

change each boron is equally coupled to all five boron hydrogens (Fig. 1 (curve e) and Fig. 2), and the suggested mechanism is probably a correct representation of the over-all process. The acceleration of the rate of intramolecular hydrogen exchange in the μ -aminodiboranes by the presence of ethers may well occur in the same way as suggested for diborane.² Nucleophilic attack by ether with bridge opening, rotation of the BH_3 group,

and subsequent nucleophilic displacement of ether by hydride to re-form the bridge would produce the observed spectral collapse provided the reactions were sufficiently rapid.

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The ρ - ρ Relation and the Reaction of *trans*-Cinnamic Acids with Diphenyldiazomethane The Basis of the Hammett Equation¹

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Rate data for the reactions of 15 *trans*-cinnamic acids (*m*- CH_3CO_2 , *m*-Cl, *p*-Cl, H, *m*-F, *p*-F, *p*-OH, *p*-(CH_3) $_2\text{CH}$, *m*- CH_3O , *p*- CH_3O , *p*- CH_3 , *m*- NO_2 , *p*- NO_2 , *p*-(CH_3) $_2\text{N}$, and 2,4-(CH_3O) $_2$) with diphenyldiazomethane (DDM) in ethanol have been obtained. The entropies of activation ($-\Delta S^* = 8$ –21 e.u.) are proportional to the activation energies ($E_{\text{act}} = 12$ –17 kcal. mole⁻¹) in this series with a slope of *ca.* 298°. Satisfactory Hammett lines for 12 substituents have been obtained: at 25° with k in l. mole⁻¹ min.⁻¹, $\log k = 0.41\sigma - 0.1705$; at 35°, $\log k = 0.43\sigma + 0.1757$. The ρ -value for the cinnamic acids follows the relation, $\rho_{\text{RGC00H}}/\rho_{\text{RGCOS}} = \text{constant}$, suggesting that the factors affecting the transmission of electronic effects in acid dissociation parallel those in the reactions of the acids with DDM. For systems of the type RGC00H, the link between ρ and the distance across G, the polarizability of G, or σ -values involving G are discussed. In some cases, field and mesomeric-inductive effects as embodied in the Kirkwood–Westheimer and Dewar–Gridale theories can generate observed rate or equilibrium properties.

Substitution in a molecule alters its reactivity. How does a substituent which is fairly remote from the site of reaction do this? The Hammett equation

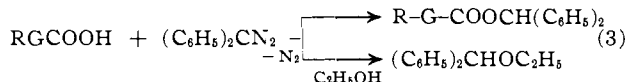
$$\log k = \rho\sigma + \text{constant} \quad (1)$$

seemed to answer this question for aryl systems. One could obtain a ρ -value which characterized the reaction, the reaction conditions (solvent, ionic strength, temperature, etc.), as well as the group G_i (often but not always equivalent to $-\text{C}_6\text{H}_4\text{T}_i-$) through which the electronic effect was relayed to the reaction site.² But after one calculated ρ appropriate to the experimental system, what did it mean?

In a previous paper it was shown that

$$\rho_{\text{RGC00H}}/\rho_{\text{RGCOS}} = \pi = \text{constant} \quad (2)$$

might be helpful in discussing ρ .³ Here the electronic effects are relayed through various groups G_i ; the reaction site in a given reaction, $-\text{COS}$, is being compared with $-\text{COOH}$ in acid dissociation. To date, line A of Fig. 1 for the hydrolysis of families of ethyl esters provided the only adequate test of eq. 2. Line B of Fig. 1 gives the available data for a second system.



In this work, rate studies are reported for the *trans*-cinnamic acids in process 3.

Results and Discussion

The kinetics and mechanism of the reaction of acids with diphenyldiazomethane (DDM) have been discussed.⁴ Suffice it to remark here that the comparison of

the slow proton-transfer process of eq. 3 with acid dissociation appears to be highly suitable for a test of the ρ - ρ relation (eq. 2).³

Rate data for the *trans*-cinnamic acids are given in Table I. For a wide range of substituents, the rate constants vary by a factor of only 3 to 4. The rate constants were determined at two temperatures chiefly

TABLE I
RATE CONSTANTS AND ACTIVATION PARAMETERS
FOR THE REACTION^a

R	k , l. mole ⁻¹ min. ⁻¹ ^b		ΔH^* , kcal. mole ⁻¹	$-\Delta S^*$, cal. deg. ⁻¹ mole ⁻¹
	(25.0 ± 0.1)°	(35.0 ± 0.1)°		
<i>p</i> -(CH_3) $_2\text{N}$	0.392 ± 0.024 ^c	1.01 ^d	16.6	8
2,4-(CH_3O) $_2$.346 ± 0.007 ^d			
<i>p</i> -OH	.679 ± 0.023	1.60 ± 0.02	15.1	12
<i>p</i> - CH_3O	.511 ± 0.019	1.20 ± 0.02	14.9	13
<i>p</i> - CH_3	.622 ± 0.003	1.34 ± 0.06 ^c	13.4	18
<i>p</i> - <i>i</i> -(CH_3) $_2\text{CH}$.645 ± 0.006	1.33 ± 0.08 ^c	12.6	21
H	.695 ± 0.041	1.52 ± 0.004 ^c	13.7	17
<i>p</i> -F	.693 ± 0.019	1.69 ± 0.023	15.6	10
<i>m</i> - CH_3O	.708 ± 0.017	1.48 ± 0.04	12.9	20
<i>p</i> -Cl	.785 ± 0.031	1.91 ± 0.04	15.6	10
<i>m</i> -F	.935 ± 0.017 ^c	1.96 ± 0.06	12.9	19
<i>m</i> -Cl	.891 ± 0.008	2.19 ± 0.08	15.8	9
<i>m</i> - CH_3COO	.873 ± 0.020	1.75 ± 0.10 ^c	12.1	22
<i>m</i> - NO_2	1.54 ± 0.02	3.62 ± 0.12	15.0	12
<i>p</i> - NO_2	1.42 ± 0.01 ^d	3.36 ± 0.15	15.1	11

^a For internal consistency, three significant figures have been retained; however see average deviations and uncertainties listed for each entry. ^b Average of 4 runs, except as indicated. ^c Average of 6–9 runs. ^d Average of 2–3 runs.

(1) Supported by the U. S. Army Research Office (Durham).

(2) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(3) R. A. M. O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 2440 (1963).

(4) J. D. Roberts and C. M. Regan, *ibid.*, **76**, 939 (1954), and previous papers.

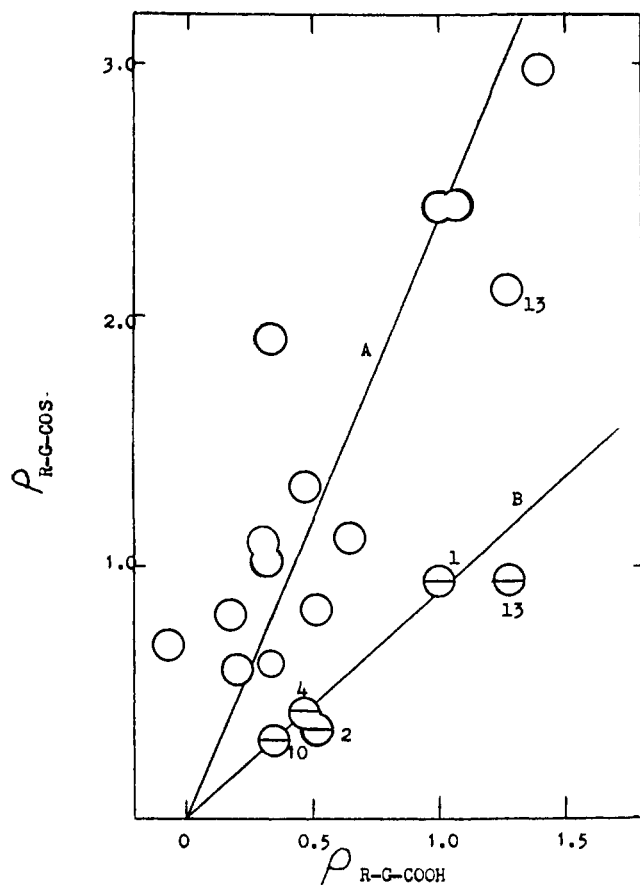


Fig. 1.— ρ - ρ relation: ρ_{RGCOOS} for reactions of acids or their derivatives vs. ρ_{RGCOOH} for the pK 's: A, the basic hydrolysis of $\text{RGCOOC}_2\text{H}_5$ in 88% ethanol at 30° ; B, the reaction of RGCOOH with DDM in ethanol at 30° . Numbers refer to the acids in Table III.

for the purpose of obtaining ρ at 30° . The calculations of the activation parameters listed in Table I were incidental to this work. It does appear, however, that the activation entropies are proportional to the enthalpies with a slope of *ca.* 298°. Review of the earlier data in the phenylacetic acid series also turns up a "compensation law" line of the same slope.³ From the point of view of entropy-enthalpy relations,⁵ the acid-DDM systems are certainly worth further investigation over a wider temperature range.

TABLE II

LINEAR CORRELATIONS FOR THE REACTION OF *trans*-CINNAMIC ACIDS WITH DIPHENYLDIAZOMETHANE

Temp., °C.	σ ^a	ρ	$\log k_0$ ^b	Std. dev. ^c	Correl. coeff. ^d	No. of compd. ^e
25	σ	0.411	-0.1705	0.0128	0.970	12
	σ^n	0.46	-0.1894	0.0075	0.959	6
35	σ	0.434	0.1757	0.0218	0.956	12
	σ^n	0.51	0.1382	0.014	0.935	6

^a See ref. 6 and 7. ^b Intercept of eq. 1. ^c Standard deviation. ^d Correlation coefficient. ^e Number of compounds used in correlation: 2,4-(CH_3O)₂, *p*-(CH_3)₂N, and *p*-OH were excluded in all cases.

Correlations of $\log k$ vs. σ -values based on the pK values of the benzoic⁶ acids were made (Table II). Acids with "difficult" substituents,² 2,4-(CH_3O)₂, *p*-

(5) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Chapter 9; R. F. Brown, *J. Org. Chem.*, **27**, 3015 (1962); R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(6) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(CH_3)₂N, and *p*-OH, were not included. We also made a limited correlation with so-called "normal" σ^n values which are presumed not to contain any contribution from the mesomeric interaction of the substituent with the reaction site.⁷ Both σ and σ^n had given satisfactory correlations for the pK data of the cinnamic acids.^{2,7} None of the present correlations was quite as good, and we are inclined to attribute this mainly to experimental errors. In any case, the value of ρ cannot be varied reasonably beyond the limits $\rho = 0.43 \pm 0.1$ at 35° even when selected data were omitted or special σ -values introduced.

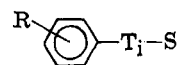
This study contributes point 4 of line B, Fig. 1, or $\rho = 0.42$ interpolated to 30° . Apart from the data for the *o*-methylbenzoic acids which were discussed previously,³ the agreement with the ρ - ρ relation is satisfactory, suggesting that electronic effects of the substituent are relayed to the reaction site in parallel fashion for both the acid dissociations and their reaction with DDM. Thus far, this applies whether the transmitting group G of RGCOOH is normal or abnormal according to any arbitrary criteria. The important point is that a mesomeric interaction through G might be expected to vary with the reaction and thereby throw off the ρ - ρ relation. If there is a weakness in this analysis, it surely stems from the low ρ values for the DDM reaction in ethanol where the transmission efficiency is 50%, $\rho_{\text{RGCOOS}}/\rho_{\text{RGCOOH}} = 0.5$.³ Clearly, reactions other than process 3, reactions with larger or negative ρ -values, should also be investigated.

Further Interpretations of ρ .—There is another set of meanings of ρ which reveals the interlocking of ρ with substituent constants. For example, in previous work the relation

$$\Delta\rho = q\Delta\sigma' \quad (4)$$

has been derived and illustrated for the multiple dependency $\log k = f(\sigma, \sigma')$ in which $\log k$ is separately linear in σ and σ' where $\sigma' = \sigma, \sigma^*, \sigma^+, \text{etc.}$ ^{3,8} Other workers have also provided interesting applications or tests of eq. 4.^{9,10}

Another fruitful line of argument¹¹⁻¹³ runs as follows. Consider that rate data for the system



in which T_1 is a side chain and S is a reaction site can be correlated either by the Hammett or Taft equations.¹⁴ Therefore

$$\log k/k_0 = \rho_1\sigma = \rho^*\sigma_1^* \quad (5a)$$

(7) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

(8) S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959); G. S. Krishnamurthy and S. I. Miller, *ibid.*, **83**, 3961 (1961).

(9) C. D. Ritchie, *J. Phys. Chem.*, **65**, 2091 (1961).

(10) C. D. Ritchie, W. F. Sager, and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 2349 (1962); C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *ibid.*, **83**, 4601 (1961).

(11) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

(12) M. Charton, Ph.D. Thesis, Stevens Institute of Technology; Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 92-O; Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 57T; *J. Org. Chem.*, **28**, 3121 (1963).

(13) W. F. Sager and C. D. Ritchie, *J. Am. Chem. Soc.*, **83**, 3498 (1961).

(14) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956. Chapter 13.

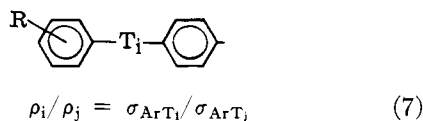
For another side chain

$$\log k/k_0 = \rho_j \sigma = \rho^* \sigma_j^* \quad (5b)$$

so that

$$\rho_i/\rho_j = \sigma_i^*/\sigma_j^* \quad (6)$$

Similarly, for the system



Because σ_{ArT} values are not generally available, only eq. 6 was tested. Since Taft has shown that σ^* is directly proportional to pK in the acids $R\text{COOH}$,¹⁴ we looked for a correlation between the pK of the parent acid and ρ for acid dissociation in the families $RG\text{COOH}$ so that in essence we were examining eq. 4 in the form

$$\Delta\rho = q\Delta\sigma^* \quad (4a)$$

Table III lists the data which were used to construct Fig. 2. Provided that the experimental data are not in error, the points which do not fall near the line clearly represent families to which either the Taft or Hammett equations or both do not apply. The omission of these points leaves a line which extrapolates at $\rho = 0$ to $pK \approx 5.0$, a value close to that observed for long chain acids.¹⁵ The slope of this line for eq. 4a is substantial at $q \approx 0.7$ with the sensitivity factor increasing as the acid strength increases. Since both positive and negative q values have been reported for eq. 4,^{3,8,10} this

TABLE III

PROPERTIES OF THE ACID FAMILIES, $RG\text{COOH}$

$RG\text{COOH}$	ρ (25°, water) ^a	pK (25°, water) ^{a,b}	r , cm. ^c
1. ArCOOH	1.00	4.20	15.5
2. ArCH_2COOH	0.519	4.312	16.5
3. $\text{ArCH}_2\text{CH}_2\text{COOH}$	0.212	4.66	21
4. trans-ArCH=CHCOOH	0.466	4.438	21.3
5. cis-ArCH=CHCOOH	0.643	3.879	14.6
6. ArCH=CHCOCOOH	-0.054	1.971 ^e	23.5
7. $p\text{-ArC}_6\text{H}_4\text{COOH}$	(0.34)		26
8. $\text{trans-ArCHCH}_2\text{CHCOOH}$	0.182	4.709	21
9. $\text{cis-ArCHCH}_2\text{CHCOOH}$	(0.32)		14.4
10. $\text{ArC}\equiv\text{CCOOH}$	(0.34)		21.8
11. 5-Furanyl acid	1.396	2.819	12.1
12. 5-Thienyl acid	1.076	3.49	12.5
13. $\text{R}(2\text{-CH}_3\text{C}_6\text{H}_3)\text{COOH}$	1.28	3.91 ^d	15.5
14. $\text{R}(2,6\text{-(CH}_3)_2\text{C}_6\text{H}_2)\text{COOH}$		3.25 ^d	15.5
15. $\text{ArOCH}_2\text{COOH}$	0.30 ^d	3.17 ^d	20.7
16. $\text{ArSCH}_2\text{COOH}$	0.40 ^d	3.53 ^d	(22.7)
17. $\text{ArSeCH}_2\text{COOH}$	0.35 ^d	3.9 ^d	(24)

^a Ref. 2 and 3 unless otherwise noted. Values in parentheses are estimates. ^b pK of parent acid, ref. 15. ^c This is the distance on Dreiding scale models (1 cm. = 0.4 Å.) from a *para* substituent to a point midway between the oxygen atoms of the carboxyl group when the whole molecule is fully extended and the aromatic nucleus and the carboxyl group are coplanar. ^d N. V. Hayes and G. E. K. Branch, *J. Am. Chem. Soc.*, **65**, 1555 (1943); O. Behaghel, *J. prakt. Chem.*, **114**, 287 (1926); O. Behaghel and M. Rollmann, *Ber.*, **62B**, 2693 (1929). ^e E. D. Stecher and H. F. Ryder, *J. Am. Chem. Soc.*, **74**, 4392 (1952).

(15) G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths & Co., London, England, 1961.

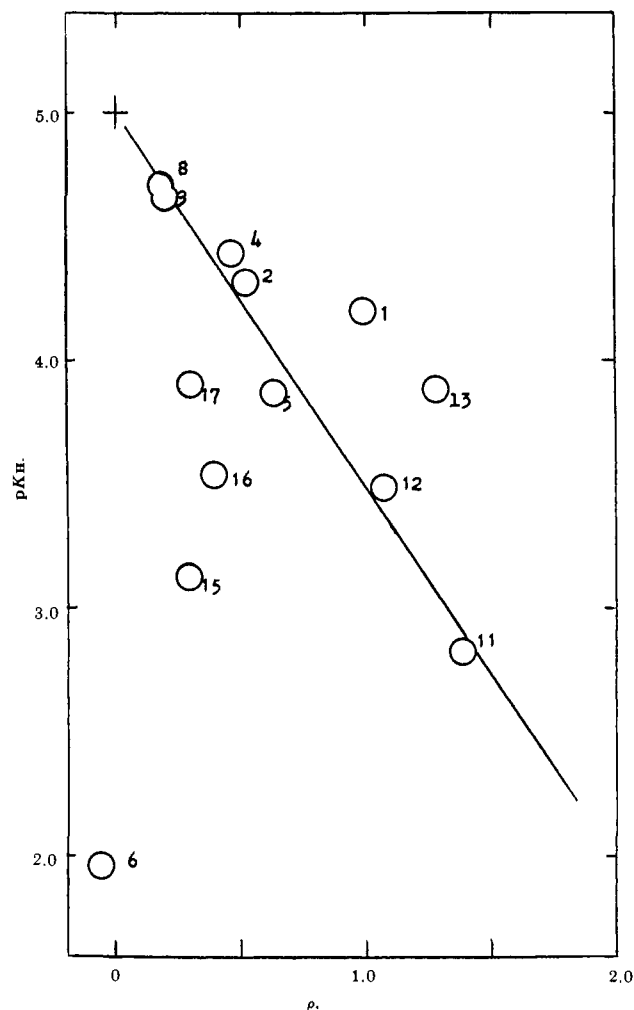


Fig. 2.—The ρ - ρ relation $\rho_i/\rho_j = \sigma_i^*/\sigma_j^*$, in which the ρ values derive from the pK values of $RG\text{COOH}$ (Table III) in water at 25° and the pK values of the parent acids are used for σ_{ArG}^* . The extrapolation to $\rho = 0$ is given by the symbol +.

result is not as odd as it might first appear. Finally, if one is hard-pressed, he can risk estimating other ρ -values from plots of this type.

Following an approach similar to that used by Hine,¹⁶ Sager and Ritchie developed the relation

$$\rho = \alpha^2(\sigma_{r_1} - \sigma_{r_2})/T \quad (8)$$

in which T is absolute temperature and σ_{r_1} and σ_{r_2} characterize the reaction site before and after reaction, e.g., σ_{COOH} and σ_{COO^-} .¹³ Equation 8 was elaborated more or less empirically to take into account the dielectric constant of the medium¹⁷ and the effect of atoms interposed between the substituent and the reaction site.¹⁸ With the further assumption that either ρ - or σ -values were proportional to group electronegativities, Sager and Ritchie were able to calculate rough ρ -values for the dissociations of oxygen acids of B, C, N, P, and S as well as ρ -values for several other equilibrium processes.^{10,13} For our present purpose, it is obvious that ρ - ρ relation 2 could also be derived from eq. 8; again there is the link between ρ and σ .

(16) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 4.

(17) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937).

(18) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1941, Chapter 6.

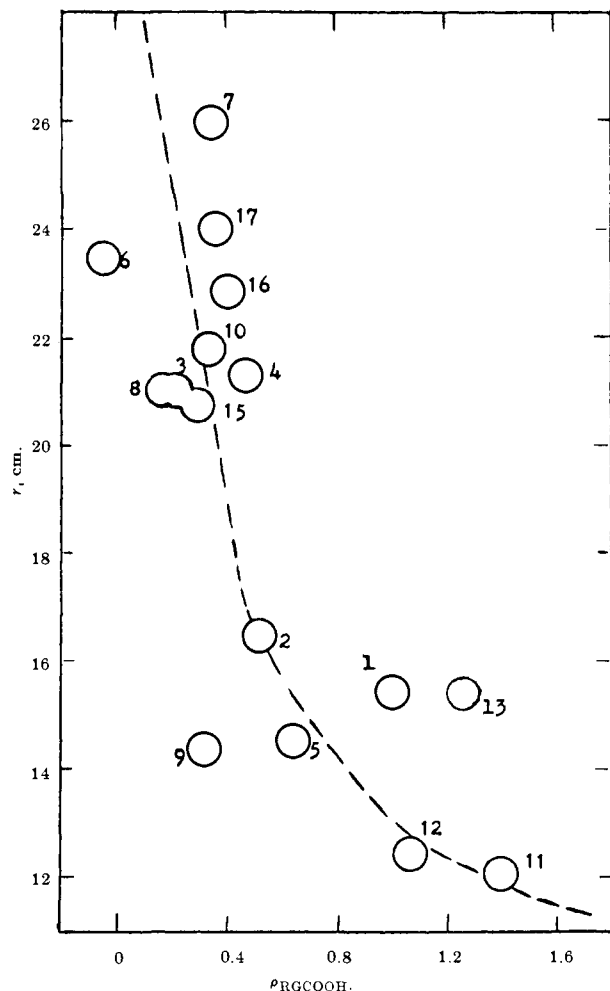


Fig. 3.—The variation of ρ for the pK values of acids in water at 25° with r , the distance from the *para* substituent to the carboxyl group in $RGCOOH$ ($1 \text{ cm.} = 0.4 \text{ \AA.}$). The acids are given in Table III.

In this section a number of sufficient but not exclusive conditions for the existence of ρ - ρ relations was indicated. Provided that linear free energy relations are applicable, eq. 4, 6, 7, and 8 all show that ρ and σ are made of the same stuff. *How effectively a group as substituent responds to the electronic demands of a reaction site is tied up with the ease with which it relays electronic effects from a substituent to a reaction site.* When a single linear free energy relation breaks down, e.g., when there is strong conjugation between the substituent and the site, either ρ or σ or both may be considered as the source of the difficulty. When a linear free energy relation does apply in a given case but its ρ departs from eq. 2 or 6, we are compelled to isolate it. Of course, the slope and intercept parameters may be valuable empirically and may even provide an indication of the cause of the deviation from relation 2 or 6. Finally, ρ - ρ relation 2 seems to be followed by several families. This suggests that there is a systematic basis underlying their behavior which should be investigated by approaches independent of linear free energy relations.

Polarizability.—In the series RG_iCOOH , how does the polarizability of G_i affect ρ ? Several years ago, Jaffé showed that the ρ -values for the acids $ArMO_nH_m$ ($M = B, C, P, As$) increase as the ionic refractivities of M increase.² For the series $ArTCH_2COOH$ ($T =$

NH, CH_2, NH_2^+), the ρ -values also increase as the polarizabilities of T increase.¹⁹ By contrast, the ρ -values for the infrared carbonyl frequency of the esters $ArTCOCH_2CH_2C_6H_5$ ($T = O, S, Se, Te$) do not vary although $\nu_{C=O}$ (cm.^{-1}) values for the unsubstituted compounds do follow the order $O > Se > S > Te$.²⁰ Likewise, there is little if any variation in ρ for dissociation of $ArTCH_2COOH$ ($T = O, S, Se$) as given in Table III. To clarify this question we have made a plot of the molar polarizability²¹ of RG_i vs. ρ . Unlike Jaffé's series, ρ increases rather irregularly as the polarizability decreases. As a trend this is really not surprising since the molar polarizability increases roughly as the size of G or the distance r across it; and we would expect ρ to decrease as r increases. A plot of ρ vs. r in Fig. 3 shows that this inverse dependence is crude at best; nor can it be improved by using r^{-2} , r^{-3} , etc. Clearly, the link between ρ and the polarizability of the group G , though real, is rather indefinite.

Electrostatic Approach.—The Kirkwood–Westheimer (K.W.) theory appears to provide the most fundamental treatment of the interaction of charges or dipoles in solution.^{22–25} Not that it is uniformly successful, but it is true that other coulombic approaches have had only limited application to structure–reactivity problems.^{2, 17, 26} The effect on an ionization rate or equilibrium process of a polar substituent as compared with a nonpolar standard, hydrogen, is given by

$$-\Delta F = RT \ln k/k_0 = \frac{q\mu \cos \theta}{D_E r^2} \quad (9)$$

where θ is the angle between the dipole axis and the line joining the charge to the dipole and r is the distance between them. D_E is a dielectric constant parameter which depends on the shape of the cavity enclosing the interacting species, on the depth of the charges or dipoles within the cavity, on D_i the dielectric constant within the cavity, and on D_0 the dielectric constant of the medium. (For a charged substituent, one inserts q_i' for $r^{-1}\mu \cos \theta$.)

In several pioneering papers Westheimer indicated how versions of eq. 9 could be applied to structure–reactivity problems. For example, the effect of *para* substituents on the pK values of benzoic and phenylacetic acids and on the rate constants for hydrolysis of their ethyl esters could be calculated.²³ Accompanying these successes was recognition of some limitations and deficiencies of the theory: systems with strong conjugation such as phenols,²³ systems subject to steric effects or conformational variation such as *m*-phenylacetic acids,^{23, 24} systems having strong intramolecular hydrogen bonding,²⁷ or systems subject to specific solvent effects²⁸ could not be treated. Although these

(19) A. Bryson, N. R. Davies, and E. P. Serjeant, *J. Am. Chem. Soc.*, **85**, 1933 (1963).

(20) J. Gosselek, *Z. Naturforsch.*, **16**, 404 (1961).

(21) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 3, p. 10.

(22) J. G. Kirkwood and F. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

(23) F. H. Westheimer, *J. Am. Chem. Soc.*, **61**, 1977 (1939); **62**, 1892 (1940).

(24) C. Tanford, *ibid.*, **79**, 5348 (1957).

(25) M. Charton of Pratt Institute is currently applying K.W. theory to structure–reactivity problems.

(26) G. A. Gallup, W. R. Gilkerson, and M. M. Jones, *Trans. Kansas Acad. Sci.*, **55**, 232 (1952).

(27) L. Ebersson, *Acta Chem. Scand.*, **13**, 211 (1959).

(28) C. D. Ritchie and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 591 (1962).

complications would probably be too difficult to incorporate into even an approximate structure-reactivity theory, we examined what seemed to be several simple systems.

We believed that the K.W. model might lead to a prediction of ρ . By combining eq. 1 and eq. 9 for two transmitting groups in ArT₁—one obtains

$$\rho/\rho' = \frac{D_E' r'^2 \cos \theta}{D_E r^2 \cos \theta'} \quad (10)$$

The ratio $\cos \theta/D_E r^2$ can be regarded as a parameter which Westheimer adjusted to give the best calculated set of p*K* values for a given family.²³ Optimizing this ratio means that the geometry, conformation, solvent, and other specific effects have effectively been averaged. The results of combining these ratios are given in Table IV. Relative to ArCOS the field effect overestimates ρ . Clearly the predictions of eq. 10 are unreliable.

TABLE IV

THE KIRKWOOD-WESTHEIMER THEORY IN THE EVALUATION OF

	$\rho/\rho' = \frac{(\cos \theta)}{r^2 D_E} / \frac{(\cos \theta')}{r'^2 D_E'}$				
	$\cos \theta^a$	r^a	D_E^a	(ρ/ρ') calcd.	(ρ/ρ') obsd. ^b
ArCOOH	1	5.9	9.4		
ArCH ₂ COOH	0.90	6.6	10.9	0.62	0.52
ArCH ₂ CH ₂ COOH	0.99	7.7	17	0.32	0.21
ArCH=CHCOOH	0.99	6.3	11	0.74	0.47
ArCOOC ₂ H ₅	1	5.2	28		
ArCH ₂ COOC ₂ H ₅	0.92	6.1	28	0.67	0.34
ArCH ₂ CH ₂ COOC ₂ H ₅	0.99	7.2	28	0.52	0.20
ArCH=CHCOOC ₂ H ₅	0.99	6.1	28	0.68	0.54

^a Data taken from ref. 23. ^b From Table III.

In fitting p*K* data for 4-substituted bicyclo[2.2.2]-octane-1-carboxylic acids, Tanford showed that each acid required its own r and D_E parameters.²⁴ Such a refined version of the K.W. theory may be necessary but then it has probably become too sensitive or too "fundamental" for our application. Since a given ρ represents the behavior of a family of compounds, it would appear that the theoretical basis of ρ must need to be based on average properties.

The *F*-*M* Method.—Dewar and Grisdale (D.G.) have recently presented a quantitative theory of substituent effects.²⁹ When strong conjugation is absent, they suggest a dependence on field effect (*F*) and inductive-mesomeric (*M*) terms

$$\log k/k_0 = \rho_{\text{ArCOS}} \sigma_{ij} = F/r_{ij} + Mq_{ij} \quad (11)$$

where r_{ij} is the distance from substituent to reaction site given in aryl C-C bond lengths and q_{ij} is the formal charge at the site produced by the substituent.³⁰ By using the usual σ -values⁶ and ρ -values from the system ArCOS as standards, they evaluated *F* and *M* for various substituents. These *F*, *M*, and appropriate r_{ij} and q_{ij} values were then used to predict rate and equilibrium data rather successfully in the naphthalene and biphenyl series. Although Dewar and Grisdale restricted their treatment to rigid systems, we believed that this would limit its utility severely. In fact, if r_{ij} were strongly variable within a family because of

(29) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

(30) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 54 and Chapter 5.

conformational variation in the side chain, for example, one would not expect eq. 1 to apply. In any case it was of interest to see what the limits of the *F*-*M* theory might be.

Therefore, we tested the *F*-*M* approach on some of the p*K* data. To obtain precise values of $(\rho\sigma)_{\text{obsd}}$ we used measured p*K* values relative to the parent acid.^{15,31-33} The comparisons are given in Table V. For the 5-furoic acids, r_{ij} was taken from the known geometry of furan³⁴ and q_{ij} was taken as $1/5$. A similar comparison was made for the 5-thienyl compounds with $r_{ij} = 1.77$ and $q_{ij} = 1/6.5$ except that the "observed" $\log K/K_0$ values were calculated from a reported ρ .³² Although the q_{ij} values are predetermined by the type of cyclic system, the theory is not applicable³⁰ to furan and thiophene so that we simply assigned q_{ij} on the basis of best fit. It turns out that these q_{ij} values are reasonable in comparison with $q_{ij} = 1/7$ for benzene and that there is a satisfactory correspondence between observed and calculated relative p*K* values.

The phenylpropionic acids provided a critical test of the *F*-*M* theory because the structures are rigid and r_{ij} and q_{ij} are fixed. The discrepancies between observed and calculated relative p*K* values in Table V are generally large—it must be admitted that the theory fails for this family.

For the remaining families, the q_{ij} are nondisposable parameters. The values to be used for r_{ij} are somewhat uncertain, particularly with *meta* substituents; therefore two *meta* r_{ij} extremes were tested. Agreement with experimental values ranges from fair in the cinnamic and phenylacetic to poor in the phenylpropionic acids. For the *para* acids, at least, it cannot be claimed that the uncertainty in r_{ij} was the root of the discrepancies. In general, the r_{ij} was a maximum and any shorter distance would lead in most cases to wider disagreement. These tests of the *F*-*M* theory must be regarded as acceptable.

When the mesomeric-inductive effect is important ($q_{ij} > 0$), the *F*-*M* approach fails in some rigid systems, e.g., ArC≡CCOOH, and possibly succeeds in others, e.g., ArCH=CHCOOH and the 5-furoic acids. As no distinction was made in the q_{ij} for the phenylpropionic and cinnamic acids, agreement in detail is not to be expected. When $q_{ij} = 0$, the theory fails in some non-rigid systems, e.g., ArCH₂CH₂COOH, and succeeds in others, e.g., ArCH₂COOH. It is possible that a portion of these discrepancies may also be ascribed to the uncertainty in the field effect term of eq. 11 which essentially includes the whole K.W. effect (eq. 9). It was anticipated that variations in the shape of the K.W. cavity should lead to variations in D_E ^{24,29} for different families (see Table IV) and should lead to variation in the *F* values of substituents. Indeed, the predicted relative p*K* values of the phenylpropionic acids are too high by the *F*-*M* approach and would naturally be reduced if the effect of an increased D_E were included in the *F*-values. Despite these criticisms, the *F*-*M* approach appears to be a useful development of the theory of the Hammett equation.

(31) W. E. Catlin, *Iowa State Coll. J. Sci.*, **10**, 65 (1955).

(32) E. Imoto and Y. Otsuji, *Bull. Osaka Prefecture*, **A6**, 115 (1958).

(33) (a) J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955); (b) I. Solomon and R. Filler, *ibid.*, **85**, 3492 (1963).

(34) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publishers, Inc., New York, N. Y., 1960, pp. 79, 104.

TABLE V
 A TEST OF THE *F-M* APPROACH OF DEWAR AND GRISDALE ON THE RELATIVE *pK* VALUES OF RCOOH^a

	5-Furyl ^b		ArC≡C ^c		<i>trans</i> -ArCH=CH ^d		ArCH ₂ COOH ^e		ArCH ₂ CH ₂ COOH ^f	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
<i>m</i> -CH ₃					0.00	-0.03, -0.04			-0.02	-0.03, -0.04
<i>p</i> -CH ₃	-0.30	-0.23			0.13	-0.10	-0.07	-0.04	-0.02	-0.03
<i>m</i> -Cl			0.15	0.27	0.14	0.19, 0.21	0.16	0.23	0.07	0.18, 0.22
<i>p</i> -Cl	0.29	0.27	0.11	0.15	0.02	0.11	0.11	0.20	0.05	0.18
<i>p</i> -Br	0.28	0.28					0.12	0.22		
<i>m</i> -NO ₂			0.31	0.51	0.32	0.34, 0.40	0.34	0.44	0.19	0.34
<i>p</i> -NO ₂	1.06	1.01	0.32	0.61	0.39	0.43	0.45	0.39	0.01	0.06, 0.07
<i>m</i> -CH ₃ O					0.06	0.06	-0.06	0.06	-0.03	0.05
<i>p</i> -CH ₃ O					-0.10	-0.18				
<i>p</i> -F			0.08	0			0.06	0.18		
<i>m</i> -CF ₃			0.24	0.31						
<i>p</i> -CF ₃			0.27	0.43						
	0.19 ^g	0.22	0.10 ^h	0.24	0.04 ⁱ	0.06, 0.07	-0.11 ^j	-0.05		

^a *pK* values relative to *pK* for R = H in water at 25° except as noted^{15,31,32}; $\rho \equiv 1.00$. ^b *r*_{ij} = 1.57, *q*_{ij} = 1/6. ^c *para* *r*_{ij} = 4.1, *meta* *r*_{ij} = 3.7, *q*_{ij} = 1/11, $\rho = 1.51$,² *pK* values in 50% ethanol.³³ ^d *para* *r*_{ij} = 4, *meta* *r*_{ij} = 3.6 or 3.1, *q*_{ij} = 1/11. ^e *para* *r*_{ij} = 3.2, *meta* *r*_{ij} = 2.8, *q*_{ij} = 0. ^f *para* *r*_{ij} = 3.7, *meta* *r*_{ij} = 3.6 or 3.0, *q*_{ij} = 0. ^g 5-I. ^h *m*-F. ⁱ *m*-OH. ^j *p*-*t*-C₄H₉.

Conclusions

Within the scope of linear free energy relations there is a rigorous phenomenological framework, *e.g.*, the ρ - ρ relations or the extended treatment of multiple linear correlations.⁸ Data can be stored compactly in analytical form and new data can be predicted. The self-consistency of the linear free energy relations and the implications of the parameters; *e.g.*, the Hammett ρ , Jaffé's ρ - ρ ratio π (eq. 2), and our cross-term *q* for dual linear variations can be examined and compared all *within* this framework.

Beyond and *outside* of methodology are the K.W. and D.G. approaches. The theories overlap in that they both emphasize a strong field effect contribution to substituent effects. In addition, the mesomeric-inductive effect is included by the D.G. approach. Both theories show only limited success to date but are presumably susceptible to refinement. Obviously more data are sorely needed to assess their value and guide their development. But their apparent failures in reproducing the parameters of linear free energy relations should not be taken in a negative sense. We are inclined to believe that the theoretical content and interpretation of these line parameters have been oversimplified. Structure-reactivity is a multidimensional problem!

Experimental

The procedure used in studying the reaction of DDM with the *trans*-cinnamic acids has been described in detail.³ The properties of the acids are given in Table VI. In the kinetic runs, the change in optical density of the DDM at 525 m μ was usually 0.6-2.7 units and was generally followed in a Cary Model 11 PM recording spectrophotometer. Although the temperature within the cell compartment was generally held to $\pm 0.1^\circ$, the actual temperature within the reaction cell was probably less well-known. The acid to DDM concentration was generally greater than 10:1 so that pseudo-first-order kinetics applied. The *p*-nitro- and dimethylaminocinnamic acids had low solubilities so that their concentrations were comparable to those of the DDM. Here the rate data was analyzed for a conventional

TABLE VI

THE *trans*-CINNAMIC ACIDS

Substituent	Equiv. wt.		Melting point, °C.	
	Calcd.	Found	Lit.	Found
<i>m</i> -CH ₃ O	178.2	180.5	117 ^a	118-118.5
<i>m</i> -CH ₃ COO	206.2	204.5	151 ^b	156-158
<i>p</i> -CH ₃ O	178.2	177.1	171 ^c	175
<i>m</i> -Cl	182.6	181.0	167 ^d	163.5-164.5
<i>p</i> -OH	164.2		206 ^e	209.5-212
<i>p</i> -Cl	182.6	182.4	247 ^a	248-249
<i>p</i> -(CH ₃) ₂ CH	190.1	190.1	157-158 ^f	159-160
<i>m</i> -F	166.1	167.2	166.5 ^g	166-167
<i>p</i> -F	166.1	170.1	208 ^a	209
<i>p</i> -CH ₃	162.2	161.9	199 ^d	198
<i>m</i> -NO ₂	193.2	197	202-204 ^c	204
<i>p</i> -NO ₂	193.2	184 ^h	286 ^c	286
<i>p</i> -N(CH ₃) ₂	190.2	185 ^h	225 ^h	226-227
2,4-(CH ₃ O) ₂	208.2	207	186 ⁱ	184-186
H	148.2	148.2	133 ^g	134

^a G. Locke and E. Bayer, *Ber.*, **72**, 1064 (1939). ^b F. Tiemann and R. Ludwig, *ibid.*, **15**, 2043 (1882). ^c E. Knoevenagel, *ibid.*, **31**, 3596 (1898). ^d J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938). ^e F. von Konek and E. Pascu, *Ber.*, **51**, 855 (1918). ^f W. H. Perkin, *J. Chem. Soc.*, **31**, 388 (1877). ^g G. Schiemann and W. Winkelmüller, *J. prakt. Chem.*, [2] **135**, 101 (1932). ^h C. W. Shoppee, *J. Chem. Soc.*, 968 (1930). ⁱ W. H. Perkin and E. Schiess, *ibid.*, **85**, 159 (1904).

second-order process. Typically, rate data for cinnamic acid were obtained with 0.083-0.187 *M* acid and *ca.* 0.0032 *M* DDM while for the *p*-nitrocinnamic acid the data were obtained with 0.0032-0.0035 *M* acid and 0.007-0.0014 *M* DDM. All of the kinetic data are collected in Table I.³⁵

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(35) NOTE ADDED IN PROOF.—The publication of this paper was delayed because it went astray in the editorial files. Citing unpublished data, K. Bowden gives $\rho = 0.416$ for the DDM reaction of the cinnamic acids in ethanol at 30° (*Can. J. Chem.*, **41**, 2781 (1963)). Bowden also applies K.W. theory to several systems.