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A Simple Method for Measuring Mass Spectra of Ions with Excess Kinetic Energy

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Synopsis. Mass spectra of ions with excess kinetic energy have been measured by applying a small negative voltage to the repeller electrode.

An important function of mass spectrometry is determination of the structure of organic compounds,[1] but this is not easy, since many rearrangement ions appear in an ordinary mass spectrum. Thus it is desirable to obtain mass spectra that are free of rearrangement ions and consist only of simple cleavage ions.

Recently, a method for measuring mass spectra of ions with excess kinetic energy was reported by Tsuchiya and Horii.[2] They used a modified ion source equipped with a metal gauze electrode between the exit slit and the focus slit. The electrode was kept at a potential a little higher than that of the ionization chamber. The term KE mass spectrum (kinetic energy mass spectrum) was given to the spectrum measured from the ion source. From the fact that simple cleavage ions consist of two kinds of ions, one with thermal energy only and the other with additional excess kinetic energy, and that the rearrangement ions usually have no kinetic energy with exception of a few instances,[3,4] they concluded that a large portion of the KE mass spectra consists of ions produced by simple cleavage, and that KE mass spectra might facilitate the determination of the structure of organic compounds. However, the method is not suitable for measuring both KE and ordinary mass spectra with an analytical mass spectrometer, since the ion source has to be modified in order to measure the KE mass spectra. A simple method for measuring the KE mass spectra with use of a commercial mass spectrometer is needed.

In the present note a simple method for measuring the KE mass spectra is reported. By applying a small negative voltage to the repeller electrode ($-V_r$), the KE mass spectra can be easily obtained without any modification of the ion source. However, the same KE mass spectra as those obtained by Tsuchiya and Horii[2] cannot be expected by the present method, sicnce the potential energy distribution inside the ionization chamber differs in the two methods.

Experimental

The mass spectra were obtained with a Hitachi RMU-5B mass spectrometer. A small negative voltage to the repeller electrode is supplied from the circuit (Fig. 1) by controlling the value of the 20-turn potentiometers R_r and R_r' (Sakae Tsushin Kogyo Co., Ltd.). The connections to the repeller electrode and ionization chamber are made by replacing the clips, so that the normal experimental condition can be recovered easily.

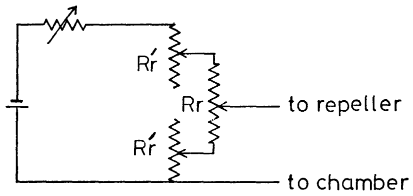

Fig. 1. Diagram of the modified electric circuit for the repeller voltage.

Other conditions of measurement were: electron accelerating voltage, 80 V; ion accelerating voltage, 2000 V; trap current, 60 μA; temperature of ion source, 250 °C; temperature of sample manifold, 20—25 °C.

The intensities of the ions in the KE mass spectra were about one-hundredth of those in ordinary mass spectra.

The samples (Kanto Kagaku Kogyo Co., Ltd.) were used without further purification.

Results and Discussion

In the usual type of mass spectrometer, a small positive voltage is applied to the repeller electrode (V_r) to draw out the ions efficiently from the ion source. Consequently, both ions with no excess kinetic energy, and those with some kinetic energy are pushed out from the ion source. However, when a small negative voltage is applied to the repeller electrode ($-V_r$), only the ions with a kinetic energy greater than half the value of the repeller voltage can emerge from the ion source. Thus it becomes possible to measure the KE mass spectra by

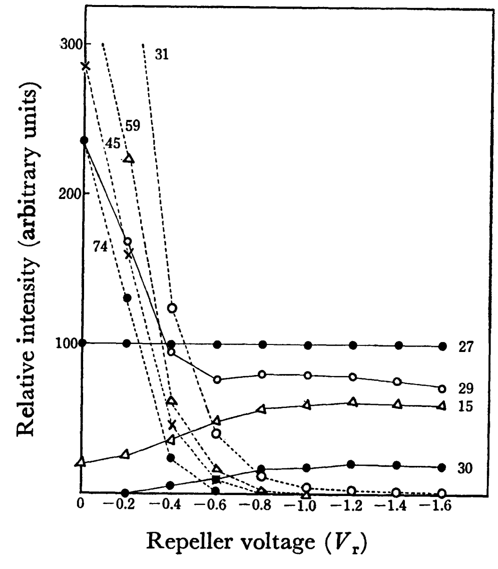

Fig. 2. Variation of the relative intensity for several intense fragment ion peaks of diethyl ether *vs.* repeller voltage.

applying an appropriate negative voltage to the repeller electrode ($-V_r$).

The intensities of several intense fragment ion peaks for diethyl ether are shown in Fig. 2 as a function of repeller voltage (V_r). The intensity of $C_2H_3^+$ (*m/e* 27) is taken as a reference. We see that the molecular ion (*m/e* 74) and the rearrangement ion (*m/e* 31), a large number of which being considered to have no excess kinetic energy, decrease rapidly with decrease in the value of V_r. While simple cleavage ions, *m/e* values of which are larger than a half of the *m/e* value of the molecular ion, *i.e.*, *m/e* 59 and *m/e* 45 ions, also decrease with the V_r value. The intensities of some simple cleavage ions (*m/e* 29, 15 *etc.*,) which are smaller in *m/e* than a half of that of the molecular ion remain approximately constant between -1.0 and -1.6 V (V_r). This implies that a reproducible KE mass spectrum can be obtained at -1.0 — -1.6 V by our method.

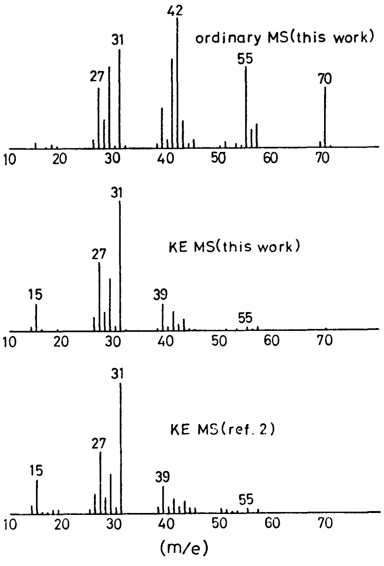

Fig. 3. KE mass spectra and ordinary mass spectrum of pentyl alcohol.

The KE mass spectrum measured at -1.5 V (V_r) and the ordinary mass spectrum (10 V (V_r)) of pentyl alcohol are shown in Fig. 3 together with the KE mass spectrum of Tsuchiya and Horii.²⁾ The KE mass spectrum measured by our method is close to the theirs, but differs from the ordinary one.

An analytical mass spectrometer can be used readily to measure the KE mass spectrum, since we can obtain the KE mass spectrum by this method without any modification of the ion source.

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