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A SIMPLE METHOD FOR MEASURING THE TRANSLATIONAL ENERGY OF IONS WITH AN ANALYTICAL MASS SPECTROMETER

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The average translational energy of ions has been readily measured by applying a variable retarding potential of negative voltage to the repeller electrode. The measured value of the methyl ion from acetonitrile at the threshold is in fair agreement with that in literature.

The measurement of the excess translational energy of ions plays an important role in studying the fragmentation mechanism of ions, in measuring the dissociation energy of molecular ions, and/or in finding the exact heat of formation which is often used in determining the structure of intermediate ions produced from various precursors.[1-4] The translational energy is usually measured by applying the retarding potential to the metal gauze electrode in front of the collector,[5] by the deflection technique, in which ions are subject to a variable electric field,[6] and by analysis of the shapes of metastable and normal ion peaks.[7-10]

In the present paper a simple method for measuring the translational energy of ions is reported. By applying a variable retarding potential of negative voltage ($-V_r$) to the repeller electrode in the ionization chamber,[11] the translational energy of ions can be readily measured without any modification of an analytical mass spectrometer.

Measurements were made on a Hitachi RMU-5B mass spectrometer. The temperatures of ion source and sample manifold were 200°C and 20-25°C, respectively. The ion accelerating voltage was 2000 V. The samples (Kanto Kasei Kogyo Co., Ltd.) were used

without further purification. A small negative voltage to the repeller electrode is supplied from the dividing circuit by means of 10-turn duplex and 20-turn potentiometers (Sakae Tsushin Kogyo Co., Ltd.).[11] Its connections to the repeller electrodes and the ionization chamber are made by detachable clips, so that the normal experimental conditions can be reproduced easily. Two repeller electrodes are kept at the same voltage. Space charge effects caused by electron beam and produced positive ions were ignored in this experiment, because they are very small.

The retarding potential curve of methyl ion produced by the reaction $CH_3CN^+ \longrightarrow CH_3^+ + CN$ at 21.1 eV electron energy is shown in Fig. 1. By regarding the electron beam as passing through the point halfway between the repeller electrodes and the exit slit of the ionization chamber, the half value of the repeller voltage is shown on the abscissa. The average translational energy $\bar{\varepsilon}_i$ of methyl ion is obtained simply by dividing the hatched area by the ion intensity at $V_r = 0$, because the area shows the total translational energy of ions.

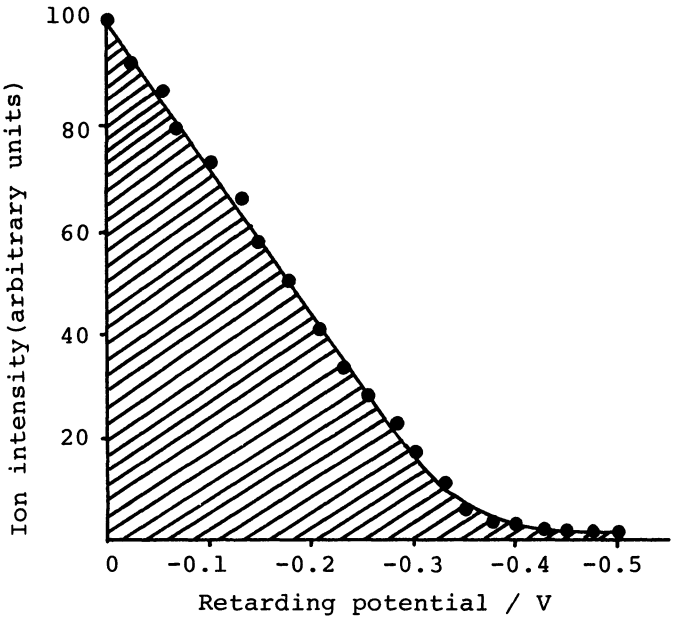

Fig. 1. Retarding potential curve of CH_3^+ from CH_3CN at 21.1 eV.

A schematic energy diagram of the ion AB^+ is shown in Fig. 2. Here E is the excitation energy, equal to the appearance potential (A.P.) of A^+ ion, and ε_t is the excess translational energy in the reaction coordinate in the activated complex. The energy ε_t will be partitioned to the A^+ ion and the B radical during the decomposition of the AB^+ ion.

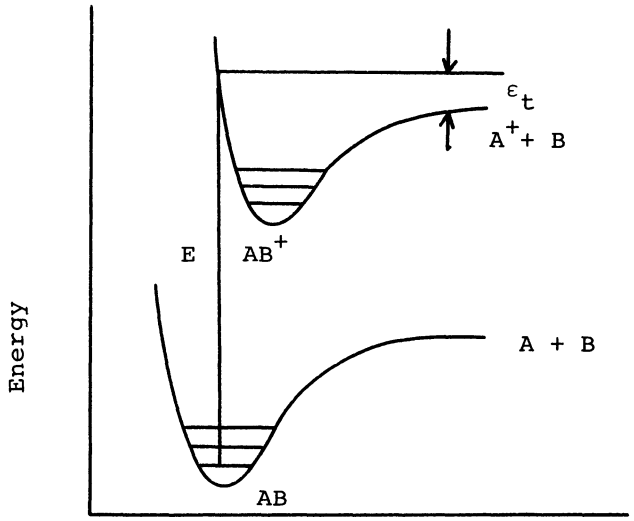

Fig. 2. Schematic energy diagram.

By assuming the application of the conservation laws of kinetic energy and momentum, $\bar{\varepsilon}_i$ of the ion A^+ is represented by the following equation;[12]

$$\bar{\varepsilon}_i = \frac{M_n}{M_n + M_i}\bar{\varepsilon}_t + \frac{M_i}{M_n + M_i} 3/2\ \kappa T + \Delta\varepsilon \qquad (1)$$

where M_n is the mass of the neutral product B, M_i is the mass of the fragment ion A^+, $3/2\ \kappa T$ is the average thermal translational energy of the molecular ion AB^+, and $\Delta\varepsilon$ is the apparent energy due to the instrumental factors, such as the steric dispersion of the electron beam.

By rearrangement we get

$$\bar{\varepsilon}_t = \frac{M_n + M_i}{M_n}(\bar{\varepsilon}_i - \Delta\varepsilon) - \frac{M_i}{M_n} 3/2\ \kappa T \qquad (2)$$

The value of $\Delta\varepsilon$ can be estimated from the $\bar{\varepsilon}_i$ of the molecular ion, since in the case of molecular ion, $M_n = 0$ in Eq. (1), therefore, $\bar{\varepsilon}_i = 3/2\ \kappa T + \Delta\varepsilon$. The average translational energy $\bar{\varepsilon}_i$ of O_2^+ ion versus electron energy is shown in Fig. 3. Electron energy was corrected by measuring the ionization potential of argon (I.P. = 15.8 eV). By extrapolating the curve to the ionization potential of oxygen (I.P. = 12.1 eV), $\bar{\varepsilon}_i$ of O_2^+ is estimated to be 1.6 kcal/mol. Therefore, $\Delta\varepsilon = \bar{\varepsilon}_i - 3/2\ \kappa T = 1.6 - 1.4 = 0.2$ (kcal/mol), as T = 473 K.

Average excess translational energy, $\bar{\varepsilon}_t$ calculated from Eq. (2) of methyl ion

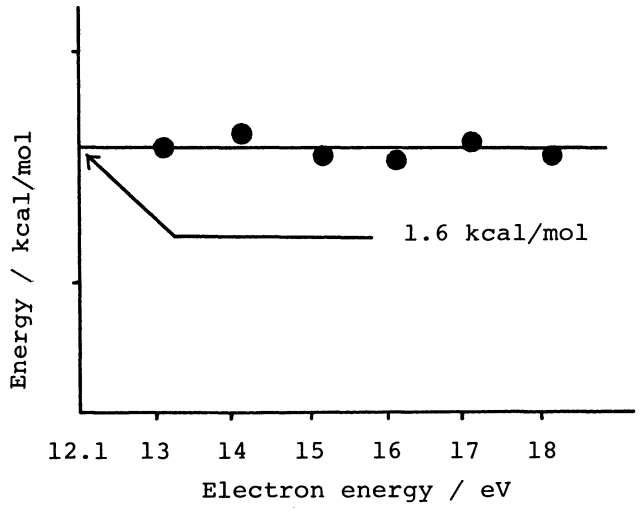

Fig. 3. Average translational energy of O_2^+ versus electron energy.

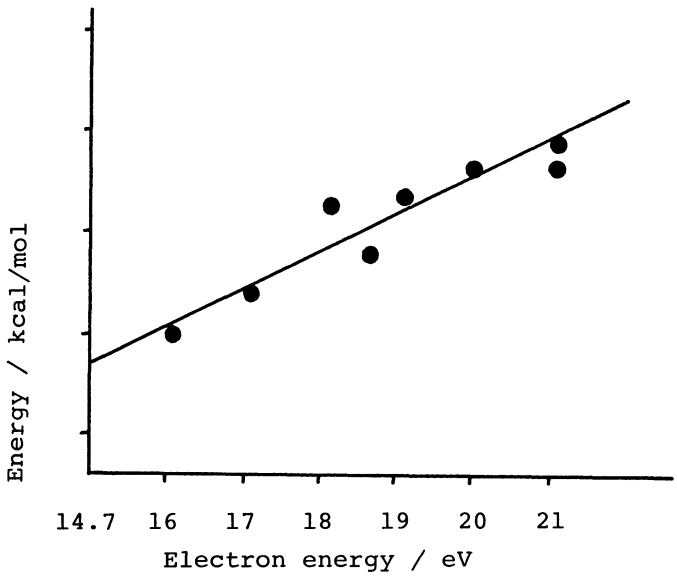

Fig. 4. Average translational energy of CH_3^+ from CH_3CN versus electron energy.

from acetonitrile versus electron energy, is shown in Fig. 4. The error in the $\bar{\varepsilon}_t$ obtained at the same experimental condition was about $\pm$ 0.1 kcal/mol. By extrapolating the curve to the appearance potential (A.P. = 14.7 eV) calculated from the thermochemical data,[12] the average excess translational energy, $\bar{\varepsilon}_t$ for methyl ion from acetonitrile at the appearance potential is estimated to be 3.6 kcal/mol. The line was drawn by the least-squares method. This measured value is in fair agreement with that in literature, *i.e.*, 3.3 kcal/mol.[13]

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