[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Ionization Constants and Rates of Esterification of Substituted Phenylpropiolic Acids

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The ionization constants of phenylpropiolic acid and the *o*-, *m*- and *p*-chloro, methoxy and nitrophenylpropiolic acids in 35% dioxane were measured as well as the rates of acid-catalyzed esterification with methanol at 25 and 35°. The *meta* and *para* derivatives esterify at a rate in conformity with the Hammett sigma–rho relationship but the *ortho* derivatives esterify at a rate greater than expected from the sigma values determined.

The utility of Hammett's sigma–rho equation in correlation of a large amount of kinetic and thermodynamic data concerning *m*- and *p*-substituted benzene derivatives is well known.[2] However, *o*-substituted benzene derivatives cannot be included because of the intrusion of steric effects. Accordingly one cannot compare the polar effects of groups in the *o*-position to the effects of those in the *m*- and *p*-positions.

In order to arrive at a measure of the relative polar effect of groups in the *o*-, *m*- and *p*-position, we thought it desirable to: (1) prepare a series of *o*-, *m*- and *p*-substituted phenylpropiolic acids; (2) measure ionization constants and compare with that of phenylpropiolic acid; (3) compute a series of sigma constants based on the ionization constants of phenylpropiolic acids; (4) measure the rate of some reaction of these acids (or esters thereof); and (5) plot the log *k* for the reaction chosen against the sigma values based on the propiolic acids. Should a straight line plot be obtained one could then compare the polar effects of groups in the *o*- as well as *m*- and *p*-positions. The phenylpropiolic acid system was chosen because of the fact that the acetylenic function is linear and hence should have a smaller steric requirement than any other function capable of joining a carboxyl group to a benzene ring. Furthermore, it is capable of transmitting polar effects and effectively removes the carboxyl group from the proximity of any *o*-substituent. Experiments showed that under the esterification conditions used for the kinetic measurements no addition of methanol to the triple bond occurred.

In this paper items 2, 3, 4 and 5 (above) are discussed. In the accompanying paper[3] the syntheses of the substituted phenylpropiolic acids are described.

Experimental

Ionization Constants.—The ionization constants were determined in 35% dioxane–65% water by weight by titration with base. At least two titrations were made on each acid and the *pK* values calculated were accurate to ±0.02 *pK* units. The following equation was used

$$pK = p\text{H} - \log \frac{\dfrac{NV_1}{V_1 + V_2} + \dfrac{1}{\text{antilog } p\text{H}}}{\dfrac{NV_3}{V_1 + V_2} - \dfrac{1}{\text{antilog } p\text{H}}}$$

where N = normality of base, V_1 = volume of base added at any point on the titration, V_2 = volume of starting solution of acid (60 ml.), V_3 = total volume of base needed to neutralize the acid V_1.

From the data *p*H was plotted against V_1. A smooth curve was drawn and three points in the range 35 to 70% neutralization were chosen for calculation of *pK*.[4] The frequently used simplification in which *pK* = *p*H at 50% neutralization cannot be used with phenylpropiolic acids because they are too strong. The results are listed in Table I.

TABLE I

IONIZATION CONSTANTS AND *pK* OF SUBSTITUTED PHENYLPROPIOLIC ACIDS IN 35% DIOXANE (WT.) AT 25°

Substituent	*pK*	$K \times 10^5$	Sigma[a]	$K \times 10^{5\,b}$	$K \times 10^{5\,c}$
H	3.24	58	0.00	3.65	6.27
o-Cl	3.08	83	.16	5.83	114
m-Cl	3.00	100	.24		14.8
p-Cl	3.07	85	.17	3.86	10.5
o-NO_2	2.83	150	.41	7.07	671
m-NO_2	2.73	190	.51		32.1
p-NO_2	2.57	270	.67	8.99	37.6
o-OCH_3	3.37	43	− .13	3.45	8.06
m-OCH_3	3.21	62	.03		8.17
p-OCH_3	3.44	36	− .20	2.73	3.38

[a] Log K_{ion} (substituted phenylpropiolic acid) − log $K°_{\text{ion}}$ (phenylpropiolic acid). [b] Ionization constants of substituted cinnamic acids in water at 25°, J. F. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938). [c] Ionization constants of substituted benzoic acids in water at 25°, Dippy and Page, ref. *b*.

Kinetic Data.—The rates of esterification of the acids in methanol were measured as described[5] at 25 ± 0.02° and 35 ± 0.02°. The initial concentration of organic acid was approximately 0.4 *M* and that of hydrogen chloride about 0.01 *M*. Exact concentrations were determined by initial titrations. The rate constants were calculated by the use of the Goldschmidt equation.[5] The values of the temperature-dependent constant γ were taken as 0.22 at 25° and 0.28 at 35° by interpolation from the data of Smith.[5] At least two runs were made for each acid and the values of the velocity constant, *k*, in Table II were obtained by averaging the individual rate constants calculated between 20 and 60% esterification.

Ionization Constants.—A plot of log K/K_0 of the ionization of the *m*- and *p*-substituted phenylpropiolic acids in 35% dioxane against Hammett σ-values gives a straight line indicating the expected agreement of the ionization with the Hammett equation. The slope, ρ, is +0.81. A similar plot for the ionization of substituted cinnamic acids in water at 25° gives ρ = +0.47,[6] while by definition ρ = 1.00 for the ionization of benzoic acids in water at 25°. The low value of ρ means that the ionization of cinnamic acid is less sensitive to variations of ring substituents than is benzoic acid. No conclusion can be drawn from the value of +0.81 with regard to the relative sensitivity of cinnamic acids and phenylpropiolic acids to substituent changes because the ioniza-

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[1] The material herein presented is taken from the Ph.D. thesis of S.H.M., O.S.U., 1953. Holder of a National Science Foundation Fellowship, 1952–1953.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., 1940, p. 184; H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[3] M. S. Newman and S. H. Merrill, THIS JOURNAL, **77**, 5549 (1955).

[4] See S. Glasstone, "The Electrochemistry of Solutions," D. Van Nostrand Co., New York, N. Y., 1930, pp. 188–189.

[5] H. A. Smith, THIS JOURNAL, **61**, 254 (1939).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 190.

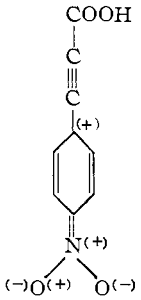
TABLE II

RATE CONSTANTS AND ENERGIES AND ENTROPIES OF ACTIVATION FOR THE ACID-CATALYZED ESTERIFICATION OF SUBSTITUTED PHENYLPROPIOLIC ACIDS, 25–35°

Substituent	$k_{25°} \times 10^3$, l./mole sec.	$k_{35°} \times 10^3$, l./mole sec.	E, kcal./mole	log PZ	$\Delta S\ddagger - \Delta S_0\ddagger$
H	0.53 ± 0.01	1.17 ± 0.02	14.5 ± 0.4	7.3 ± 0.3	0
o-Cl	.48	1.12	15.3	7.9	2.7 ± 2.6
m-Cl	.40	0.90	14.7	7.3	0.1
p-Cl	.42	.92	14.3	7.1	−0.9
o-NO_2	.41	.93	15.0	7.6	1.5
m-NO_2	.29	.63	14.4	7.1	−1.3
p-NO_2	.25	.57	14.8	7.3	−0.3
o-OCH_3	.73	1.63	14.7	7.6	1.3
m-OCH_3	.50	1.15	15.2	7.8	2.4
p-OCH_3	.56	1.28	15.1	7.8	2.2

tion constants of the phenylpropiolic acids were determined in aqueous dioxane and the constants for the cinnamic acids were determined in water. However, for the ionization of *p*-substituted benzoic acids ρ is increased from 1.00 in pure water to 1.29 in 35% dioxane.[7] Consequently the ionization of phenylpropiolic acids in pure water would probably give a ρ of less than +0.81 though it is doubtful that it would be as low as +0.47.

Examination of the data in Table I reveals that the relationship of the *ortho* to *para* acids is quite different in the phenylpropiolic and benzoic acid series. In the latter, the *ortho* isomer is markedly stronger than the *para* regardless of substituent whereas in the former the *ortho* is about the same as the *para* for the chloro group, weaker than the *para* for the nitro group, and stronger than the *para* for the methoxy group. The ionization constants for the correspondingly substituted cinnamic acids are included in Table I to show that their ionization constants are more nearly comparable to those of the phenylpropiolic than to the benzoic series with regard to the *ortho–para* relationship. An explanation for the fact that *o*-substituted benzoic acids have larger ionization constants than the *para* isomers, regardless of the substituent, has been given.[8] This explanation involves the appreciable bulk effect of groups *ortho* to the carboxyl. However, such a bulk factor cannot operate in the case of the phenylpropiolic acids because the carboxyl group is too far removed from the *ortho* substituent and the steric requirements of the linear acetylene function are not great.



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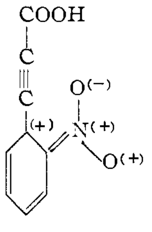

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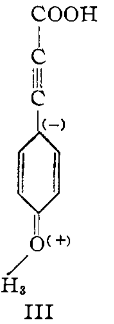

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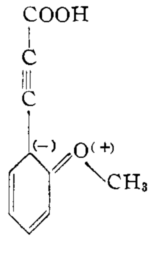

IV

One factor which is probably involved is illustrated in formulas I–IV. To whatever extent the positive charge on the ring carbon in I is effective in increasing the ionization constant the similar charge in II will be less effective because of the proximity of the negative oxygen on the nitro group. Similarly the acid weakening effect of the negative charge on the ring carbon in III will be partly offset by the positive charge on the methoxy oxygen in IV.

Rate Constants.—In Fig. 1 typical Hammett sigma–rho plots are shown for the acid-catalyzed esterification of phenylpropiolic acids with methanol at 25 and 35°. The values of sigma used are those derived by using the ionization constants of the phenylpropiolic acids listed in Table I. The straight lines were drawn by the method of least squares to include all but the points corresponding to the *o*-substituted acids. It is apparent that the points corresponding to the *meta* and *para* derivatives fall in general fairly close to this line but the *ortho* derivatives do not obey the Hammett re-

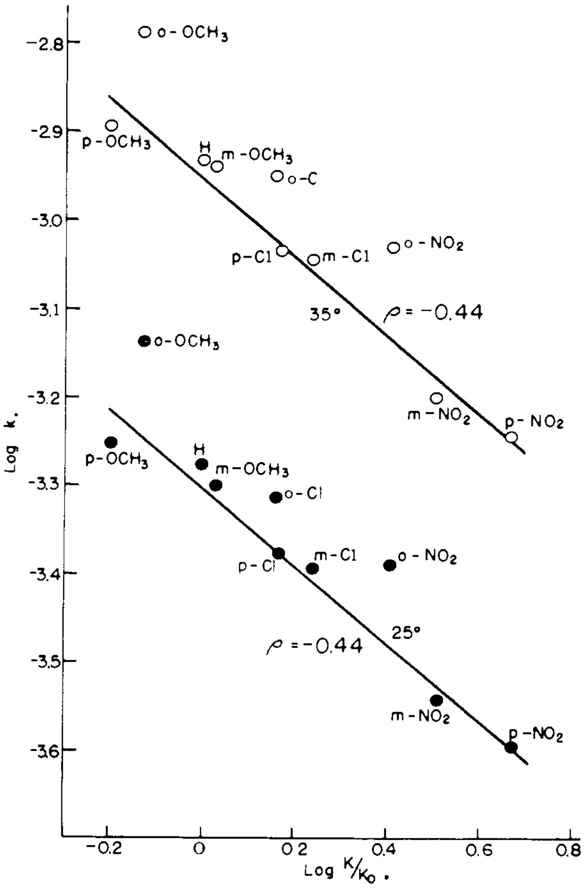

Fig. 1.—Hammett relationship between log k and log K/K_0 for substituted phenylpropiolic acids.

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[7] H. L. Goering, T. Rubin and M. S. Newman, THIS JOURNAL, **76**, 787 (1954).

[8] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 744.

lationship. Furthermore, it is noteworthy that all of the *ortho* derivatives esterify at rates greater than those to be expected from the magnitude of the ionization constants of the corresponding *o*-substituted phenylpropiolic acids. A steric effect is undoubtedly at the root of this behavior since the sigma values for the *ortho* derivatives are derived from the ionization constants of the corresponding phenylpropiolic acids. A convincing explanation for this example of steric assistance is not apparent to the authors.

The selection of a proper rho value for the esterification of benzoic acids with methanol is difficult because the experimental values for the rate constants for all of the *m*- and *p*-substituted benzoic acids do not yield a good Hammett plot. Considerable variation in the rho value can be obtained if certain acids are included or excluded. All of the recorded data come from two papers[9] and in these a rho value of -0.56 is derived. On the other hand Jaffe[1] gives a rho value of -0.23, obtained by recalculation according to certain standardized procedures. For the esterification of the phenylpropiolic acids herein reported a rho value of -0.44 was obtained at 25 and at 35°. This fact indicates that transmission of polar effects from substituent to carboxyl groups is about the same when either a $-C_6H_4-$ or a $-C_6H_4C{\equiv}C-$ group intervenes. The above findings are of interest in view of the fact that as a class the phenylpropiolic acids are about 6–10 times stronger than the corresponding benzoic acids (see Table I).[10] The spread in esterification rates was insufficient to permit accurate evaluation of the E and PZ terms. However, they are recorded in Table II.

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF ETHYL ESTERS OF PHENYLPROPIOLIC ACIDS

	Principal		Secondary	
Substituent	mμ	$E_{max} \times 10^{-3}$	mμ	$E_{max} \times 10^{-3}$
H	258	15.2		
o-Cl	259	12.6		
m-Cl	256	14.4		
p-Cl	266	18.7		
o-NO_2	232	20.2	307	4.0
m-NO_2	250	22.3		
p-NO_2	286	19.6		
o-OCH_3	268	9.3	310	6.7
m-OCH_3	262	12.7	301	4.3
p-OCH_3	286	19.0		

Infrared and Ultraviolet Spectra.—The position of the principal maxima and intensities in the ultraviolet absorption spectra of the ethyl esters of the phenylpropiolic esters studied are given in Table III. The spectra were taken in the hope that some light might be shed on the abnormal *ortho* effect noted in the section above.

No significant shifts in the position of the 4.5–4.6 μ band characteristic for the $-C{\equiv}C-$ grouping were found in the spectra of the ethyl esters.

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[9] R. J. Hartman and A. M. Borders, THIS JOURNAL, **59**, 2107 (1937); R. J. Hartman and A. G. Gassman, *ibid.*, **62**, 1559 (1940).

[10] It should be pointed out, however, that the ionization constants for the benzoic acids are for water whereas the constants of the phenylpropiolic acids were taken in 35% dioxane.

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

Electrical Effects of Substituent Groups. Reactivities of Substituted Phenylpropiolic Acids

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Measurements have been made of the reactivities of some substituted phenylpropiolic acids. It is concluded that the inductive and field effects are of comparable importance in the transmission of the electrical influences of dipolar substituents to a reactive center.

In a previous study[2] of the reactivities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids, the magnitudes of the polar effects of the 4-substituents were found to be comparable to those of the corresponding *m*- and *p*-substituted benzoic acids. It was deduced that the π-electron systems in aromatic compounds play a relatively minor role in the transmission of electrical effects from dipolar substituents to other parts of the molecule in the absence of direct and important conjugation between the substituent and ring. The magnitudes of the relative reactivities of the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids were about twice as large as predicted from the Kirkwood–Westheimer equations[3] which only take into account the effect on the reaction center of direct electrostatic influences of substituents and might be regarded as giving a first approximation of the field effect.[2] The saturated nature of the bicyclo[2.2.2]octane ring system clearly precluded resonance effects involving conjugated unsaturation but no experimental information was obtained concerning the importance, relative to the field effect, of the *inductive effect* which was taken as transmission of polarity through a chain of atoms by displacement of binding electrons between successive atoms. With all of the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids which were studied, the field and inductive effects might be expected to operate in the same direction to influence the reactivity of the carboxyl group.

It should be clear that any attempt to separate quantitatively electrical influences of dipolar substituent groups into field and inductive effects must ultimately run afoul of the formidable difficulty of evaluation of dielectric constants in very electrically inhomogeneous systems at the molecular level. As a result, it is not surprising that the field and inductive effects have been often regarded as even qualitatively indistinguishable and have been treated practically as a composite influence. Nonetheless, the effects can be regarded as differing fundamentally because, while the efficiency of

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[1] (a) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4; (b) United States Rubber Company Fellow, 1952–1953.

[2] J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953).

[3] (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).