-protonation and ortho- or para-ring-protonation are small (0.4–0.6 eV).³³ The (PhNH₃+C₅H₅)⁺ ion can be formed through association to the lone-pair electrons of the N-atom or to the benzene ring, as shown in Scheme 1. Since the association is a reversible process without an energy barrier, it will be controlled thermodynamically. According to the potential-energy diagrams of association pathways in the C₅H₅/PhNH₃ reactions,³⁴ N-adduct ions are more stable than para-ring-adduct ions by 0.30–0.42 eV. It is therefore reasonable to assume that the attack of C₅H₅⁺ ions occurs preferentially on the substituent for PhNH₃. The preferential occurrence of radiative association in the C₅H₅/PhNH₃ reaction implies that the formation rate of association products, which decay radiatively, increases with decreasing the bulkiness of NR'R''⁺. In general, the association rate will decrease with increasing the kinetic energy of the reactant ion.²⁹,¹¹,¹² The adduct ion could be observed even though the average kinetic energy of the C₅H₅⁺ ion is higher than 1.7 eV. This can be explained by the facts that the reactant C₅H₅⁺ ion has a wide kinetic energy distribution involving a low energy component and that an initial kinetic energy of C₅H₅ is partially converted into the third-body CH₃ molecule in the case of three-body association.

3.3 Nitrobenzene

Only PT channel was found in the reactions of CH₃⁺ and C₆H₅⁺ with PhNO₂ which agreed with our previous observation.³⁶ The lack of CT channel was attributed to a high ionization potential of PhNO₂ (Table 1). It should be noted that (PhNO₂+C₆H₅)⁺ and PhNO₂⁺ ions as well as (PhNO₂+H)⁺ ion are observed in the C₆H₅/PhNO₂ reaction. Figure 4 shows the dependence of branching ratios of product ions on the reaction time in the C₆H₅/PhNO₂ reaction. The branching ratio of (PhNO₂+H)⁺ increases, while that of (PhNO₂+C₆H₅)⁺ decreases, as the reaction time decreases. The disappearance of (PhNO₂+C₆H₅)⁺ at zero reaction time indicates that this adduct ion is exclusively produced by collisional stabilization process. This conclusion disagrees with our previously prediction that (PhNO₂+C₆H₅)⁺ is produced via radiative association process.³⁵

In Scheme 2 are shown observed major reaction pathways of the RH⁺/PhNO₂ reactions. The (PhNO₂+H)⁺ and (PhNO₂+C₆H₅)⁺ ions can be formed through
an attack on the O-atom in the substituent or on the benzene ring. Since the NO₂ group has electron-withdrawing properties, the formation of ring adducts will be suppressed. Actually O-protonated and O-adduct ions are more stable than meta-ring-protonated and ring-adduct ions by 0.9 and 0.5–0.6 eV, respectively. Therefore, the major (PhNO₂⁺+H)⁺ and (PhNO₂⁺+C₆H₅)⁺ ions will be more stable O-protonated and O-adduct ions. Although the (PhNO₂⁺+C₆H₅)⁺ ion was formed, the (PhNO₂⁺+C₆H₅)⁺ ion could not be detected. This difference will be discussed in Section 3.5.

The PhNO₂⁺ ion was found only in the C₆H₅⁺/PhNO₂ reaction. It is probably formed via the following O⁻-abstraction processes:

\[ \text{Scheme 2. Possible reaction pathways for the ion-molecule reactions of RH⁺ with nitrobenzene.} \]

C₆H₅⁺ + PhNO₂
\[ \rightarrow \text{PhNO⁺⁺ + C₆H₅COCH₃ (acetonyl radical)} +1.00 \text{ eV} \]  
\[ \rightarrow \text{PhNO⁺⁺ + C₆H₅CO (propionyl radical)} -0.06 \text{ eV} \]

Since the endoergic energy in process (R-6b) can be supplied from the translational energy of C₆H₅⁺, both processes are energetically accessible.

3.4 Benzonitrile

The observed product channels for PhCN with a high ionization potential are similar to those for PhNO₂. Only PT channel was found in the CH₃⁺/PhCN and C₆H₅⁺/PhCN reactions, while PT and association reaction were found in the C₆H₅⁺/PhCN reaction. The most outstanding feature of the C₆H₅⁺/PhCN reaction is the observation of a large amount of the adduct (PhCN⁺+C₆H₅⁺) ion. Figure 5 shows the dependence of branching ratios of product ions on the reaction time in the C₆H₅⁺/PhCN reaction. Although the branching ratio of the (PhCN⁺+C₆H₅⁺) ion decreases with decreasing the reaction time, it converges into a high value of 94% at zero reaction time. On the basis of this finding, it was concluded that the initial adduct ion is produced through both collisional stabilization and radiative association.

In Scheme 3 are shown the observed major reaction pathways of the RH⁺/PhCN reactions. The (PhCN⁺+H)⁺ and (PhCN⁺+C₆H₅⁺) ions can be formed through electrophilic attack on the CN bond in the substituent or on the benzene ring. The CN group has electron-withdrawing properties. Therefore, the ring-protonated ions will be suppressed, while the triple C≡N bond will have high reactivity for electrophiles. Actually, N-protonated and N-adduct ions are more stable than ring-protonated and ring-adduct ions by 1.2 and 1.4–1.9 eV. On the basis of above findings, the major (PhCN⁺+H)⁺ and (PhCN⁺+C₆H₅⁺) ions will be the most stable N-protonated and N-adduct ions.

3.5 Radiative association

An important finding of this work is the observation of radiative association in the reactions of C₆H₅⁺ with PhNH₂ and PhCN. According to many experimental studies using a low pressure ion-cyclotron-resonance
spectrometer and theoretical studies based on Ramaspger–Rice–Kassel–Marcus (RRKM) theory by Dunbar and his co-workers, the ratio of radiative association to redissociation of collision complex depends on the binding energy and the number of internal degrees of freedom (N) of the collision complex, and the reaction temperature. In general, it increases with increasing the binding energy and the number of internal degrees of freedom and with decreasing the reaction temperature. Their calculations showed that radiative association rate is dominantly governed by the binding energy of the complex; compared with the effects of changing the binding energy, the effects of changes in radiative rate or reaction temperature are much weaker. Thus, one reason for the observation of adduct ions in this study, even though the reactant \( \text{C}_2\text{H}_4^+ \) ion has a relatively high average kinetic energy of 1.7 eV, is a weak temperature dependence of radiative association rate. According to our PM3 calculations, the binding energies of adduct ions produced from the reactions of \( \text{C}_2\text{H}_4^+ \) and \( \text{C}_2\text{H}_4^+ \) with anilines, nitrobenzene, and benzonitrile are 0.9–3.0 eV. These values and N values (57–81) are sufficiently large to form association products: for example, the ratio of radiative association to the redissociation of educt ion at 300 K is estimated to be \( >1 \) for molecules having a binding energy of 2.0 eV and an N value of 60 using Fig. 1 in ref. 11. Dunbar predicted that the rate of radiative association will be enhanced by the presence of bright IR chromophores. In the present reagents, the NR'R', NOx, and CN groups are bright IR chromophores. Therefore, radiative association can occur for the reactions of \( \text{C}_2\text{H}_4^+ \) and \( \text{C}_2\text{H}_4^+ \) with all the five reagents studied here. However, radiative association was observed only in the \( \text{C}_2\text{H}_4^+ \) reactions.

In the present reaction systems, protonation competes with association. The structures and energies of \( \text{C}_2\text{H}_4^+ \) were calculated at the RHF/6-31G**, MP2/6-31G**, and B3LYP/6-31G** levels for the non-classical \( \text{C}_2 \) bridged structure 1 and the two Cs classical structures 2 and 3, shown in Fig. 6. The results obtained are shown in Table 2. Our results are in good agreement with previous \textit{ab initio} data of Pope's group, though \( R(\text{C-C}) \) values were not calculated in their study. The structure 1 is most stable in all the three methods, being consistent with their data. Although a positive charge is localized on H in the bridged position for the case of \( \text{C}_2\text{H}_4^+ \), it is delocalized on CCC bond for the case of \( \text{C}_2\text{H}_4^+ \). The protonation channel will be promoted by the localization of the positive charge on H in the bridged position for the case of \( \text{C}_2\text{H}_4^+ \), and it will be suppressed by delocalization of the positive charge among CCC bond for the case of \( \text{C}_2\text{H}_4^+ \). This will be a major reason for the lack of radiative association in the \( \text{C}_2\text{H}_4^+ \) reactions.

Although radiative association was observed in the \( \text{C}_2\text{H}_4^+ /\text{PhNH}_2 \) reaction, it could not be found in the \( \text{C}_2\text{H}_4^+ /\text{PhNHCH}_3 \) and \( \text{C}_2\text{H}_4^+ /\text{Ph(NCH}_2) \) reactions. One reason for the lack of radiative association in the latter reactions is competition of fast CT channel. Since association products are expected to be produced through the attack of \( \text{C}_2\text{H}_4^+ \) on the lone-pair of the N atom, their relative formation rates will decrease with increasing the mass of amino group due to steric hindrance. On the other hand, such a steric hindrance is not expected for PT. Therefore, radiative association channel is found in the \( \text{C}_2\text{H}_4^+ /\text{PhNH}_2 \) reaction. The lack of steric hindrance is a reason for the formation of N-adduct ion in the \( \text{C}_2\text{H}_4^+ /\text{PhCN} \) reaction. One reason for the lack of radiative association in the \( \text{C}_2\text{H}_4^+ /\text{PhNO}_2 \) reaction will be occurrence of fast competitive O' abstraction channel. The large fraction of radiative association in the \( \text{C}_2\text{H}_4^+ /\text{PhCN} \) reaction is explained by the large binding energy (2.36 eV) and by the lack of competitive CT channel due to a high ionization potential of PhCN. The IR absorption of NH and C=N group is located at 3,300–3,500 and 1,500–2,000 cm\(^{-1}\) respectively. Therefore, adduct ions will be stabilized by radiating IR emissions in the 1,500–3,500 cm\(^{-1}\) region.

4. Conclusion

The gas-phase ion-molecule reactions of \( \text{CH}_2^+, \text{C}_2\text{H}_4^+, \)
and C$_3$H$_5$ with five N-containing monosubstituted benzenes [PhX: X = NH$_2$, NHCH$_3$, N(CH$_3$)$_2$, NO$_2$, CN] have been reinvestigated using an ion-trap type of GC/MS at a low CH$_4$ pressure. The major product channels for anilines with low ionization potentials were PT and CT, while that for PhNO$_2$ and PhCN with high ionization potentials was PT. The M$^+$/M+H$^+$ ratios increased with decreasing the acidity of the reactant hydrocarbon ion and decreasing the ionization potential of reagent. We predicted in the previous study that adduct ions and their decomposition products were produced via radiative association because of a low operating pressure of 10$^{-4}$ Torr.\textsuperscript{31} However, we found here that most of all adduct ions are produced via collisional stabilization due to a relatively long residence time of product ions in the ion-trap cell. In was found that besides collisional stabilization, radiative association is responsible for the formation of (PhNH$_2$+C$_3$H$_5$)$^+$ and (PhCN+C$_3$H$_5$)$^+$ ions.

References


Keywords: Hydrocarbon ions, N-Containing benzene derivatives, Chemical ionization, Ion trap, Collisional stabilization, Radiative association