

# Mass-Spectroscopic Studies on Ion-Molecule Reactions of $\text{Ar}_2^+$ , $\text{N}_3^+$ , and $\text{N}_4^+$ Cluster Ions with Simple Aliphatic Hydrocarbons at Thermal Energy

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Ion-molecule reactions of  $\text{Ar}_2^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$  cluster ions with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  have been studied by using a thermal ion-beam apparatus. Rate constants were determined and compared with those obtained from Langevin theory. Rate constants of the  $\text{Ar}_2^+ + \text{C}_2\text{H}_2$ ,  $\text{Ar}_2^+ + \text{C}_2\text{H}_4$ , and  $\text{N}_3^+ + \text{C}_2\text{H}_6$  reactions, which have not been measured, were determined to be 1.4, 8.1, and  $3.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively. These values correspond to 14%, 74%, and 28% of calculated rate constants from Langevin theory, respectively.

**Key words:**  $\text{Ar}_2^+$  ion,  $\text{N}_3^+$  ion,  $\text{N}_4^+$  ion, Aliphatic hydrocarbon, Thermal ion-beam apparatus, Rate constant, Langevin theory

## 1. Introduction

Gas phase ion-molecule reactions at thermal energy have been studied extensively by using flowing afterglow (FA), selected ion flow tube (SIFT), and ion trapping methods for use in modeling the chemistry of gas discharge plasma, planetary atmospheres, and interstellar clouds. Anicich<sup>1)</sup> compiled product ion distributions and reaction rate constants of bimolecular ion-molecule reactions over 2,300 references in 2003.<sup>1)</sup>

We have previously made a systematic mass-spectroscopic studies on ion-molecule reactions of  $\text{Ar}^+$ ,  $\text{ArN}_2^+$ , and  $\text{CO}_2^+$  with simple aliphatic hydrocarbons using a thermal ion-beam apparatus.<sup>2-8)</sup> Reaction mechanisms were discussed from product ion distributions and reaction rate constants.

In this study, ion-molecule reactions of  $\text{Ar}_2^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$  cluster ions with such simple aliphatic hydrocarbons as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  are investigated by using a thermal ion-beam apparatus. Total reaction rate constants

are determined and compared with those obtained from Langevin theory.

## 2. Experimental

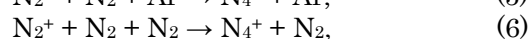
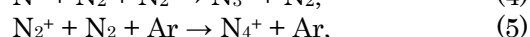
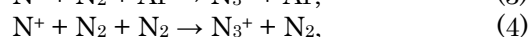
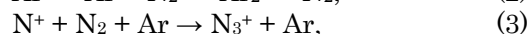
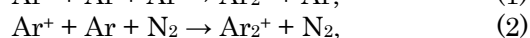
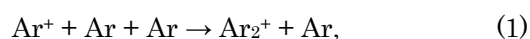
The thermal ion-beam apparatus used in this study was essentially the same as that reported previously.<sup>2,7)</sup> The apparatus consisted of a FA ion source, a low-pressure reaction chamber, and a quadrupole mass spectrometer. The ground-state  $\text{Ar}^+(^2P_{3/2})$  ions and metastable  $(\text{Ar}^+)^*$  ions were generated by a 2.45 GHz microwave discharge of high purity Ar gas in a quartz flow tube, and  $\text{N}_2$  was added about 10 cm downstream from the center of the discharge. The product ions were then expanded into an interaction chamber through a nozzle centered on the flow tube axis. At low Ar buffer gas pressures,  $\text{Ar}^+$  and  $\text{N}_2^+$  were found as reactant ions, whereas besides these ions,  $\text{Ar}_2^+$ ,  $\text{ArN}_2^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$  cluster ions were observed at high Ar buffer gas pressures by the following bi-molecular and ter-molecular reactions.

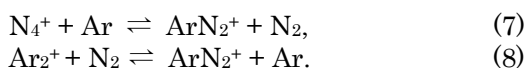
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Since the reactions of  $\text{Ar}^+$ ,  $\text{N}_2^+$ , and  $\text{ArN}_2^+$  with aliphatic hydrocarbons at thermal energy have already been studied,<sup>1,4,5,7,8)</sup> the present study focuses on the reactions of  $\text{Ar}_2^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$  cluster ions with aliphatic hydrocarbons.

The sample gas was kept at a constant mass flow and injected into the reaction chamber from a stainless-steel orifice placed 5 cm downstream from the nozzle. The reactant and product ions were sampled through a molybdenum orifice (2 mm in diameter) placed 3 cm further downstream and analyzed using a quadrupole mass spectrometer. The mass spectra were averaged using a digital storage oscilloscope and the data were stored in a microcomputer. Typical operating pressures were 1.5 Torr (1 Torr = 133.3 Pa) in the FA

ion-source chamber,  $3 \times 10^{-3}$  Torr in the reaction chamber, and  $2 \times 10^{-5}$  Torr in the mass analyzing chamber. The partial pressures of the sample gases in the reaction chamber were less than  $1 \times 10^{-5}$  Torr.

### 3. Results and Discussion

#### 3.1 Mass spectra obtained before and after addition of reagent aliphatic hydrocarbons

Figures 1(a)–4(a) show typical mass spectra observed before addition of reagent gases, where  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{N}_3^+$ ,  $\text{N}_4^+$ ,  $\text{ArN}_2^+$ , and  $\text{Ar}_2^+$  ions are observed. The relative concentrations of  $[\text{N}_2^+]$ ,  $[\text{Ar}^+]$ , and  $[\text{ArN}_2^+]$  ions are much higher than those of  $[\text{N}_3^+]$ ,  $[\text{N}_4^+]$  and  $[\text{Ar}_2^+]$  ions in our conditions. Figures 1(b)–4(b) show mass spectra obtained after addition of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ , respectively, where the following primary and secondary product ions

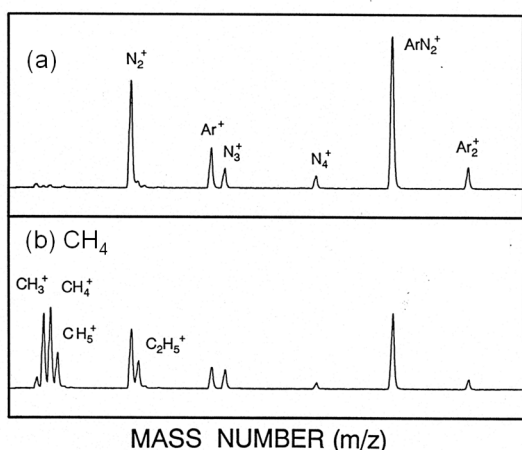


Fig. 1. Mass spectra obtained (a) before and (b) after  $\text{CH}_4$  addition.

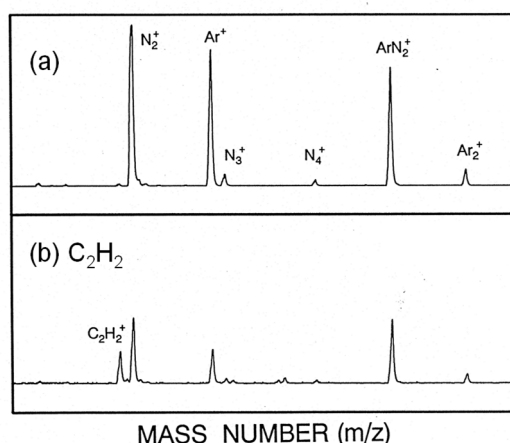


Fig. 2. Mass spectra obtained (a) before and (b) after  $\text{C}_2\text{H}_2$  addition.

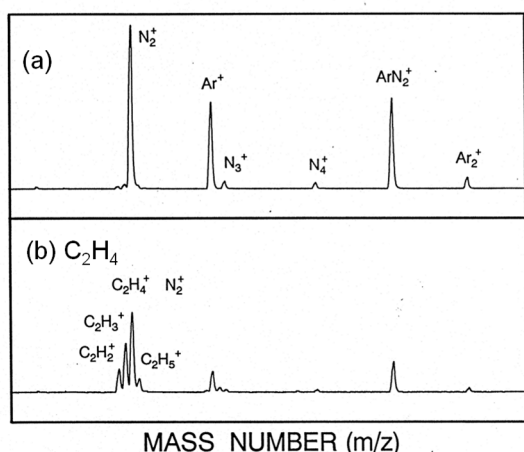


Fig. 3. Mass spectra obtained (a) before and (b) after  $\text{C}_2\text{H}_4$  addition.

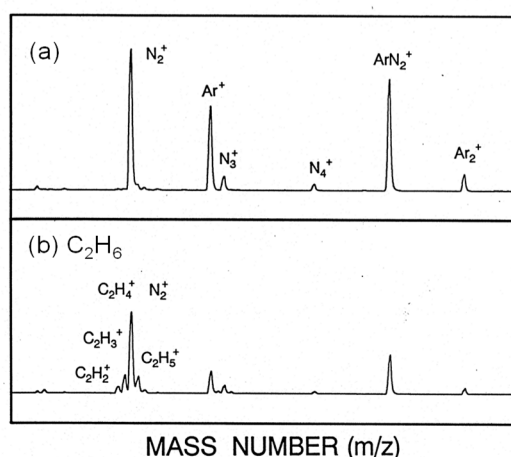
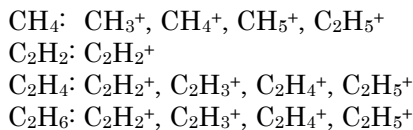


Fig. 4. Mass spectra obtained (a) before and (b) after  $\text{C}_2\text{H}_6$  addition.

are detected for each reagent:



These products ions are dominantly formed by the ion-molecule reactions of major  $\text{N}_2^+$ ,  $\text{Ar}^+$ , and  $\text{ArN}_2^+$  ions with the above four aliphatic hydrocarbons, denoted as  $\text{C}_m\text{H}_n$ .

### 3.2 Rate constants of ion-molecule reactions of $\text{Ar}_2^+$ , $\text{N}_3^+$ , and $\text{N}_4^+$ cluster ions with simple aliphatic hydrocarbons

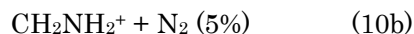
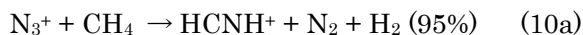
Total rate constants  $k_{\text{C}_m\text{H}_n}(\text{R}^+)$  are determined from the decay of reactant ions, which is governed by the pseudo-first-order rate law.

$$I(\text{R}^+) = I_0(\text{R}^+) \exp(-k_{\text{C}_m\text{H}_n}(\text{R}^+) [\text{C}_m\text{H}_n] t) \quad (9)$$

Here,  $I_0(\text{R}^+)$  represents the initial  $\text{R}^+$  ion current and  $t$  is the reaction time. Because of the difficulty in evaluating the accurate  $t$  value, the  $k_{\text{C}_m\text{H}_n}(\text{R}^+)$  values are evaluated by reference to known rate constants of the  $\text{Ar}^+ + \text{C}_m\text{H}_n$  and  $\text{N}_2^+ + \text{C}_m\text{H}_n$  reactions,  $k_{\text{C}_m\text{H}_n}(\text{Ar}^+)$  and  $k_{\text{C}_m\text{H}_n}(\text{N}_2^+)$ .<sup>1)</sup>

Figures 5–8 show the decay of  $\text{ArN}_2^+$ ,  $\text{Ar}_2^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$  upon addition of  $\text{C}_m\text{H}_n$ . Satisfactory linearities are found, indicating that relation (9) holds for all cases. The rate constants obtained from slopes are summarized in Table 1. The accuracy of the present value

was estimated to be  $\pm 25\%$ . The  $k_{\text{obs}}$  values obtained in this study are in reasonable agreement with reported data except for the  $k_{\text{obs}}$  values for the reactions of  $\text{N}_3^+$  and  $\text{N}_4^+$  with  $\text{C}_2\text{H}_2$ . The  $k_{\text{obs}}$  values for the reactions of  $\text{N}_3^+$  and  $\text{N}_4^+$  with  $\text{C}_2\text{H}_2$  obtained in this study at low pressures ( $3 \times 10^{-3}$  Torr) are smaller than those of SIFT data<sup>1,9)</sup> at a He buffer gas pressure of 0.47 Torr by factors of 5.5 and 7.1, respectively. The stabilization of intermediates by collisions with third-body He atoms may enhance the reaction rate in the SIFT experiment. The  $k_{\text{obs}}$  values of the  $\text{Ar}_2^+ + \text{C}_2\text{H}_2$ ,  $\text{Ar}_2^+ + \text{C}_2\text{H}_4$ ,  $\text{N}_3^+ + \text{C}_2\text{H}_6$  reactions, which have not been measured, are determined to be 1.4, 8.1, and  $3.6 \times 10^{-10}$   $\text{cm}^3 \text{s}^{-1}$ , respectively. It should be noted that the  $k_{\text{obs}}$  value for the  $\text{N}_3^+ + \text{CH}_4$  reaction,  $4.5 \times 10^{-11}$   $\text{cm}^3 \text{s}^{-1}$  is small. Since the recombination energy of  $\text{N}_3^+$  (11.06 eV) is lower than the ionization energy of  $\text{CH}_4$  (12.61 eV), as shown in Table 1, the charge-transfer channel is energetically closed for the  $\text{N}_3^+ + \text{CH}_4$  reaction. Therefore, only the following  $\text{N}^+$  insertion product channels are open.<sup>1)</sup>



The small rate constant probably arises from an existence of relatively high energy barrier in the reaction pathway leading to the major  $\text{HCNH}^+$  ion from the  $(\text{N}_3 + \text{CH}_4)^+$  intermediate.

Total rate constants of thermal-energy ion-molecule reactions have been evaluated by using Langevin theory for nonpolar molecules

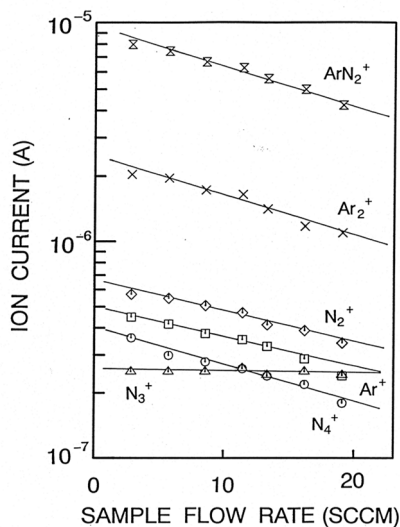


Fig. 5. Variation in the reactant ion currents with  $\text{CH}_4$  flow rate.

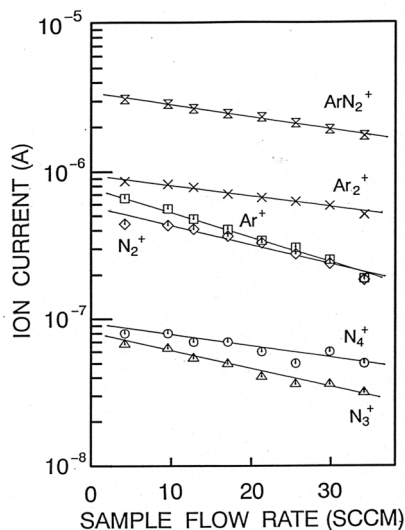


Fig. 6. Variation in the reactant ion currents with  $\text{C}_2\text{H}_2$  flow rate.

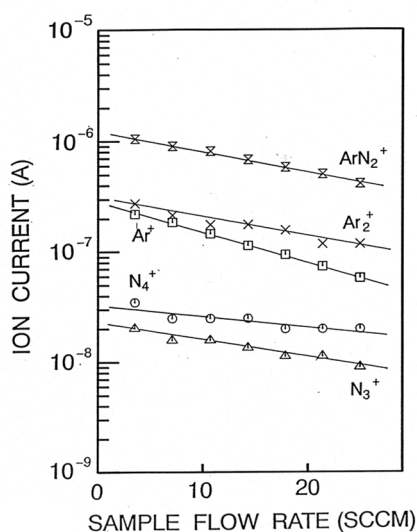


Fig. 7. Variation in the reactant ion currents with  $C_2H_4$  flow rate.

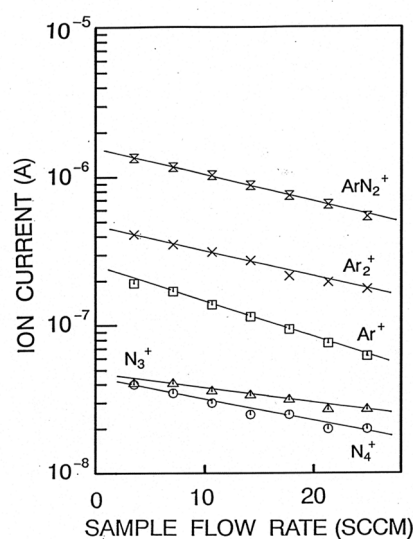


Fig. 8. Variation in the reactant ion currents with  $C_2H_6$  flow rate.

with small dipole moments,<sup>10)</sup>

$$k_L = 2\pi e(\alpha/\mu)^{1/2} \quad (11)$$

where  $e$ , the elementary charge,  $\alpha$ , the polarizability of the reagent, and  $\mu$ , the reduced mass of the ion-reagent pair. The  $\alpha$  values for aliphatic hydrocarbons used here are the same as reported previously.<sup>2)</sup> The ratio of the observed and calculated rate constants serves as a measure for the efficiency of a reaction. The  $k_{\text{obs}}/k_{\text{calc}}$  ratios are 0.52–1.3 in most cases, indicating that the ion-molecule reactions of

$Ar_2^+$ ,  $N_3^+$ , and  $N_4^+$  cluster ions with  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  occur efficiently. The  $k_{\text{obs}}/k_{\text{calc}}$  ratio for the  $N_3^+ + CH_4$  reaction is exceptionally small, 0.041. It may be due to the existence of some energy barrier along  $N^+$  insertion and rearrangement reaction pathway.

#### 4. Summary and Conclusion

Ion-molecule reactions of  $Ar_2^+$ ,  $N_3^+$ , and  $N_4^+$  cluster ions with  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  have been studied by using a thermal ion-beam apparatus. Rate constants were determined and compared with those obtained from

**Table 1.** Rate constants of ion-molecule reactions of  $Ar_2^+$ ,  $N_3^+$ , and  $N_4^+$  cluster ions with  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  at thermal energy

Reactant cluster ion	$Ar_2^+$ (14.46 eV) <sup>a)</sup>				$N_3^+$ (11.06 eV)				$N_4^+$ (14.51 eV)			
	$k_{\text{obs}}$		$k_{\text{calc}}$		$k_{\text{obs}}$		$k_{\text{calc}}$		$k_{\text{obs}}$		$k_{\text{calc}}$	
Reagents	$(\times 10^{-9} \text{ cm}^3 \text{ s}^{-1})$		$k_{\text{obs}}/k_{\text{calc}}$		$(\times 10^{-9} \text{ cm}^3 \text{ s}^{-1})$		$k_{\text{obs}}/k_{\text{calc}}$		$(\times 10^{-9} \text{ cm}^3 \text{ s}^{-1})$		$k_{\text{obs}}/k_{\text{calc}}$	
$CH_4$ (12.61 eV) <sup>b)</sup>	1.3	This work	1.0	1.3	0.045	This work	1.1	0.041	1.2	This work	1.1	1.1
	0.93	Ref. 1			0.058	Ref. 1			1.1	Ref. 1		
$C_2H_2$ (11.40 eV)	0.14	This work	0.97	0.14	0.22	This work	1.1	0.20	0.13	This work	1.0	1.3
					1.2	Ref. 1			0.92	Ref. 1		
$C_2H_4$ (10.51 eV)	0.81	This work	1.1	0.74	0.75	This work	1.3	0.58	0.62	This work	1.2	0.52
					1.1	Ref. 1			1.1	Ref. 1		
$C_2H_6$ (11.52 eV)	0.70	This work	1.1	0.64	0.36	This work	1.3	0.28	0.62	This work	1.2	0.52
	0.71	Ref. 1							1.24	Ref. 1		

a) Recombination energy

b) Ionization potential

Langevin theory. Rate constants of the  $\text{Ar}_2^+ + \text{C}_2\text{H}_2$ ,  $\text{Ar}_2^+ + \text{C}_2\text{H}_4$ , and  $\text{N}_3^+ + \text{C}_2\text{H}_6$  reactions, which have not been measured, were determined. The  $k_{\text{obs}}/k_{\text{calc}}$  ratios are 0.52–1.3 in most cases, indicating that the ion-molecule reactions of  $\text{Ar}_2^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$  cluster ions with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  occur efficiently.

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