Studies on Fragment Ion Distribution and Reaction by the Use of a Charge Spectrometer. I. Mass Spectra of Methylamine after Charge Exchange with Fast Positive Ions and Their Recombination Energies

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Charge exchange reactions with fast positive ions were used to obtain the break down curve and internal energy distribution function of methylamine which differ in several points from those obtained by Sjögren with very slow ions. In the higher region, our results on the population in internal energy distribution function is greater than the previous ones. A valley of the internal energy distribution curve was found in the region 12.0—13.8 eV which is higher than that obtained by Sjögren. The values of RE were reestimated according to recent results.

From our interest in fragment ion distribution and reactivity in nuclear transformations we have studied ion-molecule reactions which might determine the chemical fate of the recoil atom. For direct detection of the reaction paths it was thought that mass spectroscopic methods would be suitable, and a specially designed mass spectrometer, was constructed.[1] This was found useful for studying basic ion-molecule reactions as well as initial charge distributions of decayed atoms.[2]

As regards ion-molecule reactions, typical studies of the ion-molecule reaction initiated by charge exchange have been successfully performed by the use of double mass spectrometers. Lindholm and his co-workers[3] extensively studied the break down curves and internal energy distribution functions of relatively simple gases by means of charge exchange. Valuable information has been obtained on the breaking up of the parent ions and the successive ion-molecule reactions in the reaction chamber. Energy of the incident beam in their work was limited to a low range (900 eV).

In the case of methylamine, Sjögren[4,5] studied the break down curve after the charge exchange reactions with slow ions, and elucidated the internal energy distribution function of the target molecule from the experimental results. It was found that a region with low probability for ionization exists between 11 and 12 eV, and above 15 eV the probability of ionization decreases again. The relation between the electronic structure of the molecule and the break down curve was discussed.

We have studied the dissociation of methylamine with fast ions and compared the results with those by Sjögren who studied it with slow ions. Using fast ions seems to be advantageous as dispersion of energy distribution is much narrow. Interesting findings were obtained on the internal energy distribution function of methylamine.

Experimental

Methylamine as a target molecule was prepared from methylamine hydrochloride (Tokyo Kasei Co.) of guaranteed grade. Methylamine hydrochloride was treated with a saturated solution of potassium hydroxide. Gas of methylamine evolved was dried and vacuum-distilled several times.

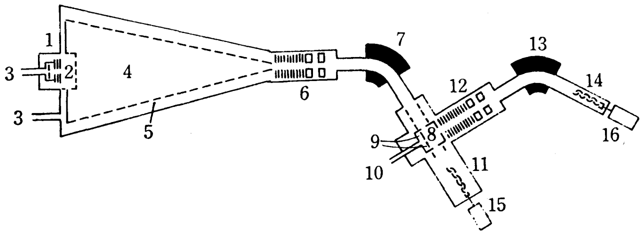

Fig. 1. Schematic diagram of the charge spectrometer.
1. X-ray tube or external ion source 2. Internal ion source 3. Gas inlet 4. Source volume 5. Guide rings 6. Lenses 7. Magnet 8. Reaction chamber 9. Repeller 10. Gas inlet 11. Electron multiplier 12. Lenses 13. Magnet 14. Electron multiplier 15. Recorder 16. Recorder or counter

The mass charge spectrometer is shown in Fig. 1. In place of the X-ray tube an external electron ion source T-2 (Hitachi Co.) may be used, as was the case in this work. Ions generated in an external ion source are introduced into 8 through 7, and impact the neutral atoms or molecules. The produced ions are led into the second analyzing system perpendicular to the incident ion, and detected by 14. Energy of the bombarding electrons in T-2 is 70.0 eV. Positive ions of various gases are produced and selected by the first analyzing system. Details of operation of this assembly have been described previously.[1]

Results and Discussion

The mass spectra of methylamine after charge exchange with 13 kinds of positive ions are shown in Table 1. Acceleration of the incident ions was set at 1850 V. All the values in the table are given when total ionization is normalized to 100. $C_6H_6^+$ was obtained from benzene, C^+ and CO_2^+ from carbon

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

[2] Y. Takita, M. Hiraga, K. Yoshihara, and T. Shiokawa, *Radiochem. Radioanal. Lett.*, **7**, 313 (1971).

[3] E. Lindholm, "Ion-Molecule Reactions in Gases," Advances in Chemistry Series 58, American Chem. Soc., Washington, D. C. (1966), p. 1.

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

[5] H. Sjögren, *ibid.*, **33**, 597 (1966).

Table 1. Mass spectra after charge exchange of methylamine with various positive ions

Primary ion	m/e										
	12	13	14	15	16	26	27	28	29	30	31
He^+	1.0	1.5	3.2	3.6	1.7	2.6	27.5	49.7	2.6	3.3	1.3
C^+			0.4	1.0	0.1		1.3	7.9	3.2	22.1	59.8
Ne^+	1.4	2.6	4.5	4.8	2.9	0.9	14.4	63.9	2.6	1.3	0.2
Cl^+			0.2	1.0	0.2		0.7	10.2	8.4	74.4	4.2
Ar^+	0.2	0.4	1.3	9.5	1.6	0.3	2.0	57.3	7.5	18.2	0.6
Kr^+		0.1	0.5	2.5	0.4	0.1	1.0	21.2	6.0	66.9	1.2
Xe^+			0.2	0.7	0.2		0.3	6.9	8.7	78.9	3.5
Ne^{2+}	1.0	0.9	1.2	1.0	0.7	1.2	2.8	3.9	0.8	11.9	73.0
Ar^{2+}	0.8	1.6	3.3	3.0	2.3	1.3	15.9	41.8	3.1	5.2	21.0
Kr^{2+}	0.2	0.7	2.3	3.7	1.7	0.7	11.4	64.5	4.7	2.4	6.9
Xe^{2+}		0.2	1.0	10.6	1.9	0.2	3.2	60.3	12.2	5.6	2.8
CO_2^+		0.4	1.0	2.4	0.8		1.5	16.2	7.3	64.2	6.1
$C_6H_6^+$							0.4	1.7	1.2	14.7	80.8

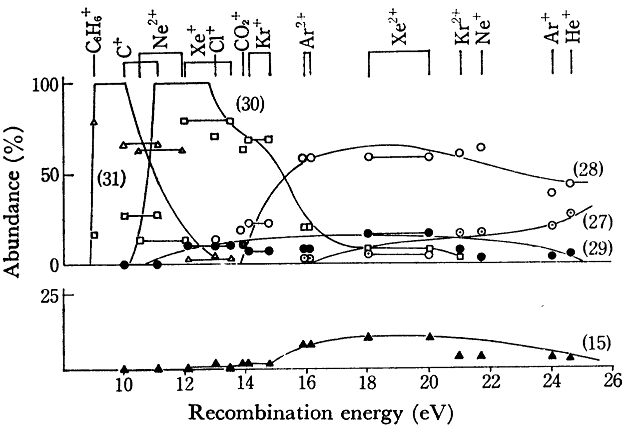

Fig. 2. Breakdown curve of methylamine.

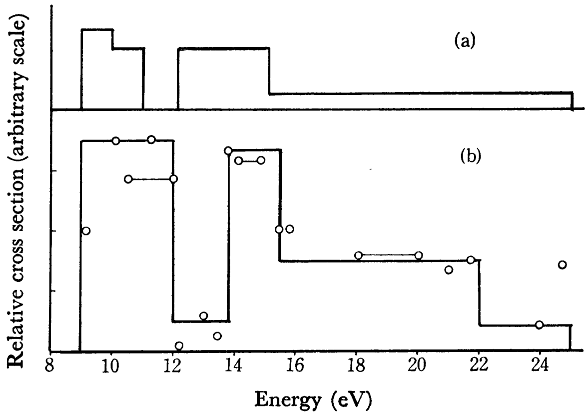

Fig. 3. Internal energy distribution function of methylamine. (a) Results obtained by Sjögren.[4] (b) Present results.

dioxide, Cl^+ being a fragment ion of trichlorofluoromethane ($m/e=35$). All the other ions were produced from the corresponding rare gases.

The break down curve of methylamine has been constructed from Table 1 and is shown in Fig. 2. The relation between m/e and chemical formulas is as follows.

(31) $CH_3NH_2^+$
(30) $CH_2NH_2^+$
(29) $CHNH_2^+$
(28) $CHNH^+$
(27) CHN^+
(16) NH_2^+
(15) CH_3^+
(14) CH_2^+, N^+
(13) CH^+
(12) C^+

Figure 3 shows the internal energy distribution function determined by the measurement of a relative cross section to the charge exchange reactions. The shape of the break down curve in Fig. 2 agrees as a whole with that of Sjögren,[4] but our energy distribution function differs somewhat.

Appearance potentials of the major fragment ions from methylamine in Table 1 were determined by experiments in which the target gas was bombarded by ions He^+, Ar^+, and Xe^+ with kinetic energy of 4.0—40.0 eV. Values obtained for the mass peaks are: (31), 9.0; (30), 10.2; (28), 13.6; and (15), 14.4 eV. They are in line fairly good with the values reported.[4,6–10]

Recombination Energies of Bombarding Positive Ions. The recombination energies of positive ions and their abundances are corrected by evaluation of the data in Table 1. They differ somewhat from the published data.[4]

1. He^+ Recombination energy of He^+ was reported to be 24.58 eV. From the break down curve (Fig. 2), however, it seems that there may be a small contribution (5%) of the lower energy level which does not greatly exceed the lowest ionization potential of methylamine. This can be argued from the presence of mass peaks 31 and 30 (Table 1).

2. C^+ Electronic structures, recombination energies and their abundances are reported to be[4]

$2p^2P^0$: 11.26, 10.00, 8.58 eV 74%
$2p^2\,{}^4P$: 16.58, 12.40 eV 25%

However, the ratio $2p^2P^0$: $2p^2\,{}^4P$ is concluded to be

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[6] F. H. Fried, J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York (1957), p. 243.

[7] J. E. Collin, *Colloq. Spectros. Intern. 9th.*, (Lyon 1961), **3**, 596 (1962).

[8] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.* **1963**, 5141.

[9] M. I. Al-Joboury and D. W. Turner, *ibid.*, **1964**, 4434.

[10] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

80: 20 from our results.

3. Ne^+ The recombination energies 21.56, 21.66 eV are adopted in this work.

4. Cl^+ The recombination energies of Cl^+ from CCl_3F are reported as follows.[4]

$3p^4\ ^3P$:	13.13, 13.01, 12.96 eV	80%
$3p^4\ ^1D$:	14.45, 14.34 eV	20%
$3p^4\ ^1S$:	16.47, 16.36 eV	0%
$3d^5D$:	15.66, 15.2 eV	0%

The intensity of (15) is extremely small as shown in Table 1. Thus, it is concluded that the level of $3p^4\ ^3P$ is predominant and the effect of the other levels can be neglected.

5. Ar^+ Recombination energies of the ion are 15.76 and 15.94 eV except those of higher levels. These values are adopted in this work.

6. Kr^+ 14.00 and 14.67 eV.

7. Xe^+ 12.13 and 13.44 eV.

8. Ne^{2+} Recombination energy of 10.5—12.0 eV was given when the process $2s^22p^4 \rightarrow 2s^22p^43x$ occurred. However, the mass peak (28) should be present in almost equal probability with that of (27), and (14) is greater than (15). Therefore, the influence of the level having recombination energy higher than 25 eV is estimated to be about 10%. Probably this is casued by the process $2s^22p^4 \rightarrow 2s^22p^5$.

9. Ar^{2+} Recombination energy of about 9 eV is given for the process $3s^23p^4 \rightarrow 3s^23p^4nx$ which produces (31) by 21%. The remainder is based on the process $3s^23p^4 \rightarrow 3s^23p^5$ (recombination energy: about 24 eV).

10. Kr^{2+} The mass peak 31 of 6.9% is produced by the process $4s^24p^4 \rightarrow 4s^24p^4nx$ with recombination energy of about 9 eV. The remainder is based on the process $4s^24p^4 \rightarrow 4s^24p^5$ (recombination energy: about 21 eV).

11. Xe^{2+} Recombination energy is 18—20 eV (the process $5s^25p^4 \rightarrow 5s^25p^5$ occurs).

12. CO_2^+ In addition to recombination energy of 13.8 eV, the level very near the ionization potential of methylamine contributes about 5%. This increases (13).

13. $C_6H_6^+$ In addition to recombination energy of 9.2 eV, the levels of 10—12 eV are expected to be present. However, these effects are negligibly small and bring no noticeable influence. Absence of the species such as (15) and (14) confirms this argument.

Comparison of Results with Mass Spectra by Electron Impact. When mass spectra are obtained by electron impact, electron energy is usually less than 100 eV. These electrons produce many molecular ions in various excited states, and the average energy of the excited state is considered to be the order of 10 eV. These mass spectra may be computed by taking into consideration the break down curve (Fig. 2) and the internal energy distribution function as in Sjögren's case.[4] Table 2 gives the results calculated with our data, in comparison with the published ones.[4,11–13] Agreement with the observed spectra is satisfactory. However, discrepancy of the fragments produced in the higher energy region is present because population is approximately taken to be zero above 25 eV.

Electronic Structure and Dissociation of Methylamine. The electronic structure of methylamine is shown in Table 3. The data are taken mainly from those of Mulliken[14] and of Turner[15] revised by Sjögren.[5]

In comparison with the results by Sjögren[4] who studied similar phenomena in the low energy region of incident ions, the present results indicate that the [x] electrons are localized on the CH_3 group (IP 15.07 eV after Turner[15]), the [z] electrons on the NH_2 group (IP 16.57 eV after Turner[15]) having large efficiency for charge exchange (Fig. 3). Sjögren has shown only low probabilities for ionization of these groups.

Table 2. Comparison of observed mass spectra of methylamine by electron impact with those calculated from the data of charge exchange

m/e	Observed value API[11]	Observed value Collin[12,13]	Calculated value Sjögren[4]	Calculated value This work
(15)	—	5.1	3.6	3.0
(27)	5.7	—	4.4	3.0
(28)	31.4	29.6	27.0	29.4
(29)	5.7	—	5.1	10.0
(30)	35.5	35.1	35.5	31.0
(31)	19.8	19.9	22.0	23.6

Table 3. Electronic structure of methylamine

Location	$1s^2$ N	$1s^2$ C	$2s^2$ NH_2	$2s^2$ CH_3	z^2 NH_2	x^2 CH_3	y^2 CN	z^2 CH_3	x^2 N
Calculation[a]			27	22	16	14.5	13.5	14.5	11
Photoelectron spectroscopy[b]	421	304	30	24	16.57	15.07	13.94	12.16	9.18

a) According to data of Mulliken[14] (in eV).

b) According to data of Turner[15] revised by Sjögren[5] (in eV).

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[11] American Petroleum Institute Research Project 44. Catalogue of Mass Spectral Data, Carnegie Institute of Technology, Pittsburgh, 1953, Serial No. 1123.

[12] J. Collin, *Bull. Soc. Sci. Liege*, **11**, 446 (1952).

[13] J. Collin, *Bull. Soc. Chim. Belg.*, **62**, 441 (1953).

[14] R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

[15] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.

According to Mulliken, ionization of [y] electrons localized on the CN group is expected to occur at 13.5 eV. If this is the case, a steep rise of CH_3^+ or NH_2^+ will be seen at 13.5 eV in the break down graph. However, such an ionization seems to be suppressed by the weak interaction of the CH_3 and the NH_2 groups in the neighorhood of 13.5 eV (Fig. 2, Table 1). A similar discussion has been given by Sjögren,[4)] but our experimental data seem to support this arguement more clearly.

The cause of the difference between our results and Sjögren's has not yet been completely explained. Dynamic treatment would be necessary to solve the problem.

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