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Studies on Fragment Ion Distribution and Reactions with the Use of a Charge Spectrometer. IV. Dependence of Cross Sections of Some Ion-Molecule Reactions on the Kinetic Energy of Ions

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Cross sections of methylamine and methanol for ion-molecule reactions with various rare gases have been studied by means of a charge spectrometer used as a double mass spectrometer. The results differed from those predicted by the Gioumousis-Stevenson theory. The difference was most pronounced for helium ion, the lightest ion.

It was reported by Field, Franklin, and Lampe[1] and also by Gioumousis and Stevenson[2] that the cross section of the ion-molecule reaction was inversely proportional to the square root of the kinetic energy of ions. Their argument was based on the theory of ion-induced dipole interaction. However, interpretation of the results by such a model is not always simple. The reaction cross section is predominantly determined by the collision cross section in gas kinetics when the energy of ions increases.[3]

The present report deals with the specific features of the reaction cross sections of methylamine and of methanol for various ions of rare gases.

Expreimental

Details of the charge spectrometer which also served as a double mass spectrometer of a perpendicular type were reported elsewhere.[4,5] The procedure was modified by applying a different electric field gradient. The primary ions of 10^{-13}—10^{-12} A were introduced into the source volume filled with target gases. The maximum pressure of the gases was 1.0×10^{-5} Torr. The reaction products in the source volume were abstracted into the analyzer system by the action of the installed lenses and measured with an electron multiplier of 16 stages.

An example of the mass spectrum of methylamine bombarded with Xe^+ with energy of 8.0 eV is shown in Fig. 1. We see that there are two series of product ions: one with mass-charge ratio of an integer produced through collision complex formation (open bars); the other with non-integer

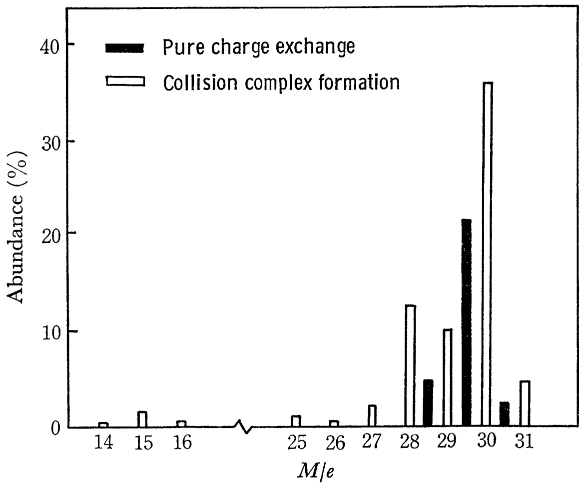

Fig. 1. Mass spectrum of methylamine bombarded with X^+.

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[1] F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Amer. Chem. Soc.*, **79**, 2419 (1957).

[2] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

[3] D. A. Kubose and W. H. Hamill, *J. Amer. Chem. Soc.*, **85**, 125 (1963).

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

[5] T. Nagatani, K. Yoshihara, and T. Shiokawa, *ibid.*, **20**, 97 (1972).

values of mass-charge ratio produced by pure charge exchange (closed bars). Since kinetic energy is transferred to the product in the complex formation, the apparent *m/e* ratio of the same fragment ion appears in the higher position as compared with that derived from pure charge exchange. Thus, the ions of the *m/e* ratio (30.5), (29.5), and (28.5) are considered to be the products by pure exchange whose net *m/e* ratios are (31), (30), and (29), respectively. The intensity of the ions caused by the charge exchange is 28.5% for the total ionization (Fig. 1). The same treatment is applicable to the other gases.

Results and Discussion

The ions abstracted into the analyzer system are classified as follows.

1) Primary ions,

a) having unchanged kinetic energy without interaction with target gases.

b) having altered kinetic energy by interaction with target gas molecules, *i.e.* inelastic scattering.

2) Stripping reaction products,

$$A^+ + B_1B_2 \longrightarrow AB_1^+ + B_2$$

where A^+ is the primary ion, B_1B_2 denotes the target molecule composed of parts B_1 and B_2, and AB_1^+ is the stripping reaction product.

3) Product ions formed through complex formation,

$$A^+ + B_1B_2 \longrightarrow [A-B_1B_2]^+ \longrightarrow B_1^+ + B_2 + A$$
$$\text{or } B_1 + B_2^+ + A \text{ etc.}$$

4) Product ions formed by charge exchange,

$$A^+ + B_1B_2 \longrightarrow A + B_1B_2^+$$

This is often accompanied by dissociation reactions.

$$A^+ + B_1B_2 \longrightarrow A + B_1B_2^+$$
$$B_1B_2^+ \longrightarrow B_1^+ + B_2$$
$$\text{or } B_1 + B_2^+$$

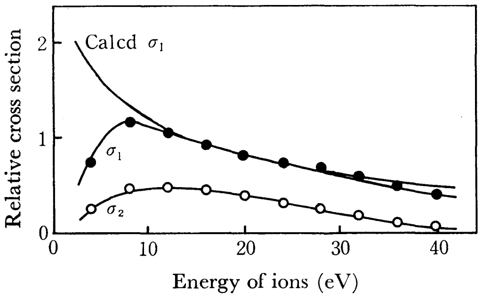

Fig. 2. Two kinds of cross sections of methylamine bombarded with Xe+.

We defined the reaction cross section σ_1 according to complex formation and σ_2 according to charge exchange. The intensity of the stripping reaction products is very small and can be neglected. The relations of σ_1 and σ_2 with energy are shown in Fig. 2 which corresponds to the experiment of methylamine bombarded with Xe+. The error of each experimental point does not exceed 20%. The calculated values are obtained by application of the Gioumousis-Stevenson's theory of inverse-square-root dependence of kinetic energy. Experimental values of σ_1 fit the calculated values in the range 12.0—32.0 eV. The charge exchange cross section σ_2 shows a somewhat different inclination from that of σ_1. Increase of σ_1 in the very low energy region implies that fragmentation increases as translational energy carried into the methylamine molecule from the xenon ion increases and the activated complex highly excited in its vibrational states increases.

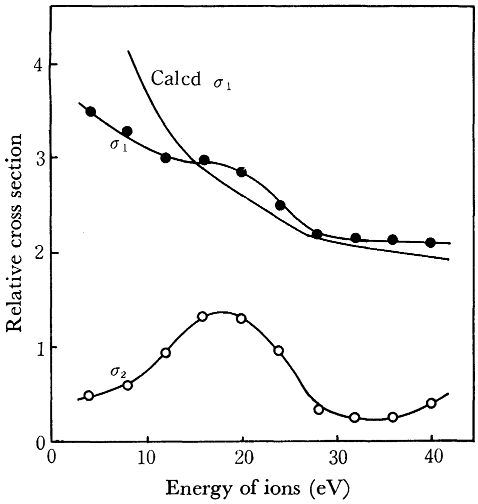

Fig. 3. Two kinds of cross sections of methanol bombarded with Xe+.

The results for methanol are plotted in Fig. 3. The calculated values for σ_1 according to the Gioumousis-Stevenson's theory can nearly account for the experimental values in the range 16.0—36.0 eV. It seems that the inverse-square-root dependence of the cross section on ion energy fits the energy range below 40 eV irrespective of ions. The trend of σ_2 for methanol differs from that of σ_1. It has a maximum at 16.0—20.0 eV. For both systems the fragment ions which contribute to σ_2 include the same ionic species of the approximately same relative intensity.[6,7] This shows that the separation of σ_2 from σ_1 is quite good.

However, when Ar+ is introduced into the source volume as the primary ion, there is a large difference

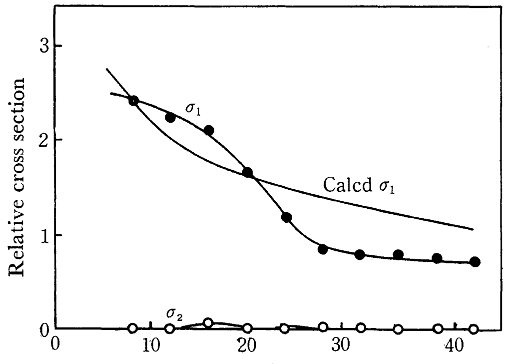

Fig 4. Ionization cross sections of methylamine bombarded with Ar+.

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

7) T. Nagatani, K. Yoshihara, and T. Shiokawa, *ibid.*, **46**, 1450 (1973).

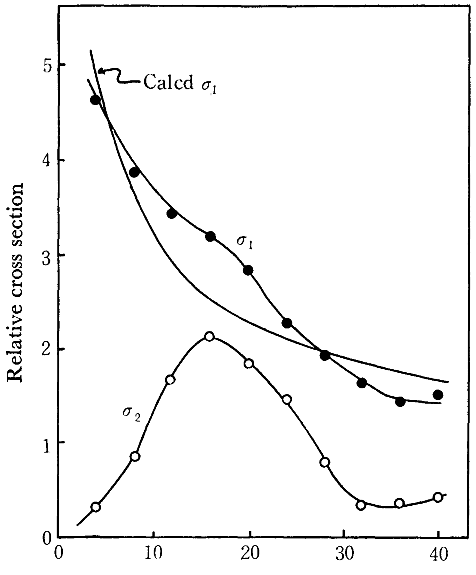

Fig. 5. Ionization cross sections of methanol bombarded with Ar^+.

between the systems of methylamine and methanol (Figs. 4 and 5). For the primary ion whose recombination energy is about 15 eV, the ratio σ_2/σ_1 is very small in methylamine. When translational energies of primary ions increase to 100—200 eV, σ_2 becomes 10% for σ_1, and negligible for the ions of 2 keV. The trend of σ_1 in 30—40 eV fits the calculated value.

σ_1 in the methanol system is in good accordance with the calculated value (Fig. 5). However, σ_2 has a maximum at about 16 eV. At this energy σ_2 contributes 40.1% of the total ionization cross section.

σ_2 is small for the primary ions of He^+. It is negligibly small in methylamine (Fig. 6). Similar results for methanol are shown in Fig. 7. The calculated values of σ_1 for methylamine and for methanol using the Gioumousis-Stevenson's theory largely differ from the experimental ones. Replacement of inverse-square-root dependence by inversely proportional dependence does not essentially change the situation. These discrepancies suggest some factors other than induced dipole interaction. In this connection recent reports by Koski and his co-workers are of interest.[8-11] Their results show that complicated factors are included in determining the formation of ionic species in the reaction of C^+ with hydrocarbons. However, it is not easy to understand why in the case of the lightest rare gas ion the deviation from the Gioumousis-Stevenson's theory is most pronounced. It is possible that the energy carried into the activated complex through the collision is not kept in vibronic states or that the contributed energy is limited through the collision which resembles an elastic one.

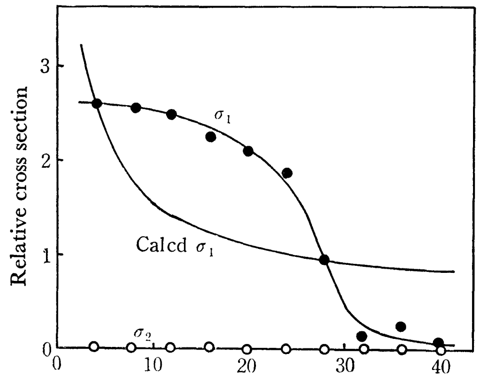

Fig. 6. Ionization cross sections of methylamine bombarded with He^+.

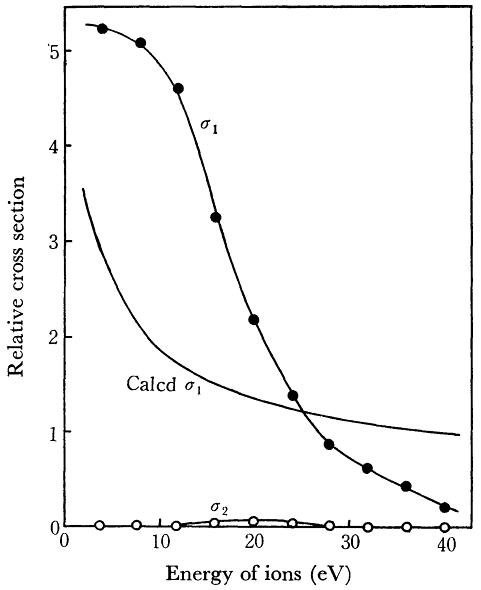

Fig. 7. Ionization cross sections of methanol bombarded with He^+.

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[8] R. C. C. Lao, R. W. Rozett, and W. S. Koski, *J. Chem. Phys.*, **49**, 4202 (1968).

[9] P. S. Wilson, R. W. Rozett, and W. S. Koski, *ibid.*, **52**, 5321 (1970).

[10] P. S. Wilson, R. W. Rozett, and W. S. Koski, *ibid.*, **53**, 1276 (1970).

[11] P. S. Wilson, R. W. Rozett, and W. S. Koski, *ibid.*, **53**, 3494 (1970).