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Studies on the Fragment Ion Distribution and Their Reactions by the Use of a Charge Spectrometer. II.
The Charge Exchange Reactions in Methanol with Fast Positive Ions

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Distribution of fragment ions after bombardment of a methanol molecule with various positive ions has been studied by the use of a double mass spectrometer. It was found that the internal energy distribution function has fine structures. The appearance potentials of the fragment ions were re-estimated. From the results the mass spectra of methanol by electron impact were interpreted fairly accurately. The successive ion-molecule reactions after the charge exchange were studied by increasing pressure in the reaction chamber. The behaviors of the metastable ions were also investigated.

Friedman *et al.*[1] studied electron impact of methanol with a mass spectrometer, and observed unimolecular decomposition of the molecular ions of the excited states. They tried to interpret their results by the theory of the rate processes.[2] Their results showed a discrepancy from the theoretical values, which seems to result from the inaccuracy of the internal energy distribution function they used.

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[1] L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).

[2] H. M. Rosenstock, M. B. Wahlenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

Wilmenius and Lindholm[3] also studied dissociation of methanol by impact of slow positive ions and tried to interpret the results by means of an internal energy distribution function. Their results showed no essential change from those of Friedman *et al.* in which a flat distribution 10.9(ionization potential)—18.1 eV was assumed. It is not appropriate to assume such a simple distribution if a more precise consideration is adopted.

The authors studied the break down curve and the internal energy distribution function of methanol by impact of fast positive ions by means of a double mass spectrometer. This study is an extention of the previous work on methylamine[4,5] which is of an isoelectric structure with methanol. A more accurate interpretation of mass spectra by electron impact has been made by improvement of the internal energy distribution function.

Successive ion-molecule reactions in the reaction chamber have been studied by increasing pressure of the neutral molecules. The behaviors of metastable ions were traced.

Experimental

Details of the apparatus[6a] have been described.[6b] Methanol of a reagent grade was purified by repeated distillation. The gases used for the positive ion sources were almost the same as in the previous work.[6b]

The mass spectra of methanol after charge exchange with fast positive ions (1850 eV) are shown in Table 1. The recombination energies are not always considered to be the same as those for the experiment of methylamine. Evaluation of the recombination energy is as follows.

(1) He^+. 24.58 eV.

(2) Ne^+. 21.56 and 21.66 eV.

(3) Cl^+. This ion is of *m/e* ratio 35, produced by electron bombardment of CCl_3F. As the contribution from $3p^4\ ^1S$ and $3d\ ^5D$ is very small, ions with *m/e* ratios (32) and (31) are produced predominantly. The ion with the ratio (15) is obtained through the contribution of $3p^4\ ^1D$ by 5.4%.

(4) Ar^+. 15.76 and 15.94 eV.

The minor peak which is present near peak (27) comes from the metastable transition $CH_2OH^+ \rightarrow CHO^+$. This is not a collision induced dissociation reaction but a unimolecular decomposition.

(5) Kr^+. 14.00 and 14.67 eV.

Contribution from the high energy levels is negligibly small.

(6) Xe^+. Mainly 12.13 and 13.44 eV.

About 5% contibution is derived from the higher energy levels.

(7) Ne^{2+}. Besides the recombination energies of 10.5—12.0 eV, recombination of $2s^22p^4 \rightarrow 2s2p^5$ can contribute to the charge exchange. The latter is about 10% in methylamine,[4] while it is as large as about 30% in methanol. The absolute value of this energy is higher than 25 eV which is the upper limit of the energy we considered, since the relation (13)>(14)>(15) holds among the abundances of the ions (Table 1, Fig. 1). Contribution of this recombination energy in the higher region will give a small error in estimation of the cross section of charge exchange.

(8) Ar^{2+}. A mass peak (32) of 5.6% is given by the process $3s^23p^4\ ^3P$ or ^1D to $3s3p^6$ which has a recombination energy of 11.5—12.5 or 13—14 eV. Peak (31) is produced by 8.0% due to the same process. Contribution from the

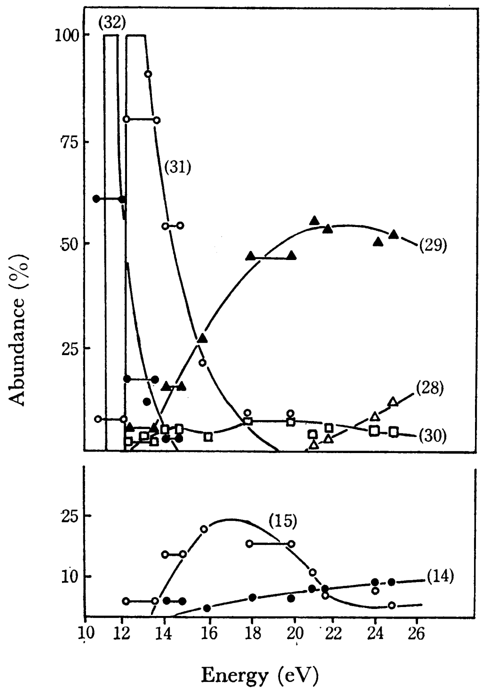

Fig. 1. Breakdown curve of methanol.

Table 1. Mass spectra after charge exchange of methanol with various positive ions (in %)

Primary Ion	*m/e*											
	(12)	(13)	(14)	(15)	(16)	(17)	(27)	(28)	(29)	(30)	(31)	(32)
He^+	4.1	6.6	9.4	2.7	1.4	2.7		10.0	53.3	3.8	4.7	1.0
Ne^+	3.6	6.3	9.7	4.4	1.2	3.3		6.3	56.4	4.5	3.0	0.6
Cl^+	0.1	0.6	1.6	5.4		0.4		0.7	9.4	3.8	64.6	12.7
Ar^+	0.6	1.6	4.2	29.2	0.6	1.0	0.4	1.3	35.0	2.7	24.8	1.9
Kr^+	0.2	0.8	3.1	15.7	0.1	0.6		0.6	15.9	4.9	54.4	3.7
Xe^+	0.1	0.6	2.0	2.4		0.2		0.2	7.7	3.8	66.3	16.3
Ne^{2+}	6.3	7.4	3.6	1.4	3.7	3.4		8.0	10.7	1.1	6.5	47.9
Ar^{2+}	2.1	4.1	8.5	6.1	0.9	3.2		7.6	49.7	3.6	8.0	5.6
Kr^{2+}	1.9	4.2	9.8	9.9	0.7	4.9		5.5	53.6	5.1	3.7	0.7
Xe^{2+}	0.4	1.3	5.3	17.9	0.2	0.9		1.7	55.9	6.8	8.8	0.6

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3) P. Wilmenius and E. Lindholm, *Arkiv Fysik*, **21**, 97 (1962).

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

5) T. Nagatani, K. Yoshihara, and T. Shiokawa, to be published.

6) a) This can be used also for the study of the ion-molecule reaction as a tandem mass spectrometer. b) T. Shiokawa, K. Yoshihara, M. Yagi, T. Omori, H. Kaji, M. Hiraga, T. Nagatani, and Y. Takita, *Mass Spectrosc.*, **18**, 1230 (1970).

process $3s^23p^4 \rightarrow 3s^23p^4$ nx can be neglected. When the breakdown curve is drawn, the fragment ions such as (29), (28), and (14) produced by the charge exchange of recombination energy 24.0 eV should be corrected by about 15%.

(9) Kr^{2+}. 21.0 eV.

(10) Xe^{2+}. 18—20 eV.

Breakdown Curve and Energy Distribution Function. The breakdown curve determined from the fragment distribution (Table 1) and the recombination energies of the ions is shown in Fig. 1. The internal energy distribution function of methanol obtained from the measured values of the cross section for the charge exchange reactions is shown in Fig. 2.

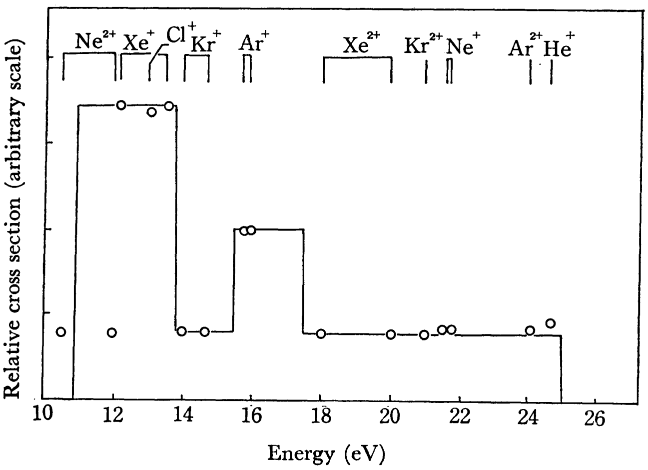

Fig. 2. Internal energy distribution function of methanol.

The behaviors of the seven dominant fragment ions (Fig. 1) are in line with the results of Wilmenius and Lindholm[3] but the appearance potentials are not always the same as those of Friedman *et al.* Potentials will be considered as follows.

(32) CH_3OH^+: 10.9 eV.

(31) CH_2OH^+: 12.0 eV.

These values are slightly lower than those of Friedman *et al.*,[1] but in good accrodance with those of Wilmenius and Lindholm.[3]

(30) $CHOH^+$: Formation of this ion starts from 12.3 eV, and it increases and then decreases, showing the second increase at about 16 eV. This indicates that there are two processes in the formation of the ion of *m/e* (30). The precursor ions corresponding to these processes are the ion of *m/e* (32) and (31).

(29) CHO^+: 13.1 eV.

Wilmenius and Lindholm[3] adopted the value of 14.2 eV. However, we have good evidence that the energy is lying at 13.1 eV from the experiment using the source volume as a cascade type double mass spectrometer.[7]

(28) CO^+. It was difficult to decide the appearance potential accurately. As shown in Table 1, a small quantity of the ion with *m/e* already appeared in the lower energy region (this might be due to contamination of N_2^+), but it is obvious that the value of the appearance potential is beyond 20.0 eV (Fig. 1). In this work we adopted 20.0 eV. The value supports the view that the formation of species (28) is due to the dissociation $(32) \rightarrow (28) + 4H$.[1]

(15) CH_3^+: 13.3 eV.

This is slightly lower than the value 14.0 eV previously reported.[1,2,8] In the experiment using a charge spectrometer as a cascade-type double mass spectrometer[7] it was determined to be 13.3 eV. This value is best responsible to the trend of the break down curve in the present study.

(14) CH_2^+: 14.2 eV.

The internal energy distribution function has a valley as in the case of methylamine[4] in the range 14.0—15.5 eV (Fig. 2). The ionization potential of (y) electron localized in CO has been reported to be 13.1 eV[3] or 14.64 eV.[9] Thus, the valley shows the presence of interaction which suppresses the formation of CH_3^+ and/or OH^+ by breaking of the C–O bond after the ionization of the (y) electrons. Up to now, the energy distribution function of methanol was assumed to be rectangular while that for methylamine[4,10] and for acetylene[11] were reported to possess valleys. The fact that a valley can be seen also in methanol suggests the presence of the interaction between the CH_3 and OH groups, although it is weaker than in the case of methylamine and acetylene.

Discussion

Comparison of the Present Data with Those of Mass Spectra by Electron Impact. The integrated value taken from the breakdown curve is expected to agree with the mass spectra by electron impact regardless of the contribution of high energy excitation of the molecules. Usually mass spectra obtained by electron bombardment is considered to satisfy these conditions, because the bombarding electrons used for ionization have kinetic energy less than 100 eV. The mass spectra are shown in Table 2. Results for ions of energy higher than 20 eV tend to disagree (Table 2, see (28)). This is because the contribution of ions with energies beyond 25 eV has been neglected in the energy distribution curve (Fig. 2). Except for this the agreement is quite satisfactory.

Reactions of Excited Ions. As in the case of methylamine the reactions of excited ions produced by charge exchange were investigated as a function of increasing gas pressure. The results for Cl^+ as a source material of the charge exchange are shown in Fig. 3. The experiments using He^+, Ne^+, Ar^+, Kr^+, Xe^+, Ne^{2+},

Table 2. Comparison of mass spectra by electron impact with those calculated from the results of charge exchange (in %)

m/e	Electron impact		Calculated from charge exchange
	Friedman[1]	Cummings[12]	
14	1.5	2.1	2.9
15	8.5	12.4	10.5
28	5.5	2.1	1.2
29	19.5	26.2	27.3
30	2.6	3.1	4.2
31	37.2	34.5	33.6
32	25.2	19.7	20.6

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[7] T. Nagatani, K. Yoshihara, and T. Shiokawa, *Mass Spectrosc.*, **20**, 97 (1972).

[8] F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954).

[9] H. Sjögren, *Arkiv Fysik*, **33**, 597 (1966).

[10] H. Sjögren, *ibid.*, **29**, 565 (1965).

[11] E. Lindholm, I. Szabo, and P. Wilmenius, *ibid.*, **25**, 417 (1963).

[12] C. S. Cummings and W. Bleakney, *Phys. Rev.*, **58**, 787 (1940).

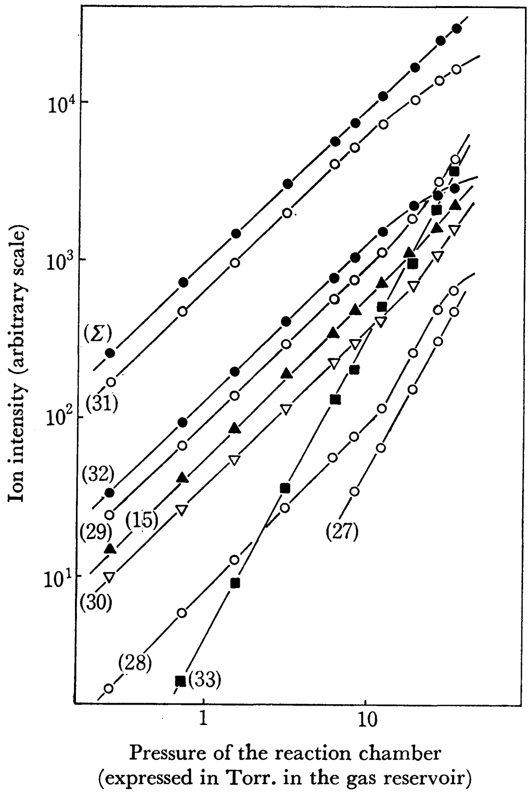

Fig. 3. Pressure dependence of the fragment ion intensity in methanol bombarded by Cl$^+$.

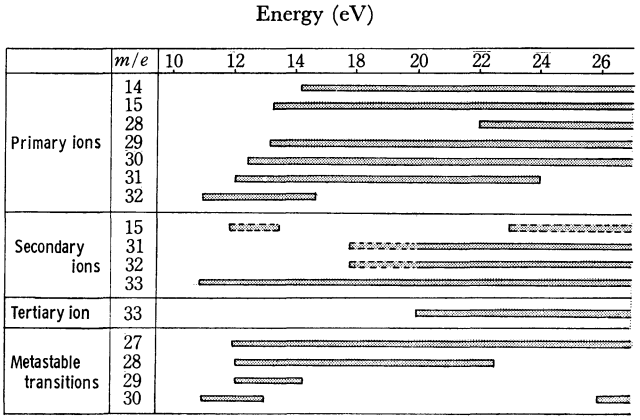

Fig. 4. Occurrence of various ions and its relation to the energy range.

Ar^{2+}, Kr^{2+}, and Xe^{2+} have also been carried out in the same way.[13] From the results we can analyze the relation between the appearance of ions and their energy range as shown in Fig. 4. Some interesting aspects in four energy regions are discussed.

(i) 10.9—12.0 eV: The parent ion is predominantly produced for the primary process. A secondary ion (33) is produced by proton transfer or hydrogen atom transfer between the parent ion and the methanol molecule. Metastable transition can be explained by elimination of a hydrogen atom from the parent ion (32) at the moment of collision with the methanol molecules.

(ii) 12.0—15.0 eV: (31) is the principal fragment ion for the primary process although (32) contributes to some extent. Its regeneration can be observed as a secondary process for methylamine. In the case of methanol, however, such a process cannot be observed. It was revealed[7] that the charge transfer cross section for methanol is very small in this region compared to the total ionization cross section. This supports the view that there is no secondary process producing (31) except for the formation of (33).

Metastable transition is caused by elimination of a hydrogen atom or molecule from (31) or (30). A possibility of the presence of the isomers $CH_2{=}O^+H$ and $C^+H_2{-}OH$ could be detected in this case.

(iii) 15.0—18.0 eV: Main primary ions are (31), (29), and (15). (33) is again produced in this region as a secondary product, but the mechanism of its formation is not clear.

(iv) 18.0—25.0 eV: (29) is predominant, various secondary and tertiary ions being also observed. Proton transfer, charge transfer and hydride ion transfer between (29) and methanol produce the ions (33), (32), and (31), respectively.

With regard to metastable transition, the metastable peak (27) is observed according to the process

$$(29) + CH_3OH \longrightarrow (28) + H + CH_3OH$$

This causes an apprarent peak at (27). We also see the presence of the metastable peak (30) above 24 eV. This species may be produced by the dissociation of the ion (32) through its regeneration reaction on collision between ions (29) or (28) and methanol molecules. It was revealed that (32) easily dissociated above 24 eV.[7]

TABLE 3. ION-MOLECULE REACTIONS IN METHANOL

Energy	Process	Mass peak
10.9—12.0 eV	H$^+$ transfer:	
	$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+$	(33)
	H transfer:	
	$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+$	(33)
	Metastable transition:	
	$CH_3OH^+ \xrightarrow{-H} CH_2OH^+$	(30)
12.1—15.0 eV	H$^+$ transfer:	
	$CH_2OH^+ + CH_3OH \longrightarrow CH_3OH_2^+$	(33)
	Metastable transition:	
	$CH_2OH^+ \xrightarrow{-H} CHOH^+$	(29)
	$CH_2OH \xrightarrow{-2H} CHO^+$	(27)
	$CHOH \xrightarrow{-H} CHO^+$	(28)
18.0—25.0 eV	H$^+$ transfer:	
	$CHO^+ + CH_3OH \longrightarrow CH_3OH_2^+$	(33)
	Electron transfer:	
	$CHO^+ + CH_3OH \longrightarrow CH_3OH^+$	(32)
	H$^-$ transfer:	
	$CHO^+ + CH_3OH \longrightarrow CH_2OH^+$	(31)
	Metastable transition:	
	$CHO^+ \xrightarrow{-H} CO^+$	(27)

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[13] T. Nagatani, Thesis Tohoku Univ., (1970).

The C–O bond rupture leads to the formation of ions (15) *etc*. There is only a weak interaction between the CH_3 group and the OH group, which makes breaking of the bond easy.

The ion-molecule reactions in methanol are summarized in Table 3.

Kotoyori *et al.*[14] studied the reactions of methanol with accelerated rare gas ions and discussed the formation of the final chemical species. They concluded that charge exchange reactions are not important in determination of the final chemical products.

The authors thank Mr. M. Hiraga for his kind cooperation throughout this work.

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[14] T. Kotoyori, M. Takahashi, and A. Ichinose, This Bulletin, **44**, 2893 (1971).