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EXAMINATION OF DEGREE-OF-FREEDOM EFFECT IN THREE CONSECUTIVE MASS SPECTRAL FRAGMENTATIONS

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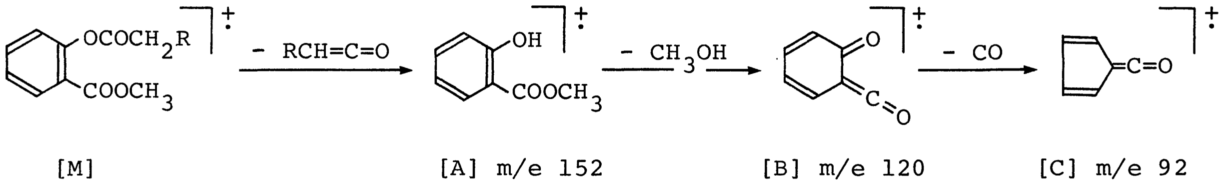
By using mass spectra of five aliphatic acid esters of methyl salicylate, the effect of vibrational degrees of freedom in the molecular ion on three consecutive fragmentations is examined. The effect was clearly observed in the second fragmentation, but the intensity ratio of ions involved in the third step is found to be essentially constant.

The fundamental concept of quasi-equilibrium theory (QET) of mass spectra$^{1)}$ is based on an assumption that the internal energy of the molecular ion $[M]^{+\cdot}$ is completely randomized throughout all the vibrational modes before fragmentation. Therefore, if the expelled group [N] is large and it carries off more vibrational energy in the primary fragmentation, the smaller average internal energy of the fragment ion $[X]^{+\cdot}$ is expected, and consequently, the smaller intensity ratio of $[m^*]/[X]^{+\cdot}$ or $[Y]^{+\cdot}/[X]^{+\cdot}$ for further fragmentations of $[X]^{+\cdot}$ may be observed.

$$\begin{tikzcd} {[M]^{+\cdot}} \arrow[r] & {[X]^{+\cdot} + [N]} \arrow[d, "m^*"] \\ & {[Y]^{+\cdot} + [R]} \end{tikzcd}$$

This "degree-of-freedom effect" has been exemplified by the intensity ratios for $C_2H_5O^+$ ion from aliphatic alcohols and for $C_3H_6O^{+\cdot}$ ion from aliphatic ketones,$^{2)}$ and by relative rates of fragmentation of benzoyl ions generated from different precursors.$^{3)}$ A similar effect in the field ionization spectra of 2-alkanones and n-alkyl thiols was also reported.$^{4)}$

In connection with other studies,[5)] we had an occasion to examine spectra of some aliphatic acid esters of methyl salicylate. The primary fragmentation of these compounds is the elimination of a substituted ketene molecule through a four-membered cyclic transition state to afford a common fragment ion at m/e 152, the structure of which is considered to be identical with that of methyl salicylate itself.[5)] This ion then loses methanol and carbon monoxide in two consecutive fragmentations.

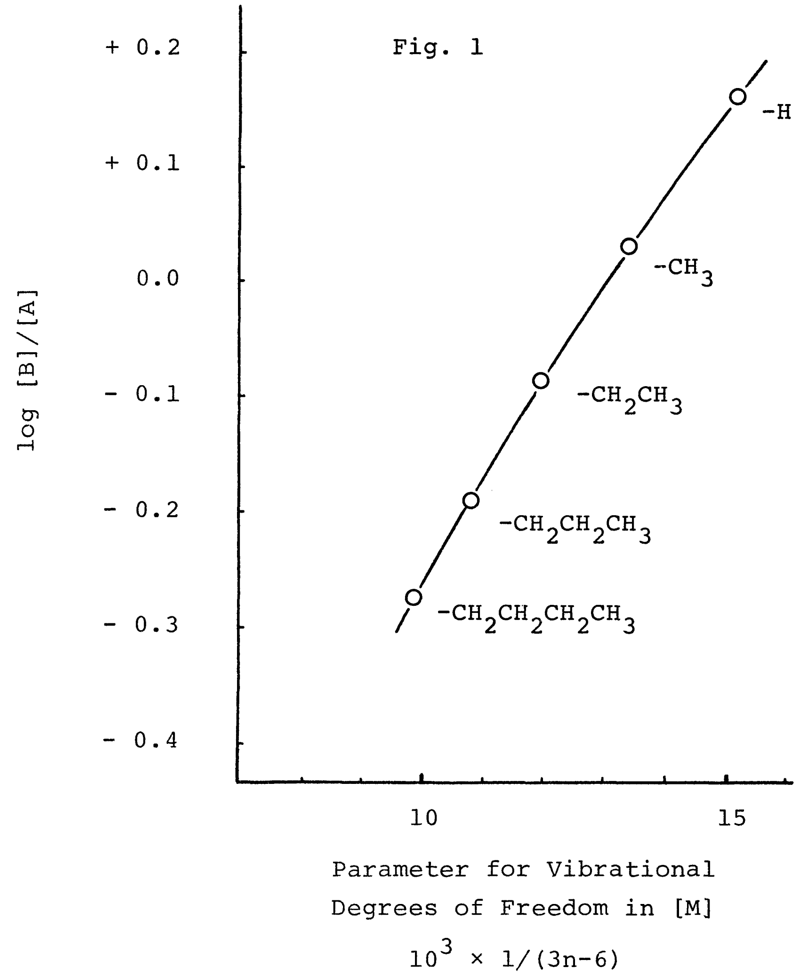


As we were unable to determine accurate metastable ion peak intensities, comparisons of the relative intensity ratio of fragment ions for these homologous esters were made. As is seen from Table 1, the intensity ratio of [B]/[A] decreases with increasing alkyl chain length, and thus, the degree-of-freedom effect in this step of fragmentation is clearly indicated. The similar trend was also found in the 20 eV spectra.

When the log of the intensity ratio of [B]/[A] is plotted against the inverse vibrational degrees of freedom in [M], a very slightly curved correlation was obtained (Fig. 1). It is of interest to note that a recent theoretical calculation[6)] on the degree-of-freedom effect of some simple model compounds resulted a similar, slightly convexed curvature for these correlations.

Table 1. Intensity Ratios of Fragment Ions from Methyl Salicylate Esters (70 eV).

Methyl Salicylate Esters [M]	Intensity Ratios [B]/[A]	[C]/[B]	Vibrational Degrees of Freedom in [M]
R = H (Acetate)	1.44	0.23	66
CH_3	1.07	0.22	75
CH_2CH_3	0.81	0.23	84
$CH_2CH_2CH_3$	0.65	0.23	93
$CH_2CH_2CH_2CH_3$	0.54	0.24	102



On the other hand, the vibrational degrees of freedom in the molecular ion did not affect the third step of the fragmentation, [B]$\longrightarrow$[C]; the ratios of [C]/[B] for these esters remain constant within the experimental error (Table 1). This is considered to be a particular case, because it has already been reported that the degree-of-freedom effect is opperative even in the third step of three consecutive fragmentations of aliphatic ketones.7)

One of the explanations of the present result is to assume the distinct nature of the third step of the fragmentation in that the intensity ratio is virtually independent of the energy content of the precursor ion [B]. Since the structures of the ions [B] and [C] are common in each homologous ester, we may expect both energy distribution P(E) and rate constnat k(E) functions, respectively, to be more or less similar shape in this series of compounds. Therefore, the constnat intensity ratio requires the activation energy lowering when the energy of the precursor ion decreases. This is highly improbable.

The alternative possibility is the disappearance of the energy differences in [A] at the second step of fragmentation, and thus the intervention of the ion [B] that has essentially the same amount of internal energies. While this release of excess energy could take a number of forms, the most probable situation may be its conversion to the translational energy of the fragment ions, provided that the electronically excited species are not involved, and that the expelled methanol molecule is not effective in carrying off enough vibrational energies. However, the explanations are still tentative and further studies are in progress in our laboratories.

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