

## Substituent Effects in Unimolecular Ion Decompositions. VIII. Rearrangement Ions in the Mass Spectra of Substituted Phenyl Methyl Ethers

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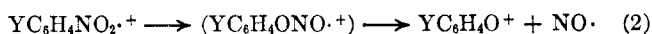
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The effect of a variety of substituents on the mass spectral behavior of anisoles has been compared to previous studies on phenetoles and nitrobenzenes. The rearrangement loss of  $\text{CH}_2\text{O}$  in anisoles is not analogous to the corresponding loss of  $\text{C}_2\text{H}_4$  in phenetoles; there are substantial differences in ring position effects. Formation of the major product ions  $\text{YC}_6\text{H}_4\text{O}^+$  and  $\text{YC}_5\text{H}_4^+$  parallel closely their formation in the spectra of nitrobenzenes. Mechanisms are proposed to account for these data.

A surprising loss of ring position identity appears to occur in the formation of the abundant, rearranged  $(\text{M} - \text{C}_2\text{H}_4)^{\cdot+}$  ions in the mass spectra of many substituted phenyl ethyl ethers (reaction 1).<sup>1</sup> Although loss of ring position identity is observed for ions from alkylbenzenes,<sup>2,3</sup> this does not occur in the formation of the rearranged  $(\text{M} - \text{NO})^+$  ions in nitrobenzenes (reaction 2).<sup>4</sup> In an effort to elucidate the factors causing loss of ring position identity, this study of substituent effects<sup>5</sup> on the formation of the rearranged  $(\text{M} - \text{CH}_2\text{O})^{\cdot+}$  ions (reaction 3) and other major ions in the spectra of substituted phenyl methyl ethers was undertaken. Previous reports<sup>6,7</sup> showed substantial differences between some isomeric compounds employing ionization by higher (70 ev) energy electrons; direct comparisons of reaction rates are difficult owing to further decompositions of the primary products at this energy.<sup>8,9</sup> Harrison and coworkers<sup>10</sup> report normal substituent effects on the appearance potentials for the formation of  $(\text{M} - \text{CH}_3)^+$  ions from such compounds (reaction 4), indicating no loss of ring position identity for this reaction at low energy.



**Substituent Effects on Ion Intensities.**— $\text{YC}_6\text{H}_4\text{O}^+$ ,  $\text{YC}_6\text{H}_5^+$ , and  $\text{YC}_5\text{H}_4^+$  are major possible fragment ions in the mass spectra of phenyl methyl ethers; Table I summarizes the ratios of their ion intensities, relative to the intensities of their precursors, for a series of substituted anisoles. The data for anisole ( $\text{Y} = \text{H}$ ) itself are taken as standards. In order to relate intensity

TABLE I  
SUBSTITUENT EFFECTS ON THE ABUNDANCES OF  $\text{YC}_6\text{H}_5^+$ ,  $\text{YC}_6\text{H}_4\text{O}^+$ , AND  $\text{YC}_5\text{H}_4^+$  AT 5.0 V ABOVE IONIZATION POTENTIAL

Y	Log Z/Z <sub>0</sub>			
	Z = [YC <sub>6</sub> H <sub>5</sub> <sup>+</sup> ] [YC <sub>6</sub> H <sub>4</sub> - OCH <sub>3</sub> <sup>+</sup> ]	Z = [YC <sub>6</sub> H <sub>4</sub> O <sup>+</sup> ] [YC <sub>6</sub> H <sub>4</sub> - OCH <sub>3</sub> <sup>+</sup> ]	Z = [YC <sub>6</sub> H <sub>4</sub> O <sup>+</sup> ] + [YC <sub>5</sub> H <sub>4</sub> <sup>+</sup> ] [YC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> <sup>+</sup> ]	Z = [YC <sub>5</sub> H <sub>4</sub> <sup>+</sup> ] [YC <sub>6</sub> H <sub>4</sub> O <sup>+</sup> ]
H	0.00	0.00	0.00	0.00
<i>p</i> -NH <sub>2</sub>	-1.50	0.95	0.78	-2.16
<i>m</i> -NH <sub>2</sub>	-0.01	-0.76	-0.84	-0.36
<i>p</i> -OH	-1.54	0.81	0.65	-2.36
<i>m</i> -OH	0.42	-0.41	-0.49	-0.36
<i>p</i> -OCH <sub>3</sub> <sup>a</sup>	-2.02	0.58	0.42	-1.96
<i>m</i> -OCH <sub>3</sub> <sup>a</sup>	-0.92	-1.27	-1.25	0.04
<i>p</i> -F	-0.70	0.73	0.58	-1.08
<i>m</i> -F	0.18	-0.59	-0.57	0.04
<i>p</i> -Cl	-1.13	0.63	0.50	-0.88
<i>m</i> -Cl	0.00	-0.54	-0.50	0.12
<i>p</i> -Br	-1.40	0.47	0.38	-1.03
<i>m</i> -Br	-0.13	-0.40	-0.23	0.41
<i>p</i> -I	-1.71	0.51	0.34	-1.18
<i>m</i> -I	-1.40	-1.70	-1.54	0.34
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	-2.74	0.21	0.05	-1.66
<i>m</i> -C <sub>6</sub> H <sub>5</sub>	-0.65	-0.61	-0.56	0.12
<i>p</i> -CH <sub>3</sub>	-0.82	0.30	0.18	-0.64
<i>m</i> -CH <sub>3</sub>	-0.38	0.06	0.02	-0.18
<i>p</i> -CHO	-2.3	-1.7	-1.8	0.3
<i>m</i> -CHO	-1.64	-1.8	-1.2	1.0
<i>p</i> -COOH	-1.55	-1.6	-1.6	0.0
<i>m</i> -COOH	-0.88	-0.84	-0.98	-0.90
<i>p</i> -NO <sub>2</sub>	<0.17 <sup>b</sup>	<-1.5	<-1.6	>0.0
<i>m</i> -NO <sub>2</sub>	<-0.70 <sup>b</sup>	<-1.6	<-1.6	>0.5
<i>p</i> -CH <sub>3</sub> CO	-2.9	<i>c</i>	<i>c</i>	<i>c</i>
<i>m</i> -CH <sub>3</sub> CO	-2.2	<i>c</i>	<i>c</i>	<i>c</i>

<sup>a</sup> Corrected by the statistical factor of 2. <sup>b</sup> Loss of NO interferes. <sup>c</sup> Loss of methyl adjacent to carbonyl interferes.

ratios to rates of the corresponding reactions, ionizing electrons of 5 v above the ionization potential were employed, at which energy no further fragmentation of the  $\text{YC}_6\text{H}_5^+$  ion occurs and the decomposition  $\text{YC}_6\text{H}_4\text{O}^+ \rightarrow \text{YC}_5\text{H}_4^+$  is significantly reduced ( $Z_0 = 0.46$ ). The experimental methods used were similar to those reported earlier.<sup>5,8,9,11</sup>

**The  $\text{YC}_6\text{H}_5^+$  Ion.**—Each of the rearrangement reactions 1–3 involves the loss of a small molecule from an aryl derivative. The data (Table I) for reaction 3 indicate that the effect of a particular substituent in the *meta* position is substantially different from its effect in the *para* position, as observed in reaction

(1) F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *J. Am. Chem. Soc.*, **88**, 5022 (1966).

(2) F. Meyer and A. G. Harrison, *ibid.*, **86**, 4757 (1964).

(3) Some data for the  $(\text{M} - \text{CO}_2)^{\cdot+}$  ion of particular aryl carbonates are consistent with this: P. Brown and C. Djerassi, *ibid.*, **89**, 2711 (1967), footnote 7.

(4) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 5023 (1966).

(5) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 529 (1966).

(6) (a) C. S. Barnes and J. L. Oocolorwitz, *Australian J. Chem.*, **16**, 219 (1963); (b) C. S. Barnes, D. J. Collins, J. J. Hobbs, P. I. Mortimer, and W. H. F. Sasse, *ibid.*, **20**, 699 (1967).

(7) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 174.

(8) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 4484 (1966).

(9) M. M. Bursey, and F. W. McLafferty, *ibid.*, **89**, 1 (1967).

(10) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, **84**, 4 (1962).

(11) F. W. McLafferty and M. M. Bursey, submitted for publication.

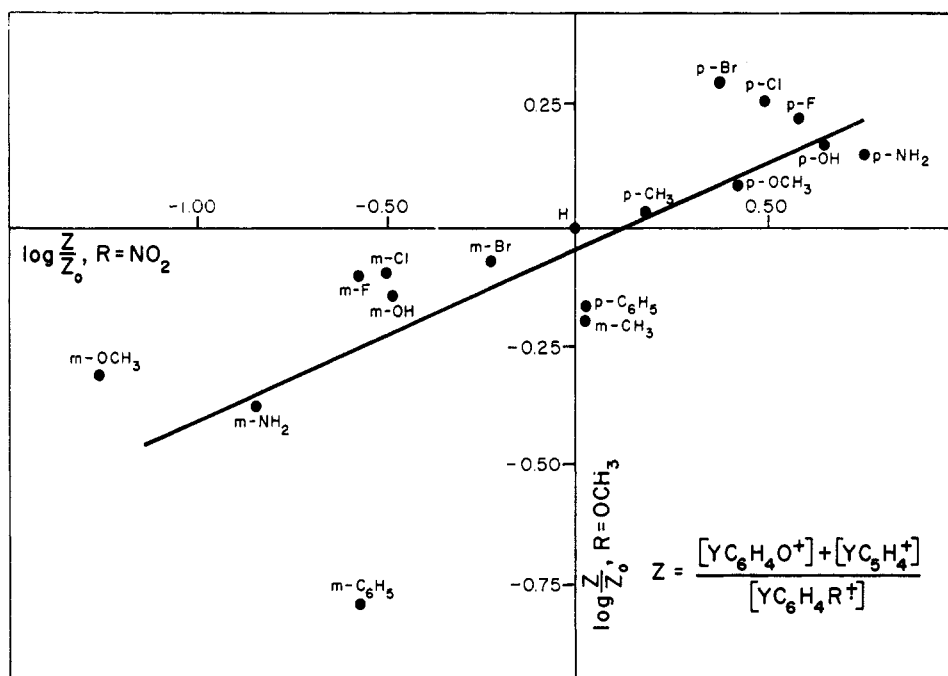
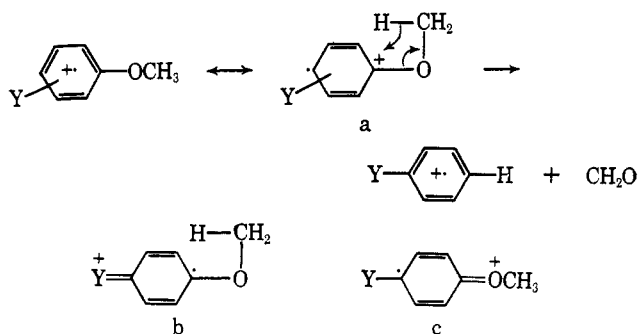


Figure 1.—Qualitative correlation of the corrected intensities of the  $YC_6H_4O^+$  ion in the spectra of substituted anisoles and nitrobenzenes. Nitrobenzene data are from ref 4; the least-squares slope is 0.35; the standard deviation is 0.08.

2,<sup>4</sup> but in contrast to substituent behavior for reaction 1.<sup>1</sup> However, there is also a sharp distinction in the substituent effects shown in reactions 2 and 3. In reaction 3, electron-donor (R) substituents in the *para* position *retard* the decomposition of the molecular ion; reaction 2,<sup>4</sup> they *accelerate* decomposition. In fact, the substituent effects observed for the simple O-methyl cleavage, reaction 4, resemble those for rearrangement in reaction 2,<sup>12</sup> as will be discussed later.

A four-center rearrangement has been proposed for reaction 3,<sup>6,7</sup> migration of hydrogen to the site of positive charge<sup>13</sup> such as in canonical form a might be expected from previous arguments. The "metastable ion characteristics"<sup>14</sup> of the  $C_6H_5Y^+$  product ion indicate that it has the same structure as the molecular ion derived from the corresponding substituted benzene ( $YC_6H_5$ ). Thus in bromobenzene the intensity of the "metastable peak" at  $m/e$  37.6 ( $C_6H_5Br^+ \rightarrow C_6H_5^+$ ) compared with the intensity of its precursor is 0.0075; in the spectrum of *m*-bromoanisole, the corresponding value is 0.0095. Again, a "flat-topped metastable ion" of 0.23-eV excess energy occurs at  $m/e$  46.4 ( $C_6H_5O^+ \rightarrow C_6H_5^+$ ) both in phenol and in resorcinol monomethyl ether, with intensity relative to that of  $C_6H_5O^+$  of 0.0023 and 0.0025, respectively; a similar "metastable peak" also occurs in the mass spectrum of phenetole.<sup>1</sup>

The large rate reduction by *para* R substituents also supports this mechanism in the such canonical forms as b which are possible with these substituents should be less reactive. This would be expected both from the lowering of the positive charge at the reaction site, and the stabilization of the ring-oxygen bond, in a fashion similar to that found for the reaction  $YC_6H_4COR^+ \rightarrow YC_6H_4^+ + RCO^+$ .<sup>5</sup> The rate of reaction 3 is also reduced, however, by +R substituents; possibly



canonical forms such as c make an important contribution to the structure of the molecular ion.

These rationales for reaction 3 all predict a substantial reduction of reaction rate by the substituent. Some *meta* substituents cause much less reduction, or actually increase the reaction rate. An important factor in this may be stabilization of the positive charge in the  $YC_6H_5^+$  product ion by donation of electrons through resonance. Although such stabilization should be equally important in the corresponding *para* derivatives, the concomitant reduction of decomposition of the molecular ion by contributing forms such as b should be much less effective in the *meta* derivatives. For the methyl derivatives, expansion to a seven-membered ring is also possible, although this apparently does not take place at threshold energies.<sup>10</sup>

**The  $YC_6H_4O^+$  Ion.**—A major decomposition pathway of anisoles produces  $YC_6H_4O^+$  ions by reaction 4, followed by loss of CO to yield  $YC_5H_4^+$  ions. To be indicative of the rate of reaction 4, the abundances of the  $YC_6H_4O^+$  ions must be corrected<sup>8,9</sup> for this further decomposition; this is done qualitatively in column 3 of Table I by summing the abundances of  $YC_6H_4O^+$  and  $YC_5H_4^+$ . The observed substituent effects resemble those for the formation of the same ions by reaction 2 (Figure 1).<sup>4</sup> The latter data were measured at a fixed electron energy of 13.8

(12) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964), and references cited therein.

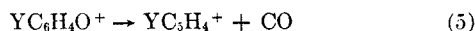
(13) F. W. McLafferty, *Chem. Commun.*, 78 (1966).

(14) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966).

ev; data for reaction 4 at 15.3 ev in general show a somewhat closer, although still qualitative, similarity. However, this resemblance provides strong support for the postulate that in both reactions 2 and 4 the rate-controlling step is loss of a substituent (NO or CH<sub>3</sub>) from the YC<sub>6</sub>H<sub>4</sub>O moiety. This is further evidence for Beynon's postulated rearrangement of the nitro group of 2 to a nitrite structure.<sup>12</sup>

Rate enhancement by *para* R substituents would be expected from stabilization of the product ion through resonance interaction: Y<sup>+</sup>=C<sub>6</sub>H<sub>4</sub>=O. If this is the main effect of the substituents, a correlation with  $\sigma^+$  constants would be expected.<sup>11</sup> However, the correlation is poor; this contrasts sharply with the correlation for the appearance potentials of YC<sub>6</sub>H<sub>4</sub>O<sup>+</sup> ions from anisoles, for which Harrison and coworkers<sup>10</sup> found a good correlation with  $\sigma^+$  constants. A possible contributing factor to the lack of correlation illustrates the dilemma of choosing a proper electron energy for such a low-voltage study. The data of Table I utilized ionizing energies 5 ev above the ionization potential to make the energy available to the molecular ions equal for the various derivatives. This has the disadvantage that this probably will not be the same energy above the appearance potential of the particular fragment ion for the various derivatives. For example, the ionizing electron energy (IP + 5 ev) is 2.9 ev above the appearance potential of *p*-methoxyanisole, but only 1.9 ev above that of *m*-methoxyanisole. Thus, if the energy distribution in the molecular ions is the same for both isomer, the *meta* compound will have a smaller proportion with sufficient energy for decomposition, thus increasing the molecular ion abundance.<sup>15</sup> Although this would reduce the Z/Z<sub>0</sub> value, it would not account for the large discrepancy found. For other *para* substituents such as the halides, this possible error can hardly account for the large positive Z/Z<sub>0</sub> values observed. It would appear that one or more additional reactive excited states are populated at energies just above the appearance potential and that these new reactions have quite different  $\rho$  values than that for the threshold decomposition.<sup>16,17</sup>

**The YC<sub>5</sub>H<sub>4</sub><sup>+</sup> Ion in Anisoles and Nitrobenzenes.**—The major path for the formation of YC<sub>5</sub>H<sub>4</sub><sup>+</sup> should be reaction 5. Table II compares the Z/Z<sub>0</sub> values for



this reaction at 15.3 ev for anisoles with those at 13.8 ev for nitrobenzenes. The qualitative similarity (Fig-

(15) Although it is convenient to use rate expression to describe these substituent effects,<sup>5</sup> kinetically the reactions are not strictly analogous to those in solution. A particular molecular ion is an isolated species, which, after formation, can neither gain nor lose energy. Energy can be transferred between various energy states in a particular ion; those ions with energies above the appearance potential decompose when sufficient excitation energy is transferred to the reaction coordinate. Thus, if some of the ions are formed with insufficient energy to decompose, the rate should be calculated on the actual abundance of the ions that are the true precursors (rate =  $k[\text{product ions}]/[\text{precursor ions}]$ ), and not on the total ions of that particular mass. Additionally, the average rate depends on the excitation energy present in the precursor. Thus the accuracy of applying these rate expressions depends on the similarity of both the amount and distribution of ion energies.

(16) Such additional reaction pathways could also cause inaccuracies in appearance potential measurements. The fractional intensity method<sup>17</sup> usually employed involves a normalization step in which ion intensities at low and high voltage are compared. Thus, if the higher voltage ion abundance was increased more by such additional paths than the abundance of reference compound, an error would be introduced.

(17) F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

ure 2) of these data suggests that the structure and energy contents for the analogous ions formed from YC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> and YC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> are the same. Values for the electron-withdrawing substituents have been omitted because of interferences in measurements.

TABLE II  
YC<sub>6</sub>H<sub>4</sub>O<sup>+</sup> AND YC<sub>5</sub>H<sub>4</sub><sup>+</sup> ABUNDANCES IN ANISOLES  
AND NITROBENZENES

$$Z = \frac{[\text{YC}_5\text{H}_4^+]}{[\text{YC}_6\text{H}_4\text{O}^+]}$$

Y	Log Z, anisoles, 15.3 ev	Log Z, nitrobenzenes, 13.8 ev
H	0.00	0.00
<i>p</i> -NH <sub>2</sub>	-1.54	-0.89
<i>m</i> -NH <sub>2</sub>	0.84	0.15
<i>p</i> -OH	-0.56	-0.68
<i>m</i> -OH	-0.03	0.63
<i>p</i> -OCH <sub>3</sub>	-1.33	-0.96
<i>m</i> -OCH <sub>3</sub>	0.54	0.54
<i>p</i> -F	-0.76	-0.47
<i>m</i> -F	0.06	0.02
<i>p</i> -Cl	-0.71	-0.32
<i>m</i> -Cl	-0.18	0.32
<i>p</i> -Br	-1.02	-0.43
<i>m</i> -Br	0.06	0.02
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	-0.98	-0.64
<i>m</i> -C <sub>6</sub> H <sub>5</sub>	0.29	0.30
<i>p</i> -CH <sub>3</sub>	-0.62	-0.40
<i>m</i> -CH <sub>3</sub>	-0.28	-0.15

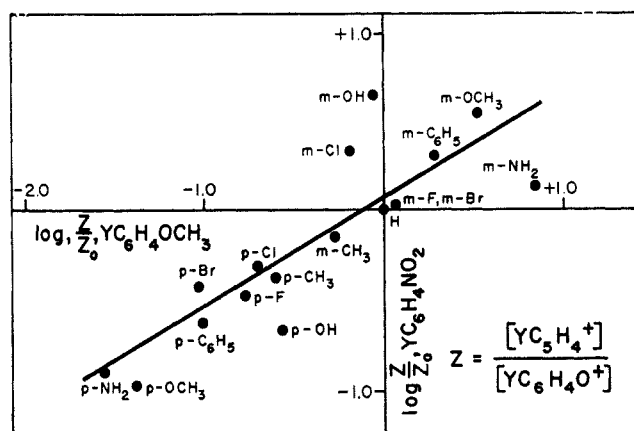


Figure 2.—Qualitative correlation of the intensity of YC<sub>5</sub>H<sub>4</sub><sup>+</sup>, the major decomposition product of YC<sub>6</sub>H<sub>4</sub>O<sup>+</sup>, in the spectra of substituted anisoles and nitrobenzenes. The least-squares slope is 0.63; the standard deviation is 0.10.

The magnitude of the Z/Z<sub>0</sub> values tends to be greater for the anisoles, but this could be due to the higher electron energy as well as the possibility that some of the YC<sub>5</sub>H<sub>4</sub><sup>+</sup> ions are formed by direct decomposition of the molecular ions. This has been postulated as a decomposition pathway in a number of substituted anisoles supported by the presence of metastable ions.<sup>6b</sup> The substantial differences between the effects of *meta* and *para* R substituents found for reaction 5 for anisoles again<sup>4</sup> appear consistent with preferential stabilization of the precursor C<sub>6</sub>H<sub>5</sub>O<sup>+</sup> ion by resonance donation of electrons from the *para* substituent and similar stabilization of the product ion (possibly cyclopentadienyl) by *meta* substituents.

### Conclusions

Reactions 2-4 appear to proceed without the loss of ring position identity in contrast to reaction 1. Reactions 1, 2, and 4 appear to be similar in that each involves the cleavage of an OY' bond in  $YC_6H_4OY' \cdot +$ ; however simple fission, which is the major pathway when  $Y' = NO$  or  $CH_3$ , is insignificant when  $Y' = C_2H_5$ , for which the rearrangement formation of  $(M - C_2H_4) \cdot +$  ions predominates. This observation seems inconsistent with the isomerization mechanisms proposed for reaction 1;<sup>1</sup> such mechanisms by analogy should be of considerable if not more importance in reactions 2 and 4. Possibly there is initial fast hydrogen rearrangement to yield a form such as  $YC_6H_4^+OHC_2H_5$  that has sufficient stability to permit isomerization of the ring positions<sup>2,4</sup> before decomposition. Studies of other systems which are possibly analogous are in progress.

### Experimental Section

Spectra were recorded on a Hitachi RMU-6D mass spectrometer at Purdue University and a Hitachi RMU-6E mass spectrom-

eter at the University of North Carolina. In both cases 75 ev was used for the high-voltage spectra; the ionizing current was 80  $\mu$ a. For low-voltage spectra a trap current of 2  $\mu$ a was maintained, and the ionization potential obtained by the vanishing current technique. Several spectra at energies approximately 5 v (measured by a digital voltmeter readable to  $\pm 0.02$  v) above the ionization potential were then recorded, and the intensities at the desired voltage were determined by interpolation of data.

Inlet system and ion source temperatures were approximately 180°.

Compounds used in this study were either gifts or commercial samples.

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## Multiple Structure-Reactivity Correlations. The Alkaline Hydrolyses of Acyl- and Aryl-Substituted Phenyl Benzoates<sup>1</sup>

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The rates of alkaline hydrolysis of acyl-substituted *p*-nitrophenyl, *m*-nitrophenyl, *p*-chlorophenyl, phenyl, and *p*-tolyl benzoates have been determined in 33% acetonitrile-water at 25°. Each of the substituted phenols generated an independent  $\sigma$ - $\rho$  plot which was correlated very precisely with the Hammett equation ( $r = 0.998 - 0.999$ ). The values of  $\rho$  so obtained show no tendency either to increase or to decrease with the intrinsic reactivity of the parent phenol and are all within  $\pm 0.040$  of the mean of 2.021. Poorer correlations were obtained with the Hammett plots made by varying the aryl moieties of the esters while holding the acyl fractions constant. These could only be improved if the  $\sigma$  of the *p*-nitrophenyl derivative was allowed to assume a "best" value of 0.89, which is intermediate between  $\sigma$  and  $\sigma^-$ . Ground-state destabilization of *p*-nitrophenyl esters by resonance is suggested as a possible explanation for the enhanced value of  $\sigma$ . The constancy of the  $\rho$  values is considered in relationship to a recently proposed multiple structure-reactivity equation.

The Hammett equation (eq 1) has been one of the most successful and most widely used of the linear free-energy relationships which have been applied in physical organic chemistry<sup>2</sup> in the resolution of structure reactivity problems. Several parameters which influence

$$\log k_i = \sigma_i \rho + \log k_0 \quad (1)$$

the values of  $\rho$  for a given set of substrates and reaction conditions have been investigated; among these are temperature and solvent composition,<sup>3</sup> distance of substituent from the reacting center,<sup>4</sup> and changes in the rate-determining step in proceeding from the most reactive to the least reactive members of the series.<sup>5,6</sup>

(1) Supported by National Institutes of Health Grant Number GM 12278 and National Science Foundation Grant Number GB 4606.

(2) For recent discussions, see (a) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

(3) An extensive compilation of relevant data is given in (a) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). Theoretical discussions of the effect of temperature on  $\rho$  are given by (b) C. C. Price, *ibid.*, **29**, 37 (1941), and in (c) ref 2b, p 177 ff.

(4) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

(5) (a) C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951); (b) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962); (c) B. M. Anderson and W. P. Jencks, *J. Am. Chem. Soc.*, **82**, 1773 (1960); (d) E. H. Cordes and W. P. Jencks, *ibid.*, **85**, 2843 (1963).

(6) J. F. Kirsch and W. P. Jencks, *ibid.*, **86**, 837 (1964).

However, the effect of the reactivity of the reactants themselves upon  $\rho$  has received scanty consideration, the main efforts in this direction being those of Brown and coworkers in an extensive series of studies on electrophilic aromatic substitution reactions. They have shown that the ratio of the rate constants for the reactions of an electrophile with toluene and with benzene ( $k_{tol}/k_{benz}$ ) approaches unity as the strength of the electrophile is increased, indicating that the absolute value of  $\rho$  decreases with increasing reactivity. The increasing reactivity is accompanied by a decrease in positional selectivity, the more highly reactive electrophiles producing greater quantities of *meta*-substituted products in addition to the usual *ortho* and *para* ones. This behavior is quantitatively reflected in the  $\rho$  values, which proceed from -12.1 in the highly selective, uncatalyzed bromination reaction where essentially no *meta*-substituted product is formed to  $\rho$  of -2.4 in the rather unselective Friedel-Craft ethylation reaction where appreciable quantities of *meta* isomers are produced.<sup>7</sup> These experiments can be considered

(7) (a) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963). See also (b) G. Å. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 2203 (1964), and earlier papers by G. A. Olah.