2-(1′-Octyl)cyclohexanone-2′,2′,-d_2. Carbonation of the Grignard reagent prepared from 1,1-d_2-heptyl bromide produced the corresponding octanoic acid. After reduction with lithium aluminum hydride and halogenation with phosphorus and iodine,[13] the resulting octyl iodide was utilized in the above-described alkylation reaction.

2-(1′Octyl)cyclohexanone-3′,3′-d_2,-4′,4′-d_2,-5′,5′-d_2. The corresponding labeled hexyl bromides were condensed with diethyl malonate;[14a] hydrolysis and decarboxylation[14b] yielded the corresponding octanoic acids, which were reduced and halogenated in the usual manner. The resulting labeled octyl iodides were used in the above-described alkylation procedure.

2-(1′-Octyl)cyclohexanone-6,6-d_2. Alkylation of cyclopentanone with 1,1-d_2-iodopropane in the usual manner resulted in a good yield of 2-(1′-propyl)cyclopentanone-1′,1′-d_2 (IX).

Anal. Calcd for $C_8H_{12}D_2O$: mol wt, 128. Found: mol wt, 128 (by mass spectroscopy).

To a solution of 1.28 g (10 mm) of IX in dichloroethane was added 2.14 g (10.5 mm) of 85% pure *m*-chloroperbenzoic acid. After the solution had been heated under reflux for 7 hr, it was allowed to cool, extracted with 1.05 equiv of sodium bicarbonate, washed with water, dried over magnesium sulfate, and distilled. The resulting clear liquid (bp 108–110° (12 mm)) was subjected to reduction with lithium aluminum hydride without further purification. The resulting 6,6-d_2-octane-1,5-diol (XI) was purified by preparative tlc using ethyl acetate eluent. The clear oil (bp 150–152° (13 mm), n_2^{20} 1.4550; lit.[20] bp 144–146° (11 mm), n_d^{17} 1.4561) exhibited a single peak when subjected to vpc (10-ft 2% SE-30 column operated at 225°). The over-all yield based on IX was 77%.

The 1-trityl derivative of XI was prepared by allowing a dry pyridine solution containing 2.10 g (7.5 mm) of trityl chloride and 1.11 g (7.5 mm) of the diol to stand for 3 days at room temperature;[15] the progress of the reaction was conveniently followed by tlc. The trityl ether was worked up in the usual manner, and purified by tlc (eluent pentane(2)–ethyl ether (1)). The product, a viscous oil, weighed 2.02 g (69% yield). The monotrityl ether was converted into the trityl ether–tosylate (XIII) using a standard procedure.[16] Purification by preparative tlc resulted in an excellent yield of viscous yellow oil, which was treated with a fourfold excess of lithium aluminum hydride at room temperature; tlc showed the reaction to be complete after 20 min. Work-up in the usual manner followed by preparative tlc (eluent pentane(9)–ethyl ether (1)) gave triphenylmethyl-6,6-d_2 octyl ether (XIV) in over-all yield of 51% based on the diol XI.

The trityl ether XIV was hydrolyzed by 30 hr reflux in 85% acetic acid.[15] The resulting 6,6-d_2-octanol was purified by vpc (10-ft 2% SE-30 column operated at 200°). The oily N-methyl isatoic ester[17] of the labeled octanol was prepared for analysis.

Anal. Calcd for $C_{16}H_{23}D_2NO$: mol wt, 265. Found: mol wt, 265 (by mass spectroscopy).

The 6,6-d_2-octanol was converted into the corresponding octyl iodide and used to effect alkylation in the usual manner.

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[20] R. Paul, *Bull. Soc. Chim. France*, 317 (1935).

Substituent Effects in Mass Spectrometry. Mass Spectra of Substituted Phenyl Benzyl Ethers

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Abstract: From a consideration of smoothed energy distributions, ionization potentials, and appearance potentials, the effect of substituents on the ratio of molecular ion to total daughter ion abundance in the mass spectra of substituted phenyl benzyl ethers ($XC_6H_4OCH_2C_6H_5$) has been calculated. The results show a qualitative agreement with experiment in 20-eV spectra, but for some substituents (*e.g.*, *m*-CH_3O, *m*-OH, and *m*-NH_2), the observed molecular ion abundance is much greater than the calculated value. In these cases it may be that the assumed energy distributions are a poor approximation to those actually occurring and/or isolated electronic states of the molecular ions may be generated upon electron impact.

When an organic molecule is ionized by an energetic electron (*e.g.*, 20 eV) to give a positive parent ion, varying amounts of energy are transmitted from the electron beam to the molecules and hence a distribution of energies in the parent ions is obtained. This energy distribution is fixed in the absence of collisions, and will in general extend from the ionization potential (IP, the minimum energy transferred to give a parent ion) to the electron beam energy, E_{el}. In earlier papers,[1] we have utilized a parabolic energy distribution extending from IP to E_{el}, and in the present paper we utilize (on purely empirical grounds) an energy distribution which weights lower internal energies (less than $(E_{el} - \mathrm{IP})/2$) more than higher internal energies (greater than $(E_{el} - \mathrm{IP})/2$) (Figure 6A).[2] In the figure the ordinate indicates the weighting of a particular internal energy, *i.e.*, $f(E)\mathrm{d}E$ is the fraction of ions having energies between E and $E + \mathrm{d}E$. This energy distribution will be used as a plausible working model for 20-eV spectra. It is probably unsuitable for much higher (*e.g.*, 70 eV) or much lower (*e.g.*, 14 eV) beam energies.

In this paper, the smoothed energy distribution is used in an approach to substituent effects in mass spectrometry. It will be seen that the approach relies to a large extent on consequences of the quasi-equilibrium theory,[3] and is somewhat different to the approach of McLafferty and Bursey,[4] which first stimulated interest in this field.

Before substituent effects can be reliably evaluated,

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[1] (a) I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, **90**, 5461 (1968); (b) R. G. Cooks, R. S. Ward, I. Howe, and D. H. Williams, *Chem. Commun.*, 837 (1968).

[2] The curve given in Figure 6 is actually a plot of $y = (1 - x^{1/3})\cdot(x - x^2)$.

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

[4] M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966). For a review, see M. M. Bursey, *Org. Mass Spectry.*, **1**, 31 (1968), and for the current status of the approach see F. W. McLafferty, *Chem. Commun.*, 956 (1968).

one must first consider the factors which determine molecular ion abundances in mass spectra. First, that fraction of ions possessing internal energy less than the lowest activation energy for decomposition must be recorded as molecular ions.. Thus, in Figure 6 (B, i) (which represents an arbitrarily drawn energy distribution of the type that will occur in practice), if E_0 represents the lowest internal energy required to cause fragmentation, the fraction of ions corresponding to the shaded area will be recorded only as molecular ions. Second, the question arises as to how the ions with internal energies in excess of E_0 will be distributed between parent ions and daughter ions, considering for the moment only the one possible mode of decomposition requiring energy E_0 or greater. Daughter ions are produced only from parent ions which decompose in the source and therefore in a typical mass spectrometer, daughter ions are formed from parent ions decomposing in approximately 1 μsec or less ($k \geqslant 10^6$ sec^{-1}). If this rate of decomposition is attained at an internal energy which is only very slightly in excess of E_0, then obviously to a good approximation, the molecular ion abundance will be given by the shaded portion of Figure 6 (B, i) and the daughter ion abundance by the unshaded portion. There is indeed evidence to suggest that in the vast majority of organic compounds, internal energies in excess of E_0 by less than 1 eV (in many cases, considerably less than 1 eV) will be effective in decomposing nearly all parent ions to daughter ions. Thus, Vestal[5] has calculated on the basis of the quasi-equilibrium theory[3] that all propane molecular ions with internal energies more than 0.01 eV in excess of the lowest activation energy decompose before reaching the collector. Thus once the activation energy for decomposition has been supplied, the rise of k with internal energy, E, is initially very rapid (see the schematic illustration in Figure 6 (C, i)). It is only if the initial rise of k with E is rapid that the difference in appearance potentials of metastable ions (formed after ~10 μsec in the second field-free region of a double focussing mass spectrometer for an ion of *m/e* 100) and daughter ions will be small or negligible. Indeed, until very recently significant differences in these appearance potentials had not been reported; the difference AP (daughter) − AP (m*) = 1.3 eV for the loss of HCN from benzonitrile[6] is certainly unusually large and differences in the range 0.1–1.0 eV seem to be more commonplace. Thus the *approximation* summarized in Figure 6 (B, i) would appear to be justified as a working model in the majority of cases. The approximation will be a poor one if the rise of k with E is unusually slow.

If one is considering substituent effects on the reaction $M^+ \rightarrow A^+$ at beam energies at which there is no significant further decomposition of A^+, the next question that must be answered is "how will the ion yield of A^+ be affected by competition with other unimolecular reactions?" The answer to this question can be found from a consideration of the quasi-equilibrium theory,[3] and much of the work which has followed (for excellent reviews of this subsequent work, see the articles by Rosenstock and Krauss[7] and by Rosenstock[8]). Consider the case where the reaction $M^+ \rightarrow A^+$ requires a minimum internal energy $E_0{}^1$ and the process of next lowest activation energy requires an energy $E_0{}^2$ (Figure 6 (B, ii)). Thus within the limits of our approximation as outlined above, the fraction of ions with energies between $E_0{}^1$ and $E_0{}^2$ will be recorded as A^+ daughter ions. For those ions with energies in excess of $E_0{}^2$ (let this be the activation energy for a reaction $M^+ \rightarrow B^+$, with no further decomposition of B^+), competition between the reactions $M^+ \rightarrow A^+$ and $M^+ \rightarrow B^+$ is now possible. To evaluate this competition, one needs to know the relative rates of these two reactions at all internal energies between $E_0{}^2$ and E_{el}. Unfortunately, such information is not readily obtained without making drastic simplifying assumptions. For example, if one assumes (or has reason to believe) that the reaction $M^+ \rightarrow A^+$ and $M^+ \rightarrow B^+$ have the same or similar frequency factors, then it can be deduced that at all internal energies between $E_0{}^2$ and E_{el}, k_A will be greater than k_B although these rates will approach each other more closely at the highest internal energies (see the convergence of the solid lines in Figure 6 (C, ii)). However, if the reaction $M^+ \rightarrow A^+$ has a lower frequency factor than the reaction $M^+ \rightarrow B^+$, then the latter reaction may become faster at high internal energies. This situation is shown schematically in Figure 6 (C, ii), where the dotted line for $M^+ \rightarrow B^+$ reaction crosses the solid line for the $M^+ \rightarrow A^+$ reaction. The situation is most readily understood if it is recognized that as internal energies tend to infinity, the reaction rates tend to equal the frequency factors. The competition between reactions near the threshold is very sensitive to the values of the activation energies and relatively insensitive to the frequency factors.[5] In contrast, at higher values of the internal energy, the competition is sensitive to the frequency factors and rather less sensitive to the values of the activation energies.

Hence, it may be seen that mass spectra can theoretically be computed from a knowledge of the variation of k with E for each fragmentation (Figure 6 (C, ii)). All the unimolecular decompositions must be treated as competing reactions at the appropriate internal energies. The relative ion abundances are then obtained by summing the relative ion yields for each internal energy over the whole energy distribution (*e.g.*, Figure 6 (B, ii)). So much has of course been long recognized,[3,5,6-8] but to the present time the approach has been almost completely ignored by organic chemists working in the field.

At this stage in the argument, the reader may well ask "Is not the consideration of exponential decay kinetics important?" or "What about the fraction of ions giving rise to metastable ions?" It is emphasized that according to the quasi-equilibrium theory there will in general be a continuous distribution of lifetimes, and the initial rise of k with E is usually sufficiently rapid that most lifetimes which are heavily weighted in 20–70-eV spectra correspond to rates $> 10^6$ sec^{-1}. Therefore on the mass spectrometer time scale, the vast majority of molecular ions with sufficient energy to decompose give rise to daughter ions. The energy segment giving rise to metastable ions is narrow (usually $\leqslant 1$ eV) and

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(5) M. L. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965).

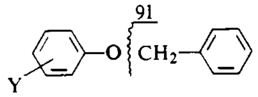
(6) I. Hertel and Ch. Ottinger, *Z. Naturforsch.*, **22a**, 40 (1967).

(7) 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.

(8) H. M. Rosenstock, *Advan. Mass Spectry.*, **4**, 523 (1968).

can therefore be ignored to a reasonable approximation for our present purposes.

To apply the outlined concepts to substituent effects in organic mass spectrometry, it is necessary to use simplified energy distribution functions, and we have chosen the energy distribution illustrated in Figure 6A. One next needs to select a system in which, for the majority of substituents, only one or two fragmentation pathways are of consequence and, at the chosen beam energy (20 eV), further decomposition of these fragment ions should be minimal. Substituted phenyl benzyl ethers (**1–15**) were selected and accordingly synthesized.

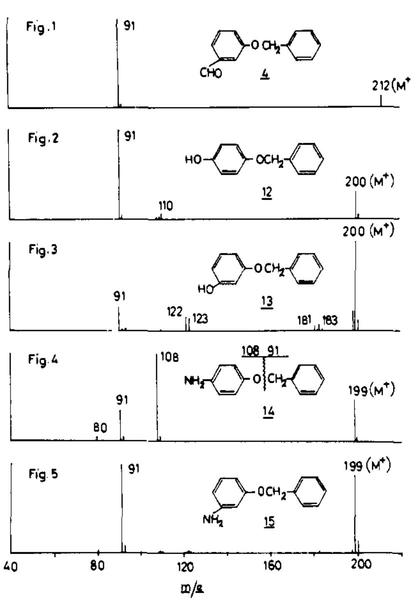


1, Y = *p*-NO_2
2, Y = *m*-NO_2
3, Y = *p*-CHO
4, Y = *m*-CHO
5, Y = *p*-Cl
6, Y = *m*-Cl
7, Y = H
8, Y = *p*-Me
9, Y = *m*-Me
10, Y = *p*-MeO
11, Y = *m*-MeO
12, Y = *p*-OH
13, Y = *m*-OH
14, Y = *p*-NH_2
15, Y = *m*-NH_2

In the 20-eV mass spectra of **3–9** and **11**, more than 95% of the total ion current is carried by *m/e* 91 ($C_7H_7^+$, base peak) and the molecular ion peak. In the 20-eV mass spectra of **1**, **2**, **12**, and **15**, more than 83% of the total ion current is carried by *m/e* 91 (base peak) and the molecular ion peak. The spectrum of **4** is reproduced in Figure 1 as being representative of the former class, and the spectra of **12** and **15** are reproduced in Figures 2 and 5 as being representative of the latter class. In the cases of **10** and **14**, more than 90% of the total ion current at 20 eV is carried by three ions (M^+, $M^+ - 91$, *m/e* 91) (see, for example, the 20 eV mass spectrum of the *p*-amino compound **14** in Figure 4). Finally, the *m*-OH compound **13** is unique for its relative lack of specificity in fragmentation, although even in this case 65% of the total ion current is carried by *m/e* 91 and M^+ (Figure 3).

It may be seen from the foregoing discussion that by use of our assumed energy distribution at 20 eV (Figure 6A), measured ionization potentials of **1–15**, and appearance potentials for the processes of lowest activation energy, we can compute in each case the anticipated molecular ion abundance, $[M^+]$, relative to the total daughter ion abundance, $[\Sigma D^+]$, *i.e.*, the ratio $[M^+]/[\Sigma D^+]$,[1b] since in our approximation the M^+ abundance is simply given by the fraction of ions with insufficient energy to decompose (*e.g.*, the shaded area in Figure 6 (B, i)). The data relevant to these calculations are summarized in Table I, and the calculated ratios are compared with the experimentally observed ratios in 20-eV spectra.

The ionization potentials of **1–15** show the expected decrease with increasing electrondonating ability of the substituent.[9-11] The spread in values is 1.5 eV, from the *p*-NH_2 compound at 7.6 eV to the *p*-NO_2 compound at 9.1 eV. It is noteworthy that the spread in values for the AP of *m/e* 91 is much less (0.5 eV) and shows no consistent trend with substitution. One possible explanation of these observations is that the reaction leading to *m/e* 91 occurs from an electronic state corresponding to ionization on the benzyl ring (**16**). This state may of course be rapidly equilibrating with other electronic states that are energetically accessible, but the important point is that one would expect this ion to be



Figures 1–5. Mass spectra (20 eV) of *m*-benzyloxybenzaldehyde (**4**), *p*-benzyloxyphenol (**12**), *m*-benzyloxyphenol (**13**), *p*-benzyloxyaniline (**14**), and *m*-benzyloxyaniline (**15**).

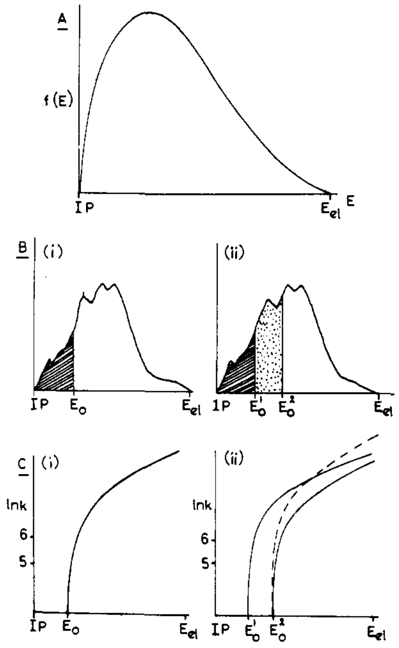


Figure 6. (A) Assumed energy distribution (plot of f(*E*) against the internal energy, *E*). (B, i and ii) Hypothetical energy distributions indicating fractions of ions with insufficient energy to decompose. (C, i and ii) Schematic plots of reaction rates (ln *k*) against internal energy (*E*).

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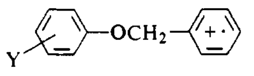
[9] G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).
[10] J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Am. Chem. Soc.*, **84**, 4 (1962).
[11] F. W. McLafferty and T. Wachs, *ibid.*, **89**, 5042 (1967).

Table I. Ionization and Appearance Potential Data (in electron volts) for **1–15**, and Calculated and Observed $[M^+]/[\Sigma D^+]$ Ratios for 20-eV Mass Spectra[a]

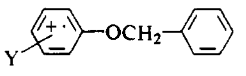
Compd	(Substitution)	IP	AP(91)	AP($M^+ - 91$)[b]	AP(91) − IP	$\frac{[M^+]}{[\Sigma D^+]_{calcd}}$	$\frac{[M^+]}{[\Sigma D^+]_{obsd}}$
1	(p-NO_2)	9.1	10.0		0.9	0.05	0.03
2	(m-NO_2)	9.0	9.9		0.9	0.05	0.03
3	(p-CHO)	8.7	9.7	11.1	1.0	0.06	0.09
4	(m-CHO)	8.6	9.7	11.5	1.1	0.07	0.11
5	(p-Cl)	8.3	9.7	12.7	1.4	0.10	0.19
6	(m-Cl)	8.5	9.6	12.6	1.1	0.07	0.15
7	(H)	8.4	9.7		1.3	0.09	0.28
8	(p-Me)	8.2	9.8	11.8	1.6	0.13	0.34
9	(m-Me)	8.4	9.9	11.9	1.5	0.12	0.39
10	(p-MeO)	8.0	10.0	10.6	2.0	0.18	0.43
11	(m-MeO)	8.3	10.1	10.4	1.8	0.16	0.52
12	(p-OH)	8.2	9.9		1.7	0.14	0.31
13	(m-OH)	8.4	9.9		1.5	0.12	1.12
14	(p-NH_2)	7.6	9.9	9.7	2.3	0.19	0.33
15	(m-NH_2)	8.0	9.9	10.1	1.9	0.18	0.83

[a] The relative (but not absolute) values of the IP's and AP's are estimated to be accurate within ±0.2 eV. The values of the AP's of $M^+ - 91$ may be subject to slightly greater variations (±0.3 eV) since these determinations were carried out on ions of lower relative abundance. [b] The absence of a value indicates that the ($M^+ - 91$) abundance was too low to permit a reliable measurement.

at a roughly constant energy level above the ground state of the neutral molecule for each substituent.[12]



16



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Therefore, if the activation energy for decomposition from **16** to give m/e 91 is similar in each case, one would expect similar AP's for the m/e 91 ions from **1** to **15** (as observed). This interpretation implies that the substituent effect on the activation energy for the reaction leading to m/e 91 from **16** is small compared to the substituent effect on the ionization potential of each compound. Hence, on the basis of this possibility it can be seen that the calculated increase in molecular ion intensity from 0.05 of the total daughter ion abundance in **1** to 0.19 in **14** (Table I) would largely be associated with a substituent effect on ionization potentials rather than a substituent effect on the activation energy for decomposition from a given excited electronic state.[1a]

Alternatively, one might also consider that m/e 91 arises from the ground electronic state of the ion which, with the possible exception of **1** and **2** will correspond to a form ionized on the phenoxy ring and/or associated substituents (**17**). In these cases, the activation energy would be given roughly by the difference AP(91) − IP (Table I). Therefore, it would transpire that the number of vibrational quanta in **17** necessary to cause dissociation into m/e 91 and a substituted phenoxy radical would approximately double on passing from **3** or **4** to **14** or **15**. This interpretation would also seem plausible since transition-state energies leading to substituted phenoxy radicals should be increased by electron-donating substituents (**14, 15**), and decreased by electron-withdrawing substituents (**3, 4**).[13] This latter interpretation would ascribe the calculated and observed increase in M^+ abundance on passing from **1** down the table as solely due to a substituent effect on activation energy for reaction from the ground state of the ion.

Our crude model leads to a calculated gradual increase of the M^+ abundance from 0.05 of the total daughter ion abundance in **1** to 0.19 in **14**, while the observed values increase from 0.03 in **1** to 1.12 in **13** (Table I). The agreement between calculation and experiment is certainly as good as can be expected for **1–6**. However, for **7–15**, the observed molecular ion abundance is consistently greater than the calculated abundance; the discrepancies are particularly pronounced for those ethers containing *meta* electron-donating substituents (m-MeO, m-OH, and m-NH_2; Table I and Figures 3 and 5). The following reasons (or combination of reasons) may be considered to account for these discrepancies. (i) The energy distribution varies from compound to compound (as indeed it will), but in such a way that our model (Figure 6A) is adequate for NO_2 and CHO substituents (**1–4**) yet does not weight sufficiently energies within 0–2 eV above the IP for the remaining compounds. (ii) Electronic states may be excited (upon electron impact) which are isolated from the electronic state which leads to decomposition *via* the dissociation of lowest AP. If, for example, a vibrationally "cold" electronic state 2 eV above the energy corresponding to the lowest AP were excited but the potential surfaces of the two states did not cross then, given an activation energy for decomposition from that isolated electronic state,[7] the highly electronically excited ion would necessarily be recorded as a molecular ion (despite the fact that its internal energy is 2 eV in excess of the lowest AP).

The problem of isolated states may be illustrated by reference to the spectra of the p- and m-hydroxy-substituted ethers (Figures 2 and 3); in the spectrum of the *meta*-substituted isomer, the molecular ion carries a much larger fraction of the total ion current than in the spec-

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[12] In ions with internal energies of a few electron volts in excess of the ionization potential, the charge is not of course localized. Thus it seems correct to argue (A. Mandelbaum and K. Biemann, *J. Am. Chem. Soc.*, **90**, 2975 (1968); see also I. Howe and D. H. Williams, *ibid.*, 5461 (1968)) that there is a dynamic distribution of charge over periods of time much greater than one vibration. However, when the requisite number of vibrational quanta corresponding to the activation energy have been gathered in the reaction coordinate, dissociation occurs in one vibration and does so from a specific electronic state.

[13] See, for example, R. S. Davidson, *Quart. Rev.* (London), **21**, 249 (1967).

Table II. Relative Abundances of Some "Metastable Peaks" due to Decomposition of the Molecular Ions of **8–15**

Compd	(Substitution)	Transition	*m/e*	Rel ab $\times 10^{-2}$ [a]
8	(*p*-Me)	$M^+ \rightarrow 108\,(M^+ - 91)$	58.9	0.5
		$M^+ \rightarrow 91$	41.8	22
9	(*m*-Me)	$M^+ \rightarrow 108\,(M^+ - 91)$	58.9	0.5
		$M^+ \rightarrow 91$	41.8	12
10	(*p*-MeO)	$M^+ \rightarrow 123\,(M^+ - 91)$	70.7	0.3
		$M^+ \rightarrow 91$	38.7	30
11	(*m*-MeO)	$M^+ \rightarrow 136\,(M^+ - 78)$	86.7	4
		$M^+ \rightarrow 123\,(M^+ - 91)$	70.7	0.1
		$M^+ \rightarrow 91$	38.7	5
12	(*p*-OH)	$M^+ \rightarrow 109\,(M^+ - 91)$	59.4	0.3
		$M^+ \rightarrow 91$	41.4	16
13	(*m*-OH)	$M^+ \rightarrow 122\,(M^+ - 78)$	74.4	13
		$M^+ \rightarrow 91$	41.4	6
14	(*p*-NH_2)	$M^+ \rightarrow 108\,(M^+ - 91)$	58.6	30
		$M^+ \rightarrow 91$	41.6	0.3
15	(*m*-NH_2)	$M^+ \rightarrow 182\,(M^+ - 17)$	166.3	5
		$M^+ \rightarrow 122\,(M^+ - 77)$	74.8	4
		$M^+ \rightarrow 121\,(M^+ - 78)$	73.8	2
		$M^+ \rightarrow 91$	41.6	5

[a] Relative to base peak as 100 units.

Table III. Melting Points of Phenyl Benzyl Ethers

Substitution	Mp, °C	Lit, Mp, °C	Ref
H	36–38	39	15
m-Me	42–43	43	15
p-Me	39–41	41	15
m-MeO	28–30	31–32	*a*
p-MeO	70–71	71	*b*
m-OH	67–69	69	16
p-OH	120–122	122	*c*
m-Cl	60–61	59	*d*
p-Cl	71–72	71–72	18
m-NO_2	54–55	55	*e*
p-NO_2	106–108	108	17
m-NH_2	62–63	61–62	*f*
p-NH_2	54–55	56	17
m-CHO	53–54	54	*g*
p-CHO	71–72	72	*h*

[a] A. Sonn and E. Patschke, *Chem. Ber.*, **58**, 1700 (1925). [b] J. C. Smith, *J. Chem. Soc.*, 251 (1931). [c] H. Schiff and G. Pellizzari, *Ann.*, **221**, 365 (1883). [d] H. Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926). [e] F. Arnall, *J. Chem. Soc.*, 811 (1924). [f] A. A. Morton and W. R. Slaunwhite, Jr., *J. Biol. Chem.*, **179**, 259 (1949). [g] W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1533 (1935). [h] E. Wörner, *Chem. Ber.*, **29**, 142 (1896).

trum of the *p* isomer despite the fact that AP(91) − IP is very similar for these compounds. Hence, we must conclude either that these *meta* and *para* isomers have very different energy distributions and/or the intervention of isolated electronic states is more important in the spectrum of the *meta* isomer.

Alternatively, it could of course be argued that had we assumed a single energy distribution which weighted much more heavily the internal energies within 0–2 eV of the IP, then reasonable agreement with experiment could be found for the *meta*-electron-donating substituents, but then the calculated molecular ion abundances would be too large in the case of the *m*- and *p*-nitro compounds. The latter situation could only be explained by assuming that such an energy distribution (weighing low internal energies very heavily) is in error for the nitro compounds. This is why we feel that our assumed energy distribution (Figure 6A) is adequate for the nitro compounds and that different energy distributions and/or the intervention of isolated states may account for the anomalously high M^+ abundances in the cases of some of the electron-donating substituents.

If one is considering only *competing* unimolecular decompositions from the molecular ion of a compound, then it is of course true that the most abundant "metastable peak" will correspond to the process of lowest activation energy.[14] Therefore, for competing reactions, the relative abundances of "metastable peaks" for decompositions of M^+ give further information on relative activation energies. Some relevant data for **8–15** are summarized in Table II.

In all cases (Table II) the data are consistent with the formation of *m/e* 91 and $M^+ - 91$ fragment ions *via* competing unimolecular decompositions. Thus when the appearance potentials for formation of *m/e* 91 ions are less than the appearance potentials for formation of $M^+ - 91$ ions (as in all instances except the *p*-amino compound **14**), intense "metastable peaks" are found for the processes $M^+ \rightarrow m/e$ 91, but the "metastable peaks" for the processes $M^+ \rightarrow M^+ - 91$ are extremely weak (Table II). On the other hand, when the appearance potential for the process $M^+ \rightarrow M^+ - 91$ is less than that for the $M^+ \rightarrow m/e$ 91 reaction (as for the *p*-amino compound, see Table I), the "metastable peak" for the $M^+ \rightarrow M^+ - 91$ (*m/e* 108) transition is by far the most intense. Most important, this latter observation, coupled with the observation of an intense "metastable peak" for the formation of *m/e* 91 in the *m*-NH_2 isomer (**15**) in the absence of a "metastable peak" for the $M^+ \rightarrow M^+ - 91$ process, establishes that the *p*- and *m*-NH_2 isomers have not isomerized to a common structure even after approximately 15 μsec (the time needed to reach the second field-free region). It is noteworthy that the *p*-NH_2 substituent is much more effective in reversing the relative activation energies for the $M^+ \rightarrow 91$ and $M^+ \rightarrow M^+ - 91$ reactions than either the *p*-OH or *p*-OMe substituents.

Another interesting observation is that electron-donating *meta* substituents (MeO, OH, and NH_2) promote the reaction $M^+ \rightarrow M^+ - 78$ accompanied by abundant "metastable peaks" (Table II, compounds **11**, **13**, and **15**). This reaction probably corresponds to the loss of a neutral benzene molecule, but the reason for this behavior is not obvious.

In summary, a consideration of crude energy distributions, in conjunction with measured appearance potentials and ionization potentials, permits the calculation of molecular ion abundances relative to total daughter ion abundances. For all compounds except **10**, **13**, and **14**, the fragmentation pathway $M^+ \rightarrow m/e$ 91 is so specific that the calculation is essentially that of the $[m/e\ 91]/[M^+]$ ratio. We emphasize that in these cases the calculation is not concerned with relative reaction rates, but is dependent upon the fractions of ions that do and do not have sufficient energy to decompose. The calculations agree qualitatively with experimental data, but quantitative correlation is poor. Where deviations between calculated and observed ratios are large, it may be that the assumed energy distributions are grossly

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(14) Reference 7, pp 43–44.

inadequate and/or isolated electronic states of the molecular ion may intervene.

Experimental Section

Preparation of Phenyl Benzyl Ethers. The amino- and formyl-substituted ethers were commercially available. The others were prepared by heating the appropriate phenol with benzyl chloride and potassium hydroxide[15-17] or potassium carbonate.[18] All samples were purified by recrystallization and their purity confirmed by melting point determination (Table III).

All mass spectra were determined on an AEI MS9 instrument operating at 20 eV (unless otherwise stated) and a source temperature of 200–220°. The trap current was 90 μA. Samples were introduced through a heated inlet system, with the exception of the *m*- and *p*-OH, and *m*- and *p*-NH_2 isomers, which were introduced *via* the direct inlet system. Ionization and appearance potentials were determined by the semilogarithmic plot method.[19]

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Stability of Molecules Containing Nonalternant Rings

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Abstract: The symbolic analysis of the Hückel molecular orbital properties developed by Dewar and Longuet-Higgins is extended to nonalternant molecules. A simple graph method is described and applied to several representative π systems.

In a recent paper[1] molecules containing single and fused 4*n* rings were treated in terms of the Longuet-Higgins and Dewar analysis of resonance formalism.[2] Their analysis had demonstrated that resonance language when modified to include an algebraic sign for each structure has firm roots in molecular orbital theory and is, as pointed out by Heilbronner,[3] only indirectly related to valance bond theory. It had been shown that molecules composed only of rings of $4n + 2$ π atoms or chains of π atoms have resonance structures with the same algebraic sign so that for these compounds the usual naive resonance structure counting rules apply. With molecules containing one or more 4*n* rings both positive and negative structures occur and this leads to quite different structure counting rules. Modified rules for a number of simple situations have been summarized and exemplified.[1] The present paper extends this approach to molecules containing odd-membered rings (nonalternants) and describes structure counting rules that can be used to correlate Hückel calculations and to estimate relative stabilities. This extension is timely because of the current general interest in nonalternant hydrocarbons. As with the earlier application to alternant hydrocarbons the resonance structure formulation does not give any information not available from an HMO calculation but it does provide a symbolism that permits the chemist to think graphically and thereby hopefully to conceive structures that might otherwise be overlooked from a purely numerical computerized examination.

The earlier conclusions about relative stability of alternant hydrocarbons[2] have two parts that must now be distinguished. The first, that molecules with a zero algebraic sum of structures have triplet Hückel ground states, applies only to alternant species because it depends on the existence of the pairing rule of energy levels. There does not appear to be a simple, rigorous way to extend this to nonalternants. The second conclusion, which was that the relative stability of isomeric hydrocarbons is proportional to the algebraic sum of signed structures, is strictly applicable only to alternant species; however, with slight modification it can be easily applied to nonalternant hydrocarbons as well.

Review of Theory for Alternant Systems. In order to explain the modified rule and its application it is useful to first outline those parts of the alternant hydrocarbon analysis that bear directly. The emphasis here is on the secular determinant in which all of the diagonal terms are set to zero since it can be shown that the numerical value of this determinant is equal to the product of the related eigenvalues.[2] With alternant molecules the contributing π atoms are divided into two classes, starred and nonstarred.[4] By definition no two starred atoms or two nonstarred atoms are adjacent. If the *n* atoms of one class are numbered sequentially followed by the *n* atoms of the second class, the resulting topological determinant[5] of order 2*n* will have the block form shown

$$\Delta=\left|\begin{array}{c|c} 0 & A \\ \hline \underbrace{A^{\mathrm{T}}}_{n} & \underbrace{0}_{n} \end{array}\right|\begin{array}{l}\}\,n\\ \}\,n\end{array}\qquad(1)$$

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