

Chemical Ionization Mass Spectra of Benzene and Toluene at Low CH₄ Pressures

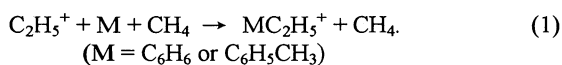
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Chemical ionization (CI) of benzene and toluene by the CH₅⁺, C₂H₅⁺, and C₃H₅⁺ ions has been studied in an ion-trap type GC/MS at low CH₄ pressures. The main product ion from benzene was C₆H₇⁺ for all the reactant ions, and that from toluene was C₇H₉⁺ for the CH₅⁺ and C₂H₅⁺ ions, and C₇H₇⁺ for the C₃H₅⁺ ion. Initial adduct ions, which had been found in previous CI spectra at high CH₄ pressures, were not observed.

Chemical ionization (CI) in a methane atmosphere is widely used as a soft ionization method of a reagent molecule.^{1,2} Most CI mass spectra have been measured at about 1 Torr (133 Pa), where CH₅⁺, C₂H₅⁺, and C₃H₅⁺ are dominant reactant ions. CI mass spectra of benzene and toluene in a methane atmosphere have been measured by Munson and Field³ without isolating a reactant ion. In addition to protonated benzene and toluene cations, which are major product ions, small amounts of such initial adduct ions as (M + C₂H₅)⁺ and (M + C₃H₅)⁺ were observed (Table 1). They predicted that these adduct ions are formed via collisional stabilization by the reactant CH₄ gas: e.g.,



However, no information about the collisional stabilization has been obtained.

In the present study, CI mass spectra of benzene and toluene were measured at low CH₄ pressures in order to determine initial product ion distributions at thermal energies. Although reactant ions produced from CH₄ have not been separated in the previous measurements,³ CI mass spectra due to the CH₅⁺, C₂H₅⁺, and C₃H₅⁺ ions were measured separately.

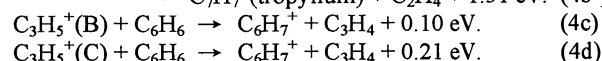
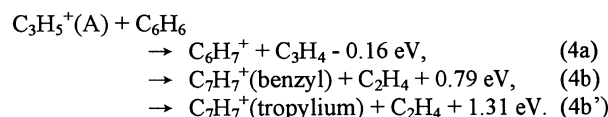
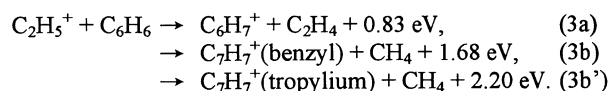
CI mass spectra were obtained by using an ion-trap type Hitachi M7200 GC/MS in a selected reactant ion mode. The time for storing a reactant ion was 5 ms and the reaction time was 20 ms. The ion-trap cell was kept at ≤170°C. The

reagents were diluted in n-heptane and injected into the GC with a carrier He gas. The partial pressures of He and CH₄ in the ion-trap cell were 5 × 10⁻⁵ and 7 × 10⁻⁵ Torr, respectively. The reactant ions produced by electron-impact ionization of CH₄ followed by ion-molecule reactions were expected to be thermalized by collisions with the carrier He gas before CI of a reagent.² The CI spectra were measured at a low reagent concentration of about 1000 pg/cm³ in order to reduce secondary reactions.

The branching ratios of product ions obtained in the present study are given in Table 1 along with previous CI data of Munson and Field³ at a CH₄ pressure of 1 Torr. In the present study, only protonated benzene cation with m/Z = 79 is found in the CH₅⁺/C₆H₆ reaction:



where ΔH° value is calculated using reported thermochemical data.⁴ On the other hand, in addition to protonated benzene cation, a small amount of C₇H₇⁺ with m/Z = 91 is found in the C₂H₅⁺/C₆H₆ and C₃H₅⁺/C₆H₆ reactions:



Here, C₃H₅⁺(A) represents the CH₂=CHCH₂⁺ ion with ΔH° = 946 kJ/mol, while C₃H₅⁺(B) and C₃H₅⁺(C) are CH₃C=CH₂⁺ and protonated cyclopropadiene ion with higher ΔH° values of 969 and 1067 kJ/mol, respectively.⁴ Since process (4a) is endoergic,

Table 1. Branching ratios of product ions in chemical ionization spectra (CH₄ reactant)

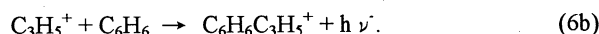
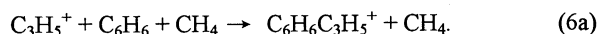
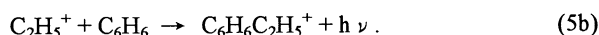
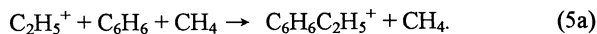
Product ions ^b	C ₆ H ₆			Ref. 3 ^a	C ₆ H ₅ CH ₃			Ref. 3
	This work				This work			
	CH ₅ ⁺	C ₂ H ₅ ⁺	C ₃ H ₅ ⁺		CH ₅ ⁺	C ₂ H ₅ ⁺	C ₃ H ₅ ⁺	
(M + C ₃ H ₇) ⁺				0.0030				0.0038
(M + C ₃ H ₅) ⁺				0.030				0.033
(M + C ₂ H ₅) ⁺				0.124				0.134
(M + CH) ⁺		0.05	0.35				0.03	
(M + H) ⁺	1.00	0.95	0.65	0.72	0.93	0.89	0.39	0.69
M ⁺				0.034				0.031
(M - H) ⁺					0.07	0.11	0.58	0.028

^aCH₄ pressure: 1 Torr, Reactant ions: CH₅⁺(48%), C₂H₅⁺(40%), C₃H₅⁺(6%), C₂H₄⁺(2%), and C₃H₇⁺(1%).

^b(M + X)⁺ represents a product ion formed by the addition of X⁺ to a reagent molecule M.

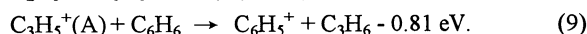
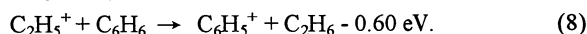
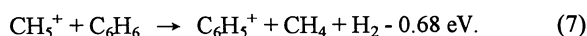
the formation of $C_6H_7^+$ by the $C_3H_5^+$ reaction probably proceeds through (4c) and/or (4d).

It should be noted that the $(C_6H_6 + C_2H_5)^+$ and $(C_6H_6 + C_3H_5)^+$ adduct ions, whose branching ratios are 12.4 and 3% in the high pressure CI spectrum, respectively, were not found in the present low-pressure CI spectrum. For the formation of these adduct ions, not only the collisional stabilization processes (5a) and (6a) but also radiative association processes (5b) and (6b), as reported for the reactions of NO^+ with carbonyl compounds,⁵ are possible:

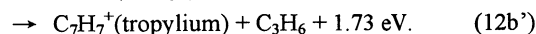
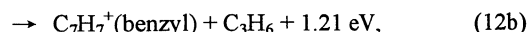
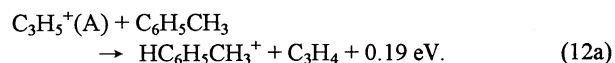
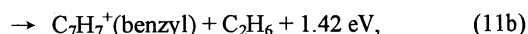
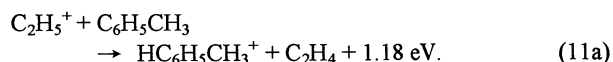
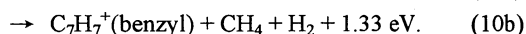
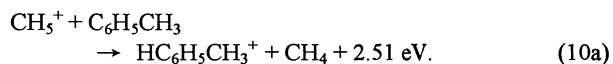


If the latter processes are dominant, the initial adduct ions will be observed at low CH_4 pressures. The lack of the $(C_6H_6 + C_2H_5)^+$ and $(C_6H_6 + C_3H_5)^+$ ions and the detection of the $(C_6H_6 + H)^+$ and $(C_6H_6 + CH)^+$ ions at low CH_4 pressures implies that the radiative association processes are insignificant and the initial adduct ions completely dissociate into fragment ions at low CH_4 pressure because of high excess energies of the $C_6H_6C_2H_5^+$ and $C_6H_6C_3H_5^+$ ions. On the basis of the present results, it is reasonable to assume that the $(C_6H_6 + C_2H_5)^+$ and $(C_6H_6 + C_3H_5)^+$ adduct ions are formed by collisional stabilization processes (5a) and (6a) at a CH_4 pressure of 1 Torr, as predicted by Munson and Field.³

No $C_6H_5^+$ ion can be found in the reactions of CH_5^+ , $C_2H_5^+$, and $C_3H_5^+$ with C_6H_6 . The lack of hydride abstraction processes can be explained by the endothermicity of the reaction processes:



When toluene was used as a reagent, protonation processes and the formation of $C_7H_7^+$ were found in all the reactions:



Here, the formation of $C_7H_7^+$ must proceed through either direct hydride abstraction from the methyl group or decomposition of adduct ions. The branching ratio of protonation process decreases with increasing the proton affinity: CH_4 (5.7 eV), C_2H_4 (7.1 eV), and C_3H_4 (8.0 eV). As minor product channels, the formation of $C_8H_9^+ = (M + CH)^+$ was found in the $C_3H_5^+/C_6H_5CH_3$ reaction:



where $\Delta H^\circ = 1.15 \text{ eV}$ for the formation of $C_6H_5CHCH_3^+$.

In the CI spectrum at a high CH_4 pressure, $(C_6H_5CH_3 + C_2H_5)^+$ and $(C_6H_5CH_3 + C_3H_5)^+$ adduct ions are found with branching ratios of 13.4 and 3.3%, respectively. The lack of them in this study led us to conclude that the $(C_6H_5CH_3 + C_2H_5)^+$ and $(C_6H_5CH_3 + C_3H_5)^+$ ions decompose completely into fragment ions at low CH_4 pressures, where secondary collisions with the CH_4 and He gases are unimportant. The initial adduct ions are formed by such a collisional stabilization process as (1) at a CH_4 pressure of 1 Torr, as reported by Munson and Field.³

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References and Notes

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