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Mass-Spectrometric Study on Ion-Molecule Reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with Benzoic Acid and Benzoates

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The gas-phase ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with PhCOOX = M (X = H, CH_3, C_2H_5, and Ph) have been studied under a reactant-ion selective chemical ionization mode of an ion-trap type of GC/MS. The major product channel is non-dissociative proton transfer leading to $(M+H)^+$ in most cases. Dissociative proton transfer leading to $(M+H-CO_2)^+$ and/or $(M+H-XOH)^+$ competes with the above channels. In the $C_3H_5^+$/PhCOOX (X = H, CH_3, and C_2H_5) reactions, initial $(M+C_3H_5)^+$ adduct ions and/or their decomposition products are found. The reaction mechanism is discussed based on the reaction-time dependence of product-ion distributions and semi-empirical calculations of the energies of intermediates and products.

Since the first introduction by Munson and Field in 1966,[1] chemical ionization (CI) mass spectrometry has been widely used as a powerful method for detecting trace levels of organic compounds. At the same time, CI studies have provided valuable information concerning gas-phase ion chemistry.[2—9] The majority of CI studies have been carried out using an ion source of magnetic sector instruments. In such experiments, CI gas pressures were 0.3—1.0 Torr (1 Torr = 133.322 Pa) and the residence time of an ion in the ionization-reaction chamber was about 10 μs. Field[3] evaluated the total number of collisions of the ion with a CI gas under these conditions to be about 200. The quadrupole ion trap has recently been used as a new device for CI. Although the operating CI gas pressures ($< 10^{-3}$ Torr) were lower than those in the magnetic sector instruments, the reaction time (ms) is longer than that in the sector instruments. Some comparative studies between medium-pressure CI at a short residence time and low-pressure CI at a long reaction time have been carried out.[10—13] In general, the CI mass spectra obtained in the ion trap were in agreement with those obtained by medium-pressure magnetic sector instruments, except that adduct ions such as $(M+C_2H_5)^+$ and $(M+C_3H_5)^+$ were absent and more fragmentation was observed because of the higher kinetic energies of the reactant ions in the trapping electric fields.

We have recently initiated a systematic mass-spectrometric study on ion-molecule reactions of hydrocarbon ions with aromatic molecules in order to clarify the reactivity of carbocations for aromatic molecules in the gas phase completely free from a solvent.[14—17] A quadrupole ion-trap type of GC/MS was used under a reactant-ion-selective CI mode. Three typical hydrocarbon ions (CH_5^+, $C_2H_5^+$, and $C_3H_5^+$) were generated using CH_4 as a CI gas, and ion-molecule reactions of each reactant ion with benzene derivatives were studied. In preceding papers, results for the following monosubstituted benzenes carrying an oxygen atom in the substituent have been reported: PhCOX (X = H, CH_3, C_2H_5, Ph, and COPh) and PhX [X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$].[15,17] The major product channels for PhCOX (X = H, CH_3, C_2H_5, Ph, and COPh) were proton transfer (PT) to the O-atom in a substituent, with or without further decomposition due to the elimination of CO, PhH, or (PhH+CO). On the other hand, the major product channel for PhOH was PT, leading to $(M+H)^+$ ions, while that for PhX [X = CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$] was dissociative PT, leading to $(MH-H_2O)^+$ ions in most cases. Small amounts of initial adduct ions, produced by association reaction, and their decomposition products were found in some reactions with $C_2H_5^+$ and $C_3H_5^+$ with O-containing monosubstituted benzenes. Although the previous CI mass spectra of PhCOX (X = H, CH_3, C_2H_5, Ph, and COPh) were measured at a constant reaction time of 20 ms, those of PhX [X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$] were obtained by changing the reaction time in the 0.5—100 ms range in order to examine the contribution of collisional stabilization. The dependence of product-ion distributions on the reaction time suggested that collisional stabilization plays a significant role for the alkylation reactions, while it is unimportant for the protonation reactions in most cases.

CH_4 CI mass spectrum of PhCOOH has been measured by Ichikawa and Harrison,[18] using a medium-pressure CI mass spectrometer without separating reactant ions. Therefore, the relative contribution of each reactant hydrocarbon ion [CH_5^+(48%), $C_2H_5^+$(40%), $C_3H_5^+$(6%), $C_2H_4^+$(2%), and $C_3H_7^+$(1%)][19] could not be determined. Since their CI spectra were measured at a high He pressure of about 1 Torr, collisional stabilization might participate in the formation of some product ions. In the present work, ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with such monosubstituted benzenes as PhCOOX (X = H, CH_3, C_2H_5, and Ph) are studied using the ion-trap type of mass spectrometer in order to examine the reactivity of each hydrocarbon ion with PhCOOX. The reaction-time dependence of product-ion distributions is measured in order to examine the contribution from the collisional stabilization. The initial product-ion distributions are determined by extrapolating the reaction-time dependence of product-ion distributions to zero reaction time. The reaction mechanism is discussed based on product-ion distributions and semi-empirical calculations of the energies of intermediates and products. Although absolute values of MNDO data may be unreliable, they will be useful and fairly reliable for comparing relative energies of related structures.

Experimental

CH_4 CI mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS in a reactant-ion selective mode. The reactant CH_5^+, $C_2H_5^+$, or $C_3H_5^+$ ion 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_5^+, 6.0 and 2.4 eV for $C_2H_5^+$, and 4.3 and 1.7 eV for $C_3H_5^+$, respectively, using a pseudo-potential well method.[20] These energies are higher than that in the medium-pressure CI experiments, which was estimated to be less than 1 eV.[21] The time for storing a reactant ion was 5 ms. The reaction time was varied from 0.5 to 100 ms for $C_2H_5^+$ and $C_3H_5^+$, and 0.5 to 50 ms for CH_5^+, because it was difficult to selectively trap CH_5^+ at reaction times above 50 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 1000—10000 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 determine rate constants from plots of a decay of a reactant ion against the reaction time or the concentration of a reagent.

The heats of formation are known for the reactant ions, reagents, and some stable products obtained in this work.[22] However, there are many species whose ΔH° values are unknown. These values were calculated using semi-empirical MNDO, AM1, and PM3 methods (MOPAC Ver. 6.0) in order to describe potential-energy diagrams of the reaction pathways. When ΔH° values of $(PhCOOH+H)^+$ and $(PhCOOCH_3+H)^+$ were calculated using the above three methods, the best fits between the calculated and experimental values were obtained using the MNDO method. Therefore, the MNDO method was used for the evaluation of ΔH° values in this study. Although we calculated ΔH° values of such initial adduct ions as $(PhCOOCH_3+C_3H_5)^+$ and $(PhCOOC_2H_5+C_3H_5)^+$ using the above three methods, ΔH° values could not be obtained for some isomers, probably due to the lack of stable structures.

Results and Discussion

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 ±10%.

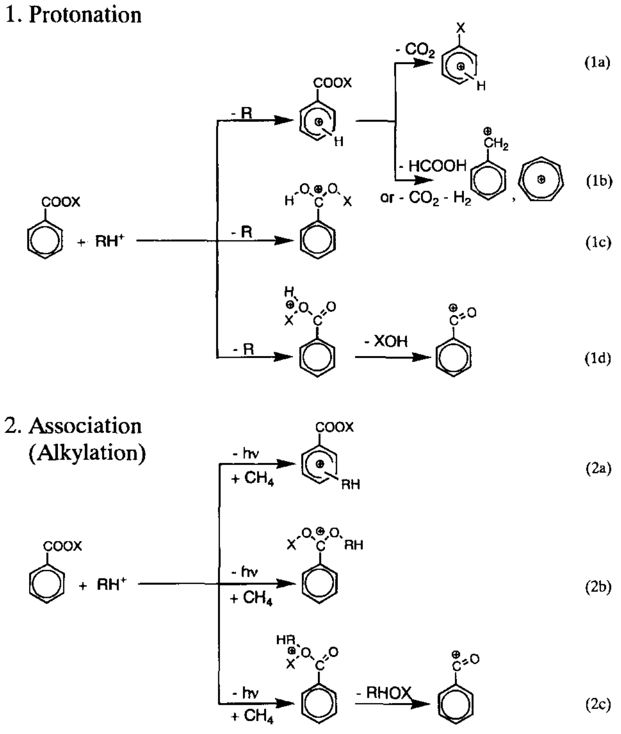
Benzoic Acid. In the CH_5^+/PhCOOH reaction, $(M+H)^+$ (m/z = 123), $(M+H-H_2O)^+$ (m/z = 105), and $(M+H-CO_2)^+$ (m/z = 79) are observed. Besides the above three ions, $(M+C_2H_5)^+$ (m/z = 151) and $(M+C_2H_5-CO_2)^+$ (m/z =

Table 1. Branching Ratios (%) of Product Ions in Reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with PhCOOX (X = H, CH_3, C_2H_5, and Ph)[a,b)]

Reagents	PhCOOH			$PhCOOCH_3$			$PhCOOC_2H_5$			PhCOOPh		
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^+	$C_2H_5^+$	$C_3H_5^+$
Product ions												
$(M+C_3H_5)^+$			2(+)			36(+)			0(+)			
$(M+C_3H_5-C_2H_4)^+$									7(+)			
$(M+C_3H_5-C_2H_4-CO_2)^+$			0(+)						17(+)			
$(M+C_3H_5-XOH)^+$						0(+)						0(+)
$(M+C_2H_5)^+$		0(+)										
$(M+C_2H_5-CO_2)^+$		0(+)										
$(M+C_2H_5-XOH)^+$											0(+)	
$(M+H)^+$	70(−)	81(−)	44(−)	51(+)	92(−)	48(−)	31(+)	81(+)	67(−)	37(−)	70(+)	47(−)
$(M+H-XOH)^+$	7(+)	9(−)	48(+)	11(0)	0(+)	10(+)	9(−)	3(0)	5(0)	56(−)	30(−)	53(+)
$(M+H-CO_2)^+$	23(0)	10(0)	6(−)	29(−)	8(0)	2(−)		3(+)		0(+)		
$(M+H-HCOOH)^+$				9(−)		4(−)						
$(M+H-CH_3COOH)^+$									4(0)			
$(M+H-C_2H_4)^+$							39(+)	11(−)				
$(M+H-C_2H_4-CO_2)^+$							21(−)	2(0)				
$(M+H-PhH)^+$										7(+)		

a) Uncertainties are within ±10%. b) Symbols, +, −, and 0 in brackets denote its branching ratio increases, decerases, or is unchanged with increasing the reaction time, respectively.

107) are observed in the $C_2H_5^+$ reaction, while $(M+C_3H_5)^+$ (m/z = 163) and $(M+C_3H_5-C_2H_4-CO_2)^+$ (m/z = 91) are detected in the $C_3H_5^+$ reaction at long reaction times. Possible reaction pathways for the RH^+/PhCOOX (R = CH_4, C_2H_4, and C_3H_4; X = H and CH_3) reactions are shown in Scheme 1. Radiative association and collisional stabilization can participate in the association reactions. They are shown using such symbols as $-h\nu$ and $+CH_4$, respectively, in Scheme 1. The $(M+H)^+$ ion is formed through PT [processes (1a)—(1d)], while the PhH_2^+ ions is formed through dissociative PT by loss of CO_2 [process (1a)]. The $PhCO^+$ ion is produced through dissociative PT by loss of H_2O in the CH_5^+ reaction [process (1d)]. The $(M+C_2H_5)^+$ and $(M+C_3H_5)^+$ adduct ions are produced through association [processes (2a)—(2c)], and the $(M+C_2H_5-CO_2)^+$ and $(M+C_3H_5-C_2H_4-CO_2)^+$ ions are formed from dissociative alkylation. It is known that two-body radiative association and three-body collisional association can participate in the formation of adduct ions. In radiative association, adduct ions are stabilized by radiating infrared emissions.[23,24] A typical rate of infrared emission would be 100 photons s^{-1}, whereas the total collision numbers in this study are estimated to be 1—240 times during reaction times of 0.5—100 ms, corresponding to the collision rate of 2400 collisions s^{-1}. Therefore, not only radiative association ($-h\nu$) but also collisional association ($+CH_4$) may participate in the formation of $(M+C_2H_5)^+$ and $(M+C_3H_5)^+$ under our operating conditions. Secondary collisional stabilization processes may also participate in the dissociative alkylation processes. In order to examine the contribution of collisional stabilization, the dependence of product-ion distributions on the reaction time was measured in the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ reactions [Figs. 1(a), 1(b), and 1(c)]. It was found that collisional stabilization plays a significant role in the non-dissociative and dissociative alkylation leading to $(M+C_2H_5)^+$, and $(M+C_2H_5-CO_2)^+$, $(M+C_3H_5)^+$, and $(M+C_3H_5-C_2H_4-CO_2)^+$. The branching ratios of the $(M+C_2H_5)^+$, and $(M+C_2H_5-CO_2)^+$ and $(M+C_3H_5-C_2H_4-CO_2)^+$ become zero at zero reaction time, indicating that they are exclusively formed via collisional stabilization. Although the branching ratio of $(M+C_3H_5)^+$ decreases with decreasing the reaction time, it does 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 $(PhCOOH+C_3H_5)^+$. The $PhCO^+$ ion can be produced through dissociative PT (1d) by loss of H_2O and/or dissociative alkylation (2c) by loss of C_2H_5OH or C_3H_5OH in the $C_2H_5^+$ and $C_3H_5^+$ reactions. If it is formed through the latter process, collisional stabilization will be significant for its production as in the formation of $(M+C_2H_5-CO_2)^+$ and $(M+C_3H_5-C_2H_4-CO_2)^+$. No evidence or only a small effect of collisional stabilization was found for the formation of $PhCO^+$. On the basis of these findings, it was concluded that $PhCO^+$ is dominantly produced via dissociative PT (1d) in the $C_2H_5^+$ and $C_3H_5^+$ reactions.



Scheme 1. Possible reaction pathways for the ion-molecule reactions of RH^+ with PhCOOX (X = H and CH_3).

The $(PhCOOH+H)^+$ ion can be formed through a PT to the benzene ring [processes (1a) and (1b)] or to the lone-pair electrons of an O-atom in the CO or OH group [processes (1c) and (1d)]. The electron-withdrawing effect of the COOH group will suppress the formation of Wheland-type ring protonated ions, while a high reactivity of the lone-pair electrons on the oxygen atoms will yield O-protonated ion preferentially. The PhCOOH molecule has two O atoms in carbonyl and hydroxy groups, denoted O(c) and O(h), respectively. Figures 2, 3, and 4 show the potential-energy diagrams of the RH^+/PhCOOH reactions obtained using known thermochemical data[22] and calculated MNDO data. For comparison, the energies of $(PhCOOH+H)^+$ + R obtained using a known experimental proton affinity of PhCOOH[22] are also shown in Figs. 2, 3, and 4, though the site of protonation was not determined. The experimental energies of $(PhCOOH+H)^+$ + R agree with the MNDO energies calculated for the formation of the most stable O(c)-protonated ion within 0.07 eV. It is, therefore, reasonable to assume that the reported proton affinity of PhCOOH is that for an O(c)-protonated ion. It is known that a major protonated ion is the most stable ion when more than two reactive sites exist in a reagent.[6] Therefore, non-dissociative PT occurs dominantly on a reactive site with the largest proton affinity, though dissociative PT takes place not only through the most stable protonated ions but also through less stable ones. In the RH^+/PhCOOH reactions, O(c)-protonated ion is more stable than the ring-protonated and O(h)-protonated ions. Therefore, it will be a dominant $(PhCOOH+H)^+$ ion.

The $(PhCOOH+C_3H_5)^+$ ion can be formed through association to the benzene ring [process (2a)] or to the lone-pair electrons of the CO or OH group [processes (2b) and (2c)]. Since the association is a reversible process with a low energy

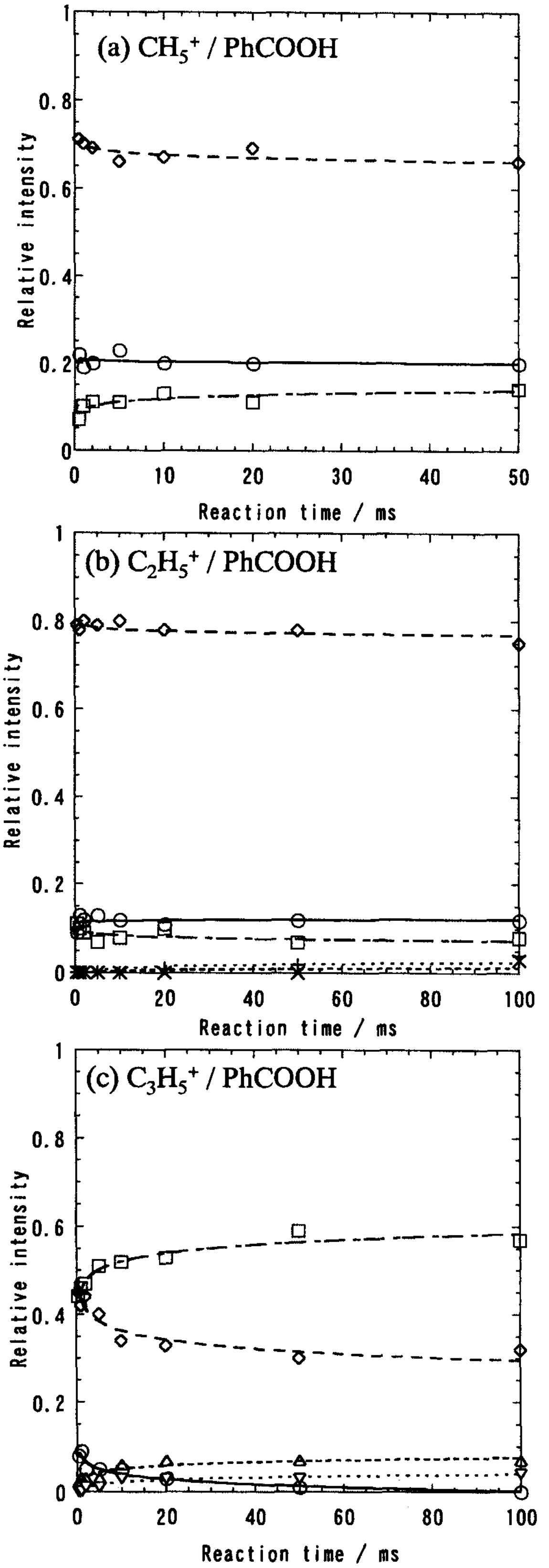


Fig. 1. Dependence of branching ratios of product ions on the reaction time in the RH^+/PhCOOH reaction. ◇ ($m/z = 123$): $(M+H)^+$, □ ($m/z = 105$): $(M+H-H_2O)^+$, ○ ($m/z = 79$): $(M+H-CO_2)^+$, × ($m/z = 151$): $(M+C_2H_5)^+$, + ($m/z = 107$): $(M+C_2H_5-CO_2)^+$, △ ($m/z = 163$): $(M+C_3H_5)^+$, and ▽ ($m/z = 91$): $(M+C_3H_5-C_2H_4-CO_2)^+$.

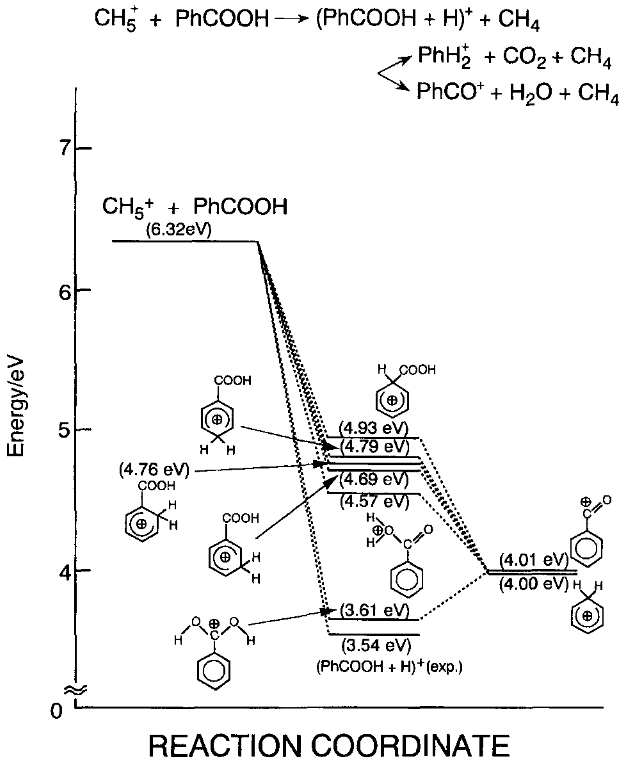


Fig. 2. Potential-energy diagram of the CH_5^+/PhCOOH reaction.

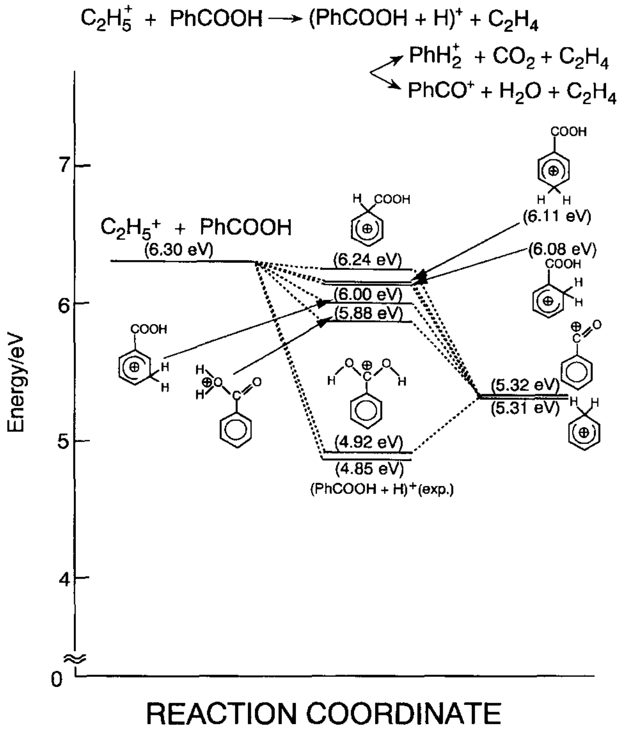


Fig. 3. Potential-energy diagram of the $C_2H_5^+$/PhCOOH reaction.

barrier, it will be controlled thermochemically. There are three possible $C_3H_5^+$ isomers, whose ΔH° values are 946, 969, and 1069 kJ mol^{-1} for $CH_2{=}CHCH_2^+$, $CH_3C{=}CH_2^+$, and protonated cyclopropene ion, respectively.[22] Since the most stable $CH_2{=}CHCH_2^+$ isomer is a significant ion produced from CH_4 CI gas,[25] all thermochemical calculations

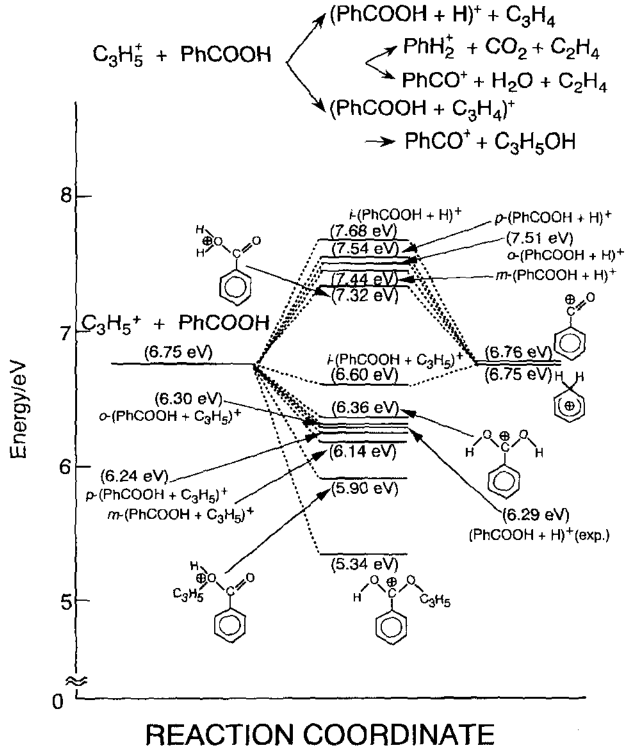


Fig. 4. Potential-energy diagram of the $C_3H_5^+$/PhCOOH reaction.

reported here for $C_3H_5^+$ are carried out using the above ΔH° value of $CH_2{=}CHCH_2^+$. According to the potential-energy diagram of association pathways in the $C_3H_5^+$/PhCOOH reaction, O(c)-adduct ion is more stable than the other ring-adduct and O(h)-adduct ions by 0.56—1.26 eV (Fig. 4). Thus, it will be a dominant $(PhCOOH + C_3H_5)^+$ ion, as in the case of the protonated ion.

Methyl Benzoate. In Table 2 are listed heats of reactions for various possible product channels in the $RH^+/PhCOOCH_3$ reactions, where an O atom in the methoxy group is denoted by O(m). For comparison, the energies of $(PhCOOCH_3+H)^++R$ obtained using a known experimental proton affinity of $PhCOOCH_3$[22] are also shown. The experimental energies of $(PhCOOCH_3+H)^++R$ agree with the MNDO energies calculated for the formation of the most stable O(c)-protonated ions within 0.52—0.53 eV. It is, therefore, reasonable to assume that the reported proton affinity of $PhCOOCH_3$ is that for the O(c)-protonated ion. The dependence of each product ion on the reaction time is shown in Figs. 5(a), 5(b), and 5(c).

The observed product channels in the CH_5^+ and $C_2H_5^+$ reactions are similar to those found for PhCOOH except for the additional formation of $(M+H-HCOOH)^+$ in the CH_5^+ and $C_3H_5^+$ reactions. The major product channel is non-dissociative PT (1a)—(1d) leading to $(PhCOOCH_3+H)^+$. Dissociative PT leading to $(PhCH_3+H)^+$ and $PhCO^+$ are found as minor competitive product channels. The $(PhCH_3+H)^+$ ion is formed through loss of CO_2 via ring-protonated ions [process (1a)]. Its branching ratios in the $CH_5^+/PhCOOCH_3$ and $C_2H_5^+/PhCOOCH_3$ reactions are comparable with those

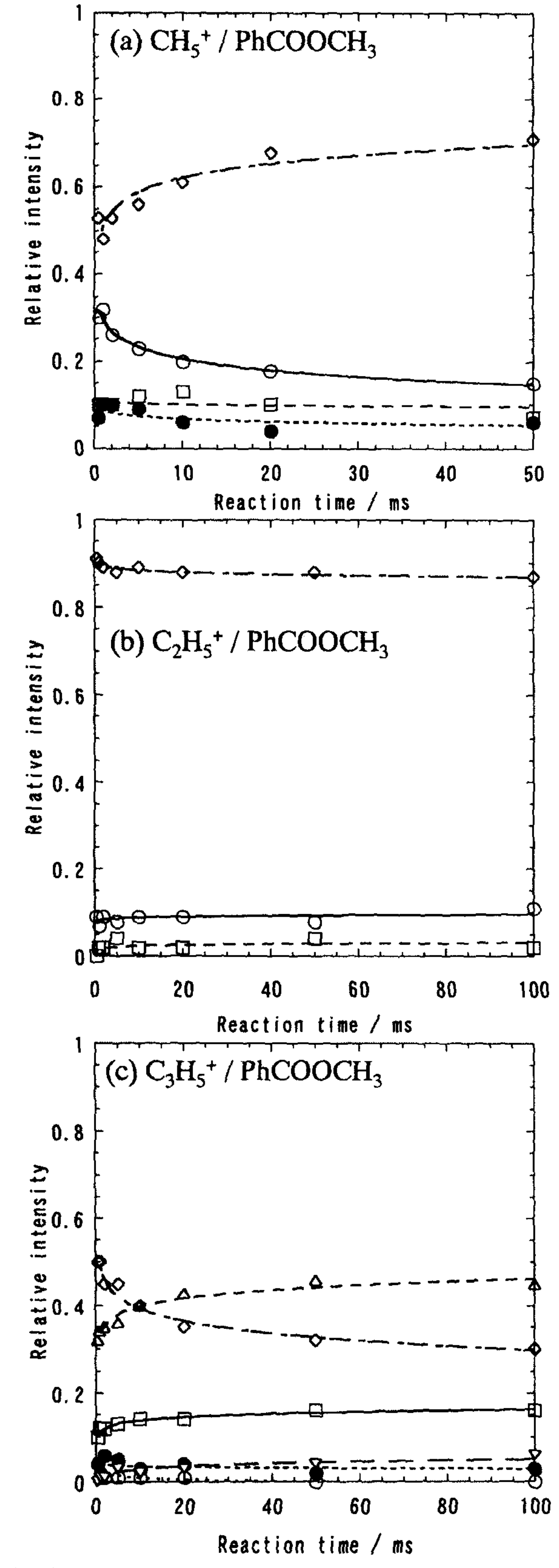


Fig. 5. Dependence of branching ratios of product ions on the reaction time in the $RH^+/PhCOOCH_3$ reaction. ◇ (m/z = 137): $(M+H)^+$, □ (m/z = 105): $(M+H-CH_3OH)^+$, ○ (m/z = 93): $(M+H-CO_2)^+$, ● (m/z = 91): $(M+H-HCOOH)^+$, △ (m/z = 177): $(M+C_3H_5)^+$, and ▽ (m/z = 145): $(M+C_3H_5-CH_3OH)^+$.

Table 2. Heats of Reactions of Each Product Channel (in eV Units)$^{a)}$

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products	$\sum\Delta H^\circ$ (Products)	ΔH° (Reactions)$^{b)}$	Processes$^{c)}$
CH$_5^+$ + PhCOOCH$_3$	6.36	o-(PhCOOCH$_3$ + H)$^+$ + CH$_4$	5.03	−1.33	(1a)
		m-(PhCOOCH$_3$ + H)$^+$ + CH$_4$	4.96	−1.40	(1a)
		p-(PhCOOCH$_3$ + H)$^+$ + CH$_4$	5.05	−1.31	(1a)
		i-(PhCOOCH$_3$ + H)$^+$ + CH$_4$	5.18	−1.18	(1a)
		O(c)–(PhCOOCH$_3$ + H)$^+$ + CH$_4$	3.83	−2.53	(1b)
		O(m)–(PhCOOCH$_3$ + H)$^+$ + CH$_4$	4.31	−2.05	(1c)
		(PhCOOCH$_3$ + H)$^+$(exp.) + CH$_4$	3.31	−3.05	
		o-(PhCH$_3$ + H)$^+$ + CO$_2$ + CH$_4$	3.78	−2.58	(1a)
		m-(PhCH$_3$ + H)$^+$ + CO$_2$ + CH$_4$	3.83	−2.53	(1a)
		p-(PhCH$_3$ + H)$^+$ + CO$_2$ + CH$_4$	3.74	−2.62	(1a)
		i-(PhCH$_3$ + H)$^+$ + CO$_2$ + CH$_4$	4.04	−2.32	(1a)
		(PhCH$_3$ + H)$^+$(exp.) + CO$_2$ + CH$_4$	3.30	−3.06	(1a)
		PhCO$^+$(exp.) + CH$_3$OH + CH$_4$	4.54	−1.82	(1c)
		PhCH$_2^+$(exp.) + HCOOH + CH$_4$	4.63	−1.74	
		C$_7$H$_7^+$(exp.) + HCOOH + CH$_4$	4.11	−2.26	
C$_2$H$_5^+$ + PhCOOCH$_3$	6.37	o-(PhCOOCH$_3$ + H)$^+$ + C$_2$H$_4$	6.34	−0.03	(1a)
		m-(PhCOOCH$_3$ + H)$^+$ + C$_2$H$_4$	6.28	−0.09	(1a)
		p-(PhCOOCH$_3$ + H)$^+$ + C$_2$H$_4$	6.36	−0.01	(1a)
		i-(PhCOOCH$_3$ + H)$^+$ + C$_2$H$_4$	6.49	0.12	(1a)
		O(c)–(PhCOOCH$_3$ + H)$^+$ + C$_2$H$_4$	5.14	−1.23	(1b)
		O(m)–(PhCOOCH$_3$ + H)$^+$ + C$_2$H$_4$	5.62	−0.75	(1c)
		(PhCOOCH$_3$ + H)$^+$(exp.) + C$_2$H$_4$	4.61	−1.76	
		o-(PhCH$_3$ + H)$^+$ + CO$_2$ + C$_2$H$_4$	5.09	−1.28	(1a)
		m-(PhCH$_3$ + H)$^+$ + CO$_2$ + C$_2$H$_4$	5.14	−1.23	(1a)
		p-(PhCH$_3$ + H)$^+$ + CO$_2$ + C$_2$H$_4$	5.06	−1.31	(1a)
		i-(PhCH$_3$ + H)$^+$ + CO$_2$ + C$_2$H$_4$	5.35	−1.02	(1a)
		(PhCH$_3$ + H)$^+$(exp.) + CO$_2$ + C$_2$H$_4$	4.62	−1.75	(1a)
C$_3$H$_5^+$ + PhCOOCH$_3$	6.81	o-(PhCOOCH$_3$ + H)$^+$ + C$_3$H$_4$	7.78	0.97	(1a)
		m-(PhCOOCH$_3$ + H)$^+$ + C$_3$H$_4$	7.71	0.90	(1a)
		p-(PhCOOCH$_3$ + H)$^+$ + C$_3$H$_4$	7.80	0.99	(1a)
		i-(PhCOOCH$_3$ + H)$^+$ + C$_3$H$_4$	7.93	1.12	(1a)
		O(c)–(PhCOOCH$_3$ + H)$^+$ + C$_3$H$_4$	6.58	−0.23	(1b)
		O(m)–(PhCOOCH$_3$ + H)$^+$ + C$_3$H$_4$	7.06	0.25	(1c)
		(PhCOOCH$_3$ + H)$^+$(exp.) + C$_3$H$_4$	6.05	−0.76	
		PhCO$^+$(exp.) + CH$_3$OH + C$_3$H$_4$	7.17	0.36	(1c)
		PhCO$^+$(exp.) + C$_3$H$_5$OCH$_3$	5.94	−0.87	(2c)
		PhCH$_2^+$(exp.) + HCOOH + C$_3$H$_4$	7.22	0.41	
		C$_7$H$_7^+$(exp.) + HCOOH + C$_3$H$_4$	6.70	−0.11	
		o-(PhCOOCH$_3$ + C$_3$H$_5$)$^+$	6.57	−0.24	(2a)
		m-(PhCOOCH$_3$ + C$_3$H$_5$)$^+$	6.41	−0.40	(2a)
		p-(PhCOOCH$_3$ + C$_3$H$_5$)$^+$	6.51	−0.30	(2a)
		i-(PhCOOCH$_3$ + C$_3$H$_5$)$^+$	6.87	0.06	(2a)
		O(c)–(PhCOOCH$_3$ + C$_3$H$_5$)$^+$			(2b)
		O(m)–(PhCOOCH$_3$ + C$_3$H$_5$)$^+$	6.88	0.07	(2c)
CH$_5^+$ + PhCOOC$_2$H$_5$	6.03	o-(PhCOOC$_2$H$_5$ + H)$^+$ + CH$_4$	4.90	−1.13	(3a)
		m-(PhCOOC$_2$H$_5$ + H)$^+$ + CH$_4$	4.78	−1.25	(3a)
		p-(PhCOOC$_2$H$_5$ + H)$^+$ + CH$_4$	4.80	−1.23	(3a)
		i-(PhCOOC$_2$H$_5$ + H)$^+$ + CH$_4$	4.93	−1.10	(3a)
		O(c)–(PhCOOC$_2$H$_5$ + H)$^+$ + CH$_4$	3.55	−2.48	(3b)
		O(e)–(PhCOOC$_2$H$_5$ + H)$^+$ + CH$_4$	4.09	−1.94	(3c)
		o-(PhCOOH + H)$^+$ + C$_2$H$_4$ + CH$_4$	5.31	−0.72	(3a)
		m-(PhCOOH + H)$^+$ + C$_2$H$_4$ + CH$_4$	5.23	−0.80	(3a)
		p-(PhCOOH + H)$^+$ + C$_2$H$_4$ + CH$_4$	5.33	−0.70	(3a)
		i-(PhCOOH + H)$^+$ + C$_2$H$_4$ + CH$_4$	5.47	−0.56	(3a)
		O(c)–(PhCOOH + H)$^+$ + C$_2$H$_4$ + CH$_4$	4.15	−1.88	(3b)
		O(h)–(PhCOOH + H)$^+$ + C$_2$H$_4$ + CH$_4$	5.11	−0.92	(3c)
		(PhCOOH + H)$^+$(exp.) + C$_2$H$_4$ + CH$_4$	4.08	−1.95	

Table 2. (Continued)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products	$\sum\Delta H^\circ$ (Products)	ΔH° (Reactions)[b)]	Processes[c)]
		$\mathrm{PhH_2^+(exp.) + CO_2 + C_2H_4 + CH_4}$	5.85	−0.18	(3a)
		$\mathrm{PhCO^+(exp.) + C_2H_5OH + CH_4}$	4.08	−1.95	(3d)
$\mathrm{C_2H_5^+ + PhCOOC_2H_5}$	6.01	$o\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_2H_4}$	6.22	0.21	(3a)
		$m\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_2H_4}$	6.10	0.09	(3a)
		$p\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_2H_4}$	6.11	0.10	(3a)
		$i\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_2H_4}$	6.24	0.23	(3a)
		$\mathrm{O(c)\text{–}(PhCOOC_2H_5 + H)^+ + C_2H_4}$	4.86	−1.15	(3b)
		$\mathrm{O(e)\text{–}(PhCOOC_2H_5 + H)^+ + C_2H_4}$	5.41	−0.60	(3c)
		$o\text{-}(\mathrm{PhCOOH + H})^+ + \mathrm{2C_2H_4}$	6.62	0.61	(3a)
		$m\text{-}(\mathrm{PhCOOH + H})^+ + \mathrm{2C_2H_4}$	6.55	0.54	(3a)
		$p\text{-}(\mathrm{PhCOOH + H})^+ + \mathrm{2C_2H_4}$	6.65	0.64	(3a)
		$i\text{-}(\mathrm{PhCOOH + H})^+ + \mathrm{2C_2H_4}$	6.79	0.78	(3a)
		$\mathrm{O(c)\text{–}(PhCOOH + H)^+ + 2C_2H_4}$	5.47	−0.54	(3b)
		$\mathrm{O(h)\text{–}(PhCOOH + H)^+ + 2C_2H_4}$	6.42	0.41	(3c)
		$\mathrm{(PhCOOH + H)^+(exp.) + 2C_2H_4}$	5.39	−0.62	
		$\mathrm{PhH_2^+(exp.) + CO_2 + 2C_2H_4}$	5.31	−0.70	(3a)
		$\mathrm{PhCO^+(exp.) + C_2H_5OH + C_2H_4}$	5.39	−0.62	(3d)
$\mathrm{C_3H_5^+ + PhCOOC_2H_5}$	6.46	$o\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_3H_4}$	7.65	1.19	(3a)
		$m\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_3H_4}$	7.53	1.07	(3a)
		$p\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_3H_4}$	7.55	1.09	(3a)
		$i\text{-}(\mathrm{PhCOOC_2H_5 + H})^+ + \mathrm{C_3H_4}$	7.68	1.22	(3a)
		$\mathrm{O(c)\text{–}(PhCOOC_2H_5 + H)^+ + C_3H_4}$	6.30	−0.16	(3b)
		$\mathrm{O(e)\text{–}(PhCOOC_2H_5 + H)^+ + C_3H_4}$	6.84	0.38	(3c)
		$\mathrm{PhCH_2^+(exp.) + CH_3COOH + C_3H_4}$	6.82	0.36	
		$\mathrm{C_7H_7^+(exp.) + CH_3COOH + C_3H_4}$	6.30	−0.16	
		$\mathrm{PhCO^+(exp.) + C_2H_5OH + C_3H_4}$	6.83	0.37	(3c)
		$\mathrm{PhCO^+(exp.) + C_3H_5OC_2H_5 + C_3H_4}$	5.71	−0.75	(4c)
		$o\text{-}(\mathrm{PhCOOC_2H_5 + C_3H_5})^+$	6.32	−0.14	(4a)
		$m\text{-}(\mathrm{PhCOOC_2H_5 + C_3H_5})^+$	6.24	−0.22	(4a)
		$p\text{-}(\mathrm{PhCOOC_2H_5 + C_3H_5})^+$	6.25	−0.21	(4a)
		$i\text{-}(\mathrm{PhCOOC_2H_5 + C_3H_5})^+$	6.62	0.16	(4a)
		$\mathrm{O(c)\text{–}(PhCOOC_2H_5 + C_3H_5)^+}$			(4b)
		$\mathrm{O(e)\text{–}(PhCOOC_2H_5 + C_3H_5)^+}$			(4c)
		$o\text{-}(\mathrm{PhCOOH + C_3H_5})^+ + \mathrm{C_2H_4}$	6.84	0.38	(4a)
		$m\text{-}(\mathrm{PhCOOH + C_3H_5})^+ + \mathrm{C_2H_4}$	6.68	0.22	(4a)
		$p\text{-}(\mathrm{PhCOOH + C_3H_5})^+ + \mathrm{C_2H_4}$	6.78	0.32	(4a)
		$i\text{-}(\mathrm{PhCOOH + C_3H_5})^+ + \mathrm{C_2H_4}$	7.14	0.68	(4a)
		$\mathrm{O(c)\text{–}(PhCOOH + C_3H_5)^+ + C_2H_4}$	5.89	−0.57	(4b)
		$\mathrm{O(h)\text{–}(PhCOOH + C_3H_5)^+ + C_2H_4}$	6.45	−0.01	(4d)
		$\mathrm{PhHC_3H_5^+ + CO_2 + C_2H_4}$	6.19	−0.27	(4a),(4b),(4d)
$\mathrm{CH_5^+ + PhCOOPh}$	7.89	$o\mathrm{(b)\text{-}(PhCOOPh + H)^+ + CH_4}$	6.44	−1.45	(5a)
		$m\mathrm{(b)\text{-}(PhCOOPh + H)^+ + CH_4}$	6.40	−1.49	(5a)
		$p\mathrm{(b)\text{-}(PhCOOPh + H)^+ + CH_4}$	6.46	−1.43	(5a)
		$i\mathrm{(b)\text{-}(PhCOOPh + H)^+ + CH_4}$	6.64	−1.25	(5a)
		$o\mathrm{(ph)\text{-}(PhCOOPh + H)^+ + CH_4}$	5.86	−2.03	(5c)
		$m\mathrm{(ph)\text{-}(PhCOOPh + H)^+ + CH_4}$	6.24	−1.65	(5c)
		$p\mathrm{(ph)\text{-}(PhCOOPh + H)^+ + CH_4}$	5.81	−2.08	(5c)
		$i\mathrm{(ph)\text{-}(PhCOOPh + H)^+ + CH_4}$	6.63	−1.26	(5c)
		$\mathrm{O(c)\text{–}(PhCOOPh + H)^+ + CH_4}$	5.08	−2.81	(5g)
		$\mathrm{O(p)\text{–}(PhCOOPh + H)^+ + CH_4}$	6.09	−1.80	(5e)
		$o\text{-}(\mathrm{PhPh + H})^+ + \mathrm{CO_2 + CH_4}$	5.04	−2.85	(5b)
		$m\text{-}(\mathrm{PhPh + H})^+ + \mathrm{CO_2 + CH_4}$	5.43	−2.46	(5b)
		$p\text{-}(\mathrm{PhPh + H})^+ + \mathrm{CO_2 + CH_4}$	4.98	−2.91	(5b)
		$i\text{-}(\mathrm{PhPh + H})^+ + \mathrm{CO_2 + CH_4}$	5.43	−2.46	(5b)
		$\mathrm{PhCOO^+ + PhH + CH_4}$	7.37	−0.52	(5d)
		$\mathrm{PhOCO^+ + PhH + CH_4}$	7.47	−0.42	(5d)
		$\mathrm{PhCO^+(exp.) + PhOH + CH_4}$	5.52	−2.37	(5f)

Table 2. (Continued)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products	$\sum\Delta H^\circ$ (Products)	ΔH° (Reactions)$^{\rm b)}$	Processes$^{\rm c)}$
$C_2H_5^+$ + PhCOOPh	7.87	*o*(b)-(PhCOOPh + H)$^+$ + C_2H_4	7.76	−0.11	(5a)
		m(b)-(PhCOOPh + H)$^+$ + C_2H_4	7.71	−0.16	(5a)
		p(b)-(PhCOOPh + H)$^+$ + C_2H_4	7.78	−0.09	(5a)
		i(b)-(PhCOOPh + H)$^+$ + C_2H_4	7.95	0.08	(5a)
		o(ph)-(PhCOOPh + H)$^+$ + C_2H_4	7.18	−0.69	(5c)
		m(ph)-(PhCOOPh + H)$^+$ + C_2H_4	7.56	−0.31	(5c)
		p(ph)-(PhCOOPh + H)$^+$ + C_2H_4	7.12	−0.75	(5c)
		i(ph)-(PhCOOPh + H)$^+$ + C_2H_4	7.94	0.07	(5c)
		O(c)–(PhCOOPh + H)$^+$ + C_2H_4	6.39	−1.48	(5g)
		O(p)–(PhCOOPh + H)$^+$ + C_2H_4	7.40	−0.47	(5e)
		$PhCO^+$(exp.) + PhOH + C_2H_4	6.83	−1.04	(5f)
		$PhCO^+$(exp.) + $PhOC_2H_5$	6.29	−1.58	(6c)
		$PhCOC_2H_5^+$ + PhOH	7.19	−0.68	(6f)
		o-$C_2H_5C_6H_4CO^+$ + PhOH	6.28	−1.59	(6d)
		m-$C_2H_5C_6H_4CO^+$ + PhOH	6.32	−1.55	(6d)
		p-$C_2H_5C_6H_4CO^+$ + PhOH	6.29	−1.58	(6d)
$C_3H_5^+$ + PhCOOPh	8.33	*o*(b)-(PhCOOPh + H)$^+$ + C_3H_4	9.19	0.86	(5a)
		m(b)-(PhCOOPh + H)$^+$ + C_3H_4	9.15	0.82	(5a)
		p(b)-(PhCOOPh + H)$^+$ + C_3H_4	9.21	0.88	(5a)
		i(b)-(PhCOOPh + H)$^+$ + C_3H_4	9.39	1.06	(5a)
		o(ph)-(PhCOOPh + H)$^+$ + C_3H_4	8.61	0.28	(5c)
		m(ph)-(PhCOOPh + H)$^+$ + C_3H_4	8.99	0.66	(5c)
		p(ph)-(PhCOOPh + H)$^+$ + C_3H_4	8.56	0.23	(5c)
		i(ph)-(PhCOOPh + H)$^+$ + C_3H_4	9.38	1.05	(5c)
		O(c)–(PhCOOPh + H)$^+$ + C_3H_4	7.83	−0.50	(5g)
		O(p)–(PhCOOPh + H)$^+$ + C_3H_4	8.84	0.51	(5e)
		$PhCO^+$(exp.) + PhOH + C_3H_4	8.27	−0.06	(5f)
		$PhCO^+$(exp.) + $PhOC_3H_5$	7.41	−0.92	(6c)
		$PhCOC_3H_5^+$ + PhOH	8.68	0.35	(6d)
		o-$C_3H_5C_6H_4CO^+$ + PhOH	7.32	−1.01	(6d)
		m-$C_3H_5C_6H_4CO^+$ + PhOH	7.28	−1.05	(6d)
		p-$C_3H_5C_6H_4CO^+$ + PhOH	7.25	−1.08	(6d)

a) The symbols *o*-, *m*-, *p*-, *i*-, and O– represent *ortho*-, *meta*-, *para*-, *ipso*-, and O-adduct ions, respectively. The symbols h, m, e, p, c, b, and ph gibven in parentheses denote hydroxy, methoxy, ethoxy, phenoxy, carbonyl, benzoyl, and phenyl, respectively. Thermochemical data calculated using reliable experimental values for ions in Ref. 22 are shown by exp., and the other values for ions are calculated using a MNDO method. b) ΔH°(Reaction) = $\sum\Delta H^\circ$(Product) − $\sum\Delta H^\circ$(Reactant). c) Processes in Schemes 1, 2, 3, and 4.

in the CH_5^+/PhCOOH and $C_2H_5^+$/PhCOOH reactions. This implies that the probability of migration of methyl group to ring is similar to that of hydrogen atom.

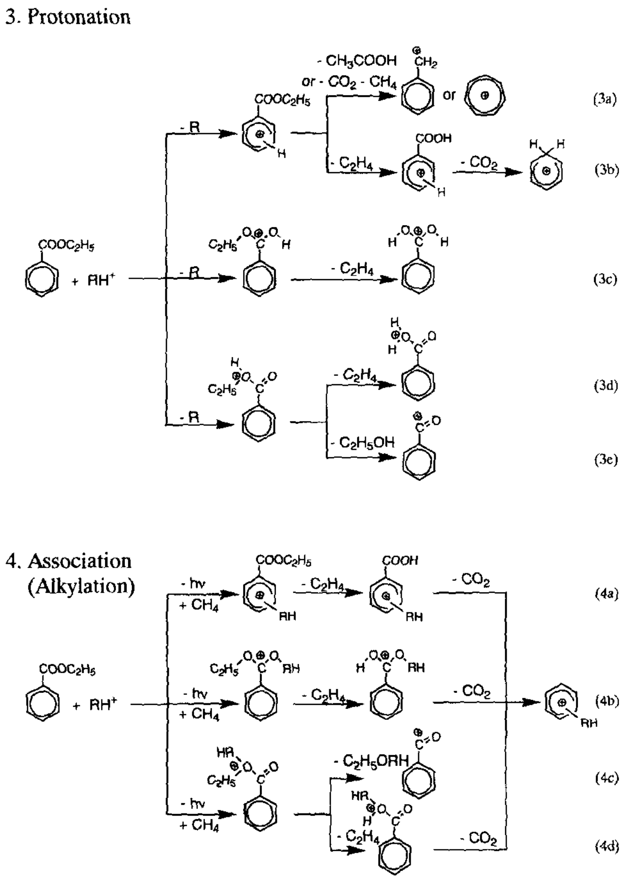
The $PhCO^+$ ion is expected to be formed via a loss of CH_3OH from the O(m)-protonated ion in the $CH_5^+/PhCOOCH_3$ reaction [process (1d)]. The branching ratio of $PhCO^+$ in the $C_2H_5^+$ reaction decreases to zero at zero reaction time, indicating that it is exclusively produced via collision-induced dissociative alkylation [process (2c)]. Although the formation of $PhCO^+$ through dissociative PT (1d) by loss of CH_3OH is endoergic (ΔH° = 0.36 eV) in the $C_3H_5^+$ reaction, this process cannot be excluded from the possible reaction processes, taking account of the kinetic energy of $C_3H_5^+$. The branching ratio of $PhCO^+$ in the $C_3H_5^+$ reaction greatly decreases from 20 to 4% with decreasing the reaction time from 100 to 0 ms. This implies that $PhCO^+$ is formed via dissociative protonation (1d) at short reaction times, while collision-induced dissociative alkylation (2c) becomes significant with increasing the reaction time.

The $(PhCOOCH_3+H)^+$ ion can be formed through a PT to the benzene ring [processes (1a) and (1b)] or to the lone-pair electrons of the CO or OCH_3 group [processes (1c) and (1d)]. On the basis of the energetics given in Table 2, the formation of O(c)-protonated ion is more favorable than the ring-protonated and O(m)-protonated ions. It is, therefore, reasonable to assume that it will be a major protonated ion.

The most outstanding feature in the $C_3H_5^+$ reaction is the formation of the initial adduct $(PhCOOCH_3+C_3H_5)^+$ ion with a high branching ratio. Its branching ratio decreases from 45 to 36% with decreasing the reaction time from 100 to 0 ms, indicating that it is dominantly produced through radiative association. The adduct $(PhCOOCH_3+C_3H_5)^+$ ion can be formed through attack on a ring, O(c), or O(m). Although the formation of the *o*-, *m*-, *p*-ring-alkylated ion is energetically accessible, the formation of the O(m)-alkylated ion is slightly endoergic (ΔH° = 0.07 eV). However, it cannot be energetically excluded, taking account of the uncertainty of the calculated ΔH° value and the kinetic energy of $C_3H_5^+$. Actually, the observation of a small amount of $PhCO^+$, formed via collisional stabilization, is a piece of evidence of the formation of O(m)–$(PhCOOCH_3+C_3H_5)^+$ ion as a precursor ion in dissociative alkylation (2c).

Ethyl Benzoate. In Table 2 are shown heats of reactions for various product channels in the $RH^+/PhCOOC_2H_5$, where an O atom in the ethoxy group is denoted by O(e). The dependence of each product ion on the reaction time is shown in Figs. 6(a), 6(b), and 6(c). Possible reaction pathways for the $RH^+/PhCOOC_2H_5$ (R = CH_4, C_2H_4, and C_3H_4) reactions are shown in Scheme 2. Although major product channels in the CH_5^+ and $C_2H_5^+$ reactions are non-dissociative and dissociative PT (3a)—(3e), as in the cases of PhCOOH and $PhCOOCH_3$, additional elimination processes of C_2H_4 are open for $PhCOOC_2H_5$. The total branching ratios of loss processes of C_2H_4 and $C_2H_4+CO_2$ from $(PhCOOC_2H_5+H)^+$ are larger than those of a loss process of CO_2 from $(PhCOOC_2H_5+H)^+$ in the CH_5^+ and $C_2H_5^+$ reactions. These facts indicate that the loss of C_2H_4 takes precedence over the loss of CO_2 in the dissociative PT reactions of CH_5^+ and $C_2H_5^+$. Major product channels in the $C_3H_5^+$ reaction are non-dissociative PT (3a)—(3e) and dissociative alkylation (4a)—(4d). Although loss processes of C_2H_4 and $C_2H_4+CO_2$ from $(PhCOOC_2H_5+C_3H_5)^+$ are observed, those from $(PhCOOC_2H_5+H)^+$ are absent in the $C_3H_5^+$ reaction.

The $(PhCOOC_2H_5+H)^+$ ion can be formed through a PT to



Scheme 2. Possible reaction pathways for the ion-molecule reactions of RH^+ with $PhCOOC_2H_5$.

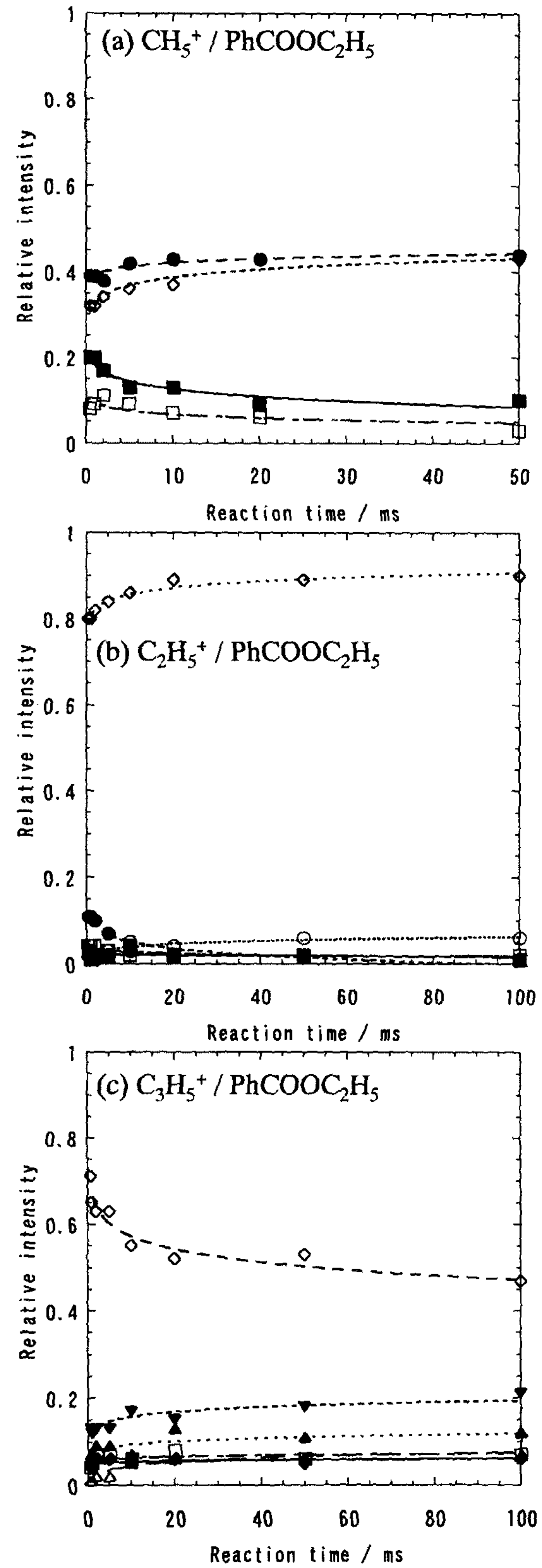
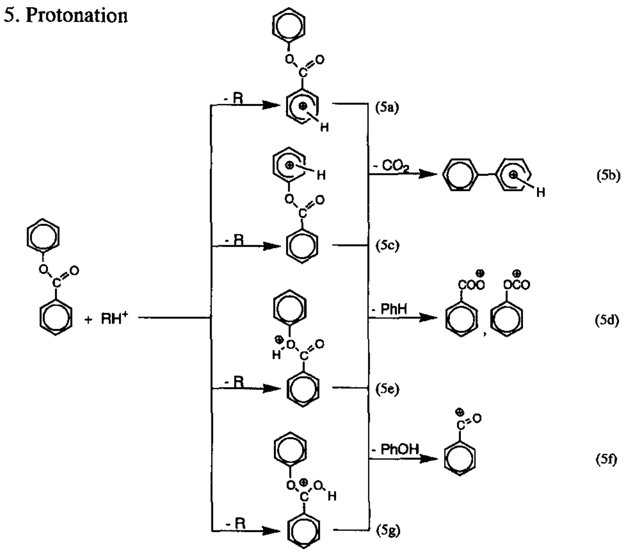


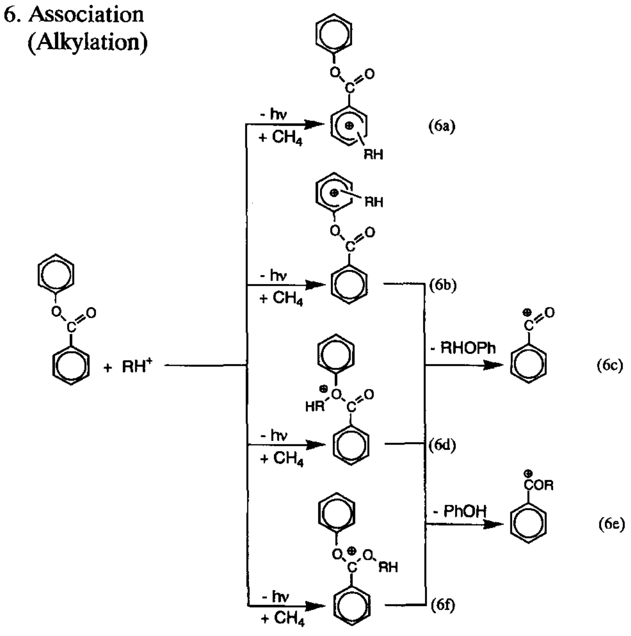
Fig. 6. Dependence of branching ratios of product ions on the reaction time in the $RH^+/PhCOOC_2H_5$ reaction. ◇ (m/z = 151): $(M+H)^+$, □ (m/z = 105): $(M+H-C_2H_5OH)^+$, ● (m/z = 123): $(M+H-C_2H_4)^+$, ■ (m/z = 79): $(M+H-C_2H_4-CO_2)^+$, ○ (m/z = 107): $(M+H-CO_2)^+$, △ (m/z = 191): $(M+C_3H_5)^+$, ▲ (m/z = 163): $(M+C_3H_5-C_2H_4)^+$, ▼ (m/z = 119): $(M+C_3H_5-C_2H_4-CO_2)^+$, and ◆ (m/z = 91): $(M+H-CH_3COOH)^+$.

the benzene ring [processes (3a) and (3b)] or to the lone-pair electrons of the CO or OC_2H_5 group [processes (3c)—(3e)]. On the basis of the energetics given in Table 2, O(c)-protonated ion is more stable than the ring-protonated and O(e)-protonated ions. Therefore, it will be a major protonated ion.

The $PhCO^+$ ion, whose branching ratio decreases with increasing the reaction time in the CH_5^+ reaction, is formed via a loss of C_2H_5OH from the O(c)-protonated ion. It is produced through dissociative PT (3e) and/or dissociative alkylation (4c) in the $C_2H_5^+$ and $C_3H_5^+$ reactions. Although the formation of O(e)-protonated ion is endoergic by 0.38 eV in the $C_3H_5^+$ reaction, it cannot be excluded from possible product ions. The branching ratios of $PhCO^+$ in the $C_2H_5^+$ and $C_3H_5^+$ reactions were essentially independent of



Scheme 3. Possible protonation pathways for ion-molecule reactions of RH^+ with PhCOOPh.



Scheme 4. Possible association pathways for ion-molecule reactions of RH^+ with PhCOOPh.

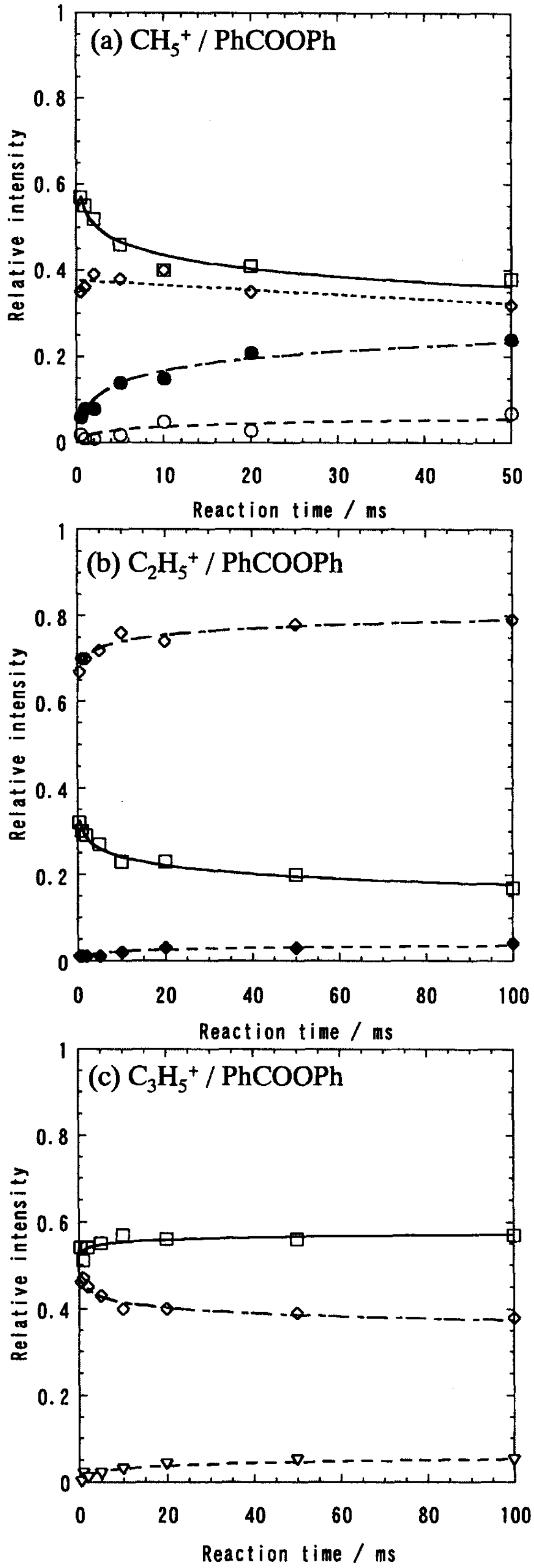


Fig. 7. Dependence of branching ratios of product ions on the reaction time in the RH^+/PhCOOPh reaction. ◇ (m/z = 199): $(M+H)^+$, □ (m/z = 105): $(M+H-PhOH)^+$, ○ (m/z = 155): $(M+H-CO_2)^+$, ● (m/z = 121): $(M+H-PhH)^+$, ◆ (m/z = 133): $(M+C_2H_5-PhOH)^+$, and ▽ (m/z = 145): $(M+C_3H_5-PhOH)^+$.

the reaction time. Therefore, it will be dominantly formed via dissociative PT (3e).

In the $C_3H_5{}^+$ reaction, the initial adduct $(PhCOOC_2H_5+C_3H_5)^+$ ion and its decomposition product ions, $(PhCOOC_2H_5+C_3H_5-C_2H_4)^+$ and $(PhCOOC_2H_5+C_3H_5-C_2H_4-CO_2)^+$, are found. The reaction time dependence of the branching ratios of these ions implies that $(PhCOOC_2H_5+C_3H_5)^+$ is exclusively formed via collisional stabilization, while the latter two ions are dominantly formed though the two-body dissociative alkylation. The O(c)–$(PhCOOH+C_3H_5)^+$ ion is most stable, as shown in Table 2. If the alkylation takes place through the lowest potential surface, it will occur via process (4b).

Phenyl Benzoate. In Table 2 are shown heats of reactions for various product channels in the $RH^+/PhCOOPh$, where an O atom in the phenoxy group is denoted by O(p). Possible reaction pathways for the $RH^+/PhCOOPh$ (R = CH_4, C_2H_4, and C_3H_4) reactions are shown in Schemes 3 and 4. The dependence of each product ion on the reaction time is shown in Figs. 7(a), 7(b), and 7(c). Major product channels in the $CH_5{}^+/PhCOOPh$ reaction are non-dissociative PT (5a), (5c), (5e), and (5g) and dissociative PT (5f) by loss of PhOH. An outstanding feature is that dissociative PT (5d) by loss of PhH is also open as a minor competitive channel in the $CH_5{}^+$ reaction. It should be noted that dissociative PT (5b) by loss of CO_2 is found in the $CH_5{}^+$ reaction, though it exclusively occurs through a collision-induced process. This shows that the migration of a large phenyl group occurs if a sufficient excess energy is supplied and it is collisionally removed in the PT process.

The $(PhCOOC_2H_5+H)^+$ ion can be formed through a PT to the benzene rings [processes (5a) and (5c)] or to the lone-pair electrons of the O atom in the OPh or CO group [processes (5e) and (5g)]. On the basis of the energetics given in Table 2, O(c)-protonated ion is more favorable than the ring-protonated and O(p)-protonated ions. Therefore, it will be a major protonated ion, as in the cases of X = H, CH_3, and C_2H_5. Since there is little difference in the ΔH° values for the formation of $PhCOO^+$ and $PhOCO^+$ (0.1 eV) in the $CH_5{}^+$ reaction, both ions are energetically accessible.

The $PhCO^+$ ion is formed via loss of PhOH from the O(p)-protonated ion in the $CH_5{}^+$ reaction [process (5f)]. Both dissociative PT (5f) via the O(p)-protonated ion and dissociative alkylation (6c) via O(p)-alkylated ions are possible for the formation of $PhCO^+$ in the $C_2H_5{}^+$ and $C_3H_5{}^+$ reactions. The decrease in the branching ratio of $PhCO^+$ in the $C_2H_5{}^+$ reaction with increasing the reaction time led us to conclude that $PhCO^+$ is dominantly formed by dissociative PT in the $C_2H_5{}^+$ reaction. On the other hand, a slight increase in the branching ratio of $PhCO^+$ in the $C_3H_5{}^+$ reaction with increasing the reaction time suggests that there is a small contribution of collisional stabilization for the formation of $PhCO^+$ at long reaction times.

In the $C_3H_5{}^+/PhCOOPh$ reaction, a small amount of $(PhCOOPh+C_3H_5-PhOH)^+$ is observed. Its disappearance at zero reaction time indicates that it is exclusively produced via a collision-induced process. It should be noted that two-body alkylation channels, as observed in the $C_3H_5{}^+/PhCOOX$ (X = H, CH_3, and C_2H_5) reactions, were absent in the $C_3H_5{}^+/PhCOOPh$ reaction. In general, alkylation reactions proceed through the formation of an activated complex, $(PhCOOX+C_3H_5)^{+*}$, which reversibly dissociates into the reactants (7), stabilized by emitting infrared emissions (8a) or collisions with CH_4 (8b), or directly dissociates into fragment species (8c):

$$C_3H_5{}^+ + PhCOOX \rightleftharpoons [PhCOOX+C_3H_5]^{+*} \qquad (7)$$

$$\begin{aligned} [PhCOOX+C_3H_5]^{+*} &\xrightarrow{-h\nu} [PhCOOX+C_3H_5]^+, && (8a)\\ &\xrightarrow{+CH_4} [PhCOOX+C_3H_5]^+, && (8b)\\ &\longrightarrow \text{Dissociation into fragments.} && (8c) \end{aligned}$$

The efficiency of radiative association generally increases with increasing the size of the activated complex and the binding energy of the complex.[23,24] Since the size of activation complex increases in the order of X = H, CH_3, C_2H_5, and Ph, the radiative association becomes favorable in this order. Although the higher branching ratio of radiative association for $PhCOOCH_3$ than that for PhCOOH agrees with this prediction, the lack of radiative association for PhCOOPh disagrees with this prediction. The binding energy of $[PhCOOPh + C_3H_5]^+$ is 1.68 eV for the most stable *p*-ring adduct, though it is not given in Table 2. Since this value is larger than that of $[PhCOOH+C_3H_5]^+$ (1.41 eV), the radiative association channel will be more favorable for PhCOOPh. The experimental observation contradicts the pre-

Table 3. Branching Ratios (%) of Each Product Channel in Reactions of $CH_5{}^+$, $C_2H_5{}^+$, and $C_3H_5{}^+$ with PhCOOX (X = H, CH_3, C_2H_5, and Ph)[a)]

Reagents		PhCOOH			$PhCOOCH_3$			$PhCOOC_2H_5$			PhCOOPh		
Reactant ions		$CH_5{}^+$	$C_2H_5{}^+$	$C_3H_5{}^+$	$CH_5{}^+$	$C_2H_5{}^+$	$C_3H_5{}^+$	$CH_5{}^+$	$C_2H_5{}^+$	$C_3H_5{}^+$	$CH_5{}^+$	$C_2H_5{}^+$	$C_3H_5{}^+$
Protonation	(Non-dissociative)	70	81	44	51	92	48	31	81	67	37	70	47
	(Dissociative)	30	19	54	49	8	16	69	19	9	63	30	53
Total		100	100	98	100	100	64	100	100	76	100	100	100
Association	(Non-dissociative)			2			36			0			0
	(Dissociative)			0			0			24			0
Total				2			36			24			0

a) Uncertainties are within ±10%.

diction from the binding energy. The lack of radiative association for $PhCOOC_2H_5$ is attributed to the presence of the fast dissociation process of activation complex via loss of stable C_2H_4 molecule [process 8(c)]. Such an elimination process of stable neutral molecules from complexes was absent for PhCOOX (X = H, CH_3, and Ph). In the RH^+/PhCOOPh reactions, PT channels leading to $(PhCOOPh+H)^+$ and $(PhCOOPh+H-H_2O)^+$ occur efficiently. One reason for the lack of radiative association for PhCOOPh will be the occurrence of fast competitive PT channels. Further detailed experimental and theoretical studies will be required in order to obtain a major factor which determines the branching ratio of each product channel.

Concluding Remarks

Ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with PhCOOX (X = H, CH_3, C_2H_5, and Ph) have been studied using an ion-trap of GC/MS. Although the contribution of each reactant hydrocarbon ion produced from CI CH_4 gas to the formation of product ions had not been determined earlier, it was determined in this study. Major product channels are PT with or without further decomposition. In general, elimination of HOX and of CO_2 compete with each other in most of the reactions. For the reactions with $PhCOOC_2H_5$, elimination of C_2H_4 takes precedence over the above decomposition processes. In Table 3 are summarized the branching ratios of each product channel. The observed product channels in the CH_5^+ and $C_2H_5^+$ reactions are non-dissociative and dissociative PT. The branching ratios of dissociative PT in the CH_5^+ reactions are larger than those in the $C_2H_5^+$ reactions, because excess energies released in each PT process in the CH_5^+ reactions are higher than those in the $C_2H_5^+$ reactions by 1.33 eV. The large excess energies make more dissociation channels possible. Association channels are open only for the $C_3H_5^+$ reactions with PhCOOX (X = H, CH_3, and C_2H_5). One reason for this is a larger proton affinity of C_3H_4 (8.0 eV) than that of CH_4 (5.7 eV) and C_2H_4 (7.1 eV),[22] reducing the proton-donating ability to a reagent. The other reason is the difference in the delocalization of a charge. Although a positive charge is localized on one C atom for $C_2H_5^+$, it is delocalized on two C atoms for $C_3H_5^+$. Therefore, protonation channels will be suppressed by the delocalization of the positive charge in the $C_3H_5^+$ reactions. The radiative association is involved in the formation of adduct ions in the $C_3H_5^+$/PhCOOX (X = H and CH_3) reactions. All product ions formed by non-dissociative and dissociative alkylation are collisionally stabilized. It should be noted that not only non-dissociative alkylation (association) but also dissociative alkylation are collisionally stabilized. The enhancement of dissociative alkylation by collisional stabilization probably results from the increased probability that $(M+C_2H_5)^{+*}$ and $(M+C_3H_5)^{+*}$ complexes will be partially deexcited by collision prior to decomposition, thus reducing the rate of dissociation back to $C_2H_5^+ + M$ and $C_3H_5^+ + M$ compared to that of rearrangement through elimination processes.

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