# Physical and Inorganic Chemistry

## Substituent Effects in Unimolecular Ion Decompositions. IV. Correlations of Intensities of Ions Retaining the Substituent[1]

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**Abstract:**  Although a close correlation is found between relative ion intensities in several sets of aromatic compounds, the effect of a substituent on the abundance of a product ion containing the substituent is not correlated by the Hammett equation.[2]  Elimination of further decomposition of such a product ion by using low-energy electrons allows a satisfactory Hammett correlation to be obtained, and these data can be used to evaluate the influence of the substituent on further decomposition of the ion at higher electron energies.  These studies yield Hammett $\rho$ values for the principal reactions involved in the mass spectra of a series of benzoyl compounds.  The $\rho$ values are consistent with previous views of reaction mechanisms and provide strong support for the postulation that product ion stability is an important driving force in ion decomposition reactions.[3]

The identification and characterization of the individual unimolecular decomposition reactions which the molecular ion and intermediate ions undergo is basic to the understanding and interpretation of mass spectra. Few tools have been found useful for this problem because of the complex nature of the kinetic scheme. This paper explores further the applicability of substituent effects to evaluation of reaction pathways in mass spectra.

The relative abundance of an unsubstituted fragment ion formed by a one-step decomposition of a variety of substituted molecular ions, e.g., acyl ions from substituted acylbenzenes (eq 1), correlates with Hammett $\sigma$ constants[2] for ordinary solution reactions, and the $\rho$ value for such reactions has a magnitude and sign

$$YC_6H_4COR^{.+} \longrightarrow RCO^+ \qquad (1)$$

consistent with the electronic effects predicted.[4]  The abundance of an ion formed in a two-step process can

be similarly correlated if only one step involves a substituent effect. The $\rho$ value of $+1.0$ found for the over-all scheme (eq 2) at low electron voltage is the same as that found for reaction 1 where $R = C_6H_5$.[5]

$$YC_6H_4COC_6H_5^{.+} \longrightarrow C_6H_5CO^+ \longrightarrow C_6H_5^+ \qquad (2)$$

When two competing decomposition paths form an ion, e.g., the formation of $C_6H_5^+$ from $YC_6H_4COC_6H_5^{.+}$ (eq 2 and 3), $\sigma$ constants may be used to ascertain the

$$YC\text{-}H_4COC_6H_5^{.+} \longrightarrow C_6H_5^+ \qquad (3)$$

portion of the product which each process contributes to the total amount of $C_6H_5^+$ produced. The much smaller $\rho$ value for eq 3 (0.0) again is consistent with the greater distance of the substituent from the reaction site.

Thus substituent effects are applicable for the elucidation of pathways leading to a product ion through a single reaction, consecutive reactions, or competing reactions when the product ion *does not contain the substituent.* However, the substituent is retained in roughly half of the observed product ions; formation of these important ions will be considered here. For such ions the substituent should influence not only the reactions by which the ion is formed, but should also

(1) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(3) F. W. McLafferty in "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 318.

(4) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

(5) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 4484 (1966).
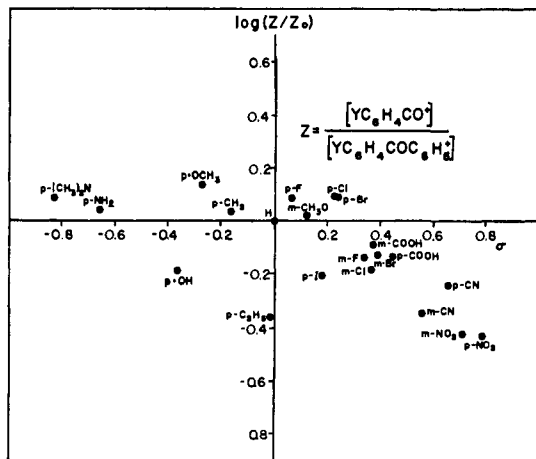
Figure 1. Relative intensities of the $YC_6H_4CO^+$ ions in substituted benzophenones vs. $\sigma$ values.[6]

Figure 2. Relative intensities of the $YC_6H_4CO^+$ ion in the mass spectra of substituted benzophenones recorded at 15.3 v vs. $\sigma$ and $\sigma^+$ values.[6]

influence all of the reactions by which the ion can decompose. Let us consider first the case in which there is only one reaction by which the ion is formed.

**Case with One Formation Pathway.** The concentration of an ion in the source of the mass spectrometer is dependent on its rates of formation and depletion (whether by decomposition or instrumental removal) according to eq 4, where A may be formed from several

$$
\begin{array}{c}
N_1 \xrightarrow{k_1} \quad \xrightarrow{k_{11}} B_1 \\
\quad A \\
N_2 \xrightarrow{k_2} \quad \xrightarrow{k_{12}} B_2
\end{array}
\tag{4}
$$
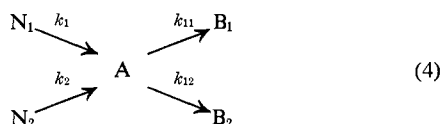
different N and decompose to give different B. This situation yields eq 5 as the rate of appearance of A in the source; by the steady-state approximation, eq 6 is obtained. For the case in which A is formed from the
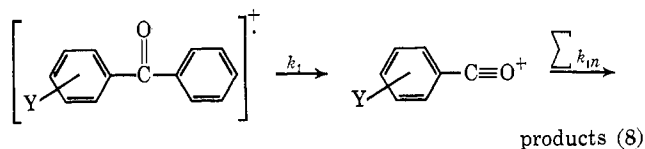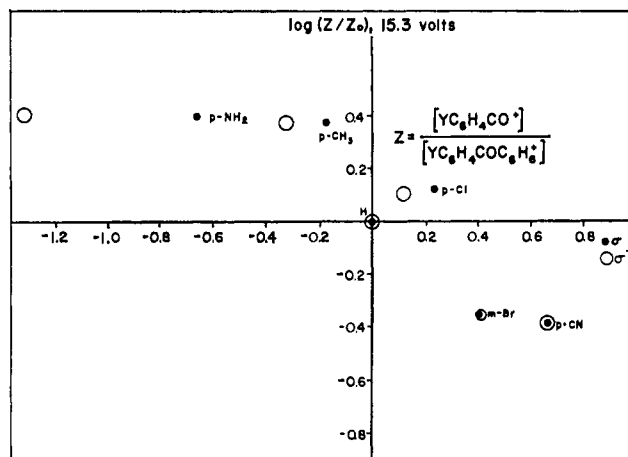
$$
\frac{d[A]}{dt} = \Sigma k_m[N_m] - \Sigma k_{1n}[A] - \Sigma k'_{inst}[A]
\tag{5}
$$

$$
[A] = \frac{\Sigma k_m[N_m]}{\Sigma k_{in} + \Sigma k'_{inst}}
\tag{6}
$$

molecular ion M alone, eq 7 is obtained. To illustrate this point, $Z/Z_0$ values are plotted vs. $\sigma$ values for the formation of substituted benzoyl ions from substituted

$$
\frac{Z}{Z_0} = \frac{[A]/[M]}{[A]_0/[M_0]} = \frac{k_1}{k_1^0} \frac{\Sigma k_{1n}^0 + \Sigma k'_{inst}}{\Sigma k_{1n} + \Sigma k'_{inst}}
\tag{7}
$$

benzophenone ions (eq 8) in Figure 1. There is no

$$
\left[ Y-\underset{\displaystyle \bigcirc}{\bigcirc}-\overset{O}{\underset{\|}{C}}-\bigcirc \right]^+ \xrightarrow{k_1} Y-\bigcirc-C\equiv O^+ \xrightarrow{\Sigma k_{1n}}
$$

products (8)

particularly meaningful correlation, either for plots vs. $\sigma$ or $\sigma^+$ because the terms for the decomposition $\Sigma k_{1n}$ are variable for different Y. By lowering the electron energy until the $\Sigma k_{1n}$ rates are negligible, a direct determination of $k_1$ may be achieved (if A is of sufficient abundance). Such an approach has been used to demonstrate changes in the relative importance of the

two routes of formation of $C_6H_5^+$ ion in the spectra of benzophenones.[5] In the present case, if the voltage of the ionizing electrons is so low that no decomposition products of the substituted benzoyl ion appear in the mass spectrum, then $\Sigma k_{1n}$ vanishes and eq 7 is reduced to eq 9, since the instrumental parameters do not vary greatly from compound to compound.[7] Accordingly, the data recorded for the relative intensities of $YC_6H_4$-

$$
\frac{Z}{Z_0} = \frac{k_1}{k_1^0} \frac{\Sigma k'_{inst}}{\Sigma k'_{inst}} = \frac{k_1}{k_1^0}
\tag{9}
$$

$CO^+$ ions at 15.3 v (Figure 2) represent relative rates of formation for these ions. The substituents used in this study were chosen to avoid products of further decomposition; ions reasonably formed from the substituted benzoyl ions are of insignificant intensity in the spectrum. It might be argued that $\sigma^+$ values would be more appropriate for this reaction because of the full positive charge on the substituted ion product; the data do not give a clear experimental conclusion on this point.

By analogy to eq 3, this reaction, which involves breaking the same bond, would be expected to have a negligible substituent effect ($\rho$ value of 0.0); yet the $\rho$ value (based on $\sigma$ values) from Figure 2 is about $-0.4$, which is *opposite in sign* to that of reaction 1.[4] In reaction 1 the reduction of product ion abundance by electron-donating groups was ascribed to increased stabilization of the decomposing bond. The present case parallels the reduction of ionization and appearance potentials caused by electron-donating substituents[8] and leads to the conclusion that *stabilization of the ion provides an important driving force* for such decomposition reactions. This has been proposed previously as one of the important general effects of molecular structure on mass spectra[1,9] paralleling general effects observed in ordinary chemical reactions.[10,11] Cases have been

(6) Values tabulated by C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 323 (1964), were used.

(7) Inaccuracies of intensity measurements resulting from mass discrimination are evidently insignificant; no trend is observed for heavy substituents in Figure 2 of ref 4, where discrimination against molecular ions of high molecular weight would have produced positive deviations from the correlation line. It may also be demonstrated that rates of collection of ions at the detector have no effect in this flow system.

(8) Reference 4, footnotes 9 to 15.

(9) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, p 81.

(10) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 34, 11 (1938).
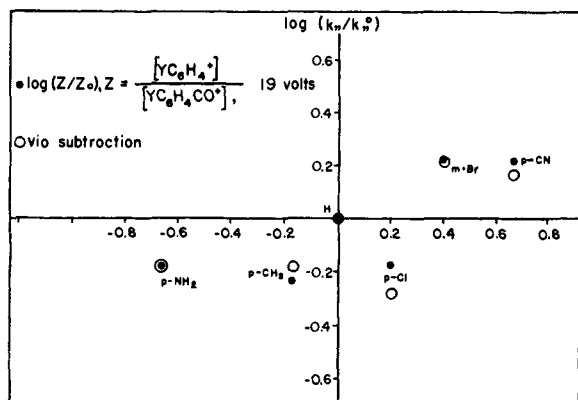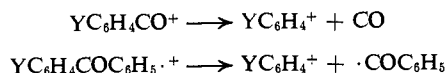
(11) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

noted where stabilization of the neutral product is an important driving force; however, the ability of a substituent to stabilize the charged product of reaction 8 is more important than its ability to stabilize the neutral product of reaction 3.

These data for rates of formation of $YC_6H_4CO^+$ can be substituted in eq 7 to yield relative values for $\Sigma k_{1n}$; values for substituents examined are found in Table I. Such numbers are in the first place an empirical device for the prediction of spectra. Positive values indicate greater over-all rates of decomposition of $YC_6H_4CO^+$ relative to the parent compound; negative values, smaller rates of decomposition. Table I indicates that these rates are neither uniform nor predictable by the Hammett equation. The major decomposition pathway not directly involving cleavage of the substituent, decarbonylation of the substituted benzoyl ion, will be examined in the subsequent discussion of the abundance of the $YC_6H_4^+$ ion. Further discussion of the significance of the substituent effects on $\Sigma k_{1n}$ will be postponed until this important contribution is evaluated.

**Table I**[a]

|  | Log $(Z/Z_0)$ |  | log $\dfrac{\Sigma k_{1n}}{\Sigma k_{1n}^0}$ |
|---|---|---|---|
| Y | 75 v | 15.3 v |  |
| p-CN | −0.34 | −0.38 | −0.04 |
| m-Br | −0.12 | −0.35 | −0.23 |
| p-Cl | 0.09 | 0.13 | 0.04 |
| H | 0.00 | 0.00 | 0.00 |
| p-CH₃ | 0.04 | 0.38 | 0.34 |
| p-NH₂ | 0.04 | 0.41 | 0.37 |

[a] $Z = [YC_6H_4CO^+]/[YC_6H_4COC_6H_5^+]$.

**Case with Two Formation Pathways.** The $YC_6H_4^+$ ion may be formed, analogously to the $C_6H_5^+$ ion,[5] via two routes from the molecular ion at normal ionizing voltages, as eq 10 illustrates. An attempt to correlate the

$$
\left[ Y\!\!-\!\!\overset{O}{\underset{\parallel}{C}}\!\!-\!\! \right]^+ \begin{array}{c} \overset{k_1}{\nearrow} \quad YC_6H_4CO^+ \longrightarrow products \\ \Big\downarrow k_{11} \quad \Sigma k_{2n} \\ \underset{k_2}{\searrow} \quad YC_6H_4^+ \xrightarrow{\quad} products \end{array} \qquad (10)
$$

effects of substituents with $[YC_6H_4^+]$ produces a distribution indicated in Figure 3. As in eq 8, no correlation is obtained because of the variable decomposition rate constants. Simplification of the kinetic scheme is again based on the determination of low-voltage intensity ratios; at sufficiently low energies, all decomposition pathways will be removed and all but one pathway of formation, by analogy to the results for the $C_6H_5^+$ ion.[5] Spectra recorded for study of $YC_6H_4^+$ at 19 v indicate that the analogy is also valid using most Y substituents at this voltage. The spectra which were used for study contained no ion below $m/e$ of $YC_6H_4^+$ except $C_6H_5^+$, whose formation from $YC_6H_4^+$ is either impossible or else discredited by our earlier work, unless Y = $CH_3O$.[5] Data for the same substituents examined in Table I are given in Table II; values obtained from this set of experiments include the ratio of $[YC_6H_4^+]$ to $[YC_6H_4CO^+]$ and to $[YC_6H_4COC_6H_5^+]$.

On the basis of the assumption that all $YC_6H_4^+$ is produced from $YC_6H_4CO^+$ at 19 v and that $YC_6H_4^+$



Figure 3. Lack of correlation between $YC_6H_4^+$ intensities in the spectra of substituted benzophenones and Hammett $\sigma$ values.[6]

does not decompose further, the steady-state approximation leads to eq 11 as the relation between the intensities of these species. As a result, this ratio is

$$
\frac{[YC_6H_4^+]}{[YC_6H_4CO^+]} = \frac{k_{11}}{\Sigma k'_{inst}} \qquad (11)
$$

proportional to $k_{11}$ in a series of compounds. This hypothesis may now be tested by subtractive combination of the data in column 2 of Table I and column 2 of Table II, since the latter data represent the product

**Table II**

| Y | $Z = \dfrac{[YC_6H_4^+]}{[YC_6H_4CO^+]}$ | $Z = \dfrac{[YC_6H_4^+]}{[YC_6H_4COC_6H_5^+]}$ | From subtractive process |
|---|---|---|---|
| p-CN | 0.22 | −0.21 | 0.17 |
| m-Br | 0.23 | −0.13 | 0.22 |
| p-Cl | −0.17 | −0.14 | −0.27 |
| H | 0.00 | 0.00 | 0.00 |
| p-CH₃ | −0.23 | 0.20 | −0.18 |
| p-NH₂ | −0.17 | 0.24 | −0.17 |

of the rate constants for the two-step formation from the molecular ion; see eq 12. By subtracting the

$$
\frac{Z}{Z_0} = \frac{k_{11}k_1}{k_{11}^0 k_1^0} \qquad (12)
$$

values obtained in the preceding part of this paper for log $(k_1/k_1^0)$, an alternate set of values for log $(k_{11}/k_{11}^0)$ is obtained. Comparison of these data (columns 1 and 3 of Table II) indicates that the assumption of formation of $YC_6H_4^+$ solely through $YC_6H_4CO^+$ is a valid one. In further support of this mechanism, "metastable" ions corresponding to the process $YC_6H_4CO^+ \rightarrow YC_6H_4^+$ may also be detected at 19 v, and their intensities are likewise smaller for electron-donating Y. The existence of the metastable ion offers no indication of the singular nature of the pathway; only the correlation of the substituent effects rules out the existence of substantial contributions from other routes.

Figure 4. Correlation of data for the formation of $YC_6H_4^+$ at 19 v with Hammett $\sigma$ constants.[6]

Correlation of these data with Hammett $\sigma$ constants indicates a small positive $\rho$ value (+0.4) for this reaction, as shown in Figure 4. This is substantially less than that (+1.0) for reaction 1, which involves cleavage of the same bond, again probably reflecting the opposing effect of the stabilization of the product ion by the substituent Y.[12]

Electron-withdrawing substituents cause a more rapid decarbonylation of the benzoyl ion; yet at 75 v, the over-all effect of the $m$-Br and $p$-CN substituents is actually to prevent the substituted benzoyl ion from decomposing as rapidly as the unsubstituted, as Table I indicates. Decarbonylation is apparently not so important a decomposition process for benzoyl ion as we had previously assumed.[5]

Possible causes for deviations from the $\sigma$-predicted values for $k_{11}/k_{11}^0$, such as for the $p$-Cl derivative, should follow our earlier arguments.[4,5] The fact that the $C_6H_5^+$ ion, and thus at least some $YC_6H_4^+$ ions, are not phenyl ions but have a linear structure[13,14] demands that ring carbon–carbon bonds be broken in addition to the ring–CO bond; if for any substituent the latter cleavage is not the rate-controlling step, the substituent effect would not necessarily follow the prediction.

At high voltages, two paths for formation of $YC_6H_4^+$ are presumably present (eq 10), paralleling the case for $C_6H_5^+$.[5] The substituent dependence of the path through the $YC_6H_4CO^+$ ion can be evaluated from Table II, assuming this data is applicable at high voltage. The substituent dependence of the one-step process is difficult to measure, but a reasonable assumption would be that the two reactions

$$YC_6H_4CO^+ \longrightarrow YC_6H_4^+ + CO$$

$$YC_6H_4COC_6H_5 \cdot^+ \longrightarrow YC_6H_4^+ + \cdot COC_6H_5$$

might have similar substituent profiles, since in each case the effect of the substituent on the energy of the cleaved bond and the stability of the product ion would be similar. A $\rho$ value of about 0.4 would be

predicted in this way. The relative contributions of the one-step and two-step pathways in the case where Y = H have been shown to be in the ratio 1.2:1 at 75 v.[5] An approximate total rate of formation may therefore be constructed for the substituents investigated in detail, and the influence of the substituent on $\Sigma k_{2n}$ may be estimated from these and the relative intensities actually found. Such data are given in Table III.[15]
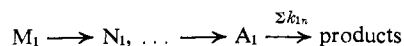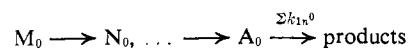
Table III

| Y | — $Z/Z_0$ — Two step | One step | — Log $Z/Z_0$ — Total formed | Obsd | Log $\Sigma k_{2n}/\Sigma k_{2n}^0$ |
|---|---|---|---|---|---|
| $p$-CN | 0.74 | 1.83 | 0.07 | −0.10 | 0.17 |
| $m$-Br | 0.89 | 1.44 | −0.01 | −0.20 | 0.19 |
| $p$-Cl | 0.87 | 1.22 | −0.02 | −0.12 | 0.14 |
| H | 1.20 | 1.00 | 0.00 | 0.00 | 0.00 |
| $p$-CH$_3$ | 1.90 | 0.85 | 0.10 | −0.07 | 0.17 |
| $p$-NH$_2$ | 2.09 | 0.54 | 0.06 | −0.22 | 0.28 |

There is no good agreement between these values and those for destabilization of the $YC_6H_4CO^+$; therefore, the decompositions of these ions at 75 v must be quite different in general character. Both electron-donating and -attracting substituents appear to be capable of causing destabilization; ions containing the former, such as $p$-NH$_2$C$_6$H$_4^+$, may decompose to produce small especially stabilized fragments. At the other end of the scale, one explanation for the decrease in the $Z/Z_0$ can be the rearrangement of the substituent. For example, even at 19 ev the $O_2NC_6H_4^+$ ion still loses NO, indicating that substituent is rearranged so that it has a very large destabilization factor even at low voltages.
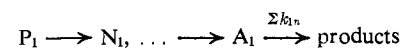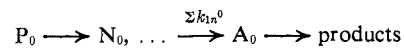
**Correlations between Different Groups of Compounds.** Consider the relation of two sets of compounds which might produce the same series of ions by a set of similar processes (for example, $YC_6H_4COCH_3$ and $YC_6H_4$-$COC_6H_5$ both producing $YC_6H_4^+$).

$$M_0 \longrightarrow N_0, \ldots \xrightarrow{\Sigma k_{1n}^0} A_0 \longrightarrow \text{products}$$

$$M_1 \longrightarrow N_1, \ldots \xrightarrow{\Sigma k_{1n}} A_1 \longrightarrow \text{products}$$

and

$$P_0 \longrightarrow N_0, \ldots \xrightarrow{\Sigma k_{1n}^0} A_0 \longrightarrow \text{products}$$

$$P_1 \longrightarrow N_1, \ldots \xrightarrow{\Sigma k_{1n}} A_1 \longrightarrow \text{products}$$

An equation relating four specific data—two ratios from each set of processes—by an arbitrary constant may be written, as illustrated by

$$\log\left(\frac{Z_2}{Z_1}\right)_M = C \log\left(\frac{Z_2}{Z_1}\right)_P \qquad (13)$$

If the constant also relates other similar data, a stand-

(12) This reaction is therefore not analogous to the decomposition of aryldiazonium ions, which is also decelerated both by electron-withdrawing substituents and by substituents capable of direct resonance donation to the reaction site: M. L. Crossley, R. H. Kienle, and C. H. Benbrook, *J. Am. Chem. Soc.*, **62**, 1400 (1940).

(13) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2935, 2943 (1965).

(14) J. Momigny, L. Brakier, and L. D'Or, *Bull. Sci. Acad. Roy. Belg.*, **48**, 1002 (1962).

(15) The significance of the last column may be judged from its sensitivity to different assumed $\rho$ values for the one-step process: for $\rho = 0.2, 0.4,$ and $0.6$, the figures are, respectively: for $p$-CN, 0.08, 0.17, and 0.27; for $p$-Cl, 0.07, 0.14, and 0.14; and $p$-NH$_2$, 0.33, 0.28, and 0.28.
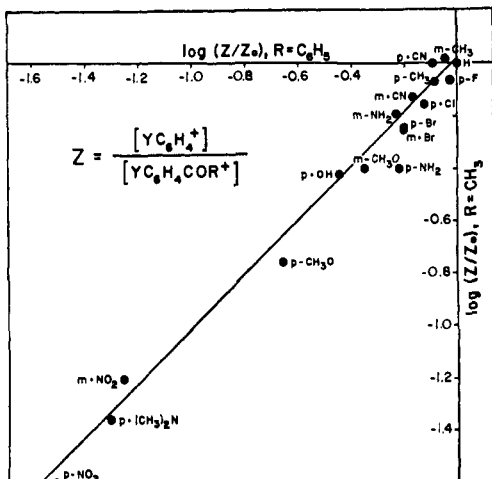
Figure 5. Correlation of $YC_6H_4^+$ ion intensities in the spectra of benzophenones with their intensities in acetophenones; slope = 0.97; correlation coefficient = 0.991.

ard compound may be chosen so that the equation becomes eq 14. Data for three sets of aromatic car-

$$\log\left(\frac{Z}{Z_0}\right)_M = C \log\left(\frac{Z}{Z_0}\right)_P \qquad (14)$$

bonyl compounds, substituted benzophenones, acetophenones, and methyl benzoates, are examined in Figures 5 and 6. The existence of a correlation, especially in view of the lack of correlation shown in Figure 3, suggests that the individual modes of formation and decay are themselves similarly related. For simplicity let $\Sigma Q_n$ equal the sum of the combinations of rate constants which is the coefficient of [M] in eq 15. The existence of a correlation line with slope

$$0 = \frac{d[A]}{dt} = \left(k_1 + \frac{k_{11}k_1}{\Sigma k_{1n} + \Sigma k'_{inst}} + \cdots\right)[M] - (\Sigma k_{1n} + \Sigma k'_{inst})[A] \qquad (15)$$

of approximately 1 indicates that eq 16 holds. It is unlikely that random irregular increase in one term on

$$\log\left(\frac{\Sigma Q_n}{\Sigma Q_n^0}\right)_M + \log\left(\frac{\Sigma k_{2n}^0}{\Sigma k_{2n}}\right)_M = 1\left\{\log\left(\frac{\Sigma Q_n}{\Sigma Q_n^0}\right)_P + \log\left(\frac{\Sigma k_{2n}^0}{\Sigma k_{2n}}\right)_P\right\} \qquad (16)$$

either side would be balanced by a corresponding decrease in the other so that for a large number of cases it follows that eq 17 and 18 must be true. From these

$$\log\left(\frac{\Sigma Q_n}{\Sigma Q_n^0}\right)_M = \log\left(\frac{\Sigma Q_n}{\Sigma Q_n^0}\right)_P \qquad (17)$$

$$\log\left(\frac{\Sigma k_{2n}^0}{\Sigma k_{2n}}\right)_M = \log\left(\frac{\Sigma k_{2n}^0}{\Sigma k_{2n}}\right)_P \qquad (18)$$

statements, each of the rate constants in $\Sigma Q_n$ and $\Sigma k_{2n}$ must be similar in the two series of compounds M and P for eq 17 and 18 to hold generally; in general, then, eq 19 holds for all $k_{ab}$ related to $YC_6H_4^+$, provided

$$(k_{ab})_M = (k_{ab})_P \qquad (19)$$

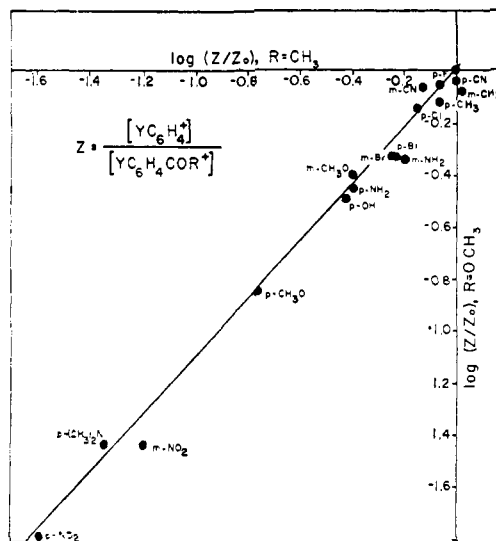the $k_1$'s are similar. This is a serious assumption, but



Figure 6. Correlation of $YC_6H_4^+$ ion intensities in the spectra of acetophenones with their intensities in methyl benzoates; slope = 1.10; correlation coefficient = 0.983.

a reasonable one, based on the demonstration of the formation of benzoyl ion from a series of substituted benzophenones with a similar distribution of energy states in every case.[4] The correlation line with slope of approximately 1 indicates that $YC_6H_4^+$, regardless of its decomposition paths, undergoes the same decompositions to the same extent whether it is formed from a substituted benzophenone, a substituted acetophenone, or a substituted methyl benzoate; this parallels the deduction for the benzoyl ion. Also, R has no appreciable substituent effect on any decomposition pathways examined which affect the benzene ring. In the transition states for the loss of $R\cdot$ or $COR\cdot$ from the molecular ion, the extent of the dissociation of the breaking bond at the transition state is equal in each series.

## Conclusion

Substituent effects for the decompositions of substituted benzophenones in eq 20 have now been estab-



(20)
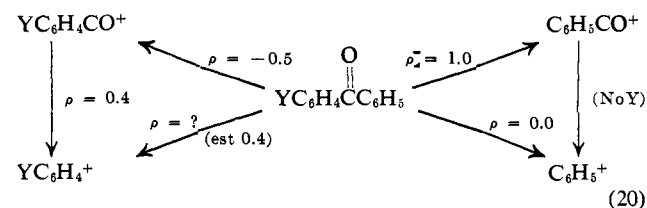
lished. These conclude the pathways for which reasonable correlation may be expected.

## Experimental Section

Compounds used in this study were either gifts or commercial samples with no impurities detectable by mass spectrometry. Spectra were recorded on a Hitachi RMU-6A single-focusing instrument with inlet temperature at 185 ± 5° and source at 160 ± 10°. For the high-voltage spectra, a 80-μa beam of 75-v electrons was used; the low-voltage data were recorded at 2 μa target current. Spectra of the substituted benzoyl ions were standardized against the intensity of the molecular ion of $CO_2$ and recorded at the voltage at which this ion attains 2% of its value at 75 v. This point is 1.5 v

above that where the intensity of the ion is 1%, which was assigned the appearance potential value[16] of 13.8 v. Data for the substituted phenyl ions were obtained at the voltage at which the intensity of $Ar^+$ is 10% of its value at 48 v on this instrument. As explained in the preceding paper,[4] this potential is assigned a value of 19 v.[17]

(16) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 280.
(17) Laurence Dusold assisted with several spectra.

# Catalyst-Controlled Monomer Distributions in Copolymers. Copolymerization of Propylene Oxide and Maleic Anhydride

## R. J. Kern and Jacob Schaefer

*Contribution from the Central Research Department, Monsanto Company, St. Louis, Missouri 63166. Received August 5, 1966*

**Abstract:** The monomer distribution in the copolymer propylene oxide–maleic anhydride, prepared by seven different homogeneous catalysts, has been obtained by high-resolution nuclear magnetic resonance spectroscopy of the copolymer and by vapor phase chromatography of the hydrolyzed copolymer. The nmr analysis yields the relative concentrations of triads in the completed chain, and the vpc analysis yields the relative concentrations of runs of propylene oxide up to a length of four. Greatly differing monomer distributions are observed depending on which catalyst is used in the copolymerization. However, in all cases, the monomer distributions can be described by Markoffian statistics of order either one, two, or three.

Monomer distributions in copolymers formed by free-radical propagation can be characterized by the statistics of Markoffian processes.[1] From the order of such statistics one knows to what extent monomers previously added to the chain affect further additions. Normally, this effect is short range. In fact, for ethylene–vinyl chloride[2] and ethylene–vinyl acetate[2] the growing chain has no (instantaneous) memory and the monomer distribution is described by zeroth-order Markoffian statistics. The monomer distribution for completely alternating copolymers[3] can be described by first-order Markoffian statistics. This implies a mechanism in which the terminal free-radical unit is involved in determining the chain propagation.

Some catalytic homopolymerizations of methyl methacrylate[4] and of propylene[5] produce diastereosequence distributions for which the parameters of Markoffian descriptions cannot be evaluated or reliably confirmed, so that the applicability of Markoffian statistics is not clear. Coleman and Fox proposed an alternative to explain such distributions.[6] Their general mechanism assumes that the end of the growing chain has two reactive states in equilibrium, both capable of adding monomer, each with its own stereospecificity. When the rates involved in the equilibrium step are comparable with the rates of chain propagation, the diastereosequence distribution is non-Markoffian and strongly depends explicitly on monomer concentration. When

the equilibrium rates are very fast or slow compared to the propagation, the mechanism predicts a distribution which is indistinguishable from that arising from a Markoffian process. The Coleman–Fox mechanism can also be applied to catalytic copolymerizations with analogous predictions.

Maleic anhydride and propylene oxide can be copolymerized[7] to yield an unsaturated poly(ester–ether) (*i.e.*, $[-C(=O)CH=CHC(=O)OCHCH_3CH_2O-]$) with a number of different catalysts. The monomer distributions for these copolymers have been obtained using a combination of high-resolution proton magnetic resonance spectroscopy on the copolymers and vapor phase chromatography on the glycol ethers produced by hydrolyzing the copolymers. The nmr analysis yields the relative concentrations of triads in the completed chain (AAA, AAB and BAA, ABA, BBB, BBA and ABB, and BAB, where A is propylene oxide and B is maleic anhydride). Vpc analysis yields the relative concentrations of runs of A (BAB, BAAB, BAAAB, BAAAAB, BAAAA...AB) up to a length of four.

From the experimental monomer distributions it can be shown that any plausible mechanism of chain propagation in this particular copolymerization does not involve a non-Markoffian process with dynamic equilibrium between two or more states. The monomer distributions produced by the various catalysts differ greatly but still can be described by Markoffian statistics of order either one, two, or three. Factors are

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