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Studies on Fragment Ion Distribution and Reactions by the Use of a Charge Spectrometer. III. Reactivities of the Excited Ions from Methylamine after Charge Exchange with Positive Ions

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The behavior of the excited ions produced by positive ion impact in methylamine has been studied in the reaction chamber of a double mass spectrometer at elevated pressure. The ion-molecule reactions have been discussed for three energy regions. Metastable transitions taking place in the reaction chamber and in the Giese lens have also been studied in the corresponding regions.

Ordinary mass spectrometry deals with cases in which molecular ions or their fragment ions initially produced in the ionization chamber collide with sample gases and form secondary or tertiary products when gas pressure is enhanced. Studies have been carried out on these phenomena using electron impact but only a few have been made using positive ion impact.[1,2,3]

Positive ions accelerated to the order of kilo electron volt are extremely useful for charge exchange reactions with neutral molecules.[4] If the reaction chamber is filled with methylamine, the fragment ions from the excited molecular ions after charge exchange with the positive ions react with methylamine having kinetic energy given by the repeller voltage.

This paper deals with the reaction of the ionic species which are pulled in the second optical system and various processes of ion-molecule reactions in the reaction chamber of the charge spectrometers. Flying ions in the Giese lens system have shown characteristic features because the lens is long and located in a position neighboring the reaction chamber of high pressure. The behavior of the excited ions in particular has been investigated.

Experimental

The charge spectrometer was described in detail.[5] It consists of a double mass spectrometer having a large source volume for the study of charge distribution. Two sets of mass analyzers are connected perpendicular to each other and there is a reaction chamber in the crossing. A Hitachi T-2 ion source was used. The pressure of the reaction chamber could not be measured directly since distribution of gas density was not at all uniform. However, relative values of pressure in the reaction chamber could be expressed by reading the McLeod gauge of the gas-inlet system which leads gases through an orifice (0.300 ml/s).

All the gases used were of high purity or purified several times before use when necessary. Other details were reported previously.[4]

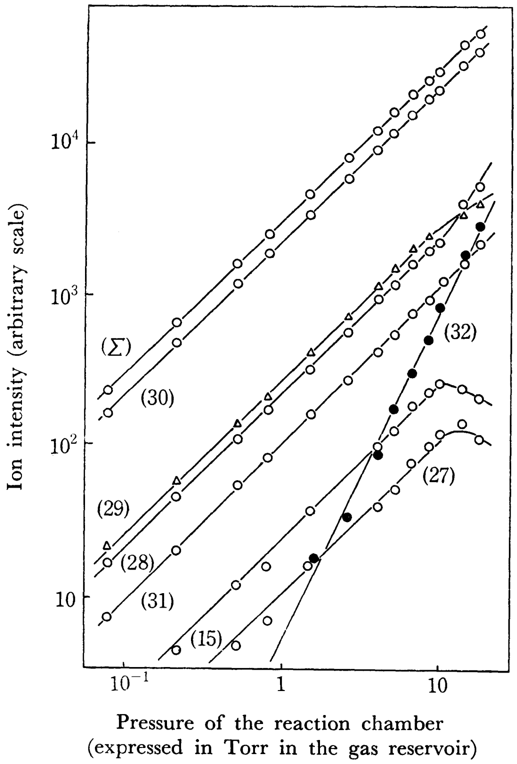

Fig. 1. Pressure dependence of the fragment ion distribution in methylamine bombarded with Xe$^+$.

An example of the relationship between gas pressure and the intensities of various ionic species after charge exchange is shown in Fig. 1. Methylamine molecules were subjected to the impact of Xe$^+$ ions. The pressure given in the abscissa is that of methylamine in the gas reservoir of the sample inlet system. The repeller field was set at a sufficient strength 15.0 V/cm) expected to protect it from the phenomena of an unsuitable reaction order as pointed out by Hamill for CD$_4$.[6] Fig. 1 shows satisfactory results for determination of the reaction order, the gradient of the straight line representing the reaction order. In the low pressure region all the ions except that of m/e=32(abbreviated as (32), see Table 2) have the gradient of unity. This indicates that they are primary fragment ions after charge exchange with Xe$^+$. On the other hand, (32) is observed when the pressure in the reaction chamber increases, and its gradient differs from that of others showing the value of 2. It is obvious that (32) is the secondary product of an initially formed ion with methylamine.

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1) I. Szabo, *Arkiv Fysik*, **33**, 57 (1967).

2) I. Szabo, *ibid.*, **35**, 339 (1968).

3) G. Sahlström and I. Szabo, *ibid.*, **38**, 145 (1968).

4) T. Nagatani, K. Yoshihara, and T. Shiokawa, This Bulletin **46**, 1306 (1973).

5) T. Shiokawa, K. Yoshihara, M. Yagi, T. Omori, H. Kaji, M. Hiraga, T. Nagatani, and Y. Takita, *Mass Spectroscopy*, **18**, 1230 (1970).

6) N. Boelrijk and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 730 (1962).

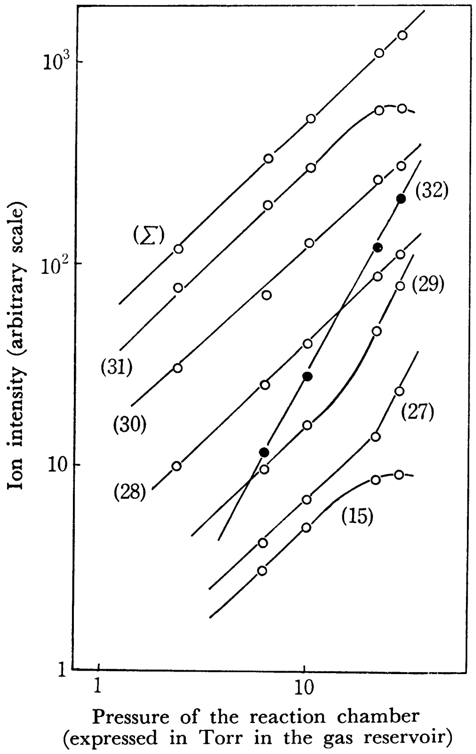

Fig. 2. Pressure dependence of the fragment ion distribution in methylamine bombarded with C$^+$.

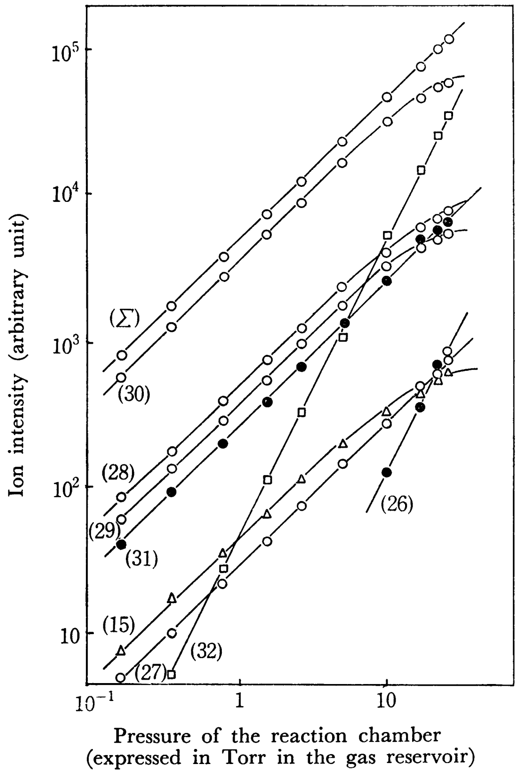

Fig. 3. Pressure dependence of the fragment ion distribution in methylamine bombarded with Cl$^+$.

Results and Discussion

Impact of methylamine with various positive ions has been performed in the reaction chamber at elevated pressure. The results with C$^+$, Cl$^+$ and Xe^{++} are shown in Figs. 2–4. Similar experiments using benzene, Ne^{++}, Xe$^+$, CO$_2$$^+$, Kr$^+$, Ar$^+$, Kr^{++}, Ne$^+$, Ar^{++} and He$^+$ have been described.[7] Detailed features depend on the energy received by the charge exchange. The break down curve should be taken into consideration.[4] The relation between the appearance of certain ions and their energy region is indicated graphically (Fig. 5).

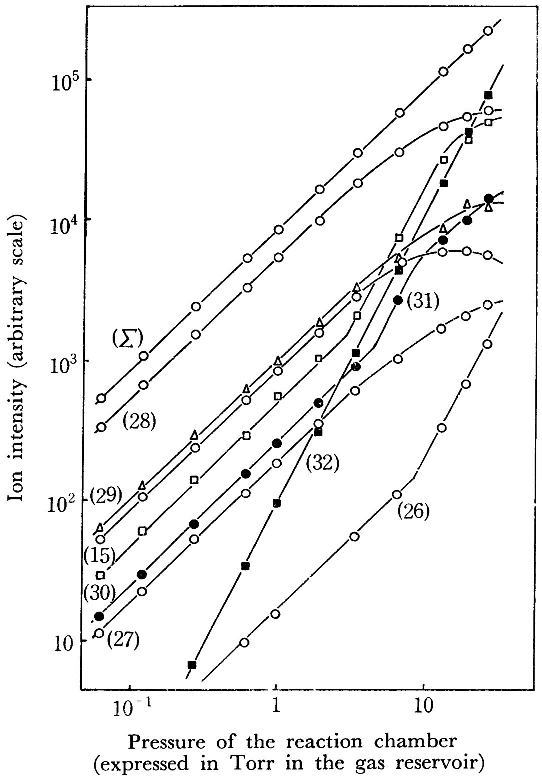

Fig. 4. Pressure dependence of the fragment ion distribution in methylamine bombarded with Xe^{++}.

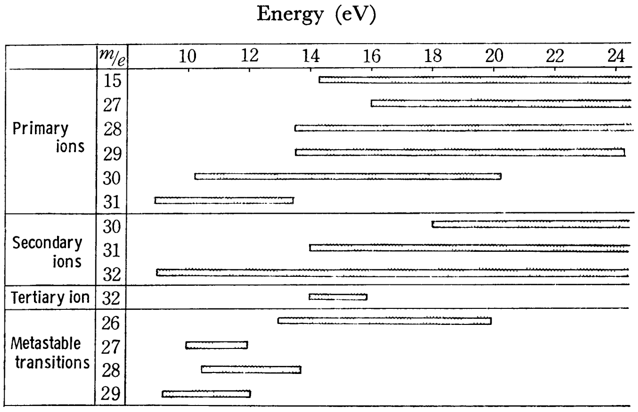

Fig. 5. Occurrence of various ions and its relation to the energy range.

The metastable transitions are considered to correspond to those shown in Table 1. These transitions take place during passage through the accelerating system before entering the magnetic field. The resolving power of this apparatus is about 50 for 1 mm slit width, and the peaks due to the metastable transi-

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[7] T. Nagatani, Thesis, Tohoku Univ., 1971.

Table 1. Metastable transition in positive ion impact of methylamine

M_1		M_2	M*	M_1		M_2	M*
31	⟶	30	29.03	29	⟶	27	25.14
31	⟶	29	27.13	28	⟶	27	26.04
30	⟶	29	28.03	28	⟶	26	24.14
30	⟶	28	26.13	27	⟶	26	25.04
29	⟶	28	27.03				

M* observed *m/e* ratio which can be calculated theoretically.[8]

tions may overlap with the ordinary ions. In the higher pressure region (Figs. 1–4), however, the behavior of the metastable ions seems to differ from that of the other ions.

The relation between excitation energy of methylamine molecule ion and the behavior of ionic species can be treated according to classification of the energy regions into three parts. Dominant ionic species are (31), (30) and (28).

i) 9.0—12.0 eV

Ion (31) collides with the parent molecule to give (32) through transfer of a hydrogen atom or a proton. A part of (31) releases a hydrogen atom or molecule to produce (30) or (29) during the flying path in the Giese lenses of 126 mm length. These species will be observed as the peaks of (29) or (27). This process is collision-induced dissociation as was reported by Melton and Well.[9]

ii) 12.1—14.7 eV

The products of ion-molecule reactions in this region are (32) and (31). (31) may be given by charge exchange or hydrogen atom transfer.[10]

The recombination energy of (30) is expected to be not so far from 13 eV, and charge exchange may be important in this case.

Metastable peaks of (28) and (26) are observed after release of a hydrogen atom or molecule from the most abundant ion (30).

A set of isomers $CH_2{=}N^+H_2$ and C^+H_2-NH_2 might exist for the mass peak (30).[11] Probably the former is formed in the low energy region not much above 9.0 eV which is the ionization potential of nonbonding nitrogen orbital [za′]. The latter will be formed in the higher energy region. It is plausible that these isomers in the reaction chamber show different behavior at elevated pressure, though detection of the difference is difficult. The meatstable peak (28) is observed in the low energy region and (26) in the higher energy region (Fig. 5). It is not clear whether this difference is due to the different behavior of the isomers or to the difference of the excited states of the produced ion (30). It seems that the latter is more important for determining the number of hydrogen atoms eliminated from the ion, since this is possible for the other cases.

iii) 15.8—25.0 eV.

The fragment ion (28) is present most abundantly. This reacts with methylamine to produce three kinds of secondary ions (32), (31) or (30) through the processes of proton transfer.

The secondary ion (30) after the change exchange with Xe^{++} seems to be highly excited, being raised up to 2.8 eV above its appearance potential. This is rarely observed in usual molecules. Metastable transition in this energy region is observed not in the initially produced ions but in the secondary ions. No collision-induced dissociation takes place in the case of (28).

As the recombination energy of (28) is considered to be appreciably high, He$^+$ in the cascade-type mass spectrometer was used as the monitor of the collision induced reactions. It was shown that the maximum probability for the charge exchange was observed in acceleration of 100—200 eV. The ion flying through the Giese lenses will attain this acceleration energy

Table 2. Classification of ion-molecule reactions in methylamine after charge exchange with positive ions

Energy range	Process	Mass Peak
9.0—12.0 eV	H transfer:	
	$CH_3NH_2^+ + CH_3NH_2 \rightarrow CH_3NH_3^+$	(32)
	H^+ transfer:	
	$CH_3NH_2^+ + CH_3NH_2 \rightarrow CH_3NH_3^+$	(32)
	Metastable transition:	
	$CH_3NH_2^+ \xrightarrow{-H} CH_2NH_2^+$	(29)
	$CH_3NH_2^+ \xrightarrow{-2H} CHNH_2^+$	(27)
12.1—14.0 eV	H^+ transfer:	
	$CH_2NH_2^+ + CH_3NH_2 \rightarrow CH_3NH_3^+$	(32)
	Electron transfer:	
	$CH_2NH_2^+ + CH_3NH_2 \rightarrow CH_3NH_2^+$	(31)
	H transfer:	
	$CH_2NH_2^+ + CH_3NH_2 \rightarrow CH_3NH_2^+$	(31)
	Metastable transition:	
	$CH_2NH_2^+ \xrightarrow{-H} CHNH_2^+$	(28)
	$CH_2NH_2^+ \xrightarrow{-2H} CHNH^+$	(26)
15.8—25.0 eV	H^+ transfer:	
	$CHNH^+ + CH_3NH_2 \rightarrow CH_3NH_3^+$	(32)
	Electron transfer:	
	$CHNH^+ + CH_3NH_2 \rightarrow CH_3NH_2^+$	(31)
	H^- transfer:	
	$CHNH^+ + CH_3NH_2 \rightarrow CH_2NH_2^+$	(30)
	Metastable transition:	
	$CH_2NH_2^+ \xrightarrow{-2H} CHNH^+$	(26)

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[8] J. H. Beyon and A. E. Fontaine, "Modern Aspect of Mass Spectrometry," ed. by R. I. Reed, Plenum Press, New York (1968), p. 113.

[9] C. E. Melton and C. F. Well, *J. Chem. Phys.*, **27**, 1132 (1957).

[10] When xenon ions of low recombination energy were bombarded to methylamine molecules filled in the source volume, it was indicated that more than 50% of total ionization is due to charge exchange above 12 eV.

[11] H. Sjögren, *Arkiv Fysik*, **29**, 565 (1965).

very easily.

In the whole energy range from the ionization potential of methylamine to 25 eV, contributions from (15) and (29) are quite low.

The rate constant of the ion-molecule reaction $CH_3NH_2^+ + CH_3NH_2 \rightarrow CH_3NH_3^+ + CH_2NH_2(CH_3NH)$ is given as 0.6×10^{-9} cm^3 $molecule^{-1}$ sec^{-1} by Jones and Harrison,[12] who carried out experiments by electron impact. In this study, however, this type of reaction can be neglected because in the energy region of the secondary product (30) there is no primary ion of (31) as shown in Fig. 5.

The ion- molecule reactions of various ionic species are classified in Table 2.

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[12] E. G. Jones and A. G. Harrison, *Can. J. Chem.*, **45**, 3119 (1967).