# Substituent Effects in Unimolecular Ion Decompositions: Formation of $PhCO^+$ Ions with Varying Internal Energies

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WE have recently reported that the relative intensities of the benzoyl ions in the mass spectra of substituted benzophenones (reaction 1) are well correlated with Hammett's $\sigma$-constants.[1]

$$PhCO{\cdot}C_6H_4Y^{+\cdot} \rightarrow PhCO^+ + C_6H_4Y\cdot \quad (1)$$

This surprisingly precise correlation (linear correlation coefficient = 0·976) was assumed to require that the decomposition of each of the various substituted benzophenones produces $C_7H_5O^+$ ions that are identical in structure and average internal energy.

We now report that these benzoyl ions are formed instead with different average energies, as indicated by the relative intensities of their metastable ions arising from reaction (2). The relative metastable-ion intensities (measured at 22·5 ev) are greatest for those benzophenones substituted with strong electron-releasing groups and smallest for those substituted with strong electron-withdrawing groups, indicating that the benzoyl ions from the former case possess higher average internal energies than those from the latter. The metastable-ion intensities are fairly well correlated with Hammett's $\sigma$-constants (linear correlation coefficient = 0·918, standard deviation = 0·067, determined by omitting the $p$-$NMe_2$ and $p$-Ph benzophenones, as discussed later), exhibiting a $\rho$-value of −0·38 as shown in the Figure.†

$$PhCO^+ \rightarrow Ph^+ + CO \ (m^* = 56{\cdot}5) \quad (2)$$

These results can be rationalized in terms of the statistical theory of mass spectra,[2] which assumes that mass spectral processes are a series of competing unimolecular reactions. Two of the competing decomposition pathways of the molecular

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† The $\sigma$-constant for $p$-phenyl was chosen to be −0·25 instead of −0·01 as discussed in ref. 1.

ion in a series of substituted benzophenones are formation of the benzoyl ion and formation of the substituted benzoyl ion. When the substituent is electron-releasing, the less-favoured pathway (higher activation energy) is formation of the benzoyl ion.[3] Thus in order that a significant number of benzoyl ions be observed in the mass spectrum, decompositions must result from higher energy states on the average than those required to produce the substituted benzoyl ion. When the substituent is electron-withdrawing, the favoured pathway (lower activation energy) is formation of the benzoyl ion,[3] and now these decompositions should originate from lower energy states.[4] This is supported by preliminary data on the appearance potentials of the $C_7H_5O^+$ ions from $Y{\cdot}C_6H_4{\cdot}COPh$ in which $p$-$NO_2$ $<$ H $<$ $m$-$NH_2$ $<$ $p$-$NH_2$. Thus the particular molecular ion decomposing by reaction (1) will have a higher average internal energy when Y is electron-releasing than when Y is an electron-withdrawing group. This rationalization appears to account for the data from all of the substituted benzophenones studied except for the $p$-dimethylamino and the $p$-phenyl cases.

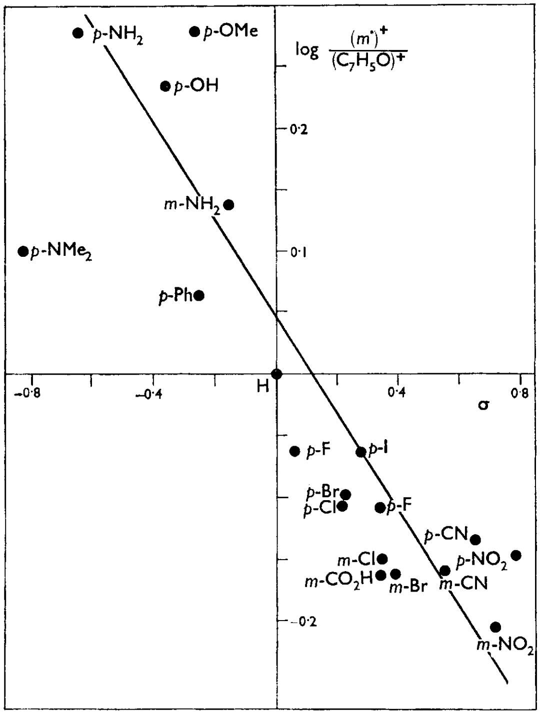

FIGURE. *Correlation of metastable-ion intensities for the decomposition of* $C_7H_5O^+$ *in substituted benzophenones (linear correlation coefficient* = 0·918, *standard deviation* = 0·067)

We have recently observed that the metastable-ion intensities for the $EtO^+$ and $PrO^+$ ions are well correlated with the number of degrees of freedom of the molecular ion.[5] Since for $p$-dimethylamino- and $p$-phenyl-benzophenone the number of degrees of freedom of the molecular ion have been substantially increased compared to the other compounds, it would be expected that the metastable-ion intensities would be smaller than predicted by the correlation.[5]†

The results also suggest that the $Z/Z_0$ values determined at 75 ev do not exactly indicate the relative rate of reaction (1) for the various benzophenones. A correlation of $Z/Z_0$ with $\sigma$ would still be expected, but the correlation of the actual rate of (1) would exhibit a lower $\rho$-value. Since the energy distribution for the benzoyl ion from benzophenones with electron-releasing substituents is higher than that for other benzophenones, the rate constant for the disappearance of the benzoyl ion from these electron-releasing compounds is larger and thus the relative rate of reaction (1) is also larger than that indicated by the $Z/Z_0$ value. Similar reasoning would predict the opposite effect for electron-withdrawing groups, resulting in a lower $\rho$-value. Low voltage measurements are in process to settle this matter.

In conclusion, the metastable-ion intensities are clearly affected by the energy distribution of the precursor ion. This energy distribution seems to be a function of the number of degrees of freedom of the molecular ion as well as the activation processes required to form the precursor ion.

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[2] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhafting, and H. Eyring, *Proc. Nat. Acad. Sci., U.S.A.*, 1952, **38**, 667.

[3] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1967, **89**, 1.

[4] P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 1965, **69**, 2943, have found that the benzoyl ion from benzophenone is formed with approximately 34 kcal./mole of excess internal energy, consistent with the above argument.

[5] F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, 1967, **89**, 5951, 5953.