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APPLICATION OF MASS SPECTRA OF IONS WITH EXCESS KINETIC ENERGY TO THE ISOTOPE-LABELLING TECHNIQUE FOR ORGANIC CHEMISTRY

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Precursors of ions with excess kinetic energy (KE ions) have higher internal energy than those of ordinary ions (thermal ions), so that rearrangement reactions like H/D scrambling may be less probable in the mass spectra of KE ions. For example, the location and number of deuterium atoms in 1,4-butanediol-2,2,3,3-d_4 has been correctly indicated by the mass spectrum of KE ions, while the ordinary mass spectrum gives no reliable information because of rearrangement. Information obtained from mass spectrum of KE ions has also been described.

The value of the isotope-labelling techniques[1],[2] for the investigation of chemical or biological reaction mechanisms and for the determination of the structure of organic compounds is very well known and mass spectrometry is the most useful method for determining the number and location of stable isotopes within a molecule. The large volume of publications, however, concerning the mass spectra of isotopically-labelled organic molecules has revealed that hydrogen and carbon scrambling may be extensive on the time scale of the mass spectrometer ($10^{-6} \sim 10^{-5}$ sec). Studies on the loss of H and D from the singly charged molecular ions of partially-deuterated toluenes have revealed that the extent of H/D scrambling prior to decomposition decreased with increasing internal energy and hence with decreasing lifetime[3]. It has also been shown from deuterium labelling[3] and from ^{13}C labelling[4] in toluene that the $C_7H_7^+$ ion is completely scrambled prior to acetylene loss, consistent with the tropylium structure. A scrambling reaction is just another rearrangement in which the precursor and product ions have the same elemental composition, causing complex information on mass spectra of stable isotopes.

Tsuchiya et al. have reported[5][6][7] that ions with excess kinetic energy (KE ions) are formed mainly from direct cleavage of highly-excited parent molecules, i.e., the precursor of a KE ion has more internal energy (higher than 10 eV) than does an ordinary ion (thermal ion) observed in an ordinary mass spectrum. Therefore, it is likely that the scrambling reaction is less probable for the reaction producing KE ions and thus the mass spectra of KE ions (excess-KE mass spectra) are easier to be interpreted than ordinary mass spectra.

Three examples will be cited in this paper in order to describe what kinds of information can be obtained from excess-KE mass spectra. The instrument and method used are almost same as described in earlier papers,[5)7)] and, in addition, the mass spectra were measured for several different electron energies and ion retarding potentials.

a) 1,4-butanediol The mass spectra of 1,4-butanediol and 1,4-butanediol-2,2,3,3-d_4 were measured. The latter had been synthesized by the Daiichi Seiyaku Co. and it was found by the chemical ionization mass spectrometry that the latter is a mixture of about 90 % d_4-, 7.5 % d_3- and 2.5 % d_2-butanediol. In the ordinary mass spectrum of 1,4-butanediol at 70 eV, the peaks at m/e 42 (mainly $C_3H_6^+$) and at m/e 31 (CH_2OH^+) are significant and the intensity ratio of the peak at m/e 32 to that at m/e 31 is almost equal to the ratio of the natural abundance of ^{13}C to that of ^{12}C. The ordinary mass spectrum of 1,4-butanediol-d_4 at 20 eV shown in Fig.1, however, indicates that the peaks at m/e 32 and 33 are much higher than those of unlabelled species as shown in Table 1.

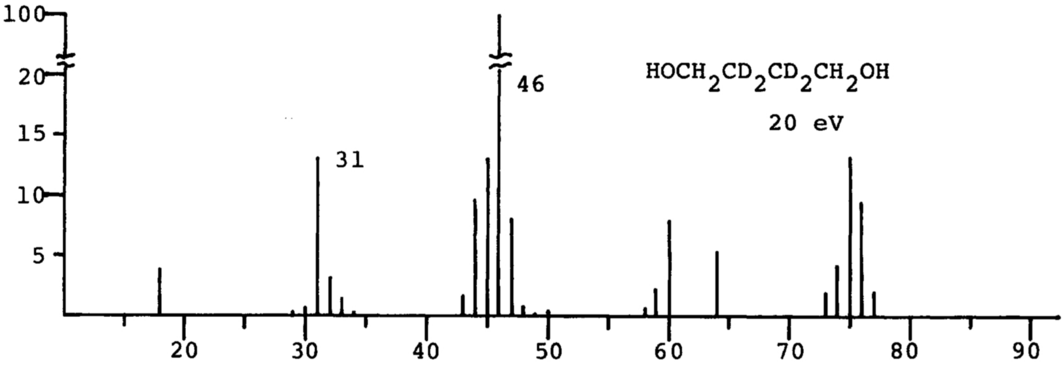


Fig.1 Ordinary mass spectrum of 1,4-butanediol-d_4, 20 eV.

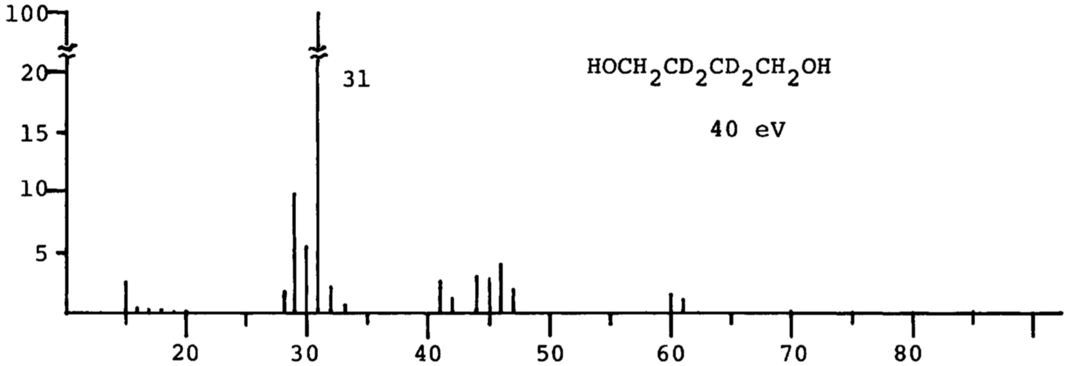


Fig.2 Excess-KE mass spectrum of 1,4-butanediol-d_4, 40 eV.

Both peaks at m/e 32 and 33 consist of CX_2OX^+ ions (X means H and/or D) and $C_2X_n^+$ ions and there may be two possibilities of forming the mixture of different CX_2OX^+ (e.g. $CHDOH^+$ and $CHDOD^+$) ions. These are (i) the sample itself is a mixture of different compounds containing different CX_2OX groups produced during synthesis and (ii) H/D scrambling occurs prior to decomposition in the ion source, even in the case when the sample is pure.

Table 1 shows the relative intensities of the peaks at m/e 31, 32 and 33 corresponding to the CH_2OH^+ ions, the CH_2OD^+ (and/or $CHDOH^+$) ions and the $CHDOD^+$ (and/or CD_2OH^+) ions, respectively, as recorded at higher resolution ($M/\Delta M$ = 900).

In the ordinary mass spectra of the labelled sample both at 20 and 70 eV, the intensities of the mass-32 peaks (about 25 %) and the mass-33 peaks (about 10 %) are much higher than the natural abundance. In contrast, the intensities of these peaks in the excess-KE mass spectra (Table 1 and Fig.2) are small and are less than one-tenth of those observed in the ordinary mass spectra, being only about 1 % higher than the natural abundance. This indicates that (i) the peaks at m/e 32 and 33 are mainly produced by H/D scrambling within a molecule, and are not caused from impurities in the sample, (ii) the excess-KE mass spectra show the exact deuterium content in the CH_2OH fragment group of 1,4-butanediol-d_4 and (iii) the extent of rearrangements is remarkably reduced at high internal energy (seen in the excess-KE mass spectra).

Table 1 Relative abundances of CX_2OX^+ ions (X means H and/or D) of 1,4-butanediol [A] and 1,4-butanediol-2,2,3,3-d_4 [B]

Compound	Mass Spectrum	Electron energy	m/e 31	32	33
			d_0	d_1	d_2
[A]	Ordinary	70 eV	100	0.9	0
	Excess-KE	70	100	0.9	0
[B]	ordinary	20	100	25	12
		70	100	24	10
	Excess-KE	40	100	2.3	0.7
		70	100	2.4	0.5
		90	100	2.1	0.6

b) Toluene The excess-KE mass spectra of toluene and toluene-αd_3 were measured to determine the isotope distribution in the mass spectra of αd_3-species and also to investigate how quickly the scrambling occurs. Toluene-αd_3 was obtained from the Merck Co.. The purity was greater than 99 %. The isotope distribution for the methyl ions (KE ions) of toluene-αd_3 calculated from the excess-KE mass spectra of toluene-αd_3 and -d_0 is as follows: the CD_3^+ ion is 55 %, the CHD_2^+ ion 17 %, the CH_2D^+ ion 20 % and the CH_3^+ ion 8 % of the total methyl ions having excess kinetic energy more than about 1 eV. It was also found that the percentage of CD_3^+ is a little larger for methyl ions having higher kinetic energy (e.g. higher than 2 eV). The value of 55 % for the CD_3^+ ions is neither 100 % (no scrambling) nor 1.8 % (complete scrambling), indicating that the tropylium ion formation process is so rapid that H/D scrambling occurs partly even in the process producing KE ions. Even at 55 %, it gives some information about the number of deuterium atoms in the methyl group, and thus in the molecule, while the ordinary mass spectrum gives no information about this because of almost complete scrambling.

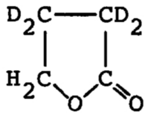
c) γ-butyrolactone Mass spectra of γ-butyrolactone and γ-butyrolactone-α_2, β_2-d_4, [C], were measured. The latter had also been synthesized by the Daiichi Seiyaku Co. and its d_4 content was found to be about 65 % from the ordinary mass spectrum. The major fragmentation processes were found to be as shown in the next page:

in the ordinary mass spectrum,

$$M^{+} \longrightarrow C_3H_6^{+} + CO_2 \quad ---- \quad (1)$$

$$M^{+} \longrightarrow CH_2CH_2CO^{+} + H_2CO \quad --- \quad (2)$$

$$CH_2CH_2CO^{+} \longrightarrow C_2H_4^{+} + CO \quad ---- \quad (3)$$


[C]

and in the excess-KE mass spectra, significant ions are H_2CO^+ and HCO^+, CH_2CO^+, $C_2H_4^+$, and CO_2^+. It is interesting to note that CO_2^+ ions are observed. The fragmentation mechanism will be described in detail elsewhere. The H_2CO^+ with HCO^+ ions and the CH_2CO^+ ion are common ions observed in excess-KE mass spectra and can often give information about the location of isotopes in a molecule. In the case of γ-butyrolactone, for instance, the peak at m/e 42 corresponding to the CH_2CO^+ ions in the unlabelled species has shifted to the peak at m/e 44 in the d_4-species, [C], because the latter is due to the CD_2CO^+ ions, while the peak at m/e 30 corresponding to the CH_2O^+ ions in the former has not shifted because the latter [C] can also give rise to CH_2O^+ ions. Information obtained from ordinary mass spectra is also useful in this case. Both spectra can be used at the same time, resulting in more accurate information.

It is concluded that the time necessary for rearrangement reactions like H/D scrambling depends on the excess internal energy of the molecule as well as on the structure of the compound. The information obtained from the excess-KE mass spectra of isotopically labelled compounds is as follows.

1) Fragmentation mechanism, involving the effect of internal energy which is higher than normal, the effect of shorter lifetime ($<10^{-7}$ sec) and the effect of translational energy of ions.

2) The number and location of isotopes within a molecule, especially in fragment groups located at the terminal of a molecule.

Such information makes the isotope labelling technique more useful. A detailed discussion of this will be published elsewhere.

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