Chemical Ionization Mass Spectra of Benzene and Toluene at Low CH_4 Pressures

Masaharu Tsuji,* Erika Oda, and Yukio Nishimura
Institute of Advanced Material Study and Department of Molecular Science and Technology,
Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

(Received April 15, 1997; CL-970274)

Chemical ionization (CI) of benzene and toluene by the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions has been studied in an ion-trap type GC/MS at low CH_4 pressures. The main product ion from benzene was $C_6H_7^+$ for all the reactant ions, and that from toluene was $C_7H_9^+$ for the CH_5^+ and $C_2H_5^+$ ions, and $C_7H_7^+$ for the $C_3H_5^+$ ion. Initial adduct ions, which had been found in previous CI spectra at high CH_4 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 CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ are dominant reactant ions. CI mass spectra of benzene and toluene in a methane atmosphere have been measured by Munson and Field[3] 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 $(M + C_2H_5)^+$ and $(M + C_3H_5)^+$ were observed (Table 1). They predicted that these adduct ions are formed via collisional stabilization by the reactant CH_4 gas: e.g.,

$$C_2H_5^+ + M + CH_4 \rightarrow MC_2H_5^+ + CH_4. \qquad (1)$$
$$(M = C_6H_6 \text{ or } C_6H_5CH_3)$$

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 CH_4 pressures in order to determine initial product ion distributions at thermal energies. Although reactant ions produced from CH_4 have not been separated in the previous measurements,[3] CI mass spectra due to the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ 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 CH_4 in the ion-trap cell were 5×10^{-5} and 7×10^{-5} Torr, respectively. The reactant ions produced by electron-impact ionization of CH_4 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/cm^3 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 Field[3] at a CH_4 pressure of 1 Torr. In the present study, only protonated benzene cation with m/Z = 79 is found in the CH_5^+/C_6H_6 reaction:

$$CH_5^+ + C_6H_6 \rightarrow C_6H_7^+ + CH_4 + 2.15\ \text{eV}, \qquad (2)$$

where ΔH° value is calculated using reported thermochemical data.[4] On the other hand, in addition to protonated benzene cation, a small amount of $C_7H_7^+$ with m/Z = 91 is found in the $C_2H_5^+/C_6H_6$ and $C_3H_5^+/C_6H_6$ reactions:

$$\begin{aligned} C_2H_5^+ + C_6H_6 &\rightarrow C_6H_7^+ + C_2H_4 + 0.83\ \text{eV}, && (3a)\\ &\rightarrow C_7H_7^+(\text{benzyl}) + CH_4 + 1.68\ \text{eV}, && (3b)\\ &\rightarrow C_7H_7^+(\text{tropylium}) + CH_4 + 2.20\ \text{eV}. && (3b') \end{aligned}$$

$$\begin{aligned} &C_3H_5^+(A) + C_6H_6 \\ &\qquad \rightarrow C_6H_7^+ + C_3H_4 - 0.16\ \text{eV}, && (4a)\\ &\qquad \rightarrow C_7H_7^+(\text{benzyl}) + C_2H_4 + 0.79\ \text{eV}, && (4b)\\ &\qquad \rightarrow C_7H_7^+(\text{tropylium}) + C_2H_4 + 1.31\ \text{eV}. && (4b')\\ &C_3H_5^+(B) + C_6H_6 \rightarrow C_6H_7^+ + C_3H_4 + 0.10\ \text{eV}. && (4c)\\ &C_3H_5^+(C) + C_6H_6 \rightarrow C_6H_7^+ + C_3H_4 + 0.21\ \text{eV}. && (4d) \end{aligned}$$

Here, $C_3H_5^+(A)$ represents the $CH_2{=}CHCH_2^+$ ion with ΔH° = 946 kJ/mol, while $C_3H_5^+(B)$ and $C_3H_5^+(C)$ are $CH_3C{=}CH_2^+$ 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 (CH_4 reactant)

	C_6H_6				$C_6H_5CH_3$			
	This work			Ref. 3[a]	This work			Ref. 3
Product ions[b]	CH_5^+	$C_2H_5^+$	$C_3H_5^+$		CH_5^+	$C_2H_5^+$	$C_3H_5^+$	
$(M + C_3H_7)^+$				0.0030				0.0038
$(M + C_3H_5)^+$				0.030				0.033
$(M + C_2H_5)^+$				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

[a] CH_4 pressure: 1 Torr, Reactant ions: CH_5^+(48%), $C_2H_5^+$(40%), $C_3H_5^+$(6%), $C_2H_4^+$(2%), and $C_3H_7^+$(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:

$$C_2H_5^+ + C_6H_6 + CH_4 \rightarrow C_6H_6C_2H_5^+ + CH_4. \quad (5a)$$

$$C_2H_5^+ + C_6H_6 \rightarrow C_6H_6C_2H_5^+ + h\nu. \quad (5b)$$

$$C_3H_5^+ + C_6H_6 + CH_4 \rightarrow C_6H_6C_3H_5^+ + CH_4. \quad (6a)$$

$$C_3H_5^+ + C_6H_6 \rightarrow C_6H_6C_3H_5^+ + h\nu'. \quad (6b)$$

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:

$$CH_5^+ + C_6H_6 \rightarrow C_6H_5^+ + CH_4 + H_2 - 0.68\ \text{eV}. \quad (7)$$

$$C_2H_5^+ + C_6H_6 \rightarrow C_6H_5^+ + C_2H_6 - 0.60\ \text{eV}. \quad (8)$$

$$C_3H_5^+(A) + C_6H_6 \rightarrow C_6H_5^+ + C_3H_6 - 0.81\ \text{eV}. \quad (9)$$

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

$$\begin{aligned} &CH_5^+ + C_6H_5CH_3 \\ &\quad\rightarrow HC_6H_5CH_3^+ + CH_4 + 2.51\ \text{eV}. &(10a)\\ &\quad\rightarrow C_7H_7^+(\text{benzyl}) + CH_4 + H_2 + 1.33\ \text{eV}. &(10b)\\ &\quad\rightarrow C_7H_7^+(\text{tropylium}) + CH_4 + H_2 + 1.86\ \text{eV}. &(10b')\end{aligned}$$

$$\begin{aligned} &C_2H_5^+ + C_6H_5CH_3 \\ &\quad\rightarrow HC_6H_5CH_3^+ + C_2H_4 + 1.18\ \text{eV}. &(11a)\\ &\quad\rightarrow C_7H_7^+(\text{benzyl}) + C_2H_6 + 1.42\ \text{eV}, &(11b)\\ &\quad\rightarrow C_7H_7^+(\text{tropylium}) + C_2H_6 + 1.94\ \text{eV}. &(11b')\end{aligned}$$

$$\begin{aligned} &C_3H_5^+(A) + C_6H_5CH_3 \\ &\quad\rightarrow HC_6H_5CH_3^+ + C_3H_4 + 0.19\ \text{eV}. &(12a)\\ &\quad\rightarrow C_7H_7^+(\text{benzyl}) + C_3H_6 + 1.21\ \text{eV}, &(12b)\\ &\quad\rightarrow C_7H_7^+(\text{tropylium}) + C_3H_6 + 1.73\ \text{eV}. &(12b')\end{aligned}$$

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:

$$C_3H_5^+(A) + C_6H_5CH_3 \rightarrow C_8H_9^+ + C_2H_4, \quad (13)$$

where $\Delta H^\circ = 1.15$ 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 Munsòn and Field.[3]

The authors acknowledge financial support from the Mitsubishi Foundation (1996) and a Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (Nos. 06453026 and 09440201).

References and Notes

1 F. H. Field, *Acc. Chem. Res.*, **1**, 42 (1968).

2 J. R. Chapman, "Practical Organic Mass Spectrometry," 2nd Ed., A Guide for Chemical and Biochemical Analysis, Wiley, New York (1993).

3 M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **89**, 1047 (1968).

4 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).

5 G. Weddle and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Processses*, **134**, 73 (1994).