# Mass-Spectrometric Study on Ion-Molecule Reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with Monosubstituted Benzenes Carrying a Carbonyl Group

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The gas-phase ion-molecule reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with five monosubstituted benzenes carrying a carbonyl group (PhCOX: X = H, $CH_3$, $C_2H_5$, Ph, COPh) have been studied using an ion-trap type of GC/MS at a low $CH_4$ pressure. The major product channels are proton transfer to the O-atom in a substituent, with or without further decomposition due to the elimination of CO, PhH, or (PhH + CO). Small amounts of initial adduct ions and their decomposition products are found in some reactions with $C_3H_5^+$. The reaction mechanism is discussed, based on product ion distributions and semi-empirical calculations of the energies of intermediates and products.

Chemical ionization (CI) has been widely used as a soft ionization method of a reagent in mass spectroscopy.[1,2] When $CH_4$ is used as a CI gas, the major reactant ions are $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$.[3] Most CI mass spectra using $CH_4$ have been measured at a high $CH_4$ pressure of about 1 Torr (1 Torr = 133.322 Pa) without separating reactant ions. Therefore, the relative contribution of each reactant ion to the product ions could not be determined; the collisional stabilization by the CI gas often takes part in the formation of product ions. The relative concentrations of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ were measured to be 48, 41, and 6%, respectively, under a typical $CH_4$ pressure of about 1 Torr.[3] The relative concentrations of the former two ions are higher than the last ion, and the reactivity of the former two ions are higher than the last ion.[2] Therefore, the major reactant ions in the $CH_4$ atmosphere are $CH_5^+$ and $C_2H_5^+$, which can induce the following proton transfer and hydride transfer in the reaction with a reagent molecule M:

$$CH_5^+ + M \rightarrow (M+H)^+ + CH_4, \quad (1)$$

$$C_2H_5^+ + M \rightarrow (M+H)^+ + C_2H_4, \quad (2a)$$

$$C_2H_5^+ + M \rightarrow (M-H)^+ + C_2H_6. \quad (2b)$$

We have recently studied CI mass spectra of benzene and toluene at a low $CH_4$ pressure by separating the reactant $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ ions.[4] Although Munson and Field[5] have observed such initial adduct ions as $(M+C_2H_5)^+$ and $(M+C_3H_5)^+$ in CI mass spectra measured at a high $CH_4$ gas pressure of 1 Torr, they could not be found in our study. It was therefore concluded that the collisional stabilization by the reactant $CH_4$ gas participated in the formation of the adduct ions in their measurements. CI mass spectra of some benzene derivatives having a carbonyl group have been measured at a high $CH_4$ pressure without separating reactant ions.[6] In the present work, ion-molecule reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with PhCOX (X=H, $CH_3$, $C_2H_5$, Ph, COPh) were studied at a low $CH_4$ pressure using an ion-trap type of GC/MS by separating reactant ions. The reaction mechanism of monosubstituted benzenes carrying a carbonyl group for the hydrocarbon ions is discussed based on product ion distributions and semi-empirical calculations of potential energies of reaction pathways.

## Experimental

CI mass spectra were obtained by using an ion-trap type of Hitachi M7200 GC/MS in a selected reactant ion mode. The time for storing a reactant ion was 5 ms and the reaction time was 20 ms. The ion-trap cell was kept at $\leq$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 the ion-trap cell were estimated to be $5\times10^{-5}$ and $7\times10^{-5}$ Torr, respectively. The reactant ions, produced by electron-impact ionization of $CH_4$ followed by secondary ion–molecule reactions, were expected to be thermalized by collisions with the carrier He gas and $CH_4$ before CI of a regent. In order to confirm this prediction, the CI mass spectra of PhCOPh were measured by changing the storing time of the reactant $CH_5^+$ or $C_2H_5^+$ ion between 5 and 15 ms. The CI mass spectra were independent of the storing time of the reactant ion, leading us to conclude that the above prediction is valid. The CI mass spectra were measured at low reagent concentrations of about 1000—5000 pg $cm^{-3}$ in order to reduce secondary ion-molecule reactions.

The heats of formation are known for the reactant ions, reagents, and some stable products obtained in this work.[7] However, there are many species whose $\Delta H^\circ$ values are unknown. These values were calculated by using a semi-empirical MNDO method (MOPAC Ver. 6.0) in order to describe potential-energy diagram of the reaction pathways. Thermochemical data used in this work are summarized in Table 1.

## Results and Discussion

The observed product ions and their branching ratios in the reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with PhCOX (X=H, $CH_3$, $C_2H_5$, Ph, COPh) are summarized in Table 2. The un-

Table 1. Thermochemical Data Used in This Work

| Molecules | | $\Delta H°$ | | Ref. |
|---|---|---|---|---|
| | | kJ mol$^{-1}$ | eV | |
| $CH_4$ | | −74.5 | −0.772 | Ref. 7 |
| $CH_5^+$ | | 905 | 9.38 | Ref. 7 |
| $C_2H_5^+$ | | 902 | 9.36 | Ref. 7 |
| $C_2H_4$ | | 52.2 | 0.541 | Ref. 7 |
| $C_2H_6$ | | −84 | −0.87 | Ref. 7 |
| CO | | −110.53 | −1.146 | Ref. 7 |
| $CHO^+$ | | 825.6 | 8.561 | Ref. 7 |
| $COCH_3^+$ | | 653 | 6.77 | Ref. 7 |
| $COC_2H_5^+$ | | 591 | 6.13 | Ref. 7 |
| $COC_2H_3^+$ | | 751 | 7.78 | Ref. 7 |
| PhH | | 82.9 | 0.859 | Ref. 7 |
| $PhH_2^+$ | | 854 | 8.85 | Ref. 7 |
| PhCHO | | −37 | −0.38 | Ref. 7 |
| $PhCOCH_3$ | | −86.6 | −0.898 | Ref. 7 |
| $PhCOC_2H_5$ | | −109 | −1.13 | Ref. 7 |
| PhCOPh | | 50 | 0.52 | Ref. 7 |
| PhCOCOPh | | −56 | −0.58 | Ref. 7 |
| $PhCO^+$ | | 705 | 7.31 | Ref. 7 |
| $PhCOCO^+$ | | 710.08 | 7.359 | This work |
| $(PhCH_3)H^+$ | (ortho-protonated) | 833.11 | 8.635 | This work |
| $(PhCH_3)H^+$ | (meta-protonated) | 829.47 | 8.597 | This work |
| $(PhCH_3)H^+$ | (para-protonated) | 837.67 | 8.682 | This work |
| $(PhCH_3)H^+$ | (ipso-protonated) | 857.93 | 8.892 | This work |
| $(PhCHO)H^+$ | (O-protonated) | 655 | 6.789 | Ref. 7 |
| $(PhCHO)H^+$ | (ortho-protonated) | 768.39 | 7.964 | This work |
| $(PhCHO)H^+$ | (meta-protonaed) | 764.12 | 7.920 | This work |
| $(PhCHO)H^+$ | (para-protonaed) | 768.94 | 7.970 | This work |
| $(PhCHO)H^+$ | (ipso-protonaed) | 777.58 | 8.059 | This work |
| $(PhCOCH_3)H^+$ | (O-protonaed) | 584 | 6.053 | Ref. 7 |
| $(PhCOCH_3)H^+$ | (ortho-protonaed) | 733.69 | 7.604 | This work |
| $(PhCOCH_3)H^+$ | (meta-protonaed) | 729.71 | 7.563 | This work |
| $(PhCOCH_3)H^+$ | (para-protonated) | 733.27 | 7.600 | This work |
| $(PhCOCH_3)H^+$ | (ipso-protonated) | 744.82 | 7.720 | This work |
| $(PhCOC_2H_5)H^+$ | (O-protonaed) | 607.56 | 6.297 | This work |
| $(PhCOC_2H_5)H^+$ | (ortho-protonated) | 732.73 | 7.594 | This work |
| $(PhCOC_2H_5)H^+$ | (meta-protonated) | 726.53 | 7.530 | This work |
| $(PhCOC_2H_5)H^+$ | (para-protonated) | 737.46 | 7.643 | This work |
| $(PhCOC_2H_5)H^+$ | (ipso-protonated) | 723.48 | 7.498 | This work |
| $(PhCOPh)H^+$ | (O-protonated) | 699.07 | 7.245 | This word |
| $(PhCOPh)H^+$ | (ortho-protonated) | 863.67 | 8.951 | This work |
| $(PhCOPh)H^+$ | (meta-protonated) | 859.40 | 8.907 | This work |
| $(PhCOPh)H^+$ | (para-protonated) | 861.57 | 8.930 | This work |
| $(PhCOPh)H^+$ | (ipso-protonated) | 871.62 | 9.034 | This work |
| $(PhCOCOPh)H^+$ | (O-protonated) | 652.77 | 6.766 | This work |
| $(PhCOCOPh)H^+$ | (ortho-protonated) | 754.20 | 7.817 | This work |
| $(PhCOCOPh)H^+$ | (meta-protonated) | 748.38 | 7.756 | This work |
| $(PhCOCOPh)H^+$ | (para-protonated) | 753.91 | 7.814 | This work |
| $(PhCOCOPh)H^+$ | (ipso-protonated) | 765.67 | 7.936 | This work |
| $(PhCOC_2H_3)H^+$ | (O-protonated) | 716.48 | 7.426 | This work |
| $(PhCOC_2H_3)H^+$ | (ortho-protonated) | 824.61 | 8.547 | This work |
| $(PhCOC_2H_3)H^+$ | (meta-protonated) | 821.01 | 8.509 | This work |
| $(PhCOC_2H_3)H^+$ | (para-protonated) | 824.11 | 8.541 | This work |
| $(PhCOC_2H_3)H^+$ | (ipso-protonated) | 837.00 | 8.675 | This work |

certainties of the branching ratios are estimated to be within ±7%.

**Benzaldehyde:** In the $CH_5^+$/PhCHO reaction, the $PhH_2^+$ and $(PhCHO)H^+$ ions are observed with branching ratios of 62 and 38%, respectively. Beside these two ions, small amounts of the $PhCO^+$ and $C_4H_3^+$ ions are found in the $C_2H_5^+$/PhCHO reaction. It should be noted that the $PhH_2^+$/$(PhCHO)H^+$ ratio decreases greatly from 1.6 to 0.29, when the reactant ion is changed from $CH_5^+$ to $C_2H_5^+$. In the $C_3H_5^+$/PhCHO reaction, the number of product chan-

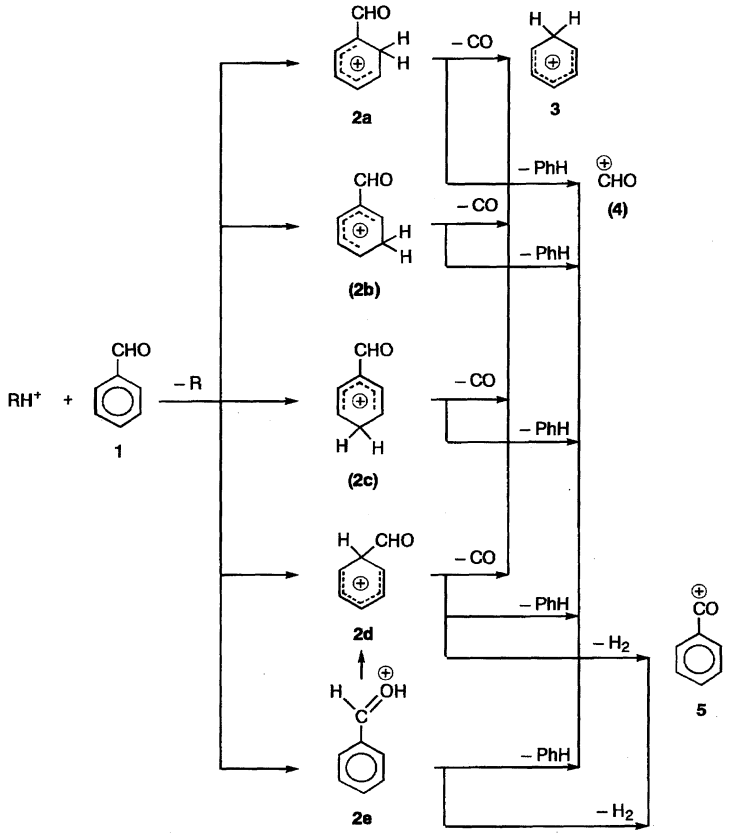
Table 2. Branching Ratios (%) of Product Ions in the Reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with PhCOX (X=H, $CH_3$, $C_2H_5$, Ph, COPh)

| Reagents | PhCHO | | | $PhCOCH_3$ | | | $PhCOC_2H_5$ | | | PhCOPh | | | PhCOCOPh | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reactant ions | $CH_5^+$ | $C_2H_5^+$ | $C_3H_5^+$ | $CH_5^+$ | $C_2H_5^+$ | $C_3H_5^+$ | $CH_5^+$ | $C_2H_5^+$ | $C_3H_5^+$ | $CH_5^+$ | $C_2H_5^+$ | $C_3H_5^+$ | $CH_5^+$ | $C_2H_5^+$ | $C_3H_5^+$ |
| Product ions | | | | | | | | | | | | | | | |
| $(M+C_3H_5)^+$ | | | | | | 0.4 | | | | | | 8.7 | | | |
| $(M+C_3H_5-PhH)^+$ | | | | | | | | | | | | 3.0 | | | |
| $(M+C_3H_5-PhCHO)^+$ | | | | | | | | | | | | | | | 3.4 |
| $(M+H)^+$ | 38 | 73 | 26 | 28 | 76 | 22 | 30 | 42 | 12 | 24 | 62 | 23 | 1.6 | 9.3 | 12 |
| $(M-H)^+$ | | | | | | | 7.2 | 6.4 | | | | | | | |
| $PhCOCO^+$ | | | | | | | | | | | | | | 2.5 | |
| $PhCO^+$ | | 2.0 | 21 | 2.9 | 7.2 | 3.8 | 4.2 | 3.9 | 2.4 | 76 | 38 | 48 | 98 | 85 | 63 |
| $C_7H_7^+$ | | | 6.5 | | | | | 1.7 | 3.3 | | | 2.0 | | | |
| $PhH_2^+$ | 62 | 21 | 15 | | 2.8 | 2.7 | | | | | | | | | 6.3 |
| $C_4H_3^+$ | | 4.2 | 23 | | 6.9 | 7.8 | | 3.6 | 14 | | | 12 | | 3.3 | 13 |
| $C_4H_2^+$ | | | 9.1 | | | 2.2 | | | 3.0 | | | 2.5 | | | 2.1 |
| $COHCH_3^+$ | | | | | | 1.2 | | | | | | | | | |
| $COCH_3^+$ | | | | 69 | 7.6 | 60 | | | | | | | | | |
| $COC_2H_5^+$ | | | | | | | 51 | 37 | 56 | | | | | | |
| $COC_2H_3^+$ | | | | | | | 7.2 | 5.1 | 9.0 | | | | | | |

Uncertainties are within ±7%.

nels increases, and the $C_7H_7^+$ and $C_4H_2^+$ ions, which are absent in the $CH_5^+$/PhCHO and $C_2H_5^+$/PhCHO reactions, are found. There are three possible $C_3H_5^+$ ions. They are $CH_2$=$CHCH_2^+$, $CH_3C$=$CH_2^+$, and protonated cyclopropene ion with $\Delta H°$=946,969, and 1069 kJ mol$^{-1}$, respectively.[7] The most stable $CH_2$=$CHCH_2^+$ isomer may be most significant under the present experimental condition.

Possible reaction mechanisms of the $CH_5^+$/PhCHO and $C_2H_5^+$/PhCHO reactions are given in Scheme 1. The $(PhCHO)H^+$ ion can be formed through a proton transfer to the benzene ring or the lone-pair electrons of the O-atom in the substituent. The electron-withdrawing effect of the CHO




Scheme 1. Numbers in parentheses are minor or unimportant intermediates and products.

group will suppress the formation of Wheland-type adduct ions **2a**—**2d**, while a high reactivity of the lone-pair electrons on the oxygen atom will yield O-protonated ion **2e** preferentially. Actually, we have recently studied ion-molecule reactions of a typical carbocation, $CF_3^+$, with PhCOX (X=H, $CH_3$, $C_2H_5$), and found that almost all electrophilic attack (93—96%) occurs on the O-atom in the substituent.[8] Since the protonation is a reversible process with a low energy barrier, it will be controlled thermochemically. Figures 1 and 2 show the potential energy diagrams of the protonation/molecular-elimination pathways in the $CH_5^+$/PhCHO and $C_2H_5^+$/PhCHO reactions. It is clear from Figs. 1 and 2 that the O-protonated ion **2e** is much more stable than ring-protonated ions **2a**—**2d**. These facts support our prediction that **2e** is a dominant $(PhCHO)H^+$ ion. The $PhH_2^+/(PhCHO)H^+$ ratio in the $C_2H_5^+$/PhCHO reaction is lower than that in the $CH_5^+$/PhCHO reaction. This can be explained by a higher proton affinity of $C_2H_4$ (7.1 eV) than that of $CH_4$ (5.7 eV), so that a lower excess energy is released in the former protonation reaction (Figs. 1 and 2).

It is highly likely that the $PhH_2^+$ ion (**3**) is formed by loss of CO from ring-protonated ions **2a**—**2d**, as shown in Scheme 1. The initial protonation is expected to occur preferentially in the substituent. It is, therefore, reasonable to assume that almost all precursor ring-protonated ions are not produced directly but they are formed via such an intramolecular proton transfer as **2e**→**2a** and **2e**→**2d**. Only the intramolecular proton transfer from **2e** to **2d** is shown in Scheme 1 and Figs. 1 and 2 for the sake of clarity. The $PhCO^+$ ion (**5**) can be formed by loss of $H_2$ from **2d** and/or **2e**. Although the $\Delta H°$ value of $PhCO^+$ (**5**)+$H_2$ is lower than that of $PhH_2^+$ (**3**)+CO (Figs. 1 and 2), the branching ratio of

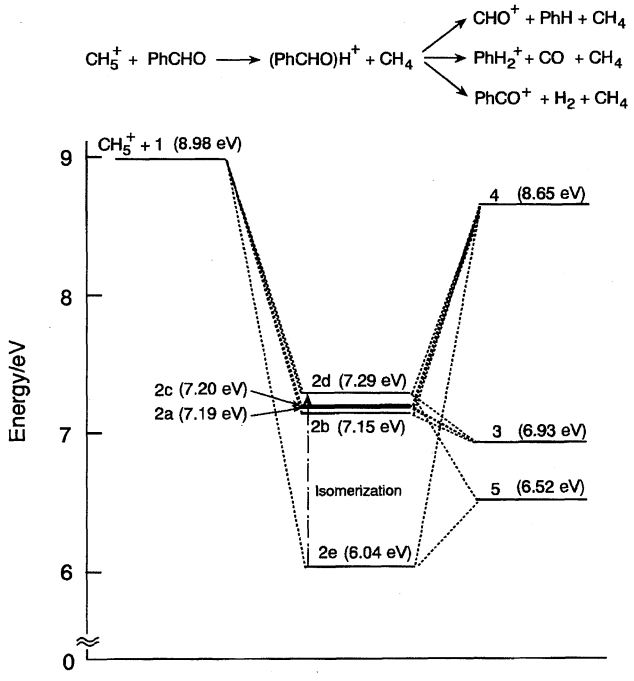



Fig. 1. A potential-energy diagram for the protonation/dissociation pathways in the $CH_5^+$+PhCHO system.

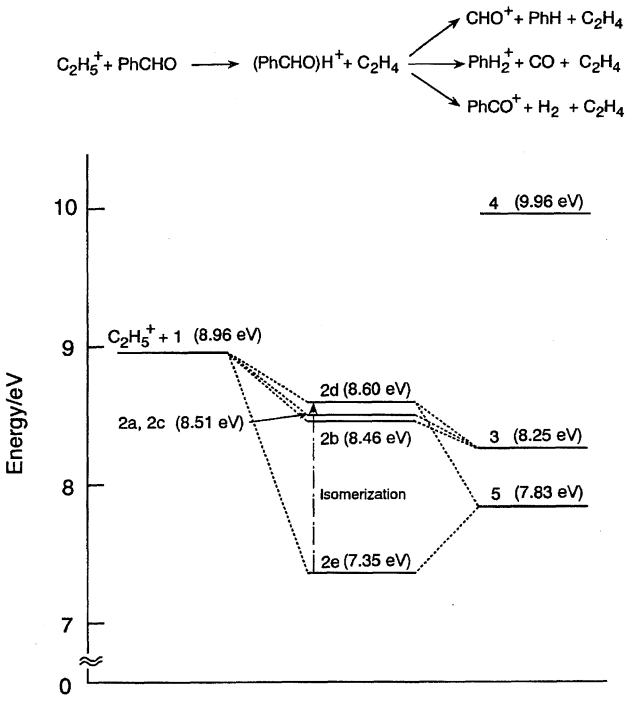
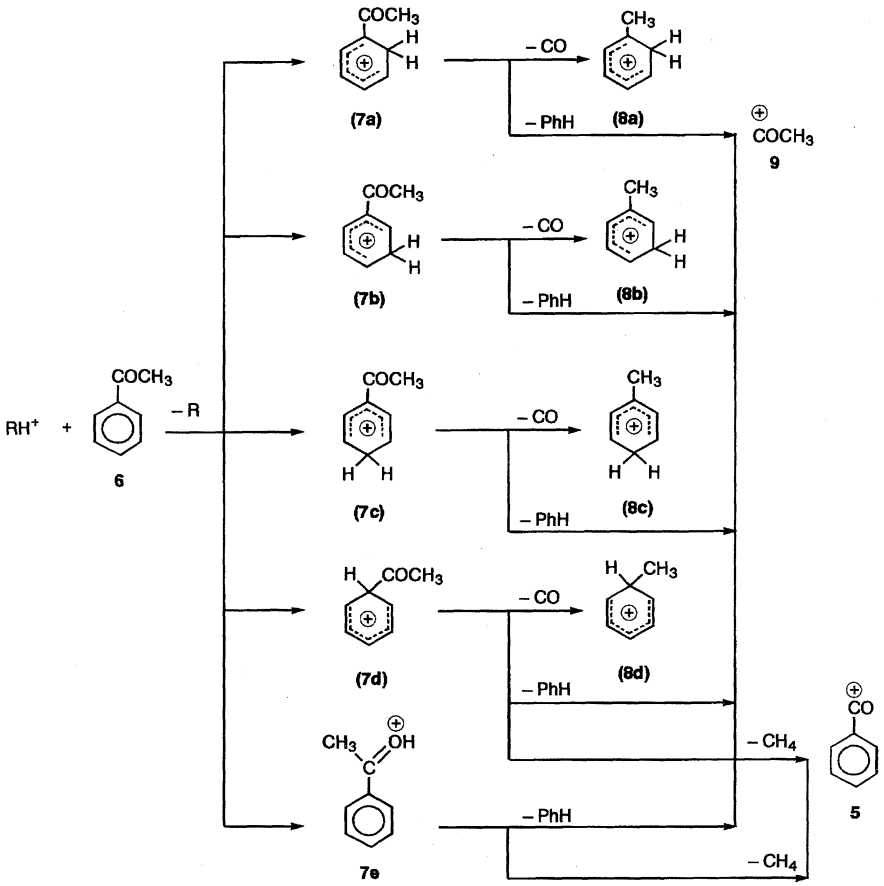



Fig. 2. A potential-energy diagram for the protonation/dissociation pathways in the $C_2H_5^+$+PhCHO system.

**5** is either zero or very small in the $CH_5^+$ and $C_2H_5^+$ reactions. In general, elimination channels from protonated ions are expected to be controlled kinetically, because the elimination processes are irreversible. Thus, the small branching ratios of **5** are attributed to higher energy barriers for the formation of **5** from **2d** and **2e** than those for the formation of **3** from **2a**—**2d**. Although the formation of $CHO^+$ (**4**) is energetically accessible in the $CH_5^+$ reaction, it cannot be detected. The lack of **4** in the $CH_5^+$ reaction is explained by the fact that the potential energy for the formation of **4** is much higher than that of **3**, so that an efficient conversion of the excess internal energy to dissociation energy is required for the formation of **4** (Fig. 1). On the other hand, the lack of **4** in the $C_2H_5^+$ reaction is due to the endothermicity of its formation (Fig. 2).

**Methyl Phenyl Ketone:** A possible reaction scheme and the potential-energy diagrams of the $CH_5^+$/$PhCOCH_3$ and $C_2H_5^+$/$PhCOCH_3$ reactions are given in Scheme 2 and Figs. 3 and 4, respectively. If the reaction mechanism of the $CH_5^+$/$PhCOCH_3$ and $C_2H_5^+$/$PhCOCH_3$ reactions is similar to that of the $CH_5^+$/PhCHO and $C_2H_5^+$/PhCHO reactions, the $(PhCOCH_3)H^+$ ion (**7**) and the $PhHCH_3^+$ ion (**8**) are expected to be produced preferentially. Although the former ion was found as a major product ion, the latter ion could not be detected. Since **7e** is themochemically most favorable among possible $(PhCOCH_3)H^+$ ions (**7a**—**7e**) due to electron-withdrawing properties of the $CH_3CO$ group, it will be a major $(PhCOCH_3)H^+$ ion. On the basis of energy-level diagrams shown in Figs. 3 and 4, the formation of **8a**—**8d** is energetically allowed and the potential energies of **8a**—**8d**+CO are comparable with those of the precursor **7a**—**7d** ions. We have recently found that the $PhHCH_3^+$ ion is produced in the




Scheme 2.

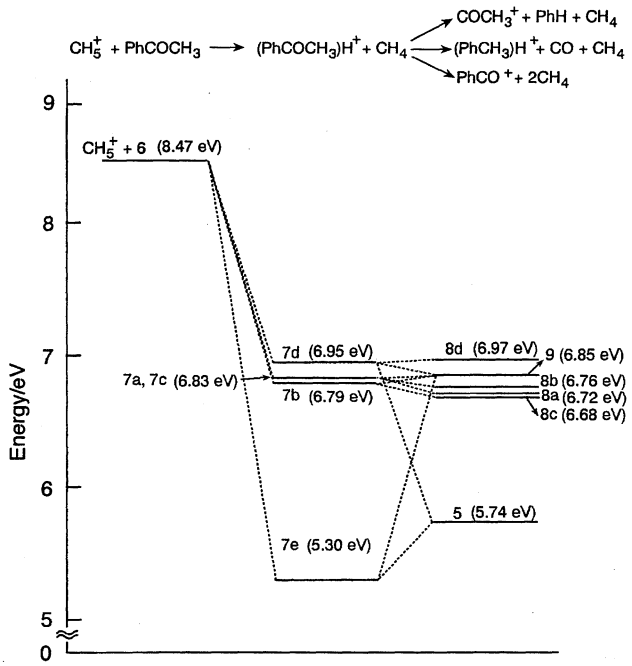



Fig. 3. A potential-energy diagram for the protonation/dissociation pathways in the $CH_5^+$+$PhCOCH_3$ system.

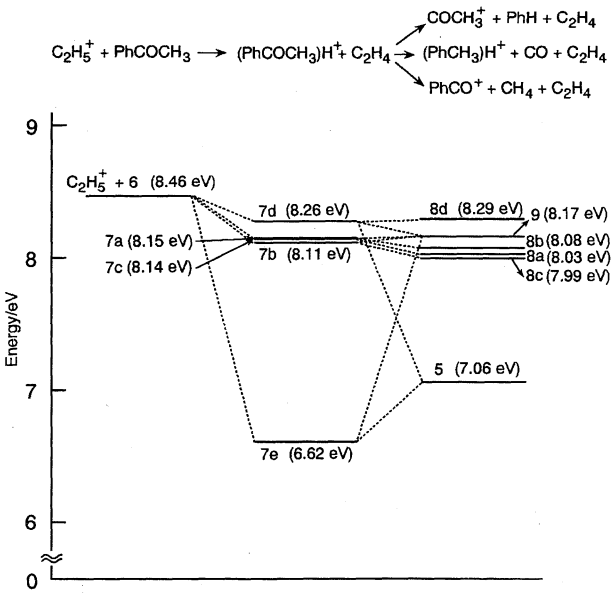



Fig. 4. A potential-energy diagram for the protonation/dissociation pathways in the $C_2H_5^+$+$PhCOCH_3$ system.

reactions of $CH_5^+$ and $C_2H_5^+$ with $PhCH_3$ with high branching ratios of 93 and 89%, respectively.[4] This implies that the $PhHCH_3^+$ ion is a stable detectable ion. Thus, the lack of **8a**—**8d** from $PhCOCH_3$ suggests that the CO elimination from **7a**—**7d** due to the migration of a heavy $CH_3$ group to the benzene ring is less efficient.

It should be noted that the $COCH_3^+$ ion (**9**) is found as

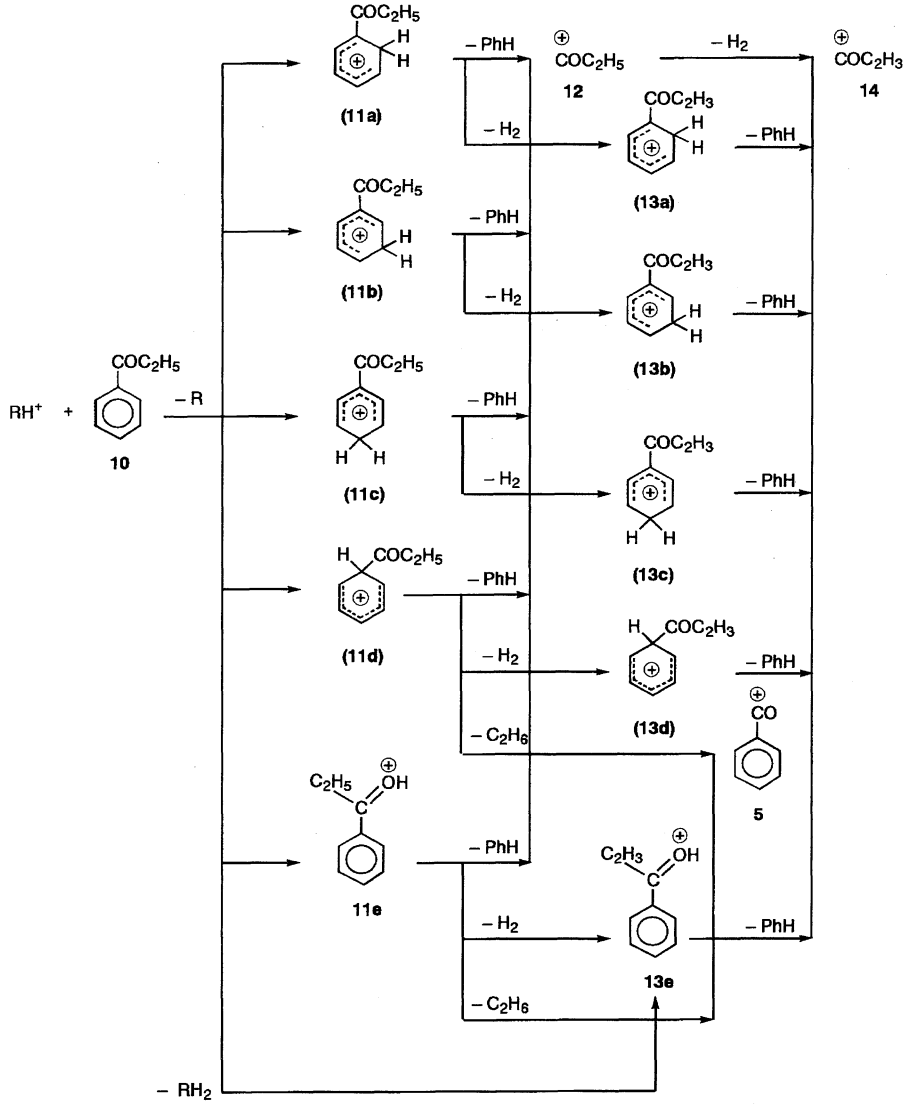
a dominant product ion (69%) in the $CH_5^+$ reaction. It can be produced through the elimination of PhH from the ring protonated ions (**7a**—**7d**) and the O-protonated ion (**7e**). Since the initial protonation occurs preferentially to the O-atom, it is highly likely that **9** is dominantly produced through **7e**. The branching ratio of $COCH_3^+$ is very small in the $C_2H_5^+$ reaction in comparison with that in the $CH_5^+$reaction. This is attributed to a lower excess energy in the $C_2H_5^+$ reaction, so that an efficient conversion of the excess internal energy to the dissociation energy is required for the formation of $COCH_3^+$ (Fig. 4). Small amounts of the $PhCO^+$ ion (**5**) are found in the $CH_5^+$ and $C_2H_5^+$ reactions. Although **5** can be formed by loss of $CH_4$ from the ipso-protonated ion **7d** and the ring-protonated ion **7e**, the major precursor ion is expected to be the more stable latter ion.

The number of product channels increases in the $C_3H_5^+$/$PhCOCH_3$ reaction, as found in the $C_3H_5^+$/PhCHO reaction. It should be noted that a small amount of the initial adduct $(M+C_3H_5)^+$ ion is found. Since the collisional stabilization is insignificant in the present experimental conditions, it may be stabilized by radiative association, as reported for the reactions of $NO^+$ with carbonyl compounds:[9]

$$C_3H_5^+ + PhCOCH_3 \rightarrow (C_3H_5 + PhCOCH_3)^+ + h\nu. \quad (3)$$

**Ethyl Phenyl Ketone:** Major products in the $CH_5^+$/$PhCOC_2H_5$ and $C_2H_5^+$/$PhCOC_2H_5$ reactions are the $(PhCOC_2H_5)H^+$ and $COC_2H_5^+$ ions, indicating that the reaction mechanism is similar to that of $PhCOCH_3$. In Scheme 3 and Figs. 5 and 6 are shown a possible reaction scheme and the potential-energy diagrams of the $CH_5^+$/$PhCOC_2H_5$ and $C_2H_5^+PhCOC_2H_5$ reactions. The $COC_2H_5^+$ group has electron-withdrawing properties. Therefore, the major $(PhCOC_2H_5)H^+$ ion will be more stable O-protonated ion (**11e**), and the $COC_2H_5^+$ ion (**12**) is dominantly produced via loss of PhH from **11e**. The $COC_2H_5^+/(PhCOC_2H_5)H^+$ ratio in the $C_2H_5^+$/$PhCOC_2H_5$ reaction is lower than that in the $CH_5^+$/$PhCOC_2H_5$ reaction by a factor of 1.9 due to a lower excess energy (Figs. 5 and 6).

Small amounts of the $(M-H)^+=PhCOC_2H_4^+$, $PhCO^+$, and $COC_2H_3^+$ ions are found in the $CH_5^+$ and $C_2H_5^+$ re-




Scheme 3.

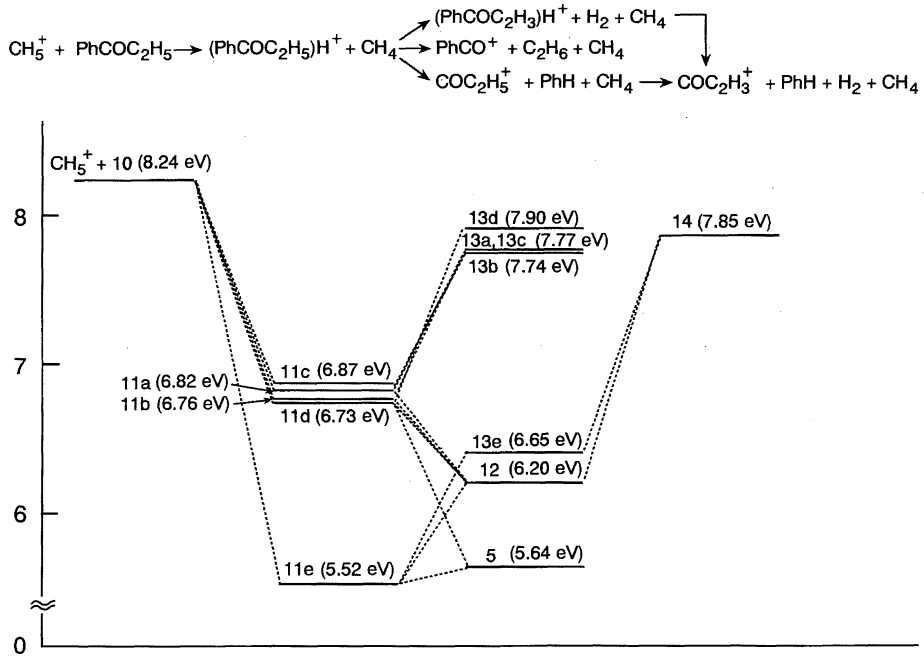



Fig. 5. A potential-energy diagram for the protonation/dissociation pathways in the $CH_5^+$+$PhCOC_2H_5$ system.

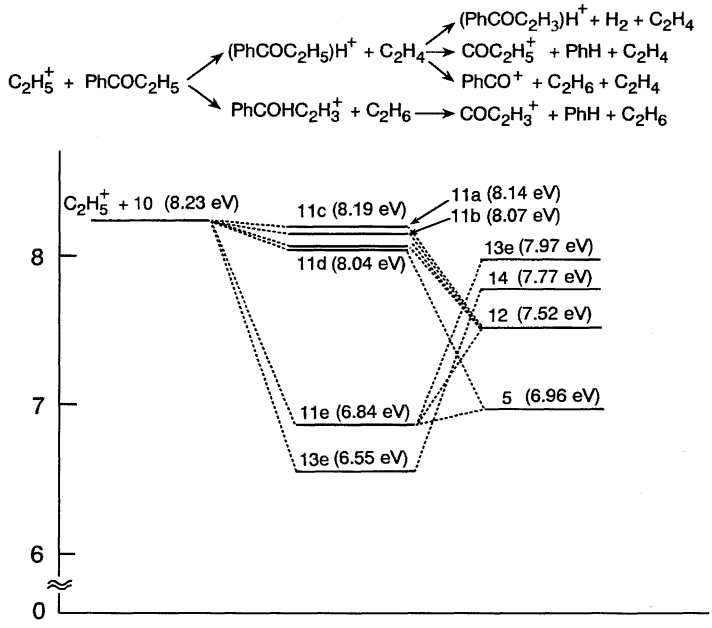



Fig. 6. A potential-energy diagram for the protonation/dissociation pathways in the $C_2H_5^+$+$PhCOC_2H_5$ system.

actions. Possible candidates of the $(M-H)^+$ ions are ring-protonated ions **13a—13d** and the O-protonated ion **13e** in the $CH_5^+$ reaction, because the formation of $PhCOCH_2CH_2^+$ and $PhCOCHCH_3^+$ are endoergic:

$$CH_5^+ + PhCOC_2H_5 \rightarrow PhCOCH_2CH_2^+ + H_2 + CH_4 - 0.42\ eV, \quad (4a)$$

$$CH_5^+ + PhCOC_2H_5 \rightarrow PhCOCHCH_3^+ + H_2 + CH_4 - 0.48\ eV, \quad (4b)$$

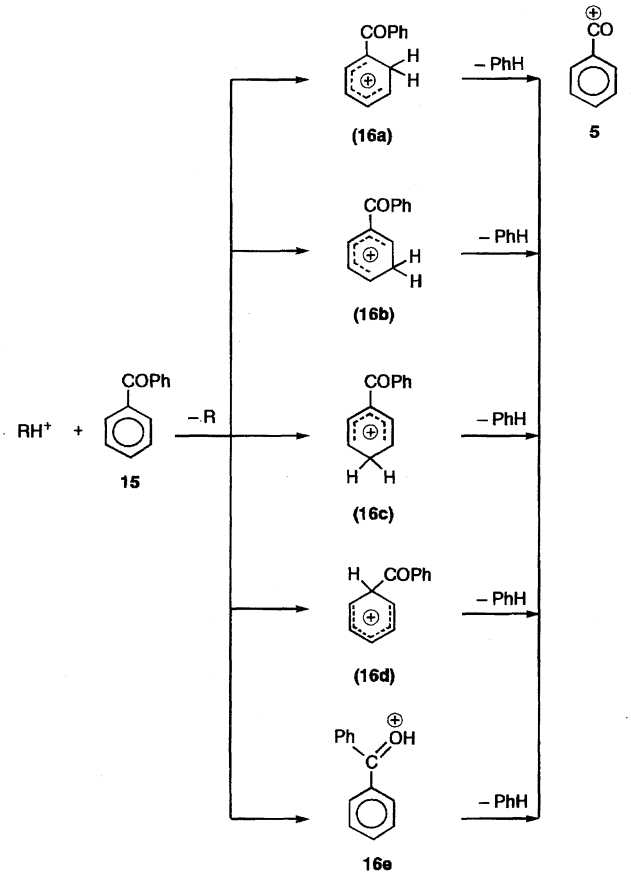
Among them, the ion **13e**, formed by the $H_2$ elimination from **11e**, will be a dominant $(M-H)^+$ ion in the $CH_5^+$ reaction. Only the formation of **13e** is energetically possible in the $C_2H_5^+$ reaction (Fig. 6). There are two possible processes for the formation of **13e** in the $C_2H_5^+$ reaction, as shown in Scheme 3. One is protonation to the O-atom followed by loss of $H_2$, as found in the $CH_5^+$ reaction, and the other is hydride abstraction from the $C_2H_5$ group involving intramolecular proton transfer from the $C_2H_4$ group to the O-atom. The formation of the $COC_2H_3^+$ ion (**14**) probably proceeds through loss of PhH and $H_2$ from the O-protonated ion (**11e**) in the $CH_5^+$ reaction (Scheme 3 and Fig. 5). On the other hand, such an elimination process is energetically closed for the formation of **14** in the $C_2H_5^+$ reaction, and only the hydride-

abstraction process followed by the PhH elimination is energetically possible (Scheme 3 and Fig. 6). Since the hydride-abstraction process is found to be involved in the formation of **14** in the $C_2H_5^+$ reaction, some part of **13e** will be also produced through the hydride-abstraction process. Although the $PhCO^+$ ion (**5**) can be formed through loss of $C_2H_6$ from the ipso-protonated ion **11d** and the O-protonated ion **11e**, the latter thermochemically favored ion will be a major precursor ion. The product ions, observed in the $C_3H_5^+$ reaction, are similar to those in the $C_2H_5^+$ reaction except for the lack of the $(M-H)^+$ and $C_4H_2^+$ ions.

**Diphenyl Ketone:** A possible reaction scheme and the potential-energy diagrams in the $CH_5^+$/PhCOPh and $C_2H_5^+$/PhCOPh reactions are given in Scheme 4 and Figs. 7 and 8, respectively. Major product ions are the $(PhCOPh)H^+$ and $PhCO^+$ ions. The dominant $(PhCOPh)H^+$ ion will be the more stable O-protonated ion (**16e**), and the $PhCO^+$ ion (**5**) is expected to be preferentially formed by the PhH elimination from **16e**. The $PhCO^+/(PhCOPh)H^+$ ratio in the $C_2H_5^+$ reaction is smaller than that in the $CH_5^+$ reaction by a factor of 5.2 because of a lower excess energy.

In the $C_3H_5^+$/PhCOPh reaction, the adduct $(M+C_3H_5)^+$ ion and its decomposition product $(M+C_3H_5-PhH)^+$ ion are found. A radiative association process probably takes part in the formation of these adduct ions:

$$C_3H_5^+ + PhCOPh \rightarrow (C_3H_5 + PhCOPh)^+ + h\nu. \quad (5)$$




Scheme 4.

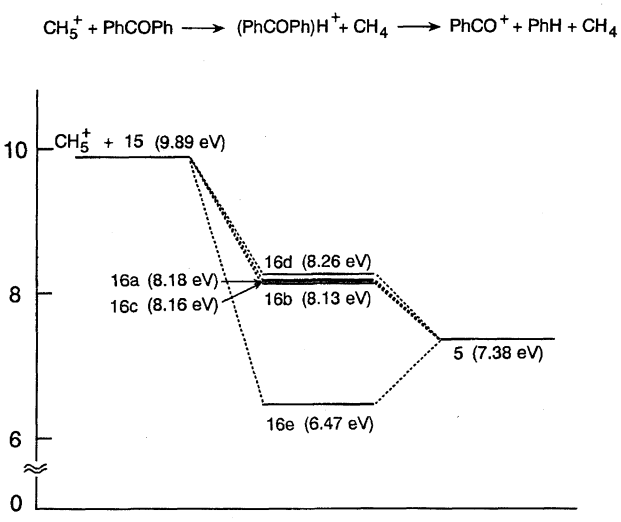



Fig. 7. A potential-energy diagram for the protonation/dissociation pathways in the $CH_5^+$+PhCOPh system.

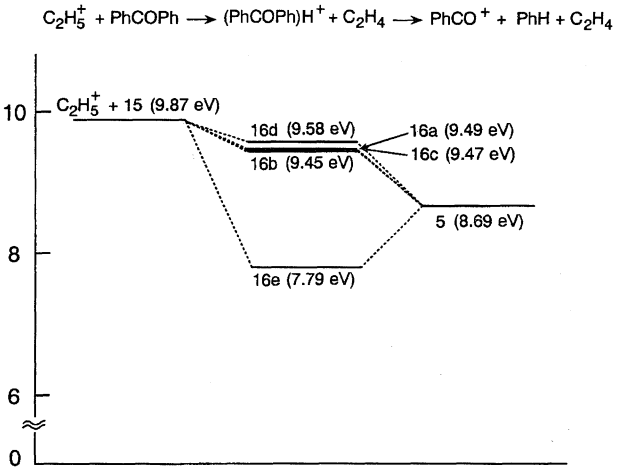
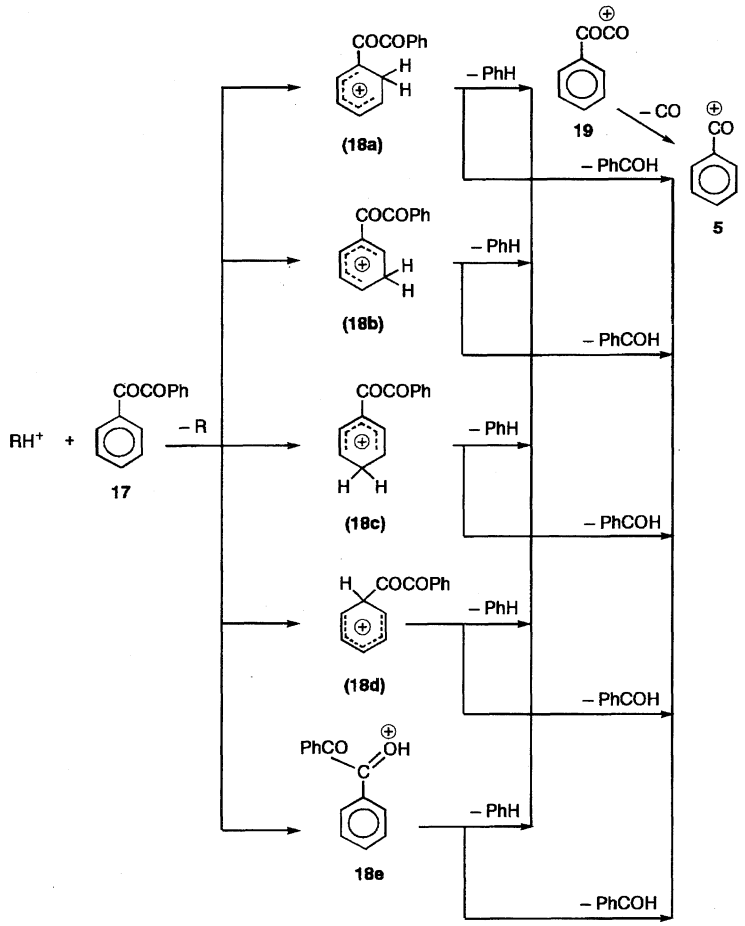



Fig. 8. A potential-energy diagram for the protonation/dissociation pathways in the $C_2H_5^+$+PhCOPh system.

**Benzil:** The $PhCO^+$ ion is a dominant product ion in the reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with PhCOCOPh, which occupies more than 63% in all three reactions (Table 2). A small amount of the $PhCOCO^+$ ion is found only in the $C_2H_5^+$ reaction. An outstanding feature for the reactions with PhCOCOPh is that the branching ratios of the $(PhCOCOPh)H^+$ ion are small in all three reactions ($\leq$12%). A possible reaction scheme and the potential-energy diagrams of the $CH_5^+$/PhCOCOPh and $C_2H_5^+$/PhCOCOPh reactions are shown in Scheme 5 and Figs. 9 and 10, respectively. The $PhCO^+$ ion (**5**) can be formed via loss of PhCHO or (PhH+CO) from ring-protonated ions (**18a**—**18d**) and the O-protonated ion (**18e**). It is expected to be formed though the decomposition of thermochemically more favorable ion **18e**. Although the $PhCOCO^+$ ion (**19**) is formed in the $C_2H_5^+$ reaction, it is absent in the $CH_5^+$ reaction. This implies that **19**, formed in the $CH_5^+$ reaction, completely dissociates into $PhCO^+$+CO. It is clear from Figs. 9 and 10 that the formation of $PhCO^+$+CO is thermochemically much more favorable than that of $PhCOCO^+$, because the




Scheme 5.

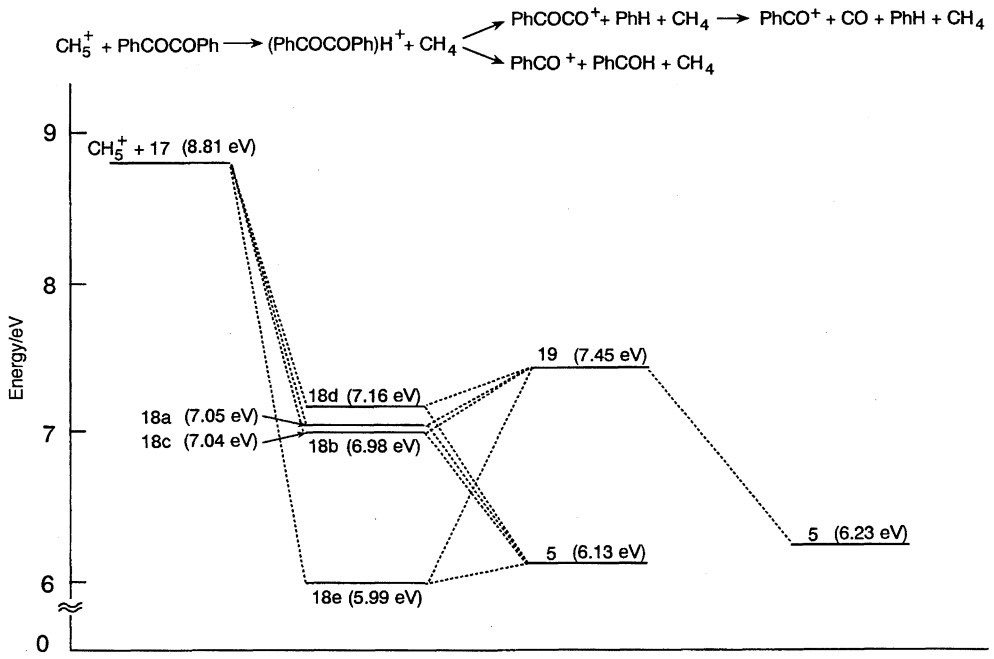



Fig. 9. A potential-energy diagram for the protonation/dissociation pathways in the $CH_5^+$+PhCOCOPh system.

$\Delta H°$ value of $PhCO^+$+CO is lower than that of $PhCOCO^+$ by 1.22 eV. There will be a low energy barrier for the formation of $PhCO^+$ from a unimolecular decomposition of the $(PhCO-CO)^+$ ion. Thus, an efficient decomposition of $PhCOCO^+$ into $PhCO^+$+CO will be the main reason for the lack of $PhCOCO^+$ in the $CH_5^+$ reaction and for its small

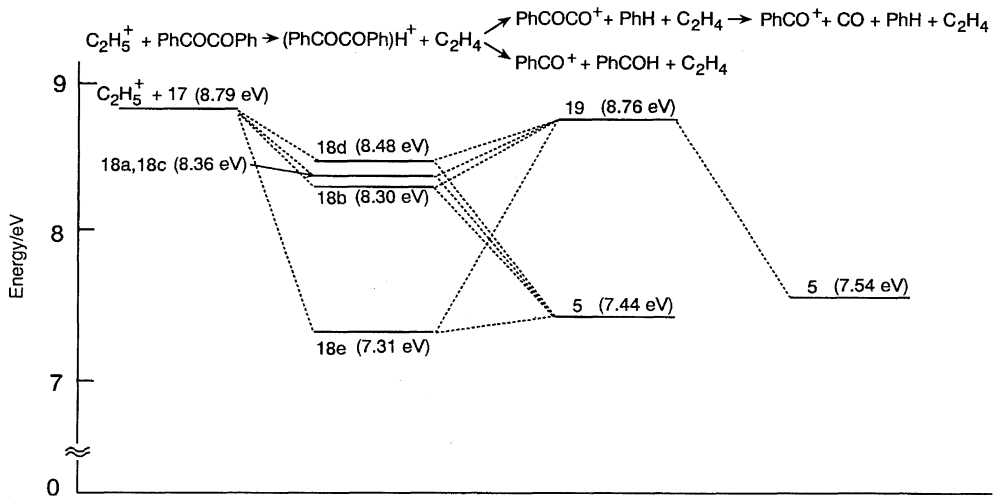
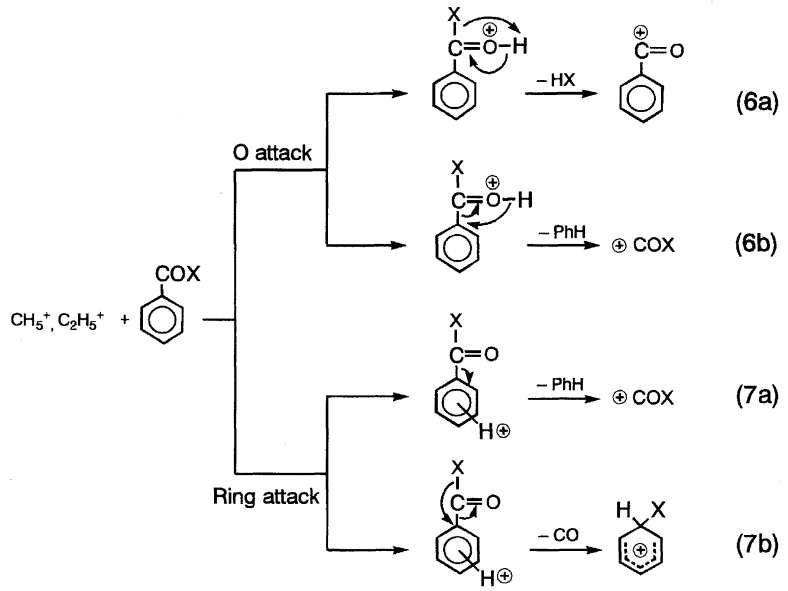



Fig. 10. A potential-energy diagram for the protonation/dissociation pathways in the $C_2H_5^+$+PhCOCOPh system.

branching ratio in the $C_2H_5^+$ reaction.

In the $C_3H_5^+$/PhCOCOPh reaction, the formation of a small amount of the adduct $(M+C_3H_5-PhCHO)^+$ ion is observed, though the initial adduct $(M+C_3H_5)^+$ ion could not be found. In addition, the $PhH_2^+$, $C_4H_3^+$, and $C_4H_2^+$ ions are also observed.

**Concluding Remarks:** Ion-molecule reactions of $CH_5^+$, $C_2H_5^+$, and $C_3H_5^+$ with PhCOX (X=H, $CH_3$, $C_2H_5$, Ph, COPh) have been studied using a GC/MS at a low $CH_4$ pressure. The product ion distributions depended strongly on the reactant ion. In general, the number of product channels increases with increasing the number of atoms in the reactant hydrocarbon ion. In some reactions with $C_3H_5^+$, initial adduct ions and decomposition products are found. Possible reaction mechanisms for $CH_5^+$ and $C_2H_5^+$ are summarized in Scheme 6. The major product channels are protonation with or without further decomposition due to molecular elimination. The branching ratios of $(M+H)^+$ in the $C_2H_5^+$ reaction were larger than those in the $CH_5^+$ reaction, because the excess energy released in the former reaction is lower than that in the latter reaction by 1.33 eV. The protonation can occur both on the O-atom and the benzene ring. The elimination of HX and PhH from an O-protonated ion gives the $PhCO^+$ and $COX^+$ ions through processes (6a) and (6b), respectively. On the other hand, the elimination of PhH and CO from a ring-protonated ion gives the $COX^+$ and $PhHX^+$ ions through processes (7a) and (7b), respectively. Since the formation of a more stable O-protonated ion due to electron-withdrawing properties of carbonyl group is more favorable than that of ring-protonated ions, the major protonations leading to $(M+H)^+$, with and without further decomposition due to the elimination of HX and PhH, are expected to occur dominantly through processes (6a) and (6b), respectively. Actually, major product ions observed from PhCOX (X=$CH_3$, $C_2H_5$, Ph, COPh) are $(M+H)^+$, $PhCO^+$, and $COX^+$ formed through processes (6a) and (6b). One reason for the




Scheme 6.

high branching ratio of $PhCO^+$ in the reactions with PhCOPh is that processes (6a) and (6b) give the same $PhCO^+$ ion. In the reactions of $CH_5^+$and $C_2H_5^+$ with PhCOX (X=$CH_3$, $C_2H_5$), the branching ratio of (6b) is much larger than that of (6a). Therefore, $PhCO^+$ produced from PhCOPh may also be formed via process (6b). Moreover, $PhCO^+$ produced from PhCOCOPh is formed via the decomposition of $PhCOCO^+$ in process (6b). Consequently, it is highly likely that the PhH-elimination pathway (6b) takes precedence over the HX-elimination one (6a) for PhCOX (X=$CH_3$, $C_2H_5$, Ph, COPh) due to a low energy barrier. It should be noted that a major product ion for PhCHO is $PhH_2^+$ formed through process (7b). Since the formation of its precursor ipso-protonated ion is unfavorable, $PhH_2^+$ is probably formed via intramolecular proton transfer from O-protonated ion to ring-protonated ions. Such intramolecular proton transfer from the substituent to ring may also occur for PhCOX (X=$CH_3$, $C_2H_5$, Ph, COPh). However, the corresponding $PhHX^+$ ions could not be found. This is probably due to the fact that ring protonated ions decompose into $COX^+$+PhH because the elimination of CO is unfavorable for PhCOX with large X substituents (X=$CH_3$, $C_2H_5$, Ph, COPh).

It is clear from Table 2 that the branching ratios of $(M+H)^+$ in the $C_3H_5^+$ reaction are lower that those in the $C_2H_5^+$ reaction, except for the case of PhCOCOPh. Since the proton affinity of $C_3H_4$ (7.65 eV for $CH_2$=$CHCH_2$)[7] is larger than that of $C_2H_4$ (7.1 eV), this result cannot be explained by the excess energies released in the proton-transfer processes. One possible explanation is that most of the fragment ions are not produced by the decomposition of proton-transfer products, but they are formed by the decomposition of the $(M+C_3H_5)^+$ adducts. In order to confirm the validity of this explanation, further experimental and theoretical studies are required.

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