mately constant factor of $\leq 1.6$ (the factor is $\sim 1.6$ assuming transfer occurs solely from C-3 and C-4). The isotope effect could arise in the transfer of H (D) from the alkyl chain to the oxygen.

## Experimental Section

The FI mass spectrometer is a modified Du Pont (C.E.C.) 21-110B double-focusing instrument.[21] The standard Du Pont combination FI/EI ion source is used with the electron collimating magnet removed to avoid mass discrimination. Source temperatures of between 50 and 150° were employed for the measurements described. Uncoated stainless steel razor blades kindly supplied by Schick were employed as emitters. The fragment ion currents $I_f$ are measured as a function of blade potential on an x–y recorder. The blade potential is varied incrementally in 10-V steps. The maximum fragment ion currents are of the order of $10^{-12}$ A at the beam monitor.

The deuterated hexanols were kindly supplied by Dr. W. H. McFadden. The preparation and estimation of purity of these molecules have been described.[45] To confirm results, the experiments were repeated with molecules synthesized in our laboratory.[46]

**Acknowledgment.** We are indebted to the National Aeronautics and Space Administration for financial support (Grant NGL 05-003-003). We wish to thank Mrs. Sydell Lewis for preparation and purification of samples.

(45) W. H. McFadden, L. E. Boggs, and R. G. Buttery, *J. Phys. Chem.*, **70**, 3516 (1966).

(46) The hexanols were intermediates in syntheses of deuterated hexanols: P. J. Derrick, A. M. Falick, S. Lewis, and A. L. Burlingame, to be submitted for publication.

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# A Reexamination of Electronic Effects in Ring-Substituted Phenyl Esters. Correlation of Spectral and Kinetic Properties with $\sigma^0$

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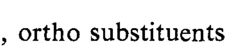
*Received June 19, 1972*

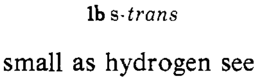
**Abstract:** The ultraviolet K bands for para-substituted phenyl acetates differ in wavelength from those of the corresponding monosubstituted benzenes by 8–10 nm, regardless of the electronic nature of the para substituent. Similarly, a constant displacement is observed in the K bands for 6-substituted hydrocoumarins. On the basis of these results, phenyl esters and lactones are considered to be devoid of "through resonance" between the aryl–oxygen atom and the para substituent. Although the ester plane of a phenyl ester is considered to be perpendicular to the benzene plane, steric inhibition is only an apparent cause for reasonance uncoupling; the true cause is the thermodynamic preference by the oxygen atom to overlap with the ester carbonyl rather than with the benzene ring. In support of this argument, the infrared carbonyl-stretching frequencies for 48 mono- and polysubstituted phenyl hydrocinnamates are shown to correlate ($r = 0.9997$) with $\sigma^0$ (or $\Sigma\sigma^0$) for the ring substituents, including a number of ortho substituents. Values of $\sigma_o^0$ (for nonpolar media) are derived by calculation: $\sigma_o^0(\mathrm{R}) = \sigma_p^0(\mathrm{R}) + 0.39\sigma^*(\mathrm{RCH_2})$. Values of $\sigma^0$ for hydroxylic media have been reevaluated on the basis of 24 sets of data for systems in which resonance coupling of the reaction site with the benzene ring is improbable. These $\sigma^0$ values are, in turn, used to correlate 33 sets of data on the intermolecular reactions of phenyl esters with various nucleophiles. The excellent correlations obtained serve to demonstrate that $\sigma^0$ is the appropriate parameter to be used in such correlations. Intramolecular reactions of phenyl esters, on the other hand, show a better correlation with $\sigma^-$. It is tentatively considered that formation of a tetrahedral intermediate is rate limiting in intermolecular reactions of phenyl esters with nucleophiles, but that breakdown of a tetrahedral intermediate is rate limiting in intramolecular cases.

The properties of aromatic systems, in which a functional group is separated from the ring by one or more methylene carbons, have been used to derive values of $\sigma^0$, a substituent parameter considered free of any component due to significant $\pi$-electronic interaction with the side-chain functional group.[2] Obviously, such systems are also devoid of "through resonance," the coupling of ring substituents with the functional group *via* the aromatic $\pi$ cloud. It has not been generally recognized, however, that phenolic esters fall into the same category, *i.e.*, that acylation of a phenol serves to uncouple virtually all resonance overlap between the phenolic oxygen atom and the aromatic $\pi$ system. In this paper we present several spectroscopic studies in support of the generalization and examine its consequences in kinetic and mechanistic studies.

Space-filling models show quite clearly that phenyl acetate is not a planar molecule. Whether the s-cis (**1a**) or s-trans (**1b**) conformation is assigned to the ester group, ortho substituents as small as hydrogen seem to be sufficient to prevent the achievement of coplanarity with the benzene ring. Dipole moment studies[3] are



**1a** s-*cis*



**1b** s-*trans*

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(1) Author to whom correspondence should be addressed.

(2) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(3) (a) M. Aroney, R. J. W. Le Fèvre, and S.-S. Chang, *J. Chem. Soc.*, 3173 (1960); (b) O. Exner, Z. Fidlerová, and V. Jehlička, *Collect. Czech. Chem. Commun.*, **33**, 2019 (1968); (c) V. Balish and K. Gana-

consistent with a model in which the ester plane is rotated 80–90° out of the benzene plane, even in so strongly electron-demanding a system as *p*-nitrophenyl acetate.[3b] The relatively low dipole moments of phenyl esters suggest further that the s-trans conformation (**1b**) is strongly preferred.[3b,4,5] In general, this conclusion is also supported by infrared spectral studies.[4,6]

**Ultraviolet Spectra.** It has long been known that the ultraviolet spectrum of phenyl acetate resembles that of benzene far more than that of phenol or of anisole. Similarly, the spectra of para-substituted phenyl acetates resemble closely those of the corresponding monosubstituted benzenes. Since the degree of displacement of the ultraviolet K band is a useful measure of the extent of "through resonance" in para-substituted phenols,[7] we have compared the positions of the K bands for a series of phenyl acetates with those of the simple benzenes. As seen from Table I, the displacement, $\Delta K_1$, falls within the narrow range of 8–10 nm despite a considerable variation in the nature of the para substituent. The virtual constancy of $\Delta K_1$ excludes any significant role for "through resonance" in phenyl acetates, the small displacement observed being attributable to an inductive perturbation of the aromatic $\pi$-system by the acetoxy substituent.

**Table I.** Ultraviolet Spectra of Phenyl Esters and Lactones[a]

| R | RPh[b] | 4-RPhOAc[c] | $\Delta K_1$[d] | **2** or **3**[e] | $\Delta K_2$[f] |
|---|---|---|---|---|---|
| H | 203.5 | 212 | 8.5 | 219.5[g] | 16 |
| F | 204 | 213[b] | 9 | 220[h] | 16 |
| $CH_3$ | 208 | 218 | 10 | 225[h] | 17 |
| Cl | 210 | 219 | 9 | 229[g] | 19 |
| Br | 210 | 219.5 | 9.5 | | |
| $OCH_3$ | 216 | 224 | 8 | 232[h] | 16 |
| CN | 222 | 231[b] | 9 | 240[h] | 18 |
| $NH_2$ | 230 | 240[b] | 10 | | |
| $COCH_3$ | 240 | 248.5 | 8.5 | | |
| CHO | 244 | 252.5 | 8.5 | | |
| $N(CH_3)_2$ | 250 | 258[b] | 8 | 266[g] | 16 |
| $NO_2$ | 262 | 270 | 8 | 281[g] | 19 |

[a] K band, nm; measured in ethanol. [b] Present work. [c] Taken from L. Skulski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **10,** 207 (1962), except as noted. [d] $\Delta K_1 = \lambda(\text{4-RPhOAc}) - \lambda(\text{RPh})$. [e] K bands for **2** and **3** coincided within 2 nm. [f] $\Delta K_2 = \lambda(\text{6-R-2 or 6-R-3}) - \lambda(\text{RPh})$. [g] Compounds described in S. Milstien and L. A. Cohen, *J. Amer. Chem. Soc.*, **92,** 4377 (1970). [h] R. T. Borchardt and L. A. Cohen, to be submitted for publication.

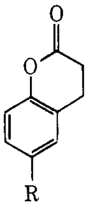
It is conceivable that the gain in stabilization derived from strong "through resonance" could serve as a restoring force to overcome, to a degree, the uncoupling effect of steric inhibition of overlap. Such a restoring force is not in evidence in the case of *p*-nitrophenyl acetate. Indeed, the even greater electron demand imposed by multiple *o*- and *p*-nitro groups (Table II) is ineffectual in restoring "through resonance." [8]

**Table II.** Ultraviolet Spectra of Nitrophenyl Esters[a]

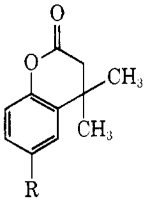
| R | RPh | RPhOAc | $\Delta K_3$ |
|---|---|---|---|
| 4-$NO_2$ | 260 | 269 | 9 |
| 2,4-$(NO_2)_2$ | 233 | 236 | 3 |
| 2,4,6-$(NO_2)_3$ | 226 | 226 | 0 |

[a] K band, nm; spectra were measured in acetonitrile to avoid solvolysis.

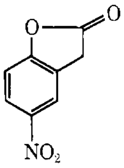
On the basis of Dreiding models, we estimate the lactone plane of a hydrocoumarin (**2** or **3**) to be *ca.* 25° out of coplanarity with the benzene ring. For simple cases of steric inhibition of resonance, this degree of twist should reduce "through resonance" by no more than 20%.[9] Yet, the $\Delta K_2$ values for 6-substituted hydrocoumarins (Table I) are sufficiently constant to deny the occurrence of "through resonance." It is interesting to note that a change from the s-trans conformation in the ester to an s-cis conformation in the lactone seems to have no significant effect on $\Delta K$ values.[10] Finally, the position of the K band of 5-nitro-2-benzofuranone (**4**) was found to be identical with that of 6-nitrohydrocoumarin, despite the virtual planarity of the bicyclic system of **4**.[11]



**2**



**3**



**4**

It is clear that the absence of "through resonance" in phenolic esters and lactones *cannot* be attributed to steric inhibition of coplanarity. Since the p-type lone pair on the $sp^2$ oxygen can engage in overlap with the carbonyl group *or* with the benzene ring (but not with both simultaneously),[12] the more effective resonance stabilization should be the determining factor. Ester resonance is at least 10 kcal/mol greater than that of phenolic resonance;[13] accordingly, ester resonance should predominate, which proves to be the case, and steric inhibition of coplanarity is a real, but coincidental, phenomenon. Thus, the 90° angle of twist found for phenyl acetates may be simply the result of conformational preference in a freely rotating system, in which the aryl–oxygen bond has little or no double bond character.

**Infrared Spectra.** For aliphatic esters ($RCH_2OCOR'$), the carbonyl-stretching frequency shows a linear correlation with $\sigma^*$ for the R substituent,[14] electronic transmission occurring either through space or along the chain. The carbonyl frequencies of phenyl esters

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pathy, *Trans. Faraday Soc.*, **59,** 1784 (1963); (d) R. J. W. Le Fèvre and A. Sundaram, *J. Chem. Soc.*, 3904 (1962).

(4) The two conformations may be estimated to differ by *ca.* 1.5 D; *cf.* H. Lee and J. K. Wilmshurst, *J. Chem. Soc.*, 3590 (1965).

(5) The literature[3,4] appears to be inconsistent in the naming of these conformations.

(6) M. Oki and H. Nakanishi, *Bull. Chem. Soc. Jap.*, **43,** 2558 (1970).

(7) L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, **85,** 3402 (1963).

(8) The progressive decrease in wavelength (and in $\Delta K_3$) with increasing nitro substitution may be due to increasing symmetry in perturbation of the $\pi$ system, as well as to increasing electron withdrawal.

(9) B. M. Wepster, *Progr. Stereochem.*, **2,** 102 (1958).

(10) The small difference between $\Delta K_1$ and $\Delta K_2$ is probably due to the electronic effect of the additional alkyl substituent in the hydrocoumarin.

(11) P. Tobias, J. H. Heidema, K. W. Loo, E. T. Kaiser, and F. J. Kézdy, *J. Amer. Chem. Soc.*, **91,** 202 (1969). We are indebted to Dr. Kaiser for a gift of this compound.

(12) Regardless of the direction of overlap, the oxygen atom should be viewed as an $sp^2$ hybrid. *Cf.* L. Radom, W. J. Hehre, J. A. Pople, G. L. Carlson, and W. G. Fateley, *J. Chem. Soc., Chem. Commun.*, 308 (1972).

(13) J. G. Aston, "Determination of Organic Structures by Physical Methods," Vol. I, E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 560.

(14) S. Takahashi, L. A. Cohen, H. K. Miller, and E. G. Peake, *J. Org. Chem.*, **36,** 1205 (1971).

**Table III.** Phenyl Esters of Hydrocinnamic Acids[a]

| Phenol substituents | Mp or bp (mm), °C | S[b] | $\sigma^0$ or $\Sigma\sigma^0$ | $\nu_{\text{C=O}}$,[c] cm$^{-1}$ | Phenol substituents | Mp or bp, °C | S[b] | $\sigma^0$ or $\Sigma\sigma^0$ | $\nu_{\text{C=O}}$,[c] cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 2,3,5,6-(CH$_3$)$_4$ | 61–62 | E | −0.46 | 1757.0 | 2-I | 157 (0.2) | | 0.62 | 1770.3 |
| 2,3,6-(CH$_3$)$_3$ | 156 (0.2) | | −0.39 | 1757.9 | 4-CN | 68–69 | E | 0.63 | 1770.5 |
| 2,6-(CH$_3$)$_2$ | 130 (0.3) | | −0.32 | 1758.8 | 2-F[e] | 128 (0.3) | | 0.63 | 1772.7 |
| 2-*t*-C$_4$H$_9$ | 171 (0.4) | | −0.20 | 1760.6 | 2-Br | 141 (0.2) | | 0.66 | 1771.1 |
| 2-CH$_3$ | 153 (0.8) | | −0.16 | 1760.7 | 2-Cl | 131 (0.1) | | 0.66 | 1771.1 |
| 4-OCH$_3$ | *d* | | −0.16 | 1760.8 | 3-NO$_2$ | *d* | | 0.68 | 1771.2 |
| 4-*t*-C$_4$H$_9$ | *d* | | −0.14 | 1760.9 | 4-NO$_2$ | *d* | | 0.73 | 1771.8 |
| 4-CH$_3$ | *d* | | −0.125 | 1761.2 | 3,5-Cl$_2$ | 147 (0.1) | | 0.76 | 1772.3 |
| 3-CH$_3$ | 22–24 | P | −0.07 | 1762.0 | 2,4-Cl$_2$ | 57–58 | C | 0.91 | 1773.6 |
| 2-OCH$_3$-4-CH$_3$[e] | 164 (0.2) | | −0.03 | 1763.8 | 2-CF$_3$ | 20–23 | C | 0.91 | 1774.2 |
| H | *d* | | 0 | 1762.8 | 2,4-Br$_2$ | 80–81 | E | 0.92 | 1774.1 |
| 3-OCH$_3$ | 33–35 | E-P | 0.04 | 1763.3 | 2-CN | 79–80 | E | 1.14 | 1776.8 |
| 2-CH$_3$-4-Cl | 60–61 | C | 0.09 | 1763.7 | 2-NO$_2$-4-CH$_3$ | 46 | E | 1.15 | 1776.7 |
| 2-OCH$_3$[e] | 31–32 | C | 0.10 | 1765.6 | 3-CF$_3$-4-NO$_2$ | 56 | E-C | 1.21 | 1777.3 |
| 4-F | *d* | | 0.17 | 1764.5 | 2-NO$_2$ | 68–69 | E-P | 1.27 | 1778.7 |
| 2,6-(OCH$_3$)$_2$[e] | 170 (0.2) | | 0.20 | 1766.8 | 2,6-Br$_2$ | 45 | C | 1.32 | 1778.7 |
| 4-Cl | *d* | | 0.25 | 1765.3 | 2,4,6-I$_3$ | 91–92 | E | 1.51 | 1781.0 |
| 4-Br | *d* | | 0.26 | 1765.4 | 2-NO$_2$-4-Cl | 39–41 | E-C | 1.52 | 1781.4 |
| 4-I | *d* | | 0.27 | 1765.7 | 2,4,6-Br$_3$ | 86–88 | E | 1.58 | 1781.8 |
| 3-F | 24–26 | P | 0.33 | 1766.5 | 2,4-(NO$_2$)$_2$ | *d* | | 2.00 | 1787.3 |
| 3-Cl | *d* | | 0.38 | 1767.5 | 2,6-Cl$_2$-4-NO$_2$ | 90–91 | E | 2.05 | 1787.0 |
| 3-Br | 41–42 | P | 0.38 | 1767.3 | 2,6-Br$_2$-4-NO$_2$ | 111–112 | E | 2.05 | 1787.8 |
| 3-I | 52–53 | P | 0.38 | 1767.5 | F$_5$[e] | 127 (0.5) | | 2.12 | 1791.5 |
| 3-CF$_3$ | 29–30 | C | 0.48 | 1769.0 | 2-Cl-4,6-(NO$_2$)$_2$ | 94–96 | E | 2.66 | 1794.5 |
| 2-CH$_3$-3-NO$_2$ | 41 | E-C | 0.52 | 1769.1 | 2,4,6-(NO$_2$)$_3$ | 93–95 | E | 3.27 | 1803.0 |
| 4-CF$_3$ | 68–70 | E | 0.54 | 1769.1 | 2,4,6-(NO$_2$)$_3$-3-CF$_3$ | 108–110 | E | 3.75 | 1808.4 |
| 3-CN | 46 | E-P | 0.62 | 1770.5 | | | | | |

[a] All new compounds provided acceptable elemental analyses. [b] Solvents used for recrystallization: E, ethyl acetate; P, petroleum ether; C, cyclohexane. [c] Measured in carbon tetrachloride. [d] Reference 24. [e] This compound was included in the correlation for eq 2, rather than that for eq 1.

should, by analogy, show a dependence on electron density in the aromatic ring. In 1960, Freedman observed that the carbonyl-stretching frequencies of phenyl acetates failed to correlate with $\sigma$ or with $\sigma^-$ for the para substituent[15] and suggested that the frequency is dependent only on the inductive component of $\sigma$. It seems more reasonable to assume, however, that the carbonyl frequency should be dependent on the *net* electron density at the ring carbon (C-1) bearing the acetoxy group. In the absence of "through resonance," the net electron density at C-1 should be a composite of field (or $\sigma$) inductive, $\pi$ inductive, and resonance effects due to a ring substituent, and should, therefore, be a function of $\sigma^0$ for the ring substituent.

For many substituents, values of $\sigma$, $\sigma^-$, and $\sigma^0$ are so similar that a statistically valid distinction becomes impossible. Accordingly, we have expanded the sampling range by the examination of 53 phenyl esters which involve a spread in $\sigma^0$ of more than 4 units. A set of such magnitude required the inclusion of esters of ortho-substituted and of polysubstituted phenols, selecting cases in which the additivity of $\sigma$ values is most likely to hold. In general, ortho-substituent constants (even for $\sigma^0$) vary widely according to the type of reaction examined,[16] being perturbed by hydrogen bonding, electrostatic, and steric factors in either the ground or transition state. Since the carbonyl group in a phenyl ester is apparently perpendicular to the aromatic plane in every case, it seemed reasonable to assume that its stretching frequency, when measured in a nonpolar solvent (CCl$_4$), should be largely free of the complications mentioned and should vary primarily with the electron density at C-1. For this study, phenyl esters of hydrocinnamic acid were used, in preference to acetates, to provide for a greater number of crystalline derivatives, to ensure a greater solubility in carbon tetrachloride, and to ensure a uniform s-trans conformation for all the esters. To avoid complications due to possible overlap of absorption bands, substituents themselves containing carbonyl groups were omitted from the study.

For the most part, values of $\sigma_m^0$ and $\sigma_p^0$ were taken from the compilation of Taft.[2] For several substituents, slight changes in $\sigma^0$ values were made to provide a better fit, these changes being justified by additional correlations given in the following section. Values of $\sigma_o^0$ were derived by calculation, making use of certain assumptions.

(1) $\sigma_m^0 = \sigma_m^I + \sigma_m^R$; $\sigma_p^0 = \sigma_p^I + \sigma_p^R$[17]

(2) $\sigma_m^I(R) = 0.45\sigma^*(RCH_2)$[18]

(3) Inductive transmission from ring positions to C-1 occurs through space—accordingly, $\sigma_p^I = (\sqrt{3}/2)\sigma_m^I$ and $\sigma_o^I = \sqrt{3}\sigma_m^I$

(4) $\sigma_p^R = \sigma_o^R$

(5) Combination and simplification of the foregoing relationships lead to the equation $\sigma_o^0(R) = \sigma_p^0(R) + 0.39\sigma^*(RCH_2)$

In calculating $\sigma_o^0$, the following values of $\sigma^*$ were used:[14] NO$_2$, 1.38; Cl, 1.05; Br, 1.03; I, 0.90; F, 1.17; CN, 1.30; CH$_3$, −0.10; CH$_3$O, 0.66; CF$_3$, 0.94; and *tert*-butyl, −0.16.

In Table III, the $\sigma^0$ (and $\Sigma\sigma^0$) values are given together with the carbonyl-stretching frequencies for the various esters studied. A plot of $\nu$ *vs.* $\sigma^0$ (Figure 1) shows that all but five compounds fit a single slope;

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(15) H. H. Freedman, *J. Amer. Chem. Soc.*, **82**, 2454 (1960).

(16) M. Charton, *J. Org. Chem.*, **36**, 882 (1971), and earlier papers cited therein.

(17) $\pi$-Inductive effects are considered to be included in $\sigma^R$.

(18) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **79**, 1045 (1957).

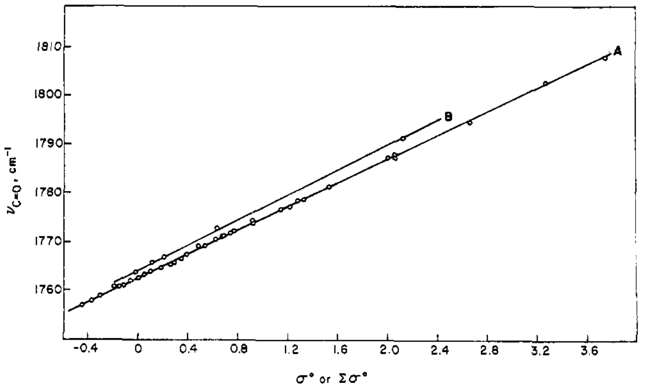

Figure 1. Correlations of carbonyl-stretching frequency for substituted phenyl hydrocinnamates (in carbon tetrachloride) with $\sigma°$ or $\Sigma\sigma°$ for phenyl substituents: (A) correlation for 48 compounds obeying eq 1; (B) correlation for five compounds (containing *o*-F or *o*-OCH$_3$ groups) obeying eq 2.

for the principal set ($n$ = 48), least-squares analysis provides eq 1, with correlation coefficient ($r$) = 0.9997

$$\nu = 12.19\sigma^0 + 1762.7 \qquad (1)$$

and standard deviation of the slope ($s$) = 0.042. Of the ten ortho substituents examined, both singly and as part of a polysubstituted ring, only in two cases (OCH$_3$ and F) do the calculated values of $\sigma_o{}^0$ result in deviations from this line. Interestingly, the five compounds examined, which contain these substituents, form a separate slope (eq 2), with $r$ = 1.000 and $s$ = 0.109. Whether

$$\nu = 12.86\sigma^0 + 1764.3 \qquad (2)$$

this method of calculating $\sigma_o{}^0$ needs refinement, or whether highly electronegative atoms such as oxygen and fluorine introduce a special perturbation of the carbonyl, may be clarified by further study. The fact that, for all five compounds, the deviation is in the same direction suggests that a special field effect may be in operation.

The excellence of the infrared correlation (well beyond expectation) for phenyl esters strengthens our thesis regarding the absence of "through resonance" and confirms the validity of the additivity principle for some adjacent substituents.[19] Despite the seemingly arbitrary basis for our derivation of $\sigma_o{}^0$, the successful correlations of $\Sigma\sigma^0$ with $\nu$ suggest that approach to warrant further exploration. Because of the variety of complicating interactions possible in ortho-substituted arylalkyl systems, these values of $\sigma_o{}^0$ should not be expected to hold for p$K_a$ or kinetic data.

**Kinetic Studies.** If, in the reactions of phenyl esters with nucleophiles, formation of a tetrahedral intermediate were the rate-limiting step, the rate constant should increase with increasing withdrawal of electron density from the carbonyl carbon atom; *i.e.*, log $k$ should be a linear function of $\sigma^0$. Conversely, if breakdown of a tetrahedral intermediate were rate limiting, the rate constant should be more dependent on the leaving ability (or p$K_a$) of a phenol or phenolate ion and log $k$ should correlate better with $\sigma^-$. Unfortunately, the majority of reported kinetic studies and Hammett correlations for phenyl esters involve relatively few substituents and, of those substituents most often utilized, only the *p*-nitro group offers a significant difference between $\sigma^0$ and $\sigma^-$. Clearly, even a modest experimental error in rate data for the *p*-nitrophenyl ester (due, usually, to a relatively high rate of reaction) can lead to a deceptively satisfactory correlation with the one parameter or the other. While many of these studies have been included in the correlations summarized below, emphasis should be placed on those involving both the larger number of substituents and the greater sampling of strongly electronegative substituents.

In his original determination of $\sigma^0$ values, Taft noted that, for certain substituents, $\sigma^0$ varies with the polarity of the medium.[2] The $\sigma^0$ values used for infrared spectral correlation are, therefore, not wholly applicable to correlations of kinetic data. The type of data available to Taft—the physical and chemical properties of arylalkyl systems—has grown considerably in volume in the intervening years; we have, accordingly, reexamined the correlation of $\sigma^0$ with the data now available. On the basis of least-squares analysis of 24 sets of ionization and kinetic data (Table IV), we recommend a slight modification of several of the original $\sigma^0$ values and propose values for some additional substituents (Table V). In keeping with the definition of $\sigma^0$, the site of reaction, in each of the sets examined, is insulated from the benzene ring by one or more sp$^3$ or sp carbon atoms. Wherever $\sigma^0$ values show a significant solvent dependence, the value in a hydroxylic solvent is consistently higher than that in nonhydroxylic media.[2] Our analysis provides a reverse order for the solvent effect on $\sigma^0$ for both the *m*-chloro and *m*-bromo substituents (Table V). This result is puzzling and is under further investigation.

Application of this $\sigma^0$ scale to 33 sets of kinetic data on interactions of nucleophiles with phenyl esters (Table VI) provides correlations which are of an even higher average level than those of Table IV. In the large majority of these cases, correlation with $\sigma^0$ is superior to that with $\sigma^-$. On this basis, we believe that *intermolecular* nucleophilic attack[20] on phenyl esters generally involves formation of a tetrahedral intermediate as the rate-limiting step. It is noteworthy, however, that in the four reported studies of *intramolecular* nucleophilic attack on phenyl esters,[21] correlation of rate data with $\sigma^0$ is inferior to that with $\sigma^-$ (Table VII), suggesting that breakdown of a tetrahedral intermediate to product is now rate limiting. This conclusion had already been anticipated in earlier studies[21,22] and, in the light of other recent investigations,[23] such a differentiation between intermolecular and intramolecular reactions of phenyl esters seems reasonable.

It will be noted that one intermolecular reaction, the reduction of phenyl esters with sodium borohydride, has been assigned to Table VII, on the basis of best fit. Although a detailed mechanistic analysis of borohydride

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[19] For substituents which do not mutually interact to any significant extent.

[20] Including general base-catalyzed attack by water.

[21] The one other case known to us, the hydrolysis of phenyl $\gamma$-(4-imidazolyl)butyrates [T. C. Bruice and J. M. Sturtevant, *J. Amer. Chem. Soc.*, **81**, 2860 (1959)], consists of too short a set for inclusion.

[22] (a) E. Gaetjens and H. Morawetz, *J. Amer. Chem. Soc.*, **82**, 5328 (1960); (b) T. C. Bruice and S. J. Benkovic, *ibid.*, **85**, 1 (1963).

[23] S. Milstien and L. A. Cohen, *ibid.*, **92**, 4377 (1970), and studies in progress.

**Table IV.** Summary of Correlations with $\sigma^0$

| Reaction | $n$[a] | $r$[a] | $s$[a] | $\rho$ | Log $k_0$[b] |
|---|---|---|---|---|---|
| Phenylacetic acids, p$K_a$, water, 25° [c] | 12 | 0.999 | 0.008 | −0.537 | 4.312 |
| Phenylacetic acids, DDM,[d] methanol, 30° [e] | 6 | 0.999 | 0.007 | 0.286 | 0.409 |
| Phenylacetic acids, DDM, ethanol, 26° [f] | 9 | 0.998 | 0.011 | 0.401 | −0.062 |
| Phenylacetic acids, DDM, ethanol, 30° [g] | 4 | 0.999 | 0.004 | 0.378 | 0.040 |
| Phenylacetic acids, DDM, ethanol, 35.6° [f] | 7 | 0.998 | 0.011 | 0.381 | 0.271 |
| Ethyl phenylacetates, saponification, 60% aq acetone, 25° [h] | 16 | 0.997 | 0.021 | 0.951 | 0.668 |
| Ethyl phenylacetates, saponification, 60% aq acetone, 25° [i] | 10 | 0.999 | 0.018 | 0.953 | −1.365 |
| Ethyl phenylacetates, saponification, 85.4% aq ethanol, 25° [j] | 10 | 0.999 | 0.021 | 1.115 | 1.071 |
| Phenylpropionic acids, p$K_a$, water, 25° [k] | 5 | 0.999 | 0.006 | −0.206 | 4.712 |
| Phenylpropionic acids, p$K_a$, water, 25° [l] | 8 | 0.999 | 0.005 | −0.220 | 4.659 |
| Phenylpropionic acids, p$K_a$, 50% aq ethanol, 25° [m] | 6 | 0.997 | 0.016 | −0.376 | 5.882 |
| Phenylpropionic acids, DDM, ethanol, 30° [g] | 4 | 0.992 | 0.018 | 0.207 | −0.120 |
| Ethyl phenylpropionates, saponification, 87.8% aq ethanol, 30° [n] | 12 | 0.999 | 0.008 | 0.659 | −2.216 |
| Phenylpropiolic acids, p$K_a$, 50% aq ethanol, 25° [o,p] | 6 | 0.999 | 0.013 | −0.448 | 3.577 |
| Phenylpropiolic acids, p$K_a$, 35% aq dioxane, 25° [q] | 6 | 0.999 | 0.021 | −0.786 | 3.248 |
| Phenylpropiolic acids, DDM, dioxane, 30° [o] | 5 | 0.999 | 0.022 | 0.916 | 0.512 |
| Phenylpropiolic acids, esterification, HCl–methanol, 35° [q] | 7 | 0.997 | 0.013 | −0.370 | −2.938 |
| Phenylpropiolic acids, TPCD,[r] phenylcyclohexane, 175° [s] | 8 | 0.998 | 0.024 | 0.823 | 0.191 |
| *trans*-Phenylcyclopropanecarboxylic acids, p$K_a$, 50% aq ethanol, 25° [m] | 11 | 0.999 | 0.008 | −0.525 | 5.775 |
| *cis*-Phenylcyclopropanecarboxylic acids, p$K_a$, 50% aq ethanol, 25° [m] | 6 | 0.997 | 0.019 | −0.391 | 6.334 |
| Ethyl *trans*-phenylcyclopropanecarboxylates, saponification, 87.8% ethanol, 30° [t] | 7 | 1.000 | 0.011 | 0.910 | −2.856 |
| Ethyl *cis*-phenylcyclopropanecarboxylates, saponification, 87.8% ethanol, 30° [t] | 7 | 0.999 | 0.023 | 1.030 | −4.036 |
| Benzylammonium ions, p$K_a$, water, 25° [u] | 11 | 0.997 | 0.028 | −1.044 | 9.373 |
| Benzyl acetates, saponification, 56% aq acetone, 25° [v,w] | 10 | 0.997 | 0.021 | 0.754 | 0.814 |

[a] $n$ = number of compounds in the set; $r$ = correlation coefficient; $s$ = standard deviation of the slope. [b] For ionization data, value = $-\log K_0$. [c] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 644 (1936); J. F. J. Dippy and F. R. Williams, *ibid.*, 161 (1934). [d] DDM = diphenyldiazomethane. [e] N. B. Chapman, J. R. Lee, and J. Shorter, *J. Chem. Soc. B*, 769 (1969). [f] R. M. O'Ferrall and S. I. Miller, *J. Amer. Chem. Soc.*, **85,** 2440 (1963). [g] K. Bowden, N. B. Chapman, and J. Shorter, *Can. J. Chem.*, **42,** 1479 (1964). [h] Reference 24a. [i] R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph, and E. M. Smith, *J. Chem. Soc.*, 3247 (1961); R. O. C. Norman and P. D. Ralph, *ibid.*, 5431 (1963). [j] J. G. Watkinson, W. Watson, and B. L. Yates, *ibid.*, 5437 (1963). [k] E. N. Trachtenburg and G. Odian, *J. Amer. Chem. Soc.*, **80,** 4018 (1958). [l] J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938). [m] R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27,** 733 (1962). [n] R. Fuchs and J. A. Caputo, *ibid.*, **31,** 1524 (1966). [o] J. D. Roberts and R. A. Carboni, *J. Amer. Chem. Soc.*, **77,** 5554 (1955). [p] I. J. Solomon and R. Filler, *ibid.*, **85,** 3492 (1963). [q] M. S. Newman and S. H. Merrill, *ibid.*, **77,** 5552 (1955). [r] TPCD = tetraphenylcyclopentadienone. [s] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23,** 885 (1958). [t] R. Fuchs and J. J. Bloomfield, *ibid.*, **28,** 910 (1963). [u] L. F. Blackwell, A. Fischer, I. J. Miller, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 3588 (1964). [v] E. Tommila and C. N. Hinshelwood, *ibid.*, 1801 (1938). [w] E. Tommila, *Ann. Acad. Sci. Fenn., Ser. A*, **57** (4), 3 (1942).

reduction of esters is not available, it would appear that, owing to the very high nucleophilicity of the reagent,[24] attack on the carbonyl group is no longer rate limiting. It would be desirable to perform similar correlation tests (with $\sigma^0$ or $\sigma^-$) for the reactions of phenyl esters with powerful $\alpha$-nucleophiles (hydroperoxides, hypochlorites); unfortunately, the necessary kinetic data are not yet available. As is evident from Table VII, those reactions believed to involve rate-limiting breakdown of an intermediate show remarkable consistency in their $\rho$ values. Evaluation of the significance of this observation also will require rate data for a larger variety of systems.

**Table V.** Normal Substituent Constants,[a,b] $\sigma^0$

| R | $\sigma_m{}^0$ | $\sigma_p{}^0$ |
|---|---|---|
| $NO_2$ | 0.68 | 0.84 (0.73)[c] |
| $COCH_3$ | 0.35 | 0.51 |
| COOR | 0.36 | 0.46 |
| CN | 0.62 | 0.72 (0.65) |
| $CF_3$ | 0.48 | 0.54 |
| I | 0.38 | 0.27 |
| Br | 0.32 (0.38) | 0.26 |
| Cl | 0.31 (0.38) | 0.25 |
| F | 0.33 | 0.17 |
| $OCH_3$ | 0.04 | −0.16 |
| $CH_3$ | −0.07 | −0.125 |

[a] Values used in the correlations of Tables IV and VI. [b] The following $\sigma^0$ values are based on a narrower sampling range (2–4 cases) than those in the table: *p*-COPh, 0.50; *p*-N=NPh, 0.36; *p*-CHO, 0.56; *p*-$NH_2$, −0.34; *p*-Ph, 0; *p*-*t*-Bu, −0.14; 3,4-$(OCH_3)_2$, −0.03; 3,4-methylenedioxy, −0.02; 3,4-$Cl_2$, 0.56. [c] Nonpolar $\sigma^0$ values, where different from polar values, are given in parentheses. Nonpolar $\sigma^0$ values for some carbonyl-containing substituents are given in ref 2.

The high levels of correlation shown in Tables IV and VI, which are based on $\sigma^0$, appear to eliminate the need for adjustable $\sigma$ parameters and for a range of values for the *p*-nitro group,[25] at least as far as the kinetic properties of phenyl esters are concerned. In Hammett correlations for the intermolecular reactions of nucleophiles with phenyl esters, the use of $\sigma^0$ as the appropriate substituent parameter seems obligatory.

## Experimental Section[26]

**Substituted Phenyl Hydrocinnamates.** All of the esters listed in Table III were prepared from commercial samples of the appropriate phenols, by use of the trifluoroacetic anhydride method.[14] In

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(24) S. Takahashi and L. A. Cohen, *J. Org. Chem.*, **35,** 1505 (1970).

(25) (a) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Soc. Chem. Jap.*, **39**, 2274 (1966); (b) Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 971 (1959); (c) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968); (d) C. G. Mitton, R. L. Schowen, M. Gresser, and J. Shapley, *ibid.*, **91**, 2036 (1969); (e) J. F. Kirsch, W. Clewell, and A. Simon, *J. Org. Chem.*, **33**, 127 (1968); (f) J. J. Ryan and A. A. Humffray, *J. Chem. Soc. B*, 842 (1966); (g) A. A. Hummfray and J. J. Ryan, *ibid.*, 468 (1967); (h) Z. S. Chaw, A. Fischer, and D. A. R. Happer, *ibid.*, 1818 (1971); (i) R. J. Washkuhn, V. K. Patel, and J. R. Robinson, *J. Pharm. Sci.*, **60,** 736 (1971).

(26) Melting points and boiling points are uncorrected. Microanalyses were performed by the Microanalytical Services Section of this laboratory, under the direction of Dr. W. C. Alford. Infrared spectra were recorded and measured as previously described.[14] Least-squares analyses were performed by use of a General Electric 265 computer.

Table VI. Reactions of Phenyl Esters with Nucleophiles. Correlations of Rate Data with $\sigma^0$ [a]

| Leaving group | Nucleophile | Conditions | $n$ | $r$ | $s$ | $\rho$ | Log $k_0$ |
|---|---|---|---|---|---|---|---|
| Acetate[b] | $OH^-$ | 60% acetone, 25° | 5 | 0.999 | 0.039 | 1.474 | −0.299 |
| Acetate[c] | $OH^-$ | 56% acetone, 1.0° | 12 | 0.998 | 0.039 | 1.793 | −1.057 |
| Acetate[c] | $OH^-$ | 56% acetone, 20° | 12 | 0.998 | 0.033 | 1.574 | −0.443 |
| Acetate[d] | $OH^-$ | Water, 25° | 5 | 0.999 | 0.025 | 1.044 | 1.885 |
| Acetate[e] | $H_2O$ | 28% ethanol, 30° | 5 | 0.999 | 0.049 | 1.785 | −3.889 |
| Acetate[f] | $MeO^-$ | Methanol, 27° | 5 | 0.997 | 0.070 | 1.561 | 0.521 |
| Acetate[g] | $AcO^-$ | Water, 25° | 5 | 1.000 | 0.012 | 1.380 | −6.407 |
| Acetate[h] | $NH_3$ | Water, 30° | 5 | 1.000 | 0.031 | 2.425 | −0.597 |
| Acetate[i] | $N_2H_4$ | Water, 18° | 5 | 0.996 | 0.175 | 3.402 | −0.520 |
| Acetate[j] | Tris | Water, 30° | 4 | 0.998 | 0.036 | 0.804 | −2.969 |
| Acetate[k] | $C(CH_2OH)_4$ | Water, 30° | 4 | 1.000 | 0.011 | 1.037 | 0.006 |
| Acetate[d] | Imidazole | Water, 25° | 6 | 0.999 | 0.038 | 2.229 | −0.345 |
| Acetate[e] | Imidazole | 28% ethanol, 30° | 4 | 1.000 | 0.061 | 2.710 | −0.968 |
| Acetate[i] | Imidazole | Water, 34° | 5 | 0.997 | 0.101 | 2.166 | −0.214 |
| Acetate[k] | Aziridine | Water, 30° | 5 | 0.995 | 0.155 | 2.586 | 0.626 |
| Acetate[k] | HMPA[l] | Water, 30° | 6 | 0.998 | 0.094 | 2.920 | 1.709 |
| Acetate[k] | MPA[m] | Water, 30° | 6 | 1.000 | 0.018 | 2.705 | 2.241 |
| Benzoate[n] | $OH^-$ | 60% ethanol, 25° | 16 | 0.998 | 0.034 | 1.839 | −0.929 |
| Benzoate[o] | $OH^-$ | 60% acetone, 25° | 11 | 0.999 | 0.033 | 1,891 | −1.422 |
| Benzoate[o] | $OH^-$ | 60% acetone, 40° | 10 | 0.999 | 0.024 | 1.589 | −0.817 |
| Benzoate[p] | $OH^-$ | 33% acetonitrile, 25° | 5 | 0.999 | 0.030 | 1.403 | 0.503 |
| Benzoate[q] | $OH^-$ | 50% acetonitrile, 25° | 6 | 0.999 | 0.030 | 1.464 | −2.475 |
| *p*-Toluate[q] | $OH^-$ | 50% acetonitrile, 25° | 6 | 1.000 | 0.004 | 1.404 | −2.816 |
| *p*-Toluate[p] | $OH^-$ | 33% acetonitrile, 25° | 5 | 0.999 | 0.035 | 1.406 | 0.123 |
| *p*-Cl-Benzoate[p] | $OH^-$ | 33% acetonitrile, 25° | 5 | 0.998 | 0.049 | 1.280 | 0.963 |
| *p*-Cl-Benzoate[q] | $OH^-$ | 50% acetonitrile, 25° | 6 | 1.000 | 0.019 | 1.370 | −1.971 |
| *p*-F-Benzoate[q] | $OH^-$ | 50% acetonitrile, 25° | 5 | 1.000 | 0.015 | 1.400 | −2.281 |
| *p*-CN-Benzoate[q] | $OH^-$ | 50% acetonitrile, 25° | 6 | 0.999 | 0.012 | 1.431 | −1.125 |
| *p*-$NO_2$-Benzoate[q] | $OH^-$ | 50% acetonitrile, 25° | 7 | 0.998 | 0.040 | 1.439 | −0.948 |
| *p*-$NO_2$-Benzoate[p] | $OH^-$ | 33% acetonitrile, 25° | 5 | 1.000 | 0.024 | 1.315 | 2.098 |
| *p*-$Me_2N$-Benzoate[p] | $OH^-$ | 33% acetonitrile, 25° | 4 | 1.000 | 0.026 | 1.295 | −1.152 |
| Hydrocinnamate[r] | $OH^-$ | 70% acetone, 0° | 5 | 0.998 | 0.056 | 1.525 | 0.362 |
| Carbonate[f] | $MeO^-$ | Methanol, 27° | 8 | 1.000 | 0.022 | 1.557 | −0.061 |

[a] For key to column headings, see Table IV, footnote *a*. [b] Table IV, footnote *v*. [c] Reference 25f. [d] J. F. Kirsch and W. P. Jencks, *J. Amer. Chem. Soc.*, **86,** 837 (1964). [e] T. C. Bruice and G. L. Schmir, *ibid.*, **79,** 1663 (1957). [f] Reference 25d. [g] V. Gold, D. G. Oakenfull, and T. Riley, *J. Chem. Soc. B*, 515 (1968). [h] T. C. Bruice and M. F. Mahayi, *J. Amer. Chem. Soc.*, **82,** 3067 (1960). [i] T. C. Bruice and S. J. Benkovic, *ibid.*, **86,** 418 (1964). [j] T. C. Bruice and J. L. York, *ibid.*, **83,** 1382 (1961). [k] T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *ibid.*, **89,** 2106 (1967). [l] HMPA = 3-hydroxymethyl-3-phenylaziridine. [m] MPA = 3-methyl-3-phenylaziridine. [n] Reference 25h. [o] Reference 25g. [p] Reference 25e. [q] Reference 25i. [r] J. Gosselck, H. Barth, and L. Béress, *Justus Liebigs Ann. Chem.*, **671,** 1 (1964).

Table VII. Reactions of Phenyl Esters with Intramolecular Nucleophiles[a,b]

| Nucleophile and leaving group | Conditions | $n$ | $r$ | $s$ | $\rho$ | Log $k_0$ | $r'$ [c] | $\rho'$ [c] |
|---|---|---|---|---|---|---|---|---|
| γ-*N*,*N*-Dimethylbutyrate[d] | Water, 20° | 5 | 1.000 | 0.042 | 2.700 | 0.952 | 0.968 | 3.529 |
| δ-*N*,*N*-Dimethylvalerate[d] | Water, 20° | 5 | 0.999 | 0.075 | 2.747 | 0.582 | 0.972 | 3.607 |
| Glutarate[e] | Water, 25.3° | 7 | 0.999 | 0.047 | 2.604 | −4.996 | 0.980 | 2.820 |
| Succinate[e] | Water, 25.3° | 4 | 1.000 | 0.022 | 2.573 | −2.865 | 0.995 | 3.368 |
| Hydride–hydrocinnamate[f] | DME,[g] 40° | 8 | 0.999 | 0.048 | 2.602 | −2.357 | 0.930 | 2.518 |

[a] Correlations based on $\sigma^-$ values, as given in ref 7 and 23. [b] For key to column headings, see Table IV, footnote *a*. [c] Correlations based on $\sigma^0$ values in Table V. [d] Reference 22b. [e] Reference 22a. [f] Reference 24. [g] DME = 1,2-dimethoxyethane.

the cases of very acidic phenols, the reaction mixtures were maintained at 40–50° for 2 hr, then stored at ambient temperature overnight. Physical properties and crystallization solvents are given in Table III.