tion of the peroxide gave *o*-iodosobenzoic acid, *p*-nitrobenzoic acid, and an estimated 60% yield of compound IV. Decomposition of the peroxide in benzene at 50° or heating compound IV gave a highly insoluble substance (VIII) believed to be the noncyclic polymer of IV.

Compounds IV *and* VIII. To 8 g. of *o*-iodobenzoic acid dichloride suspended in methylene chloride was added 15.2 g. of silver *p*-nitrobenzoate and the mixture was then extracted with hot methylene chloride. The filtrate was concentrated to dryness and extracted with ether to remove *p*-nitrobenzoic acid. The residue was essentially pure IV, but could be recrystallized from methylene chloride if necessary. Compound IV showed some signs of decomposition at 200° and melted with decomposition at 204–205°. The infrared spectra in Nujol of the synthetic material and the material from the decomposition of the peroxide were nearly identical and had the following bands: 1715s, 1630s, 1330s, 1270s, 1240s, 1120s, 842m, 742s, 723s cm.$^{-1}$. The spectrum of the closely related compound (II) from the decomposition of bis(*o*-iodobenzoyl) peroxide was very similar and had the following bands: 1695s, 1610s, 1320s, 1270s, 1230s, 1110s, 738s cm.$^{-1}$. Both spectra closely resembled that of the cyclic acetyl derivative of *o*-iodosobenzoic acid.

Anal. of Compound IV: Calcd.: Active oxygen, 3.87. Found: Active oxygen, 3.90.

Hydrolysis of compound IV in water at 60° for 3 hr. gave an equimolar mixture of *o*-iodosobenzoic acid and *p*-nitrobenzoic acid. Reduction of compound IV gave *o*-iodobenzoic acid and *p*-nitrobenzoic acids in equimolar amounts.

Heating compound IV in benzene at 50° for 2 hr. converted it in about 50% yield to the polymeric material compound VIII. Melting point (dependent on rate of heating) was varied from 214–216° to 219–221°. Compound VIII was remarkably stable against hydrolysis in water, but was quantitatively reduced by a mixture of sodium iodide and sodium sulfite in methanol, acidified with hydrochloric acid, to an equimolar mixture of *o*-iodobenzoic acid and *p*-nitrobenzoic acid. Compound VIII dissolved readily in warm acetic acid giving a precipitate of *o*-iodosobenzoic acid on addition of petroleum ether.

Anal. Calcd. for ($C_{14}H_8O_6NI$): C, 40.70; H, 1.95; N, 3.39; active oxygen 3.87. Found: C, 40.52; H, 1.68; N, 3.25; active oxygen 3.86.

The infrared spectrum of compound VIII in Nujol differed somewhat from that of compound IV and had the following bands: 1690s, 1660s, 1525s, 1270s, 1240s, 1120s, 1110s, 842m, 765s, 723s cm.$^{-1}$.

Decomposition of the peroxide in acetone. Heating 0.150 g. of the peroxide in 10 cc. of acetone for 2 hr. at 50° gave a precipitate of 0.060 g. of *o*-iodosobenzoic acid.

Decomposition of the peroxide in thionyl chloride. The peroxide was reduced by this reagent to a mixture of *o*-iodobenzoyl chloride and *p*-nitrobenzoyl chloride. In contrast to *p*-methoxy-*p*′-nitrobenzoyl peroxide[3] it did not appear to give the carboxy inversion reaction.

Decomposition of the peroxide in the presence of acids. In benzene containing acetic acid a precipitate of *o*-iodosobenzoic acid was formed. In benzene containing chloroacetic or trichloroacetic acid precipitates were also formed. These substances have been tentatively identified as the chloroacetyl and trichloroacetyl derivatives of *o*-iodosobenzoic acid. Their infrared spectra in Nujol resembled that of the acetyl derivative of *o*-iodosobenzoic acid.

Polymerization experiments. A solution of 0.050 g. of the peroxide in 5 cc. of acrylonitrile at room temperature quickly became opaque and began to deposit solid polymer within 2 min., followed shortly by a rapid exothermic reaction converting almost all of the acrylonitrile to solid polymer. Solutions of 0.09 g. of the peroxide in 4 cc. portions of mixed nitrobenzene and acrylonitrile (1:2, 1:1, and 2:1 proportions by volume) became warm and appeared to give complete polymerization within 15 min. Nitrobenzene retarded the initiation of polymerization by benzoyl peroxide. Compound IV did not initiate the polymerization of pure acrylonitrile at room temperature.

Decomposition in the solid state. The solid peroxide on standing at room temperature showed no significant change in its infrared spectrum in Nujol in 24 hr., but appeared to be about half decomposed in 2 weeks.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STEVENS INSTITUTE OF TECHNOLOGY]

Application of the Hammett Equation to Acetylenic Systems[1a,b,c]

MARVIN CHARTON

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Ionization constants of 3-substituted propiolic acids, rates of alkaline hydrolysis of 3-substituted ethyl propiolates, and dipole moments of substituted acetylenes, 1-hexynes, 1-heptynes, and cyanides are correlated with the Hammett equation using the σ_p substituent constants. Transmission of substituent effects through the *trans*-vinylene, acetylene, and *p*-phenylene groups is in the order *p*-phenylene≪acetylene < *trans*-vinylene.

The Hammett equation, Equation 1, has been widely applied to the correlation of rate and equilibrium data, and of certain physical properties, for *meta*- and *para*-substituted benzene reaction series.[2,3] The Hammett equation has also been applied to heterocyclic systems including furan, thiophene and pyridine.[2,4,5] Recently it has been shown that the Hammett equation is directly applicable to olefins, using the σ_p constants.[6–8]

$$\log \frac{K_X}{K_H} = \rho\sigma_X \qquad (1)$$

(1a) Presented at the 136th Meeting, ACS, Atlantic City, September 1959.

(1b) Abstracted from part of the doctoral dissertation of M. Charton, Stevens Institute of Technology, Hoboken, N. J.

(1c) Present address: Dept. of Chemistry, Pratt Institute, Brooklyn 5, N. Y.

(2) L. P. Hammett, *Physical Organic Chemistry,* McGraw-Hill Book Co., New York, 1940, pp. 118–123.

(3) H. H. Jaffé, *Chem. Revs.* **53**, 191 (1953).

(4) E. Imoto and Y. Otsuji, *Bull. Univ. Osaka Prefect.,* Ser. **A, 6,** 115 (1958).

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TABLE I

1. Ionization constants of 3-substituted propiolic acids[a]

Substituent	CH_3	C_2H_5	C_4H_9	t-C_4H_9	C_6H_5	CO_2H	CO_2^-	H^b
$K.10^3$	2.56	2.47	2.50	2.21	5.88	70.7	3.55	14.5
Ref.	11	11	11	11	11	12	12	11

2. Rates of alkaline hydrolysis of ethyl 3-substituted propiolates[a,c]

Substituent	H	CH_3	CO_2^-	$CO_2C_2H_5$
k.10	4.68	0.568	2.40	69.0
Ref.	13.	13	14	14

3. Dipole moments of substituted acetylenes[d,e]

Substituent,	H	CH_3	C_2H_5	C_3H_7	C_4H_9	C_2H_5O	C_4H_9O	Cl
μ	0^e	$(-)0.74^e$	$(-)0.80^e$	$(-)0.85^e$	$(-)0.88^e$	$(-)1.98$	$(-)2.03$	0.44^f

4. Dipole moments of 1-substituted hexynes

Substituent	H	Cl	Br	I	CN	Ac	CHO^f
μ	$(-)0.88^e$	1.23	1.1	0.8	4.21	3.2	3.2

5. Dipole moments of 1-substituted 1-heptynes

Substituent	H	Cl	Br	I	CN	Ac	CHO^f
μ	$(-)0.86^e$	1.27	1.1	0.8	4.22	3.2	3.2

6. Dipole moments of substituted cyanides[f]

Substituent	H	CH_3	C_2H_5	C_3H_7	C_4H_9	Cl	CN	$C_6H_5^g$
μ	2.93^e	3.94^e	4.00^e	4.05^e	4.09^e	2.80^e	0^e	4.39

[a] All data in water at 25°. [b] Wilson and Wenzkie[15] report a value of 14.1×10^{-3}. [c] Units of k in series 2 are l/mole sec. [d] All dipole moments taken from Ref. 16. [e] (−) indicates sign used in correlation. [f] Not included in correlation. [g] Determined in vapor state; all other values in solution.

Data for two ferrocene and one azulene reaction series[9] are also correlated by the Hammett equation. The applicability of the Hammett equation to olefins suggested the possible extension to acetylenic reaction series in which the substituent is directly attached to the triply bound carbon atom.[10a,b] A search of the literature revealed sufficient data for the correlation of five acetylenic reaction series; the data used in the correlations are shown in Table I."

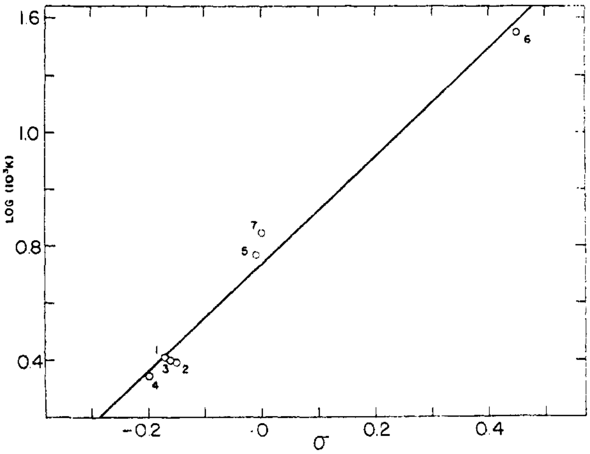

Fig. 1. Log 10^3K *vs.* σ for ionization constants of 3-substituted propiolic acids. The substituents are: 1. CH_3, 2. C_2H_5, 3. C_4H_9, 4. t-C_4H_9, 5. C_6H_5, 6. CO_2H, 7. CO_2^-.

RESULTS AND DISCUSSION

Correlations. The correlations were made by the method of Jaffé[3] using the σ_p substituent constants taken from the computations of Jaffé, and McDaniel and Brown.[17] The results of these correlations are shown in Table III. A plot of log K for the ionization of 3-substituted propiolic acids against σ_p is shown in Fig. 1. The correlation is reasonably good in view of the fact that the data

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(8) J. Hine and W. C. Bailey, *J. Am. Chem. Soc.*, **81**, 2075 (1959).

(9) Ferrocene series: E/4 values of substituted ferrocenes, O. E. Bublitz, G. Hoh, and T. Kuwana, *Chem. & Ind.* (*London*), 635 (1959); ionization constants of substituted ferrocene carboxylic acids, A. Nesveyanov and O. A. Reutov, *Doklady Akad. Nauk. S. S. S. R.*, **115**, 578 (1957); Azulene series: E0.5 values for 1-substituted azulenes; W. Triebs and K. Grundel, *Chem. Ber.*, **91**, 143 (1958).

(10a) M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955).

(10b) J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955), have studied reaction series of the type $XC_6H_4C{\equiv}CY$ where the substituent X is attached to a phenylene group and the C≡C group is a side chain joining the phenylene group and the reaction site Y.

(11) G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4761 (1956).

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(13) E. A. Halonen, *Acta Chem. Scand.*, **9**, 1492 (1955).

(14) E. Tommila and A. Kivinen, *Suomen Kemistilehti* **B27**, 1 (1954).

(15) C. J. Wilson and H. H. Wenzkie, *J. Am. Chem. Soc.*, **57**, 1266 (1935).

(16) C. P. Smyth, *Dielectric Behavior and Structure*, McGraw-Hill Book Co., Inc., New York, 1955.

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

TABLE II

Reaction Series[a]	ρ	r[b]	s[c]	n[d]	Q_H[e]
1	1.891	0.990	0.0161	7	2.39
2	2.690	0.965	0.239	4	1.40
3	4.707	0.927	0.344	8	(−)0.30
4	7.982	0.988	0.312	6	(−)0.89
5	7.958	0.987	0.317	6	(−)0.87
6	−4.860	0.981	0.316	7	3.30

[a] Numbers refer to Table I. [b] Correlation coefficient. [c] Standard deviation. [d] Number of compounds in series. [e] 1. $-\log K_H$ calculated; 2. $\log K_H$ calculated; 3., 4., 5., 6., μ_H calculated.

in each reaction series came from more than one source.

Ionization constants and hydrolysis rates. In the case of the first and second ionization constants of acetylenedicarboxylic acid, the values used were obtained by graphical extrapolation of data obtained by M. L. Dondon[12] in aqueous methanol and aqueous ethanol. It should be noted that Ashton and Partington[18] have reported values of 1.85×10^{-2} for the first and for the second ionization constant of acetylenedicarboxylic acid. These values differ considerably from those used in the correlation.

Dondon has reported that the results of Ashton and Partington are confirmed for acetylenedicarboxylic acid dihydrate, but were not obtained with the anhydrous acid. The values used in the correlations are extrapolated from values for the anhydrous acid. The value for the unsubstituted acid reported by Wilson and Wenzkie[15] and by Mansfield and Whiting,[11] appears to deviate considerably from the best line for the other points, and has not been included in the correlation.[19]

Statistical factors of $^1/_2$ and 2 were used with the first and second dissociation constants, respectively, of acetylenedicarboxylic acid. A statistical factor of $^1/_2$ was also required for the rate of alkaline hydrolysis of diethyl acetylene-dicarboxylate.

Dipole moments. Taft[20] has used Equation 2 to correlate the dipole moments of alkyl chlorides, iodides, cyanides, and tertiary amines with the σ^* constants.

$$\mu_X - \mu_H = \rho^*\sigma_X^* \tag{2}$$

Kross and Fassel[21] have used a similar equation, 3, to correlate the dipole moments of *para*-substituted nitrobenzenes

$$\mu_X - \mu_H = \rho\sigma_X \tag{3}$$

Van Beek[22] has recently reported the correlation of dipole moments of disubstituted benzenes with Equation 4.

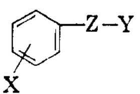
$$\log \frac{\mu_X}{\mu_H} = \rho\sigma_X \tag{4}$$

The correlations in this paper were made with Equation 4.

The dipole moments of substituted cyanides have also been correlated with the σ_p constants. They were studied because cyanides may be considered heteroanalogs of alkynes just as pyridines are heteroanalogs of benzenes.

In performing the correlations, the dipole moments were given signs indicative of the direction of the moment. The values for the formyl substituent in the 1-substituted 1-hexyne and the 1-substituted 1-heptyne reaction series were not included in the correlation, as the value of σ_p for the formyl group given by Jaffé appears to be too low when compared with the values of the acetyl, benzoyl, and carbomethoxy groups. A value of about 0.45 for σ_p for this substituent seems more likely. Goering and Jacobson[23] have suggested a value of 0.465 for σ_p^+ for the formyl group. For electron-withdrawing substituents, σ_p and σ_p^+ values are approximately equal.

Transmission of substituent effect. It is of considerable interest to compare the transmission of substituent effects through the benzene ring and the double bond. The problem of transmission of substituent effects through a group was first discussed by Jaffé.[3] He proposed that the effect of the group Z, in compounds of type I, on the transmission of substituent effect to the reaction site was given by ρ_{ZY}/ρ_Y where ρ_{ZY} is the reaction constant for a reaction series of type I undergoing some reaction with specified conditions, and ρ_Y is the reaction constant for the reaction series in which Y is attached directly to the ring, undergoing the same reaction under the same conditions. This treatment may be extended to any reaction series of type II, provided that the same substituent constants have been used in all correlations. By choosing some group G_0 as a standard group, transmission of substituent effects through some



I

X–G–Y

II

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[18] H. W. Ashton and J. B. Partington, *Trans. Faraday Soc.*, **30**, 548 (1934).

[19] It has been pointed out by one of the referees that σ_p values depend upon bonding of substituent to a carbon atom in sp^2 hybridization, whereas in substituted propiolic acids the substituent is bonded to a carbon atom in sp hybridization. It is well known that the apparent electronegativity of carbon varies with the hybridization state. Correlation with the σ_p substituent constants would require that replacement of sp^2 carbon by sp carbon shift the electronegativity of all groups by the same amount. This may not be the case for hydrogen.

[20] R. W. Taft Jr., in M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley & Sons, New York, 1956.

[21] R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, **78**, 4225 (1956).

[22] L. K. H. Van Beek, *Rec. trav. chim.*, **76**, 729 (1957).

[23] H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

group G relative to the standard group G_0 will be given by,

$$\frac{\rho_G}{\rho_{G_0}} = \gamma \quad (5)$$

where ρ_G and ρ_{G_0} are the reaction constants for reaction series XGY and XG_0Y both of which are undergoing the same reaction under the same conditions. The group chosen as the standard is the *p*-phenylene group. Values of γ for several common groups from the ionization of the carboxylic acids are given in Table III.

TABLE III

TRANSMISSION OF SUBSTITUENT EFFECTS

Group	γ	Ref.[a]	τ
t-Vinylene	2.23	6	6.52
Ethynyl	1.89	—	5.13
4-Phenyl	1.00		2.94[c]
4-Styryl	0.466	3	
4-Phenylethynyl	0.63[b]	10[a]	
4-Diphenyl	0.341	3	
4-Phenylmethyl	0.489	3	
2-(4-Phenyl)ethyl	0.212	3	
Ferrocenyl	0.677	9	2.4
4-Phenylcyclopropyl	0.182	24	
5-Furanyl	1.40	3	
5-Thienyl	1.08	4	

[a] Source of ρ values for γ. [b] From Ref. 10a, values of γ of 0.25 or 0.28 depending upon which of the two ρ values for the ionization of benzoic acids in 50% ethanol given by Jaffé[3] is used. Thus the average value of γ in this case is about 0.44–0.45. [c] Ref. 25.

Hine[25] has recently proposed that the transmission of substituent effect through the *m*- or *p*-phenylene group is given by

$$\tau = \frac{\rho^2}{\log \frac{K_1}{4K_2}} \quad (6)$$

where ρ is the reaction constant for the ionization of a benzene acid or base reaction series, and K_1 and K_2 are the first and second ionization constants for the member of the series which possesses two identical reaction sites. Examples of such compounds ate isophthalic and terephthalic acids, resorcinol and hydroquinone, and *m*- and *p*-phenylenediamine. This relationship is readily extended to other groups if the reaction constants have been obtained with the same substituent constants. Values of τ for several groups are given in Table III.

It is noteworthy that in both treatments of the transmission of substituent effects the acetylene group is found to be somewhat less effective than the *trans* ethylene group. This is in accord with the observations of Sinn[26] who reports that the carbon-carbon triple bond is less polarizable than the carbon-carbon double bond, and that the electrons in both π bonds of the triple bond are more strongly held than those of the double bond. The energies are 35–36 Kcal./mole for the double bond π electrons, and 44 Kcal./mole for each of the two π bonds of the triple bond.

HOBOKEN, N. J.

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(24) E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

(25) J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).

(26) H. Sinn, *Z. Elektrochem.*, **61**, 989 (1957).

[CONTRIBUTION FROM MELLON INSTITUTE]

On the Correlation of Hydrogen Bridging Equilibria with Acidity

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The relationship $\Delta \log K_{\text{assn.}} = a\Delta \log K_a^{\text{HA}}$ is proposed for correlation of hydrogen bridging equilibria with acidity in the system variable acid-reference base: $\text{HA} + \text{B} \overset{K_{\text{assn}}}{\rightleftharpoons} \text{AH} \cdots \text{B}$. The available chemical and spectroscopic data are found to be largely in accord with this and the analogous expression for variation of the proton acceptor moiety. Analogous expressions are found applicable to formation of the bridged ion pair, $\text{A}^- \cdots \text{HB}^+$, and on inclusion of the Brønsted catalysis law, the formation of each of the species ($\text{AH} \cdots \text{B}$, proton transfer transition state, $\text{A}^- \cdots \text{HB}^+$) intermediate between $\text{AH} + \text{B}$ and $\text{A}^- + \text{BH}^+$ can be described by $\Delta \log K = x\Delta \log K_{\text{ion}}$ with suitable coefficient x. Numerical results of the correlations are compared and related to structure using this model, as are the formation of complex ions of the type $\text{BHB}^{\pm}$ and the influence of proton acceptor polarizability on hydrogen bridge stability.

The concept of a relationship between the strength of a hydrogen bridge, $\text{AH} \cdots \text{B}$, and the acidity and basicity of the proton donor and acceptor moieties involved is not a new one; indeed, it finds common qualitative employment in the literature.[1] The basis and scope of this generalization, and the possibilities of a quantitative extension thereof, however, have not been explored as fully as existing data permit. Such exploration is the purpose of the present article. Several authors[2–5] have plotted data on association through

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(1) See, for example, H. Van Looy, and L. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959).

(2) R. Denyer, A. Gilchrist, J. Pegg, J. Smith, T. Tomlinson, and L. Sutton, *J. Chem. Soc.*, 3889 (1955).