reaction mixture was decomposed with sodium acetate solution. Acetylferrocene was recovered.

A solution of acetylferrocene and benzaldehyde in methylene chloride was similarly treated with boron fluoride (deep purple solution) followed by sodium acetate. The ketone was recovered.

When a methylene chloride solution containing only acetylferrocene was saturated with boron fluoride a deep purple colored solution was again obtained. Evaporation of the solvent in a vacuum desiccator left purple crystals which appeared to be stable on standing in the desiccator for one week. These crystals were hygroscopic but did not fume in air. They reacted readily with water to regenerate

acetylferrocene (orange needles), the purple color being destroyed.

When a solution of acetophenone in methylene chloride was similarly saturated with boron fluoride at 0° and the resulting yellow solution evaporated, a yellow solid was obtained which fumed in air.[6a] The solid reacted readily with water to regenerate acetophenone.

Under similar conditions, a solution of ferrocene in methylene chloride failed to absorb boron fluoride. No color change was noted and ferrocene was recovered.

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# A Quantitative Treatment for Electrophilic Reactions of Aromatic Derivatives[1-3]

Y. OKAMOTO AND HERBERT C. BROWN

Electrophilic reactions do not obey the usual Hammett treatment, presumably because of resonance interactions of the *para*- substituents with the electron deficient center of the transition states. The utility of the $\sigma^+$ constants, recently developed for aromatic substitution, was examined. Excellent agreement between the calculated and observed rates was observed for the nineteen electrophilic reactions for which quantitative rate data are available. A statistical analysis of the results indicates that the measure of agreement is as good as that realized by the usual Hammett treatment in reactions where it has been considered applicable. These $\sigma^+$ values should have considerable utility in correlating both the nuclear and the side-chain electrophilic reactions of aromatic systems.

The Hammett Equation 1 has provided a quantitative approach to the correlation of a large number of side-chain reactions of aromatic derivatives.[4,5]

$$\log k/k^\circ = \rho\sigma \tag{1}$$

However, this treatment has not been satisfactory for electrophilic aromatic substitutions or for side-chain reactions involving resonance interactions between an electron-deficient center and the substituents.[6]

An attempt was made to develop a set of substituent constants suitable for electrophilic reactions, but the data available were too few to provide a satisfactory test of the idea.[6] The prevailing view has been that the resonance contributions by the substituent will vary quite markedly from reaction to reaction, so that the electronic contribution of the substituent could not be reproduced by a constant, as required by the Hammett treatment.[7]

This view is quite reasonable. However, our success in correlating rate and orientation data in electrophilic aromatic substitution by means of $\sigma^+$ constants developed from the solvolysis of phenyldimethylcarbinyl chlorides[8] led us to explore their possible utility in other types of electrophilic reactions.

*Solvolysis reactions.* The $\sigma^+$ constants were developed from the rate data for the solvolysis of the substituted phenyldimethylcarbinyl chlorides.[8].This solvolysis is believed to proceed to the incipient formation of the phenyldimethylcarbonium ion in the transition state. A rigorous test of the utility of the $\sigma^+$ constants should be provided by an examination of their ability to correlate rate data in solvolytic reactions where the carbonium ions will be both more and less stable than the phenyldimethyl derivative.

Fortunately, there exist in the literature data on the solvolysis of substituted triphenylcarbinyl chlorides, benzhydryl chlorides and benzyl tosyl-

(1) Directive Effects in Aromatic Substitution. XV.

(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, 1940, chap. VII.

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

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

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

(8) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 79, 1913 (1957). A number of resonance enhanced substituent constants based on the conversion of di- and triarylcarbinols into carbonium ions and on the ionization of triarylmethyl chlorides have recently been proposed by N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3051 (1955) and N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, 60, 164 (1956), respectively. For the limited number of cases where these constants can be compared with the $\sigma^+$ values based on the solvolysis data of the present study, the agreement is quite good.

ates.[9] Certainly, the triphenylcarbonium ion should be far more stable, and the benzyl cation should be far less stable, as compared to the derivative utilized for the determination of the $\sigma^+$ constants.

In Fig. 1 are shown plots of log $k$ for the solvolysis of the triphenylcarbinyl chlorides versus $\sigma$ and $\sigma^+$. Unfortunately, there are no *meta*- derivatives to assist in fixing the line. However, it is apparent that both *p*-methoxy and $\beta$-naphthyl exhibit serious deviations in the $\sigma$-plot. On the other hand, all rate constants give an excellent linear relationship with the $\sigma^+$ values.
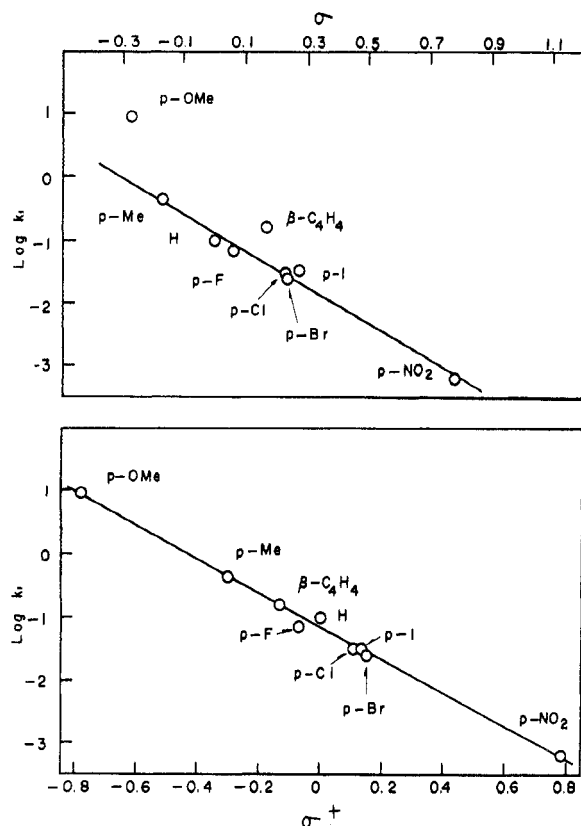


FIG. 1. SOLVOLYSIS OF TRIPHENYLCARBINYL CHLORIDES IN 40% ETHANOL–60% ETHYL ETHER AT 0° ($\beta$-C₄H₄ INDICATES $\beta$-NAPHTHYL DERIVATIVE) (19)

In the corresponding plots for the ethanolysis of the benzhydryl chlorides (Fig. 2), the $\sigma$ values reveal large deviations for the *p*-halo, *p*-alkyl, and *p*-methoxy substituents. These deviations disappear when relative rates are correlated with the $\sigma^+$ values. The solvolysis results in isopropyl alcohol include a point for $\beta$-naphthyl. No correlation between the rate constants and the $\sigma$ values is indicated by the data, whereas an excellent linear relationship is exhibited by the $\sigma^+$ treatment (Fig. 3).

(9) For convenience, all references for the data discussed in this paper are summarized in Table II, together with the reaction constants and the results of a statistical analysis of the data. The numbers in parentheses in the caption for each Figure refer to the reaction and to the literature reference in this Table.
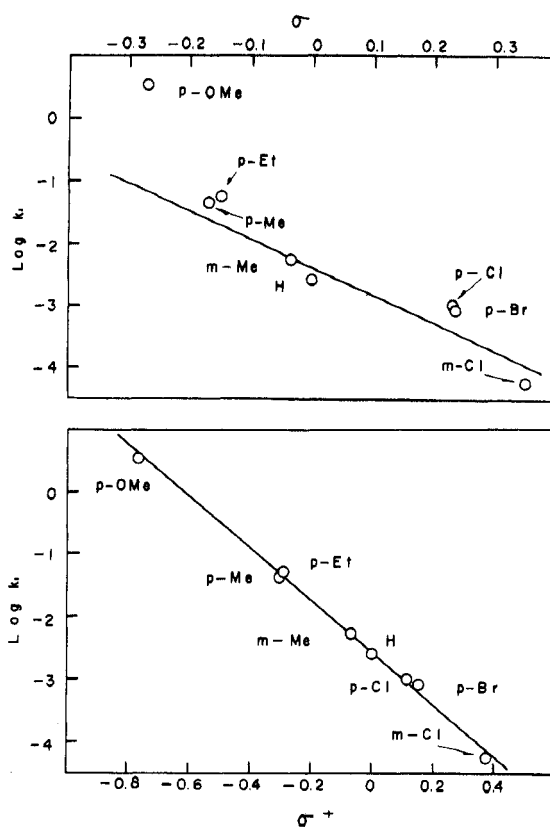


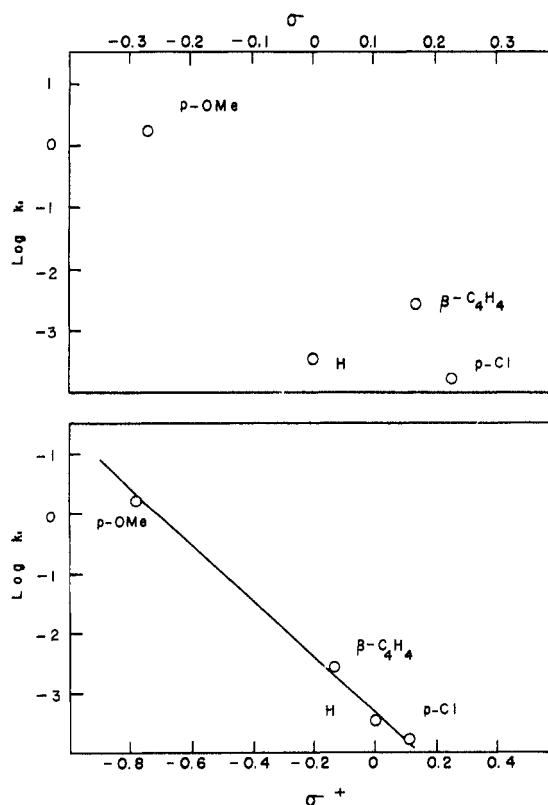FIG. 2. SOLVOLYSIS OF BENZHYDRYL CHLORIDES IN ETHANOL AT 25° (10)



FIG. 3. SOLVOLYSIS OF BENZHYDRYL CHLORIDES IN ISOPROPYL ALCOHOL AT 25° ($\beta$-C₄H₄ INDICATES $\beta$-NAPHTHYL DERIVATIVE) (9)

The benzyl tosylate results are particularly interesting (Fig. 4). As was pointed out by the authors, Kochi and Hammond, both $p$-methyl and $p$-methoxy exhibit marked deviations in the usual Hammett plot. However, the other substituents exhibit a satisfactory linearity. They attributed the deviations to resonance of the type previously mentioned.[10]
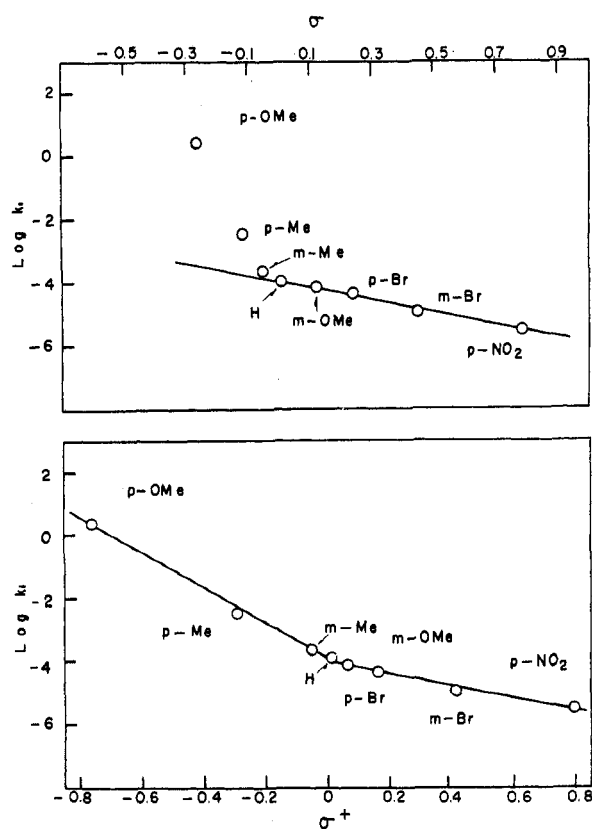
FIG. 4. SOLVOLYSIS OF BENZYL TOSYLATES IN 76.6 MOLAR % AQUEOUS ACETONE AT 25.3°

Contrary to the previous cases, the $\sigma^+$ constants do not lead to a simple linear relationship. Interestingly enough, the data appear to define two distinct lines with markedly different slopes.

It is, of course, possible that we are observing a breakdown in the $\sigma^+$ treatment. However, in view of the excellent correlation observed in all other of the reactions considered in this paper, it is reasonable to seek another explanation.

One of the two lines includes electron-supplying substituents ($m$- and $p$-methyl, $p$-methoxy), and the other includes electron-withdrawing substituents. A possible explanation for the dual linear relationship lies in the duality of mechanism concept of substitution reactions.[11] According to this interpretation, the benzyl tosylates containing electron-supplying substituents undergo solvolysis via a mechanism involving the benzyl cation ($S_N1$) and

the reaction therefore follows the $\sigma^+$ constants. With electron-withdrawing substituents this path becomes less favorable than a bimolecular displacement by the solvent ($S_N2$) and the reaction rates correspond to the $\sigma$ values.

Within recent years arguments have been advanced that substitution reactions do not fall into two distinct classes, $S_N1$ and $S_N2$, as originally proposed by Ingold and his coworkers,[10] but exhibit instead a complete spectrum of mechanism from essentially pure displacement ($S_N2$) to pure ionization ($S_N1$).[12] However, the results shown in Fig. 4 argue for the existence of two essentially distinct mechanisms in the solvolysis of benzyl tosylates.

Recently Deno and Schriesheim have determined equilibrium constants for the formation of substituted benzhydryl carbonium ion for solutions of the benzhydrols in sulfuric acid. A quantitative parallelism was demonstrated between the stability of these carbonium ions, as measured by their equilibrium constants in sulfuric acid solution, and their stability, as measured by the rates of solvolysis of the corresponding benzhydryl chlorides. Here also the data reveal an excellent correlation with the $\sigma^+$ constants (Fig. 5).

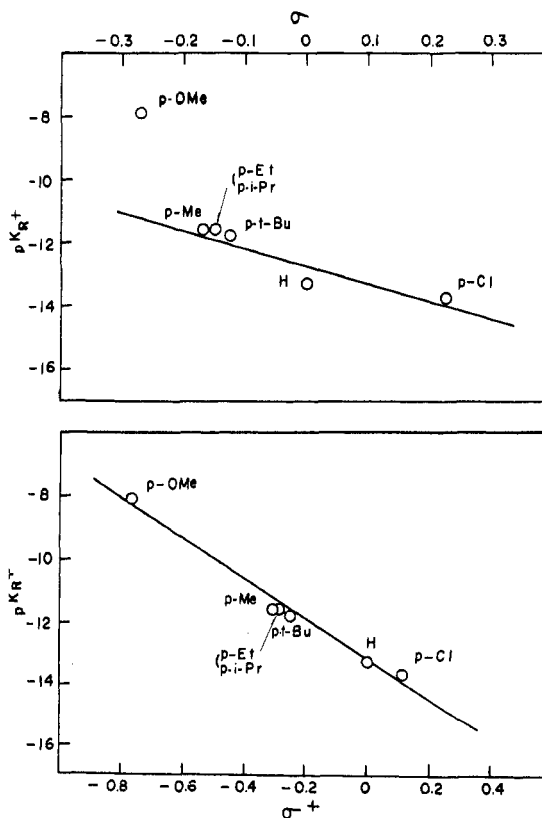Rearrangement reactions. The acid catalyzed re-



FIG. 5. EQUILIBRIUM CONSTANT FOR IONIZATION OF SUBSTITUTED DIPHENYLCARBINOLS IN AQUEOUS SULFURIC ACID AT 25° (3)

(10) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953).

(11) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953.

(12) S. Winstein, E. Grunewald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951).

arrangement of oximes (Beckmann rearrangement) is believed to proceed through an electron-deficient transition state[13] which can be stabilized by resonance interaction with suitable substituents in the *para-* position. Pearson was led to his proposal of electrophilic substituent constants as a result of the deviations he observed in the usual Hammett-type plot (Fig. 6). (In actual fact, the deviations from the least squares line are not large. This is probably because the rate data do not include any *meta-* derivatives which would serve to fix the line in a lower position). The use of the $\sigma^+$ constants leads to a satisfactory correlation (Fig. 6).
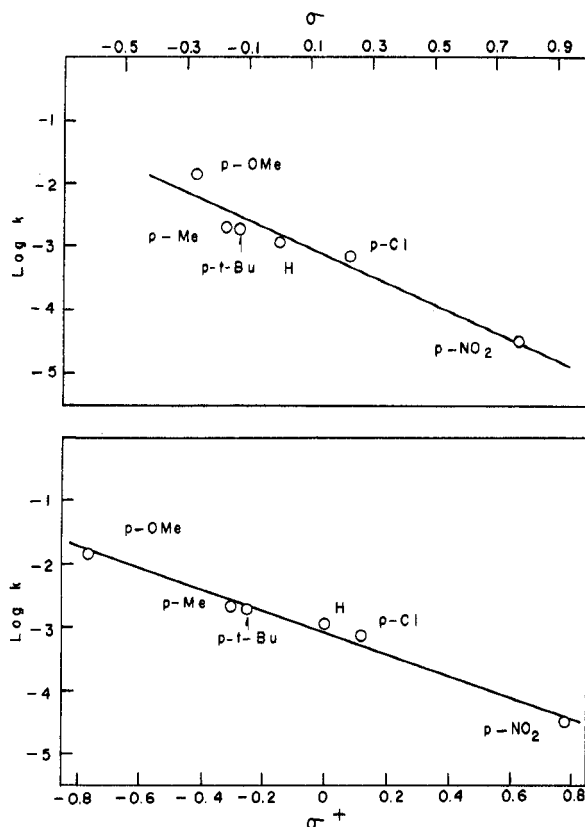


FIG. 6. REARRANGEMENT OF OXIMES IN 94.5% SULFURIC ACID AT 50.9° (*22*)

The migration aptitudes of the symmetrically substituted tetraarylpinacols was studied by Bachmann and his coworkers by utilizing what is essentially a competition technique. The relative amounts of the two isomeric ketones in the product were established and, from the data, the relative migration aptitudes were calculated.
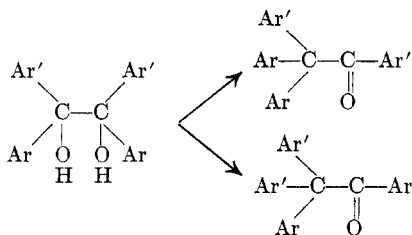


(13) D. E. Pearson and F. Ball, *J. Org. Chem.*, **14**, 118 (1949).

The transition state for the migration of the aromatic groups must resemble the transition state for aromatic substitution. Similar structural effects are observed. The values for the migration aptitudes disagree sharply with the $\sigma$ constants in the case of *p*-alkyl and *p*-methoxy (Fig. 7). However, with the possible exception of *p*-ethyl, the various substituents correspond closely with the $\sigma^+$ values.
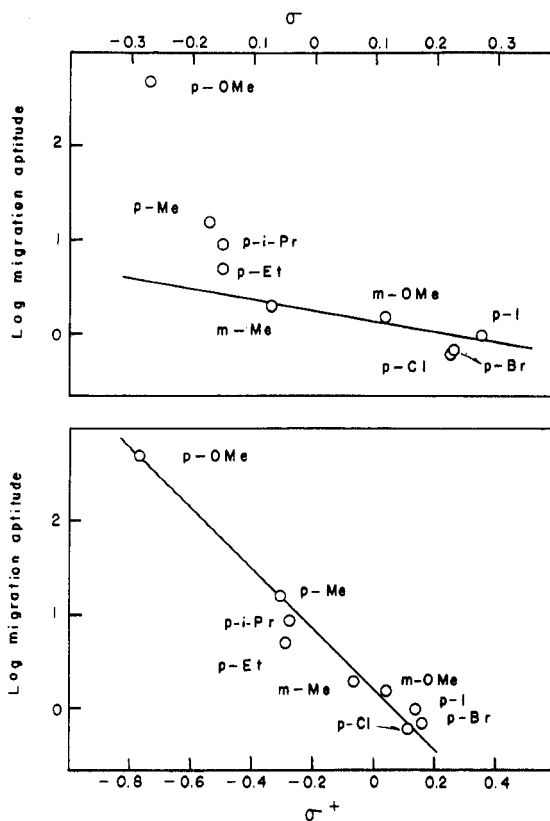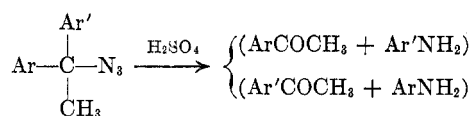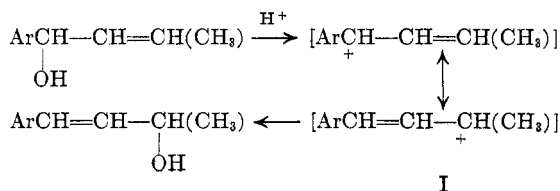


FIG. 7. MIGRATION APTITUDE IN THE REARRANGEMENT OF PINACOLS (*16*)

Diphenylmethylcarbinyl azides undergo rearrangement under the influence of sulfuric acid to yield a mixture of isomeric anilines and acetophenones.

$$\underset{\underset{CH_3}{|}}{\overset{\overset{Ar'}{|}}{Ar-C-N_3}} \xrightarrow{H_2SO_4} \begin{cases} (ArCOCH_3 + Ar'NH_2) \\ (Ar'COCH_3 + ArNH_2) \end{cases}$$

Here also the migration aptitudes exhibited by various substituted aryl rings correspond far better to the $\sigma^+$ values (Fig. 8).

The acid-catalyzed allylic rearrangement of the substituted phenylpropenylcarbinols presumably proceeds through a carbonium ion intermediate (I).

$$\underset{\underset{OH}{|}}{ArCH-CH=CH(CH_3)} \xrightarrow{H^+} [ArCH-CH=CH(CH_3)]$$

$$\underset{\underset{OH}{|}}{ArCH=CH-CH(CH_3)} \longleftarrow [ArCH=CH-CH(CH_3)]$$
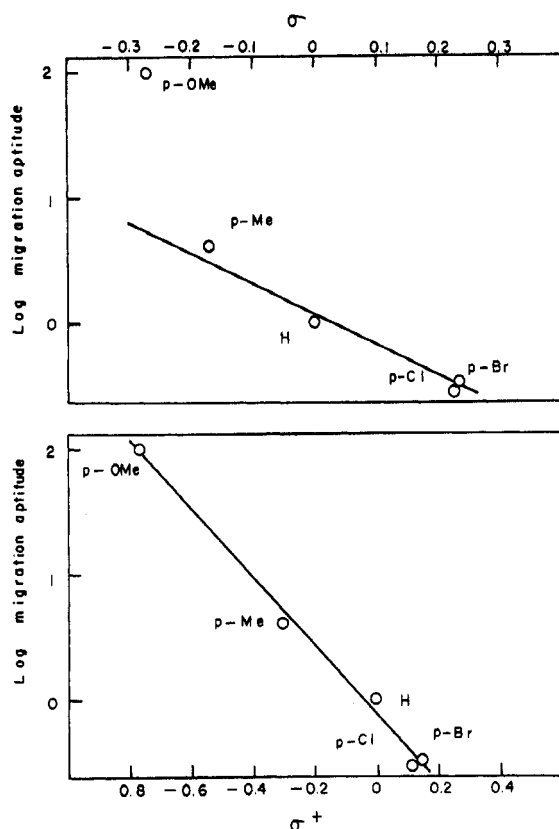
I

FIG. 8. MIGRATION APTITUDES IN THE ACID-CATALYZED REACTION OF DIPHENYLMETHYLCARBINYL AZIDES (18)

Consequently, this reaction also presents the possibility for resonance interaction between *para*-substituents and the incipient carbonium ion in the transition state. In their kinetic study of this system, Braude and Stern observed a marked enhancement in the rate of rearrangement of the $p$-methyl and $p$-methoxy derivatives. Here also the results are correlated satisfactorily by the $\sigma^+$ constants (Fig. 9).

*Addition reactions.* The ionic addition of halogen to a double bond has been demonstrated to be a two-stage process involving the transfer of a halogen cation from the halogen molecule to the double bond.[14]
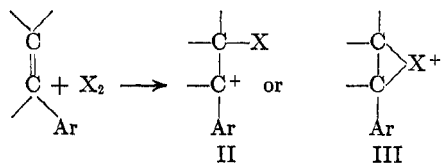


Irrespective of whether the reaction proceeds to form the carbonium ion (II) or the bridged intermediate[15](III), resonance interaction between an electron deficient structure and *para*- substituents should occur.

Fortunately, kinetic studies have been made by

(14) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).

(15) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

Robertson for the addition of chlorine to substituted cinnamic acids and benzalacetophenones. Data for the latter reaction are shown in Fig. 10. Deviations are indicated in the $\sigma$ plot for the $p$-methyl and $p$-chloro derivations. An excellent linear relationship results from the use of the $\sigma^+$ constants.
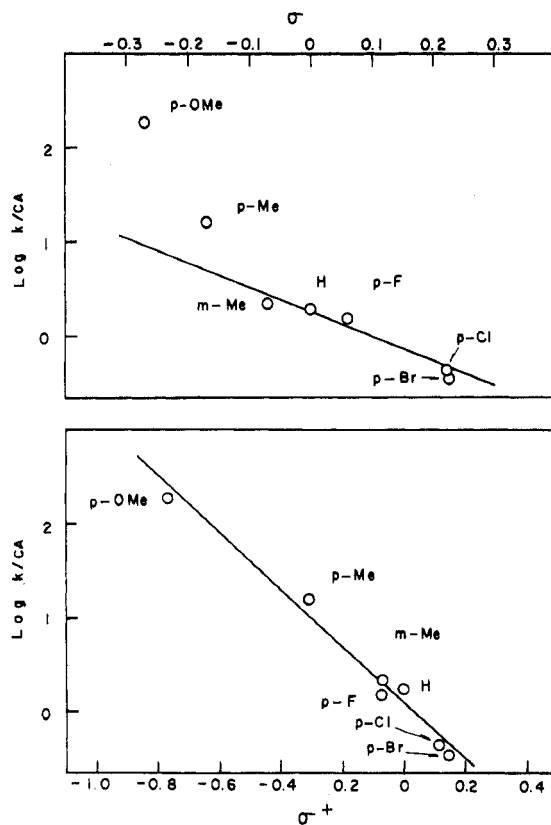


FIG. 9. ACID-CATALYZED REARRANGEMENT OF PHENYL-PROPENYLCARBINOLS, $XC_6H_4CH(OH)CH{=}CHCH_3$ in 60% AQUEOUS DIOXANE AT 30° (15)

The acid catalyzed polymerization of olefins involves the formation and addition of a carbonium ion to an olefin. The relative ability of a carbonium ion to add to various substituted styrenes should be related to the stability of the carbonium ions which result (IV). The stability of these carbonium ions will obviously be influenced by resonance interaction with substituents in the *para*- position.
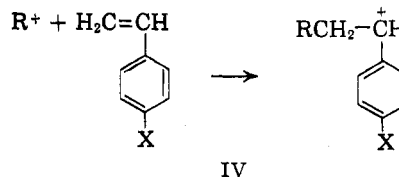


Overberger and his coworkers have determined the reactivity ratios for several substituted styrenes in their copolymerization under the influence of stannic chloride. Once again the $\sigma^+$ values yield a highly satisfactory correlation with the data (Fig. 11).

Fig. 10. Addition of Chlorine to Substituted Benzylideneacetophenones, $XC_6H_4CH$=$CHCOC_6H_5$, in Acetic Acid at 24° (*13*)

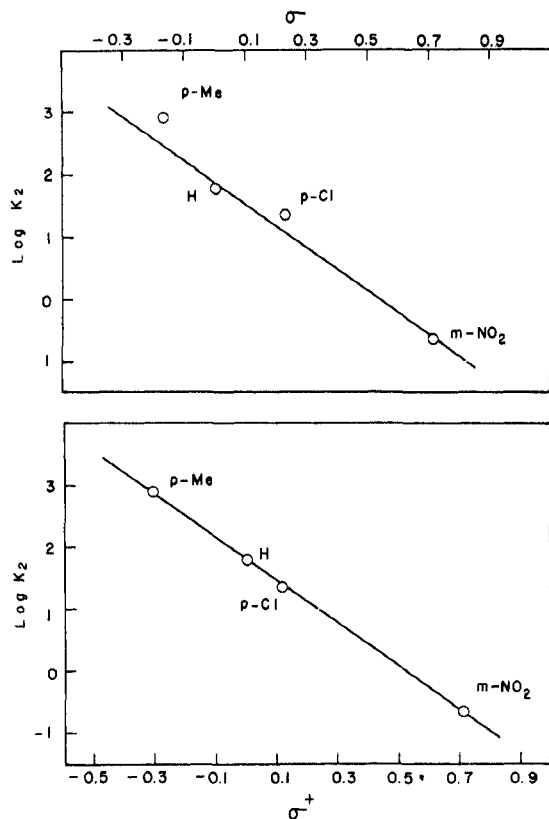*Application to reaction mechanism study.* It is quite apparent that a knowledge of whether a given reaction follows the Hammett $\sigma$ constants or the present $\sigma^+$ constants should prove of valuable diagnostic assistance in the study of reaction mechanisms. As already discussed, the behavior of the benzyl tosylates strongly suggests that their solvolysis in aqueous acetone actually proceeds by two different mechanisms. Clearly, those reactions which follow the $\sigma^+$ constants, must involve an electronic deficient intermediate of some type in the transition state, whereas reactions which agree with the Hammett $\sigma$ values must proceed without the formation of such an intermediate.

For example, Wiberg and Skryne examined the decomposition of $\alpha$-phenylethyl chlorocarbonate at 80° into $\alpha$-phenylethyl chloride and carbon dioxide. By using optically active alcohol, they demonstrated that the oxygen atom is replaced with retention of configuration. Moreover, the reaction proceeds readily in the gas phase[16] and, in the case of the benzyl and $\alpha$-phenylethyl derivatives, in such non-polar solvents as toluene and dioxane.

One hesitates to ascribe a carbonium ion intermediate to a reaction of such characteristics. However,

the authors point out that the reaction rate is influenced by structural changes in the same way as reactions which clearly involve carbonium ion intermediates. They therefore conclude that the rate-determining stage must proceed through the forma-
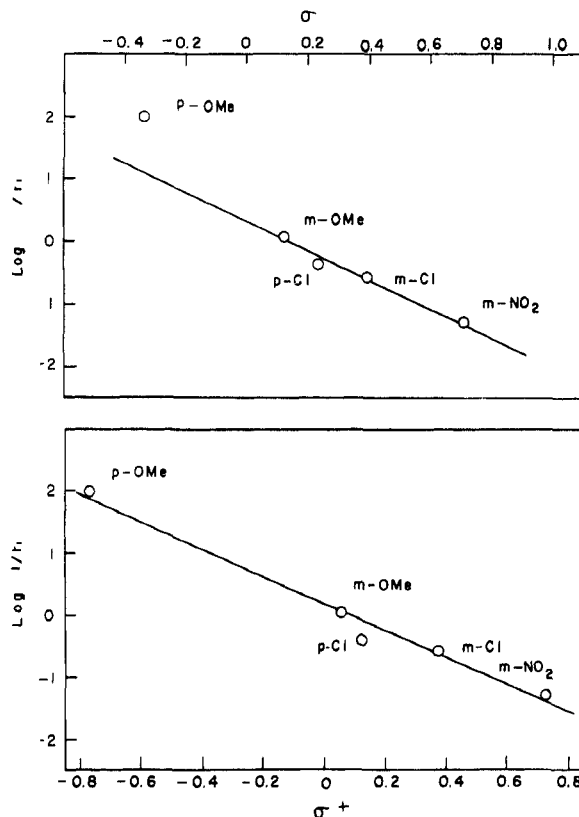


Fig. 11. Reactivity Ratio in the Stannic Chloride Catalyzed Copolymerization of Styrenes (*21*)

tion of a carbonium ion intermediate (ion-pair) (V).

$$R\!-\!O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!Cl \longrightarrow [R^+ \quad \overset{\overset{\displaystyle -O}{\diagdown}}{\underset{\underset{\displaystyle Cl}{\diagup}}{C}}\!\!=\!\!O] \longrightarrow RCl + CO_2$$

V
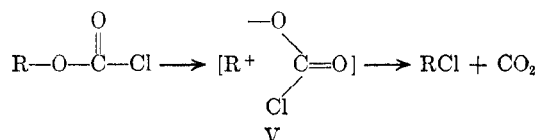
Support for this conclusion is provided by Fig. 12. The reaction rates parallel the $\sigma^+$ values closely, as would be expected for the formation of an electron-deficient intermediate in the transition state, as proposed by the authors. No correlation is obtained with the $\sigma$ values.[17]

The mechanism of the Diels-Alder reaction is believed to involve a direct condensation between the diene in the *cis* configuration and the dienophile

(16) A. R. Choppin, H. A. Frediani, and G. F. Kirby, Jr., *J. Am. Chem. Soc.*, **61**, 3176 (1939); A. R. Choppin and G. F. Kirby, Jr., *J. Am. Chem. Soc.*, **62**, 1592 (1940); A. R. Choppin and E. L. Compere, *J. Am. Chem. Soc.*, **70**, 3797 (1948).

(17) The authors report a plot of their rate constants versus $\sigma$. They draw a straight line through the four points other than hydrogen and consider that only this point deviates from the Hammett treatment. However, because of the considerations which have been presented in this series of papers, we believe that the line is more properly drawn through the hydrogen and *m*-bromo points, with the deviations exhibited by *p*-chloro, *p*-fluoro, and *p*-methyl attributed to resonance interaction.

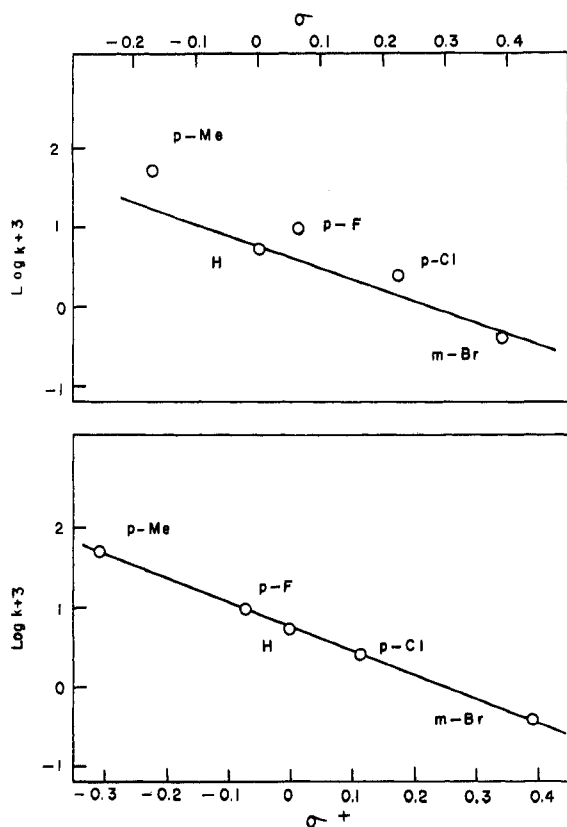FIG. 12. DECOMPOSITION OF $\alpha$-PHENYLETHYL CHLORO-CARBONATES IN DIOXANE AT 80° (17).

oriented in a plane above and parallel to the *cis* diene structure.[18] Woodward suggested that there is formed in the course of the reaction an intermediate in which an electron has been transferred from the diene to the dienophile. In this process the diene is converted into a radical carbonium ion.[19] It follows that considerable resonance interaction should occur with suitably placed substituents.

Recently a study was made by DeWitt, Lester, and Ropp on the rates of reaction of substituted 1-phenyl-1,3-butadienes with maleic anhydride. As was noted by the authors, the rates deviate somewhat from the Hammett equation. However, they give excellent agreement with the $\sigma^+$ values (Fig. 13). Such agreement would appear to support the mechanistic proposal by Woodward and Baer.[19]

*Summary of data.* The available data on the substituent constants and reaction constants for electrophilic reactions are summarized in Tables I and II. A statistical analysis of the data was made, following Jaffe's treatment,[5] and the results of this analysis are included in the Tables. A comparison of the data with those reported by Jaffé indicates that the agreement here realized for electrophilic

(18) A. Wassermann, *J. Chem. Soc.*, 828 (1935); G. A. Benford, H. Kaufmann, B. S. Khambata, and A. Wassermann, *J. Chem. Soc.*, 381 (1939).

(19) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 3058 (1942); R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944).

reactions is quite as satisfactory as that obtained in the usual Hammett correlation.[5]

TABLE I

ELECTROPHILIC SUBSTITUENT CONSTANTS ($\sigma^+$)

| Substituent | $\sigma^+$ | $n^a$ | $r^b$ |
|---|---|---|---|
| *p*-Methoxy | −0.764 | 14 | 0.072 |
| *p*-Methyl | −0.306 | 19 | 0.048 |
| *p*-Ethyl | −0.291 | 5 | 0.024 |
| *p*-Isopropyl | −0.276 | 4 | 0.016 |
| *p-t*-Butyl | −0.250 | 5 | 0.029 |
| 3,4-$C_4H_4^c$ | −0.132 | 3 | 0.054 |
| *p*-Fluoro | −0.0714 | 10 | 0.050 |
| *m*-Methyl | −0.069 | 7 | 0.021 |
| *m*-Ethyl | −0.0625 | | |
| *m*-Isopropyl | −0.0589 | | |
| *m-t*-Butyl | −0.0581 | | |
| Hydrogen | 0 | | |
| *m*-Methoxy | 0.0465 | 3 | 0.014 |
| *p*-Chloro | 0.112 | 19 | 0.047 |
| *p*-Iodo | 0.132 | 5 | 0.044 |
| *p*-Bromo | 0.148 | 11 | 0.043 |
| *m*-Fluoro | 0.337 | 1 | |
| *m*-Iodo | 0.352 | 2 | 0.048 |
| *m*-Chloro | 0.373 | 4 | 0.057 |
| *m*-Bromo | 0.391 | 4 | 0.048 |
| *m*-Nitro | 0.662 | 5 | 0.071 |
| *p*-Nitro | 0.777 | 6 | 0.043 |

$^a$ The number of reactions for which data for each substituent are available. $^b$ Probable error (deviation), calculated from r = 0.8453Ā, where Ā is the average deviation of experimental measurements from the $\sigma$ value. $^c$ $\beta$-Naphthyl derivatives.
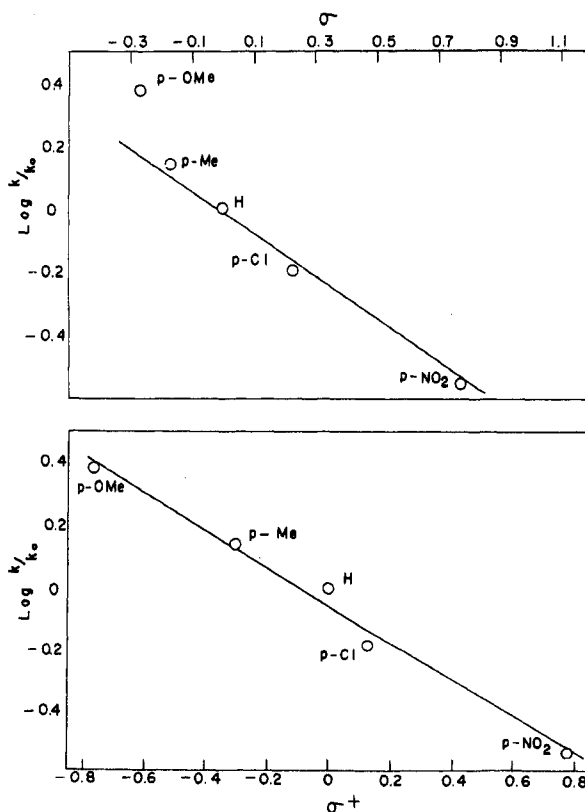


FIG. 13. DIELS-ALDER REACTION OF *para*-SUBSTITUTED 1-PHENYL-1,3-BUTADIENES WITH MALEIC ACID ANHYDRIDE IN DIOXANE AT 45° (24)

TABLE II

REACTION CONSTANTS

| Reaction No. | Reaction | $\rho$ | $s^a$ | $c^b$ | $n^c$ |
|---|---|---|---|---|---|
| 1. | Solvolysis of phenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25° [d] | −4.62 | 0.274 | 0.980 | 8 |
| 2. | Halogenation of monosubstituted benzenes by bromine and chlorine in acetic acid | −11.35 | 0.690 | 0.987 | 6 |
| 3. | Equilibrium constants for carbonium ions from benzhydrols in sulfuric acid at 25° | −6.67 | 0.296 | 0.990 | 7 |
| 4. | Nitration of monosubstituted benzenes in nitromethane or acetic anhydride at 25° | −6.53 | 0.335 | 0.975 | 9 |
| 5. | Solvolysis of p-alkylbenzhydrylchlorides in ethanol at 25° | −4.63 | 0.076 | 0.994 | 5 |
| 6. | Protonolysis of phenyltrimethylsilanes by perchloric acid in 72% aqueous methanol at 50° | −4.59 | 0.215 | 0.986 | 8 |
| 7. | Brominolysis of benzeneboronic acids in 20% acetic acid and 0.40$M$ sodium bromide at 25° | −4.30 | 0.224 | 0.991 | 12 |
| 8. | Solvolysis of p-halobenzhydryl chlorides in 70% aqueous acetone at 25° | −4.11 | 0.016 | 0.999 | 4 |
| 9. | Solvolysis of benzhydryl chlorides in isopropyl alcohol at 25° | −4.06 | 0.250 | 0.992 | 4 |
| 10. | Solvolysis of benzhydryl chlorides in ethanol at 25° | −4.05 | 0.251 | 0.998 | 8 |
| 11. | Addition of chlorine to cinnamic acids in acetic acid at 24° | −4.01 | 0.097 | 0.999 | 4 |
| 12. | Equilibrium constants for carbonium ions from triphenylcarbinols in sulfuric acid at 25° | −3.55 | 0.181 | 0.982 | 4 |
| 13. | Addition of chlorine to benzalacetophenones in acetic acid at 24° | −3.66 | 0.032 | 0.999 | 4 |
| 14. | Thermal rearrangement of α-phenylethyl chlorocarbonates in dioxane at 80° | −3.08 | 0.014 | 0.999 | 5 |
| 15. | Acid-catalyzed rearrangement of phenylpropenylcarbinols, $XC_6H_4CH-(OH)CH=CHCH_3$, in 60% aqueous dioxane at 30° | −3.02 | 0.154 | 0.990 | 7 |
| 16. | Migration aptitudes in the rearrangement of sym. tetraarylpinacols by acetyl chloride in acetic acid or by iodine in acetic acid and benzene | −2.99 | 0.195 | 0.979 | 9 |
| 17. | Thermal rearrangement of α-phenylethyl chlorocarbonates in toluene at 80° | −2.87 | 0.100 | 0.993 | 5 |
| 18. | Migration aptitudes in the acid-catalyzed reaction of diphenylmethylcarbinyl azides | −2.77 | 0.093 | 0.997 | 4 |
| 19. | Solvolysis of triphenylcarbinyl chlorides in 40% ethanol-60% ethyl ether at 0° | −2.68 | 0.078 | 0.997 | 9 |
| 20. | Same as 19, but at 25° | −2.34 | 0.099 | 0.992 | 7 |
| 21. | Reactivity ratio in the stannic chloride-catalyzed copolymerization of styrenes | −2.34 | 0.191 | 0.991 | 5 |
| 22. | Rearrangement of oximes in 94.5% sulfuric acid at 50.9° | −1.76 | 0.094 | 0.995 | 8 |
| 23. | Reactivity ratio in the stannic chloride-catalyzed polymerization of styrenes with α-methylstyrene | −1.70 | 0.181 | 0.969 | 5 |
| 24. | Reaction of 1-phenyl-1,3-butadienes with maleic anhydride in dioxane at 45° | −0.62 | 0.012 | 0.997 | 4 |

[a] The standard deviation of experimental measurements from the regression line. [b] The correlation coefficient. [c] The number of compounds involved in the calculation of $\rho$. [d] The reaction constant, $\rho$, was determined by the data for m-Me, m-Et, m-F, m-Cl, m-Br, m-I, m-NO₂ and H.

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*Theoretical implications.* As Hammett has pointed out,[4] the existence of a linear relationship between the logarithms of the constants (1) is equivalent to a linear relation between the free energies of reaction or activation. The reactions of *meta-* and *para-* derivatives exhibit similar entropies of reaction. The limitation of the treatment to reactants with similar entropies of reaction implies that the linear relationship must be one between the potential energies of the reactants.

The substituent constant, $\sigma$, is considered to be a measure of the effect of the substituent in modifying the electron density at the reaction center. A negative value of the substituent indicates an increase in the electron density; a positive value of $\sigma$, a decrease. The larger the numerical value of $\sigma$, the greater the effect of the substituent on the electron density (and on the potential energy). The reaction constant $\rho$ reflects the sensitivity of the rate or equilibrium constant to changes in the electron density (and potential energy). In the *meta-* position the substituent must exert its effect largely through induction. In the *para-* position induction is still of major importance, but a small resonance factor must be introduced to account for the observed differences in the values of the *meta-* and *para-* $\sigma$ values.

The inductive effect should be essentially independent of the reaction. However, the resonance contribution would be expected to vary with the electronic demands of the reaction and should, therefore, be a function of $\rho$. Using the symbols $\sigma_I$ and $\sigma_R$ to represent the inductive and resonance components of the substituent constants, we can write,

$$\sigma_m = \sigma_{I_m} \tag{2}$$

$$\sigma_p = \sigma_{I_p} + \sigma_R f(\rho) \tag{3}$$

The Hammett equation is found to be operable for an enormous number of reactions of various types. For the great majority of these, with widely varying values of $\rho$, the rate and equilibrium constants are represented satisfactorily by a single set of $\sigma$ values. It follows that the changes in $\sigma_R$ must be no larger than the usual limits of precision in applying the Hammett treatment. This can only be true if $\sigma_R$ changes only slightly with relatively large changes in $\rho$. Consequently, we can write, as a first approximation,[20]

(20) This approximation is not satisfactory for systems where a powerful electron-withdrawing substituent, such as *p*-nitro and *p*-cyano, is coupled with a powerful electron-supplying substituent, such as *p*-methoxy or *p*-amino. In these cases it is no longer possible to utilize the usual $\sigma$ values and a corrected value must be introduced to reduce the discrepancy (ref. 5).

$$\sigma_p \cong \sigma_{I_p} + \sigma_R \tag{4}$$

Electrophilic reactions provide far greater opportunity for resonance contributions by the substituent. The difference in the $\sigma$ and $\sigma^+$ values is attributed to such resonance (Table III). The magnitude of the resonance contributions measured in this way agree with current interpretations of the factors controlling reactivity in organic structures.

In these reactions also, the resonance contributions of the substituent, $\sigma_R^+$, would be expected to vary as a function of the electronic demands of the reaction.[21,22]

$$\sigma_m^+ = \sigma_{I_m} \tag{5}$$

$$\sigma_p^+ = \sigma_{I_p} + \sigma_R + \sigma_R^+ f(\rho) \tag{6}$$

$$\sigma_p^+ = \sigma_p + \sigma_R^+ f(\rho) \tag{7}$$

(21) The variation of the resonance contribution as a function of $\rho$ was discussed by Hammett at the Bryn Mawr Conference on Reaction Mechanisms (ref. 5).

(22) In recent years considerable research activity has been evidenced in studying the different components of the Hammett substituent constants and in exploring the extension of the Hammett treatment to reaction systems not now amenable to this treatment. In the course of these studies a considerable number of different symbols have been proposed and utilized by various authors: sigma*e* (Pearson[6]), $\sigma^*$ (Jaffe[6]), $\sigma^*$ (R. W. Taft, Jr., in M. S. Newman, ed., *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, Chap. 13), $\sigma_R$ (Deno[6]), $\sigma'$, [J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953)], $\sigma^{**}$ [J. Miller, *Aust. J. Chem.*, **9**, 61 (1956)], etc.

In some cases the same symbol has been utilized for different quantities; in others, different symbols have been utilized for the same quantity. The situation was discussed at the Reaction Mechanism Conference at Swarthmore (Sept., 1956) by a number of workers in the field, including H. Jaffé, R. W. Taft, Jr., N. C. Deno, H. C. Brown, and others. In order to avoid the confusion arising from the present situation, it appeared desirable to adopt a standard set of symbols and to propose them in the hope that others would find them satisfactory. These symbols have been used in the above treatment.

(a) $\sigma = \sigma_I + \sigma_R$ where $\sigma$ is the usual Hammett substituent constant and the subscripts I and R refer to its inductive and resonance components.

(b) $\sigma^- = \sigma_I + \sigma_R^-$ where $\sigma^-$ is the "dual" value[5] for use with derivatives of phenol and aniline and for nucleophilic substituents in aromatic nuclei. [J. F. Bennett, *et al.*, *J. Am. Chem. Soc.*, **75**, 642 (1953); J. Miller, *loc. cit.*]

(c) $\sigma^+ = \sigma_I + \sigma_R^+$ where $\sigma^+$ is the substituent constant applicable to electrophilic reactions.

According to this scheme, $\sigma^*$ as used by Jaffé is replaced by $\sigma^-$. The symbol $\sigma^*$ as used by Taft is retained for the aliphatic series and for *ortho* substituted benzene derivatives. The symbol $\sigma_R$ as used by Deno and sigma*e* as used by Pearson is replaced by $\sigma^+$. The symbol $\sigma'$ used by Roberts (*loc cit.*) for 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid derivatives is retained. By the arguments of Roberts and Moreland and Taft (*loc. cit.*), $\sigma'$ and $\sigma_I$ may be equated, *i.e.* $\sigma_I \equiv \sigma'$. The symbol $\chi$ ($p$-$\sigma$-$\sigma' \equiv \chi$) as used by Taft (*loc. cit.*), is replaced by $\sigma_R$.

TABLE III

RESONANCE CONTRIBUTIONS IN ELECTROPHILIC REACTIONS

| Substituent | $\sigma_m^+ - \sigma_m$ | $\sigma_p^+ - \sigma_p$ |
|---|---|---|
| Methoxy | −0.069 | −0.496 |
| 3,4-C$_4$H$_4$ ($\beta$-naphthyl) | | −0.302 |
| Methyl | 0.004 | −0.136 |
| Fluoro | 0.009 | −0.133 |
| Chloro | 0.018 | −0.115 |
| Bromo | 0.008 | −0.084 |
| Iodo | 0.001 | −0.144 |
| Nitro | −0.048 | −0.001 |

In the present paper we have examined all of the data now available on electrophilic reactions. Admittedly the reactions are relatively few and the data all too sparse. However, with these limitations in mind, it has been possible to achieve a reasonable correlation between a single set of $\sigma^+$ constants and all of the experimental data without any serious discrepancies. Indeed, the measure of agreement realized appears to be of the same quality as that obtained in the usual Hammett treatment. It follows that here also $\sigma_R^+$ must be either a constant, which appears improbable, or that it changes relatively moderately with large changes in $\rho$. In other words, with $\sigma_R^+$ a relatively insensitive function of $\rho$ (7), we can, to a first approximation, treat $\sigma_R^+$ as a constant, independent of $\rho$ (8).

$$\sigma_p^+ \cong \sigma_p + \sigma_R^+ \tag{8}$$

That this is a reasonable approximation is indicated by the constancy of the calculated values of $\sigma_p^+ \left( \sigma_p^+ = \dfrac{\log k/k^0}{\rho} \right)$ for all of the reactions listed in Table II. Values of $\sigma_p^+$ are plotted as a function of $\rho$ for three representative substituents, methoxy, methyl, and chloro (Fig. 14). The scatter about the $\sigma_p^+$ value (solid line) is of the same order of magnitude as that observed in the usual Hammett treatment. It is of particular interest that the scatter in values appears to be haphazard and exhibits no trend with decreasing values of $\rho$.

The widespread use of the Hammett equation is justified by its evident utility in correlating rate and equilibrium constants and not by any theoretical basis for its existence. In the same way, the justification for the extension of the Hammett treatment presented in this paper lies in its appar-
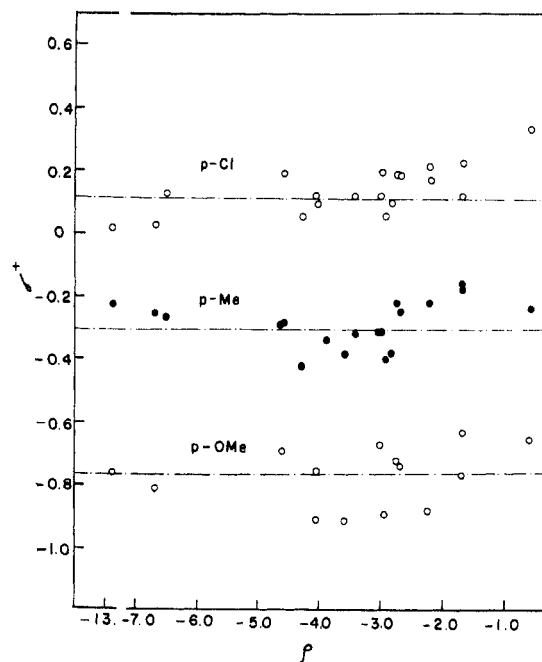


FIG. 14.  VARIATION IN $\sigma^+$ FOR $p$-METHOXY, $p$-METHYL AND $p$-CHLORO AS A FUNCTION OF $\rho$

ent utility in providing a quantitative correlation of aromatic substitution and other electrophilic reactions. It is to be hoped that additional data will soon be forthcoming to provide a rigorous test of the full utility and possible limitation of the $\sigma^+$ constants in correlating electrophilic reaction data.

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