Substituent Effects in Unimolecular-ion Decompositions: An Attempt to Enumerate Basic Factors

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ALTHOUGH a simple kinetic approach appeared to provide a sufficient explanation for our original studies of substituent effects in mass spectra,[1] in further investigations it has become apparent that several factors can contribute to the overall kinetic scheme.[2] This is an attempt to clarify the ways in which a substituent can affect the abundance of ions formed by a particular decomposition path.‡ Factors that can be affected are:

(1) *The distribution of the internal energy values of the precursor ions.* The energy transferred from the bombarding electron in the ionization of a particular molecule can vary over a wide range of values, so that the internal energies of the molecular ions

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produced in the ion source have a distribution of values. Unlike reactions at higher pressures in which the reactants are in thermal equilibrium, there is little probability that an ion, once formed, will gain or lose energy before it undergoes decomposition; thus the rate of its decomposition by a particular path depends on the internal energy acquired when it is formed.[4] The abundance of the product ion relative to the precursor ion (the "Z" value[1]), which we previously related to a "rate" of the overall reaction, is thus determined by the rates and abundances of the different energy forms of the precursor.

If the only effect of adding a substituent to a molecule is to shift the molecular ion energies to (for example) lower values (*e.g.* by lowering the ionization potential), the number of molecular ions with sufficient energy to decompose through a particular reaction should decrease, and those with insufficient energy to decompose before leaving the ion source should increase, thereby lowering the "Z" value. For example,[2b] changing $Y = -NO_2$ to $Y = -NH_2$ in p-RCO·C_6H_4·CH_2·CH_2Ph-Y-p dramatically lowers the abundance of ions produced by reactions at the carbonyl group, consistent with the large decrease in ionization potential.§ Also, this factor offers an alternative explanation for the observations that the *m*- and *p*-isomers of certain substituted phenetoles exhibit nearly identical substituent effects, which has been explained as isomerization to a common structure.[5] We find that these isomeric pairs also have the same ionization potentials;[6] if no other factor has an important differential effect on the decomposition, the isomers might then exhibit identical substituent effects without isomerization.

It is also possible to change the shape of the curve describing the ion-energy distribution without appreciably changing the onset (*e.g.* ionization) potential. This appears to offer a partial explanation for the degree-of-freedom effect on the relative abundance of metastable ions.[7]

(2) *Stabilization of the product ion.* This well-recognized effect arises through the fact that in such endothermic ionic decompositions the transition state and products are structurally similar. Thus if the substituent is retained in the product ion, the substituent effect on the activation energy can offset its effect on the moleculer ion energy [factor (1)]. In the reaction $\text{YPhCOPh}^{+\cdot} \rightarrow \text{YPhCO}^{+} + \text{Ph}\cdot$, the negative q-value observed[8] indicates that the effect of the substituent on the even-electron product ion is more important than its effect on the odd-electron molecular ion. In general the parallel factor, the substituent effect on the rate through stabilization of the neutral product, is much less important.

(3) *Bond strength of all bonds cleaved or formed in the reaction.* In contrast to the formation of YPhCO^{+}, in the reaction $\text{YPhCOPh}^{+\cdot} \rightarrow \text{PhCO}^{+} + \text{YPh}\cdot$ the substituent should have a much smaller effect by factor (2), but should have a much greater effect on the electron density at the reaction site.[1] Factor (1) should also affect this reaction with a positive ρ-value; the good correlation with σ-constants observed attests to the additivity of these factors, if factor (3) makes an appreciable contribution to this system.¶

4. *Competitive reactions.* According to the quasi-equilibrium theory,[4] a number of reaction pathways may be possible for the decomposition of ions of a particular internal energy, and the relative proportions of the product ions formed will be determined by the rates of these reactions. If the substituent affects the rate of an important competitive reaction pathway to a much greater extent than the pathway under study, this could affect the number of energetic ions available for decomposition. A change in the mechanism of a decomposition reaction represents this type of effect.

5. *Secondary decompositions of the product ion.* If the product ion bears the substituent, the effect of secondary decompositions must be considered[1,8] unless the rates of these reactions are low.** Apparently there can be a substituent effect on such rates even when the product ion does not contain the substituent.[2e]

Thus factors (1) and (4) can make the total number of precursor ions of all energies a poor measure of the ions available for reaction, and factor (5) has a similar effect on the product ions. The presence of isomers can give misleading "Z" values.[1,8] Within the same spectrum a measure of relative reaction rates can be obtained by comparing the abundances of different product ions arising from the same precursor,[7] but to use this technique to compare the relative rates of a particular reaction in two compounds with different

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§ Although factor 4, below, could also lower the ion abundance to some extent, factors 2 and 5 would act in the opposite direction.

¶ Note that factors 2 and 3 are attempts to predict the effect of structure on the shape of the curve relating the energy of the precursor ion to the reaction rate. Thus any factors which affect the activation energy and "frequency factor" should also be included.

** Such rates can often be made negligible by lowering the electron energy.

substituents, it is necessary that the rate of the reaction used as a reference does not change with change of substituents.

This large number of factors emphasizes that caution must be exercised in interpreting the effects of substituents on mass spectral reactions. However, if particular factors can be controlled or held constant, substituent effects should give much more specific information than previously possible; this appears to be possible by comparing the reactivity of the substituted moiety with its unsubstituted counterpart in the same molecule. For example, comparison[6] of the formation of $YPhCH_2^+$ and $PhCH_2^+$ from $YPhCH_2{\cdot}CH_2Ph^{+\cdot}$ eliminates differences caused by factors (1) and (3). In the reaction[9] $YPh(Y'Ph)(Ph)COH^{+\cdot} \rightarrow YPh(Ph)COH^+$ or $Y'Ph(Ph)COH$ or $YPh(Y'Ph)COH^+$ the effect of three substituents can be compared intramolecularly. Of perhaps greater importance, it appears that it may be possible to incorporate these factors as separate terms in an overall substituent effect equation.[2a,6]

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