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Mass-Spectroscopic Studies on Ion-Molecule Reactions of Ar_2^+, N_3^+, and N_4^+ Cluster Ions with Simple Aliphatic Hydrocarbons at Thermal Energy

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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 Langevin theory. Rate constants of the $Ar_2^+ + C_2H_2$, $Ar_2^+ + C_2H_4$, and $N_3^+ + C_2H_6$ reactions, which have not been measured, were determined to be 1.4, 8.1, and 3.6 × 10^{-10} cm^3 s^{-1}, respectively. These values correspond to 14%, 74%, and 28% of calculated rate constants from Langevin theory, respectively.

Key words: *Ar_2^+ ion, N_3^+ ion, 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[1] complied product ion distributions and reaction rate constants of bimolecular ion-molecule reactions over 2,300 references in 2003.[1]

We have previously made a systematic mass-spectroscopic studies on ion-molecule reactions of Ar^+, ArN_2^+, and CO_2^+ with simple aliphatic hydrocarbons using a thermal ion-beam apparatus.[2-8] Reaction mechanisms were discussed from product ion distributions and reaction rate constants.

In this study, ion-molecule reactions of Ar_2^+, N_3^+, and N_4^+ cluster ions with such simple aliphatic hydrocarbons as CH_4, C_2H_2, C_2H_4, and C_2H_6 are investigated by using a thermal ion-beam apparatus. Total reaction rate constants are determined and compared with those obtained from Langevin theory.

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2. Experimental

The thermal ion-beam apparatus used in this study was essentially the same as that reported previously.[2,7] The apparatus consisted of a FA ion source, a low-pressure reaction chamber, and a quadrupole mass spectrometer. The ground-state $Ar^+(^2P_{3/2})$ ions and metastable $(Ar^+)^*$ ions were generated by a 2.45 GHz microwave discharge of high purity Ar gas in a quartz flow tube, and 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, Ar^+ and N_2^+ were found as reactant ions, whereas besides these ions, Ar_2^+, ArN_2^+, N_3^+, and N_4^+ cluster ions were observed at high Ar buffer gas pressures by the following bi-molecular and ter-molecular reactions.

$$Ar^+ + Ar + Ar \rightarrow Ar_2^+ + Ar, \quad (1)$$
$$Ar^+ + Ar + N_2 \rightarrow Ar_2^+ + N_2, \quad (2)$$
$$N^+ + N_2 + Ar \rightarrow N_3^+ + Ar, \quad (3)$$
$$N^+ + N_2 + N_2 \rightarrow N_3^+ + N_2, \quad (4)$$
$$N_2^+ + N_2 + Ar \rightarrow N_4^+ + Ar, \quad (5)$$
$$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2, \quad (6)$$

$N_4^+ + Ar \rightleftharpoons ArN_2^+ + N_2$, (7)

$Ar_2^+ + N_2 \rightleftharpoons ArN_2^+ + Ar$. (8)

Since the reactions of Ar^+, N_2^+, and ArN_2^+ with aliphatic hydrocarbons at thermal energy have already been studied,[1,4,5,7,8] the present study focuses on the reactions of Ar_2^+, N_3^+, and 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, 3×10^{-3} Torr in the reaction chamber, and 2×10^{-5} Torr in the mass analyzing chamber. The partial pressures of the sample gases in the reaction chamber were less than 1×10^{-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 N_2^+, Ar^+, N_3^+, N_4^+, ArN_2^+, and Ar_2^+ ions are observed. The relative concentrations of [N_2^+], [Ar^+], and [ArN_2^+] ions are much higher than those of [N_3^+], [N_4^+] and [Ar_2^+] ions in our conditions. Figures 1(b)–4(b) show mass spectra obtained after addition of CH_4, C_2H_2, C_2H_4, and C_2H_6, respectively, where the following primary and secondary product ions

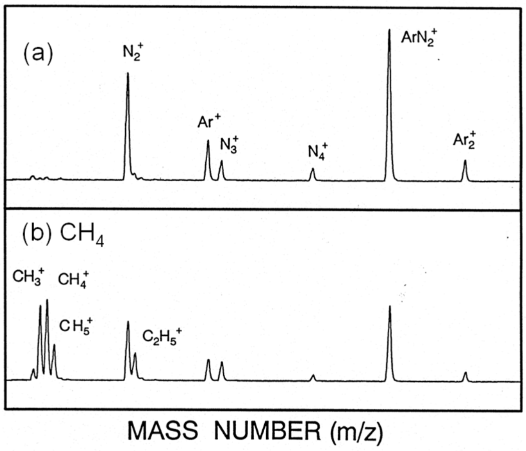

Fig. 1. Mass spectra obtained (a) before and (b) after CH_4 addition.

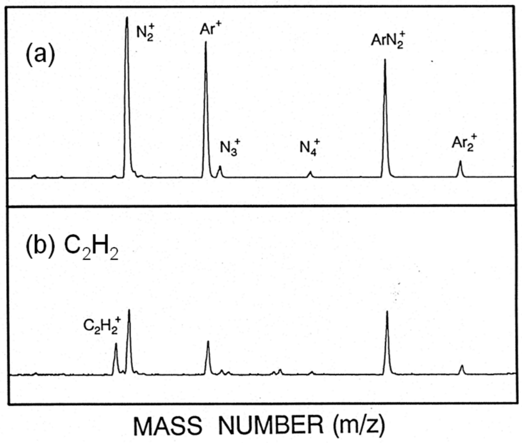

Fig. 2. Mass spectra obtained (a) before and (b) after C_2H_2 addition.

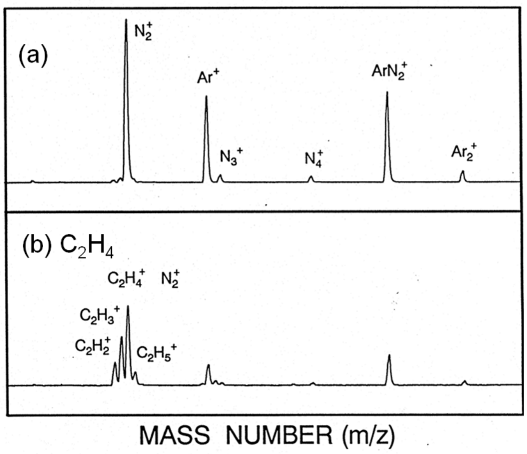

Fig. 3. Mass spectra obtained (a) before and (b) after C_2H_4 addition.

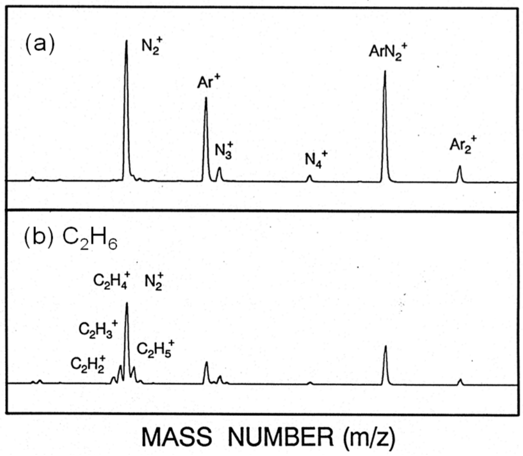

Fig. 4. Mass spectra obtained (a) before and (b) after C_2H_6 addition.

are detected for each reagent:

CH_4: CH_3^+, CH_4^+, CH_5^+, $C_2H_5^+$
C_2H_2: $C_2H_2^+$
C_2H_4: $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$
C_2H_6: $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$

These products ions are dominantly formed by the ion-molecule reactions of major N_2^+, Ar^+, and ArN_2^+ ions with the above four aliphatic hydrocarbons, denoted as C_mH_n.

3.2 Rate constants of ion-molecule reactions of Ar_2^+, N_3^+, and N_4^+ cluster ions with simple aliphatic hydrocarbons

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

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

Here, $I_0(R^+)$ represents the initial R^+ ion current and t is the reaction time. Because of the difficulty in evaluating the accurate t value, the $k_{\mathrm{C}_m\mathrm{H}_n}(R^+)$ values are evaluated by reference to known rate constants of the Ar^+ + C_mH_n and N_2^+ + C_mH_n reactions, $k_{\mathrm{C}_m\mathrm{H}_n}(\mathrm{Ar}^+)$ and $k_{\mathrm{C}_m\mathrm{H}_n}(\mathrm{N}_2^+)$.[1)]

Figures 5–8 show the decay of ArN_2^+, Ar_2^+, N_2^+, Ar^+, N_3^+, and N_4^+ upon addition of C_mH_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 ±25%. The k_{obs} values obtained in this study are in reasonable agreement with reported data except for the k_{obs} values for the reactions of N_3^+ and N_4^+ with C_2H_2. The k_{obs} values for the reactions of N_3^+ and N_4^+ with C_2H_2 obtained in this study at low pressures (3×10^{-3} Torr) are smaller than those of SIFT data[1,9)] 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_{obs} values of the Ar_2^+ + C_2H_2, Ar_2^+ + C_2H_4, N_3^+ + C_2H_6 reactions, which have not been measured, are determined to be 1.4, 8.1, and 3.6×10^{-10} $cm^3\ s^{-1}$, respectively. It should be noted that the k_{obs} value for the N_3^+ + CH_4 reaction, 4.5×10^{-11} $cm^3\ s^{-1}$ is small. Since the recombination energy of N_3^+ (11.06 eV) is lower than the ionization energy of CH_4 (12.61 eV), as shown in Table 1, the charge-transfer channel is energetically closed for the N_3^+ + CH_4 reaction. Therefore, only the following N^+ insertion product channels are open.[1)]

$$N_3^+ + CH_4 \rightarrow HCNH^+ + N_2 + H_2\ (95\%) \quad (10a)$$
$$CH_2NH_2^+ + N_2\ (5\%) \quad (10b)$$

The small rate constant probably arises from an existence of relatively high energy barrier in the reaction pathway leading to the major $HCNH^+$ ion from the $(N_3 + CH_4)^+$ intermediate.

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

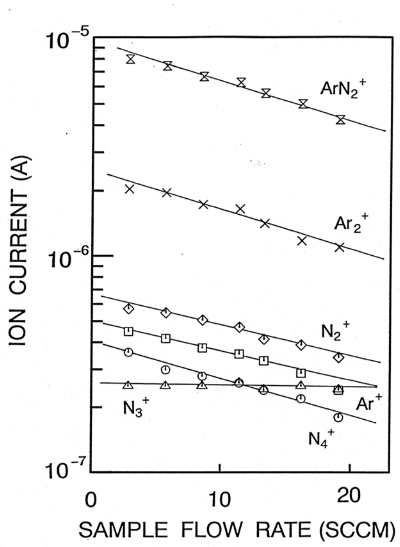

Fig. 5. Variation in the reactant ion currents with CH_4 flow rate.

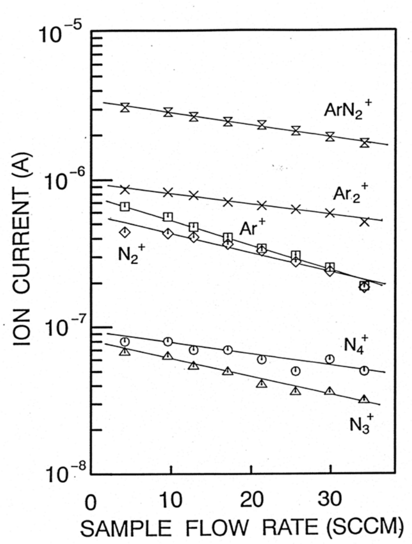

Fig. 6. Variation in the reactant ion currents with C_2H_2 flow rate.

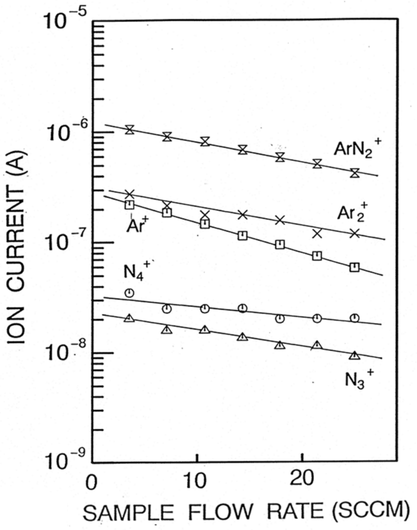

Fig. 7. Variation in the reactant ion currents with C_2H_4 flow rate.

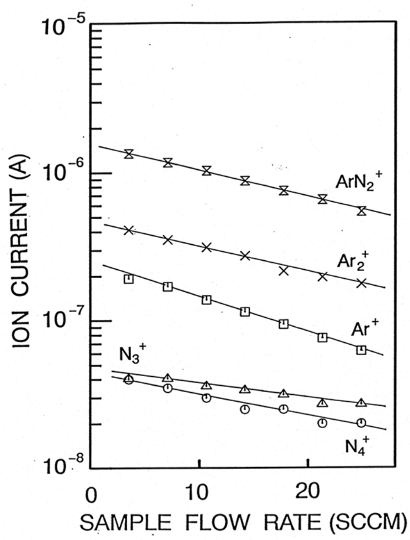

Fig. 8. Variation in the reactant ion currents with C_2H_6 flow rate.

with small dipole moments,[10)]

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

where e, the elementary charge, α, the polarizability of the reagent, and μ, the reduced mass of the ion-reagent pair. The α values for aliphatic hydrocarbons used here are the same as reported previously.[2)] The ratio of the observed and calculated rate constants serves as a measure for the efficiency of a reaction. The k_{obs}/k_{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_{obs}/k_{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)[a)]				N_3^+ (11.06 eV)				N_4^+ (14.51 eV)			
Reagents	k_{obs} (× 10^{-9} cm^3 s^{-1})		k_{calc}	k_{obs}/k_{calc}	k_{obs} (× 10^{-9} cm^3 s^{-1})		k_{calc}	k_{obs}/k_{calc}	k_{obs} (× 10^{-9} cm^3 s^{-1})		k_{calc}	k_{obs}/k_{calc}
CH_4	1.3	This work	1.0	1.3	0.045	This work	1.1	0.041	1.2	This work	1.1	1.1
(12.61 eV)[b)]	0.93	Ref. 1			0.058	Ref. 1			1.1	Ref. 1		
					0.048	Ref. 1						
C_2H_2	0.14	This work	0.97	0.14	0.22	This work	1.1	0.20	0.13	This work	1.0	1.3
(11.40 eV)					1.2	Ref. 1			0.92	Ref. 1		
C_2H_4	0.81	This work	1.1	0.74	0.75	This work	1.3	0.58	0.62	This work	1.2	0.52
(10.51 eV)					1.1	Ref. 1			1.1	Ref. 1		
C_2H_6	0.70	This work	1.1	0.64	0.36	This work	1.3	0.28	0.62	This work	1.2	0.52
(11.52 eV)	0.71	Ref. 1							1.24	Ref. 1		

a) Recombination energy
b) Ionization potential

Langevin theory. Rate constants of the Ar_2^+ + C_2H_2, Ar_2^+ + C_2H_4, and N_3^+ + C_2H_6 reactions, which have not been measured, were determined. The k_{obs}/k_{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.

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