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REGULAR PAPERS

Study on Charge Transfer Reaction of Several Organic Molecules with Accelerated Rare Gas Ions

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Observing the charge transfer mass spectra of ethylbenzene, cyclobutane and methanol in Ar and Xe ion impacts, we investigated the dependence of the secondary ion peak intensities (normalized to primary ion current and target pressure) on the translational energy of primary ions (0–3500 eV). In the case of ethylbenzene, several maxima of the secondary ion peak intensities were observed in Ar and Xe ion impacts. The correlation between the maxima and the primary ion energy was examined in terms of near adiabatic theory of Massey. Supplementary studies on the energy distribution of primary ion, charge transfer cross section between methanol and Xe ion, and final product analysis in rare gas ion irradiation on cyclobutane were described.

1. Introduction

Reactions of molecules with ions in gas phase have been studied from various aspects by many workers, and a number of literatures and reviews have been published. Here we restrict our concern mainly to the studies on charge transfer (CT) mass spectra of polyatomic molecules. Pioneering works by Lindholm and his coworkers include the studies on CT mass spectra of methanol, ethanol, and propane with various primary ions of different

electron recombination energies (RE).^{1,2,3)}

They plotted relative abundance of secondary ions as a function of RE of projectile ions (break-down curve), and applied the statistical theory to the interpretation of CT mass spectrum in comparison with electron impact spectrum, but the agreement of the calculated secondary ion intensity distribution with the observed one was not satisfactory. S. Ikuta *et al.*⁴⁾ attempted to interpret the reported fragmentation patterns of cycloalkanes in the charge transfer reactions with ions of

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various RE , and they examined the applicability of MO theory by Hirota⁹⁾ to the fragment ion distribution.

Homer *et al.*⁸⁾, Lehrle and Parker⁷⁾, Lehrle *et al.*⁹⁾, Milner and Parker⁹⁾, and Lehrle and Mason¹⁰⁾ studied CT mass spectra of several hydrocarbons, and Parker and Milner¹¹⁾ on ammonia. They investigated the dependence of the secondary ion intensities on the primary ion translational energy, and applied near adiabatic theory of Massey to the interpretation of the dependence.

A technically important point in this kind of experiments as Lehrle *et al.*^{8,10)} pointed out is the collection efficiency of secondary ions, when the tandem mass spectrometer is a so-called perpendicular type one. When some secondary ions receive a fairly large amount of translational energy from primary ions (probably by momentum transfer in collision with a small impact parameter), a part of the secondary ions may not be extracted from the collision chamber.¹⁰⁾ Actually L'Hote *et al.*¹²⁾ and Yoshihara *et al.*¹³⁾ showed CT mass spectra which were obtained with a longitudinal type tandem mass spectrometer were different from those with a perpendicular type tandem mass spectrometer. It is interesting that L'Hote *et al.* found a large difference in the mass spectrum of propane in I^+ ion impact when the primary ion translational energy was varied from 3 to 30 eV in the perpendicular type tandem mass spectrometer. In the studies of CT mass spectra with perpendicular type tandem mass spectrometer, Lehrle *et al.*^{8,10)} overcame the difficulty in secondary ion collection efficiency by applying a high extraction potential to the

collision chamber to collect ions of high translational energy as well as slow ions.

In the present study we used a longitudinal ion impact system, without using any primary ion mass separating arrangement. CT mass spectra of ethylbenzene, cyclobutane and methanol by Ar and Xe ion impacts were studied with special concern on the primary ion energy dependence of the secondary ion intensities.

2. Experimental

2.1. Apparatus and Operation. Ion source.

At the time when this project was started, counting technique was not available to us, and we are obliged to obtain a primary ion beam of sufficient intensity (more than 1 nA) in order to observe CT mass spectrum without counting technique. Our ion source was low voltage discharge type, and similar to that developed by Menzinger and Wählin¹⁴⁾ with some modifications. It was designed in consideration of easy fabrication and cleaning of the ion source, and frequent replacements of

Fig. 1. Schematic diagram of ion source and collision chamber for CT mass spectrum (see Experimental Part for details).

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filament. Schematic diagram of the ion source is shown in Fig. 1. It consists of a stainless steel cylindrical cup (20 mm i.d. $\times$ 30 mm length) with a 2 mm diameter hole at its top for ion extraction, a quartz disk (19.8 mm diameter $\times$ 2 mm thickness) with a hole of 2 mm diameter, a quartz pipe (19 mm o.d. $\times$ 28 mm length) and a Ta disk of the same diameter with a hole of 1.5 mm diameter as anode. Both the quartz pipe and disk confine discharge to the center region near the ion extraction hole of Ta disk. As Pohlit *et al.*¹⁵⁾ pointed out, a clean surface of Ta disk is crucial to obtain a high intensity ion beam. An ion extracting electrode (a cone type nozzle) was screwed into a support. The ion extracting electrode was on earth potential and insulated by a boron nitride ring (BN) from a high voltage applied to the ion source for ion acceleration.

In order to perform a stable operation of ion source, a long life of filament is important. Filaments of various types were tested (tungsten wire and strip, and BaO matrixed tungsten powder sintered disk), but the electron emissions from these filaments were not sufficient to maintain stable discharge under our prescribed experimental conditions (low filament current, low discharge voltage, and low gas loading).

A fairly satisfactory performance was achieved with BaO-SrO sprinkled Ni net (100 mesh). A nichrome strip (2 mm $\times$ 0.175 mm) was wrapped by a Ni net and shaped as U type. The strip ends were inserted into each cut of Kovar supporting rods (6 mm diameter) which were mounted by screws into pins of hermetic sealed electrodes. The electrodes were mounted

on a small flange of 75 mm diameter. Before use, the filament was dipped in a suspension of Chemical R-500 solution (Ba-Sr double carbonate suspension in a mixture of butyl alcohol, butyl acetate and pyroxylin cotton, T. Baker Chem. Co.). Double carbonate suspension in water glass was also tested, but Chemical R-500 gave better results, since the latter assured the strong binding of BaO-SrO powder to Ni net. One disadvantage in use of Chemical R-500 is that it gave impurity ions at m/z 28 and 30 (probably N_2 and NO from pyroxylin), but their ion abundances were less than one to thousandth of the main primary ion abundance. The average life of the filament was 100–150 hours, provided filament heating current was kept below 20 A.

Ion source gas was fed through a hole drilled in the flange, a thick Tygon tubing, a U tube packed with molecular sieves, a Cu pipe of 8 mm i.d. and finally *via* a needle valve. The molecular sieve packing was baked under vacuum. The packing generates a pressure difference between ion source and gas supplying line, preventing electric breakdown up to 6 kV between ion source and gas supplying system.

2.2. Ion source operation.

For the discharge between the filament and Ta disk anode, DC voltage (initially 300 V) was supplied from DC power which was floated through an insulating transformer. Filament was heated with AC power (7 V/30 A rating) which was also floated from ground potential. After introduction of ion source gas, striking of DC arc was started when the filament heating current was raised to 30 A and

DC voltage up to 300 V referred to the filament potential. Initial high gas feeding rate was gradually reduced to the steady discharge limit. The approximate gas consumption was 10^{-8} mol/s for Ar and about its half for Xe. When the discharge started, anode voltage dropped spontaneously below 20 V due to the voltage drop across a guard resistor of 100 Ω /100 W. Maximum discharge current was limited below 1 A due to the current capacity of insulating transformer. The anode voltage was kept below 20 V to suppress the generation of double charged ions, and no voltage stabilizing circuit was used. To maintain the temperature of vacuum housing of the ion source below 60°C, air cooling from outside with a small electric fan was sufficient. Primary ions were extracted from the ion source through a hole of Ta disk, applying a positive voltage from 2500 to 6000 V directly to the ion source chamber. The ion extracting efficiency depended on the accelerating voltage. The ion source flange was insulated from pumping line by a Delurin flange (D). The high voltage power was supplied from Fluke 408 B (John Fluke Mfg., 6000 V/20 mA).

2.3. Collision chamber arrangement.

Two types of collision chamber were used. For the experiments of CT mass spectrum a small drum type chamber (C) was installed in a cavity of a steel block by a Delurin supporting ring (R). Thickness of the drum was 5 or 10 mm, and it had a hole of 1 mm diameter at each side of the drum. A target gas was introduced into the collision chamber through a polyvinyl chloride

tube of 3 mm i.d., which was joined to a glass pipe of 12 mm i.d. fixed by an O ring seal to a flange. The middle part of the glass pipe was capillary (0.5 mm i.d. and 100 mm length) and the pipe was connected to Cu pipe, leading to a gas feeding system. A Pirani gauge was attached to the glass pipe in between the capillary and Cu pipe in order to monitor the gas flow rate. The pressure at the Pirani gauge position was usually set at 20 – 25 mTorr (nominal reading) and in the early experiments at more than 100 mTorr. Direct measurement of the pressure in the collision chamber was not attempted. The pressure difference between the collision chamber and gas supplying line generated by the capillary could prevent electric discharge toward gas supplying system, when the collision chamber voltage was set at 2500 V for the secondary ion extraction.

Two electrodes, E_1 and E_2 in front of the collision chamber were served as collimating plates, and E_1 also as a monitoring electrode for the total primary ion current extracted from the ion source. The primary ion accelerating voltage was varied from 2500 to 6000 V. When the ion accelerating voltage was reduced close to the collision chamber voltage, a large fraction of the primary ions were reflected back in front of the collision chamber. As the reflected ions disturbed stable operation of the system, the double electrode system was useful to collect the reflected ions.

At another side of the collision chamber, an ion extracting electrode E_3 and an ion current monitoring electrode E_4 were placed. The electrode E_3 was usually grounded and no measurable current (less

than 0.1 nA) was observed, provided the primary ion beam alignment was proper. The electrode E_4 had a hole of 5 mm diameter covered with a Ni grid of 100 mesh. The transmittance of the grid was about 30% by the estimation of geometrical size of the grid. We assumed that the ion current measured at E_4 was proportional to the primary ion current injected into the collision chamber, and the secondary ion intensities measured at the ion detecting position were normalized to the ion current at E_4 . When target gas was introduced into the collision chamber, the current measured at E_4 was a mixture of primary and secondary ions formed in the collision chamber by charge transfer, but we confirmed the current did not show any difference either in the presence or absence of the target gas in the collision chamber.

In the original arrangement the ion source was placed as close as possible to the collision chamber (*ca* 20 mm). This arrangement made possible to inject several more than 100 nA of the primary ions into the collision chamber, and the primary ion current collected at Faraday cage were of order of 10^{-11} – 10^{-12} A and ion current of secondary peak was also 10^{-11} – 10^{-13} A. Some disturbing problem in this arrangement was that weak secondary ion peaks were still observed, nevertheless that the primary ion accelerating voltage was reduced below the collision chamber voltage (usually 2500 V). We presumed that the secondary ions were probably generated by fast neutral atoms formed by the resonance charge transfer in front of the ion source, since the secondary ion peaks still persist even when the primary ion accel-

erating voltage was reduced to 1000 V. This may be due to the inefficient pumping of ion source gas in the region in front of the ion source, and we modified the arrangement of ion source- collision chamber, shifting the ion source 300 mm away from the collision chamber, and evacuated the region with 6' DP. In this arrangement no formation of the secondary ions was observed, while the primary ion accelerating voltage was reduced below 2500 V. However, the primary ion current passing through the collision chamber was reduced (0.1–several nA) despite of focussing with Einzel lens, and electron multiplier (Paralleltron S kindly donated by Nihon Denshi Co.) was indispensable to take CT mass spectrum. Essentially CT spectrum obtained in both arrangements were similar, but rather better in the original arrangement.

For the experiments to determine the energy distribution of primary ions and the charge transfer cross section, another type of collision chamber was used. Some details of the collision chamber are described in the supplementary experiment section.

2.4. Some points in CT mass spectrum with present longitudinal mass spectrometer.

In obtaining CT mass spectrum, we used magnetic field scan technique with a fixed voltage of 2500 V for extracting the secondary ions from the collision chamber. Primary ion accelerating voltage was varied from 2500 up to 6000 V with a step of increment of 50 or 100 V. Ion current collected at Faraday cage or electron multiplier was fed through Keithley electrometer 610C to a pen recorder. The MS obviously

includes primary ion peaks as well as secondary ion peaks, but their discrimination can be easily done by checking whether the peak moves or not with change of primary ion accelerating voltage. Overlapping of secondary ion peak with primary ones takes places occasionally in the course of changing the primary ion accelerating voltage. This is a trouble in the present technique, and we need to pay special caution in order to avoid observation of artifact maximum in plot of secondary ion intensities as a function of primary ion energy. We attempted to separate and eliminate the primary ion peaks from the secondary ones using an energy analyser after the mass analysis, but the reduction of the ion current in our energy analyser was so large that this attempt was abandoned. Such an overlapping was observed mainly in CT mass spectrum of small molecular weight compounds in Ar ion impact. In the present reaction systems CT mass spectra of ethylbenzene are free from this trouble as far as peak heights of high m/z values are concerned, while in the case of methanol satisfactory results are not obtained. (see Results section)

2.5. Materials

Rare gases were obtained from Taka-chiho Chem. Ind. Co. Cyclobutane from Merck, Sharp and Dohme, Ltd. was kindly donated by Prof. I. Tanaka (Tokyo Institute of Technology).

3. Results

3.1. Charge transfer mass spectra.

Dependence of intensity of secondary ions on pressure of

target molecule and primary ion intensity.

In Fig. 2 is shown CT mass spectrum of ethylbenzene obtained by Xe ion impact. In CT mass spectrum of ethylbenzene, the most intense peak is at m/z 91 ($C_7H_7^+$), and the secondly intense one is molecular ion, at m/z 106. Other fragment ion peaks such as $C_6H_6^+$, $C_6H_5^+$, $C_5H_5^+$, $C_4H_3^+$, $C_3H_3^+$, $C_2H_3^+$ and CH_3^+ are also observed. The features of CT mass spectrum of ethylbenzene both in Ar and Xe ion impacts are similar.

Fig. 2. CT mass spectrum of ethylbenzene in Xe ion impact. Xe ion accelerating voltage (V_p), 4000 V; extracting voltage of secondary ions from collision chamber (V_c), 2485 V. Pressure of ethylbenzene at monitoring Pirani gauge, 200 mTorr (nominal). Total ion current at E_4 , 19 nA.

Figure 3. gives a plot of peak heights at m/z 91 *vs.* ethylbenzene pressure by Pirani gauge reading. We see that a linear relationship between secondary ion intensity and Pirani gauge reading holds below 100 mTorr (nominal reading). Since we were not concerned with the absolute values of secondary ion intensity, we kept

Fig. 3. Plot of peak heights at m/z 91 in CT mass spectrum of ethylbenzene *vs.* ethylbenzene pressure at monitoring Pirani gauge. Primary ion, Ar ion (2 nA at E_4). Primary ion accelerating voltage, 2600 V; extracting voltage of secondary ions, 2500 V.

the flow rate of target vapor constant only by monitoring the Pirani gauge reading in a series of experiments (in a plot of secondary ion intensities as a function of primary ion energy). The actual pressure in the collision chamber is not known, but it may be less than 1 mTorr in the course of usual experiments where Pirani nominal reading is around 10 mTorr order. The deviation of peak intensity plot against pressure from linearity above 100 mTorr of target pressure (Pirani reading) is supposed to be mainly due to decrease of sensitivity of Pirani gauge above 100 mTorr. In Fig. 4 a plot of peak heights at m/z 91 in CT mass spectrum of ethylbenzene *vs.* total ion current at E_4 is shown. Since the large range variation of primary ion current at a fixed ion energy is extremely difficult in ion impact experiments, the variable range of ion current is very limited. The variation of ion current in the present study was performed by adjusting Einzel lens focussing. In the experiments to examine the dependence of secondary

Fig. 4. Plot of peak heights at m/z 91 in CT mass spectrum of ethylbenzene *vs.* total ion current at E_4 . Primary ion, Ar ion. Primary ion accelerating voltage, 2700 V; extracting voltage of secondary ions, 2500 V. Pressure of ethylbenzene at monitoring Pirani gauge, 100 mTorr (nominal).

ion intensities on primary ion energy, the primary ion intensity varies from several to hundred nA, depending on the primary ion accelerating voltage. We could not confirm the linear relationship between secondary ion intensity and primary ion intensity over the whole range of the primary ion current (0.1 – 100 nA), but we assumed that the secondary ion peak heights could be normalized to primary ion current over the whole energy range of primary ion in the plots of secondary ion peak heights *vs.* primary ion energy.

3.2. CT mass spectrum of cyclobutane in Ar^+ and Xe^+ impacts.

CT mass spectrum of cyclobutane taken under specified conditions are shown in Fig. 5 (a) and (b). In the case of Ar ion impact, the secondary ion peaks at m/z 28, 27, and 26 are well resolved and identified.

Peaks of C_3 and C_4 groups are not clearly identified, since their peak intensities are very weak, and the overlapping of the primary ion peak(s) (Ar, NO and N_2) with C_3 peaks interrupts their identification. In the case of Xe ion impact, peaks in each group of C_4 , C_3 , and C_2 were clearly observed, but they showed tailing to lower mass side, and individual peak positions in each group were not definitely established. Although the reason for such tailing is not certain, the decomposition of the energized precursor ions may produce the secondary ions having a kinetic energy of broad range, resulting in broad peaks. Another interesting thing is that the intensities of C_4 group peaks are very weak, while in 70 eV electron impact the peak intensities at m/z 56 ($C_4H_8^+$), 41 ($C_3H_8^+$) and 28 ($C_2H_4^+$) are nearly comparable, suggesting that more violent decomposition of precursor ions is involved in the ion impact.

3.3. CT mass spectrum of methanol.

CT mass spectrum of methanol is taken in both Ar and Xe ion impacts, but not shown in figure, since the feature is essentially similar to that reported by Wilmenius and Lindholm.²⁹ The intense peaks are at m/z 32 and 31, and the ratio of the peak height at m/z 32 to that at m/z 31 is around 0.1 – 0.3 in the energy range from 50 to 3000 V of Xe ion, while Wilmenius and Lindholm²⁹ reported its ratio of 0.1 at 9 V of Xe ion.

3.4. Dependence of secondary ion peak heights on primary ion energy.

Although the experimental difficulty is large in this kind of experiments, the

Fig. 5. CT mass spectrum of cyclobutane. (a) Ar ion impact, Ar ion accelerating voltage, 2900 V. Extracting voltage of secondary ions from collision chamber, 2486 V. Pressure of cyclobutane at monitoring Pirani gauge, 350 mTorr (nominal). Total ion current at E_4 , 300 nA. (b) Xe ion impact, ion accelerating voltage, 3000 V; extracting voltage of secondary ions, 2500 V. Pressure of cyclobutane at monitoring Pirani gauge, 400 mTorr (nominal). Total ion current at E_4 , not measured. In the MS, p indicates primary ion.

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fairly clear results were obtained in the case of ethylbenzene. In Fig. 6 a plot of peak height at m/z 91 in Ar and Xe ion impact on ethylbenzene is shown as a function of primary ion energy in the collision chamber, which is assumed to be $V_p - V_c$, (V_p , primary ion accelerating potential and V_c , secondary ion extracting potential applied to collision chamber, usually fixed at 2500 V). All the peak heights are normalized to total ion monitor current, the pressure of ethylbenzene in the collision chamber being kept constant in a series of energy dependence experiments. We took as well a plot of peak heights at m/z 106 as a function of primary ion energy, but the essential feature of the plot is similar to that at m/z 91, apart from gradual increase of ratio of peak height at m/z 106 to that at m/z 91 with increase of primary ion energy. Plot of other weak secondary ion peaks was not attempted.

In Fig. 7 (a) and (b) similar plots of secondary ion peak heights in Ar and Xe ion impacts on cyclobutane are shown. For Ar ion impact, plots of most definite secondary ion peaks, *i. e.*, at m/z 28, 27, and 26 are given, while for Xe ion impact plots of the strongest ion peaks for each of C_4 , C_3 , and C_2 groups (the definite m/z values of these

Fig. 6. Plot of peak heights at m/z 91 in CT mass spectrum of ethylbenzene (peak heights normalized to total ion current at E_0) as a function of energy of primary ion (Ar and Xe ions) at collision chamber, ($V_p - V_c$). In the case of Ar ion impact, pressure of ethylbenzene, 6.0 mTorr (nominal). In the case of Xe ion impact, pressure of ethylbenzene, 24 mTorr (nominal), extracting voltage of secondary ions, 2560 V.

Fig. 7. Plot of peak heights in CT mass spectrum of cyclobutane (peak heights normalized to total ion current) as a function of energy of primary ion (Ar and Xe ions) in the collision chamber. (a) Ar ion impact, peak heights of secondary ions at m/z 26 ($C_2H_2^+$), $\circ$; 27 ($C_2H_3^+$), $\square$; and 28 ($C_2H_4^+$), $\bullet$ are plotted. Pressure of cyclobutane at monitoring Pirani gauge, 300 mTorr (nominal). (b) Xe ion impact, peak heights of the strongest intensity peaks, $\circ$ for C_2 group, $\square$ for C_3 group and $\bullet$ for C_4 group are plotted, since peaks in each group are not well resolved. Pressure of cyclobutane at monitoring Pirani gauge, 300 mTorr (nominal).

peaks were not certain) are shown as a function of primary ion energy.

In Fig. 8 a similar plot of peak heights of secondary ions at m/z 31 in the case of methanol in Xe ion impact is shown. For Ar ion impact on methanol a plot of secondary ion peak was obtained in a similar way, but not shown for lack of good reproducibility in the location of position of $V_p - V_c$ for maximum of secondary ion intensities. Probably the overlapping interference of primary ion peaks of impurity (N_2 and NO) with secondary ion peaks may be the main reason.

4. Discussions

In the charge transfer of atom-atomic ion systems the dependence of the charge transfer cross sections on the primary ion energy has been interpreted in terms of near adiabatic theory of Massey or of further sophisticated quantitative calculation of energy level correlation in many cases. However, in ion-molecule system only a limited number of studies have been reported on the dependence of the charge transfer cross sections on the primary ion energy. As described in Introduction, Lehrle and Parker and their group proposed that the primary ion energy dependence of the secondary ion intensities may be interpreted in terms of near adiabatic theory. With the similar concerns on this problem we attempted to see whether a maximum of secondary ion intensities ap-

Fig. 8. Plot of peak heights at m/z 31 in CT mass spectrum of methanol (peak heights normalized to total ion current at E_t) as function of energy of primary ion (Xe ions) at collision chamber. Pressure of methanol at monitoring Pirani gauge, 30 mTorr (nominal).

Fig. 9. Comparison of RE values of reactant ions (Ar and Xe), IP values of ethylbenzene and AP values of fragment ion from ethylbenzene. E_{max} values are the primary ion energy values where secondary ion peak heights are maximum.

pears at the position of energy resonance

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in terms of primary ion energy. In Figs. 9, 10, and 11 *RE* values (electron recombination energy of projectile ions), *IP* values (ionization energy of target molecules, ethylbenzene, cyclobutane, and methanol)

Fig. 10. Similar diagram for cyclobutane to that in Fig. 9.

Fig. 11. Similar diagram for methanol to that in Fig. 9.

and *AP* values (appearance energy of fragment ions from parent target molecule, ethylbenzene only) are shown. In these figures *RE* values of Ar and Xe ions are given for both of different *J* (3/2 and 1/2). Since we do not know the abundance ratios of these ions of different *J* under our experimental conditions, we assume both ions might participate in the production of secondary ions. *IP* values of the target molecules (cyclobutane and methanol) are from the published papers^{16,17)} which give vertical ionization energies determined by photoelectron spectroscopy measurements. For ethylbenzene no published *IP* values are available, and the values shown are kindly communicated by Prof. Nagakura and Dr. Kobayashi.¹⁸⁾ *AP* values of some fragment ions are also shown for ethylbenzene.¹⁹⁾

In the right columns we give $E_{\max}$ (obs.) and $E_{\max}$ (cal.). $E_{\max}$ (obs.) is the primary ion energy where the secondary ion peak height shows a maximum, while $E_{\max}$ (cal.) is the primary ion energy calculated by Massey's equation:

$$E_{\max}(\text{cal.}) = 3.08 (aJE)^2 m,$$

where *JE* is the difference, $|RE - IP|$; *a*, Massey's parameter (7Å adopted); and *m*, mass of reactant ions in a.m.u. (for Xe, average atomic weight for isotopes, 131.29 is used).

Looking at these diagrams (Fig. 9, Fig. 10, and Fig. 11), we consider that a meaningful comparison between $E_{\max}(\text{cal.})$ and $E_{\max}(\text{obs.})$ is possible only in the case of ethylbenzene. Fairly good correspondence is seen in the case of $\text{Xe}^+(^2P_{3/2})$, that is $E_{\max}(\text{cal.})$ are at 1550 and 2160 eV, while

E_{max} (obs.) are at 1380 and 2030 eV. For $\text{Xe}^+ (^2\text{P}_{1/2})$, which is 1.31 eV above $\text{Xe}^+ (^2\text{P}_{3/2})$, the expected E_{max} (cal.) are at 3330 and 7130 eV, but in our experiments the primary ion energy range was limited to 2400 eV, being below the expected E_{max} (cal.) values. Since the abundance of $\text{Xe}^+ (^2\text{P}_{1/2})$ in the present discharge ion source is supposed to be far less than that of $\text{Xe}^+ (^2\text{P}_{3/2})$, we would not expect that these E_{max} for $\text{Xe}^+ (^2\text{P}_{1/2})$ could be observed, even if the primary ion energy range could be extended above E_{max} (cal.) values.

In the case of Ar ion-ethylbenzene system, we observed three E_{max} (obs.) at 270, 850 and 1700 eV, while E_{max} (cal.) are at 470, 1270 and 1400 eV. The agreement of E_{max} (obs.) with E_{max} (cal.) is not so good as in the case of $\text{Xe}^+ (^2\text{P}_{3/2})$ -ethylbenzene system. At present we have no satisfactory explanation on this disagreement, but we need consider the arbitrariness in the calculation of E_{max} (cal.) as well as the experimental errors in the location of E_{max} (obs.). In Massey's equation, a parameter α is of semiempirical nature, and its value ranges from 6 to 8 Å, and the value of 7 Å adopted is a tentative one. At the same time, we need consider experimental errors in the location of E_{max} (obs.) which are probably due to the experimental fluctuations of the normalized secondary ion peak heights. In particular, in the case of Ar ion impact, the variation of the secondary ion peak heights (difference between its top and bottom) as a function of primary ion energy is not so distinguished as in the case of Xe ion, and consequently the location of E_{max} (obs.) values involves more errors. Reason for such a

different feature in the variation of the plots is not certain, but we presume that the shorter interacting time of Ar ions with ethylbenzene than that of Xe ions due to the lighter mass (or larger velocity) of the Ar ions might reduce the transition probability between Ar ion and ethylbenzene.

In the case of cyclobutane, the primary ion energy range in our experiment was so narrow, that it is difficult to see the correlation clearly. For Ar ion impact the energy differences, ΔE , for both $\text{Ar}^+ (^2\text{P}_{3/2})$ and $\text{Ar}^+ (^1\text{P}_{1/2})$, are very small, and strong intensity (normalized) of the secondary ions near 0 eV may be ascribed to the small ΔE values, but E_{max} (obs.) at near 500 eV cannot be assigned to any values of E_{max} (cal.), and some unknown autoionization level might be responsible. For Xe ion impact on cyclobutane actually no E_{max} (obs.) is seen in the present experimental range, apart for an appreciable secondary ion peak height close to 0 eV. For $\text{Xe}^+ (^2\text{P}_{3/2})$ the energy difference, ΔE is so large and E_{max} (experiment) is out of experimental energy range. On the other hand for $\text{Xe}^+ (^2\text{P}_{1/2})$ we would expect E_{max} at 500 V, but no indication of the maximum is seen. This might be ascribed to the small abundance of $\text{Xe}^+ (^2\text{P}_{1/2})$ in the present experiment, but we would not go further into this matter.

In the case of methanol the result is more ambiguous. For Xe ion impact on methanol no definite intensity maximum was observed except increase near the energy zero of primary ion, but the increase of the apparent secondary ion in the energy zero region must be considered carefully, since the primary ion intensity

is so weak in this energy range and some contribution of neutral fast atoms might be involved. The diagram (Fig. 11) suggests a maximum of secondary ion peak intensity at 6900 eV, but we could not extend our primary ion energy beyond 3500 eV.

Summarizing these results, we admit that our results are still not conclusive, and further experiments in future are required in order to establish clearly the correlation of dissociative ionization cross sections in charge transfer with near adiabatic theory in the ion-molecule systems. Experimentally the results obtained until today are suggesting that the choice of favorable ion-molecule system is important in order to be able to find the correlation between the secondary ion intensities and primary ion energies.

5. Supplementary experiments relating with CT mass spectra

5.1. Determination of energy distribution of primary ion.

We assumed that the primary ion translational energy is equal to the ion accelerating potential applied to the ion

source. However, considering that our ion source is discharge type, we felt that it is desirable to determine the ion energy distribution by experiments. In Fig. 12 a schematic diagram of collision chamber and of movable Faraday cage arrangement used for this experiment and for the determination of charge transfer cross section is shown. The ion source chamber and the collision chamber were separated by a skimmer with a 2 mm diameter hole. The collision chamber was a cylinder of 60 mm i. d. and 200 mm length. The chamber had an ionization gauge port, a target gas inlet port, and three viewing windows for observing the photoemissions in ion impact. A movable Faraday cage was installed at a flange on the end of the collision chamber cylinder. The collision chamber had no pumping system apart from pumping through the skimmer hole, but a vacuum of 10^{-6} Torr could be attained before introducing the ion source gas, and that of 10^{-5} Torr after that.

First we tried a retarding potential method in which a mesh grid was placed in front of Faraday cage and a retarding potential was applied to the grid. However, the measured ion energy values were not well reproducible and the apparent FWHM of the ion energy distribution was 30 – 60 eV. We also tried the electrostatic parallel electrode energy analyzer method, but our laboratory-made energy analyzer did give neither sufficient energy resolution nor high ion transmission. Here we describe the results obtained by a modified

Fig. 12. Schematic diagram of collision chamber for the determination of ion energy and its distribution and of the charge transfer cross section. E, Einzel lens; S, skimmer; F, Faraday cage; G₁ and G₂, gas inlet; IG, ionization gauge.

retarding potential method which is similar to that used by Zehr and Berry.²⁹⁾

A retarding potential was applied directly to Faraday cage, and ion current was measured as a function of the retarding potential. Since Faraday cage was on a high voltage, special cautions on insulation were required in measuring the ion current of order less than 1 nA. Zehr and Berry floated electrometer and recorder at the retarding potential, but we inserted a high voltage power supply between Faraday cage and electrometer. In this arrangement DC high voltage power supply must be sufficiently insulated at negative potential side (ground side) as well as positive potential side to eliminate any current leakage through the DC power supply line. In the preliminary experiment we used a series of dry cell battery piles placed on an insulated board. We met no serious problem on insulation, but a minimum step of voltage change was limited to 1.5 V. (We would not use potentiometer circuit to avoid any battery voltage drop due to power consumption of batteries). In order to achieve more fine voltage setting a DC high voltage power supply of high frequency converter type (Towa Keisoku Co., KT-05 K, output voltage 0 – 5000 V; output current, 1 mA) was an inexpensive and convenient choice, although it was found necessary that primary DC power supply from AC line must be substituted by a dry cell battery of 15 V. In this arrangement we were able to vary the retarding potential with 0.2 V step at 1000 V. The voltage applied to Faraday cage was determined by a digital voltmeter (Takeda Riken Co., TR-6855).

First we placed a grid (grounded) in front of Faraday cage for the purpose to obtain an electric field as parallel as possible to the bottom plate of Faraday cage. We obtained a median value of 982 V with FWHM of 20 V for Xe ions accelerated at 1000 V. However, when the retarding potential exceeded the ion accelerating voltage, a negative current was observed amounting to more than 10 % (1.0 nA) to the positive current obtained at zero retarding potential. We confirmed that this negative current was not due to secondary photoelectrons produced by UV irradiation from ion source discharge plasma on Faraday cage surface, because the current went to zero, when the ion accelerating voltage was reduced to zero (no incoming of positive ions to Faraday cage) with continuation of discharge in the ion source. We presumed that a part of projectile ions which collided on grid wire surface generated secondary electrons, and some portions of the secondary electrons were collected at positive Faraday cage. Although the amount of the negative current was not known when the retarding potential voltage was below the primary ion accelerating voltage, it might contribute heavily to the distribution of ion current in the region where the positive current entering to Faraday cage is reduced steeply by the application of retarding potential, resulting in a distortion of ion current distribution *vs.* retarding voltage, as Simpson pointed out.²⁹⁾ In consideration of this effect, finally we removed the grid and obtained the improved result as shown in Fig. 13. The median value of ion energy was 898 eV with FWHM of 4.0 eV at the ion acceler-

Fig. 13. Plot of primary ion current *vs.* retarding potential applied to Faraday cage, and its differential plot. Primary ion, Xe ion. Primary ion accelerating voltage, 900 V.

ating voltage of 900 V, and no negative current was observed above 900 V. Thus we concluded that the primary ion energy is fairly close to the ion accelerating potential with a narrow FWHM, although some distortion of ion energy distribution may still remain left.

It is to be noted that the results obtained above may not assure our assumption that the primary ion energy in the collision chamber is equal to $V_p - V_c$, since the arrangement of the collision chamber which retards primary ions with the application of 2500 V potential (V_c) is different from the arrangement of ion energy distribution measurement.

5.2. Charge transfer cross section between Xe ions and methanol and its primary ion energy dependence.

Using our ion impact apparatus, we attempted to determine the total cross section of charge transfer between Xe ions and methanol. The main arrangement of the apparatus was the same as described

above, but we placed a secondary electron suppressor grid kept at -50 V in front of Faraday cage, and fed the ion current directly to electrometer. The cross sections were determined by the usual ion intensity attenuation method according to the equation:

$$i = i_0 \exp(-\sigma l n),$$

where i and i_0 are the ion current in the presence and in the absence of target molecule, σ is the cross section, l is the path length, and n is the number density of the target molecule. We can determine σ by varying either l or n . For the variation of l Faraday cage was moved in the range 5 – 70 mm from the skimmer position. Faraday cage can accept all ions experienced single elastic collisions as well as uncollided ions, since the span angle of Faraday cage (36 mm diameter) viewed from the skimmer nozzle position was 28 degree, when the Faraday cage was at 70 mm far from the nozzle hole position, while the calculated maximum angle of elastic scattering is 14 degree in the system of Xe ion and methanol (assuming the effective mass of methanol is 32 in a. m. u.). We assumed that the energy of methanol ions or its fragment ions formed by the charge transfer is nearly thermal, and that these ions are not collected in Faraday cage. In Fig. 14 (a) a plot of $\ln i$ *vs.* ion path length l is shown, and in Fig. 14 (b) a plot of $\ln i$ *vs.* pressure of methanol measured by an ionization gauge in the collision chamber is shown. The cross sections determined by the first procedure in the energy range from 1000 eV to 3000 eV are shown in Fig. 15. Any appreciable

change of the cross sections was not observed in the energy range, apart from a slight increase with ion energy increase. The absolute value of the charge transfer cross section could not be evaluated, but the approximate value of the charge transfer cross section was 0.1 nm^2 , assuming the reading of the ionization gauge is the true pressure.

For Ar ion-methanol system we found no appreciable attenuation of ion current, and we presumed that the charge transfer cross sections between Ar ion and methanol are much smaller, although CT mass spectrum of methanol were observed both for Ar and Xe ion impact. From the view of energy resonance in charge transfer the cross section between Ar ion-methanol (ΔE values, 0.21, 0.44 and 0.61 eV) is expected to be larger than that in Xe ion-methanol (ΔE , 0.59 and 0.72 eV) (Fig. 11), but the result is opposite to the expectation, and we have to consider other unknown factors.

Fig. 15. Plot of charge transfer cross section between Xe ion and methanol as a function of primary ion energy. Pressure of methanol measured by ionization gauge, 8 mTorr.

Fig. 14. Charge transfer cross section determination. (a) Plot of $\ln i$ vs. ion path length l . Pressure of methanol measured by ionization gauge, 8 mTorr. Primary ion, Xe ion; ion accelerating voltage, 1000 V. (b) Plot of $\ln i$ vs. pressure of methanol measured by ionization gauge. Primary ion Xe ion; ion accelerating voltage, 2000 V.

It is desirable to determine the charge transfer cross section between ethylbenzene or cyclobutane and rare gas ions as a function of ion energy with this apparatus, but we did not attempt further experiments, considering that the collisions between heavier target molecules and rare gas ions do not necessarily satisfy the scattering angle requirement described above.

5.3. Final product distribution in rare gas ion impact on cyclobutane.

In order to see the correlation between CT mass spectrum of cyclobutane and its final product distribution in ion impact, we attempted the final product analysis in ion impact on cyclobutane. As reported previously in the ion impact of methanol,²³⁾ the product analysis in ion impact is technically difficult, and the results did not lead to the straightforward elucidation of the mechanism to yield the final products. In the case of cyclobutane, originally we expected that the product distribution may be simpler than that in the case of methanol. As far as the product distribution is con-

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cerned, this is the case, but unexpected difficulty (formation of hydrocarbon polymer) interrupted the continuation of experiments. Here we describe our tentative results of ion impact on cyclobutane very briefly.

The detailed description of ion irradiation and the product recovery procedures were reported elsewhere.²²⁾ The analysis of the products was performed by gas chromatography with 8 m active alumina column with He carrier at 50°C. The products were ethane, ethylene, acetylene, propane, and propene. We confirmed that these products were not formed in the absence of cyclobutane in the ion injection into the reaction chamber. We also confirmed that a plot of product yields (in unit of molecule/primary ion) *vs.* ion irradiation time was linear in the range of 10 to 20 min, passing through origin at zero minute (in Ar ion irradiation at 5.7 kV and at the pressure of 1 mTorr by Pirani gauge (nominal)). We also confirmed that a plot of the product yields *vs.* cyclobutane pressure was linear in the pressure range from 10 to 30 mTorr (nominal), passing through origin at zero pressure (in Ar ion irradiation at 5.7 kV). Table I shows the

relative ratios of the product yields, including the results of photolysis (below and above the photoionization threshold) by Doecker and Ausloos²³⁾ for comparison. It is interesting that the yield of acetylene is comparable with that of ethylene in the ion impact, while in the photolysis the yield of acetylene is much less. According to Depker and Ausloos,²³⁾ and K. Obi *et al.*²⁴⁾ the main processes to yield ethylene and acetylene are as follows:

where C_2H_4^* is energy rich ethylene. Since in the present ion impact the pressure of cyclobutane is lower by a factor of one to thousandth than in the case of the photolysis, the decomposition of energized ethylene (and/or energized ethylene ion) may proceed, being free from collision with another cyclobutane. Another interesting thing is that the yield of propylene in the present case is relatively high, considering that Depker and Ausloos predicted the increase of propylene yield in the radiolysis of cyclobutane compared with the case of

Table I. Product Distribution in Ion Impact on Cyclobutane in Comparison with Photolysis

	Pressure	Product yields (relative to ethylene yield)						
		H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆
Ion impact with Ar ion at 5.7kV, RE of Ar ⁺ (² P _{3/2}) 15.8 eV.	1 mTorr	not determined		17.4	(100)	80.7	3.9	20.3
Photolysis ²²⁾								
147 nm photon, (8.3 eV)	15 Torr	14.4	0.52	0.88	(100)	12.0	—	2.1
123.6 nm photon, (9.9 eV)	15 Torr	38.0	1.1	1.58	(100)	29.0	—	3.4
106.7–104.8 nm photon (11.5–11.7 eV)	5.2 Torr	—	—	1.58	(100)	35.0	—	4.86

photolysis. Under the present reaction conditions it was not possible to differentiate the ionic, free radical, and molecular processes to give these products, and the detailed reaction mechanism is left for future investigations.

We studied also the reactions of ion impact with Kr and Xe ions, but the results were similar, and no appreciable difference was observed in the product distributions.

Although it was expected originally to study the primary ion energy dependence of the product yields, it was found that the amounts of ethylene and acetylene in the blank experiments were gradually increasing after many ion irradiation runs. Every effort to reduce the blank values of the compounds was not so successful to assure the continuation of further experiments.

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