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Reaction of Methanol with Accelerated Rare Gas Ions

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Reaction of methanol with accelerated rare gas ions was studied. The yields of the reaction products, H_2, CO, CH_4, HCHO, and ethylene glycol, were determined, varying the initial kinetic energy of ion (2—6 kV), ionic species, (Ar, Xe, and Kr), and pressure of methanol ((2—14)$\times 10^{-3}$ Torr). No appreciable effect on the product yields was observed by adding carbon tetrachloride as electron scavenger or propylene as radical scavenger. The product yields are found to be linear against ln E_i, (E_i is initial kinetic energy of ions). Although the detailed reaction mechanism is left for future investigation, the reaction seems to be interpreted in terms of billiard model, momentum of ion being transferred directly to a local part of the target molecule at the contact time.

Studies on the chemical reaction of neutral compounds with accelerated ions have been rather few except in the field of mass spectrometric studies and radiation chemistry. It is well known that the ion-molecule reaction takes an important part in the processes of radiation chemistry and plasma chemistry in electrical discharge, but the studies on the reaction initiated directly by accelerated ions are few, apart from the radiation chemical studies with α-particles. In these recent years, a remarkable progress has been achieved in elucidating the characteristics of ion-molecule reaction using single or tandem-type mass spectrometer technique. Study of ion-molecule reaction with mass spectrometer has a pronounced advantage, in observing directly the behavior of the secondary ions produced by impact of primary ions. However, we consider it is also important and interesting to get the information on the final reaction products obtained by ion impact. For this purpose, a small chemical accelerator was constructed which is furnished with an ion source of relatively strong beam intensity and enables us to obtain enough amount of reaction products to be analysed by the conventional analytical methods. With this apparatus we studied the reaction of methanol with accelerated rare gas ions and obtained some preliminary results on the reaction mechanism.

Experimental

Apparatus and Procedures. Figure 1 shows a schematic drawing of the apparatus. Details of the construction and performance of this apparatus is described elsewhere.[1] Impact ions are generated by electrical discharge of 70 MHz radio waves. Discharge tube is made of Pyrex glass, and is similar to that used in some neutron generator. Gas pressure in discharge tube is adjusted to obtain maximum ion intensity, and the optimum rate of gas feeding is about 10 m*l* STP per hour. The ions are accelerated by DC voltage from 2 to 6 kV. The efficiency of ion extraction is found to be very sensitive to the shape and size of quartz tube for ion exit. The ion extraction efficiency from discharge tube increases with increase of DC voltage, and maximum intensity of ion obtained is about 70 μA. F is an ion focussing lens to which DC voltage is applied, and the optimum ratio of ion focussing voltage to source voltage in the present apparatus is about 1.16. The reaction tube is made of Pyrex glass of 30 cm of length and 3 cm in diameter. A cold trap C is provided to collect condensable vapours and methanol

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[1] T. Kotoyori and M. Takahasi, *Mass Spectrometry*, **17**, 619 (1969).

and reaction products (formaldehyde and ethylene glycol) can be collected almost quantitatively in the trap. Incondensable gases such as argon, hydrogen, methane, and carbon monoxide are collected in an evacuated bulb of 2 *l* through oil diffusion pump, closing the valve V during the irradiation time. It was checked beforehand that oil diffusion pump does not give any decomposition products, although mercury diffusion pump may be more preferable. Ion current is measured by a Faraday cup attached at the end of the reaction tube, and auxiliary electrodes are furnished to remove charge accumulated on the glass wall. At present, the reaction tube of 5 cm in diameter instead of that of 3 cm in diameter is used, and in this case, it is found that these auxiliary electrodes are unnecessary. Target vapour is supplied from the end of the reaction tube, and the rate of feeding is regulated by a needle valve, monitoring the pressure with Pirani gauge. The gauge was calibrated for methanol in the range of 0.001 to 10 Torr. The working pressure of methanol in the experiment is $(2-14)\times 10^{-3}$ Torr. Methanol is purified by refluxing with magnesium metal and distilled in the vacuum line. The irradiation time is 5 min for collecting condensable products, and 2 min for collecting incondensable gases. Incondensable gases collected in an evacuated bulb are compressed by a Toepler pump and analysed by gas chromatography with Molecular Sieve 5 A column. The amount of formaldehyde was determined by spectrophotometric method after being treated with chromotropic acid.[2] The amount of ethylene glycol was determined separately after being oxidized with periodic acid to formaldehyde.[3] To collect these reaction products quantitatively, it is necessary to heat the reaction tube with electrical heater of nichrome wire wound on outside of the reaction tube. Water may also be produced, but its analysis was not attempted in the present experiment.

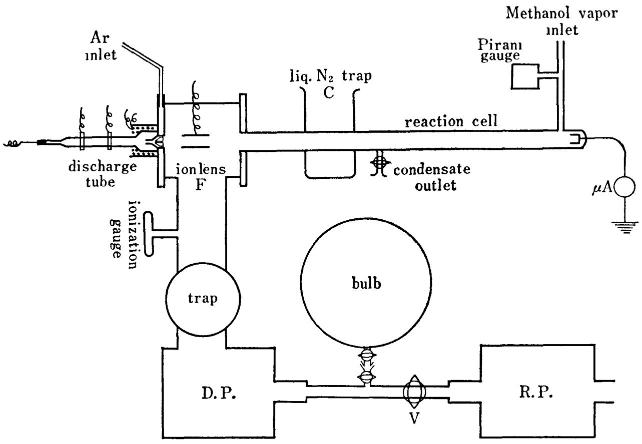

Fig. 1. Diagram of ion impact apparatus.

Results

Spread of Energy of Incident Ar Ion and Abundance of Double Charged Ion. It is generally known that the spread of energy of ion beam generated by electrical discharge is fairly large, and in order to determine the magnitude of the energy spread under the present experimental condition, the ion source is installed to a mass spectrometer which is 60° sector type with analysing tube of 20 cm radius. The maximum beam intensity of Ar at the ion accelerating voltage of 5kV is about 6μA, but the intensity fluctuates slowly. Since it can be easily recovered by adjusting the magnetic field, this fluctuation must be due to that of the energy, which seems to be caused by the periodic slow instability of plasma in the discharge tube. Due to this fluctuation of beam intensity, it is difficult to determine the exact shape of the beam against magnetic field, but the approximate energy spread of Ar at 5 kV is estimated to be about 150 V. The relative abundance Ar^{2+} to Ar^+ is also estimated to be about 1 to 40 by scanning the magnetic field. In the actual impact experiments, the ion source is directly attached to the reaction tube as shown in Fig. 1, to obtain enough intensity of the ion beam, without eliminating double charged ions, assuming that their contribution is negligible.

Proportionality of Product Yields with Ion Intensity and Product Distribution Pattern. In order to confirm the reliability of our apparatus and the reproducibility of the product yields, the proportionality of the yields of the reaction products per unit irradiation time with the intensity of impact ion was investigated in the range from 20 to 40 μA in the impact experiment of methanol with Ar ion. The proportionality of the yields is satisfactory.

As will be described later, the product distribution in the methanol impact experiment depends to some extent on the pressure of methanol and the energy of impact ions, but an example of the product distribution under a specified condition is presented in Table 1, including the photochemical and radiation chemical results obtained by the other authors for comparison.[4,5]

TABLE 1. PRODUCT DISTRIBUTION PATTERNS IN THE REACTION OF METHANOL WITH 5 kV Ar^+ AT[6] 8.5×10^{-3} Torr OF METHANOL AND OTHER DATA FOR COMPARISON

	Unit	H_2	CO	CH_4	$(CH_2\text{-}OH)_2$	HC-HO
5kV Ar^+	molecule per Ar^+	41.0	10.7	2.7	3.2	1.0
Co γ-ray[4]	*G* value	10.4	0.84	0.26	3.1	5.6
1849 Å photon[5]	mole per cc sec, 10^{-13}	86	2	1.5	60	16

Hitherto, in interpreting the product distribution patterns of the radiolysis of organic compounds, calculations have been made by several authors[7,8] on the basis of the relative abundance of ions observed in mass spectra. In the case of methanol radiolysis,

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[2] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem. Anal. Ed.*, **17**, 400 (1945).

[3] N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

[4] J. H. Baxendale and R. D. Sedgwick, *Trans. Faraday Soc.*, **57**, 2157 (1961).

[5] J. Hagege, S. Leach, and C. Vermeil, *J. Chem. Phys.*, **62**, 736 (1965).

[6] The atom ratio (H:C:O) calculated from the experimental result from Table 1 is 25:5:4.4. From the material balance, the ratio 4:1:1 should be expected. The incomplete material balance may be due to some missing of carbon products or to hydrogen production by some unknown reaction with contaminated water or oil of diffusion pump.

[7] G. G. Meisels, W. H. Hamil, and R. R. Williams, *J. Phys. Chem.*, **61**, 1456 (1957).

[8] J. H. Futrell, *J. Amer. Chem. Soc.*, **81**, 5921 (1959).

Table 2. Product distribution patterns calculated on the basis of various assumptions of the primary ion product distributions and successive ion-molecule reaction schemes

Assumption adopted		Final products ratio[a)]					
Distribution of primary ions	Secondary ion-molecule reaction scheme	H_2	$(CH_2OH)_2$	HCHO	CO	CH_4	H_2O
Proposed values by Lindholm	Proposed scheme by Lindholm	10	8.3	5.7	0.51	4.0	4.0
Observed values by Lindholm(10VAr$^+$)	Lindholm	10	9.1	11.2	2.8	9.6	9.6
Same as above	Baxendale	10	3.4	5.3	1.2	1.0	—
Observed values in electron impact	Baxendale	10	3.4	5.1	0.9	0.3	—
Present experimental values		10	0.78	0.25	2.6	0.66	—

a) normalized to hydrogen

calculations by Lindholm *et al.*[9] and Baxendale *et al.* show fairly good agreement with the experimental results. We attempted the similar calculation to our ion impact case, assuming that the primary ion distribution in the present case is same as that of ion impact spectrum of 10 V Ar$^+$ reported by Lindholm.[9] This assumption may be acceptable because it is known that the ion impact spectra do not vary so much with the kinetic energy of ion in the case of charge transfer. Since Lindholm and Baxendale assumed slightly different reaction schemes for the successive secondary processes, we made calculations on the both reaction schemes. As shown in Table 2, the calculated results do not agree with our experimental result. The distiguished feature in our observed result is very low yields of formaldehyde and ethylene glycol, and the calculation cannot give high yield of carbon monoxide, unless a fundamentally different mechanism is introduced.

Variations of Yields of the Reaction Products with Different Incident Ionic Species. Several authors[9–11] proposed that the secondary ion spectra of organic compounds obtained by ion impact may be explained assuming that the most part of energy required to produce secondary ions from the original target molecule comes from the charge neutralization energy of the incident ions due to the charge transfer process. Lindholm observed the ion impact mass spectra of methanol due to charge transfer with various positive ions of low kinetic energy (4—900 V). He concluded that for most ions the mass spectra of methanol are almost independent of the kinetic energy of the incident ions, and that the energy transferred to methanol equals the electron recombination energy of the incident ions. If this could be applied to the present impact case, we would expect the variation of yields of the reaction products with ionic species of various electron recombination energies. To investigate the effect of recombination energy of impact ions, Ar (I_p=15.75, 15.95 eV), Kr (I_p=14.0, 14.67 eV), and Xe (I_p=12.15, 13.44 eV) are used as source gas. Since the ionization potential of methanol is 10.88 eV, the gain of energy due to the charge transfer is at most 4.87 eV for Ar$^+$, 3.12 eV for Kr$^+$, and 1.27 eV for Xe$^+$ for each ground state of ions. As Fig. 2 shows, the yields of the reaction products per ion at a fixed translational energy are almost the same within the experimental errors irrespective of the species of ion used.

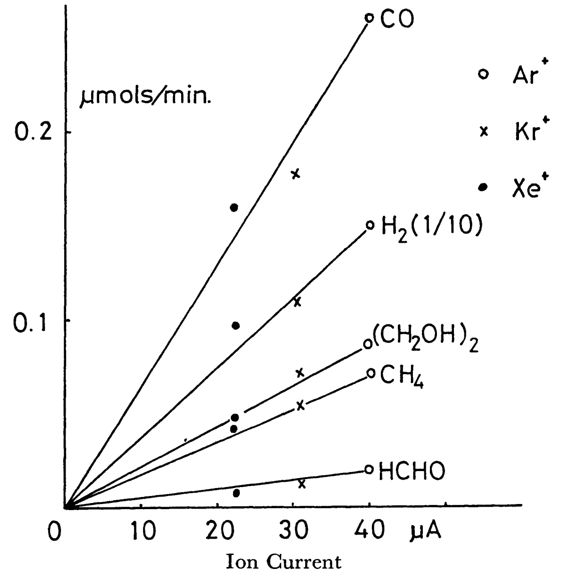

Fig. 2. The yields of the reaction products per ion with Ar$^+$, Xe$^+$, and Kr$^+$.

This figure shows that the product yields of five components, if normalized to ion intensity, do not show any appreciable difference. (In Fig. 2, the beam intensities are not normalized, since the extraction efficiencies of ions from ion source depend on the ionic species). Therefore, the present result cannot be interpreted in terms of charge transfer process. It can be understood if we consider that our experimental conditions (high energy of incident ion, long reaction path, and higher pressure of methanol in the reaction chamber than in the ionization chamber of mass spectrometer) result in the multiple collisions of incident ion. Table 1 shows that a single ion reacts with more than one molecule of methanol, although we have not definite evidence that all of these products are produced by the reaction with initial ions. At any rate, we may conclude that the charge transfer process does not contribute predominantly, although it may be involved in the initial step to some extent.

The Effect of Initial Kinetic Energy of Impact Ion and of Pressure of Methanol. The variation of product

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[9] P. Wilmenius and E. Lindholm, *Arkiv Fysik*, **21**, 97 (1962).

[10] J. B. Homer, R. S. Lehrle, J. C. Robb, M. Takahasi, and D. W. Thomas, "Advances in Mass Spectrometry," Vol. 2, Pergamon Press, London (1961), p. 503.

[11] V. Čermák and Z. Herman, *Nucleonics*, **19**, 106 (1961).

yields with the initial kinetic energy of ion (2 to 6 kV) was investigated. The plot of product yields with logarithm of the initial energy E_i shows a fairly good linear relationship, as Fig. 3 shows. Another interesting point to be noted is that the extrapolations of slopes for carbon monoxide, ethylene glycol, and methane intercept the abscissa nearly at the same position. Interpretation of these results will be given in discussion part.

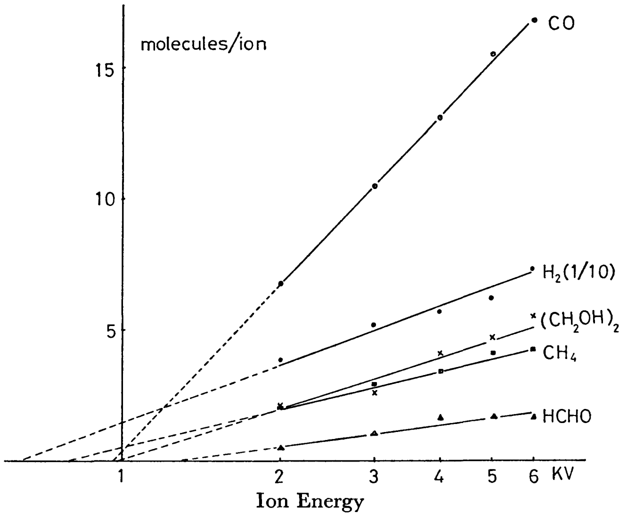

Fig. 3. The plots of the yields of the reaction products against logarithm of the initial energy, ln E_i.

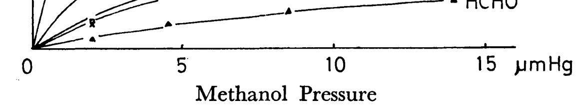

Fig. 4. The variation of the reaction product yields with the increase of the pressure of methanol.

The variation of the reaction product yields with the increase of the pressure of methanol was also investigated in the range (2—14)$\times 10^{-3}$ Torr. (Fig. 4). When the pressure of methanol is increased, the yields of all the reaction products increase, approaching to constant values. Five components of the reaction products do not show the same behavior, particularly the yields of hydrogen and carbon monoxide increasing more rapidly with methanol pressure than those of the other reaction products. If the simple bimolecular collision of methanol with ion is assumed, we would expect for the product yields to be proportional to flux of incident ions, length of the reaction tube and pressure of methanol. It is already shown that the product yields are proportional to the ion intensity. The fact that the product yields increase first and approach to limiting values with the increase of methanol pressure indicates some more complicated mechanism is involved in the present reaction. We have not yet definite interpretation for the pressure effect, but some ideas will be given later.

Effect of the Addition of Carbon Tetrachloride and Propylene. It is well known that in the radiolysis of organic compounds with γ-ray the energetic secondary electrons produced by Compton scattering take an important role. However, in the present case, the average energy of the electrons produced by ionizing penetration of heavy charged particles is supposed to be very near to the thermal energy, since the kinetic energy of incident ion is at most 6 kV. Therefore, the direct excitation of methanol by energetic electrons is unlikely, but the production of excited methanol by charge neutralization of methanol ion might be possible, resulting the decomposition of excited methanol.

$$CH_3OH^+ + e \longrightarrow CH_3OH^*$$

$$CH_3OH^* \longrightarrow \text{Products}$$

Meaburn and Mellows[12] found the reduction of the yield of hydrogen in the radiolysis of methanol vapour with the addition of 0.01% of carbon tetrachloride ($G(H_2)=4.1$), and assumed that carbon tetrachloride interrupts the following process, scavenging slow electrons.

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2{}^+ + CH_3O\cdot$$

$$CH_3OH_2{}^+ + e \longrightarrow CH_3OH + H$$

To know whether these processes play any role in the present case, we examined the effect of the addition of carbon tetrachloride. As Fig. 5 shows, no appreciable effect in the product yields was observed except in formaldehyde, and it is concluded that these processes seem not to contribute appreciably in the production of hydrogen. The increase of the yield of formaldehyde with the addition of carbon tetrachloride was noticed. Any conclusive interpretation for this

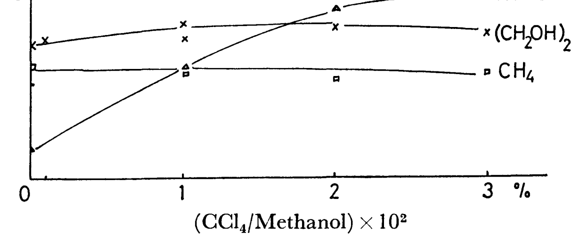

Fig. 5. The effect of the addition of carbon tetrachloride on the yields of the reaction products.

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[12] M. Meaburn and P. W. Mellows, *Trans. Faraday Soc.*, **61**, 1701 (1965).

finding is not available at present, but if chlorine atom is assumed to be produced by impact of carbon tetrachloride, it may induce the abstraction of hydrogen from methanol, resulting $\cdot CH_2OH$ or $CH_3O\cdot$ which may be finally converted into formaldehyde.

In view of the existence of ethylene glycol among the reaction products, the formation of free radicals (hydrogen atom and methylol radical $\cdot CH_2OH$) is supposed to be quite probable, and propylene was added as radical scavenger to find the extent of the contribution of free radicals to the whole reaction. Contrary to out expectation, no remarkable decrease of yields of the reaction products was observed, as Fig. 6 shows. It seems to be difficult to assume that the whole hydrogens were produced by molecular mechanism, so that an alternative possible explanation may be that produced hydrogen atoms are hot. Hatano and Shida[13] found that hot hydrogen atoms produced in irradiation of liquid olefins with Co 60 γ-rays do not add to olefins and rather abstract hydrogen. No reduction of ethylene glycol with addition of propylene may be understood, if we consider the fact that methylol radical is stabilized by conjugation of odd electron with oxygen and cannot add to propylene at room temperature.

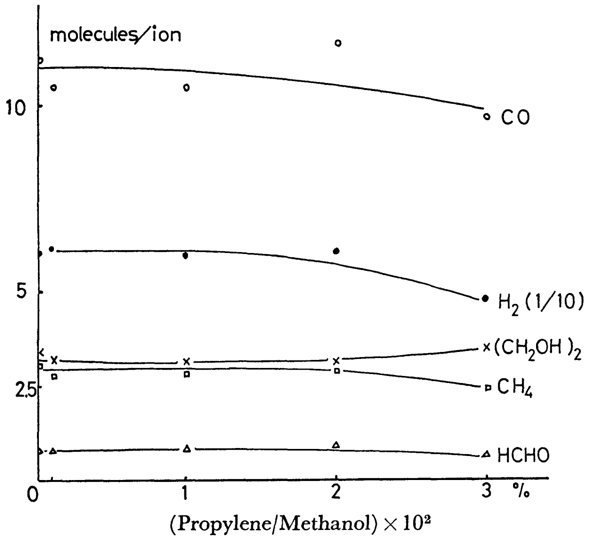

Fig. 6. The effect of the addition of propylene on the yields of the reaction products.

Luminescence by Ion Impact. Faint purple luminescence was observed in the reaction tube, when methanol vapour was introduced. Spectra in the visible region were taken by a spectrograph, with exposure time of 30 min. The spectra consisted of line spectra of hydrogen Balmer series and some unidentified bands (band heads at 4311.8 Å, 3978 Å, and 3955 Å). More detailed investigations for the interpretation of these spectra are left for future study.

Discussions

Summarizing the above experimental results, the contributions of the possible processes are considered and evaluated.

(1) Charge Transfer Process.

$$X^+ + CH_3OH \longrightarrow X + CH_3OH^{*+}$$
$$CH_3OH^{*+} \longrightarrow \text{Products}$$

As described in experimental results, no variation of the yields of the reaction products with different ionic species was observed. As excess energy left on methanol ion, CH_3OH^{*+}, must depend on the amount of recombination energy of incident ion X^+, different product distribution patterns would be expected, depending on the ionic species used. Present results are incompatible with this expectation, and the charge transfer process appears not to play an important role under the present conditions.

(2) Complex Formation Process as Considered in Ion-molecule Reaction. Now it is generally admitted that the complex formation mechanism in ion-molecule reaction takes place only in the very low translational energy range,[14,15] and the energy range of the present experiment is well above this energy range. Therefore, the contribution of this type of reaction may not be necessary to be considered.

(3) Excitation Process by Secondary Electrons. At present, we have no direct experimental evidence whether the excitation of methanol by secondary electrons produced by ionizing penetration of heavy charged particles is involved or not. The data of cross sections for the ionization of methanol by rare gas ions in the energy range of several kV are not available, but the cross sections reported in the case of accelerated ion with various atomic particles are in 10^{-16} cm^2 range,[16,17] indicating that the probability of ionization by charged heavy particles in several kV range is generally large. However, it is less likely that the electrons produced have enough energy to excite methanol, since the relative velocity of ion is fairly low compared with the velocity of orbital electron.

(4) Dissociative Excitation of Methanol Ions by Charge Neutralization. If methanol ion is produced by ionization, excited methanol may be formed through charge neutralization, resulting in its decomposition. However, our experimental result on the effect of addition of carbon tetrachloride seems not to favour this process.

(5) Direct Dissociation Process by Momentum Transfer.

$$X^+ + M \longrightarrow X^+ + R_1 + R_2,$$

or

$$X^+ + M \longrightarrow X^+ + M^* \longrightarrow X^+ + R_1 + R_2.$$

The collision dynamics by classical or semiclassical treatment has been recently developed for interpreting the product yields, the isotope effect and the moderator

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[13] Y. Hatano, S. Shida, and S. Sato, This Bulletin, **41**, 1120 (1968).

[14] "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series 58, Amer. Chem. Soc., (1966).

[15] *Discussions Faraday Soc.* **44** (1967).

[16] J. B. Hasted, "Physics of Atomic Collisions," Butterworth, London (1964).

[17] E. W. McDaniel, "Collision Phenomena in Ionized Gases," John Wiley & Sons, New York, N. Y. (1964), p. 238.

effect in hot atom chemistry.[18–20] The main characteristic of this type of reaction is transfer of momentum of hot atom to molecule in the collision process. The same type of collision is also observed in molecular beam experiment of alkali atom with halogen[21] and ion-molecule reaction in relatively high energy impact.[22] In these experiments, only the reactions to give stable association products such as HT in the reaction, $T+H_2$, MX in the reaction, M (alkali metal) $+X_2$, and ArH^+ in the reaction, $Ar^+ + H_2$ have been considered. However, if the energy of incident particles is high, more drastic reactions to give fragmental products must be considered. We presume that this type of reaction takes an important role in the present ion impact experiment, considering that the processes (1)—(4) mentioned above are rather less likely. To interprete the relation of the product yields with the initial kinetic energy of ions, a similar formula as derived for the relative yields of hot atom products is considered.

Miller and Dodson[23] gave the following formula for the yield of hot product,

$$N_{\mathrm{hot}j} = N_s\int f_j p_j(E) n(E)\mathrm{d}E, \qquad (1)$$

where N_{hot} is the number of hot product, N_s is the total number of hot atoms available for the reaction, f_j, the relative probabilty of collision, $p_i(E)$, the probability of hot combination reaction in such collision at energy E, and $n(E)$ is the average number of collision per unit energy at E (collision density). Estrup and Wolfgang[24] derived the following equation for the number of collisions between energies E and $E+\mathrm{d}E$ of a hot atom not undergoing hot combination reaction, assuming elastic and reactive collisions are taking place competitively,

$$n(E)\mathrm{d}E = -\frac{\mathrm{d}E}{\alpha E}\left\{1-\sum_j\int_{E_i}^{E} f_j p_j(E) n(E)\mathrm{d}E\right\}, \qquad (2)$$

where $\alpha = \sum f_i\alpha_i$, and for hard sphere collision,

$$\alpha_j = 1 + \frac{\beta_j \ln \beta_j}{1-\beta_j} \quad \text{and} \quad \beta_j = \left[\frac{(M_j-m)}{(M_j+m)}\right]^2,$$

where m is the mass of hot atom and M_j, that of the particle struck. The quantity in the bracket of Eq. (2) is the probabiliy that the hot atom has escaped reaction in the energy interval E_2 to E. Here, the reactions to form stable products by hot atom combination (such as CH_3T in the reaction, $T+CH_4$) are only considered.

In the present ion impact system, the incident ions are not lost, since they do not form any stable products by collision, and therefore we may simply assume that the number of ion impact products N_j is proportional to the collision number of methanol with incident ions in the energy range between E_i (initial energy of ion) and E_f (final energy). In this case, the formula similar to the equation (1) can be used, redifining N_s as the total number of incident ions.

$$N_j = N_s\int_{E_f}^{E_i} p_j n(E)\mathrm{d}E \qquad (3)$$

Since the form of scattering function for reactive and nonreactive collision is not known, the exact form of $n(E)$ cannot be derived. However, if we simply assume that the collision density function approaches rapidly to the following well known asymptotic solution[23]

$$n(E) = 1/\alpha E, \qquad (4)$$

the equation (3) can be simplified,

$$N_j = N_s\int_{E_f}^{E_i} p_j\left(\frac{1}{\alpha E}\right)\mathrm{d}E = N_s\frac{p_j}{\alpha}\ln(E_i/E_f), \qquad (5)$$

assuming p_j and α are both independent of energy, although this is obviously an approximation.[25] From the experimental point of view, since Fig. 3 shows that the yields per ion, (N_j/N_s) are proportional to logarithm of initial ion energy E_i, p_j/α can be determined as slope and $\ln E_f$ as intercepts with abscissa. Here, E_f can be interpreted as the lowest limits of energy to give appreciable reaction products.

In Table 3, the values calculated by least squares method are given. Here, it is interesting to compare

Table 3. Average logarithmic energy loss α and minimum energy to give reaction rpoduct calculated by the least squares method from the experimental results shown in Fig 3.

	α/p_j	$\ln E_f$	E_f, volt
H_2	0.035	6.2	490
CO	0.11	6.9	980
$(CH_2OH)_2$	0.24	6.9	980
CH_4	0.51	6.6	740

Table 4. Calculated α values for several sets of collision pair in the case of isotropic scattering for

$$\alpha = 1+\frac{\beta\ln\beta}{1-\beta},\ \beta = \left(\frac{m_1-m_2}{m_1+m_2}\right)^2$$

	Ar	Kr	Xe
H	0.05	0.02	0.02
He	0.19	0.09	0.06
Ne	0.73	0.23	0.16
Ar	1.00	0.70	0.50
Kr	0.70	1.00	0.85
Xe	0.50	0.85	1.00
CH_3OH	0.94	0.60	0.41

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[18] R. Wolfgang, "Progress in Reaction Kinetics," Vol. 3, Pergamon Press, London (1965), p. 97.

[19] R. N. Porter and S. Kunt, *J. Chem. Phys.*, **52**, 3240 (1970).

[20] C. Hsiung, K. L. Verosub, and A. A. Gordus, *ibid.*, **41**, 1595 (1964).

[21] R. Herschbach, "Molecular Beams," Advances in Chemical Physics, Vol. X, Interscience, New York, N. Y. p. 319.

[22] A. Henglein, K. Lacmann, and G. Jacobs, *Ber. Bunsenges. Phys. Chem.*, **69**, 279, 286, 292 (1965).

[23] J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 865 (1950).

[24] P. J. Estrup and R. Wolfgang, *J. Amer. Chem. Soc.*, **82**, 2665 (1960). See also, for example, S. Glasstone, "The Elements of Nuclear Reactor Theory," Van Nostrand, Inc., New York, N. Y. (1955), p. 147.

[25] In a strict sense, the asymptotic equation (4) cannot be applied to the region near E_i. However, Placzek (*Phys. Rev.* **67**, 423 (1964)) and Hsiung, Verosub, and Gordus (*J. Chem. Phys.*, **41**, 1595 (1964) have shown that $n(E)$ approaches rapidly to $1/\alpha E$, if β is much less than 1.

p_j/α with values α calculated for isotropic elastic scattering for several collision pairs.

The values of p_j are not known, but they must be less than unity, so the values of α in the experiment must be below 0.035, indicating that the average energy fraction lost in reactive collision is rather small corresponding to a small value of β. This seems to suggest that momentum is transferred to a part of light mass in a molecule (possibly to hydrogen atom), not to the whole molecule at the collision instant. After collision, the struck atom may depart from molecule, carrying kinetic energy, or dissipate energy to the whole molecule as in unimolecular decomposition. The latter process is taken into consideration, in view of the pressure effect on the product yields described below.

Pressure Effect on the Product Yields. Apparently, the pressure effect shown in Fig. 4 might be explained in terms of exponential law like Lambert-Beer type as

$$N_j = N_s \exp(-n_{CH_3OH}\sigma_j l) \qquad (6)$$

However, under the present experimental conditions, "so-called single collision condition" is not the case, and our experimental result of pressure dependency itself does not fit to Lambert-Beer type law. Although plot of logarithm of product yields against pressure of methanol is linear, the extrapolation of plot does not pass through origin at pressure zero, but rather intercepts the ordinate at much larger values. Instead, if the reciprocals of the product yields per ion are plotted against the reciprocal of pressure, again linear relationships are obtained. This type of linear relationship is known in the unimolecular decomposition mechanism, fluorescence and photochemical quenching, indicating the involvement of deactivation process of excited species by collision. Since the detailed reaction mechanism is not yet established, the following reaction scheme might be oversimplified one, but it may be helpful for understanding the feature of the reaction.

$$X^+ + CH_3OH \xrightarrow{\sigma_j l} X^+ + CH_3OH^* \qquad 1$$

$$CH_3OH^* + CH_3OH \xrightarrow{k_{2j}} 2CH_3OH \qquad 2$$

$$CH_3OH^* \xrightarrow{k_{3j}} \text{Product}\ j \qquad 3$$

The rate of formation of primary products to give j-th final product per ion, R_j may be as follows,

$$R_j = n_{CH_3OH}\sigma_j l\left(\frac{k_{3j}}{k_{3j}+n_{CH_3OH}k_{2j}}\right), \qquad (7)$$

or

$$1/R_j = \frac{1}{\sigma_j l}(k_{2j}/k_{3j} + 1/n_{CH_3OH}),$$

assuming steady state condition. n_{CH_3OH} is the number of methanol per ml, l, the length of reaction tube (30 cm), σ_j, macroscopic cross section for the process 1, and k_{2j} and k_{3j} are the rate constants for the processes 2 and 3, respectively.[26] The values σ_j[27] and k_{2j}/k_{3j} determined from the experimental values are given in Table 5. We consider a very large cross section for hydrogen production is an apparent one, since more than one hydrogen molecule must be produced per single collision. Relating to our observation, it is interesting that Tachikawa and Kahara[28] recently reported the similar pressure dependence of the reaction of recoil Br produced from ^{80m}Br with CH_4 and CD_4. They concluded the lifetime of the excited species is in the range of 10^{-8} to 10^{-9} sec. In the present case, much longer life-time (10^{-3} sec) must be assigned on the basis of our experimental values of k_{2j}/k_{3j}.

We are now undertaking the experiment in the presence of moderator, and more definite scheme for ion impact process will be obtained in near future.

TABLE 5. SLOPES AND INTERCEPTS CALCULATED FROM THE PLOTS OF $1/R_j$ AGAINST $1/p$, CROSS SECTIONS σ_j, AND k_{2j}/k_{3j}

Product	Slope (molecule ion)$^{-1}$/ (10^{-3} Torr)$^{-1}$	Intercept (molecule/ ion)$^{-1}$	σ_j (10^{-14} cm^2)	k_{2j}/k_{3j} (10^{-14}cc/ molecule)
H_2	0.023	0.012	4.2	1.5
CO	0.086	0.051	1.1	1.7
$(CH_2OH)_2$	0.601	0.12	0.16	0.55
CH_4	0.743	0.13	0.09	0.34
HCHO	1.955	0.19	0.05	0.27

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[26] In order to introduce the pressure effect into the equation (5), Eq. (7) must be combined with Eq. (5), but this is left for future investigation. We point out here only that it is necessary to modify the meaning of p_j to some extent.

[27] As Table 5 shows, σ for each reaction product is not constant. This seems to be peculiar, but the appropriate interpretation is not available at present.

[28] E. Tachikawa and T. Kahara, This Bulletin, **43**, 1293 (1970).