benzaldehydes is generally accepted, the markedly increased basicity of acetophenones relative to benzophenones is a new observation and worthy of further documentation.[35] This order seems to be a manifestation more of the electron-withdrawing inductive effects of phenyl substituents in the "onium" ion than of their potential electron-donating conjugative ability and is also evident from comparison of the heat of protonation of ethyl acetate (-17.4 kcal/mol) with ethyl benzoate (-14.5 kcal/mol). Conjugative stabilization in the free base would also give the same order. Taft[36] concluded, on the basis of fluorine nmr shielding effects in substituted benzophenones, that thermodynamic substituent effects are the resultants of substantial effects in both complexed ($\bar{p} = -7.00$ for H_2SO_4 adduct) and uncomplexed ($\bar{p} = -2.43$) ketone. The observed order acetone $\approx$ acetophenone $\gg$ benzophenone tends to eliminate π-complex interaction of the phenyl ring with FSO_3H as an important contributing factor to the high basicity estimates for aromatic carbonyl compounds on this scale. The opposite order would be expected if these interactions were significant.

(5) Within the alicyclic ketone series, increasing ring strain is manifested in a decrease in basicity. Thus, a difference of 4 kcal/mol in heats of protonation exists between cyclohexanone and cyclobutanone.

(6) Fluorenone, which would produce a potentially antiaromatic cation,[37] is one of the weakest bases examined, even though it possesses the potential for conjugation with two coplanar phenyl rings in the conjugate acid.

(7) The very low basicity of benzoyl chloride and hexachloroacetone bears witness to the dramatic sensitivity of the basicity of carbonyl compounds to inductive effects.

(35) One of us (J. W. L.) has observed this order in several other systems. Extension of Dewar's SCF-MO calculations for conjugated molecules to this series might be interesting. See M. J. S. Dewar and T. Morita, J. Amer. Chem. Soc., 91, 802 (1969).

(36) P. G. Pews, Y. Tsuno, and R. W. Taft, ibid., 89, 2391 (1967).

(37) (a) R. Breslow, H. W. Chang, R. Hill, and E. Wassermann, J. Amer. Chem. Soc., 89, 1112 (1967); (b) R. Breslow, Angew. Chem. Intern. Ed. Engl., 7, 565 (1968); (c) R. Breslow and H. W. Chang, J. Amer. Chem. Soc., 83, 3727 (1961); (d) R. Breslow, J. Brown, and J. Gajewski, ibid., 89, 4383 (1967).

Calculation of Partial Mass Spectra of Some Organic Compounds Undergoing Competing Reactions from the Molecular Ions

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Abstract: Methyl o-toluate, methyl salicylate, p-chloroaniline, nitrobenzene, and diethyl ketone each undergo two important reactions from their molecular ions, one involving rearrangement and the other formally corresponding to a simple bond cleavage. These reactions are treated as competing unimolecular reactions within the framework of the quasi-equilibrium theory (QET). To preserve mathematical simplicity, an empirical modification is made to the original and simplest QET equation relating the rate constant (k) and internal energy (E), in the hope that this will compensate for inadequacies of the original equation near threshold. Treating only the frequency factors for the rearrangement reactions as adjustable parameters, good agreement is obtained between calculated and observed partial mass spectra of methyl o-toluate, methyl salicylate, and p-chloroaniline. It is suggested that the QET may be applied in calculation of the mass spectra of organic compounds in general, at least up to the degree of functional complexity considered in the present paper.

I nterpretation of the mass spectra of organic compounds has during the last 10 years proceeded almost entirely on empirical grounds.[1,2] Notable exceptions are, however, found in calculation of the mass spectra of simple hydrocarbons, such as propane, by means of the quasi-equilibrium theory (QET).[3-6] The application of this theory to complex organic molecules containing heteroatoms has been questioned[1,7] and organic chemists have not applied its principles in attempts to calculate ion abundances in mass spectra. This paper deals with the partial calculation of simple mass spectra of some organic molecules, where hitherto only empirical interpretations have been available.[8]

(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

(2) J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier Publishing Co., Amsterdam, The Netherlands, 1968.

(3) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, Proc. Nat. Acad. Sci. U. S., 38, 667 (1952).

(4) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 1.

(5) H. M. Rosenstock in "Advances in Mass Spectrometry," Vol. 4, E. Kendrick, Ed., The Institute of Petroleum, London, 1968, pp 523–545; see also M. L. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 2.

(6) For calculations of the mass spectra of hydrocarbons and simple monofunctional compounds, see (a) A. Kropf, E. M. Eyring, A. L. Wahrhaftig, and H. Eyring, J. Chem. Phys., 32, 149 (1960); (b) E. M. Eyring and A. L. Wahrhaftig, ibid., 34, 23 (1961); (c) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, ibid., 37, 1276 (1962); (d) L. Friedman, F. A. Long, and M. Wolfsberg, ibid., 27, 613 (1957); (e) J. Collin, Bull. Soc. Roy. Sci. Liege, 7, 520 (1956); (f) A. B. King and F. A. Long, J. Chem. Phys., 29, 374 (1958); (g) W. A. Chupka, ibid., 30, 191 (1959); (h) W. A. Chupka and J. Berkowitz, ibid., 32, 1546 (1960); (i) B. Steiner, C. F. Giese, and M. G. Inghram, ibid., 34, 189 (1961); (j) W. A. Chupka and M. Kaminsky, ibid., 35, 1991 (1961).

(7) G. Spiteller and M. Spiteller-Friedmann, Justus Liebigs Ann. Chem., 690, 1 (1965).

Discussion

In an earlier paper,[9] we have applied the principles of the QET to the calculation of the mass spectra of monosubstituted benzenes, considering only a single dominant fragmentation from M[+]. However, it may validly be argued that the moderately good agreement there found between calculation and experiment does not constitute a test of the theory that is in any way demanding since, in the absence of competing unimolecular decompositions, the critical factor in determining daughter ion/parent ion ratios is the measured energy of activation (approximated by A.P.-I.P.); the results are relatively insensitive to the exact form of the k vs. E curves (rate constant for reaction vs. internal energy) and to the chosen frequency factors (ν). A more exacting test is, however, found when competing reactions from M[+] are considered and cases of two competing reactions are discussed in the present study.

The first problem which must be faced is that of estimating the distribution of energies when the parent molecule is ionized by electron impact. Such distribution can in fact be obtained experimentally by taking the second derivative of the total ionization efficiency curve, as has been done for propane[4] (see, for example, Figure 1). Although the energy distribution will vary from compound to compound, the variations should not in general be large.[6j] In our preliminary calculations[8,9] we chose a simplified energy distribution curve (i.e., plot of $f(E)$ vs. E, Figure 2) such that

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

where $f(E)\delta E$ is the fraction of ions having energies between E and $E + \delta E$ and E_{max} is the electron beam energy; α is a normalizing constant given by $\alpha = 3.75/E_{max}^{5/2}$.[9] This type of distribution appears to weight high energy ions excessively in spectra between 12 and 20 eV. For the present work we have therefore chosen the distribution illustrated in Figure 3 (cf. Figure 1). When the total area under the curve has been normalized to unity, the distribution curve is defined by the following equations.

$$f(E) = 12.5E/E_{max}^2 \text{ for } 0 \leqslant E \leqslant E_{max}/5$$

$$f(E) = (3.5E_{max} - 5E)/E_{max}^2 \text{ for }$$
$$E_{max}/5 \leqslant E \leqslant 8E_{max}/15 \qquad (ii)$$

$$f(E) = 12.5(E_{max} - E)/7E_{max}^2 \text{ for }$$
$$8E_{max}/15 \leqslant E \leqslant E_{max}$$

The second problem is that of calculating the rate constant (k) for each reaction at an internal energy E (in excess of the activation energy E^0). Expressions relating k with E in the modified QET[4-6] are mathematically very complex and certainly not suitable for the present purpose of developing a mathematically simple procedure for the approximate calculation of the mass spectra of complex molecules. Yet the original expression relating k and E, namely

$$k = \nu \left(\frac{E - E^0}{E}\right)^{s-1} \qquad (iii)$$

(8) For a preliminary communication, see A. N. H. Yeo and D. H. Williams, Chem. Commun., 956 (1969).

(9) I. Howe and D. H. Williams, J. Amer. Chem. Soc., 92, 7137 (1970).
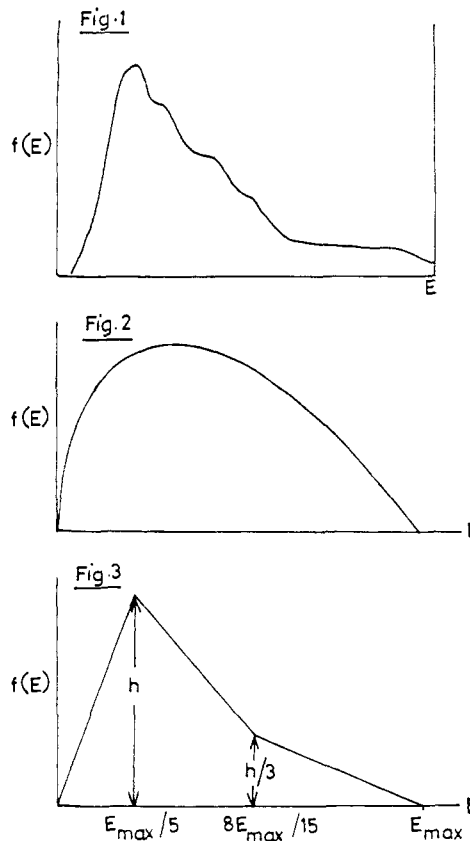
Figures 1-3. Energy distribution curves for propane (Figure 1 experimental; see, for example, ref 4): a general model calculated according to eq i (Figure 2): a general model according to eq ii (Figure 3).

where ν is a frequency factor and s the number of oscillators in the decomposing ion, has been found to be an exceedingly poor approximation near threshold. Thus there are indications that for propane near threshold, only one-fifth of the oscillators are effective on the basis of the approximate relationship (iii) [i.e., $(s - 1)$ must be replaced by $(s - 1)/5$ to give a realistic rise of k with E just above the activation energy for decomposition]. The gross inadequacies of eq iii near threshold may be illustrated by the calculation of the internal energies necessary to produce rate constants of 10^6 sec^{-1}. Taking $s = 57$, $\nu = 4 \times 10^{13} \text{ sec}^{-1}$, and $E^0 = 2.7$ eV (parameters for loss of OMe from methyl o-toluate), the internal energies necessary to attain k values of 10^6 sec^{-1} are ~ 5.8 and 4.4 eV even when considering the effective numbers of oscillators to be $(s - 1)/2$ and $(s - 1)/3$, respectively (Figure 4). Such slow rises of k with E near threshold are clearly unrealistic since kinetic shifts of the order of 1 eV or more are only found in instances where the activation energy is very high and the frequency factor for reaction low.[10,11] Yet the metastable ion abundances calculated when using $(s - 1)/2$ as the effective number of oscillators in the mass spectra of monosubstituted benzenes[9] are in good agreement with experiment. Therefore, we have considered modification of eq iii such that the energy spread giving rise to metastable transitions (log $k \simeq 4$-6) will be only slightly reduced,

(10) I. Hertel and Ch. Ottinger, Z. Naturforsch., A, 22, 40 (1967).

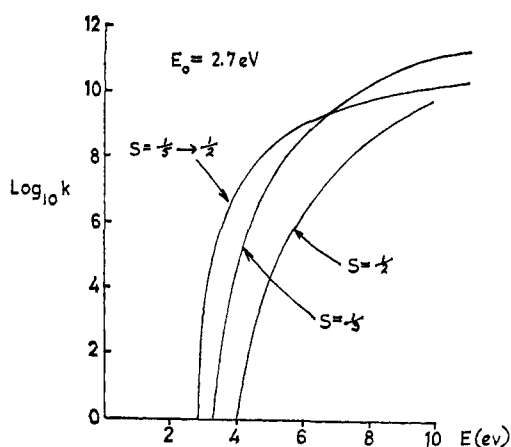(11) J. H. Beynon, J. A. Hopkinson, and G. R. Lester, J. Mass Spec. Ion Phys., 2, 291 (1969).

Figure 4. k vs. E curves for the loss of a methoxyl radical from the molecular ion of methyl o-toluate (1) for various values of the fraction (x) of effective oscillators used in calculations.

Figure 5. Variation of the fraction x of effective oscillators used as a function of internal energy E.

and yet the internal energy (in excess of E^0) required to raise the rate constant k from 0 to 10^4 sec^{-1} will be greatly reduced. This has been achieved by the use of the equation

$$k = \nu \left(\frac{E - E^0}{E}\right)^{(s-1)x} \qquad \text{(iv)}$$

where x is a fraction varying from one-fifth at the activation energy to one-half at the maximum internal energy of the ion at 20 eV. For simplicity, a linear variation of x with E is used (eq v and Figure 5). In

$$x = 0.2 + 0.3(E - E^0/((E_{max})_{20eV} - E^0) \qquad \text{(v)}$$

this way we compensate for the fact that eq iii is a very poor approximation near threshold but becomes a better approximation at higher internal energies. Using eq iv with a continuous variation of x from one-fifth to one-half with increasing E gives a much sharper rise of k with E near threshold (Figure 4); the theoretical kinetic shift of $\sim$0.5 eV is now eminently reasonable.

To calculate the mass spectrum, k for each reaction must be calculated, and the parent and various daughter ion abundances computed by allowing for competition between the unimolecular reactions, and weighting each $k(E)$ value according to the energy distribution. Total ion abundances are obtained by integrating over the whole energy distribution.[12] If a molecular ion undergoes n competitive unimolecular decompositions characterized by the parameters $(\nu_1, E_1^0) \ldots (\nu_i, E_i^0) \ldots (\nu_n, E_n^0)$, then at voltages at which secondary decomposition is negligible

$$[M_E^+] = \int_{E_i^0}^{E_{max}} f(E) \exp(-\sum_{i=1}^{i=n} k_i t_4) \, dE \qquad \text{(vi)}$$

$$[A_1^+] =$$

$$\int_{E_i^0}^{E_{max}} f(E) \frac{k_i}{\sum\limits_{i=1}^{i=n} k_i} (1 - \exp(-\sum_{i=1}^{i=n} k_i t_1)) \, dE \qquad \text{(vii)}$$

$$[m_1^*] = \int_{E_i^0}^{E_{max}} f(E) \frac{k_i}{\sum\limits_{i=1}^{i=n} k_i} (\exp(-\sum_{i=1}^{i=n} k_i t_2) -$$

$$\exp(-\sum_{i=1}^{i=n} k_i t_3)) \, dE \qquad \text{(viii)}$$

where $[M_E^+]$ is the fraction of ions with energy in excess of the lowest activation energy (E_1^0) which do not decompose on the mass spectrometer time scale, $[A_1^+]$ and $[m_1^*]$ are, respectively, the fractions of ions giving rise to daughter ions and metastable ions appropriate to reaction i. The times t_4, t_1, t_2, and t_3 are those required to reach the collector, leave the source, and enter and leave the field-free region giving rise to the "metastable peaks," respectively. To compute the total molecular ion abundance, the fraction of ions $[M_0^+]$ with insufficient energy to decompose (i.e., those with less than the lowest activation energy, E_1^0) must be added to $[M_E^+]$; $[M_0^+]$ is given by the expression

$$[M_0^+] = \int_0^{0E_1} f(E) \, dE \qquad \text{(ix)}$$

To calculate the value of k at each internal energy from eq iv it is necessary to assign frequency factors, ν, to each reaction. For simple bond cleavage reactions, the vibrational frequency of the bond in the neutral molecule is taken as the frequency factor (except where explicitly stated to the contrary). For reactions involving rearrangement, it is more difficult to assign such frequency factors. The approach adopted was to assign plausible frequency factors to such rearrangements and to compare the calculated and observed spectra; the frequency factor for rearrangement was then adjusted until reasonable agreement was achieved. The frequency factor for rearrangement is the only adjustable parameter available to give good fits of calculated and observed spectra since (i) E_i^0 is approximated by A.P.$_{.i}$ — I.P.$_{.i}$; (ii) the effective number of oscillators and the energy distribution are chosen and fixed prior to calculation; and (iii) ν_1 for simple bond cleavage is fixed by the bond vibrational frequency. The test of the assumptions involved in the approach has been made more rigorous by comparing calculated and observed spectra at intervals of 1 eV in the range of beam energies from 12 to 20 eV.

The principles associated with calculation of t_1, t_2, t_3, and t_4 for the AEI MS 9 mass spectrometer have been considered previously[9,13,14] and therefore are not discussed further in the present context.

(12) For a discussion of the principles involved, see R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, Chapter 7.
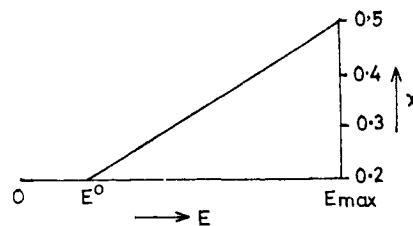
(13) I. Howe and D. H. Williams, Chem. Commun., 220 (1968).
(14) J. H. Beynon, J. A. Hopkinson, and G. R. Lester, J. Mass Spec. Ion Phys., 1, 343 (1968).
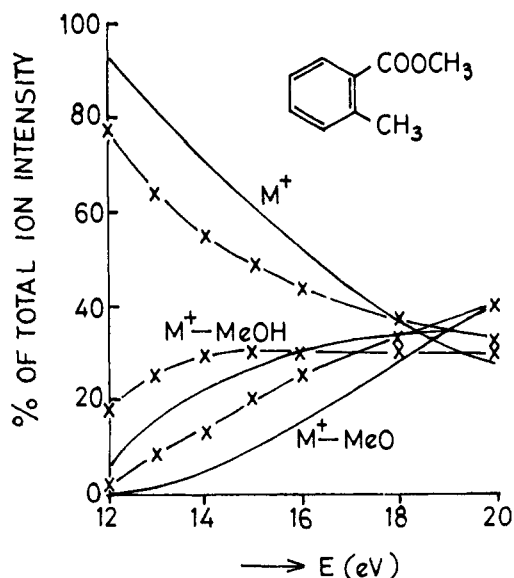
Figure 6. Plot of ion intensity $vs.$ electron beam energy; crossed lines, experimental; solid lines, calculated using the energy distribution given in Figure 3 and the k $vs.$ E relation given in eq iv.
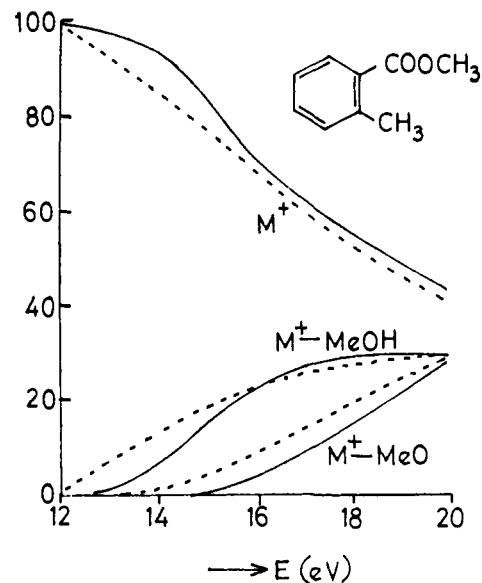

Figure 7. Plot of ion intensity $vs.$ electron beam energy; dashed lines, calculated using the energy distribution in Figure 3 and one-third the number of oscillators; solid lines, calculated using the energy distribution given in Figure 2 and one-half the number of oscillators.

Results

The compounds chosen for study were methyl o-toluate (1), methyl salicylate (2), p-chloroaniline (3), nitrobenzene (4), and diethyl ketone (5) because in each of these compounds two competing reactions from M^+ are found. Since low voltage (12–20 eV) spectra have been studied, further decomposition of the primary daughter ions has been minimized. Where further decomposition occurs to a significant extent, the experimental abundance of secondary daughter ions has been added to that of the precursor primary daughter ions
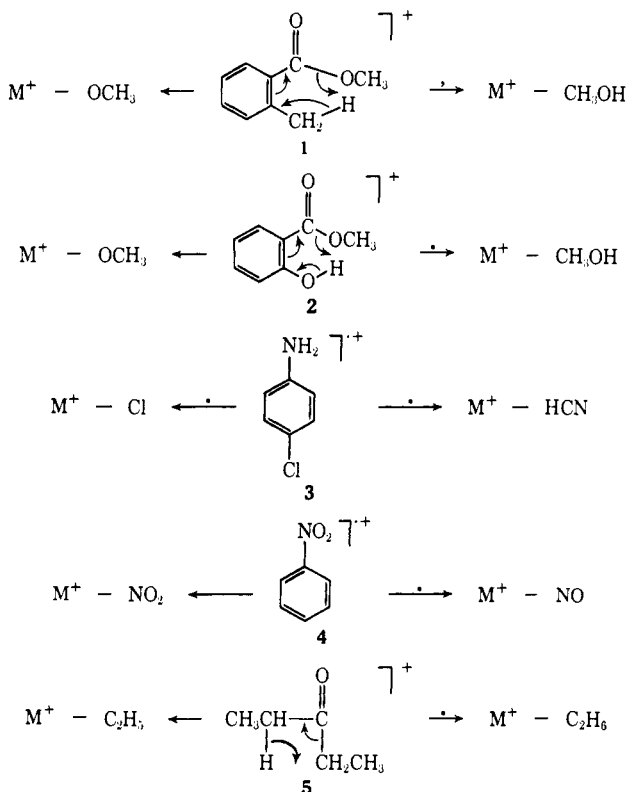
since our calculations do not allow for secondary decompositions. The reactions studied are given in Scheme I.

In all cases a reaction which must involve rearrangement (see right-hand side of molecular formulas) is in competition with one which formally does not involve rearrangement(see left-hand side of molecular formulas). Relevant parameters for the calculations are given in Table I, the rearrangement reactions being described by

Scheme I

Table I. Parameters Used in the Calculation of the Partial Mass Spectra of 1-5[a]

	1	2	3	4	5
I.P.	8.5	7.65	9.18	10.13	9.50
N[b]	21	19	14	14	16
E_1	1.54	2.20	3.24	0.40	0.37
E_2	2.72	3.62	3.38	2.00	2.00
ν_1	3×10^{10}	6×10^{11}	1×10^{10}	3×10^6	3×10^6
ν_2	4×10^{13}	4×10^{13}	3×10^{10}	3×10^{13}	8×10^{13}
t_1	1.9	1.9	1.8	1.7	1.4
t_2	10.9	10.9	9.9	9.8	8.2
t_3	15.8	15.8	14.6	14.5	12.1
t_4	21.0	21.0	18.0	18.0	15.0

[a] Energies of activation are given in eV, frequency factors in sec^{-1}, and times in μsec. [b] N is the number of atoms in the molecule.

the parameters (E_1, ν_1) and the formally simple bond cleavages by (E_2, ν_2). Only ν_1 is adjusted to fit the spectra [with the sole exception of p-chloroaniline $(vide\ infra)$].

According to the QET, in the cases of competing unimolecular decomposition an abundant metastable ion will be observed only for the lowest activation energy reaction.[4] For 1–5 the rearrangement reaction always has the lowest activation energy, and in 1, 2, 4, 5, in accordance with the requirements of competing unimolecular reactions, only these processes give rise to abundant metastable ions due to decomposition in the second field-free region of the MS9 mass spectrometer.
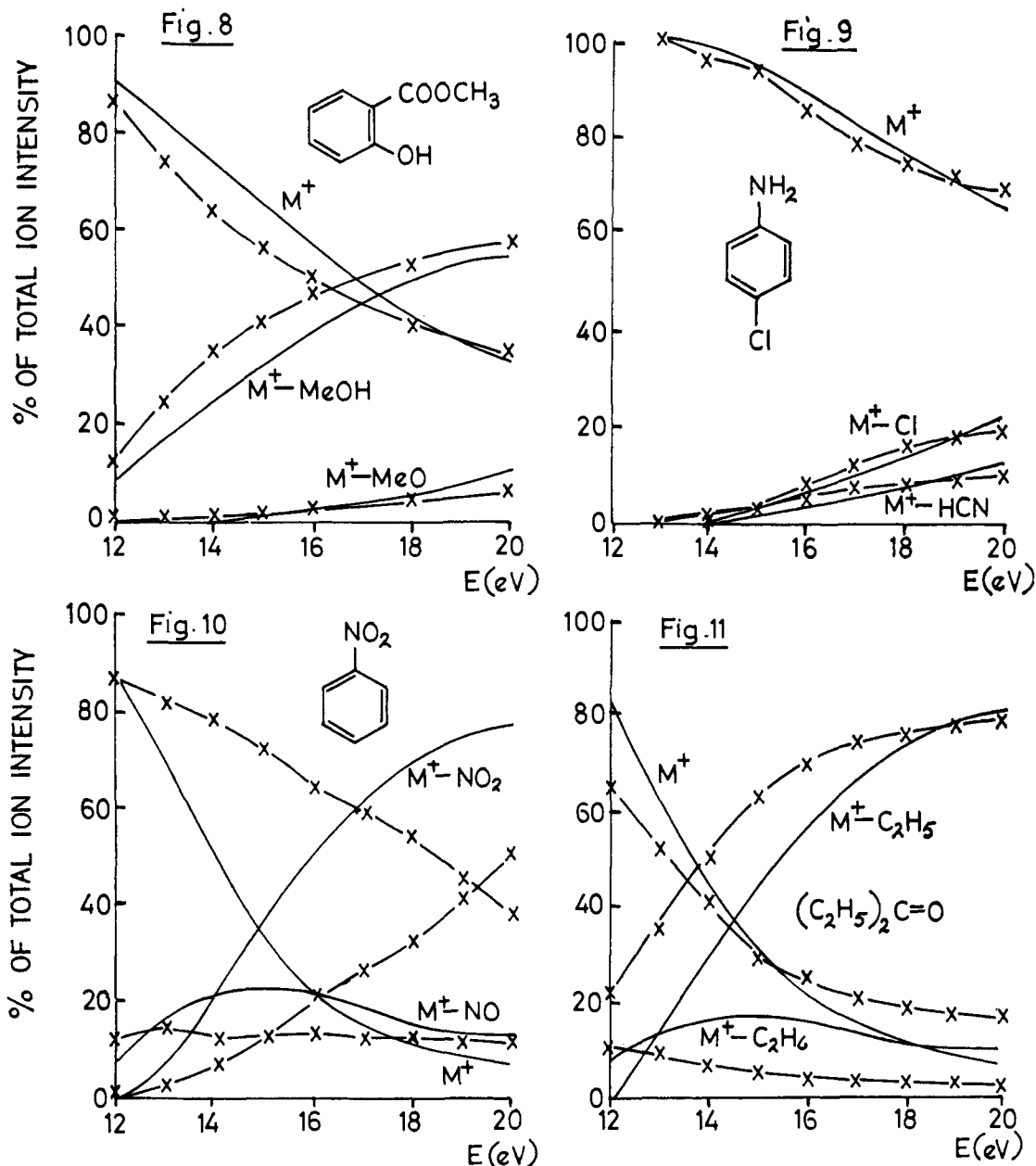
Figures 8-11. Same legend as for Figure 6.

In the case of p-chloroaniline (3), the energies of activation for HCN and Cl loss are almost identical (Table I) and, in accord with QET predictions, competing metastable transitions are observed here (abundant metastable transitions are indicated by asterisks over the arrows in the reaction scheme).

Calculated and observed parent and daughter ion abundances are discussed briefly below for each compound in turn. The data are summarized in Figures 6 and 8–11. The observed spectra are indicated by the crossed lines and the calculated spectra by solid lines. At each voltage the total ion abundance is normalized to 100%.

Methyl o-Toluate (1). Moderately good agreement between observed and calculated spectra (Figure 6) is observed if the rearrangement process is assigned a frequency factor of 3×10^{10} sec^{-1}. Other calculations were also made using (i) the effective number of oscillators as $(s - 1)/2$ over the whole energy range in

conjunction with the energy distribution given in Figure 2 and (ii) the effective number of oscillators as $(s - 1)/3$ over the whole energy range in conjunction with the energy distribution given in Figure 3. The calculations are summarized by solid and dashed lines, respectively, in Figure 7. In both cases the fit is poorer than that given in Figure 6. The effect of using $(s - 1)/2$ as the effective number of oscillators over the whole internal energy range greatly reduces the initial rise of k with E for both reactions and so the k vs. E curves cross at an internal energy which is too high. Thus in our preliminary communication,[8] using $(s - 1)/2$ gave good agreement between calculation and experiment only when the electron beam energy was correlated with absolute values by taking the beam energy giving 10^{-5} of the Kr$^+$ (or Xe$^+$) ion current at 50 eV as the ionization potential of Kr$^+$ (or Xe$^+$). This procedure interprets an instrumentally measured beam energy of 14 eV as being an absolute value of 16

eV, whereas the procedure employed in the present study (see Experimental Section) accords with agreement between instrumentally measured and absolute beam energies. Of course, the present procedure is still arbitrary, but it is preferable to the 10^{-5} criterion.[8] The latter must be unrealistic because it gave a good correlation between measured and absolute beam energies when the initial rise of k with E taken was certainly too slow (this gives extremely large kinetic shifts, as may be seen from the log k vs. E curves reproduced in ref 8, where $(s - 1)/2$ is the effective number of oscillators used).

Methyl Salicylate (2). A satisfactory fit of calculated and observed spectra (Figure 8) requires a frequency factor of 6×10^{11} sec^{-1} for methanol loss. It is noteworthy that this value is somewhat higher than the toluate **1** ($\nu = 3 \times 10^{10}$ sec^{-1}). Such a difference is required because although the ratios of the energies of activation for methoxyl radical and methanol loss are similar in **1** and **2** ($2.72/1.54 = 1.76$ and $3.62/2.20 = 1.65$), in the 20 eV spectrum of the salicylate **2**, M$^+$ − MeOH is still much more abundant than M$^+$ − OMe (contrast Figures 6 and 8).

p-**Chloroaniline (3).** Inspection of the mass spectra of *p*-chloroaniline (**3**) shows the presence of an abundant molecular ion (base peak even at 70 eV) and low abundance ions due to loss of HCN and Cl from M$^+$. An excellent fit between experimental and calculated spectra can be obtained (Figure 9) but only if *both* reactions are given relatively low frequency factors (1×10^{10} sec^{-1} for HCN loss and 3×10^{10} sec^{-1} for Cl loss). Indeed, so much might be concluded even on a qualitative basis, since the reactions have very similar activation energies and the relative ion yields of M$^+$ − HCN and M$^+$ − Cl do not change greatly between 16 and 20 eV (Figure 9). Therefore their k vs. E curves must lie close to each other (*i.e.*, the reactions have similar frequency factors). Since HCN loss involves extensive rearrangement, the rise of k with E for this reaction must surely be slow (ν low) and hence ν for Cl loss must also be relatively low. This result is somewhat surprising, although it would be understandable if chlorine loss were preceded by a rearrangement process.

Nitrobenzene (4). The mass spectra of nitrobenzene (**4**) show the loss of NO and NO$_2$, with the loss of NO predominating at low electron voltage (*e.g.*, 12 eV) but that of NO$_2$ predominating at higher electron voltage (*e.g.*, 20 eV). These findings are in accord with a three-center rearrangement for NO loss.[15,16] Calculations using only the frequency factor for NO loss as an adjustable parameter give rise to a poor fit between calculated and observed spectra. With such limitations the best agreement (still poor) is found using frequency factors of 3×10^{13} sec^{-1} for NO$_2$ loss and 3×10^6 sec^{-1} for NO loss (see Figure 10). The calculation gives a molecular ion abundance which is only about one-fifth of the observed abundance at 20 eV. While better fits could obviously be obtained by juggling numerous parameters, the nature of the problem is best illustrated by emphasizing that although the activation energy for

NO loss is only 0.4 eV,[16] 40% of the total ion current is still carried by M$^+$ in 20 eV spectra (Figure 10). The calculated M$^+$ abundance could be increased by lowering the frequency factor for NO$_2$ loss. This situation may not be artificial since we have earlier concluded that Cl loss from aromatic carbon atoms proceeds with a relatively low frequency factor (*vide supra*). However, the problem that then arises is that the calculated M$^+$ − NO abundance is too large at high eV (20 eV). Frequency factors much lower than 3×10^6 sec^{-1} for NO loss are inadmissible since the daughter ion abundance for this reaction then becomes negligible at all internal energies. In view of these difficulties we feel that serious consideration might be given to the suggestion that NO loss from nitrobenzene only gives rise to a very low abundance daughter ion (in spite of the low activation energy for this reaction) because NO loss is only possible from parent ions of long lifetime. Such would be the case if the reaction were spin-forbidden.[17] The nitrobenzene molecular ion is a doublet in its ground state, as is the neutral particle NO. If the phenoxy cation were a triplet in its ground state (with two unpaired electrons, as seems plausible), then NO loss would be a spin-forbidden process ($\Delta S = 1$) and would occur only from molecular ions of long lifetime. It has been reported that such spin-forbidden dissociations may occur onto repulsive surfaces, resulting in a well-defined kinetic energy release.[17] Since nitrobenzenes containing electron-donating *para* substituents undergo metastable transitions for NO loss with well-defined releases of kinetic energy,[18,19] spin-forbidden dissociations onto repulsive surfaces seem worthy of consideration in these cases also. No concrete proof of these suggestions is currently available, but we emphasize that the mass spectrum of nitrobenzene cannot readily be interpreted by our approach in terms of simple competing unimolecular dissociations at all internal energies up to 20 eV.

Diethyl Ketone (5). Diethyl ketone loses ethane from its molecular ion *via* a four-center process.[20] Although this reaction has the lower energy of activation (Table I), the abundance of the M$^+$ − C$_2$H$_6$ ion is less than $^1/_{20}$ of the abundance of M$^+$ − C$_2$H$_5$ at 20 eV (Figure 11). Fairly good agreement is found between observed and calculated spectra if C$_2$H$_5$ loss is given a frequency factor of 8×10^{13} sec^{-1} and C$_2$H$_6$ loss a frequency factor of 3×10^6 sec^{-1}.

Metastable Transitions. The "metastable peak" intensities observed for second field-free region transitions in the mass spectra of **1–5** are summarized in Table II, and are compared with the calculated intensities.

Considering the approximations in the approach, the agreement between calculated and observed values is surprisingly good for methyl *o*-toluate (**1**), methyl salicylate (**2**), and *p*-chloroaniline (**3**). In the cases of nitrobenzene (**4**) and diethyl ketone (**5**) agreement is poor. In the case of nitrobenzene (**4**), the reservations noted earlier may account for the disagreement. We can currently offer no explanation for the poor agreement for diethyl ketone (**5**), except to note that con-

(15) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964); see also R. H. Shapiro and J. W. Serum, *Org. Mass Spec.*, **2**, 533 (1969).

(16) This appearance potential was measured using first field-free region metastable transitions, since nitrobenzene is catalytically reduced to aniline (in trace amounts) in the mass spectrometer. Aniline parent ions have the same *m/e* value as M$^+$ − NO daughter ions.[11]

(17) G. G. Rowland, J. H. D. Eland, and C. J. Danby, *Chem. Commun.*, 1535 (1968).

(18) Reference 2, pp 60–63.

(19) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5023 (1966).

(20) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Org. Mass Spec.*, **2**, 985 (1969).

Table II. Calculated and Observed "Metastable Peak" Intensities[a] in the Mass Spectra of **1–5**

Compd	Process		Electron beam energy, eV								
			12	13	14	15	16	17	18	19	20
1	M^+ − MeOH	Obsd	1.6	1.9	1.6	1.5	1.3		1.1		0.6
		Calcd	0.8	0.9	1.2	1.3	1.2		1.2		1.0
2	M^+ − MeOH	Obsd	0.5	0.4	0.4	0.3	0.3		0.3		0.3
		Calcd	0.5	0.6	0.7	0.7	0.8		0.7		0.6
3	M^+ − HCN	Obsd			0.2	0.3	0.3	0.5	0.5	0.5	0.5
		Calcd			0.2	0.3	0.4	0.4	0.5	0.5	0.5
3	M^+ − Cl	Obsd			0.2	0.3	0.3	0.4	0.4	0.5	0.5
		Calcd			0.2	0.3	0.3	0.4	0.4	0.5	0.5
4	M^+ − NO	Obsd	0.1	0.4	0.6	0.5	0.6	0.6	0.5	0.5	0.5
		Calcd	4.5	7.0	7.2	6.4	5.1	3.9	3.1	2.3	1.8
5	M^+ − C_2H_6	Obsd		0.3	0.2	0.1	0.1	0.04	0.04	0.04	0.05
		Calcd		7.7	7.5	6.6	5.5	4.3	3.4	2.6	2.1

[a] In terms of percentage of total ion current accounted for by the "metastable peak."

siderations of minimum rate phenomena[21,22] and isolated states[4] may be relevant.

Our calculations indicate that significant metastable ion abundances should not be observed for loss of OMe, OMe, NO_2, and C_2H_5 from **1, 2, 4**, and **5**, respectively. These are in fact the experimental observations.

Conclusion

It has been shown that a mathematically simple equation of the QET can be used to calculate the mass spectra of complex organic compounds. The results suggest that the basic tenets of the QET are applicable in interpreting the mass spectra of disubstituted benzenes.

Experimental Section

All mass spectra were taken on an AEI MS9 double focussing mass spectrometer operating at 8 kV. Samples were introduced via the heated inlet. Xenon and krypton were used to calibrate the electron voltage scale. The points at which the ion intensities of xenon and krypton were 10^{-3} of their ion intensities at 50 eV were assigned as the values of their ionization potentials. All ionization and appearance potentials were measured by the method of semilogarithmic plots, with the same two rare gases as internal standards.

(21) M. Wolfsberg, *J. Chem. Phys.*, **36**, 1072 (1962).
(22) M. L. Vestal, *ibid.*, **41**, 3997 (1964).

Table III. Secondary Decomposition "Metastable Peaks" in the Mass Spectra of **1–5**

	m/e	Reactions	
Methyl o-toluate (**1**)	69.5	119 → 91	(M^+ − MeO) − CO
	68.7	118 → 90	(M^+ − MeOH) − CO
Methyl salicylate (**2**)	71.5	121 → 93	(M^+ − MeO) − CO
	70.6	120 → 92	(M^+ − MeOH) − CO
	45.9	92 → 65	(M^+ − Cl) − HCN
p-Chloroaniline (**3**)	42.2	120 → 65	(M^+ − HCN) − Cl
	41.4	100 → 65	(M^+ − HCN) − Cl
Nitrobenzene (**4**)	45.4	93 → 65	(M^+ − NO) − CO
	33.8	77 → 51	(M^+ − NO_2) − C_2H_2
Diethyl ketone (**5**)	14.8	57 → 29	(M^+ − C_2H_5) − CO

When present in the mass spectra, secondary decomposition peaks are added to the precursor ion peaks, as established by the metastable peaks (Table III). In general this correction is relatively small even at 20 eV. The total ion intensity due to secondary decompositions in compounds **1–5** is 12.5, 9.0, 10.8, 10.4, and 22.6%, respectively, of the total ion intensity at 20 eV; at about 15 eV, no decomposition occurs. For p-chloroaniline, M^+ − HCN and M^+ − Cl ions both give secondary decomposition peaks at m/e 65. The intensities of the appropriate metastable peaks for (M^+ − Cl) − HCN and (M^+ − HCN) − Cl are in a ratio of 3:1. As a first approximation, a quarter of the peak intensity at m/e 65 is added to the (M^+ − HCN) intensity and the remainder to the (M^+ − Cl) intensity.

Calculations were made on a Titan (prototype Atlas 2) computer, University Mathematical Laboratory, Cambridge, with standard library subroutines for integration.