Substituent Effects in Mass Spectrometry

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AN important and useful kinetic approach to mass spectrometry has recently been suggested to study substituent effects.[1] We think that a modified approach may be necessary, and point out the importance of some factors which have not hitherto been emphasised.

Since ions in the mass spectrometer source are non-interacting, the energy distribution in the molecular ion is fixed and uniquely determines which ions do or do not have sufficient energy to undergo a given dissociation. To derive crude and simple energy distributions, we have recently derived[2] and attempted to justify the expression (1)

$$f(E)\cdot dE = A(E_{el} - E)(E - \text{I.P.})\cdot dE \qquad (1)$$

where $f(E)\cdot dE$ is the fraction of ions with energies between E and $E + dE$, and A is a constant; for a given excitation probability the cross section is assumed to be linear in the energy excess $E_{el} - E$, and the excitation probability is assumed to be linear in E — I.P. (where E_{el} is the electron-beam energy and I.P. is the ionisation potential of the compound). This expression results in parabolic-shaped energy distributions extending from I.P. to E_{el}, and it is here assumed that this simple approach provides an adequate working model for 20 ev spectra.

We recently emphasised that for a molecular ion (M^+) undergoing the single reaction $M^+ \longrightarrow A^+$, with no significant further decomposition of A^+, the ratio $[A^+]/[M^+]$ is a function of accelerator potential.[3] While this effect has important consequences for a kinetic approach in some instances (*e.g.*, when there is an abundant "metastable peak" for the $M^+ \longrightarrow A^+$ transition), it is frequently observed that varying the time t_2 needed for ions to travel from the source exit slit to the collector (from approximately 15 to 30 μsec.) does not have

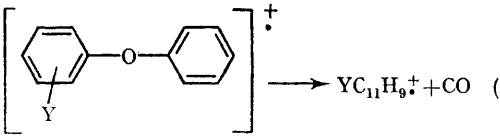
TABLE[a]

Y		$[M^+]/[\Sigma_{30}f]$		$[M^+ - CO]/[M^+]$	$([M^+]/\Sigma_{30}f])^{t\to\infty}_{calc.}$
		8kv	2 kv		
(1) p-NH_2	..	0·51	0·45	0·02	0·52
(2) m-NH_2	..	0·45	0·38	0·10	0·25
(3) p-MeO	..	0·62	0·54	—	0·33
(4) m-MeO	..	0·51	0·45	0·006	0·29
(5) H ..	..	0·59	0·47	0·12	0·26
(6) p-Cl ..	..	0·47	0·40	0·017	0·20
(7) p-Br ..	..	0·35	0·29	0·012	0·20
(8) m-Br ..	..	0·32	0·27	0·010	0·19
(9) p-MeCO	..	0·31	0·28	—	0·13
(10) p-NO_2	..	0·58	0·46	—	0·09
(11) m-NO_2	..	0·52	0·47	—	0·06

[a] All spectra were determined at a nominal 20 ev.

a very marked effect on relative fragment ion/molecular ion abundances. In these cases, Bursey and McLafferty's postulate[1] that the relative abundances of ions recorded by the collector reflect the relative concentrations in the source is a useful working model. However, if the M^+ abundance shows only a small dependence on t_2, one must then consider the possibility that a large fraction of the molecular ions with sufficient energy to dissociate do so in less than 5 μsec. Therefore, the recorded molecular ion abundance can reflect to an important degree merely those ions which have insufficient energy to undergo any dissociation process. Under these circumstances, it will not be valid to equate the rate of formation of A^+ to $k_1[M^+]$ (where k_1 is the 'rate constant' for the $M^+ \longrightarrow A^+$ reaction, and $[M^+]$ is the recorded molecular ion abundance).[1]

To illustrate the important consequences of the above considerations, we have studied substituent effects on the loss of CO from diphenyl ether and m- and p-substituted derivatives (equation 2). Relevant data are summarised in the Table.



$\longrightarrow YC_{11}H_9^{+\cdot} + CO$ (2)

A change in accelerating voltage from 8 kv to 2 kv corresponds to an increase in t_2 from ~15 μsec. to ~30 μsec. in the AEI MS9 mass spectrometer;[3] yet in all cases (compounds 1—11), the fraction of total ion current $[\Sigma_{30}]$ carried by the molecular ions changes by a relatively small amount upon almost doubling the decay time. These experimental data support the contention that a large fraction of molecular ions with sufficient energy to decompose do so in less than 15 μsec., and therefore a large fraction of the measured M^+ abundance may correspond to ions with insufficient energy to dissociate. This point may be emphasised by comparing the behaviour of diphenyl ether (5) and p-methoxydiphenyl ether (3). In the spectrum of the latter there is no significant loss of CO from M^+, but the $M - CH_3$ peak is 24% of the abundance of the base-peak molecular ion. It must be concluded that in states where there is possible competition between loss of CO and CH_3, the loss of CH_3 is more than an order of magnitude faster.† Despite this fact, the fraction of total ion current carried by M^+ (at both 8 kv and 2 kv) in the spectra of (5) and (3) is very similar. Taking the viewpoint that the rates of formation of $M - CH_3$ and $M - CO$ peaks can be represented by the expressions $k_{Me}[M^+]$ and $k_{CO}[M^+]$,[1] one would be forced to conclude that k_{CO} for p-methoxydiphenyl ether (3) is much less than k_{CO} for diphenyl ether (5). From an extension of the argument, it would follow that there is a general trend for all substituents to decelerate the loss of CO.‡ However, while there probably is a substituent effect on the rate of CO loss, it would seem unlikely that both electron-withdrawing and electron-donating substituents would retard that rate process. The

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† This conclusion assumes that there are no drastic differences between the rates of further decomposition of $M - CO$ and $M - CH_3$ ions, which would appear to be a reasonable assumption for 20 ev spectra.

‡ A similar conclusion was recently made regarding the loss of CH_2O from substituted anisoles (M. M. Bursey and F. W. McLafferty, *J. Org. Chem.*, 1968, **33**, 124). Footnote 15 of this paper points out some of the considerations emphasised in this communication, but the practical importance of these considerations is here demonstrated for the first time.

true explanation of the data would appear to be that the rates of loss of CO from (1—11) are not necessarily drastically different. Rather, when dissociations involving the Y substituents take place much faster than CO loss (3, 9—11), a large reduction in M^+ intensity does not occur because the competition is not possible in a considerable proportion of M^+. Hence, in the presence of M^+ ions with insufficient energy to dissociate, the ratio $[A^+]/[M^+]$ will not be independent of the rate constants for competing unimolecular decompositions (as hitherto assumed[1]). In (9—11), where CO loss does not compete with loss of Me, NO, and NO, respectively, the appearance potentials of the fragment ions formed by rupture of the substituent are less than 12 ev, whereas the appearance potential for loss of CO from diphenyl ether (5) is 12·6 ev.[4] In compounds (1—2) and (4—8) where CO loss is competitive with other fragmentation modes, the appearance potentials for the alternative fragmentations are in all cases equal to or greater than 12 ev. In *p*-methoxydiphenyl ether (3) where the appearance potential for loss of Me is 12·4 ev, loss of CO probably fails to compete because of a slightly higher activation energy (and perhaps lower frequency factor) for CO loss.

By use of the smoothed energy distributions referred to at the outset, in conjunction with measured ionisation potentials of (1—11), and the appearance potentials corresponding to the processes of lowest activation energy, a rough estimate of $[M^+]/[\Sigma_{30}]$ as $t_2 \rightarrow \infty$ can be made. The calculated values are given in the Table. It is apparent that on the basis of the simple model, considerable fractions of the molecular ions from (1—9) will have insufficient energy to dissociate. If it is assumed that the vast majority of reaction which is going to take place has done so when t_2 ~30 μsec. (column 3 of the Table), then the agreement between the figures for (1—9) in columns 3 and 5 is as good as can be expected, considering the crudity of the approach. When $Y = p\text{-}NO_2$ or $m\text{-}NO_2$ (10 and 11), the difference between the figures is large (0·46 as against 0·09, and 0·47 as against 0·06). The ionisation potentials of (10) and (11) are 9·3 and 9·2 ev and the appearance potentials for loss of NO from M^+ are estimated to be as low as 11·4 and 10·9 ev.§ The surprisingly large observed intensity of M^+ in the spectra of (10) and (11) may be related to loss of NO from an isolated electronic state.

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§ The appearance potentials of the *M* — NO fragments are 8·6 and 8·1 ev, respectively [*less* than the corresponding ionisation potentials of (10) and (11)]. These values are estimated to be less than the appearance potentials for loss of NO *from* M^+ by an amount equal to the electron affinity of NO (~2·8 ev) [Dr. J. H. Beynon, personal communication].

[1] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 529.
[2] I. Howe and D. H. Williams, *J. Amer. Chem. Soc.*, in the press.
[3] I. Howe and D. H. Williams, *Chem. Comm.*, 1968, 220.
[4] P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 1965, **69**, 2943.