Chemical Ionization of *n*-Paraffins (C_{14}-C_{18}) by CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ in an Ion-Trap Type of Mass Spectrometer

Masaharu Tsuji,* Yuki Tanaka,† Takeshi Arikawa,† and Yukio Nishimura
Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816-8580
†*Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580*

(Received September 1, 1999; CL-990756)

Chemical ionization of *n*-paraffins (C_nH_{2n+2}:n=14~18) by the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions has been studied using an ion-trap type of GC/MS under a reactant-ion-selected mode. In all the reactions, $C_nH_{2n+1}^+$ and $C_mH_{2m+1}^+$ (m=3~n-3) ions were observed. The most favorable fragment $C_mH_{2m+1}^+$ ion in the CH_5^+ reaction was m = 8, while that in the $C_2H_5^+$ and $C_3H_5^+$ reactions was m = n-5 or n-6.

Chemical ionization (CI) mass spectra in a methane atmosphere provide valuable information on the reactivity of carbocations in the gas phase. Field *et al.*[1,2] measured CH_4 CI mass spectra of *n*-paraffins (C_nH_{2n+2}:n=8~28) at a CH_4 pressure of 1 Torr (= 133 Pa), where dominant reactant ions were CH_5^+(48%), $C_2H_5^+$(40%), and $C_3H_5^+$(6%). They observed $(M-1)^+=C_nH_{2n+1}^+$ and fragment alkyl $C_mH_{2m+1}^+$ (m=3~n-1) ions. On the basis of later isotopic studies using an ion-cyclotron-resonance spectrometer,[3] it was demonstrated that these ions were formed through the following pathways.

$$CH_5^+ + C_nH_{2n+2} \xrightarrow{-CH_4} [C_nH_{2n+3}^+] \begin{array}{l} \nearrow C_nH_{2n+1}^+ + H_2 \qquad\qquad\qquad\quad (1a) \\ \searrow C_mH_{2m+1}^+ + C_{(n-m)}H_{2(n-m)+2} \quad (1b) \end{array}$$

$$C_2H_5^+ + C_nH_{2n+2} \xrightarrow{-C_2H_6} C_nH_{2n+1}^+ \rightarrow C_mH_{2m+1}^+ + C_{(n-m)}H_{2(n-m)} \quad (2)$$

More recently, Dorey[4] measured CH_4 CI mass spectra of *n*-$C_{14}H_{30}$ at a low CH_4 gas pressure of 10^{-5} Torr in an ion trap detector (ITD) and found that the extent of fragmentation was much higher than that in the high-pressure CI spectrum obtained by Field *et al.*[1,2] Since no appreciable collisional cooling of reactant ions was found during the residence time of 1-100 ms, the increased fragmentation was explained as a consequence of the high kinetic energy of reactant ions in the ITD. Since previous high- and low-pressure CH_4 CI mass spectra reported by Field *et al.*[1,2] and Dorey[4] have been measured without separation of the reactant ions, the reactivity of each reactant ion for *n*-paraffins has not been determined.

In this study, CH_4 CI mass spectra of five typical *n*-paraffins (C_nH_{2n+2}:n=14~18) were measured by separating reactant CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions under an ion-trap type of GC/MS. The dependence of product-ion distributions on the residence time was measured and compared with the previous data of Field *et al.*[1,2] and Dorey[4] in order to examine the effects of collisional stabilization and the kinetic energy of reactant ions. The reactivity of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ for *n*-paraffins was discussed from the product-ion distributions.

CH_4 CI mass spectra were obtained using an ion-trap type of Hitachi M7200 GC/MS under a reactant-ion-selected mode. The ion-trap cell was kept at ≤170 °C. The reagents were diluted in hexane 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 time for storing a selected reactant ion was 5 ms and the reaction time between the reactant ion and *n*-paraffins was varied in the 0.2-100 ms region. The total number of collisions of a reactant ion with He and CH_4 was about 0.5-240 times during these reaction times. The total number of collisions in the high-pressure CI experiments of Field *et al.*[1,2] was about 200 times during a residence time of 10^{-5} s at a CH_4 gas pressure of 1 Torr.

As an example, Figures 1(a)-1(c) show CI mass spectra of *n*-$C_{18}H_{38}$ obtained by the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ reactions at a reaction time of 20 ms. In all the spectra, $C_nH_{2n+1}^+ = C_{18}H_{37}^+$ and fragment $C_mH_{2m+1}^+$ (m=3~n-3) ions were observed. Responsible formation processes for these ions in the CH_5^+ and $C_2H_5^+$ reactions were expected to be (1a), (1b), and (2). It

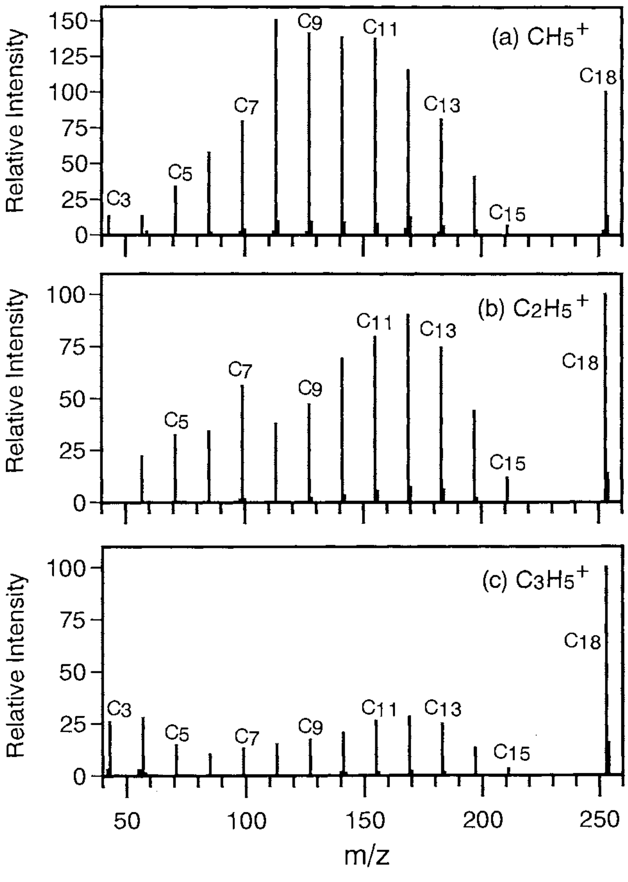

Figure 1. CH_4 CI mass spectra of *n*-$C_{18}H_{38}$.

should be noted that the intensity distributions of $C_nH_{2n+1}^+$ and $C_mH_{2m+1}^+$ (m=3~n-3) strongly depend on the reactant ion. The branching ratios of $C_nH_{2n+1}^+$ in the total product ions were 10, 15, and 29% for the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ reactions, respectively. The $C_mH_{2m+1}^+$ (m=3~n-3) ions were observed as a single modal distribution with the most intense peak at m=8 in the CH_5^+ reaction. On the other hand, the $C_mH_{2m+1}^+$ (m=4~n-3) ions having a bimodal distribution with peaks at m=7 and 12 and the $C_mH_{2m+1}^+$ (m=3~n-3) ions having a bimodal distribution with peaks at m=4 and 12 were observed in the $C_2H_5^+$ and $C_3H_5^+$ reactions, respectively.

The CI mass spectra of the other *n*-paraffins (n=14~17) by the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ reactions were composed of similar $C_nH_{2n+1}^+$ and $C_mH_{2m+1}^+$ (m=3~n-3) peaks, indicating that the reactivity of the three ions was similar for *n*-paraffins with n=14~18. Figures 2(a)-2(c) show the distributions of $C_mH_{2m+1}^+$ produced from the reactions of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with the five *n*-paraffins. The product-ion distributions in CI mass spectra of *n*-paraffins (n=14~18) were essentially independent of the reaction time in the 0.2-100 ms region. It was therefore concluded that the collisional stabilization was insignificant for the formation of $C_nH_{2n+1}^+$ and $C_mH_{2m+1}^+$ ions under these operating conditions. This finding is consistent with a previous result of Dorey[4] for *n*-$C_{14}H_{30}$ in a similar ITD.

The extent of fragmentation of *n*-paraffins was higher than that in high-pressure CI mass spectra of Field *et al.*[1,2] Although Field *et al.* observed the $C_mH_{2m+1}^+$ (m=4~n) ions, the large $C_mH_{2m+1}^+$ (m=n-2 and n-1) ions could not be detected in any spectra in this study. They found that the variation in intensities of $C_mH_{2m+1}^+$ was quite small except for the large intensity of $C_nH_{2n+1}^+$. However, we found here that the variation in intensities of $C_mH_{2m+1}^+$ was large and that the intensity distributions of $C_mH_{2m+1}^+$ strongly depended on the reactant hydrocarbon ions. No appreciable change in the product-ion distributions during the reaction time of 0.2-100 ms suggested that the higher extent of fragmentation observed here did not arise from the collisional stabilization, but it originated from the difference in the kinetic energy of reactant ions. The maximum and average kinetic energies of 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.[5] These energies are higher than those in the high-pressure CI experiments, which were estimated to be less than 1 eV.[6] The extent of fragmentation for n-$C_{14}H_{30}$ in the three reactions was lower than that in low-pressure CI mass spectra of Dorey,[4] where $C_mH_{2m+1}^+$ had a peak at m=5. This shows that the kinetic energy of reactant ions in this work is lower than that in his work using a similar ITD.

The following general tendencies are obtained from Figures 2(a)-2(c). (1) In the CH_5^+ reaction, the $C_mH_{2m+1}^+$ (m=3~n-3) ions were observed. The intensity distributions had a single peak at m=8 for all the reactions. Although the intensity distributions of m=3~8 were nearly the same, those for m>9 decreased more rapidly with decreasing n of *n*-paraffin. (2) In the $C_2H_5^+$ reaction, the $C_mH_{2m+1}^+$ (m=4~n-3) ions were observed. The intensity distributions had double peaks at m=7 and n-5 or n-6. With increasing n of reagent, the lower mass peak decreased, while the higher one shifted to high mass number. (3) In the $C_3H_5^+$ reaction, the $C_mH_{2m+1}^+$ (m=3~n-3) ions were observed. The intensity distributions had double peaks at m=4 and n-5 or n-6. With increasing n of reagent, the lower mass peak increased, while the higher one shifted to high mass number. Since the fragmentation pattern in the $C_3H_5^+$ reaction was similar to that in the $C_2H_5^+$ reaction, the responsible formation processes of $C_mH_{2m+1}^+$ in the $C_3H_5^+$ reaction would be similar to those in the $C_2H_5^+$ reaction.

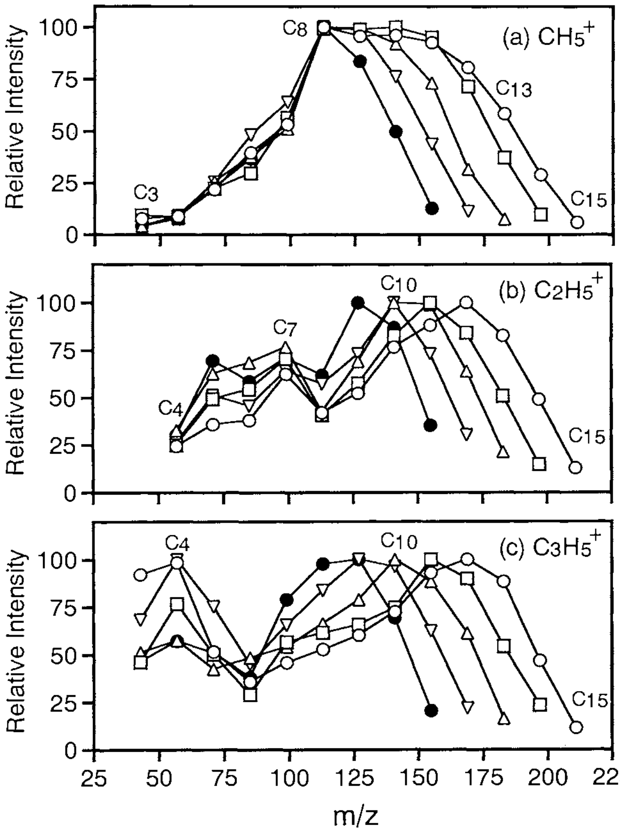

Figure 2. Intensity distributions of $C_mH_{2m+1}^+$ in the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ reactions. ○:$C_{18}H_{38}$, □:$C_{17}H_{36}$, △:$C_{16}H_{34}$, ▽:$C_{15}H_{32}$, ●:$C_{14}H_{30}$.

The most outstanding features obtained for the formation of $C_mH_{2m+1}^+$ were that the same $C_8H_{17}^+$ ion, accompanied by elimination of different neutral C_mH_{2m+2} alkanes (m=6~10), was most favorable in the CH_5^+ reactions, while the different $C_mH_{2m+1}^+$ (m=n-5 or n-6) ions, accompanied by elimination of similar neutral C_mH_{2m} alkenes (m=5 or 6), were most favorable in the $C_2H_5^+$ and $C_3H_5^+$ reactions. We are planning to make further experimental and theoretical studies in order to clarify the origin of the above tendencies.

References and Notes

1 F. H. Field, M. S. B. Munson, and D. A. Becker, "Advances in Chemistry Series," No. 58, American Chemical Society, Washington, D. C. (1966), pp. 167-192.

2 M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

3 R. Houriet, G. Parisod, and T. Gäumann, *J. Am. Chem. Soc.*, **99**, 3599 (1977).

4 R. C. Dorey, *Org. Mass Spectrom.*, **24**, 973 (1989).

5 J. F. J. Todd, R. M. Waldren, and R. F. Bonner, *Int. J. Mass Spectrom. Ion Phys.*, **34**, 17 (1980).

6 C. Chang, G. G. Meisels, and J. A. Taylor, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 411 (1973).