Chromatographic areas were corrected for detector response, and absolute yields of dichlorocyclopropanes were determined by addition of either *m*-xylene or *cis*-decalin as an internal standard. Relative rates were calculated as previously described.[1]

When *t*-BuOK was used as the base the following modifications were made: *t*-BuOK (usually ~10 mmoles) was weighed into the flask under nitrogen, followed by addition of the solvent and olefin mixture. After temperature equilibration an excess of $CHCl_3$ in isopentane was added dropwise, followed by the usual work-up procedure.

Competition results are presented graphically in Figure 1 and values at 0 and −78° are given in Table II. Except for 1-chloro-2-methylpropene and the 1-alkenes all competitions were run using isobutylene as the reference olefin. Table V lists competitions in which olefins other than isobutylene were used as the reference. In Table VI are the results of 1-octene/cyclohexene competitions run at varying total olefin concentration.

Table VI. Olefin Reactivity *vs.* Absolute Olefin Concentration[a]

Total olefin concn, moles/l	Log *k*(1-octene)/*k*(cyclohexene)	Dichlorocyclopropane yield, mmoles
~6.7[b]	−0.93	3.3
3.0[c]	−0.94	3.1
9.0×10^{-2} [c]	−0.86	0.3
9.0×10^{-3} [c]	−0.92	<0.1

[a] Reaction at 0° for 7.5–8.0 hr; 10 mmoles of *t*-BuOK and 12.5 mmoles of $CHCl_3$ were added to olefin mixture. [b] Neat olefin. [c] Isopentane solvent.

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Calculation and Qualitative Predictions of Mass Spectra. Mono- and *para*-Disubstituted Benzenes

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Abstract: A classification of the relative ease of fragmentation of substituents in 17 monosubstituted benzenes is drawn up in terms of daughter/parent ($[A^+]/[M^+]$) ion ratios at 18 eV. This order is rationalized with the aid of ionization and appearance potential measurements; the quasi-equilibrium theory calculations show good consistency in most cases with observed $[A^+]/[M^+]$ ratios and metastable ion abundances. A similar order of "ease of fragmentation" of a substituent is drawn up simply in terms of the appearance potential of the daughter ions and is tested in the spectra of *para*-substituted bromobenzenes and anilines. This classification predicts the more abundant daughter ion, which usually swamps the other process except where the two appearance potentials are close. Where a "readily fragmentable group" (*i.e.*, COMe, CO_2Me) is used as the fixed substituent in a series of disubstituted benzenes, the change in the main $[A^+]/[M^+]$ ratio is attributable to the variation in ionization potential and the accompanying change in activation energy E_0. Results are presented to illustrate that the process of lowest appearance potential gives the most abundant "metastable peak."

A feature of recent papers concerned with substituent effects[1–5] has been a more rigorous approach to the factors governing daughter/parent ion ratios. This development has led to a broader understanding of substituent effects measured in terms of ion ratios.

The factors influencing $[A^+]/[M^+]$ ratios at the collector for the reaction $M^+ \rightarrow A^+$ are now established,[1–4] the most important ones being as follows.

1. The rate constant k_A for fragmentation and its variation with internal energy E. These k *vs.* E curves depend on (i) the activation energy E_0 for formation of A^+ and (ii) the frequency factor ν for the fragmentation.
2. The fraction of M^+ ions not having the energy to fragment to A^+. This fraction is larger for a larger difference between ionization potential (I.P.) and appearance potential of A^+ (A.P.) and larger for a smaller electron beam energy, but its exact value is dependent on the internal energy distribution of M^+.
3. Secondary decompositions of A^+ (which influence the intensity of A^+). This problem may be largely alleviated by using low electron beam energies.
4. Competitive decompositions from M^+. In the general case, $[A^+]/[M^+]$ will be dependent on the rates of all competing unimolecular reactions from M^+ and the extent of this dependence is of considerable importance to the discussions in this paper.

Discussion

Monosubstituted Benzenes. Toward a classification and ordering of substituents in terms of relative ease of fragmentation and toward the empirical prediction of the spectra of disubstituted benzenes, we have measured the mass spectra of a number of monosubstituted benzenes at 18 eV. The daughter/parent ion ratios $[A^+]/[M^+]$, together with the I.P. of M^+ and the A.P. of A^+, are listed in Table I.

From the data in Table I, the general trend toward a decrease in $[A^+]/[M^+]$ as A.P. − I.P. is increased is clearly evident.

The quasi-equilibrium theory (QET) of mass spectra[6]

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(1) I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, **90**, 5461 (1968).

(2) R. G. Cooks, R. S. Ward, I. Howe, and D. H. Williams, *Chem. Commun.*, 837 (1968).

(3) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass. Spectrom.*, **2**, 137 (1969).

(4) F. W. McLafferty, *Chem. Commun.*, 956 (1968).

(5) P. Brown, *J. Am. Chem. Soc.*, **90**, 4459 (1968).

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

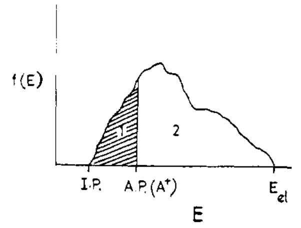

Figure 1. A feasible energy distribution of M^+, illustrating "subdecomposition energy" ions.

in its simplest form predicts that the rate constant k_A varies with internal energy E^7 according to the relationship

$$k_A = \nu\left(\frac{E - E_0}{E}\right)^{s-1} \qquad (1)$$

where ν is a frequency factor, $E_0{}^7$ is the activation energy, and s is the number of vibrational degrees of freedom. This equation may be used, along with Figure 1, to interpret semiquantitatively the results of Table 1.

Table I. Variation of $[A^+]/[M^+]$ Ratios[a] at 18 eV, I.P. of M^+ and A.P. of A^+ with Substituent X in a Series of Monosubstituted Benzenes

Compd no.	X	$[A^+]/[M^+]$	Neutral fragment	I.P. (M^+)	A.P. (A^+)	A.P. − I.P.
1	COMe	2.2	CH_3	9.57	9.99	0.42
2	CMe_3	2.1	CH_3	9.04	10.26	1.22
3	CO_2Me	1.5	OCH_3	9.50	10.80	1.30
4	$CHMe_2$	1.3	CH_3	9.05	10.65	1.60
5	C_2H_5	0.95	CH_3	9.12	11.25	2.13
6	CHO	0.75	H	9.70	10.99	1.29
7	NO_2	0.72	NO_2	10.18	12.16	1.98
8	NMe_2	0.61	H	7.95	10.80	2.85
9	Me	0.53	H	9.18	11.80	2.62
10	I	0.43	I	9.27	11.46	2.19
11	Br	0.36	Br	9.52	12.02	2.50
12	OMe	0.23	CH_2O	8.83	11.30	2.47
13	Cl	0.16	Cl	9.60	13.20	3.60
14	NH_2	0.11	HCN	8.32	12.50	4.18
15	OH	0.11	CO	9.16	11.67	2.51
16	CN	0.090	HCN	10.09	14.60	4.51
17	F	0.044	C_2H_2	9.73	14.73	5.00

[a] A^+ is the characteristic fragment ion of the substituent and is virtually the only fragment ion at 18 eV in the spectra listed.

Figure 1 shows a plausible energy distribution of M^+ and illustrates the importance of "subdecomposition energy" ions[1-4] in influencing $[M^+]$ and therefore $[A^+]/[M^+]$. Area 2 represents those M^+ ions which have energy to decompose, and the extent to which these ions fragment to A^+ in the source is influenced by the k_A *vs.* E curve and the shape of the energy distribution.[8] So from consideration only of area 2, it is evident from eq 1 that, for a given electron beam energy (E_{el}), a larger $[A^+]/[M^+]$ is encouraged by (i) a low E_0 (*i.e.*, a low A.P. − I.P.),[9] (ii) a high frequency factor, and (iii) a smaller molecule.

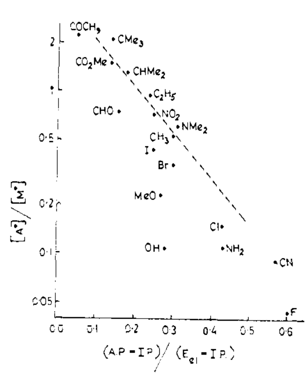

Figure 2. An illustration of the dependence of $[A^+]/[M^+]$ on activation energies and on other molecular parameters.

Area 1 represents the "subdecomposition energy" ions. It is evident from Figure 1 that, given similar shapes of energy distributions for different molecules, this area will be smaller when the ratio (A.P. − I.P.)/(E_{el} − I.P.) is smaller[1] and the result will be an increase in $[A^+]/[M^+]$.

A suitable illustration of the dependence of $[A^+]/[M^+]$ on some of these parameters is presented in Figure 2. The variation of $[A^+]/[M^+]$ with (A.P. − I.P.)/(E_{el} − I.P.) is plotted semilogarithmically from the results in Table I.

It is seen from Figure 2 that the correlation of log $[A^+]/[M^+]$ with (A.P. − I.P.)/(E_{el} − I.P.) is reasonably good.[10] It is noticeable that substituents which lead to A^+ ions *via* rearrangement (*i.e.*, X = MeO, OH, NH_2, CN, F) have $[A^+]/[M^+]$ values rather lower than might be expected from their A.P. − I.P. values. This is probably due to lower frequency factors for rearrangement,[11-13] which would produce lower k values for a given E. Hence there is an increased probability that ions with energies just above the threshold for decomposition will arrive at the collector without fragmenting and so contribute to the M^+ intensity. Similarly, the slightly lower $[A^+]/[M^+]$ values for X = I, Br, Cl may be due, in part, to the lowering of ν due to the lower frequency of vibration of the C–I, –Br, –Cl bonds. The further decomposition of $C_6H_5CO^+$ in the 18-eV spectra of compounds **1** and **6** should result in the lowering of the expected value of $[A^+]/[M^+]$.

Since QET calculations of relative ion abundances have been confined largely to small nonaromatic organic molecules,[8] it was felt that such calculations for aromatic compounds **1–17** would be instructive. This series of compounds would seem to be a reasonable starting point (*i.e.*, only one decomposition pathway and no secondary decompositions in most cases).

First, the k_A *vs.* E relationship must be evaluated for the fragmentation $M^+ \rightarrow A^+$ in each compound. This has been done here by substituting suitable values for the parameters ν, E_0, and s in eq 1.[14] The frequency

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(7) E and E_0 are relative to the ground state of the ion.

(8) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall Inc., Englewood Cliffs, N. J., 1965, pp 145–161, and references cited therein.

(9) The kinetic shift [W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959)] is neglected, although in certain cases this may be unjustified [*e.g.*, for benzonitriles, see I. Hertel and Ch. Ottinger, *Z. Naturforsch.*, *A*, 22, 40 (1967)].

(10) Although it is recognized that the distribution is not drastically altered by omitting the (E_{el} − I.P.) factor.

(11) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968).

(12) F. W. McLafferty and R. B. Fairweather, *J. Am. Chem. Soc.*, **90**, 5915 (1968).

(13) R. S. Ward, R. G. Cooks, and D. H. Williams, *ibid.*, **91**, 2727 (1969).

(14) Insufficient information is available about "activated complex" parameters[8] in these cases to make a more rigorous approach worthwhile.

Table II. Parameters Used in QET Calculations of $[A^+]/[M^+]$ at 18 eV in Some Monosubstituted Benzenes

Compd no.	Substituent, X	E_{max}, eV	E_0, eV	t_1, µsec	t_2, µsec	ν, sec^{-1}	$(S - 1)/2$
1	COMe	8.43	0.42	1.7	18	4×10^{13}	22
2	CMe_3	8.96	1.22	1.8	20	12×10^{13}	32.5
3	CO_2Me	8.50	1.30	1.8	20	4×10^{13}	23.5
4	$CHMe_2$	8.95	1.60	1.7	18	8×10^{13}	28
5	C_2H_5	8.88	2.13	1.6	18	4×10^{13}	23.5
6	CHO	8.30	1.29	1.6	18	8×10^{13}	17.5
7	NO_2	7.82	1.98	1.7	19	3×10^{13}	17.5
8	NMe_2	10.05	2.85	1.7	19	48×10^{13}	26.5
9	Me	8.82	2.62	1.5	16	27×10^{11}	19
10	I	8.83	2.19	2.2	24	2×10^{13}	14.5
11	Br	8.48	2.50	2.0	21	2×10^{13}	14.5
12	OMe	9.17	2.47	1.6	18	1×10^{11}	20.5
13	Cl	8.40	3.60	1.7	18	2×10^{13}	14.5
14	NH_2	9.68	4.18	1.5	16	1×10^{11}	17.5
15	OH	8.84	2.51	1.5	16	1×10^{11}	16
16	CN	7.91	3.21	1.6	17	1×10^{11}	16
17	F	8.27	5.00	1.5	17	1×10^{12}	14.5

factor ν is equated to the frequency of vibration[15] of the bond broken in the transition state, multiplied by a factor σ which represents the number of ways of choosing the reaction coordinate [*e.g.*, $\sigma = 3$ for loss of CH_3 from *t*-butylbenzene (**2**)].[8] In view of the observations[16, 17] that loss of a hydrogen from aliphatic hydrocarbon ions proceeds with a frequency factor of about 100 times slower than that expected from the neutral CH stretching frequency, we have corrected ν for loss of H from toluene (**9**) by a factor of 10^{-2}. The frequency factors for the rearrangement reactions (compounds **12** and **14–17**) are difficult to assign. For compounds **12** and **14–16** a ν value of 10^{11} has been used, and for loss of C_2H_2 from fluorobenzene (**17**) a value of 10^{12} was employed (*cf.* the loss of HCN from pyrazine).[18]

The activation energy E_0 was equated to A.P. − I.P. (neglecting the kinetic shift),[9] except for benzonitrile, where the observed A.P. − I.P. is known to be at least 1.3 eV greater than the true E_0[19] and was therefore reduced by this amount.

In previous applications of the QET, it has been found that only a fraction of the total number of oscillators are effective.[20] Here $(s - 1)/2$ is used as the number of effective oscillators ($s = 3n - 6$, where n is the number of atoms).

Another requirement is the energy distribution and since such distributions are not experimentally available for electron-impact spectroscopy for the compounds used here, a reasonable estimation is made

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

where $f(E)dE$ is the fraction of ions possessing energy between E and $E + dE$ and α is a normalizing constant ($\alpha = 3.75/E_{max}^{5/2}$). For consistency with eq 1, all values of E are relative to the ground state of the ion and $E_{max} = E_{el} - \text{I.P.}$ The distribution is shown in Figure 3. Distributions of this general shape have been found for aliphatic hydrocarbon ions in electron-impact spectroscopy[21] and for a number of aromatic compounds in photoelectron spectroscopy,[22] although the factors influencing the energy distribution from electron and photon impact are somewhat different.

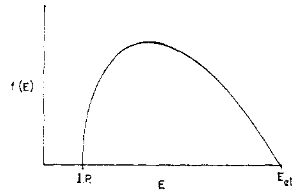

Figure 3. Assumed energy distribution for QET calculations, $f(E)$ *vs.* E.

The final requirements for the QET calculation are the source residence time t_1 and the total time of flight t_2 to the collector. t_1 is difficult to estimate and here we have used as a basis the value $t_1 = 1.4$ sec calculated for pyridazine by Beynon, *et al.*,[18] for an AEI MS 9 source, with the additional assumption that t_1 is proportional to the square root of the mass of M^+.[23] t_2 is calculated from knowledge of t_1, the accelerator potential, and instrument geometry.

All the parameters necessary for the calculations are listed in Table II.

For reasons of clarity, it is convenient to divide the M^+ ions at the collector into two classes: (i) subdecomposition energy ions (M_0^+); and (ii) those ions which have energy to decompose, but which reach the collector without decomposing (M_E^+). The latter class of ions have rate constants between zero and $\sim 10^5$ sec^{-1}.

If it is assumed that A^+ ions do not decompose further and that M^+ and A^+ ions are both removed by instrument parameters (*i.e.*, collision with walls, slits, etc.) at equal rates, then the fractions of $[A^+]$, $[M_0^+]$, and $[M_E^+]$

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(15) All frequencies are taken from the ir spectra of the neutral molecule since no vibrational information about the ion is available.

(16) L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).

(17) A. Kropf, E. M. Eyring, A. L. Wahrhaftig, and H. Eyring, *ibid.*, **32**, 149 (1960).

(18) J. H. Beynon, J. A. Hopkinson, and G. R. Lester, *J. Mass Spectrosc. Ion Phys.*, **1**, 343 (1968).

(19) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *J. Chem. Soc., B*, 149 (1969).

(20) See, for example, Chupka, ref 9.

(21) See, for example, (a) W. A. Chupka and M. Kaminsky, *J. Chem. Phys.*, **35**, 1991 (1961); (b) M. L. Vestal, *ibid.*, **43**, 1356 (1965).

(22) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc., B*, 22 (1968).

(23) See, for example, ref 8, p 134.

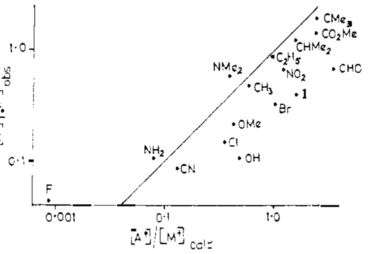


Figure 4. Plot of observed *vs.* calculated $[A^+]/[M^+]$ ratios in monosubstituted benzenes at 18 eV

at the collector are given by

$$[A^+] = \int_{E_0}^{E_{max}} f(E)[1 - \exp(-k_A t_1)]\,dE$$

$$[M_0^+] = \int_0^{E_0} f(E)\,dE$$

$$[M_E^+] = \int_{E_0}^{E_{max}} f(E)\exp(-k_A t_2)\,dE$$

where $f(E)$ and k_A are given by eq 2 and 1, respectively. Standard computer facilities are available for numerical integrations of simple finite functions such as these and the solutions have been computed using one of these standard techniques (Gauss six-point quadrature). The results are shown in Table III.

Table III. Computed Relative Ion Abundances in the Mass Spectra of Some Monosubstituted Benzenes at 18 eV Using QET

Compd no.	Substituent X	$[A^+]^a$	$[M_0^+]$	$[M_E^+]$	$[M_0^+ + M_E^+]^b$	$[A^+]/[M^+]^c$
1	COMe	95.2	2.7	2.1	4.8	20 (2.2)
2	CMe_3	65.6	11.5	17.3	28.8	2.3 (2.1)
3	CO_2Me	69.4	13.6	15.9	29.5	2.3 (1.5)
4	$CHMe_2$	57.8	16.9	22.0	38.9	1.5 (1.3)
5	C_2H_5	46.2	25.2	23.8	49.0	0.94 (0.95)
6	CHO	77.1	13.9	12.9	26.8	3.4 (0.75)
7	NO_2	53.0	27.0	15.9	42.9	1.2 (0.72)
8	NMe_2	26.3	31.3	37.6	68.9	0.38 (0.61)
9	CH_3	34.5	33.3	26.5	59.8	0.57 (0.53)
10	I	58.5	26.3	10.5	36.8	1.6 (0.43)
11	Br	50.4	33.0	14.6	47.6	1.0 (0.36)
12	OMe	26.6	29.3	35.5	64.8	0.41 (0.23)
13	Cl	25.1	52.1	18.7	70.8	0.35 (0.16)
14	NH_2	7.00	52.6	37.2	89.8	0.078 (0.11)
15	OH	28.1	31.4	26.7	58.1	0.48 (0.11)
16	CN	10.9	48.9	33.2	82.1	0.13 (0.090)
17	F	0.86	74.9	22.0	96.9	0.0089 (0.044)

[a] All ion abundances are expressed as percentages of M^+ ions produced in the source at $t = 0$. [b] $[M_0^+ + M_E^+] = [M^+]$. [c] The values in brackets refer to observed values (Table I).

In view of the number of approximations involved, the correlation between observed and calculated $[A^+]/[M^+]$ values is quite good. This correlation is illustrated graphically in Figure 4. The observed value of $[A^+]/[M^+]$ is plotted against the calculated value (on a logarithmic scale for reasons of clarity).

It is evident from Figure 4 that the observed value is in most cases somewhat lower than the calculated value. This general trend could be corrected by choosing for example (i) a number of effective oscillators greater than $(s - 1)/2$ or (ii) an energy distribution weighted more to lower energies than that shown in Figure 3.

Table IV. Computed Metastable Ion Abundances Using QET in the Mass Spectra of Some Monosubstituted Benzenes at 18 eV

Compd no.	Substituent X	t_3, μsec	t_4, μsec	$[m^*]$,[a] Calcd	$[m^*]/[M^+]$, % Calcd	Obsd
1	COMe	9.7	14.3	0.094	2.0	2.2
2	CMe_3	10.2	15.1	0.51	1.8	1.8
3	CO_2Me	10.3	15.2	0.44	1.5	0.3
4	$CHMe_2$	9.7	14.3	0.60	1.5	0.6
5	C_2H_5	9.1	13.4	0.70	1.4	0.9
6	CHO	9.1	13.4	0.29	1.1	1.0
7	NO_2	9.8	14.5	0.55	1.3	0.0[b]
8	NMe_2	9.7	14.4	0.71	1.0	1.4
9	CH_3	8.5	12.5	0.87	1.5	1.5
10	I	12.6	18.6	0.43	1.2	0.2
11	Br	11.1	16.3	0.51	1.1	0.6
12	OMe	9.2	13.6	1.3	2.0	1.8
13	Cl	9.4	13.8	0.63	0.8	0.6
14	NH_2	8.5	12.6	1.1	1.2	1.0
15	OH	8.6	12.7	1.1	1.9	2.4
16	CN	9.0	13.2	1.1	1.3	0.8
17	F	8.7	12.8	0.42	0.43	0.3

[a] Metastable ion abundances are expressed as percentages of M^+ ions produced in the source at $t = 0$, as in Table III. [b] Lowest A.P. process is loss of NO, but this gives only a very low abundance daughter ion, possibly due to a very low frequency factor for this reaction.

However, we feel that there is little merit to be gained by manipulating the parameters to achieve a very good correlation. With the information available at present the error in the calculated value must be large; but it is emphasized that the general *order* of the $[A^+]/[M^+]$ ratios for compounds **1–17** is independent of the exact form of the energy distribution and the number of effective oscillators chosen. The calculations presented here do not of course, in the absence of competing reactions, rigorously test the assumed frequency factors.

In acetophenone (**1**) the calculated $[A^+]/[M^+]$ value is over nine times as large as the observed value. Even allowing for errors in the treatment and for the secondary decomposition of $C_6H_5CO^+$ to $C_6H_5^+$, this difference is large and may be in part a consequence of there being isolated states in M^+, from which decomposition cannot occur even though there is sufficient internal energy for decomposition. Hopefully, as more information becomes experimentally available, the possibility of isolated states in this and other cases will be uncovered.

Several authors have recently emphasized[1-4,13] that subdecomposition energy ions may make an important contribution to M^+ intensity at the collector. Table III illustrates that this assumption is valid. With reasonable chosen values of parameters (see Table II), M_0^+ and M_E^+ make comparable contributions to M^+ intensity at the collector. This is a useful extension to assumptions previously made.[13] The relative proportions of M_0^+ and M_E^+ would, of course, change if instruments using different times of flight t_2 were employed. It is noteworthy that M_E^+ may be conveniently represented graphically as the low-energy segment of area 2 in Figure 1. The calculated $[M_E^+]$ values are probably maximum values as it is generally considered that the effective number of oscillators may be considerably less than $(s - 1)/2$ near threshold, leading to a much more rapid rise of log k in the region 0–3 than that assumed here, thus leading to a decrease in $[M_E^+]$.

An additional test of the approach is made if the relative abundance $[m^*]$ of the metastable peak in each

Table V. Variation of Relative Abundance of $M^+ - Br$ (A^+) to the Other Characteristic Fragment Ion B^+ in the 18-eV Spectra of a Series of *para*-Substituted Bromobenzenes, YC_6H_4Br

Compd no.	Substituent Y	B^+	$[M^+ - Br]/[B^+]$	A.P. ($M^+ - Br$),[a] eV	A.P. (B^+),[a] eV
18	COMe	$M^+ - CH_3$	0.0042		10.58
19	NMe_2	$M^+ - H$	0.0090		11.15
20	C_2H_5	$M^+ - CH_3$	0.52	10.80	10.75
21	OMe	$M^+ - CH_2O$[b]	0.83		
22	I	$M^+ - I$	0.022		12.04
23	OH	$M^+ - CO$	29	12.17	
24	Me	$M^+ - H$	7.2	11.30	12.48
25	NH_2	$M^+ - HCN$	61	11.95	
26	Cl	$M^+ - Cl$	63	12.70	
27	CN	$M^+ - HCN$	$\sim$1000	13.21	

[a] The absence of an A.P. measurement means that the relative abundance of the ion was too low to permit an accurate measurement. [b] The $M^+ - Me$ ion (A.P. = 11.80 eV) is the major fragment ion in this spectrum.

18-eV spectrum is calculated. This quantity is defined by the equation

$$[m^*] = \int_{E_0}^{E_{\max}} f(E)[\exp(-k_A t_3) - \exp(-k_A t_4)]\, dE$$

where t_3 and t_4 are the respective times taken to reach the beginning and end of the field-free region between the electrostatic and magnetic analyzers in a double-focusing mass spectrometer. t_3 and t_4 are listed in Table IV for compounds **1–17**.

The solutions to this integral have been computed using the same parameters and assumptions quoted previously and are also listed in Table IV. The ratio $[m^*]/[M^+]$ is evaluated and compared with the observed value.

In view of the approximations involved, the calculated values of $[m^*]/[M^+]$ shown in Table IV compare favorably with the observed values. So it appears that the chosen number of effective oscillators is adequate in the range $\log k \simeq 4$–6.

Disubstituted Benzenes. Daughter/Daughter Ion Ratios. In order to investigate the extent to which the parameters listed in Table I might be used in qualitative prediction of spectra, we have measured the spectra of several series of disubstituted benzenes.

The following problems arise on further substitution of the monosubstituted benzene C_6H_5X to give the disubstituted compound YC_6H_4X:

1. The fraction M_0^+ of subdecomposition energy ions will change, because of the different energy distribution of YC_6H_4X which is influenced by the I.P. and by the lowest E_0 for fragmentation. An electron-donating substituent will increase this fraction, because of the lower I.P.[24] (all other factors being equal).

2. There is the possibility of competition between the two characteristic fragmentation modes.[25] The effectiveness of the competition depends on the relative appearance potentials and frequency factors for the two processes (*i.e.*, on the k *vs.* E curves).[12,13] The frequency factor should not differ greatly between the monosubstituted and disubstituted case for a given fragmentation reaction and it will be seen in the subsequent discussion that E_0 values are seldom changed drastically on introduction of a further substituent into a monosubstituted benzene. The interplay of these two factors will provide the basis for the further discussions in this paper.

The question of relative daughter ion abundances will be considered first. If the parent ion $YC_6H_4X^+$ gives two daughter ions, A^+ and B^+, characteristic (*cf.* Table I) of X and Y, respectively, then the ratio $[A^+]/[B^+]$ ought to be qualitatively predictable in terms of some parameter in Table I. An order of "fragmentation probability" based on $[A^+]/[M^+]$ ratios in monosubstituted benzene would be unsuitable, since this parameter is influenced by the fraction of subdecomposition energy ions M_0^+, whereas $[A^+]/[B^+]$ is not. Therefore, an order based simply on the A.P. of the A^+ ions in Table I is felt to be more suitable, since $[A^+]/[B^+]$ should be governed largely by the relative appearance potentials of the two ions. Starting with the lowest A.P. process, the order is as follows: COMe, CMe_3, $CHMe_2$, CO_2Me, NMe_2, CHO, C_2H_5, OMe, I, OH, Me, Br, NO_2, NH_2, Cl, CN, F. Table V lists $[A^+]/[B^+]$ ratios together with some relevant appearance potentials for some *para*-substituted bromobenzenes.

It is evident from Table V that an order of fragmentation probability, based on A.P., is quite reliable. Fragmentations of lower characteristic A.P. than $M^+ - Br$ are almost invariably preferred, and $M^+ - Br$ dominates where the A.P. of the other fragmentation is higher.

The actual appearance potentials (where measurable) listed in Table V show that the lower A.P. process is *always* preferred. The results also show that the A.P. of the $M^+ - Br$ ion may vary considerably throughout the series.

However, any quantitative prediction of $[A^+]/[B^+]$ is difficult. Low A.P. processes tend to swamp high A.P. processes (unless the lower A.P. process has a low frequency factor)[11,26] and the high A.P. process may be almost unobeservable even though it was observable in the monosubstituted benzene. This means that a simple prediction using the ratio of the two relevant $[A^+]/[M^+]$ values (from Table I) as being the expected value of $[A^+]/[B^+]$ in the disubstituted compound is, of course, inadequate. The reason for this is evident from eq 1. Ions which have the energy to undergo the high A.P. process[25] are likely to undergo the low A.P. reaction at a rate up to several orders of magnitude faster than the high A.P. reaction (as can be seen by substituting suitable values for the parameters in eq 1). The high A.P. process was only observable in the monosubstituted compounds because at energies at which it can proceed at an apprecia-

[24] G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).
[25] See, for example, Figure 4 in ref 3.
[26] I. Howe, D. H. Williams, D. G. I. Kingston, and H. P. Tannenbaum, *J. Chem. Soc.*, *B*, 439 (1969).

ble rate there are no other, faster, low A.P. processes to compete.

We have measured further spectra to illustrate the general applicability of the order of "fragmentation probability" of substituents based on A.P. values. Relative abundances of daughter ions are listed in Table VI for *para*-substituted anilines.

Table VI. Variation of Relative Abundance of $M^+ - HCN$ (A^+) to the Other Characteristic Fragment Ion B^+ in the 18-eV Spectra of a Series of *para*-Substituted Anilines, $YC_6H_4NH_2$

Compd no.	Substituent Y	B^+	$[M^+ - HCN]/[B^+]$	A.P. $(M^+ - HCN)$,[a] (eV)	A.P. (B^+),[a] eV
28	COMe	$M^+ - CH_3$	$<10^{-3}$		10.19
29	OMe	$M^+ - CH_3$	$<10^{-3}$		10.23
30	CH_3	$M^+ - H$	0.01		10.80
25	Br	$M^+ - Br$	0.015		11.95
31	Cl	$M^+ - Cl$	1.3	12.24	12.37
32	OH	$M^+ - CO$	2.0		

[a] The absence of an A.P. measurement indicates either that the low relative abundance or the interference from other peaks made this impossible with any accuracy.

Table VI illustrates that the characteristic loss of HCN from aniline is observed in compounds **25** and **28–32** only when the other substituent occurs close to NH_2 or further down the "fragmentation probability" series (based on appearance potentials).

HCN loss from aniline is not a low A.P. process and since the frequency factor will be low (rearrangement), it would only be expected to compete with reactions which have higher appearance potentials and/or low frequency factors.

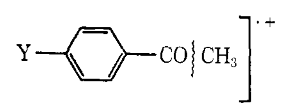
Table VI shows that the fragment ion characteristic of Y has an A.P. lower than that of the $M^+ - HCN$ ion of aniline (12.50 eV) in compounds **25** and **28–30**, and in these cases $M^+ - HCN$ is negligible. However, in compound **31** the fragment $M^+ - Cl$ has an A.P. around that for $M^+ - HCN$ and competition is effective. In compound **32**, interference by an $M^+ - H_2CN$ peak made A.P. measurement impossible.

These results are further supplemented by the spectra of a random selection of *para*-disubstituted benzenes. In the spectra of *p*-*t*-butylphenol (**33**), *p*-*t*-butylbenzonitrile (**34**), *p*-methoxybenzonitrile (**35**), the ions $M^+ - CH_3$, $M^+ - CH_3$, and $M^+ - CH_2O$, respectively, exclude the formation of the fragment ion characteristic of the other substituent, and in the 18-eV spectrum of *p*-chlorophenol (**36**) where the appearance potentials of the fragment ions are sufficiently close to permit competition, $[M^+ - CO]/[M^+ - Cl] = 2.4$.

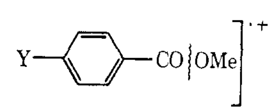
As a general guide, in *meta*- or *para*-disubstituted benzenes, substituents occurring in the top left-hand portion of Figure 2 are expected to fragment more readily than those occurring in the lower right-hand portion. although the predictive usefulness of the diagram is limited when the two substituents come in the same region of the diagram (*e.g.*, CH_3 and Br).

Daughter/Parent Ion Ratios. The discussion of $[A^+]/[B^+]$ ratios in disubstituted benzenes has neglected subdecomposition energy ions M_0^+.[1-4] However this consideration is important in determining $[A^+]/[M^+]$ ion ratios in disubstituted benzenes and is pertinent to the general topic of substituent effects in mass spectrometry.

We will first consider the substituent effect on $[A^+]/[M^+]$ ratios in *para*-substituted acetophenones and methyl benzoates (see a and b). These substituent effects at 18 eV are shown in Tables VII and VIII, respectively, together with the associated ionization and appearance potentials.



a



b

Table VII. Variation of $[M^+ - CH_3]/[M^+]$ with Substituent in the 18-eV Mass Spectra of *para*-Substituted Acetophenones

Compd no.	Substituent	$[M^+ - CH_3]/[M^+]$	I.P.	A.P. $(M^+ - CH_3)$
1	H	2.17	9.67	9.99
37	F	2.18	9.65	10.41
38	Cl	2.10	9.63	10.69
39	Br	2.03	9.55	10.58
40	CH_3	1.60	9.14	10.08
41	OH	1.57	9.11	10.42
42	OMe	1.57	8.85	10.45
43	NH_2	1.01	8.42	10.19

Table VIII. Variation of $[M^+ - OMe]/[M^+]$ with Substituent in the 18-eV Mass Spectra of *para*-Substituted Methyl Benzoates

Compd no.	Substituent	$[M^+ - OMe]/[M^+]$	I.P.	A.P. $(M^+ - OMe)$
44	CN	2.08	9.72	11.60
45	NO_2	2.02	9.70	11.52
3	H	1.54	9.50	10.80
46	CMe_3	0.24[a]	9.38	11.02
47	Cl	1.80	9.57	11.02
48	Br	1.61	9.47	11.11
49	I	0.73	9.10	11.08
50	NH_2	0.99	8.65	10.91

[a] $[M^+ - CH_3]/[M^+] = 3.5$; A.P. of $M^+ - CH_3 = 10.10$ eV.

The results in both Tables VII and VIII may be considered together. Since COMe and CO_2Me are readily fragmentable groups (see appearance potentials in Table I) fragmentations involving the other substituent Y are virtually absent[27] (with the exception of compound **46**, see below). The appearance potentials of $M^+ - CH_3$ and $M^+ - OCH_3$ in Tables VII and VIII, respectively, are not altered much by the substituent Y and it is this that encourages the belief that the ratio $[A^+]/[M^+]$ may be rationalized in terms of the variation in ionization potential. Whatever the exact form of the energy distribution, it is reasonable to assume that lower I.P. substituents will, in general, increase the fraction of subdecomposition energy ions M_0^+[1-4] and hence decrease $[A^+]/[M^+]$. Further, a lowering in I.P. will in general cause an increase in E_0 and this will increase the fraction M_E^+ of molecular ions which *have* energy to decompose but reach the collector without decomposing.

The notable anomaly in Table VIII is methyl *p*-*t*-butylbenzoate (**46**) in which $[M^+ - OMe]/[M^+]$ is only 0.24. This is because $M^+ - CH_3$ is the lowest A.P. process, competing effectively with loss of OMe.

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(27) There is a small peak in all cases for further loss of CO from $M^+ - CH_3$ and $M^+ - OCH_3$, respectively, but this should not invalidate the general arguments presented here.

The situation regarding substituent effects on [A$^+$]/[M$^+$] ratios becomes more complicated when the fixed substituent occurs lower down Table I (or toward the bottom right in Figure 2). Since the A.P. of the ion A$^+$ formed by fragmentation of the fixed group is often not the lowest A.P. in the molecule, the question of competitive decompositions, as well as I.P. effects, is an important consideration.

Tables IX and X show [A$^+$]/[M$^+$] ratios at 18 eV in the mass spectra of *para*-substituted bromobenzenes and anilines, respectively.

Table IX. Variation of [M$^+$ − Br]/[M$^+$] with Substituent in the 18-eV Mass Spectra of *para*-Substituted Bromobenzenes

Compd no.	Substituent	[M$^+$ − Br]/ [M$^+$]	A.P. (M$^+$ − Br)	Other A.P.'s
11	H	0.36	12.02	
18	COMe	0.0095		10.58 (M$^+$ − CH$_3$)
19	NMe$_2$	0.0068		11.15 (M$^+$ − H)
20	C$_2$H$_5$	0.44	10.80	10.75 (M$^+$ − CH$_3$)
21	OMe	0.0021		
22	I	0.074		12.04 (M$^+$ − I)
23	OH	0.10	12.17	
24	Me	0.50	11.30	12.48 (M$^+$ − H)
25	NH$_2$	0.18	11.95	
26	Cl	0.18	12.70	
27	CN	0.23	13.21	

Table X. Variation of [M$^+$− HCN]/[M$^+$] with Substituent in the 18-eV Mass Spectra of *para*-Substituted Anilines

Compd no.	Substituent	[M$^+$ − HCN]/ [M$^+$]	A.P. (M$^+$ − HCN)	Other A.P.'s
11	H	0.11	12.50	
21	COCH$_3$	$<10^{-3}$		10.19 (M$^+$ − CH$_3$)
29	OMe	$<10^{-3}$		10.23 (M$^+$ − CH$_3$)
30	CH$_3$	0.003		10.80 (M$^+$ − H)
25	Br	0.003		11.95 (M$^+$ − Br)
31	Cl	0.09	12.24	12.37 (M$^+$ − Cl)
32	OH	0.06		

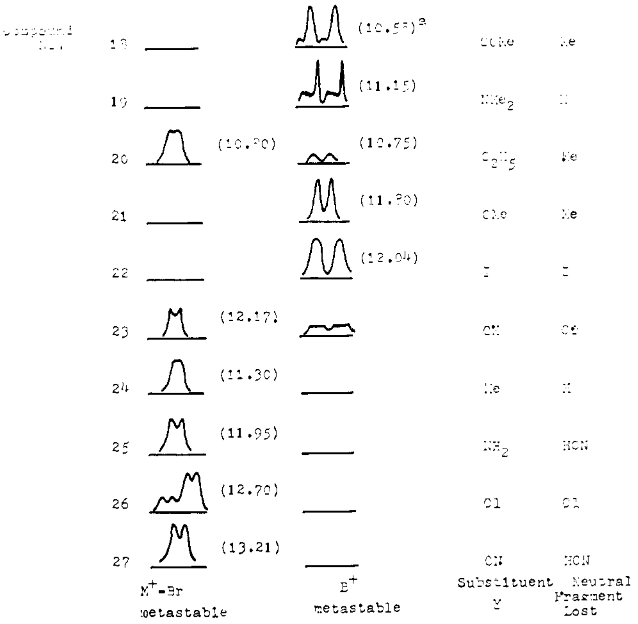
The results illustrate the complications in this type of substituent effect. In the substituted bromobenzenes the [A$^+$]/[M$^+$] ratio is very small where the variable substituent forms a low A.P. ion (see compounds **18, 19, 21, 22**). Where the loss of bromine is the dominant process, subdecomposition energy ions become important and there is also a moderate substituent effect on A.P. for loss of bromine.

In summary, it is reasonable to expect regular substituent effects (in terms of σ or σ^+) if the fixed substituent is readily fragmentable (see Table I or Figure 2). But if the fixed substituent occurs toward the lower right of Figure 2, there will be effective competition with fragmentation of some of the variable substituents. This will result in irregular substituent effects.

Relative Metastable Ion Abundances. Since metastable ions will result from decompositions of M$^+$ within a relatively narrow energy segment and since QET predicts that only the lower energy processes of a set of competitive reactions will be observed as metastables,[28] the lowest A.P. process will give the most intense metastable. Hence "metastable peaks" will only be of comparable intensity when appearance potentials are close. It is pertinent to an investigation on disubstituted benzenes to illustrate competition between different decomposition modes in terms of relative "metastable peak" intensities.

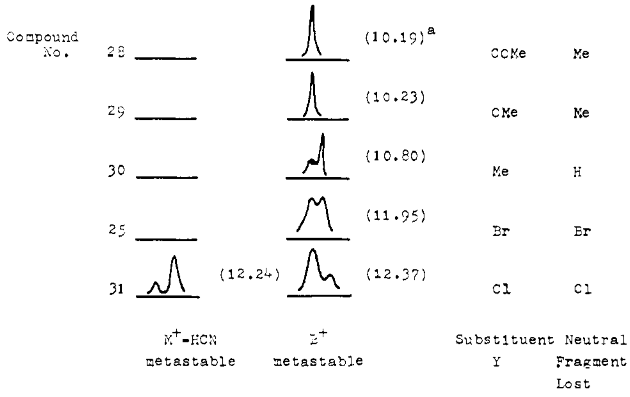
Tables XI and XII illustrate the relative abundances of the metastable ions formed from the two characteristic fragmentation pathways in a series of *para*-substituted bromobenzenes and anilines, respectively. The metastable ion intensities were measured in the second field-free region of a double-focusing AEI MS 9 mass spectrometer. In most cases one of the "metastable peaks" is very small, or unobservable, relative to the other. For each metastable ion, the A.P. of the corresponding daughter ion (formed in the source) is shown in parentheses.

Table XI. "Metastable Peak" Intensities in Some *para*-Substituted Bromobenzenes



^{a} A. P. of daughter ion (eV).

Table XII. "Metastable Peak" Intensities in Some *para*-Substituted Anilines



^{a} A. P. of daughter ion.

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(28) M. Krauss and V. H. Dibeler in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., Chapter 3, p 152.

It is evident from Table XI that the fragmentation of lower A.P. gives the more abundant metastable. In the cases where the $M^+ - Br$ metastable is prominent, the A.P. of the other "characteristic fragment" (although unmeasurable in most cases) would be expected to be high (see Table I). In *p*-bromoethylbenzene (**20**), where the two fragmentations have similar appearance potentials, there is effective competition. It is noteworthy that the A.P. of $M^+ - Br$ in *p*-bromoethylbenzene (**20**) is considered less (10.80 eV) than that in bromobenzene itself (12.02 eV). This observation suggests that in the transition state for loss of a bromine radical from *p*-bromoethylbenzene, the benzene ring was partially or totally rearranged in such a manner that the structure of the $M^+ - Br$ species is probably a methyltropylium ion.[29]

Similarly, in *p*-bromophenol the two metastable ions are of comparable abundance and although the A.P. of the $M^+ - CO$ ion was not measurable because of interference of other peaks, it is quite feasible that this A.P. is close to that of the $M^+ - Br$ ion.[30]

Table XII further confirms our conclusions. Note that in *p*-chloroaniline (**31**) the two characteristic "metastable peaks" are of almost equal intensity and the two appearance potentials are only 0.13 eV apart.

In the spectra of all the *para*-substituted acetophenones measured, the $M^+ - CH_3$ metastables were the only ones observable from M^+ and in all cases the $M^+ - CH_3$ daughter ions had low appearance potentials (see Table VII). In all spectra measured, relative metastable abundances were independent of electron volts.

In conclusion, it may be stated that this treatment of the spectra of *para*-disubstituted benzenes may, in principle, be extended to those of *meta*-disubstituted benzenes, heteroaromatics, and polynuclear aromatics.

Experimental Section

All relative ion abundances were determined using an AEI MS 9 mass spectrometer operating at a source temperature of 160–170° and with the slits set for a resolving power of approximately 2000 (10% valley definition). The source temperature, electron beam energy, accelerator protential (8 kV), and repeller potential remained constant within each run of a series of compounds. Samples were introduced through a heated inlet system.

Ionization and appearance potentials were determined by the semilogarithmic plot method.[31]

The relative (but not absolute) values of the I.P.'s and A.P.s. are estimated to be accurate within ±0.2 eV.

The solutions to the integrals for $[A^+]/[M^+]$ ratios were computed by the Titan (prototype Atlas 2) computer, University Mathematical Laboratory, Cambridge, using a six-point gauss quadrature, available as a Library routine for numerical integration. Dividing each of the integrals into three parts achieved an accuracy of 1%. Evaluation of the $[m^*]$ integrals required division of the integral into 0.1-eV segments. Peak areas were measured in the determination of observed $[m^*]/[M^+]$ ratios.

Acknowledgments. The award of a Junior Research Fellowship (to I. H.) at Churchill College, Cambridge, is gratefully acknowledged.

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[29] See also P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

[30] The appearance potentials of $M^+ - Br$ in bromobenzene and $M^+ - CO$ in phenol are 12.02 and 11.67 eV, respectively.

[31] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

Application of the Principle of Least Motion to Organic Reactions. A Generalized Approach

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Abstract: The application of the principle of least motion to organic reactions has been facilitated by a generalized method of calculation. The results of calculations for β eliminations, acetylene formation, enolization, 1,2-hydride shifts, pseudorotation, and the thermal cyclization of butadiene are in accord with experimental observation.

The *principle of least motion*, as put forward by Rice and Teller,[1] states that *those elementary reactions will be favored that involve the least change in atomic position and electronic configuration.* The applicability of this principle to the reactions of resonance-stabilized species,[2a] and to the stereochemistry of eliminations[2b] has been shown by Hine. Recently Miller[2c] critically reviewed the principle and suggested that it be renamed as a hypothesis. It can best be applied to systems where other factors remain essentially constant, and, because of its simplicity, can be used generally, provided the results are assessed critically.[2c]

The object of the present paper is to outline a more general method of calculation than that used previously,[2b] and to give examples of calculations that have been carried out for a variety of systems. Criticism can be leveled at the approach in that atoms which are not common to both reactant and product are ignored.[2b,3] Clearly this could lead to serious error where the atoms ignored constitute a complex grouping. For this reason the approach would seem to be best applied to molecular rearrangements where the constituent atoms remain constant. Calculations carried out for elimina-

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[1] F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

[2] (a) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); (b) *J. Amer. Chem. Soc.*, **88**, 5525 (1966); (c) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968).

[3] This point was raised by one of the referees.