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

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The gas-phase ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with four monosubstituted benzenes carrying a hydroxy group in the substituent [PhX : X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$] have been studied under a reactant-ion selective chemical ionization mode of an ion-trap type of GC/MS. The major product channel for PhOH is non-dissociative proton transfer leading to $(M+H)^+$ ions, while that for the other three reagents is dissociative proton transfer leading to $(M+H-H_2O)^+$ ions in most cases. Small amounts of dissociative alkylation channels are found in some reactions with $C_2H_5^+$ and $C_3H_5^+$. The reaction mechanism is discussed based on the dependence of product-ion distributions on the reaction time and semi-empirical calculations of the energies of intermediates and products.

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.[1—3] An 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. Ion-molecule reactions of these reactant ions with benzene derivatives were studied by selectively trapping each reactant ion. In preceding papers, results for the following monosubstituted benzenes have been reported: PhH, $PhCH_3$, PhCOX (X = H, CH_3, C_2H_5, Ph, and COPh), and PhX [X = NH_2, $NH(CH_3)$, $N(CH_3)_2$, NO_2, and CN].[1—3] 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 channels for PhX [X = NH_2, $NH(CH_3)$, and $N(CH_3)_2$] with low ionization potentials were PT and charge transfer, while that for $PhNO_2$ and PhCN with high ionization potentials was PT. Small amounts of initial adduct ions, produced by association processes, and their decomposition products were found in the reactions of $C_2H_5^+$ and $C_3H_5^+$ with PhCOX, PhNX, and PhCN.

Although CH_4 CI mass spectra of substituted benzyl alcohols have been measured by Ichikawa and Harisson,[4] their measurements were carried out at a high CI gas pressure of 0.2—0.5 Torr (1 Torr = 133.322 Pa) 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%)][5] could not be determined. Brodbelt et al.[6] measured the CH_4 CI mass spectrum of PhOH in an ion trap type of mass spectrometer at a low CI gas pressure of 4.2×10^{-4} Torr. However, major reactant CH_5^+ and $C_2H_5^+$ ions were not separated. In the present work, ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with such monosubstituted benzenes as PhX [X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$] are studied under a reactant-ion selective CI mode of an ion-trap type of GC/MS, in order to obtain information on the reactivity of these hydrocarbon ions for monosubstituted benzenes carrying a hydroxy group in the substituent.

The operating conditions in the ion-trap cell used in this work are significantly different from those of conventional high-pressure CI mass spectrometer developed by Munson and Field.[5,7,8] In the high-pressure CI measurements, the typical CH_4 gas pressure was 1 Torr and a residence time of reactant ions in the ionization-reaction chamber was about 10 μs. Field[7] evaluated that the total number of collisions of reactant ions with CH_4 during this residence time is about 200 under these conditions. In our previous CI measurements using an ion trap of GC/MS, the total gas pressure was 1.2×10^{-4} Torr and the reaction time in the trap was kept at a constant value of 20 ms. The total number of collisions of a reactant ion with CH_4 and He during this reaction time is about 50. Some comparative studies between high-pressure and low-pressure CI have been carried out.[6,9,10] In general, fragmentation increases and no adduct ions such as $(M+C_2H_5)^+$ and $(M+C_3H_5)^+$ are observed in the ion-trap experiments. These facts were explained by the decrease in the effects of collisional stabilization of $(M+H)^+$, $(M+C_2H_5)^+$, and $(M+C_3H_5)^+$ ions with decreasing the number of secondary collisions with CH_4 and He gases. The other reason for the higher fragmentation in the ion-trap experiments is higher kinetic energies of reactant ions.[9]

In this study, the dependence of product-ion distributions on the reaction time is measured in order to examine the effects of collisional stabilization. The initial product-ion distributions are estimated by extrapolating the reaction-time dependence of the product-ion distributions to zero reaction time. 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. The reaction mechanism is discussed based on product-ion distributions and semi-empirical PM3 calculations of potential energies of intermediates and products.

The sites of protonation, methylation, and ethylation to PhOH and $PhNH_2$ have already been studied by Wood et al.[11] using a mass spectrometry/mass spectrometry (MS/MS) technique. They found that protonation of PhOH occurs exclusively on the benzene ring, and this is also the favored site for $PhNH_2$. Although alkylation of PhOH occurs preferentially to the ring, that of $PhNH_2$ takes place to the substituent. The difference between PhOH and $PhNH_2$, and that between protonation and alkylation, were explained by thermodynamical stability. In this study, the sites of protonation and alkylation to PhX [X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$] are discussed from the product-ion distributions and thermochemical data of intermediate and product ions.

Experimental

CH_4 CI mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS in a reactant-ion selective mode. It is known that the reactant CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions are produced through the following ion-molecule reactions, when CH_4 is used as a CI gas:[5]

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 + 0.10\ \mathrm{eV}, \quad (1)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 + 1.21\ \mathrm{eV}, \quad (2)$$

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 + 0.96\ \mathrm{eV}. \quad (3)$$

Here, the $\Delta H°$ values are evaluated using reported thermochemical data.[12] Since the $\Delta H°$ values of the above reactions are lower than those of usual electronic excitation energies of molecular ions (>3 eV), all of the reactant ions are expected to be located in their electronic ground states. 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.[13] These energies are higher than that in the high-pressure CI experiments, which was estimated to be less than 1 eV.[14] The time for storing a reactant ion was 5 ms. The reaction time was varied from 0.5 to 50 ms for CH_5^+ and 0.5 to 100 ms for $C_2H_5^+$ and $C_3H_5^+$, because it was difficult to isolate CH_5^+ at long 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.

The heats of formation are known for the reactant ions, reagents, and some stable products obtained in this work.[12] However, there are many species whose $\Delta H°$ values are unknown. These values were calculated using a semi-empirical PM3 method (MOPAC Ver. 6.0) in order to describe the potential-energy diagram of the reaction pathways.

Results and Discussion

Initial product-ion distributions in each reaction were estimated by extrapolating the dependence of branching ratios of product ions on the reaction time to zero reaction time. The results obtained are given in Table 1. The uncertainties of the branching ratios were estimated to be within ±7%. Although $CH_2{=}CHCH_2^+$, $CH_3C{=}CH_2^+$, and protonated cyclopropene ion with $\Delta H° = 946$, 969, and 1069 kJ mol^{-1}, respectively,[12] are possible as $C_3H_5^+$, the most stable $CH_2{=}CHCH_2^+$ isomer will be most significant under the present experimental conditions. Therefore, all thermochemical calculations reported

Table 1. Branching Ratios (%) of Product Ions in Reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with PhX [X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$][a)]

Reagents	PhOH			$PhCH_2OH$			$PhCH_2CH_2OH$			$PhCH(OH)CH_3$		
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												
$(M+C_3H_5)^+$			9									
$(M+C_3H_5-H_2O)^+$									19			
$(M+C_3H_5-C_2H_4)^+$			36									
$(M+C_3H_5-CH_3CHO)^+$												5
$(M+C_3H_5-C_3H_4O)^+$												18
$(M+C_2H_5-H_2O)^+$								13				
$(M+C_2H_5-CH_2O)^+$					20							
$(M+C_2H_5-CH_3CHO)^+$											10	
$(M+H)^+$	100	100	55									
$(M+H-H_2O)^+$				58	63	70	100	87	77	100	82	56
$(M+H-CH_2O)^+$				42	17	27						
$(M+H-CH_3OH)^+$											8	7
$(M+H-CH_3CHO)^+$												9
$(M-H)^+$						3			4			5

a) Uncertainties are within ±7%.

here for $C_3H_5^+$ are carried out using the above ΔH° value of $CH_2{=}CHCH_2^+$.

Phenol. Possible reaction pathways for the RH^+/PhOH ($R = CH_4$, C_2H_4, and C_3H_4) reactions are shown in Scheme 1. Radiative association and collisional stabilization processes can participate in the formation of some ions. However, such symbols as $-h\nu$ and $+CH_4$, which are generally used to represent the above processes, are omitted from all the schemes presented in this work for the sake of clarity. Only non-dissociative PT leading to $(M+H)^+$ is found in the CH_5^+/PhOH and $C_2H_5^+$/PhOH reactions [processes (4a) and/or (4b)] at reaction times of 0.5—50 and 0.5—100 ms, respectively. This finding is consistent with a previous result of Brodbelt et al.,[6] who observed a strong $(M+H)^+$ peak by the CH_5^+/PhOH and $C_2H_5^+$/PhOH reactions in an ion-trap experiment. In the $C_3H_5^+$/PhOH reaction, besides similar non-dissociative PT, non-dissociative association leading to $(M+C_3H_5)^+$ and dissociative association leading to $(M+C_3H_5-C_2H_4)^+$ are observed. In our previous papers, we have reported that adduct ions are formed by radiative association at a total (CH_4+He) pressure of 1.2×10^{-4} Torr.[2,3] In radiative association, adduct ions are stabilized by radiating infrared emissions.[15,16] A typical rate of infrared emission would be 100 photons s^{-1}, whereas the total collision numbers in this study are estimated to be 1.2—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 but also collisional association may participate in the formation of the $(M+C_3H_5)^+$ and $(M+C_3H_5-C_2H_4)^+$ ions under our operating conditions. In order to examine the contribution of collisional stabilization, the dependence of product-ion distributions on the reaction time was measured in the 0.5—100 ms region (Fig. 1). With decreasing the reaction time from 100 to 0.5 ms, the branching ratios of $(M+C_3H_5)^+$ ($m/z = 135$) and $(M+C_3H_5-C_2H_4)^+$ ($m/z = 107$) decrease from 13 to 9% and from 64 to 36%, respectively, while that of $(M+H)^+$ ($m/z = 95$) increases from 23 to 55%. On the basis of the above facts, collisional stabilization participates in the formation of $(M+C_3H_5)^+$ and $(M+C_3H_5-C_2H_4)^+$. It should be noted that only a slight decrease in the branching ratio of the adduct $(M+C_3H_5)^+$ ion was found. This implies that the radiative association plays a significant role for the formation of $(M+C_3H_5)^+$.

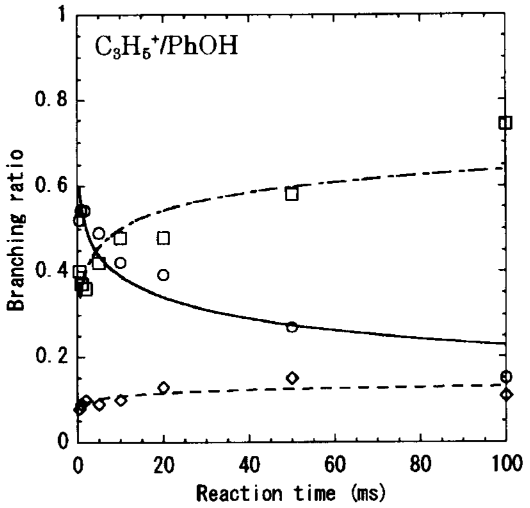
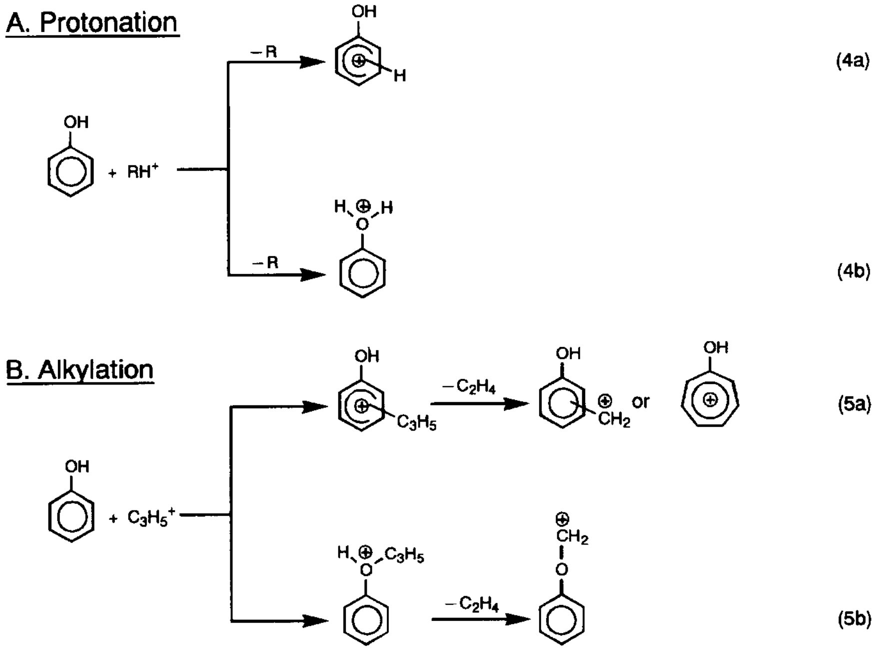


Fig. 1. Dependence of branching ratios of product ions on the reaction time in the $C_3H_5^+$/PhOH reaction. ◇: $m/z = 135$, □: $m/z = 107$, and ○: $m/z = 95$.

The $(M+H)^+$ ion can be formed through a PT to the benzene ring [process (4a)] or to the lone-pair electrons of the O-atom [process (4b)]. The electron-donating effect of the OH group will enhance the formation of Wheland-type ring protonated ions, while a high reactivity of the lone-pair electrons on the



Scheme 1. Possible reaction pathways for the RH^+/PhOH reactions.

oxygen atom will yield O-protonated ion preferentially. Figures 2, 3, and 4 show the potential-energy diagrams of the RH^+/PhOH reactions obtained using known thermochemical data[12] and calculated PM3 data. When the energies of $(M+H)^+$+R are estimated using a known experimental proton affinity of PhOH,[12] they are lower than PM3 energies calculated for the formation of stable *para*- and *ortho*-ring-protonated ions by 0.43—0.52 eV. This shows that absolute values of PM3 data are unreliable. However, they will be useful and fairly reliable for comparing relative energies of related structures. It is known that a major $(M+H)^+$ ion is the most stable ion formed by protonation to a substituent with the highest proton affinity, when more than two reactive sites are present in a reagent.[8,17] This shows that protonation is governed thermodynamically. Thus, stable *para*- and *ortho*-ring-protonated ions are expected to be more favorable than the other ring-protonated and O-protonated ions in the protonation of PhOH, which is consistent with a previous MS/MS study of Wood et al.[11]

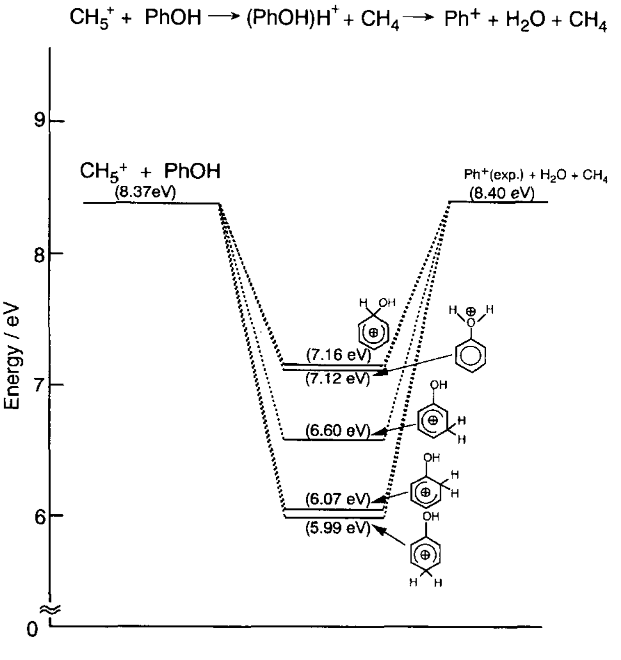


Fig. 2. Potential-energy diagram of the CH_5^+/PhOH reaction.

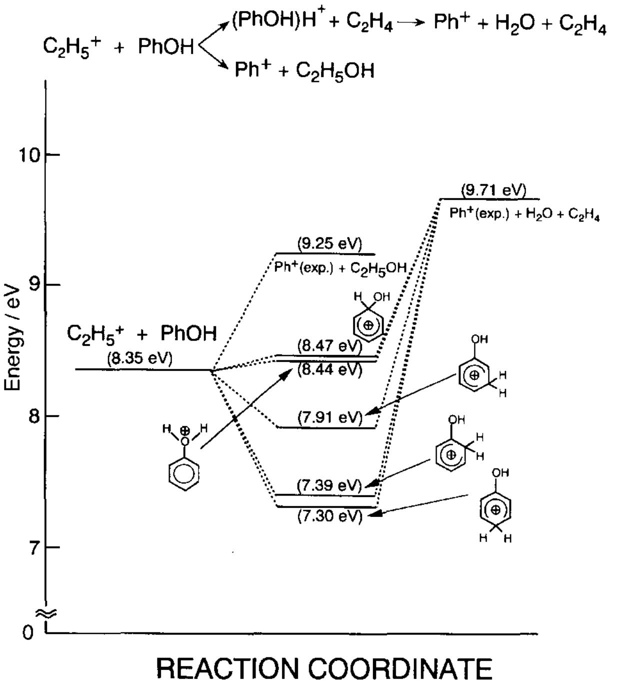


Fig. 3. Potential-energy diagram of the $C_2H_5^+$/PhOH reaction.

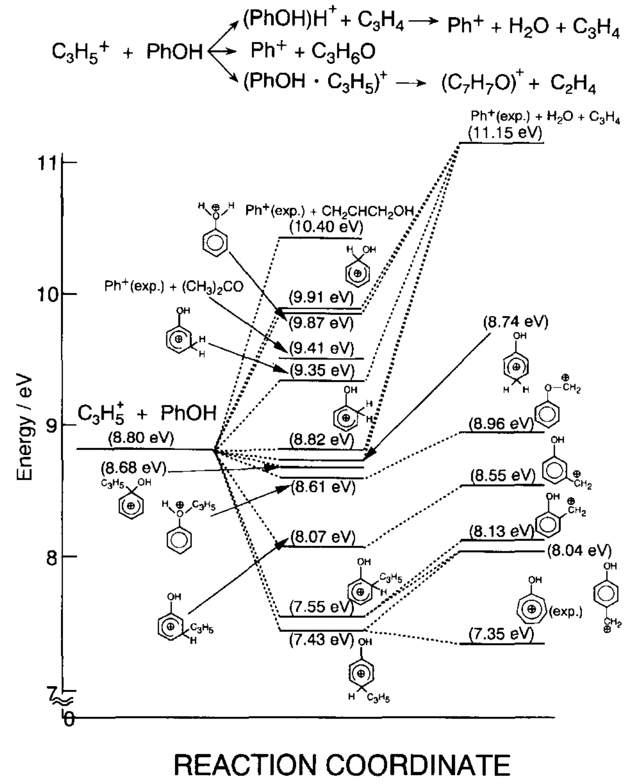


Fig. 4. Potential-energy diagram of the $C_3H_5^+$/PhOH reaction.

The most outstanding feature of the RH^+/PhOH reactions is the preferential formation of the $(M+H)^+$ ion and the lack of the subsequent elimination process of H_2O, C_2H_5OH, or $(CH_3)_2CO$. The formation of Ph^+ by loss of H_2O, C_2H_5OH, or $(CH_3)_2CO$ is endoergic due to a high ΔH° value of Ph^+, as shown in Figs. 2, 3, and 4. Thus, the lack of dissociative PT in the RH^+/PhOH reactions can be explained by its endoergicity. Brodbelt et al.,[6] observed a Ph^+ peak with a very small branching ratio of 2% in the ion-trap experiment. This is probably due to the fact that the kinetic energies of reactant $C_2H_5^+$ and $C_3H_5^+$ ions in their experiment were higher than those in this study.

The $(M+C_3H_5)^+$ ion is dominantly formed through radiative association to the benzene ring [process (5a)] or to the lone-pair electrons of the O-atom [process (5b)]. Since the association is a reversible process without an energy barrier, it will be controlled thermodynamically. According to the potential-energy diagram of association pathways in the $C_3H_5^+$/PhOH reaction, *para*- and *ortho*-ring-adduct ions are more stable than the other ring-adduct and O-adduct ions by 0.5—1.3 eV (Fig. 4). On the basis of a previous MS/MS study,[11] alkylation of PhOH occurs exclusively on the ring. These facts led us to conclude that the attack of $C_3H_5^+$ ions occurs preferentially on the ring for PhOH. Although $CH_2C_6H_4OH^+$ and $C_7H_6OH^+$ ions are possible as a minor $(M+C_3H_5-C_2H_4)^+$ ion, the more stable tropylium-type $C_7H_6OH^+$ ion formed through process (5a) will be a major ion.

Summarizing the above results, we find that $(M+C_3H_5)^+$ and $C_7H_6OH^+$ ions are formed through two-body reaction involving radiative association at short reaction times:

$$C_3H_5^+ + PhOH \rightleftarrows (PhOH+C_3H_5)^{+*} \rightarrow (PhOH+C_3H_5)^+ + h\nu, \quad (6a)$$

$$\rightarrow C_7H_6OH^+ + C_2H_4. \quad (6b)$$

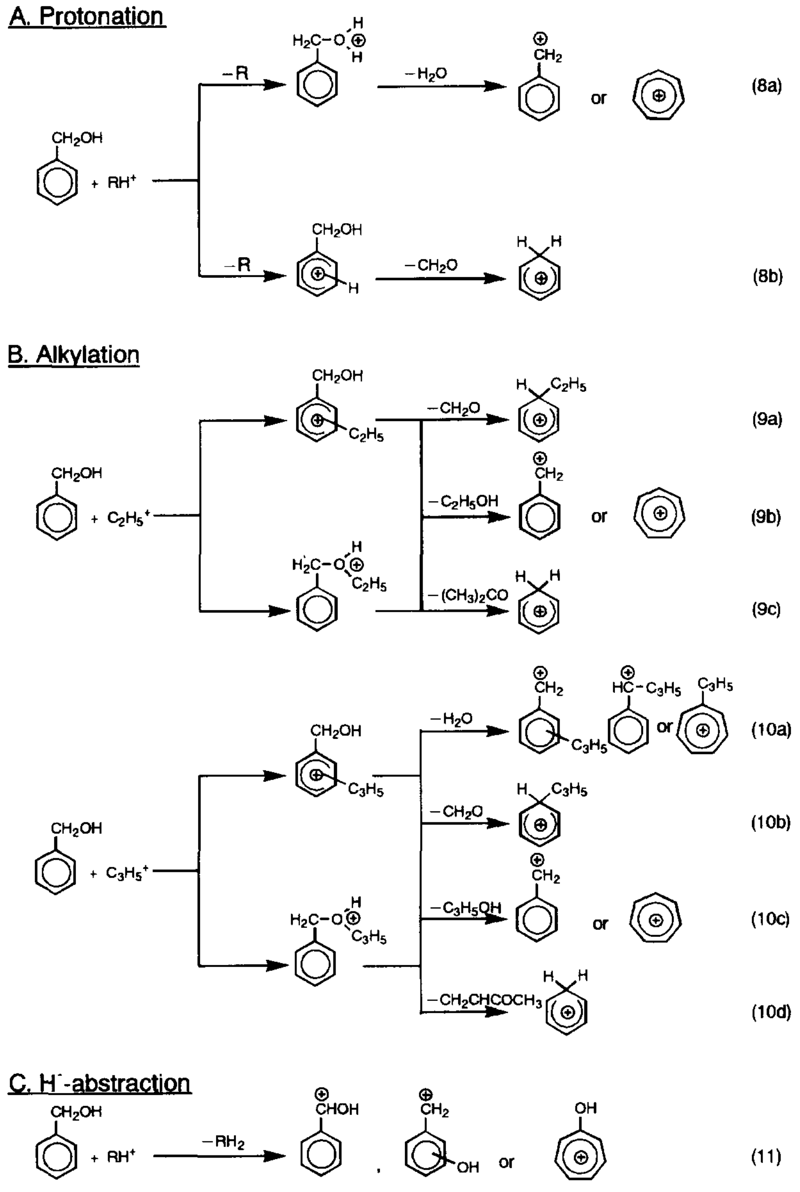
Here, $(PhOH+C_3H_5)^{+*}$ denotes a collision complex, which redissociates into the reactants, is radiatively stabilized, or dissociates by loss of C_2H_4. In addition to the above processes, the following collisional-stabilization processes participate in the formation of $(M+C_3H_5)^+$ and $C_7H_6OH^+$ ions at long reaction times:

$$C_3H_5^+ + PhOH \rightleftarrows (PhOH+C_3H_5)^{+*} \xrightarrow{+CH_4} (PhOH+C_3H_5)^+, \quad (7a)$$

$$\xrightarrow{+CH_4} C_7H_6OH^+ + C_2H_4. \quad (7b)$$

The increase in the branching ratio of (7b) with increasing the reaction time probably results from the increased probability that a $(PhOH+C_3H_5)^{+*}$ complex will be partially deexcited by collision prior to decomposition, thus reducing the rate of dissociation back to $C_3H_5^+$+PhOH compared to that of rearrangement to $C_7H_6OH^+$.

Benzyl Alcohol. A possible reaction scheme for $PhCH_2OH$ is shown in Scheme 2. In Table 2 are listed heats of reactions for various possible product channels in



Scheme 2. Possible reaction pathways for the $RH^+/PhCH_2OH$ reactions.

Table 2. Heats of Reaction of Each Product Channels (in eV Units)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products[a]	$\sum\Delta H^\circ$ (Products)	ΔH° (Reactions)[b]	Processes[c]
$CH_5^{+}+PhCH_2OH$	8.33	$o\text{-}(PhCH_2OH+H)^{+}+CH_4$	6.30	−2.03	(8b)
		$m\text{-}(PhCH_2OH+H)^{+}+CH_4$	6.36	−1.97	(8b)
		$p\text{-}(PhCH_2OH+H)^{+}+CH_4$	6.23	−2.10	(8b)
		$i\text{-}(PhCH_2OH+H)^{+}+CH_4$	6.61	−1.72	(8b)
		$O\text{-}(PhCH_2OH+H)^{+}+CH_4$	6.56	−1.77	(8a)
		$(PhCH_2OH+H)^{+}(\mathrm{exp.})+CH_4$	5.86	−2.47	
		$C_7H_7^{+}(\mathrm{exp.})+H_2O+CH_4$	5.52	−2.81	(8a)
		$PhCH_2^{+}(\mathrm{exp.})+H_2O+CH_4$	6.04	−2.29	(8a)
		$PhH_2^{+}(\mathrm{exp.})+CH_2O+CH_4$	6.60	−1.73	(8b)
		$C_7H_6OH^{+}+H_2+CH_4$	6.04	−2.29	(11)
		$PhCHOH^{+}+H_2+CH_4$	6.46	−1.87	(11)
$C_2H_5^{+}+PhCH_2OH$	8.31	$o\text{-}(PhCH_2OH+H)^{+}+C_2H_4$	7.62	−0.69	(8b)
		$m\text{-}(PhCH_2OH+H)^{+}+C_2H_4$	7.67	−0.64	(8b)
		$p\text{-}(PhCH_2OH+H)^{+}+C_2H_4$	7.54	−0.77	(8b)
		$i\text{-}(PhCH_2OH+H)^{+}+C_2H_4$	7.92	−0.39	(8b)
		$O\text{-}(PhCH_2OH+H)^{+}+C_2H_4$	7.87	−0.44	(8a)
		$(PhCH_2OH+H)^{+}(\mathrm{exp.})+C_2H_4$	7.18	−1.13	
		$PhH_2^{+}(\mathrm{exp.})+CH_2O+C_2H_4$	7.91	−0.40	(8b)
		$C_7H_7^{+}(\mathrm{exp.})+H_2O+C_2H_4$	6.84	−1.47	(8a)
		$PhCH_2^{+}(\mathrm{exp.})+H_2O+C_2H_4$	7.36	−0.95	(8a)
		$o\text{-}(PhCH_2OH+C_2H_5)^{+}$	6.67	−1.64	(9a—c)
		$m\text{-}(PhCH_2OH+C_2H_5)^{+}$	6.73	−1.58	(9a—c)
		$p\text{-}(PhCH_2OH+C_2H_5)^{+}$	6.59	−1.72	(9a—c)
		$i\text{-}(PhCH_2OH+C_2H_5)^{+}$	6.98	−1.33	(9a—c)
		$O\text{-}(PhCH_2OH+C_2H_5)^{+}$	7.02	−1.29	(9a—c)
		$C_2H_5PhH^{+}+CH_2O$	7.33	−0.98	(9a)
		$C_7H_7^{+}(\mathrm{exp.})+C_2H_5OH$	6.37	−1.94	(9b)
		$PhCH_2^{+}(\mathrm{exp.})+C_2H_5OH$	6.89	−1.42	(9b)
		$PhH_2^{+}(\mathrm{exp.})+(CH_3)_2CO$	6.60	−1.71	(9c)
		$C_7H_6OH^{+}+C_2H_6$	6.02	−2.29	(11)
		$PhCHOH^{+}+C_2H_6$	6.44	−1.87	(11)
$C_3H_5^{+}+PhCH_2OH$	8.76	$o\text{-}(PhCH_2OH+H)^{+}+C_3H_4$	9.05	0.29	(8b)
		$m\text{-}(PhCH_2OH+H)^{+}+C_3H_4$	9.11	0.35	(8b)
		$p\text{-}(PhCH_2OH+H)^{+}+C_3H_4$	8.98	0.22	(8b)
		$i\text{-}(PhCH_2OH+H)^{+}+C_3H_4$	9.36	0.60	(8b)
		$O\text{-}(PhCH_2OH+H)^{+}+C_3H_4$	9.31	0.55	(8a)
		$(PhCH_2OH+H)^{+}(\mathrm{exp.})+C_3H_4$	8.61	−0.15	
		$PhH_2^{+}(\mathrm{exp.})+CH_2O+C_3H_4$	9.35	0.59	(8a)
		$C_7H_7^{+}(\mathrm{exp.})+H_2O+C_3H_4$	8.27	−0.49	(8a)
		$PhCH_2^{+}(\mathrm{exp.})+H_2O+C_3H_4$	8.79	0.03	(8b)
		$o\text{-}(PhCH_2OH+C_3H_5)^{+}$	7.74	−1.02	(10a—d)
		$m\text{-}(PhCH_2OH+C_3H_5)^{+}$	7.81	−0.95	(10a—d)
		$p\text{-}(PhCH_2OH+C_3H_5)^{+}$	7.67	−1.09	(10a—d)
		$i\text{-}(PhCH_2OH+C_3H_5)^{+}$	8.05	−0.71	(10a—d)
		$O\text{-}(PhCH_2OH+C_3H_5)^{+}$	8.45	−0.31	(10a—d)
		$o\text{-}CH_2C_6H_4C_3H_5^{+}+H_2O$	7.78	−0.98	(10a)
		$m\text{-}CH_2C_6H_4C_3H_5^{+}+H_2O$	7.81	−0.95	(10a)
		$p\text{-}CH_2C_6H_4C_3H_5^{+}+H_2O$	7.81	−0.95	(10a)
		$PhCHC_3H_5^{+}+H_2O$	7.48	−1.28	(10a)
		$PhCH_2C_3H_4^{+}+H_2O$	7.81	−0.95	(10a)
		$C_7H_6C_3H_5^{+}+H_2O$	7.45	−1.31	(10a)
		$C_3H_5PhH^{+}+CH_2O$	8.41	−0.35	(10b)
		$C_7H_7^{+}(\mathrm{exp.})+CH_2CHCH_2OH$	7.52	−1.24	(10c)
		$PhCH_2^{+}(\mathrm{exp.})+CH_2CHCH_2OH$	8.04	−0.72	(10c)
		$C_7H_7^{+}(\mathrm{exp.})+CH_3CHCHOH(Z)$	7.00	−1.76	(10c)
		$PhCH_2^{+}(\mathrm{exp.})+CH_3CHCHOH(Z)$	7.52	−1.24	(10c)
		$C_7H_7^{+}(\mathrm{exp.})+CH_3CHCHOH(E)$	7.05	−1.71	(10c)
		$PhCH_2^{+}(\mathrm{exp.})+CH_3CHCHOH(E)$	7.57	−1.19	(10c)

Table 2. (continued)

Reactants	$\sum \Delta H^\circ$ (Reactants)	Products[a]	$\sum \Delta H^\circ$ (Products)	ΔH° (Reactions)[b]	Processes[c]
		PhH_2^+(exp.)$+CH_3COCHCH_2$	7.66	−1.10	(10d)
		$PhCHOH^+ + C_3H_6$	7.51	−1.25	(11)
		$C_7H_6OH^+ + C_3H_6$	7.09	−1.67	(11)
$CH_5^+ + PhCH_2CH_2OH$	8.17	o-$(PhCH_2CH_2OH+H)^+ + CH_4$	6.04	−2.13	(13)
		m-$(PhCH_2CH_2OH+H)^+ + CH_4$	6.20	−1.97	(13)
		p-$(PhCH_2CH_2OH+H)^+ + CH_4$	5.98	−2.19	(13)
		i-$(PhCH_2CH_2OH+H)^+ + CH_4$	6.43	−1.74	(13)
		O-$(PhCH_2CH_2OH+H)^+ + CH_4$	6.74	−1.43	(13)
		$C_7H_6CH_3^+ + H_2O + CH_4$	5.81	−2.36	(13)
		$PhCH_2CH_2^+ + H_2O + CH_4$	7.31	−0.86	(13)
$C_2H_5^+ + PhCH_2CH_2OH$	8.15	o-$(PhCH_2CH_2OH+H)^+ + C_2H_4$	7.36	−0.79	(13)
		m-$(PhCH_2CH_2OH+H)^+ + C_2H_4$	7.51	−0.64	(13)
		p-$(PhCH_2CH_2OH+H)^+ + C_2H_4$	7.29	−0.86	(13)
		i-$(PhCH_2CH_2OH+H)^+ + C_2H_4$	7.74	−0.41	(13)
		O-$(PhCH_2CH_2OH+H)^+ + C_2H_4$	8.05	−0.10	(13)
		$C_7H_6CH_3^+ + H_2O + C_2H_4$	7.12	−1.03	(13)
		$PhCH_2CH_2^+ + H_2O + C_2H_4$	8.62	0.47	(13)
		o-$(PhCH_2CH_2OH+C_2H_5)^+$	6.40	−1.75	(14a—c)
		m-$(PhCH_2CH_2OH+C_2H_5)^+$	6.57	−1.58	(14a—c)
		p-$(PhCH_2CH_2OH+C_2H_5)^+$	6.34	−1.81	(14a—c)
		i-$(PhCH_2CH_2OH+C_2H_5)^+$	6.90	−1.25	(14a—c)
		O-$(PhCH_2CH_2OH+C_2H_5)^+$	7.13	−1.02	(14a—c)
		o-$C_2H_5PhCH_2CH_2^+ + H_2O$	7.43	−0.72	(14a)
		m-$C_2H_5PhCH_2CH_2^+ + H_2O$	7.48	−0.67	(14a)
		p-$C_2H_5PhCH_2CH_2^+ + H_2O$	7.45	−0.70	(14a)
		1,2-$C_2H_5C_7H_5CH_2^+ + H_2O$	5.99	−2.16	(14a)
		1,3-$C_2H_5C_7H_5CH_2^+ + H_2O$	5.88	−2.27	(14a)
		1,4-$C_2H_5C_7H_5CH_2^+ + H_2O$	5.87	−2.28	(14a)
		o-$(PhCH_3+C_2H_5)^+ + CH_2O$	6.74	−1.41	(14b)
		m-$(PhCH_3+C_2H_5)^+ + CH_2O$	6.88	−1.27	(14b)
		p-$(PhCH_3+C_2H_5)^+ + CH_2O$	6.68	−1.47	(14b)
		i-$(PhCH_3+C_2H_5)^+ + CH_2O$	7.23	−0.92	(14b)
		$C_7H_6CH_3^+ + C_2H_5OH$	6.65	−1.50	(14c)
		$PhCH_2CH_2^+ + C_2H_5OH$	8.16	0.01	(14c)
		$PhCHCH_2OH^+ + C_2H_6$	6.81	−1.34	(16)
		$PhCH_2CHOH^+ + C_2H_6$	6.71	−1.44	(16)
$C_3H_5^+ + PhCH_2CH_2OH$	8.60	o-$(PhCH_2CH_2OH+H)^+ + C_3H_4$	8.79	0.19	(13)
		m-$(PhCH_2CH_2OH+H)^+ + C_3H_4$	8.95	0.35	(13)
		p-$(PhCH_2CH_2OH+H)^+ + C_3H_4$	8.72	0.12	(13)
		i-$(PhCH_2CH_2OH+H)^+ + C_3H_4$	9.18	0.58	(13)
		O-$(PhCH_2CH_2OH+H)^+ + C_3H_4$	9.49	0.89	(13)
		$C_7H_6CH_3^+ + H_2O + C_3H_4$	8.56	−0.04	(13)
		$PhCH_2CH_2^+ + H_2O + C_3H_4$	10.06	1.46	(13)
		o-$(PhCH_2CH_2OH+C_3H_5)^+$	7.45	−1.15	(15a,b)
		m-$(PhCH_2CH_2OH+C_3H_5)^+$	7.64	−0.96	(15a,b)
		p-$(PhCH_2CH_2OH+C_3H_5)^+$	7.42	−1.18	(15a,b)
		i-$(PhCH_2CH_2OH+C_3H_5)^+$	7.96	−0.64	(15a,b)
		O-$(PhCH_2CH_2OH+C_3H_5)^+$	8.02	−0.58	(15a,b)
		o-$C_3H_5PhCH_2CH_2^+ + H_2O$	8.53	−0.07	(15a)
		m-$C_3H_5PhCH_2CH_2^+ + H_2O$	7.26	−1.34	(15a)
		p-$C_3H_5PhCH_2CH_2^+ + H_2O$	8.54	−0.06	(15a)
		$PhCH_2CHC_3H_5^+ + H_2O$	7.95	−0.65	(15a)
		1,2-$C_3H_5C_7H_5CH_2^+ + H_2O$	7.06	−1.54	(15a)
		1,3-$C_3H_5C_7H_5CH_2^+ + H_2O$	6.97	−1.63	(15a)
		1,4-$C_3H_5C_7H_5CH_2^+ + H_2O$	7.00	−1.60	(15a)
		$C_7H_6CH_3^+$(exp.)$+CH_2CHCH_2OH$	7.80	−0.80	(15b)
		$PhCH_2CH_2^+$(exp.)$+CH_2CHCH_2OH$	9.31	0.71	(15b)
		$C_7H_6CH_3^+$(exp.)$+CH_3CHCHOH(Z)$	7.28	−1.32	(15b)
		$PhCH_2CH_2^+$(exp.)$+CH_3CHCHOH(Z)$	8.78	0.18	(15b)

Table 2. (continued)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products[a)]	$\sum\Delta H^\circ$ (Products)	ΔH° (Reactions)[b)]	Processes[c)]
		$C_7H_6CH_3^+$(exp.)+$CH_3CHCHOH$(*E*)	7.33	−1.27	(15b)
		$PhCH_2CH_2^+$(exp.)+$CH_3CHCHOH$(*E*)	8.84	0.24	(15b)
		$PhCHCH_2OH^+ + C_3H_6$	7.88	−0.72	(16)
		$PhCH_2CHOH^+ + C_3H_6$	7.78	−0.82	(16)
$CH_5^+ + PhCH(OH)CH_3$	8.18	*o*-$\{PhCH(OH)CH_3+H\}^+ + CH_4$	6.01	−2.17	(17a—c)
		m-$\{PhCH(OH)CH_3+H\}^+ + CH_4$	6.09	−2.09	(17a—c)
		p-$\{PhCH(OH)CH_3+H\}^+ + CH_4$	6.03	−2.15	(17a—c)
		i-$\{PhCH(OH)CH_3+H\}^+ + CH_4$	6.25	−1.93	(17a—c)
		O-$\{PhCH(OH)CH_3+H\}^+ + CH_4$	5.80	−2.38	(17a—c)
		$C_7H_6CH_3^+ + H_2O + CH_4$	5.81	−2.37	(17a)
		$PhCHCH_3^+ + H_2O + CH_4$	5.92	−2.26	(17a)
$C_2H_5^+ + PhCH(OH)CH_3$	8.17	*o*-$\{PhCH(OH)CH_3+H\}^+ + C_2H_4$	7.32	−0.85	(17a—c)
		m-$\{PhCH(OH)CH_3+H\}^+ + C_2H_4$	7.41	−0.76	(17a—c)
		p-$\{PhCH(OH)CH_3+H\}^+ + C_2H_4$	7.35	−0.82	(17a—c)
		i-$\{PhCH(OH)CH_3+H\}^+ + C_2H_4$	7.57	−0.60	(17a—c)
		O-$\{PhCH(OH)CH_3+H\}^+ + C_2H_4$	7.11	−1.06	(17a—c)
		$C_7H_6CH_3^+ + H_2O + C_2H_4$	7.12	−1.05	(17a)
		$PhCHCH_3^+ + H_2O + C_2H_4$	7.24	−0.93	(17a)
		$C_7H_7^+ + CH_3OH + C_2H_4$	7.25	−0.92	(17b)
		$PhCH_2^+ + CH_3OH + C_2H_4$	7.78	−0.39	(17b)
		$PhH_2^+ + CH_3CHO + C_2H_4$	7.67	−0.50	(17c)
		o-$\{PhCH(OH)CH_3+C_2H_5\}^+$	6.40	−1.77	(18a—e)
		m-$\{PhCH(OH)CH_3+C_2H_5\}^+$	6.46	−1.71	(18a—e)
		p-$\{PhCH(OH)CH_3+C_2H_5\}^+$	6.34	−1.83	(18a—e)
		i-$\{PhCH(OHCH_3+C_2H_5\}^+$	6.81	−1.36	(18a—e)
		O-$\{PhCH(OH)CH_3+C_2H_5\}^+$	6.27	−1.90	(18a—e)
		o-$C_2H_5PhCHCH_3^+ + H_2O$	7.02	−1.15	(18a)
		m-$C_2H_5PhCHCH_3^+ + H_2O$	7.15	−1.02	(18a)
		p-$C_2H_5PhCHCH_3^+ + H_2O$	7.01	−1.16	(18a)
		1,2-$C_2H_5C_7H_5CH_2^+ + H_2O$	5.99	−2.18	(18a)
		1,3-$C_2H_5C_7H_5CH_2^+ + H_2O$	5.88	−2.29	(18a)
		1,4-$C_2H_5C_7H_5CH_2^+ + H_2O$	5.87	−2.30	(18a)
		o-$(PhCH_3+C_2H_5)^+ + CH_2O$	6.74	−1.88	(18b)
		m-$(PhCH_3+C_2H_5)^+ + CH_2O$	6.88	−1.74	(18b)
		p-$(PhCH_3+C_2H_5)^+ + CH_2O$	6.68	−1.94	(18b)
		i-$(PhCH_3+C_2H_5)^+ + CH_2O$	7.23	−1.39	(18b)
		$C_2H_5PhH^+ + CH_3CHO$	7.05	−1.53	(18c)
		$C_7H_6CH_3^+ + C_2H_5OH$	6.65	−1.52	(18d)
		$PhCHCH_3^+ + C_2H_5OH$	6.77	−1.40	(18d)
		$PhH_2^+ + C_4H_8O$	6.37	−2.25	(18e)
		$PhC(OH)CH_3^+ + C_2H_6$	6.81	−1.36	(20)
		$PhCH(OH)CH_2^+ + C_2H_6$	6.71	−1.46	(20)
$C_3H_5^+ + PhCH(OH)CH_3$	8.62	*o*-$\{PhCH(OH)CH_3+H\}^+ + C_3H_4$	8.76	0.14	(17a—c)
		m-$\{PhCH(OH)CH_3+H\}^+ + C_3H_4$	8.84	0.22	(17a—c)
		p-$\{PhCH(OH)CH_3+H\}^+ + C_3H_4$	8.78	0.16	(17a—c)
		i-$\{PhCH(OH)CH_3+H\}^+ + C_3H_4$	9.00	0.38	(17a—c)
		O-$\{PhCH(OH)CH_3+H\}^+ + C_3H_4$	8.55	−0.07	(17a—c)
		$C_7H_6CH_3^+ + H_2O + C_3H_4$	8.56	−0.06	(17a)
		$PhCHCH_3^+ + H_2O + C_3H_4$	8.67	0.05	(17a)
		$C_7H_7^+ + CH_3OH + C_3H_4$	8.69	0.07	(17b)
		$PhCH_2^+ + CH_3OH + C_3H_4$	9.21	0.59	(17b)
		PhH_2^+(exp.)+$CH_3CHO + C_3H_4$	9.11	0.49	(17c)
		o-$\{PhCH(OH)CH_3+C_3H_5\}^+$	7.48	−1.14	(19a—e)
		m-$\{PhCH(OH)CH_3+C_3H_5\}^+$	7.54	−1.08	(19a—e)
		p-$\{PhCH(OH)CH_3+C_3H_5\}^+$	7.42	−1.20	(19a—e)
		i-$\{PhCH(OH)CH_3+C_3H_5\}^+$	7.88	−0.74	(19a—e)
		O-$\{PhCH(OH)CH_3+C_3H_5\}^+$	7.74	−0.88	(19a—e)
		$C_7H_6C_2H_5^+ + CH_3CHO$	6.96	−1.66	(19a)
		$C_3H_5PhH^+ + CH_3CHO$	7.97	−0.65	(19a)

Table 2. (continued)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products[a)]	$\sum\Delta H^\circ$ (Products)	ΔH° (Reactions)[b)]	Processes[c)]
		$C_2H_5PhH^+ + CH_3CHCO$	7.72	−0.90	(19b)
		$C_7H_6CH_3^+ + CH_2CHCH_2OH$	7.80	−0.82	(19c)
		$PhCHCH_3^+ + CH_2CHCH_2OH$	7.92	−0.70	(19c)
		$C_7H_6CH_3^+ + CH_3CHCHOH(Z)$	7.28	−1.34	(19c)
		$PhCHCH_3^+ + CH_3CHCHOH(Z)$	7.40	−1.22	(19c)
		$C_7H_6CH_3^+ + CH_3CHCHOH(E)$	7.33	−1.29	(19c)
		$PhCHCH_3^+ + CH_3CHCHOH(E)$	7.45	−1.17	(19c)
		$C_7H_7^+ + C_4H_8O$	6.33	−2.29	(19d)
		$PhCH_2^+ + C_4H_8O$	6.85	−1.77	(19d)
		PhH_2^+(exp.)$+CH_3CHCHCOCH_3$	7.43	−1.19	(19e)

a) The symbols *o*-, *m*-, *p*-, *i*-, and *O*- represent *ortho*-, *meta*-, *para*-, *ipso*-, and *O*-adduct ions, respectively. Thermochemical data calculated using reliable experimental values for ions in Ref. 14 are shown by exp. b) ΔH° (Reaction) = $\sum\Delta H^\circ$ (Product) − $\sum\Delta H^\circ$ (Reactant). c) Processes in Schemes 1, 2, 3, and 4.

the $RH^+/PhCH_2OH$ reactions. The heats of protonation reactions obtained using a reported proton affinity of $PhCH_2OH$[12] are also shown in Table 2 for comparison. Figures 5(a), 5(b), and 5(c) show the dependence of branching ratios of each product ion on the reaction time. In the $CH_5^+/PhCH_2OH$ reaction, $(M+H-H_2)^+$ ($m/z = 107$), $(M+H-H_2O)^+$ ($m/z = 91$), and $(M+H-CH_2O)^+$ ($m/z = 79$) are observed at the longest reaction time of 50 ms. With decreasing the reaction time, the branching ratio of $(M+H-H_2)^+$ decreases and becomes nearly zero at zero reaction time. On the other hand, the branching ratio of $(M+H-H_2O)^+$ slightly decreases from 60 to 58%, while that of $(M+H-CH_2O)^+$ increases from 31 to 42% with decreasing the reaction time from 50 to 0 ms. In the $C_2H_5^+/PhCH_2OH$ reaction, the following four product ions are observed: $(M+C_2H_5-H_2O)^+$ ($m/z = 119$), $(M-H$ and/or $M+C_2H_5-CH_2O)^+$ ($m/z = 107$), $(M+H-H_2O$ and/or $M+C_2H_5-C_2H_5OH)^+$ ($m/z = 91$), and $(M+H-CH_2O$ and/or $M+C_2H_5-(CH_3)_2CO)^+$ ($m/z = 79$). The branching ratios of $m/z = 119$ and 107 decreases from 5 to 0% and 28 to 20%, while those of $m/z = 91$ and 79 increase from 58 to 63% and 8 to 17%, respectively, with decreasing the reaction time from 100 to 0 ms.

In the $C_3H_5^+/PhCH_2OH$ reaction, the following five product ions are observed: $(M+C_3H_5-H_2O)^+$ ($m/z = 131$), $(M+C_3H_5-CH_2O)^+$ ($m/z = 119$), $(M-H)^+$ ($m/z = 107$), $(M+H-H_2O$ and/or $M+C_3H_5-C_3H_6O)^+$ ($m/z = 91$), and $(M+H-CH_2O$ and/or $M+C_3H_5-CH_2CHCOCH_3)^+$ ($m/z = 79$). The branching ratios of $(M+C_3H_5-H_2O)^+$ and $(M+C_3H_5-CH_2O)^+$ decrease with decreasing the reaction time and become nearly zero at zero reaction time, indicating that collisional stabilization is necessary for the formation of these ions. The branching ratios of $m/z = 107$ and 91 are essentially independent of the reaction time, while that of $m/z = 79$ greatly increases from 1 to 27% with decreasing the reaction time.

The most outstanding feature of the $RH^+/PhCH_2OH$ reactions is the lack of a non-dissociative PT channel leading to $(M+H)^+$, which was a dominant product channel for PhOH. The major product ion in the $RH^+/PhCH_2OH$ reactions is $C_7H_7^+$. Although benzyl ion and tropylium ion are possible as the $C_7H_7^+$ ion, the latter ion is more stable than the former one by 0.52 eV (Table 2). Therefore, it will be a more favorite $C_7H_7^+$ ion. This ion must be formed through dissociative PT by loss of H_2O in the $CH_5^+/PhCH_2OH$ reaction [process (8a)]. On the other hand, not only similar dissociative PT by loss of H_2O, but also dissociative alkylation by loss of C_2H_5OH or C_3H_6O [C_3H_5OH and/or $(CH_3)_2CO$] is possible for the formation of $C_7H_7^+$ in the $C_2H_5^+/PhCH_2OH$ and $C_3H_5^+/PhCH_2OH$ reactions [processes (9b) and (10c)]. If the $C_7H_7^+$ ion is produced through processes (8a), (9b), and (10c), its precursor ions will be O-protonated and O-alkylated ions. The formation of the O-protonated and O-alkylated ions is energetically allowed in the $C_2H_5^+/PhCH_2OH$ reaction (Table 2). Although the formation of the O-alkylated ions is energetically allowed in the $C_3H_5^+/PhCH_2OH$ reaction, that of O-protonated ion is endoergic by 0.55 eV in the $C_3H_5^+/PhCH_2OH$ reaction. This energy can be supplied from the kinetic energies of the reactant ion. Both dissociative PT (8a) and dissociative alkylation (9b) and (10c) are possible for the formation of $C_7H_7^+$ in the $C_2H_5^+/PhCH_2OH$ and $C_3H_5^+/PhCH_2OH$ reactions. If $C_7H_7^+$ is formed through the former process, collisional stabilization will be insignificant. On the other hand, if it is formed through the latter processes, collisional stabilization will take part in its production at long reaction times. Since little evidence of collisional stabilization was found for the formation of $C_7H_7^+$ in the $C_2H_5^+/PhCH_2OH$ and $C_3H_5^+/PhCH_2OH$ reactions, dissociative PT (8a) is expected to be more important than dissociative alkylation (9b) and (10c).

As a minor product ion, PhH_2^+ was found in all the three reactions. This ion must be formed through dissociative PT by the CH_2O elimination in the $CH_5^+/PhCH_2OH$ reaction [process (8b)]. On the other hand, not only similar dissociative PT by loss of CH_2O, but also dissociative alkylation by loss of $(CH_3)_2CO$ or $CH_2CHCOCH_3$ is possible for the formation of PhH_2^+ in the $C_2H_5^+/PhCH_2OH$ and $C_3H_5^+/PhCH_2OH$ reactions [processes (9c) and (10d)]. The collisional stabilization will participate in the formation of PhH_2^+, if the latter processes are significant. No evidence of collisional stabilization was found for the formation of PhH_2^+. It is therefore likely that PhH_2^+ is dominantly formed through dissociative PT (8b) in the $C_2H_5^+/PhCH_2OH$

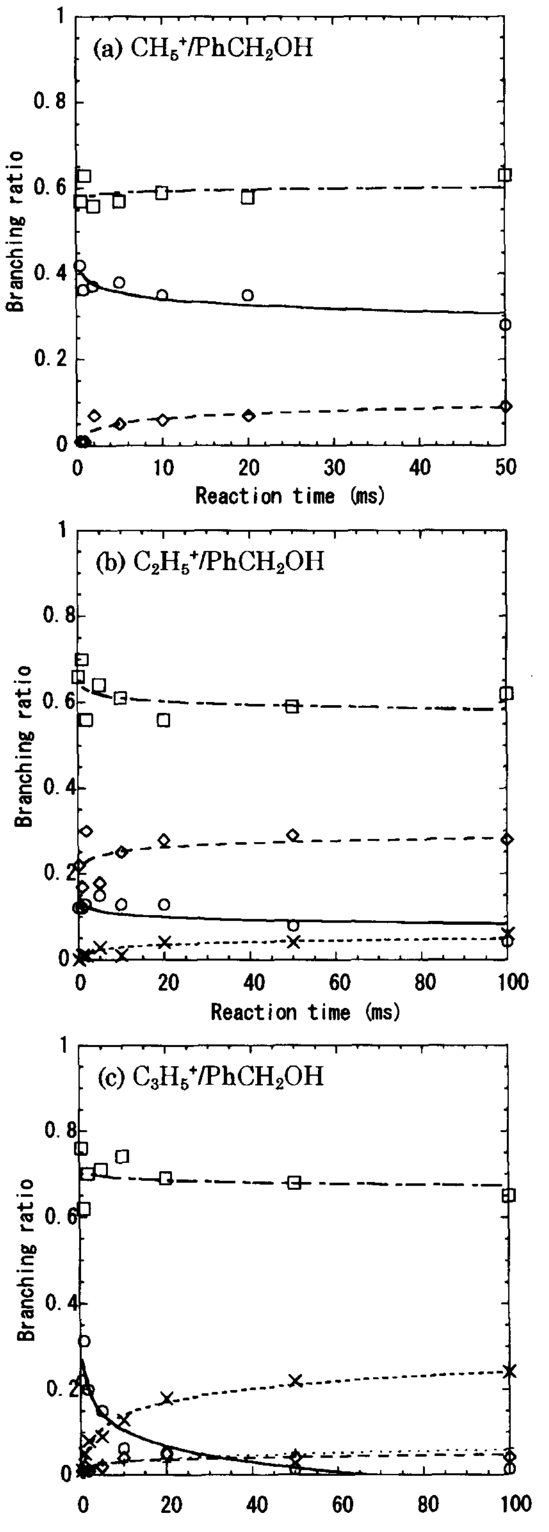


Fig. 5. Dependence of branching ratios of product ions on the reaction time in the (a) CH_5^+/$PhCH_2OH$, (b) $C_2H_5^+$/$PhCH_2OH$, and (c) $C_3H_5^+$/$PhCH_2OH$ reactions. +: $m/z = 131$, ×: $m/z = 119$, ◇: $m/z = 107$, □: $m/z = 91$, and ○: $m/z = 79$.

and $C_3H_5^+$/$PhCH_2OH$ reactions. The endoergic energy for the formation of PhH_2^+ in the $C_3H_5^+$/$PhCH_2OH$ reaction ($\Delta H = 0.59$ eV) must be supplied from the kinetic energies of the reactant ion.

The $(M-1)^+$ ion was found in all the three reactions. This ion has also been observed in a previous CI experiment of Ichikawa and Harrison[4] at a higher CI CH_4 gas pressure of 1 Torr. They concluded that the $(M-1)^+$ ion is not $(M-H)^+$ formed through H^- abstraction (11), but it is $(M+C_2H_5-CH_2O)^+$ formed through dissociative alkylation (9a) on the basis of the CI mass spectrum using CD_4. It is therefore expected that the major $(M-1)^+$ ion, observed here in the $C_2H_5^+$/$PhCH_2OH$ reaction, is the $(M+C_2H_5-CH_2O)^+$ ion formed by dissociative alkylation (9a). Possible $(M-1)^+$ ions found in the CH_5^+/$PhCH_2OH$ and $C_3H_5^+$/$PhCH_2OH$ reactions are $PhCHOH^+$, $C_6H_4CH_2OH^+$, and $C_7H_6OH^+$. Among them, the most stable $C_7H_6OH^+$ ion will be a major $(M-1)^+$ ion. Since $C_7H_6OH^+$ is formed exclusively by collisional stabilization in the CH_5^+/$PhCH_2OH$ reaction, it will be produced through the following dissociative PT:

$$CH_5^+ + PhCH_2OH \xrightarrow{-CH_4} (PhCH_2OH + H)^+ \xrightarrow{+CH_4} C_7H_6OH^+ + H_2. \tag{12}$$

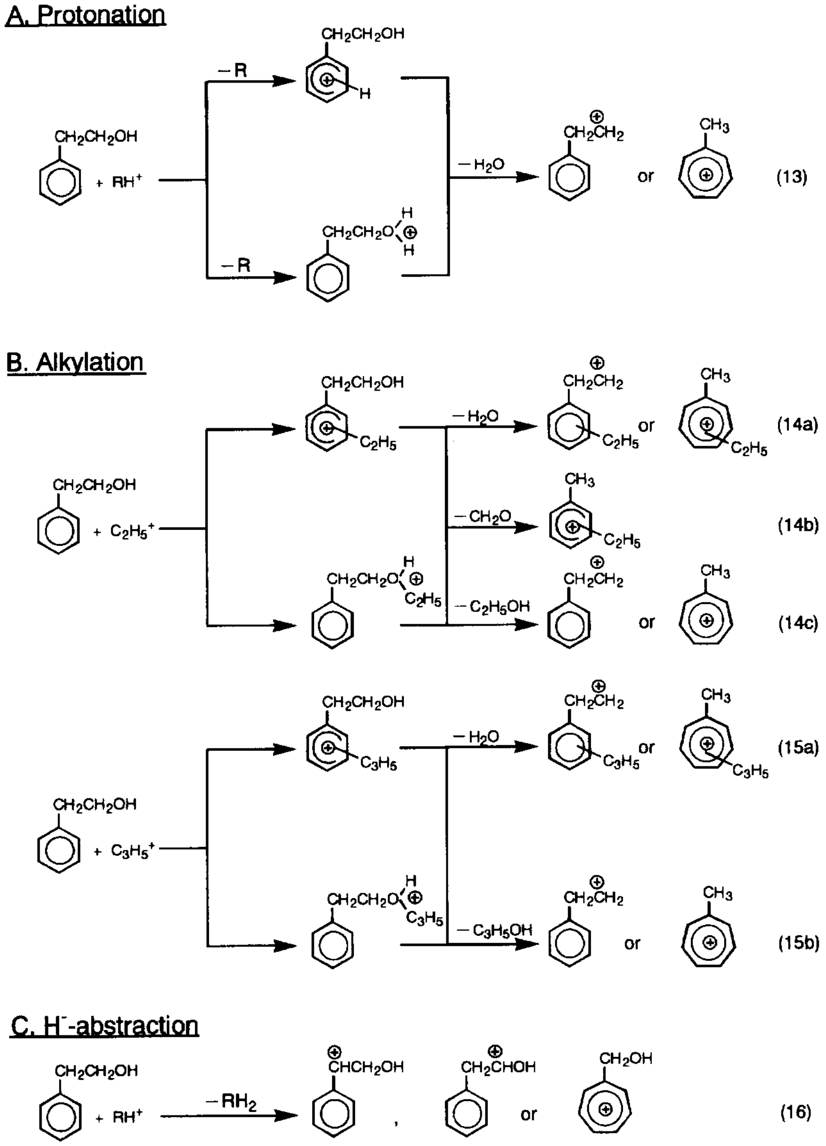
Two dissociative PT processes leading to $C_7H_7^+$ and PhH_2^+ compete with the above process. The branching ratios of $C_7H_7^+$ and PhH_2^+ slightly increase and decrease, respectively, with increasing the reaction time. On the basis of the above findings, initially formed excited $(PhCH_2OH+H)^+$ ion dissociates into $C_7H_7^+ + H_2O$ and $PhH_2^+ + CH_2O$, while collisionally deexcited $(PhCH_2OH+H)^+$ ion provides all of the $C_7H_6OH^+$ ion and a small part of the $C_7H_7^+$ ion. It is reasonable to assume that collisional stabilization is unimportant for the H^- abstraction process. Since no evidence of collisional stabilization was found for the formation of $(M-1)^+$ from the $C_3H_5^+$/$PhCH_2OH$ reaction, it will be produced through H^- abstraction (11).

In the $C_3H_5^+$/$PhCH_2OH$ reaction, $(M+C_3H_5-H_2O)^+$ and $(M+C_3H_5-CH_2O)^+$ are found. The formation processes of these ions are alkylation (10a) and (10b) in Scheme 2. The reaction-time dependence of their branching ratios indicated that collisional stabilization is necessary for the formation of these ions.

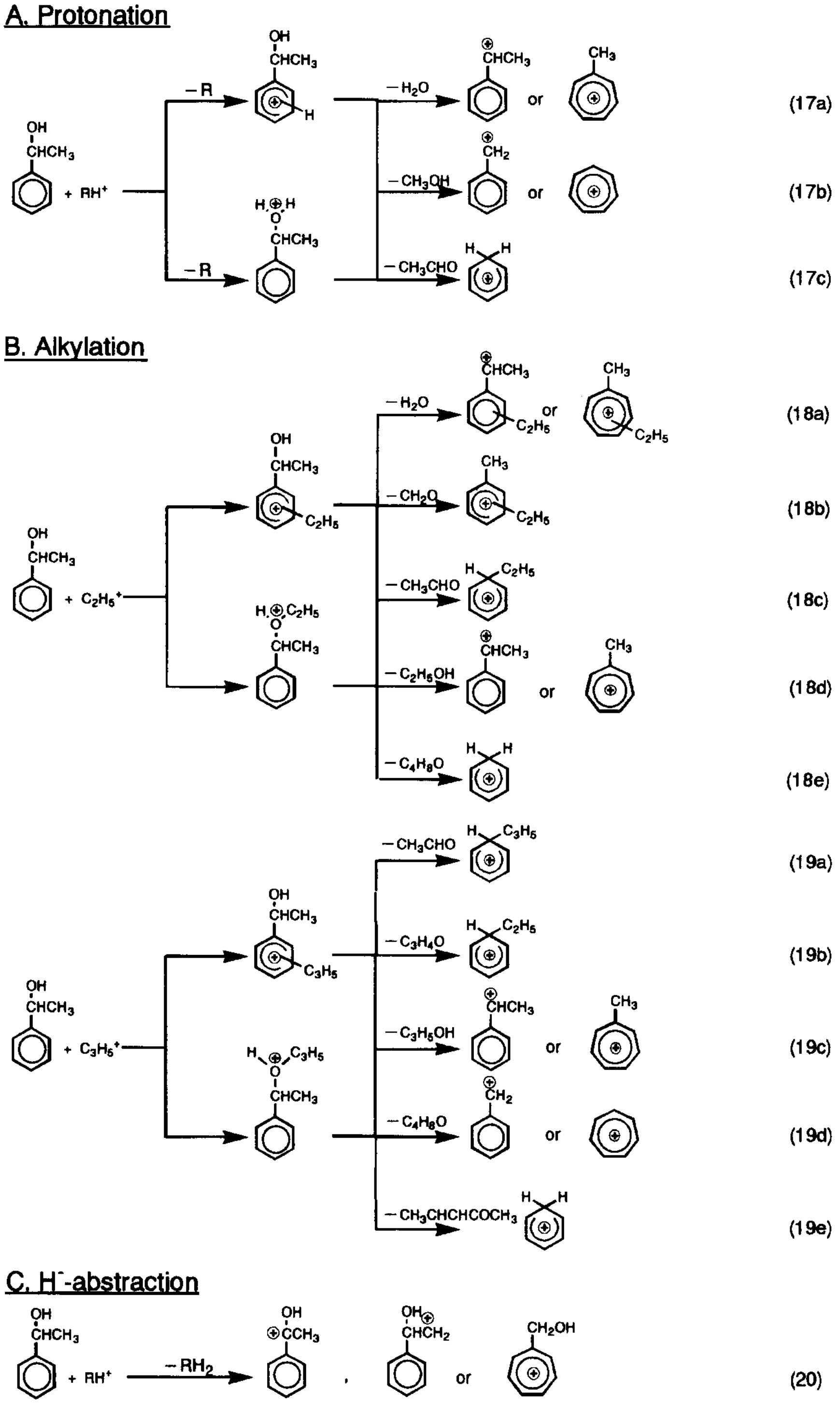
In the final part of this section, the sites of protonation and alkylation in the RH^+/$PhCH_2OH$ reactions are discussed on the basis of energetics given in Table 2. The energies for the protonation obtained using an experimentally determined proton affinity of $PhCH_2OH$[12] are 0.36—0.50 eV lower than the present PM3 data for the formation of *ortho*-, *meta*-, and *para*-ring-protonated ions. Therefore, the reported proton affinity of $PhCH_2OH$ probably corresponds to that for the ring protonation. Both protonation and alkylation can occur on the benzene ring and the substituent, as shown in Scheme 2. Since electron-donating properties of the OH group are suppressed by the insertion of a CH_2 group between phenyl and hydroxy groups, the energy differences between ring-protonated ions and the O-protonated ion and between ring-alkylated ions and O-alkylated ion will be smaller than those in the cases of PhOH. Actually, the energy differences between the *para*-ring-protonated ion and the O-protonated ion and between *para*-ring-alkylated ions and O-alkylated ions decreases from 1.1—1.2 eV for PhOH to 0.3—0.8 eV for $PhCH_2OH$. Therefore, protonation and alkylation will occur not only on the benzene ring but also on the substituent. According to an isotopic study of protonation and the subsequent elimination processes by Ichikawa and Harrison,[4] the H_2O elimination selectively takes place via O-protonated ions, while the CH_2O elimination occurs preferentially via ring-protonated ions. The branching ratios of $(M+H-H_2O)^+$ and $(M+H-CH_2O)^+$ are 58 : 42 and 79 : 21 for the $CH_5^+/PhCH_2OH$ and $C_2H_5^+/PhCH_2OH$ reactions, respectively. The higher branching ratios of the former ions indicate that the proton attacks dominantly on the O-atom, even though the calculated energies of O-protonated ions are slightly higher than the ring-protonated ions.

Only the $(M+C_2H_5-CH_2O)^+$ ion was found through dissociative alkylation in the $C_2H_5^+/PhCH_2OH$ reaction. This indicates that $C_2H_5^+$ selectively attacks on the ring, as predicted from the energetics. On the basis of the above facts, we conclude that the major sites of protonation and alkylation are different in the $C_2H_5^+/PhCH_2OH$ reaction. The $(M+C_3H_5-H_2O)^+$ and $(M+C_3H_5-CH_2O)^+$ ions are observed through collisionally-stabilized dissociative alkylation in the $C_3H_5^+/PhCH_2OH$ reaction. The former ion is formed via decomposition of O-alkylated ions, while the latter one is produced via decomposition of the ring-alkylated ion. A higher branching ratio of $(M+C_3H_5-CH_2O)^+$ than that of $(M+C_3H_5-H_2O)^+$ at every reaction times above 0.5 ms implies that the formation of the ring-alkylated ion is more favorable in the $C_3H_5^+/PhCH_2OH$ reaction.

2-Phenylethyl and 1-Phenylethyl Alcohols. A possible reaction scheme for $PhCH_2CH_2OH$ and $PhCH(OH)CH_3$ is shown in Schemes 3 and 4, respectively.



Scheme 3. Possible reaction pathways for the $RH^+/PhCH_2CH_2OH$ reactions.



Scheme 4. Possible reaction pathways for the $RH^+/PhCH(OH)CH_3$ reactions.

In Table 2 are shown heats of reactions for some representative product channels in the $RH^+/PhCH_2CH_2OH$ and $RH^+/PhCH(OH)CH_3$ reactions. Only the $(M+H-H_2O)^+$ ion was found in the $CH_5^+/PhCH_2CH_2OH$ and $CH_5^+/PhCH(OH)CH_3$ reactions within reaction times of 0.5—50 ms. Figures 6(a) and 6(b) show the reaction-time dependence of branching ratios of each product ion in the $C_2H_5^+/PhCH_2CH_2OH$ and $C_3H_5^+/PhCH_2CH_2OH$ reactions. In the $C_2H_5^+/PhCH_2CH_2OH$ reaction, the following three product ions are observed: $(M+C_2H_5-H_2O)^+$ ($m/z=133$), $(M-H$ and/or $M+C_2H_5-CH_2O)^+$ ($m/z=121$), and $(M+H-H_2O$ and/or $M+C_2H_5-C_2H_5OH)^+$ ($m/z=105$). With decreasing the reaction time, the branching ratio of $m/z=121$ decreases and becomes zero at a reaction time of 0.5 ms. Therefore, the $(M+C_2H_5-CH_2O)^+$ ion will be a major $m/z=121$ ion. Since the branching ratio of $m/z=105$ increases from 68 to 87%, $(M+H-H_2O)^+$ will be a major $m/z=105$ ion. The branching ratio of $(M+C_2H_5-H_2O)^+$

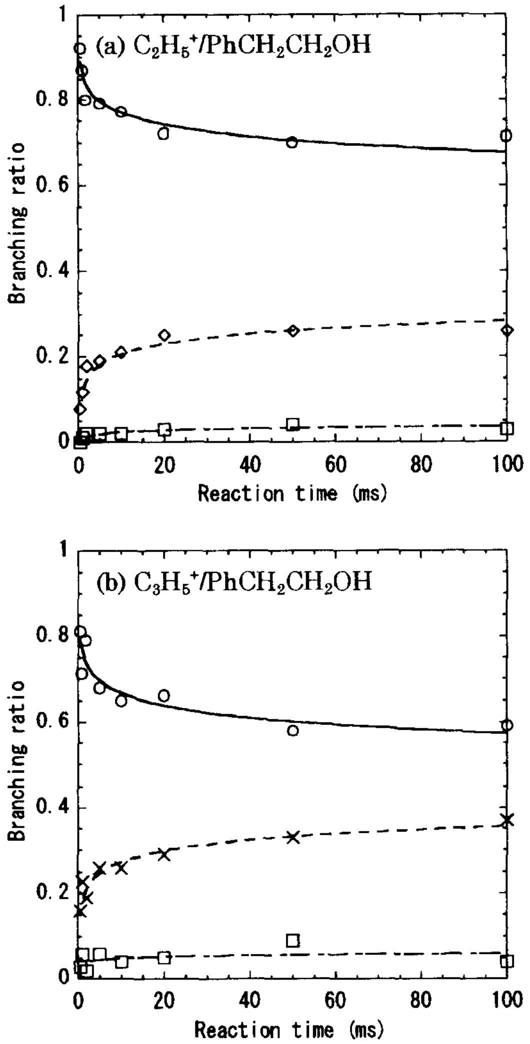


Fig. 6. Dependence of branching ratios of product ions on the reaction time in the (a) $C_2H_5^+$/PhCH$_2$CH$_2$OH and (b) $C_3H_5^+$/PhCH$_2$CH$_2$OH reactions. ×: $m/z = 145$, ◇: $m/z = 133$, □: $m/z = 121$, and ○: $m/z = 105$.

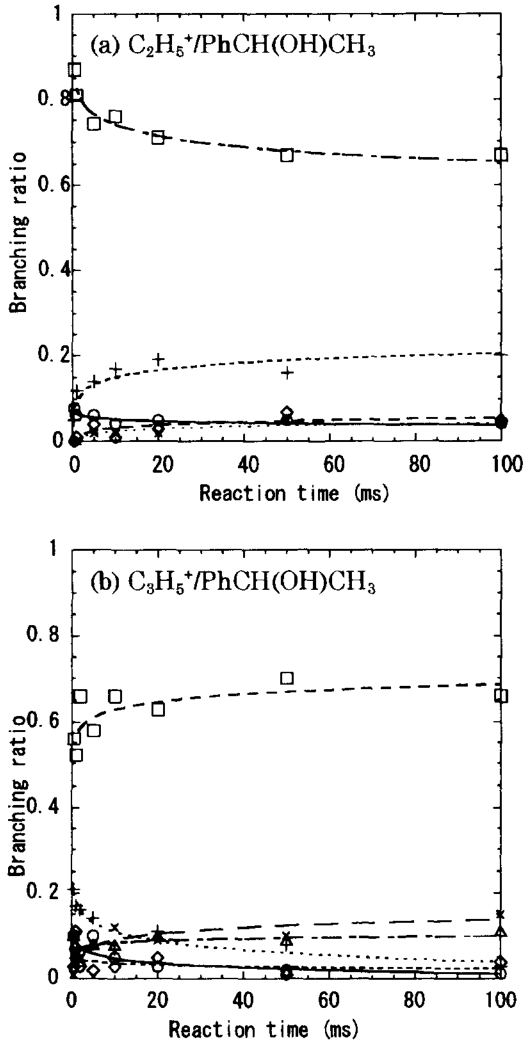


Fig. 7. Dependence of branching ratios of product ions on the reaction time in the (a) $C_2H_5^+$/PhCH(OH)CH$_3$ and (b) $C_3H_5^+$/PhCH(OH)CH$_3$ reactions. ×: $m/z = 133$ in (a) and 119 in (b), ◇: $m/z = 121$, +: $m/z = 107$, □: $m/z = 105$, and △: $m/z = 91$, ○: $m/z = 79$.

greatly decreases from 28 to 13% with decreasing the reaction time from 100 to 0 ms, indicating that collisional stabilization is significant for the formation of this ion.

In the $C_3H_5^+$/PhCH$_2$CH$_2$OH reaction, $(M+C_3H_5-H_2O)^+$ ($m/z = 145$), $(M-H)^+$ ($m/z = 121$), and $(M+H-H_2O)^+$ ($m/z = 105$) are observed. The branching ratio of $m/z = 121$ is essentially independent of the reaction time. The branching ratio of $(M+C_3H_5-H_2O)^+$ decreases from 35 to 19%, while that of $(M+H-H_2O)^+$ increases from 57 to 77% with decreasing the reaction time. These results suggest that collisional stabilization participates in the formation of $(M+C_3H_5-H_2O)^+$.

Figures 7(a) and 7(b) show the reaction-time dependence of the branching ratios of each product ion in the $C_2H_5^+$/PhCH(OH)CH$_3$ and $C_3H_5^+$/PhCH(OH)CH$_3$. In the $C_2H_5^+$/PhCH(OH)CH$_3$ reaction, the following five product ions are observed: $(M+C_2H_5-H_2O)^+$ ($m/z = 133$), (M−H and/or $M+C_2H_5-CH_2O)^+$ ($m/z = 121$), $(M+C_2H_5-CH_3CHO)^+$ ($m/z = 107$), (M+H−H$_2$O and/or $M+C_2H_5-C_2H_5OH)^+$ ($m/z = 105$), and (M+H−CH$_3$CHO and/or $M+C_2H_5-C_4H_8O)^+$ ($m/z = 79$). With decreasing the reaction time, the branching ratio of $m/z = 121$ decreases and becomes zero at zero reaction time. Since collisional stabilization is unimportant for H^- abstraction, $(M+C_2H_5-CH_2O)^+$ will be a major $m/z = 121$ ion. The branching ratio of $(M+C_2H_5-H_2O)^+$ also becomes zero at zero reaction time, indicating that collisional stabilization is necessary for the formation of this ion. The branching ratios of $m/z = 105$ and 79 ions increase, while that of $m/z = 107$ decreases with decreasing the reaction time. On the basis of these findings, we conclude that collisional stabilization participates in the formation of $(M+C_2H_5-CH_3CHO)^+$.

In the $C_3H_5^+$/PhCH(OH)CH$_3$ reaction, the following six product ions are observed: $(M-H)^+$ ($m/z = 121$), $(M+C_3H_5-CH_3CHO)^+$ ($m/z = 119$), $(M+C_3H_5-C_3H_4O)^+$ ($m/z = 107$), (M+H−H$_2$O and/or $M+C_3H_5-C_3H_6O)^+$ ($m/z = 105$), (M+H−CH$_3$OH and/or $M+C_3H_5-C_4H_8O)^+$

($m/z = 91$), and $(M+H-CH_3CHO$ and/or $M+C_3H_5-C_5H_8O)^+$ ($m/z = 79$). With decreasing the reaction time, the branching ratios of $m/z = 119$, 105, and 91 slightly decrease, while those of the other peaks either increase or are essentially independent of the reaction time. These results suggest that small parts of the $m/z = 119$, 105, and 91 ions are formed by collisional stabilization. Thus, major $m/z = 105$ and 91 ions will be $(M+H-H_2O)^+$ ($m/z = 105$) and $(M+H-CH_3OH)^+$ ($m/z = 91$), respectively.

Only PT followed by the H_2O elimination leading to $PhCH_2CH_2^+$ or $C_7H_6CH_3^+$ (tropylium type ion) is found in the reactions of CH_5^+ with these two isomers [processes (13) and (17a)]. Since $C_7H_6CH_3^+$ is more stable than $PhCH_2CH_2^+$ by 1.5 eV, the former ion will be a major $C_8H_9^+$ ion. The same ion was found as a major product ion in the reactions of $C_2H_5^+$ and $C_3H_5^+$ with the two isomers. Not only similar dissociative PT by loss of H_2O, but also dissociative alkylation by loss of C_2H_5OH or C_3H_6O [C_3H_5OH and/or $(CH_3)_2CO$] is possible for the formation of $C_7H_6CH_3^+$ [processes (14c), (15b), (18d), and (19c)]. On the basis of the energetics given in Table 2, protonation is energetically accessible in all the reactions except for the $C_3H_5^+/PhCH_2CH_2OH$ reaction, where it is endoergic by at least 0.1 eV. When we compared PM3 data with more reliable experimental data for the protonated ions of PhOH and $PhCH_2OH$, heats of formation of protonated ions obtained by PM3 calculations overestimate by about 0.5 eV (Table 2). Taking account of this overestimation and the kinetic energy of the reactant ion, PT followed by loss of H_2O cannot be excluded from the possible formation processes of $C_7H_6CH_3^+$ in the $C_3H_5^+/PhCH_2CH_2OH$ reaction. Since the contribution of collisional stabilization is either insignificant or small for the formation of $C_7H_6CH_3^+$ in the $C_2H_5^+$ and $C_3H_5^+$ reactions, it will be formed through PT followed by loss of H_2O [processes (13) and (17a)].

Finally, the sites of protonation and alkylation are discussed on the basis of energetics given in Table 2. Since the heats of reactions for ring protonation and ring alkylation are lower than those for O-protonation and O-alkylation by 0.6—0.8 eV for $PhCH_2CH_2OH$, the favorable reaction site will be a benzene ring. Actually, the $(M+C_2H_5-H_2O)^+$ and $(M+C_3H_5-H_2O)^+$ ions, produced via ring alkylation, are found as major alkylation products in the $C_2H_5^+/PhCH_2CH_2OH$ and $C_3H_5^+/PhCH_2CH_2OH$ reactions. It is known that the elimination of H_2O from OH-containing compounds in the dissociative PT reactions occurs exclusively from the O-protonated ion.[17] The branching ratios of the $(M+H-H_2O)^+$ ions in the three reactions are large (77—100%). It is therefore reasonable to assume that the protonation occurs preferentially on the substituent, or that thermochemically favored ring-protonated ions are initially formed and the subsequent proton transfer from ring to substitutent gives the O-protonated ion.

The heats of reactions for ring protonation and ring alkylation agree with O-protonation and O-alkylation within 0.3 eV for $PhCH(OH)CH_3$. It should be noted that O-protonated ions and O-$\{PhCH(OH)CH_3+C_2H_5\}^+$ ions become slightly more stable than the corresponding ring-adduct ions. Thus, protonation and alkylation will occur both on the ring and the substituent for $PhCH(OH)CH_3$. The large branching ratios of the $(M+H-H_2O)^+$ ions in the three reactions suggests that the O-protonated ion is preferentially formed either directly or by proton transfer from ring-protonated ions as in the cases of $PhCH_2CH_2OH$. The formation of $(M+C_2H_5-CH_3CHO)^+$, $(M+C_3H_5-CH_3CHO)^+$, and $(M+C_3H_5-C_3H_4O)^+$ suggests that alkylation occurs preferentially on the ring.

Conclusion

The gas-phase ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with four OH-containing monosubstituted benzenes [PhX: X = OH, CH_2OH, CH_2CH_2OH, and $CH(OH)CH_3$] have been studied using an ion-trap type of GC/MS at a low CH_4 pressure. Only PT channels were found in the CH_5^+ reactions. The lack of alkylation channels in the CH_5^+ reactions can be explained by the instability of the adduct $(M+CH_5)^+$ ions. In most of the $C_2H_5^+$ and $C_3H_5^+$ reactions, alkylation channels compete with PT. The branching ratios of the former channels in the $C_3H_5^+$ reactions are larger than those in the $C_2H_5^+$ reactions in most cases. We propose here two reasons for this different reactivity between $C_2H_5^+$ and $C_3H_5^+$. One reason is a lower acidity (proton-donating ability) of $C_3H_5^+$ than that of $C_2H_5^+$ due to a higher proton affinity of C_3H_4 (8.0 eV) than that of C_2H_4 (7.1 eV).[12] The other reason is the difference in the delocarization of cation. Although a positive charge is localized on one C atom for $C_2H_5^+$, it is delocalized on two C atoms for $CH_2{=}CHCH_2^+$. Therefore, protonation channels will be suppressed by the delocalization of the positive charge in the $C_3H_5^+$ reactions. The contribution from radiative association and collisional stabilization was examined by measuring the branching ratios of each product ion as a function of the reaction time. It was found that radiative association is responsible for the formation of the adduct $(PhOH+C_3H_5)^+$ ion. The collisional stabilization plays a significant role in many alkylation reactions followed by elimination of stable neutral molecules. On the other hand, it is generally unimportant in protonation reactions followed by elimination of stable neutral molecules. In the case of alkylation, collisional stabilization suppresses the redissociation of such collision complexes as $(M+C_2H_5)^{+*}$ and $(M+C_3H_5)^{+*}$, so that the branching ratios of dissociative alkylation channels will be enhanced by collisions with CH_4.

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