[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Substituent Constants for Aromatic Substitution[1-3]

BY HERBERT C. BROWN AND Y. OKAMOTO

RECEIVED AUGUST 29, 1956

A plot of the logarithms of the rate constants for the solvolysis of the *meta* and *para* substituted phenyldimethylcarbinyl chlorides against the Hammett σ-constants reveals an excellent correlation in the case of the *meta* derivatives but serious deviations for the *para* substituents. The deviations are in the direction to be anticipated for important resonance interactions between the *para* substituent and the electron deficient center of the incipient carbonium ion in the transition state. The *meta* derivatives are used to establish ρ for the reaction (-4.620). A new set of σ^+-constants for the *para* substituents is then calculated from this ρ-value and the observed solvolysis rates. The available data on the rates of the nitration of monosubstituted aromatics, the halogenation of aromatics, the brominolysis of arylboronic acids and the protonolysis of aryltrimethylsilanes exhibit important deviations using the Hammett σ-values, but they give good agreement with the σ^+-values. It is proposed that the σ^+-values may provide a quantitative basis for the treatment of directive effects in aromatic substitution.

The Hammett equation, limited though it is to *meta* and *para* derivatives of aromatic systems, has provided the most successful approach to a quantitative treatment of the effects of structure upon reaction rates.[4,5] Its success in treating the side-chain reactions of aromatic systems has led to a number of attempts to apply the treatment to nuclear substitution reactions. Hammett himself realized a measure of success in treating the available nitration data[6] in terms of his σ-values.[4]

As additional substitution data have become available, it has become apparent that this simple treatment cannot suffice. Thus the presently available data on aromatic nitration show serious deviations in the Hammett treatment.[7] It was pointed out that *ortho–para* directing groups, through resonance interaction with the electron deficient transition state, might be able to stabilize the transition state for *para* nitration to a far greater extent than would be expected from the value of the σ-constant for the substituents.[7]

Similarly, de la Mare pointed out that the available halogenation results fail to follow the Hammett relationship.[8] He also attributed the deviation to the importance of resonance interactions in aromatic substitution and to the fact that the σ-values reflect to a greater extent the inductive rather than the electromeric effect of the substituents. The brominolysis of phenylboronic acids likewise exhibits major deviations from the Hammett treatment.[9]

Although there is general agreement that the Hammett substituent constants cannot serve for the correlation of aromatic substitution (and other electrophilic)[10] reactions, the possibility of devising an alternative set of such constants for these reactions has been viewed with scepticism.

In 1952, Pearson suggested that a set of substituent constants might be developed which would apply to the Beckmann rearrangement and other electrophilic reactions.[11] Unfortunately, the data at his disposal did not permit the development of a satisfactory set of such constants, nor a test of their utility in the quantitative prediction of rates.

The prevailing view has been that resonance interactions by the substituent will vary widely from reaction to reaction, so that the electronic contribution of the substituent could not possibly be represented by a single constant.[8,12,13]

That this view may be unduly pessimistic is suggested by the recent observation of Kuivila and Benjamin[9] that a linear free energy relationship exists between the rates of brominolysis of the arylboronic acids and the rates of aromatic nitration.

Our attention was attracted to the possibility of developing a set of substituent constants suitable for aromatic substitution as a result of our observations on directive effects in the substitution of toluene.[14,15] It was observed that every substitution reaction of toluene for which orientation and rate data are available fits the empirical relationship

$$\log p_f = c \log (p_f/m_f) \qquad (1)$$

Moreover, this relationship can be developed by simple algebraic manipulation from the Hammett equation, in the form[16]

$$\log p_f = \left(\frac{\sigma_p}{\sigma_p - \sigma_m}\right)\log (p_f/m_f) \qquad (2)$$

However, the introduction of the Hammett values for $\sigma_{p\text{-Me}}$ and $\sigma_{m\text{-Me}}$ into the term $\sigma_p/(\sigma_p - \sigma_m)$ yields the quantity 1.68, instead of the experimentally observed value of 1.310 for the constant c.

The constancy of the experimentally determined slope (c) for some thirteen reactions argues for the conclusion that the value of c must be based upon constant values of substituent constants for *m*- and *p*-methyl. However, because of the disagreement between the experimental value of c and the calculated value of $\sigma_p/(\sigma_p - \sigma_m)$, it is apparent that the

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(1) Directive Effects in Aromatic Substitution. XIV.

(2) Supported by the Petroleum Research Fund of the American Chemical Society.

(3) Based upon a thesis submitted by Y. Okamoto, in 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

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

(6) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931); M. L. Bird and C. K. Ingold, *ibid.*, 918 (1938); C. K. Ingold and M. S. Smith, *ibid.*, 905 (1938).

(7) J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, THIS JOURNAL, **76**, 4525 (1954).

(8) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(9) H. J. Kuivila and A. R. Hendrickson, THIS JOURNAL, **74**, 5068 (1952); H. G. Kuivila and L. E. Benjamin, *ibid.*, **77**, 4834 (1955).

(10) To be discussed in a subsequent publication.

(11) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(12) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(13) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

(14) H. C. Brown and K. L. Nelson, *ibid.*, 6292 (1953).

(15) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300, 2306 (1955).

(16) C. W. McGary, Jr., Y. Okamoto and H. C. Brown, *ibid.*, **77**, 3037 (1955).

TABLE I

SUMMARY OF RATE DATA FOR THE SOLVOLYSIS OF THE SUBSTITUTED PHENYLDIMETHYLCARBINYL CHLORIDES IN 90% ACETONE AT 25°

Substituent	*Ortho* $10^5 k_1/25°$ sec.$^{-1}$	*Ortho* Relative rate	*Ortho* log k/k^0	*Meta* $10^5 k_1/25°$ sec.$^{-1}$	*Meta* Relative rate	*Meta* log k/k^0	*Para* $10^5 k_1/25°$ sec.$^{-1}$	*Para* Relative rate	*Para* log k/k^0
Hydrogen[a]	12.4	1.00	0	12.4	1.00	0	12.4	1.00	0
Methyl[a]	45.0	3.63	0.560	24.8	2.00	0.301	322	26.0	1.41
Ethyl[a]	25.7	2.07	.317	24.1	1.94	.289	273	22.0	1.34
Isopropyl[a]	10.5	0.847	− .0722	23.2	1.87	.272	233	18.8	1.27
t-Butyl[a]				23.0	1.85	.268	178	14.4	1.16
Fluoro[c]	0.622	0.0502	−1.30	0.311	0.0251	−1.60	26.5	2.14	0.330
Chloro[c]	.0975	.00786	−2.10	.194	.0156	−1.81	3.78	0.305	− .516
Bromo[c]	.0753	.00607	−2.22	.178	.0144	−1.84	2.58	.208	− .682
Iodo[c]	.137	.0110	−1.96	.289	.0233	−1.63	3.03	.244	− .612
Methoxy[d]	1300	105	2.02	7.56	.610	−0.215	41700	3360	3.53
Nitro[d]				0.0108	.000871	−3.06	0.00319	0.000257	−3.59
2,3-C_4H_4[b,e]	51.7	4.16	0.620						
3,4-C_4H_4[b,f]							50.6	4.08	0.611

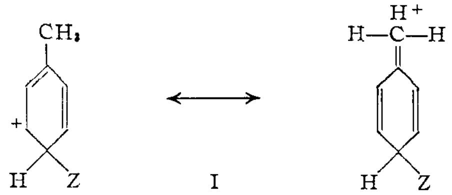
[a] Ref. 17. [b] Ref. 19. [c] Ref. 20. [d] Ref. 21. [e] α-Naphthyldimethylcarbinyl chloride. [f] β-Naphthyldimethylcarbinyl chloride.

Hammett σ-values will not serve for these reactions. It was suggested that a new set of substituent constants, designated σ^+, be developed for aromatic substitution reactions.[16]

$$\log p_f = \left(\frac{\sigma_p^+}{\sigma_p^+ - \sigma_m^+}\right) \log \frac{p_f}{m_f} \qquad (3)$$

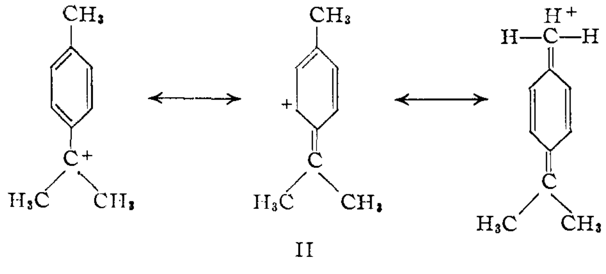
Earlier we attempted to develop such a set of substituent constants σ^+ utilizing the available data on aromatic substitution.[16] Unfortunately, the available data are few and the quality variable. Consequently, this approach proved promising but not entirely satisfactory.

In substitution reactions the *p*-methyl group behaves as a far better supplier of electrons than would be indicated by its σ-constant. This is attributed to hyperconjugative interaction in the transition state (I).



I

The methyl group in the *para* position of *p*-tolyldimethylcarbinyl chloride likewise behaves as an excellent source of electrons.[17] Here also the effect is attributed to hyperconjugation (II).



II

The similarity, both in the effects and in their interpretation, suggested an examination of the solvolysis data for the phenyl- and tolyldimethylcarbinyl chlorides in the empirical relationship (1). The excellent fit realized[18] encouraged a detailed study of the solvolysis of the substituted phenyldimethylcarbinyl chlorides as an experimental approach to substituent constants applicable to aromatic substitution.[17,19-21] The available data on the solvolysis reaction (Table I) makes possible the development of an experimentally-based set of σ^+-constants and critical examination of their utility in correlating the data on aromatic substitution.

The σ^+-Substituent Constants.—A plot of the logarithms of the rate constants for the solvolysis of the aryldimethylcarbinyl chlorides *versus* the Hammett σ-values indicated an excellent linear relationship for the *meta* derivatives. However, the *para* substituents, other than *p*-nitro, deviate from the line in a manner indicating the incursion of considerable resonance interaction between the *para* substituents and the electron-deficient center in the transition state (Fig. 1). (For convenience in examining both the fit and the deviations, the plot is shown in two parts, one for the *meta* substituents and the other for *para*. The same line, obtained by a least squares treatment of the *meta* data, is shown in both parts of the figure.)

From the slope of this line, the reaction constant ρ for this reaction is calculated to be −4.620. Using this value of ρ and the rate data for the *meta* and *para* substituents, we now proceed to calculate the values of σ^+ required to satisfy the modified Hammett equation 4.

$$\log k/k^0 = \rho\sigma^+ \qquad (4)$$

The results are summarized in Table II along with the Hammett σ-values.

Since the σ_m^+-constants agree with the Hammett σ-values well within the experimental variation in these constants, it is convenient to adopt the σ_m-values for both types of reactions. In the case of the higher alkyl groups (Et, *i*-Pr, *t*-Bu) where the σ_m-values are either lacking or are based upon measurements of questionable value, it appears

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(17) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957).

(18) Figure 3, ref. 17.

(19) Y. Okamoto and H. C. Brown, THIS JOURNAL, **79**, 1903 (1957).

(20) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957).

(21) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

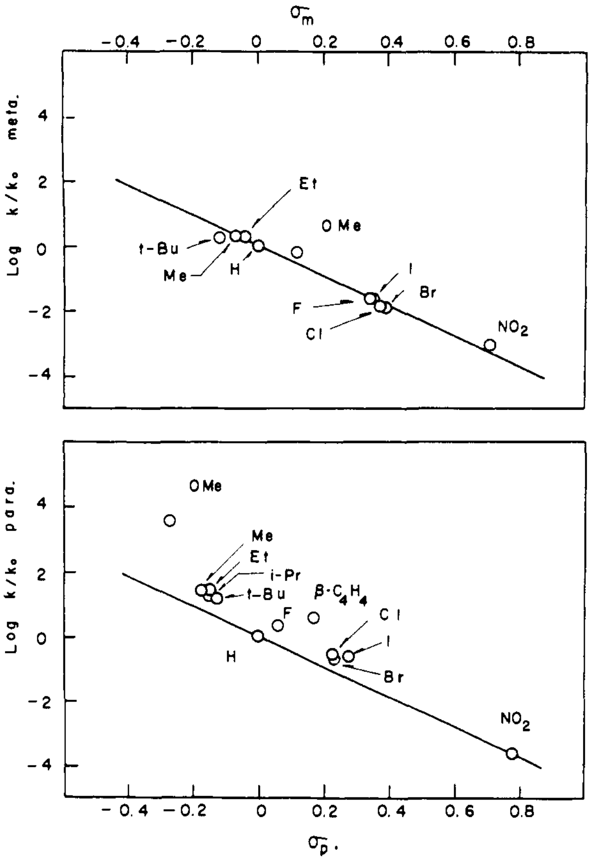

Fig. 1.—Solvolysis of 2-chloro-2-phenylpropanes, $XC_6H_4-(CH_3)_2CCl$, in 90% aqueous acetone at 25°.

desirable to retain the σ_m^+-values. Also in the case of the methoxy and nitro groups, where the σ_m-values exhibit a large variation from reaction to reaction and there exists a significant difference in the two values, it has appeared desirable to retain the σ_m^+-value.

TABLE II

SUBSTITUENT CONSTANTS FOR AROMATIC SUBSTITUTION[a,b]

Substituent	σ_m	σ_m^+	σ_p	σ_p^+
Methoxy	0.115	**0.0465**	−0.268	−**0.764**
Methyl	− **.069**	− .0652	− .170	− **.306**
Ethyl	− .043	− **.0625**	− .151	− **.291**
Isopropyl		− **.0589**	− .151	− **.276**
t-Butyl	−0.120	− **.0581**	− .197	− **.250**
Fluoro	**.337**	.346	.062	− **.0714**
Chloro	**.373**	.391	.227	**.112**
Bromo	**.391**	.399	.232	**.148**
Iodo	**.352**	.353	.276	**.132**
Nitro	.710	**.662**	.778	**.777**
3,4-C_4H_4[c]			.170	− **.132**

[a] Values of σ from the compilation by Jaffe, ref. 5. [b] Final values adopted for σ^+-values are indicated by bold-faced type. [c] β-Naphthyl.

In an earlier paper, in the absence of experimental data for the determination of σ^+-constants, we attempted to develop an empirical relationship between σ_p and σ_p^+ which might be used to calculate σ_p^+-values where these could not otherwise be estimated. It was noted that linear relationship appeared to exist between the σ^+-values calculated from nitration data and the σ-values (σ^* for carbethoxy). Accordingly, it was proposed that this empirical relationship

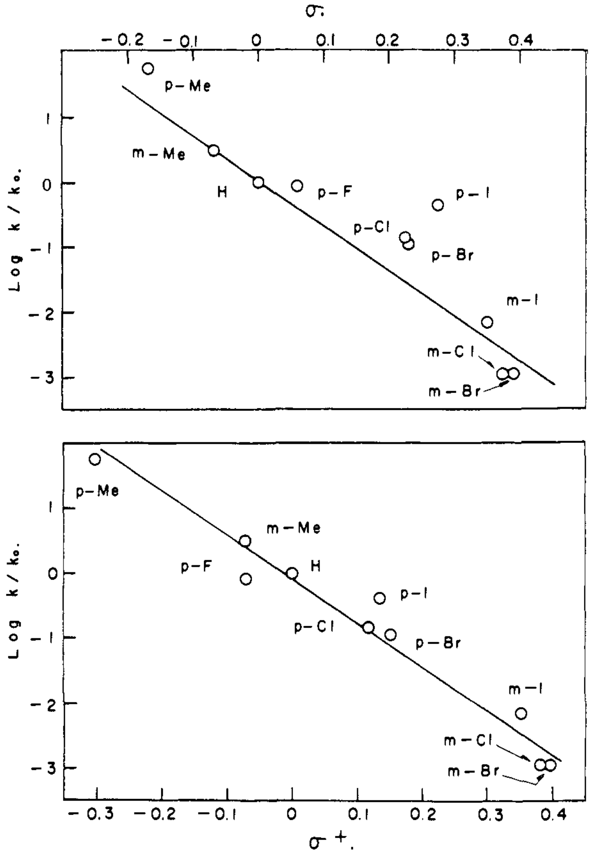

Fig. 2.—Nitration of monosubstituted benzenes in nitromethane or acetic anhydride at 25°.

$$\sigma_p^+ = \sigma_p^{(*)} - 0.134 \qquad (5)$$

might serve for the calculation of σ^+-values. Treatment of the experimental σ^+-values for the four alkyl and the four halo group yields the relationship

$$\sigma_p^+ = \sigma_p - 0.116 \qquad (6)$$

with an average deviation of 0.024. Thus these groups obey the empirical relationship (5). However, the relationship breaks down for the nitro and the methoxy groups. It appears that resonance makes a remarkably constant contribution to the σ^+-values of the alkyl and halo groups.

The marked difference in the σ_p- and σ_p^+-values for the methoxy group is noteworthy. The close agreement in these values for the nitro group is also of interest.

Application to Aromatic Substitution.—By far the largest amount of quantitative data in the area of aromatic substitution reaction involves the nitration reaction.[6,7] Unfortunately, the reaction has been carried out in different solvents, using various nitrating agents. It is by no means certain that these experimental changes do not involve changes in ρ. However, in the absence of data ob-

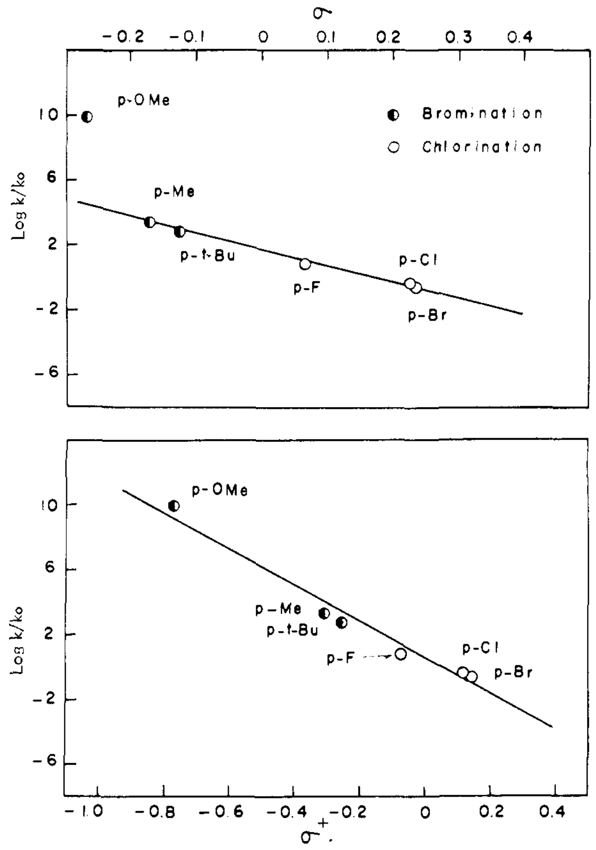

Fig. 3.—Halogenation of monosubstituted benzenes by bromine and chlorine in acetic acid.

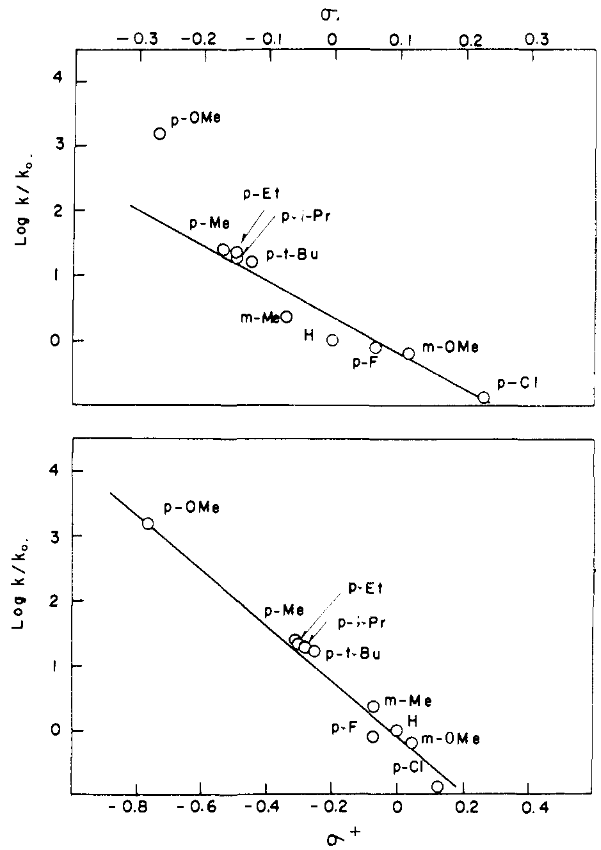

Fig. 4.—Protonolysis of phenyltrimethylsilanes by perchloric acid in 72% aqueous methanol at 50°.

tained under more carefully controlled conditions, it is of interest to examine the utility of the σ^+-values in correlating the data.

In Fig. 2 are shown plots of the nitration data *versus* the σ- and σ^+-constants. It is apparent that the σ^+-constants provide a far better fit.

Bromination data are available for some of the more reactive monosubstituted benzenes, while chlorination data are available for several of the halobenzenes.[8] There is some evidence that the two reactions must have similar ρ-values.[8] Again the results show closer agreement with the σ^+-values (Fig. 3).

Recently, Illuminati and Marino have obtained accurate partial rate factors for the bromination reaction by an ingenious procedure based upon the measurement of the rates of reaction of bromine with monosubstituted derivatives of mesitylene, durene and isodurene.[22] Their results exhibit a remarkably good fit,[23] with the values proposed in this paper.

Dr. Eaborn has measured the protonolysis of the substituted phenyltrimethylsilanes by perchloric acid in 72% aqueous methanol at 50°.[24] Again serious discrepancies are exhibited by a plot *versus* the σ-values, whereas the σ^+-values give a far better fit. It is particularly gratifying to note that *p*-fluoro, *p*-methyl and *p*-methoxy, all of which have large resonance components, agree closely with the σ^+-values for these groups (Fig. 4).

Finally, we examined the extensive data made available in recent years by Kuivila and his coworkers on the brominolysis of substituted phenylboronic acids.[9] Again the data fit the σ^+-values far more closely than they do the σ-constants (Fig. 5). However, *p*-methoxy deviates greatly in both plots. The *p*-methoxy rate is exceedingly fast and it could be determined only by utilizing extrapolations of considerable magnitude. In view of the excellent agreement realized for the methoxy substituent in the bromination (Fig. 3) and the protonolysis (Fig. 4) reactions, as well as in numerous other types of electrophilic reactions to be discussed in a subsequent paper, we question whether the disagreement is real. In our opinion a redetermination of the rate constant for the *p*-methoxy derivative would be highly desirable.

In Table III are listed the reaction constants discussed in this paper together with the results of a statistical analysis of the measure of agreement realized.

In spite of the difficulties in the available data, the fit achieved by the use of the σ^+-values, as measured by the correlation coefficient, is easily as good as that realized in the usual Hammett treatment.[5] Consequently, the results must be consid-

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(22) G. Illuminati and G. Marino, This Journal, **78**, 4975 (1956).

(23) See Fig. 2, ref. 22.

(24) Unpublished measurements of Dr. C. Eaborn of University College, Leicester, England. We are greatly indebted to Dr. Eaborn for his kindness in making his results available to us in advance of publication. Added in proof.—These data have now been published: C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

TABLE III

REACTION CONSTANTS FOR ELECTROPHILIC REACTIONS

Reaction	ρ	s^a	c^b	n^c
Solvolysis of phenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25°	− 4.62	0.274	0.980	8^d
Nitration of monosubstituted benzene in nitromethane or acetic anhydride at 25°	− 6.53	.335	.975	9
Halogenation of monosubstituted benzenes by bromine or chlorine in acetic acid at 25°	−11.35	.690	.987	6
Protonolysis of phenyltrimethylsilanes by perchloric acid in 72% aqueous methanol at 50°	− 4.59	.215	.986	8
Brominolysis of substituted phenylboronic acids in 20% acetic acid and 0.4 *M* sodium bromide at 25°	− 4.30	.224	.991	12

[a] The standard deviation of the experimental measurements from the regression line. [b] The correlation coefficient. [c] The number of compounds involved in the calculation of ρ. [d] The value of ρ determined by a least square treatment of *m*-Me, *m*-Et, H, *m*-F, *m*-Cl, *m*-Br, *m*-I, and *m*-NO_2.

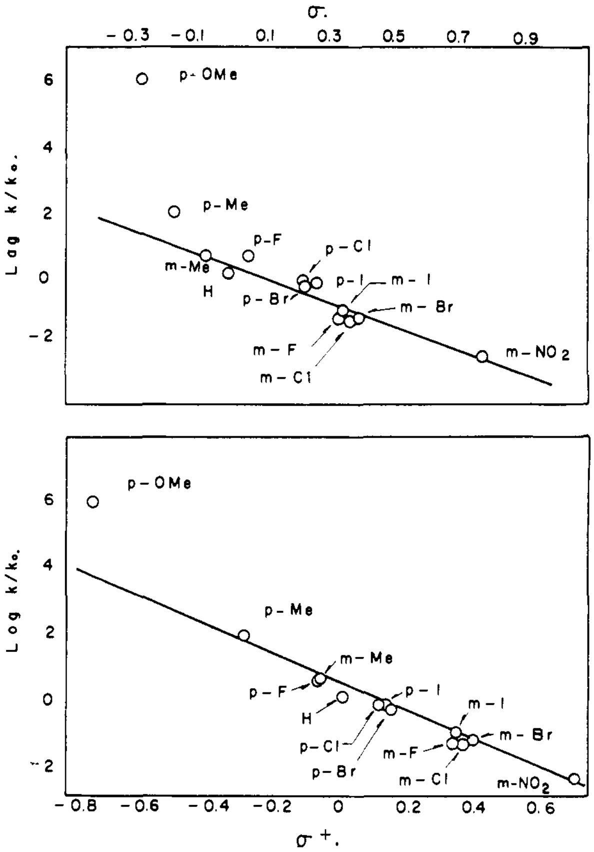

Fig. 5.—Brominolysis of phenylboronic acids in 20% acetic acid at 25°.

ered encouraging for the objective of the present study—the development of a set of substituent constants suitable for the correlation of aromatic substitution data. A rigorous test of the precise utility of these constants must await the availability of additional precise orientation and rate data for aromatic substitution.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

The Kinetics and Mechanism of the Reaction of Benzoic Acid and Substituted Diphenyldiazomethanes in Toluene[1]

BY C. KINNEY HANCOCK, RALPH F. GILBY, JR., AND JOHN S. WESTMORELAND

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Rate constants at 25° have been determined for the reaction of benzoic acid with twelve *m*- and *p*-substituted diphenyldiazomethanes in toluene. Log k_2 values show a good linear relationship with Hammett's σ-values, the σ-values being additive for disubstituted derivatives. Excluding values for methoxy derivatives, statistical treatment of the data yields the following results: (1) equation of the regression line, $\log k_2 = -0.1440 - 1.570\sigma$, where -1.570 is the reaction constant ρ; (2) standard deviation from the regression line, 0.0422; (3) correlation coefficient, 0.9987. New σ-values may be calculated from the equation, $\sigma = -0.0905 - 0.6353 \log k_2$. The σ-value for the *p*-methoxy group is -0.361. These results support a mechanism for the reaction involving a simultaneous attack of hydroxyl hydrogen and of hydroxyl oxygen (both from benzoic acid) on the diazocarbon.

Introduction

Roberts and co-workers[2] made a kinetic study of the reaction of diphenyldiazomethane (DDM) in ethanol at 30° with benzoic acid and six *m*- and *p*-substituted benzoic acids. The second-order rate constants, obtained by following the reactions colorimetrically, were correlated with Hammett's[3] σ-values to give a ρ-value of 0.937.

Roberts and others[4a] proposed the two mechanisms shown in Fig. 1 for the reaction of benzoic acid with DDM, but they had no direct evidence in favor of either mechanism over the other. Later

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[1] Presented before the Organic Section at the 11th Southwest Regional A.C.S. Meeting, Houston, Texas, December 1, 1955. Taken in part from the Ph.D. dissertation of R. F. Gilby, Jr., The A. and M. College of Texas, May, 1954.

[2] J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

[4] (a) J. D. Roberts, W. Watanabe and R. E. McMahon, THIS JOURNAL, **73**, 760 (1951); (b) **73**, 2521 (1951).