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Mass-Spectrometric Study on Ion-Molecule Reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with Anilines, Nitrobenzene, and Benzonitrile

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The gas-phase ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with five monosubstituted benzenes carrying a nitrogen atom in the substituent [PhX: X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, CN] have been studied using an ion-trap type of GC/MS at a low chemical-ionization gas pressure of CH_4. The major product channels for anilines with low ionization potentials are proton transfer and charge transfer, while the channel for $PhNO_2$ and PhCN with high ionization potentials is proton transfer. The $PhX^+/(PhX+H)^+$ ratios increases with decreasing the acidity of the reactant hydrocarbon ion and decreasing the ionization potential of reagent. Small amounts of initial adduct ions, produced by radiative association, and their decomposition products are found in the reactions with $C_2H_5^+$ and $C_3H_5^+$. The reaction mechanism is discussed based on product ion distributions and semi-empirical calculations of the energies of intermediates and products.

Chemical ionization (CI) has been widely used as a soft ionization method of a reagent in mass spectroscopy.[1—4] When CH_4 is used as a CI gas, various reactant hydrocarbon ions are produced. Most CI mass spectra using CH_4 have been measured at a high CH_4 pressure of about 1 Torr (= 133.322 Pa) without separating reactant ions. Therefore, the relative contribution of each reactant ion to the product ions could not be determined and the collisional stabilization by the CI gas often takes part in the formation of product ions. According to typical CI experiments of Munson and Field at a CH_4 pressure of 1 Torr,[4] CH_5^+, $C_2H_5^+$, $C_3H_5^+$, $C_2H_4^+$, and $C_3H_7^+$ were formed with branching ratios of 48, 40, 6, 2, and 1%, respectively. Therefore, major reactant ions in the CH_4 atmosphere are CH_5^+, $C_2H_5^+$, and $C_3H_5^+$, which occupy 94% of the total ions. These reactant ions can induce the following proton transfer (PT) and hydride transfer in the reaction with a reagent molecule M: e.g.,

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

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

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

In addition to the above products, such initial adduct ions as $(M+C_2H_5)^+$ and $(M+C_3H_5)^+$, which are important intermediates in organic reactions by carbocations, have often been observed. It was predicted that these adducts ions are formed by the three-body collisional stabilization processes:[3,4] e.g.,

$$C_2H_5^+ + M + CH_4 \longrightarrow (M+C_2H_5)^+ + CH_4, \quad (3)$$

$$C_3H_5^+ + M + CH_4 \longrightarrow (M+C_3H_5)^+ + CH_4. \quad (4)$$

However, there is a possibility that they are formed by the two-body radiative association, which has recently been predicted to occur in such ion-molecule reactions as NO^+/PhCN, CH_3^+/HCN, and $(CH_3)_2COH^+/(CH_3)_2CO$.[5—7] In order to determine the contribution of the latter two-body processes, CI mass spectra must be measured at low CI gas pressures, where the collisional stabilization is insignificant.

We have recently measured CI mass spectra of PhH, $PhCH_3$, and PhCOX (X = H, CH_3, C_2H_5, Ph, COPh) at a low CH_4 pressure by separating the reactant CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions.[8,9] A comparison between our results at ca. 10^{-4} Torr and previous data at 1 Torr indicated that the collisional stabilization by the CH_4 gas participates in the formation of adduct ions from the reactions of $C_2H_5^+$ and $C_3H_5^+$ with PhH and $PhCH_3$, while adduct ions are produced from two-body radiative association in the reactions of $C_3H_5^+$ with $PhCOCH_3$ and PhCOPh. In the present work, ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with such typical N-containing benzene monoderivatives as PhX [X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, CN] are studied at a low CH_4 pressure using an ion-trap type of GC/MS by separating reactant ions. The reaction mechanism of these monosubstituted benzenes carrying a nitrogen atom in the substituent for the hydrocarbon ions is discussed based on product ion distributions and semi-empirical PM3 calculations of potential energies of intermediates and products.

The site of protonation, methylation, and ethylation to $PhNH_2$, $PhNO_2$, and PhCN has already been studied theoretically and experimentally.[10—12] Although Pollack et al.[10] predicted that protonation to $PhNH_2$ occurs dominantly on the NH_2 group on the basis of ion-cyclotron resonance (ICR) data and ab initio calculations of ring and nitrogen proton

affinities, Wood et al.[11] found that the major site of protonation is the benzene ring on the basis of MS/MS spectroscopic data. Wood et al.[11] reported that methylation and ethylation of aniline occur preferentially on the NH_2 group. Burinsky and Campana[12] confirmed their results for aniline using collision-induced dissociation (CID) with mass-analyzed ion kinetic energy (MIKE) spectroscopy and demonstrated that the NO_2 and CN groups are active sites of alkylation. In this study, the site of protonation and alkylation is discussed from PM3 data of product ions.

Experimental

CI mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS in a selected reactant ion mode. The time for storing a reactant ion was 5 ms and the reaction time was 20 ms. The ion-trap cell was kept at $\leq$170 °C. The reagents were diluted in hexane and injected into the GC with a high-purity carrier He gas. The partial pressures of He and CH_4 in an ion-trap cell were estimated to be 5×10^{-5} and 7×10^{-5} Torr, respectively. The CI 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.[13] However, there are many species whose ΔH° values are unknown. These values were calculated using a semi-empirical PM3 method (MOPAC Ver. 6.0) in order to determine potential energies of various reaction pathways.

Results and Discussion

The observed product ions and their branching ratios in the reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with PhX [X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, CN] are summarized in Table 1. The total branching ratios of each product channel are listed in Table 2 along with ionization potentials of the reagents. The uncertainties of the branching ratios were estimated to be within ±7%. There are three possible $C_3H_5^+$ ions. They are CH_2=$CHCH_2^+$, CH_3C=CH_2^+, and protonated cyclopropene ion with ΔH° = 946, 969, and 1069 kJ mol^{-1}, respectively.[13] The most stable CH_2=$CHCH_2^+$ isomer may be most significant under the present experimental conditions.

Anilines. The most outstanding feature of anilines among the N-containing benzene monoderivatives studied here is their low ionization potentials (Table 2). They are lower than the recombination energies of $C_2H_5^+$ (8.13 eV) and $C_3H_5^+$ (8.13 eV for CH_2=$CHCH_2^+$).[13] Therefore, not only PT channels, which are generally major processes in CI, but also charge-transfer (CT) channels are energetically open. Actually, both PT leading to $(PhNR'R''+H)^+$ and CT leading to $PhNR'R''^+$ are observed as major product channels in all the reactions except for the CH_5^+/$PhNH_2$ reaction, where only the former channel is found:

$$RH^+ + PhNR'R'' \longrightarrow (PhNR'R'' + H)^+ + R, \quad \text{(Proton transfer)} \quad (5)$$

$$RH^+ + PhNR'R'' \longrightarrow PhNR'R''^+ + RH. \quad \text{(Charge transfer)} \quad (6)$$

It should be noted that CT channels are found in the reactions of CH_5^+ with $PhNHCH_3$ and $PhN(CH_3)_2$. On the basis of known thermochemical data,[13] CT followed by dissociation

Table 1. Branching Ratios (%) of Product Ions in Reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with PhX [X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, CN][a]

Reagents	$PhNH_2$			$PhNHCH_3$			$PhN(CH_3)_2$			$PhNO_2$			PhCN		
Reactant ions	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$
Product ions															
$(M+C_3H_5)^+$			21			7			2			28			63
$(M+C_3H_5-C_2H_4)^+$			6												
$(M+C_2H_5)^+$		2			7			16							
$(M+C_2H_5-CH_3)^+$					3										
$(M+H)^+$	100	77	36	82	58	50	85	43	36	100	100	62	100	100	37
$(M+H-CH_3)^+$				10											
M^+		21	37	8	32	43	15	41	62						
$(M-O)^+$												10			

a) Uncertainties are within ±7%.

Table 2. Branching Ratios (%) of Each Product Channel in the Reactions of CH_5^+, $C_2H_5^+$,and $C_3H_5^+$ with PhX [X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, CN][a]

Reagents	$PhNH_2$			$PhNHCH_3$			$PhN(CH_3)_2$			$PhNO_2$			PhCN		
Ionization potential[b] (eV)	7.72			7.33			7.12			9.86			9.62		
Reactant ions	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	CH_5^+	$C_2H_5^+$	$C_3H_5^+$
Proton transfer	100	77	36	92	58	50	85	43	36	100	100	62	100	100	37
Charge transfer		21	37	8	32	43	15	41	62						
Association		2	27		10	7		16	2			28			63
O^--abstraction												10			

a) Uncertainties are within ±7%. b) Ref. 13.

into CH_3+H_2 or CH_4+H is energetically open:

$$CH_5^+ + PhNHCH_3 \longrightarrow PhNHCH_3^+ + CH_3 + H_2 + 0.51 \text{ eV}, \quad (7a)$$

$$CH_5^+ + PhNHCH_3 \longrightarrow PhNHCH_3^+ + CH_4 + H + 0.53 \text{ eV}, \quad (7b)$$

$$CH_5^+ + PhN(CH_3)_2 \longrightarrow PhN(CH_3)_2^+ + CH_3 + H_2 + 0.74 \text{ eV}, \quad (8a)$$

$$CH_5^+ + PhN(CH_3)_2 \longrightarrow PhN(CH_3)_2^+ + CH_4 + H + 0.76 \text{ eV}. \quad (8b)$$

Therefore, the above processes will be responsible for the formation of parent ions, though the relative importance between processes 7a and 7b and between processes 8a and 8b cannot be determined in the present study.

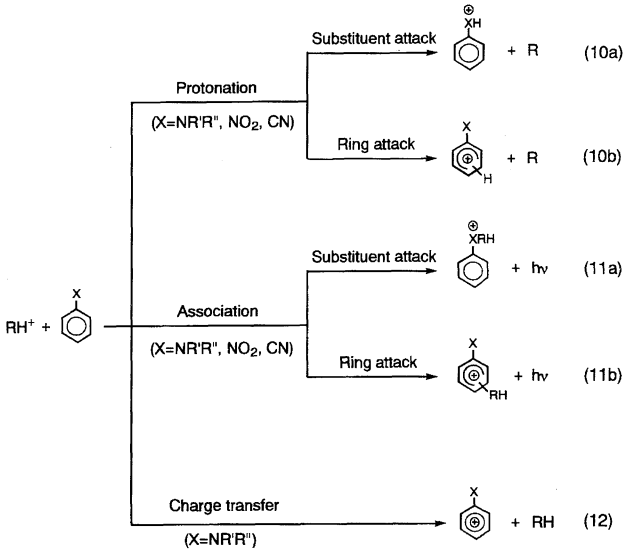
The proton-donating ability (acidity) of hydrocarbon ions decreases with increasing the dissociation energy of $RH^+ \rightarrow R+H^+$, which is denoted as D_0 ($R-H^+$). The D_0 ($R-H^+$) value increases in the order of CH_5^+ (5.7 eV), $C_2H_5^+$ (7.1 eV), and $C_3H_5^+$ (7.83 eV for $CH_2{=}CHCH_2^+$).[13] With decreasing the acidity of the reactant hydrocarbon ion, the $PhNR'R''^+/(PhNR'R''+H)^+$ ratio increases from 0 to 1.02 for $PhNH_2$, from 0.098 to 0.86 for $PhNHCH_3$, and from 0.18 to 1.72 for $PhN(CH_3)_2$. It also increases from 0 to 0.18 for CH_5^+, from 0.27 to 0.95 for $C_2H_5^+$, and from 1.02 to 1.72 for $C_3H_5^+$ with decreasing the ionization potential of anilines, probably because more CT product channels are open for molecules with low ionization potentials. Hughes and Tierman[14] investigated ion-molecule reactions of $C_4H_8^+$ with various amines and found that CT becomes more important relative to PT by nearly a factor of 10 when the ionization potential of the amine diminishes from 8.97 eV (CH_3NH_2) to 7.82 eV [$(CH_3)_3N$]. This result is consistent with our present results for aromatic amines.

It should be noted that initial adduct ions and their dissociation products are observed in all the reactions of $C_2H_5^+$ and $C_3H_5^+$ with anilines. These adduct ions are observed at a low total (CH_4+He) pressure of 1.2×10^{-4} Torr, where collisional stabilization is insignificant. Therefore, the initial adduct ions are probably formed by radiative association:

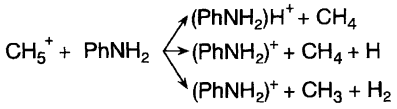
$$RH^+ + PhNR'R'' \longrightarrow (PhNR'R'' + RH)^+ + h\nu. \quad (9)$$

When the substituent $NR'R''$ becomes bulky, the total branching ratio of initial adduct ion and its dissociation products in the $C_2H_5^+/PhNR'R''$ reactions increases from 2 to 16%, while that in the $C_3H_5^+/PhNR'R''$ reactions decreases from 27 to 2% (Tables 1 and 2).

The observed major product channels of the RH^+/PhX ($X = NR'R''$) reactions are shown in Scheme 1. The $(PhNR'R''+H)^+$ ions can be formed through a PT to the lone-pair electrons of the N-atom or to the benzene ring. The electron-donating effect of the $NR'R''$ group will enhance the formation of Wheland-type ring adduct ions, while a high reactivity of the lone-pair electrons on the nitrogen atom will yield N-protonated ions preferentially. Figures 1, 2, and 3 show the potential-energy diagrams of the $CH_5^+/PhNH_2$, $C_2H_5^+/PhNH_2$, and $C_3H_5^+/PhNH_2$ reactions obtained using known thermochemical data[13] and calculated PM3 data. The corresponding data for the reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with $PhNHCH_3$ and $PhN(CH_3)_2$ are given in Table 3.



Scheme 1. Possible reaction pathways for the ion-molecule reactions of RH^+ with anilines, nitrobenzene, and benzonitrile.



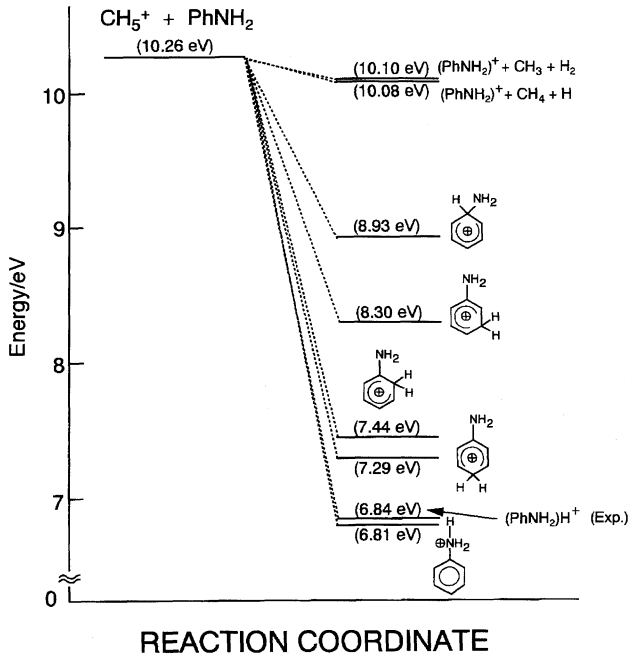


Fig. 1. Potential-energy diagram of the $CH_5^+ + PhNH_2$ reaction.

For comparison, the energies of $(PhNR'R''+H)^+ + R$ obtained using known experimental proton affinities of $PhNR'R''$[13] are also shown in Figs. 1, 2, and 3 and Table 3, though the site of protonation was not determined. The experimental energies of $(PhNR'R''+H)^+ + R$ agree with the PM3 energies calculated for the formation of the most stable N-protonated ions within ±0.52 eV. It is, therefore, reasonable to assume that the reported proton affinities of $PhNR'R''$ are those for

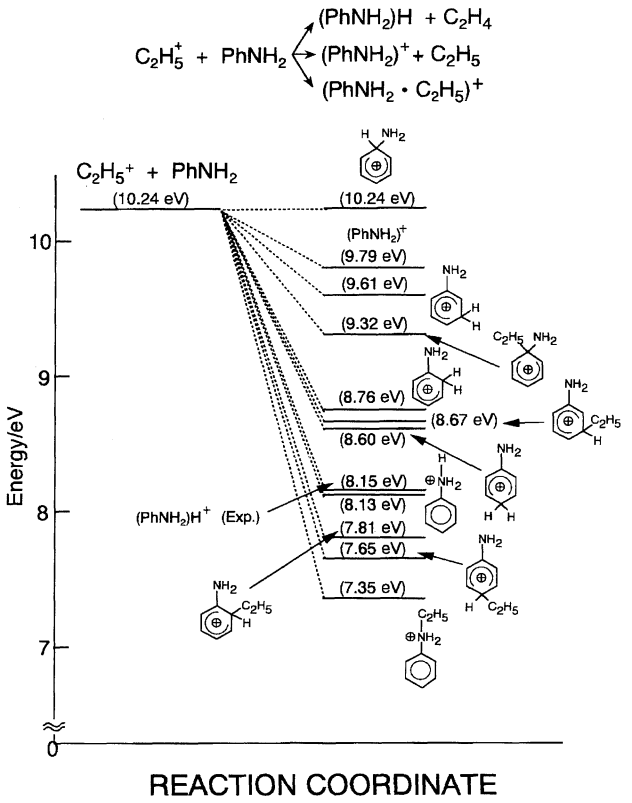


Fig. 2. Potential-energy diagram of the $C_2H_5^+$+$PhNH_2$ reaction.

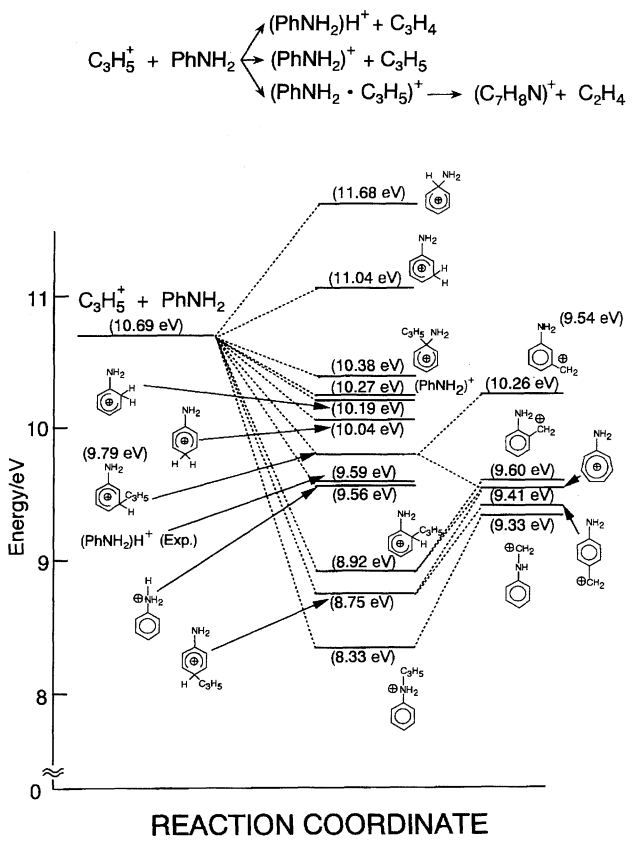


Fig. 3. Potential-energy diagram of the $C_3H_5^+$+$PhNH_2$ reaction.

N-protonated ions. It is likely that protonation is governed thermodynamically because there will be little barrier in the protonation processes. Assuming that the protonation is controlled thermodynamically, the most stable N-protonated ions are more favorable products, as predicted by Pollack et al.[10] However, a possibility of preferential protonation to a ring cannot be excluded, partly because the energy differences between N-protonation and *ortho*- or *para*-ring-protonation are small (0.4—0.6 eV), and partly because Wood et al.[11] found that protonation of aniline occurs exclusively on the ring in the MS/MS experiments.

The $(PhNR'R''+C_2H_5)^+$ and $(PhNR'R''+C_3H_5)^+$ ions can be formed through association to the lone-pair electrons of the N-atom or to the benzene ring, as shown in Scheme 1. Since the association is a reversible process without an energy barrier, it will be controlled thermodynamically. According to the potential-energy diagrams of association pathways in the $C_2H_5^+$/PhNR′R″ and $C_3H_5^+$/PhNR′R″ reactions, N-adduct ions for $PhNH_2$ are more stable than *para*-ring-adduct ions by 0.30—0.42 eV (Figs. 2 and 3). The energy difference between N-adduct ions and *para*-ring-adduct ions becomes small for $PhNHCH_3$ (0.21—0.22 eV), and *para*-ring-adduct ions become more stable than N-adduct ions for $PhN(CH_3)_2$ by 0.02—0.08 eV (Table 3). On the basis of previous MS/MS and CID/MIKE studies,[11,12] alkylation of aniline occurs exclusively on the substituent. These facts led us to conclude that the attack of $C_2H_5^+$ and $C_3H_5^+$ ions occurs preferentially on the substituent for $PhNH_2$. However, the attack on the *para*-ring site becomes important with increasing the bulkiness of substituent, because the energy difference between N-adducts and *para*-ring-adducts becomes small and steric hindrance increases with increasing the bulkiness of amino group.

In the CH_5^+/$PhNHCH_3$ and $C_2H_5^+$/$PhNHCH_3$ reactions, the formation of $PhNH_2^+$ and $PhNHC_2H_5^+$ was found with branching ratios of 10 and 3%, respectively. These ions are probably formed through the following addition/CH_3-elimination processes:

$$CH_5^+ + PhNHCH_3 \longrightarrow PhNH_2^+ + CH_4 + CH_3 + 0.90 \text{ eV}, \quad (13)$$

$$C_2H_5^+ + PhNHCH_3 \longrightarrow PhNHC_2H_5^+ + CH_3 + (0.50—0.77) \text{ eV}. \quad (14)$$

A small amount of the $C_7H_8N^+$ ion (6%) was found in the $C_3H_5^+$/$PhNH_2$ reaction. Although both monosubstituted tropylium ion and mono- and di-substituted benzene ions, as shown in Fig. 3, are energetically possible, the most stable $PhNHCH_2^+$ ion may be the most favorable product ion.

Nitrobenzene. Only PT channel was found in the reactions of CH_5^+ and $C_2H_5^+$ with $PhNO_2$. The lack of CT channel was attributed to a high ionization potential of $PhNO_2$ (Table 2). It should be noted that $PhNO^+$ and $(PhNO_2+C_3H_5)^+$ ions as well as $(PhNO_2+H)^+$ ion are observed in the $C_3H_5^+$/$PhNO_2$ reaction. The initial adduct ion is expected to be produced by a radiative association process, as predicted in the $C_3H_5^+$/PhNR′R″ reactions:

Table 3. Heats of Formation of Each Product Channels (in eV Units)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products[a)]	$\sum\Delta H^\circ$ (Products)	$-\Delta H^\circ$ (Reactions)[b)]
CH_5^++PhNHCH$_3$	10.22	PhNHCH$_3^+$+CH$_3$+H$_2$	9.71	0.51
		PhNHCH$_3^+$+CH$_4$+H	9.69	0.53
		o-(PhNHCH$_3$+H)$^+$+CH$_4$	7.35	2.87
		m-(PhNHCH$_3$+H)$^+$+CH$_4$	8.25	1.97
		p-(PhNHCH$_3$+H)$^+$+CH$_4$	7.21	3.01
		i-(PhNHCH$_3$+H)$^+$+CH$_4$	8.79	1.43
		N-(PhNHCH$_3$+H)$^+$+CH$_4$	6.94	3.28
		(PhNHCH$_3$+H)$^+$(Exp.)+CH$_4$	6.45	3.77
		PhNH$_2^+$+CH$_4$+CH$_3$	9.32	0.90
$C_2H_5^+$+PhNHCH$_3$	10.21	PhNHCH$_3^+$+C$_2$H$_5$	9.40	0.81
		o-(PhNHCH$_3$+H)$^+$+C$_2$H$_4$	8.67	1.54
		m-(PhNHCH$_3$+H)$^+$+C$_2$H$_4$	9.56	0.65
		p-(PhNHCH$_3$+H)$^+$+C$_2$H$_4$	8.52	1.69
		i-(PhNHCH$_3$+H)$^+$+C$_2$H$_4$	10.10	0.11
		N-(PhNHCH$_3$+H)$^+$+C$_2$H$_4$	8.25	1.96
		(PhNHCH$_3$+H)$^+$(Exp.)+C$_2$H$_4$	7.76	2.45
		o-(PhNHCH$_3$+C$_2$H$_5$)$^+$	7.72	2.49
		m-(PhNHCH$_3$+C$_2$H$_5$)$^+$	8.61	1.60
		p-(PhNHCH$_3$+C$_2$H$_5$)$^+$	7.57	2.64
		i-(PhNHCH$_3$+C$_2$H$_5$)$^+$	9.26	0.95
		N-(PhNHCH$_3$+C$_2$H$_5$)$^+$	7.35	2.86
		PhNHC$_2$H$_5^+$+CH$_3$	9.71	0.50
		o-C$_2$H$_5$C$_6$H$_4$NH$_2^+$+CH$_3$	9.58	0.63
		m-C$_2$H$_5$C$_6$H$_4$NH$_2^+$+CH$_3$	9.53	0.68
		p-C$_2$H$_5$C$_6$H$_4$NH$_2^+$+CH$_3$	9.44	0.77
$C_3H_5^+$+PhNHCH$_3$	10.66	PhNHCH$_3^+$+C$_3$H$_5$	9.88	0.78
		o-(PhNHCH$_3$+H)$^+$+C$_3$H$_4$	10.10	0.56
		m-(PhNHCH$_3$+H)$^+$+C$_3$H$_4$	10.99	−0.33
		p-(PhNHCH$_3$+H)$^+$+C$_3$H$_4$	9.96	0.70
		i-(PhNHCH$_3$+H)$^+$+C$_3$H$_4$	11.53	−0.87
		N-(PhNHCH$_3$+H)$^+$+C$_3$H$_4$	8.68	1.98
		(PhNHCH$_3$+H)$^+$(Exp.)+C$_3$H$_4$	9.20	1.46
		o-(PhNHCH$_3$+C$_3$H$_5$)$^+$	8.84	1.82
		m-(PhNHCH$_3$+C$_3$H$_5$)$^+$	9.70	0.96
		p-(PhNHCH$_3$+C$_3$H$_5$)$^+$	8.67	1.99
		i-(PhNHCH$_3$+C$_3$H$_5$)$^+$	10.33	0.33
		N-(PhNHCH$_3$+C$_3$H$_5$)$^+$	8.46	2.20
CH_5^++PhN(CH$_3$)$_2$	10.40	PhN(CH$_3$)$_2^+$+CH$_3$+H$_2$	9.66	0.74
		PhN(CH$_3$)$_2^+$+CH$_4$+H	9.64	0.76
		o-[PhN(CH$_3$)$_2$+H]$^+$+CH$_4$	7.25	3.15
		m-[PhN(CH$_3$)$_2$+H]$^+$+CH$_4$	8.18	2.22
		p-[PhN(CH$_3$)$_2$+H]$^+$+CH$_4$	7.16	3.24
		i-[PhN(CH$_3$)$_2$+H]$^+$+CH$_4$	8.67	1.73
		N-[PhN(CH$_3$)$_2$+H]$^+$+CH$_4$	6.88	3.52
		[PhN(CH$_3$)$_2$+H]$^+$(Exp.)+CH$_4$	6.37	4.03
$C_2H_5^+$+PhN(CH$_3$)$_2$	10.38	PhN(CH$_3$)$_2^+$+C$_2$H$_5$	9.36	1.02
		o-[PhN(CH$_3$)$_2$+H]$^+$+C$_2$H$_4$	8.57	1.81
		m-[PhN(CH$_3$)$_2$+H]$^+$+C$_2$H$_4$	9.49	0.89
		p-[PhN(CH$_3$)$_2$+H]$^+$+C$_2$H$_4$	8.48	1.90
		i-[PhN(CH$_3$)$_2$+H]$^+$+C$_2$H$_4$	9.98	0.40
		N-[PhN(CH$_3$)$_2$+H]$^+$+C$_2$H$_4$	8.20	2.18
		[PhN(CH$_3$)$_2$+H]$^+$(Exp.)+C$_2$H$_4$	7.68	2.70
		o-[PhN(CH$_3$)$_2$+C$_2$H$_5$]$^+$	7.61	2.77
		m-[PhN(CH$_3$)$_2$+C$_2$H$_5$]$^+$	8.54	1.84
		p-[PhN(CH$_3$)$_2$+C$_2$H$_5$]$^+$	7.43	2.95

a) The symbols *i*-, *O*-, and *N*- represent *ipso*-substituted ions, O-adduct ions, and N-adduct ions, respectively. Thermochemical data calculated using experimentally determined proton affinities in Ref. 13 are shown by Exp.
b) $-\Delta H$(Reactions) = $\sum\Delta H^\circ$(Reactants) − $\sum\Delta H$(Products).

Table 3. (Continued)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products[a)]	$\sum\Delta H^\circ$ (Products)	$-\Delta H^\circ$ (Reactions)[b)]
		i-$[PhN(CH_3)_2+C_2H_5]^+$	9.18	1.20
		N-$[PhN(CH_3)_2+C_2H_5]^+$	7.51	2.87
$C_3H_5^+$+$PhN(CH_3)_2$	10.83	$PhN(CH_3)_2^+$+C_3H_5	9.83	1.00
		o-$[PhN(CH_3)_2+H]^+$+C_3H_4	10.00	0.83
		m-$[PhN(CH_3)_2+H]^+$+C_3H_4	10.93	−0.10
		p-$[PhN(CH_3)_2+H]^+$+C_3H_4	9.91	0.92
		i-$[PhN(CH_3)_2+H]^+$+C_3H_4	11.41	−0.58
		N-$[PhN(CH_3)_2]H^+$+C_3H_4	9.63	1.20
		$[PhN(CH_3)_2+H]^+$(Exp.)+C_3H_4	9.12	1.71
		o-$[PhN(CH_3)_2+C_3H_5]^+$	8.70	2.13
		m-$[PhN(CH_3)_2+C_3H_5]^+$	9.62	1.21
		p-$[PhN(CH_3)_2+C_3H_5]^+$	8.53	2.30
		i-$[PhN(CH_3)_2+C_3H_5]^+$	10.28	0.55
		N-$[PhN(CH_3)_2+C_3H_5]^+$	8.51	2.32
CH_5^++$PhNO_2$	10.06	*o*-$(PhNO_2+H)^+$+CH_4	8.96	1.10
		m-$(PhNO_2+H)^+$+CH_4	8.71	1.35
		p-$(PhNO_2+H)^+$+CH_4	8.97	1.09
		i-$(PhNO_2+H)^+$+CH_4	9.16	0.90
		O-$(PhNO_2+H)^+$+CH_4	7.79	2.27
		$(PhNO_2+H)^+$(Exp.)+CH_4	7.49	2.57
$C_2H_5^+$+$PhNO_2$	10.04	*o*-$(PhNO_2+H)^+$+C_2H_4	10.27	−0.23
		m-$(PhNO_2+H)^+$+C_2H_4	10.02	0.02
		p-$(PhNO_2+H)^+$+C_2H_4	10.28	−0.24
		i-$(PhNO_2+H)^+$+C_2H_4	10.48	−0.44
		O-$(PhNO_2+H)^+$+C_2H_4	9.10	0.94
		$(PhNO_2+H)^+$(Exp.)+C_2H_4	8.80	1.24
		o-$(PhNO_2+C_2H_5)^+$	9.34	0.70
		m-$(PhNO_2+C_2H_5)^+$	9.06	0.98
		p-$(PhNO_2+C_2H_5)^+$	9.33	8.71
		i-$(PhNO_2+C_2H_5)^+$	9.55	0.49
		O-$(PhNO_2+C_2H_5)^+$	8.45	1.59
$C_3H_5^+$+$PhNO_2$	10.49	*o*-$(PhNO_2+H)^+$+C_3H_4	11.70	−1.21
		m-$(PhNO_2+H)^+$+C_3H_4	11.46	−0.97
		p-$(PhNO_2+H)^+$+C_3H_4	11.71	−1.22
		i-$(PhNO_2+H)^+$+C_3H_4	11.91	−1.42
		O-$(PhNO_2+H)^+$+C_3H_4	10.54	−0.05
		$(PhNO_2+H)^+$(Exp.)+C_3H_4	10.24	0.25
		o-$(PhNO_2+C_3H_5)^+$	10.41	0.08
		m-$(PhNO_2+C_3H_5)^+$	10.14	0.35
		p-$(PhNO_2+C_3H_5)^+$	10.40	0.09
		i-$(PhNO_2+C_3H_5)^+$	10.62	−0.13
		O-$(PhNO_2+C_3H_5)^+$	9.60	0.89
		$PhNO^+$+CH_3COCH_2	9.49	1.00
		$PhNO^+$+C_2H_5CO	10.55	−0.06
		m-$(PhCN+H)^+$+CH_4	10.38	1.23
		p-$(PhCN+H)^+$+CH_4	10.32	1.29
		i-$(PhCN+H)^+$+CH_4	10.75	0.86
		N-$(PhCN+H)^+$+CH_4	9.08	2.53
		$(PhCN+H)^+$(Exp.)+CH_4	8.93	2.68
CH_5^++PhCN	11.61	*o*-$(PhCN+H)^+$+CH_4	10.34	1.27
		m-$(PhCN+H)^+$+CH_4	10.38	1.23
		p-$(PhCN+H)^+$+CH_4	10.32	1.29
		i-$(PhCN+H)^+$+CH_4	10.75	0.86
		N-$(PhCN+H)^+$+CH_4	9.08	2.53
		$(PhCN+H)^+$(Exp.)+CH_4	8.93	2.68
$C_2H_5^+$+PhCN	11.59	*o*-$(PhCN+H)^+$+C_2H_4	11.65	−0.06
		m-$(PhCN+H)^+$+C_2H_4	11.69	−0.10
		p-$(PhCN+H)^+$+C_2H_4	11.63	−0.04

Table 3. (Continued)

Reactants	$\sum\Delta H^\circ$ (Reactants)	Products[a)]	$\sum\Delta H^\circ$ (Products)	$-\Delta H^\circ$ (Reactions)[b)]
		i-(PhCN+H)$^+$+C_2H_4	12.06	−0.47
		N-(PhCN+H)$^+$+C_2H_4	10.40	1.19
		(PhCN+H)$^+$(Exp.)+C_2H_4	10.24	1.35
		o-(PhCN+C_2H_5)$^+$	10.74	0.85
		m-(PhCN+C_2H_5)$^+$	10.75	0.84
		p-(PhCN+C_2H_5)$^+$	10.68	0.91
		i-(PhCN+C_2H_5)$^+$	11.15	0.44
		N-(PhCN+C_2H_5)$^+$	9.26	2.33
$C_3H_5^+$+PhCN	12.04	*o*-(PhCN+H)$^+$+C_3H_4	13.08	−1.04
		m-(PhCN+H)$^+$+C_3H_4	13.13	−1.09
		p-(PhCN+H)$^+$+C_3H_4	13.06	−1.02
		i-(PhCN+H)$^+$+C_3H_4	12.22	−0.18
		N-(PhCN+H)$^+$+C_3H_4	11.83	0.21
		(PhCN+H)$^+$(Exp.)+C_3H_4	11.68	0.36
		o-(PhCN+C_3H_5)$^+$	11.83	0.21
		m-(PhCN+C_3H_5)$^+$	11.83	0.21
		p-(PhCN+C_3H_5)$^+$	11.76	0.28
		i-(PhCN+C_3H_5)$^+$	12.22	−0.18
		N-(PhCN+C_3H_5)$^+$	10.32	1.72

$$C_3H_5^+ + PhNO_2 \longrightarrow (PhNO_2 + C_3H_5)^+ + h\nu. \quad (15)$$

In Scheme 1 and Table 3 are shown observed major reaction pathways and potential energies of the CH_5^+/$PhNO_2$, $C_2H_5^+$/$PhNO_2$, and $C_3H_5^+$/$PhNO_2$ reactions. The energies for the protonation obtained using an experimentally determined proton affinity of $PhNO_2$ [13] are also shown in Table 3. They are 0.3 eV lower than the present PM3 data for the formation of the most stable O-protonated ions. Therefore, the reported proton affinity of $PhNO_2$ probably corresponds to that for the O-protonation. The $(PhNO_2+H)^+$ and $(PhNO_2+C_3H_5)^+$ ions can be formed through an attack on the O-atom in the substituent or on the benzene ring, as shown in Scheme 1. Since the NO_2 group has electron-withdrawing properties, the formation of ring adducts will be suppressed. Actually O-protonated and O-alkylated ions are more stable than *meta*-ring-protonated and ring-alkylated ions by 0.9 and 0.5—0.6 eV, respectively, as shown in Table 3. Therefore, the major $(PhNO_2+H)^+$ and $(PhNO_2+C_3H_5)^+$ ions will be more stable O-protonated and O-alkylated ions. Although the $(PhNO_2+C_3H_5)^+$ ion was formed, the $(PhNO_2+C_2H_5)^+$ ion could not be detected. This difference will be discussed in the last section.

The $PhNO^+$ ion was found only in the $C_3H_5^+$/$PhNO_2$ reaction. The formation of $PhNO^+$ through the following dissociative CT process is highly endoergic:

$$C_3H_5^+ + PhNO_2 \longrightarrow PhNO^+ + O + C_3H_5 - 3.91\ \text{eV}. \quad (16)$$

Therefore, it is probably formed via the following O^--abstraction process:

$$C_3H_5^+ + PhNO_2 \longrightarrow PhNO^+ + CH_3COCH_2\ \text{(acetonyl radical)} + 1.00\ \text{eV}, \quad (17a)$$

$$\longrightarrow PhNO^+ + C_2H_5CO\ \text{(propionyl radical)} - 0.06\ \text{eV}. \quad (17b)$$

Since the endoergic energy in process 17b can be supplied from the translational and rotational energies of the reactants (9/2*RT*), both processes are energetically accessible. However, process 17a will be dominant because a significant rearrangement of chemical bonds is required for the formation of C_2H_5CO from the $C_3H_5^+$+O^- reaction.

Benzonitrile. The observed product channels for PhCN with a high ionization potential are similar to those for $PhNO_2$. Only PT channel was found in the CH_5^+/PhCN and $C_2H_5^+$/PhCN reactions, while PT and association reaction were found in the $C_3H_5^+$/PhCN reaction. The initial adduct ion is expected to be produced by radiative association, as found in the reactions of $C_3H_5^+$ with anilines and nitrobenzene:

$$C_3H_5^+ + PhCH \longrightarrow (PhCN + C_3H_5)^+ + h\nu. \quad (18)$$

In Scheme 1 and Table 3 are shown the observed major reaction pathways and potential energies of the CH_5^+/PhCN, $C_2H_5^+$/PhCN, and $C_3H_5^+$/PhCN reactions. The energies for the protonation obtained using an experimentally determined proton affinity of PhCN[13] are also shown in Table 3. They are about 0.2 eV lower than the present PM3 data for the formation of the most stable N-protonated ions. Therefore, the reported proton affinity of PhCN[13] will correspond to that for the N-protonation. The $(PhCN+H)^+$ and $(PhCN+C_3H_5)^+$ ions can be formed through electrophilic attack on the CN bond in the substituent or on the benzene ring, as shown in Scheme 1. The CN group has electron-withdrawing properties. Therefore, the ring-protonated ions will be suppressed, while the triple C≡N bond will have high reactivity for electrophiles. Actually, N-protonated and N-alkylated ions are more stable than ring-protonated and ring-alkylated ions by 1.2 and 1.4—1.9 eV, respectively, as shown in Table 3. On the basis of above findings, the major $(PhCN+H)^+$ and $(PhCN+C_3H_5)^+$

ions will be the most stable N-protonated and N-alkylated ions.

Radiative Association. An important finding of this work is the observation of radiative association in the reactions of hydrocarbon ions with N-containing monosubstituted benzenes. This implies that the radiative association is a more general product channel in ion-molecule reactions of hydrocarbons ions with N-containing compounds. According to a systematic study on radiative association by Dunbar and his co-workers,[5,6] the ratio of radiative association to redissociation of collision complex depends on the binding energy and the number of internal degrees of freedom (N) of the collision complex, and the reaction temperature. In general, it increases with increasing the binding energy and the number of internal degrees of freedom and with decreasing the reaction temperature. According to our PM3 calculations, the binding energies of adduct ions produced from the reactions of $C_2H_5^+$ and $C_3H_5^+$ with anilines, nitrobenzene, and benzonitrile are 0.9—3.0 eV, as shown in Figs. 2 and 3 and Table 3. These values and N values (57—81) are sufficiently large to form association products. For example, the ratio of radiative association to the redissociation of adduct ion at 300 K is estimated to be > 1 for molecules having a binding energy of 2.0 eV and an N value of 60 using Fig. 1 in Ref. 5. Dunbar[5] predicted that the rate of radiative association will be enhanced by the presence of bright IR chromophores. In the present case, the NR′R″, NO_2, and CN groups are bright IR chromophores. Therefore, it seems likely that the radiative-association rates for PhX (X = NR′R″, NO_2, CN) are significantly enhanced and that most of the IR radiation comes from these IR chromophores in the substituents.

A significant difference was found in the association reactions for N-containing benzene monoderivatives between $C_2H_5^+$ and $C_3H_5^+$. Although adduct ions are formed in all the reactions of $C_2H_5^+$ and $C_3H_5^+$ with anilines, they are produced in only the reactions of $C_3H_5^+$ with nitrobenzene and benzonitrile. The binding energies of $(C_2H_5^+ + PhNO_2)^+$ and $(C_2H_5^+ + PhCN)^+$ are larger than those of $(C_3H_5^+ + PhNO_2)^+$ and $(C_3H_5^+ + PhCN)^+$ by 0.5—0.7 eV, as shown in Table 3. Therefore, the association is expected to be a more favorable channel for the reactions with $C_2H_5^+$, according to the prediction of Dunbar.[5] The differences in the N value of adduct ions are only 6 between $C_2H_5^+$ and $C_3H_5^+$. On the basis of above facts, the lack of adduct ions from the $C_2H_5^+/PhNO_2$ and $C_2H_5^+/PhCN$ reactions cannot be explained from the differences in the binding energy and the N value of adduct ions. In the present reaction systems, protonation competes with association. If the branching ratios between association and protonation in the $C_2H_5^+/PhNO_2$, $C_3H_5^+/PhNO_2$, $C_2H_5^+/PhCN$, and $C_3H_5^+/PhCN$ reactions are controlled thermodynamically, association is the more favorable product channel than protonation in all the reactions, on the basis of thermochemical data given in Table 3. The lack of an association channel in the $C_2H_5^+/PhNO_2$ and $C_2H_5^+/PhCN$ reactions suggests that the branching ratios between association and protonation are not controlled thermodynamically, but they are governed kinetically. Although a positive charge is localized on one C atom for the case of $C_2H_5^+$, it is delocalized on two C atoms for the case of $C_3H_5^+$. The protonation channel will be suppressed by the delocalization of the positive charge in the hydrocarbon ion. Thus the branching ratio of association becomes large for the $C_3H_5^+/PhNO_2$ and $C_3H_5^+/PhCN$ reactions. On the other hand, there will be little energy barrier for the protonation processes in the $C_2H_5^+/PhNO_2$ and $C_2H_5^+/PhCN$ reactions. Therefore, protonation becomes the dominant product channel.

Conclusion

The gas-phase ion-molecule reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with five N-containing monosubstituted benzenes [PhX: X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, CN] have been studied using an ion-trap type of GC/MS at a low CH_4 pressure. The major product channels for anilines with low ionization potentials were PT and CT, while that for $PhNO_2$ and PhCN with high ionization potentials was PT. The $PhX^+/(PhX+H)^+$ ratios increased with decreasing the acidity of the reactant hydrocarbon ion and decreasing the ionization potential of reagent. Small amounts of initial adduct ions and their decomposition products were found in the reactions with $C_2H_5^+$ and $C_3H_5^+$ at a CH_4 pressure of 10^{-4} Torr, where collisional stabilization was insignificant. It was therefore concluded that these adduct ions are formed via radiative association. The branching ratio of adduct ions strongly depended on both the reactant hydrocarbon ion and the reagent in the present system. PM3 calculations of the energies of adduct ions led us to conclude that association occurs exclusively on the substituents. In order to gain better understanding of the radiative association processes, further detailed experimental and theoretical studies will be required.

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References

1) F. H. Field, *Acc. Chem. Res.*, **1**, 42 (1968).
2) J. R. Chapman, "Practical Organic Mass Spectrometry: A Guide for Chemical and Biochemical Analysis," 2nd ed, Wiley, New York (1993).
3) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).
4) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **89**, 1047 (1968).
5) R. C. Dunbar, *Int. J. Mass Spectrom. Ion Processes*, **100**, 423 (1990).
6) G. Weddle and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Processes.*, **134**, 73 (1994).
7) V. G. Anicich, A. D. Sen, W. T. Huntress, Jr., and M. J. McEvan, *J. Chem. Phys.*, **102**, 3256 (1995).
8) M. Tsuji, E. Oda, and Y. Nishimura, *Chem. Lett.*, **1997**, 781.
9) M. Tsuji and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, **71**, 273 (1998).

10) S. K. Pollack, J. L. Devlin, III, K. D. Summerhays, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 4583 (1977).
11) K. V. Wood, D. J. Burinsky, D. Cameron, and R. G. Cooks, *J. Org. Chem.*, **48**, 5236 (1983).
12) D. J. Burinsky and J. E. Campana, *Org. Mass Spectrom.*, **23**, 613 (1988).
13) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data*, **17**, Suppl. 1 (1988); update data were obtained from NIST Standard Ref. Database, Number69, 1998, (http://webbook.nist.gov/chemistry).
14) B. M. Hughes and T. O. Tiernan, *J. Chem. Phys.*, **58**, 4373 (1969).