Estimation of Frequency Factors for some Mass Spectral Rearrangements

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Summary Four-centre and six-centre hydrogen rearrangements occur in the molecular ions of diethyl ketone and methyl *o*-toluate, respectively, and these processes are shown to have frequency factors in the region of 3×10^6 and 3×10^{10} sec.$^{-1}$

THE rate constant k for a unimolecular decomposition of a molecular ion of internal energy E is given, according to the original and simplest form of the quasi-equilibrium theory,[1] by the expression

$$k = \nu[(E - E^0)/E]^{s-1} \qquad \text{(i)}$$

where ν may be regarded as a frequency factor for the reaction, E^0 is the energy of activation, and $(s - 1)$ the effective number of oscillators.

If a molecular ion undergoes n competing unimolecular decompositions, described by parameters $(\nu_1, E_1^0) \cdots (\nu_i, E_i^0) \cdots\cdots (\nu_n, E_n^0)$, then at voltages at which the further decomposition of the resulting daughter ions is negligible

$$[M_E^+] = \int_{E_1^0}^{E_{\max}} f(E) \exp\left\{-\sum_{i=1}^{i=n} k_i t_4\right\} \cdot \mathrm{d}E \qquad \text{(ii)}$$

$$[A_i] = \int_{E_i^0}^{E_{\max}} f(E) \frac{k_i}{\sum_{i=1}^{i=n} k_i} \left(1 - \exp\left\{-\sum_{i=1}^{i=n} k_i t_1\right\}\right) \cdot \mathrm{d}E \qquad \text{(iii)}$$

$$[m_i^*] = \int_{E_i^0}^{E_{\max}} f(E) \frac{k_i}{\sum_{i=1}^{i=n} k_i} \left(\exp\left\{-\sum_{i=1}^{i=n} k_i t_2\right\} - \exp\left\{-\sum_{i=1}^{i=n} k_i t_3\right\}\right) \cdot \mathrm{d}E \qquad \text{(iv)}$$

where $[M_E^+]$ is the fraction of molecular ions with energy in excess of the lowest activation energy (E_1^0) which do not decompose on the mass spectrometer time scale, $[A_i]$ and $[m_i^*]$ are the fraction of ions giving rise to daughter ions and metastable ions appropriate to reaction i, $E_{\max}$ is the electron-beam energy, and t_4, t_1, t_2, t_3 are the times needed to reach the collector, leave the source, and enter and leave the field-free region giving rise to the "metastable peaks," respectively. $f(E) \cdot \mathrm{d}E$ is the fraction of ions having energies between E and $E + \mathrm{d}E$. To compute the total molecular ion abundance the fraction of ions $[M_0^+]$ with insufficient energy to decompose must be added to $[M_E^+]$; the former quantity is given by the following expression

$$[M_0^+] = \int_0^{E_1^0} f(E) \cdot \mathrm{d}E$$

We have chosen an energy distribution curve (*i.e.* plot of (E) against E) such that

$$f(E) = \alpha E^{\frac{1}{2}} (E_{\max} - E)$$

where α is a normalising constant. Equating the total area under the energy distribution to unity gives $\alpha = 3{\cdot}75/E_{\max}^{5/2}$.[2] When internal energies extending from I.P. ($E = 0$)to internal energies of 11·5 ev are weighted, for example, the energy distribution appears as in Figure 1A. Such energy distributions have proved satisfactory for calculation of the mass spectra of monosubstituted benzenes in the absence of competing reactions.[2]

For calculation of ion abundances we have taken $(s - 1)/2$ as the effective number of oscillators, where s is the number of degrees of vibrational freedom in the molecule. E_1^0 is approximated by the difference between the measured appearance potential for reaction i and the ionization potential of the molecule, leaving only ν as an adjustable parameter in the calculation of k against E curves [equation (i)]. The relative ion yields due to each reaction are then computed by integrating over the whole energy distribution and allowing for competition as indicated in equations (ii)—(iv). Standard computer facilities are available for computation of the integrals. The necessary times are available from a knowledge of instrument geometry (AEI MS-9), accelerating voltage (8 kv), and ion masses.[3,4]

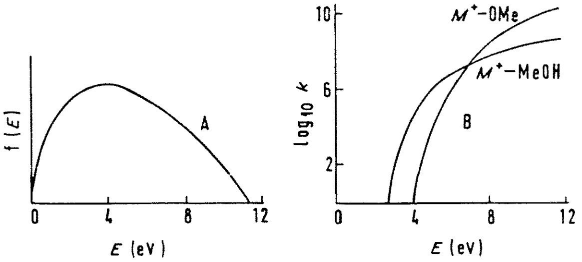


FIGURE 1

Reactions with "tight" transition states are expected to have lower frequency factors than those with "loose" transition states,[5] and hence a knowledge of the transition state should provide information about the frequency factor and *vice versa*. We have calculated the high-mass regions of the mass spectra of diethyl ketone (1) and methyl *o*-toluate (2), where in each case a reaction proceeding by simple bond cleavage (a, c) is in competition with a hydrogen rearrangement reaction (b, d). In the case of ethane loss from (1), a four-membered transition state is indicated by deuterium labelling.[6]

The parameters used in the calculations are summarized in Table 1. The frequency factors for the simple bond cleavages are taken as the relevant bond vibrational frequencies, and therefore the only adjustable parameters to "fit" the spectra at various voltages are the frequency factors for the rearrangement reactions.

In each case the rearrangement reaction has the lower activation energy and it is therefore only these reactions that should give rise to abundant metastable transitions ($\log_{10}k$ *ca.* 4—6). This is borne out by the experimental and calculated data (Table 2 and Figure 2). So far as daughter ion abundances are concerned, the rearrangement reactions of low activation energy and low-frequency factor are most prevalent in low-voltage spectra. The single-bond cleavages become faster at higher internal energies (see the k against E curves for methyl *o*-toluate in Figure 1B). The agreement between calculated and

TABLE 1

Parameters used in calculation of the mass spectra of diethyl ketone (1) *and methyl* o-*toluate* (2)

Compound	t_1 (μsec.)	t_2 (μsec.)	t_3 (μsec.)	t_4 (μsec.)	E_1^0 (ev)	ν_1 (sec.$^{-1}$)	E_2^0 (ev)	ν_2 (sec.$^{-1}$)
(1)	1·4	8·2	12·1	15·1	0·37	3×10^6	2·00	8×10^{13}
(2)	1·9	10·9	15·8	21·0	1·54	3×10^{10}	2·72	4×10^{13}

TABLE 2

Calculated and observed ion abundances (% total ionization) in the mass spectra of diethyl ketone (1) *and methyl* o-*toluate* (2)

Comp.		ev	Ion abundances (%)			
			M^+	$m^*(M^+ - C_2H_6)$	$M^+ - C_2H_6$	$M^+ - C_2H_5$
(1)	Calc.	14	70·2	6·5	8·9	14·4
	Obs.		66·2	0·4	11·3	22·5
	Calc.	16	43·5	4·8	7·8	43·9
	Obs.		41·9	0·2	7·4	50·5
	Calc.	18	32·4	3·5	6·2	60·9
	Obs.		29·4	0·05	5·2	65·4
	Calc.	20	21·4	2·7	4·5	71·4
	Obs.		24·3	0·04	4·3	71·4
			M^+	$m^*(M^+ - \text{MeOH})$	$M^+ - \text{MeOH}$	$M^+ - \text{MeO}$
(2)	Calc.	16	71·9	1·6	22·6	3·9
	Obs.		64·1	1·9	25·0	9·0
	Calc.	17	62·8	1·5	26·7	9·0
	Obs.		55·5	1·6	29·5	13·4
	Calc.	18	55·0	1·4	28·5	15·1
	Obs.		49·0	1·5	29·4	20·1
	Calc.	19	48·6	1·3	28·6	21·5
	Obs.		45·1	1·3	29·3	24.3

observed ion abundances is excellent for methyl *o*-toluate (1) at all voltages examined (15—20 ev in steps of 1 ev). Agreement is likewise very good for diethyl ketone (2), except for the calculated metastable ion abundances for ethane loss which are one or two orders of magnitude too large. Despite this discrepancy, it is obvious that in this case the reaction proceeding through the four-membered transition state is associated with a much lower frequency factor (*ca.* 10^6) than that proceeding through the six-membered transition state (*ca.* 10^{10}). Thus although ethane loss from the diethyl ketone molecular ion has a lower activation energy than ethyl loss, in 20 ev spectra the daughter ion abundance due to the latter process is approximately 17 times as great as that due to ethane loss (Table 2).

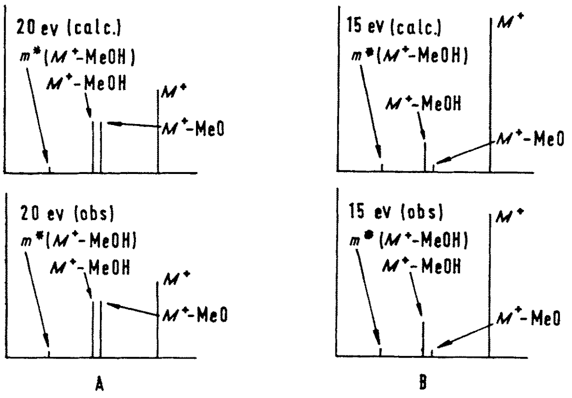
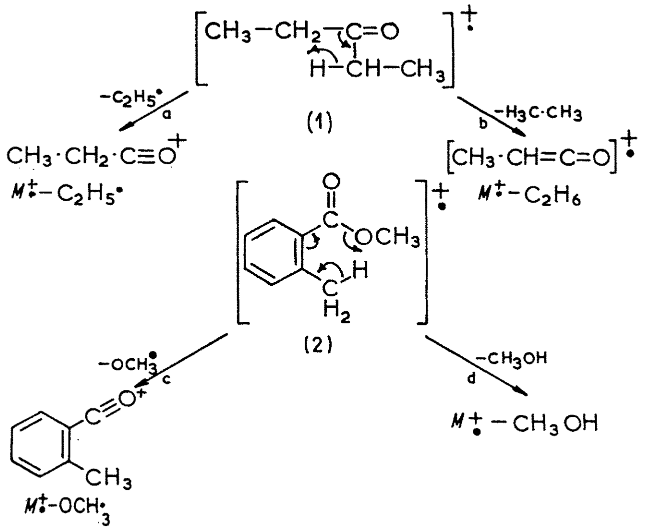


FIGURE 2



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