

solution was dried, the solvent was evaporated, and the residue was distilled under reduced pressure to give 19.4 g. (94%) of benzonitrile, b.p. 70–71° (10 mm.),  $n_D^{25}$  1.5206. The aqueous solution was made strongly acid with concentrated hydrochloric acid, and the solid which separated was recovered by filtration, washed with water and dried. There was obtained 33.3 g. of solid, much more than the 24.4 g. of benzoic acid required by theory. It appeared that sodium trifluoroacetate or sodium chloride had coprecipitated with the benzoic acid. This was removed by treating the solid with 300 ml. of ether, filtering to remove undissolved solid, washing with two 50-ml. portions of water to remove any dissolved sodium trifluoroacetate, and drying. Evaporation of the ether left 21.4 g. (88%) of benzoic acid, m.p. 120.5–122°. A mixture of this material and authentic benzoic acid melted at 120.5–122°.

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## Correlation of Polarographic Data with Structure. Use of the Hammett-Taft Relation

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The success which the Hammett polar substituent relation has had in correlating the polarographic half-wave potential data of certain series of organic compounds with their structure, prompted an examination of the applicability of the Taft elaboration on the Hammett relation for the same purpose. The Taft-Hammett equation very satisfactorily correlates data in the electrochemical reduction of a variety of functional groups in both aliphatic and aromatic compounds. In the case of aliphatic compounds, the equation is apparently not applicable for substituents larger than ethyl groups.

Considerable attention has been given in the polarographic literature to the search for consistent relationships between the half-wave potential,  $E_{1/2}$ , and the structural characteristics of electroreducible and electrooxidizable organic substances.<sup>1</sup> Generally, none of the various relationships developed has been widely applied. However, specific areas of good agreement between the observed behavior of a series of related compounds and a particular correlating equation are well known, especially in connection with the Hammett equation,<sup>2</sup>

$$\log(k/k_0) \text{ or } \log(K/K_0) = \sigma\rho \quad (1)$$

where  $k$  is a rate constant,  $K$  an equilibrium constant,  $\sigma$  a polar substituent constant based on the structure of the reacting molecule, and  $\rho$  a reaction constant which measures the susceptibility of a given reaction series to polar substituents; the zero subscript refers to some member of a reaction series arbitrarily chosen as standard;  $k$  or  $K$  sans subscript refers to any other member of the same series.

Successful correlation of polarographic half-

wave potentials with structure has been achieved through use of Equation 1 by assuming that  $E_{1/2}$  is proportional to  $\log K$ , the unknown proportionality constant being absorbed in the  $\rho$  factor, *e.g.*,

$$E_{1/2} - (E_{1/2})_0 = \sigma\rho \quad (2)$$

As in the case of rates and equilibrium constants, this correlation fails for *ortho* benzene derivatives and aliphatic compounds.<sup>3</sup>

Taft<sup>4</sup> developed an equation analogous to that of Hammett but applicable to *ortho* derivatives and aliphatic compounds, and a further equation of great generality

$$P_\sigma = \sigma^*\rho^* \quad (3)$$

where  $P_\sigma$  is any parameter proportional to energy and dependent upon the polar effect of substituent groups, *e.g.*, dipole moments, vibration frequencies and bond energies; dimensional consistency is maintained by assigning the proper dimensions to the empirical constant,  $\rho^*$ .

Taft<sup>4</sup> has applied his generalized form of the Hammett equation to predict successfully the outcome of the experimental determination of  $E_{1/2}$  of an aliphatic compound studied by the

(3) E. C. Bennett, Ph.D. Thesis, University of Michigan, 1954.

(4) (a) R. W. Taft, *J. Am. Chem. Soc.*, **74**, 2729 (1952);

(b) *J. Am. Chem. Soc.*, **74**, 3120 (1952); (c) *J. Am. Chem. Soc.*, **75**, 4231 (1953).

(1) *E.g.*, R. L. Bent, J. C. Dessloch, F. C. Duennebler, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.*, **73**, 3100 (1951); P. Zuman, *Chem. Listy*, **48**, 94 (1954).

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

authors.<sup>5,6</sup> Consequently, the study of the applicability of the Taft relationship to the correlation of the ease of polarographic reduction with structure in other series of organic compounds was undertaken. The greater applicability of the Taft equation as compared to the Hammett equation would be especially advantageous in polarography.

*Application of the Hammett-Taft equation.* The success of the Taft-Hammett equation in correlating  $E_{1/2}$  with structure is illustrated by Table I, which summarizes data for the polarographic reduction of eight series of compounds (other series, which do not follow Taft's correlation, are discussed later). The correlation is used in the form

$$E_{1/2} = \sigma^* \rho^* + (E_{1/2})_0 \quad (4)$$

in which  $(E_{1/2})_0$  corresponds to  $E_{1/2}$  for reduction of that member of a series of related compounds

TABLE I

CORRELATION OF POLAROGRAPHIC HALF-WAVE POTENTIALS BY THE TAFT-HAMMETT EQUATION

Reaction Series <sup>a</sup>	Equation Applicable	$\delta$	Ref.
1. 2-Bromoalkanoic acids $R_1R_2C(Br)COOH$	$-0.41 \sigma^* - 0.030$	0.02	6
2. Ethyl-2-bromoalkanoates $R_1R_2C(Br)COOC_2H_5$	$-0.28 \sigma^* - 2.71$	0.02	6
3. Substituted phenones $pH 5$ $pH 9$ $C_6H_5COR$	$0.33 \sigma^* - 1.27$ $0.36 \sigma^* - 1.44$	0.01	7
4. Substituted ethylenes $R_1R_2C = CR_3R_4$	$0.72 \sigma^* - 3.77$	0.05	8
5. Ethyl trichloroacetate (three waves)	$0.81 \sigma^* - 2.37$	0.03	9
6. Alkyl bromides $R_1R_2R_3CBr$	$0.63 \sigma^* - 2.71$	0.12	10
7. Bromomethane derivatives $BrCH_2R$	$1.04 \sigma^* - 2.11$	0.03	10, 11
8. Iodobenzoic acids ( <i>o</i> , <i>m</i> , and <i>p</i> )	$-0.44 \sigma^* - 1.32$	0.01	12

<sup>a</sup> Substituents corresponding to the above reaction series are given below, e.g., the pairs of substituents used in the first series of the 2-bromoalkanoic acids were H and H, H and  $CH_3$ ,  $CH_3$  and  $CH_3$ ,  $CH_3$  and  $CH_3$ , and  $C_2H_5$ , etc. (numbers are those of the tabulated values of the substituent constants in Taft's paper<sup>4c</sup>; the constants used here are the following: 1.  $Cl_3C$ , 2.65; 3.  $Cl_2H$ , 1.940; 4.  $CH_3CO$ , 1.65; 6.  $ClCH_2$ , 1.050; 7.  $CH_2Br$ , 1.030; 11.  $C_6H_5$ , 0.600; 14. H, 0.490; 23.  $CH_3$ , 0.000; 25.  $C_2H_5$ , -0.100; 26. *n*- $C_3H_7$ , -0.115; 28. *n*- $C_4H_9$ , -0.130; 30. *i*- $C_3H_7$ , -0.210): 1. 14, 14; 14, 23; 23, 23; 23, 25; 14, 25; 25, 25; 25, 28. 2. 23, 25; 14, 25; 23, 23; 25, 25. 3. 11; 14; 25; 26; 30. 4. 11, 14, 14, 14; 11, 14, 14, 23; 11, 14, 14, 11; 11, 11, 14, 14; 11, 11, 14, 11; 11, 11, 11, 11. 5. 1; 3; 6. 6. 14, 14, 14; 14, 14, 23; 14, 14, 26; 14, 14, 27; 14, 23, 25; 7, 14, 14; 7. 4; 14; 23; 26.

(5) R. W. Taft, personal communication.

(6) P. J. Elving, J. M. Markowitz, and I. Rosenthal, *J. Electrochem. Soc.*, **101**, 195 (1954).

for which  $\sigma^*$  is zero. Taft's  $\sigma^*$  parameters<sup>4c</sup> are referred in all cases to the methyl group, e.g., in compound series 1 of Table I where the general formula is  $R_1R_2C(Br)COOH$ ,  $(E_{1/2})_0$  is the half-wave potential of 2-bromo-2-methylpropanoic acid. The fit of Equation 4 to the data was performed by the method of least squares; the standard deviation,  $\delta$ , is given.

The disparate nature of the kinds of compounds which can be successfully correlated by this method is evident. However, anomalies occur, some of which are instructive in themselves. For example, in the 2-bromoalkanoic acids (series 1), the equation fails to predict  $E_{1/2}$  correctly for 2-bromo-2-ethylhexanoic acid, or, indeed, for any of the straight chain acids larger than 2-bromobutanoic acid;  $E_{1/2}$  is more positive than the equation predicts, indicating the action of structure-sensitive factors other than pure polar effects. Much the same kind of anomaly occurs with the alkyl bromides (series 6), in which the *n*-butyl and isobutyl bromides lie off the mean straight line of the equation by a distance exceeding the standard deviation for the remaining members of the series, whereas *sec*-butyl bromide lies precisely on the line. The consistency of these facts with those for series 1 may be seen by considering the structure upon which the correlation for the alkyl bromides is based:



In *n*-butyl bromide one of the substituents, R, is normal propyl and in isobutyl bromide one of them is isopropyl; however, in *sec*-butyl bromide the largest substituent is ethyl. Thus, in both the 2-bromoalkanoic acids and in the alkyl bromides the Taft-Hammett relationship, when applied to half-wave potentials, breaks down for substituents larger than ethyl groups.

In the monobromomethane derivatives (series 7), the compounds included are bromoacetone, ethyl bromide, bromoform and *n*-butyl bromide;  $E_{1/2}$  data are not available for methyl bromoacetate, which is structurally a member of this series, and Taft gives no  $\sigma^*$  value for ethyl bromoacetate, for which polarographic data are available. An attempt to correlate  $E_{1/2}$  data for chloroacetone,

(7) P. J. Elving and J. T. Leone, *J. Am. Chem. Soc.*, **80**, 1021 (1958).

(8) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).

(9) P. J. Elving and C.-S. Tang, *J. Am. Chem. Soc.*, **76**, 1412 (1954).

(10) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

(11) R. E. Van Atta, Ph.D. Thesis, The Pennsylvania State University, 1952.

(12) P. J. Elving and C. L. Hilton, *J. Am. Chem. Soc.*, **74**, 3368 (1952).

chloroform, and methyl chloroacetate was unsuccessful, suggesting that carboalkoxy groups, unlike the ketone group, cannot be successfully correlated by the present scheme (although more data would be necessary for verification). Therefore, any attempt to extend Taft's list of  $\sigma^*$  values to include the carboethoxy group by use of the polarographic data of series 7 would likely lead to an erroneous assignment.

In general, attempts to extend the list of  $\sigma^*$  values by using polarographic data did not lead to consistent results, especially for the case of halomethyl substituents. For example, Taft<sup>4c</sup> lists  $\sigma^*$  values for  $-\text{CH}_2\text{Cl}$  and  $-\text{CH}_2\text{Br}$ , but not for  $-\text{CH}_2\text{I}$ . A precise value for the substituent constant of the latter group is readily obtained by plotting the data for the three monohaloacetones. However, use of this value to correlate  $E_{1/2}$  for the three haloforms does not give a straight line. As a second example, the success of the correlation for the three polarographic waves of ethyl trichloroacetate (series 5, which is equivalent to the series of the three ethyl esters of the chloroacetic acids), encouraged the belief that the data for ethyl bromoacetate might fall on the same line; it does not.

Actually, in series 5 the Taft substituent constants are being used somewhat improperly, since they are intended to measure the effect of substituents on a *nearby* reaction center. In the reduction of the haloacetates, the halogen is being attacked, leading to carbon-halogen bond fission, *i.e.*, the entity being used as a substituent is itself at the reaction center. Whether the success of the Taft-Hammett equation in the face of this misuse is only fortuitous or whether it indicates a greater generality for this equation than has been suspected, cannot now be decided.

It should be noted that in addition to predicting

the effect of substituents on carbon-halogen bond fission, the Taft-Hammett equation is successful in predicting their effect upon the reduction of both carbonyl and carbon-carbon double bonds (series 3 and 4). Furthermore, the success of correlation is somewhat independent of solution environment, a good fit being achieved at each of two different pH values (series 3).

The Taft-Hammett equation was unsuccessful when applied to the nitroalkanes and hydroxynitroalkanes; values based on the Taft substituent values for the structure  $\text{R}_1\text{R}_2\text{R}_3\text{CNO}_2$  were completely scattered, regardless of the bulk of the R groups.

*Conclusions.* Like the Hammett equation, the Taft-Hammett equation appears to be generally useful in discussing the ease of electrochemical reduction (and presumably of oxidation) of certain series of structurally related compounds. It is likely that those series or those members of a series which follow the equation are subject to polar effects only, as far as the structural effect on  $E_{1/2}$  is concerned, or that the energetic magnitude of polar effects overshadows the energetic contributions of other effects such as adsorption. Thus, the Taft-Hammett relation may have possibilities for serving as a type of screen for pure polar effects in examining the electrode mechanisms of organic compounds, with deviations from the predicted behavior indicating the influence of factors in the electrochemical process other than polar effects due to structure.

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## Tetrabutylammonium Iodotetrachloride as a Chlorinating Agent

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Tetrabutylammonium iodotetrachloride has been used successfully as a source of chlorine for addition on a small scale to the double bonds of *cis*- and *trans*-stilbene, tetraphenylethylene, cyclohexene, and styrene, and to the triple bond of diphenylacetylene. A successful substitution was carried out on the  $\alpha$ -carbon atom of acetophenone, and some chlorination of phenol to trichlorophenol was observed. Of particular interest was the fact that with *cis*- or *trans*-stilbene stereospecific *trans* addition was observed. When molecular chlorine reacted with *cis*- or *trans*-stilbene in the dark, the addition was not stereospecific even when antimony pentachloride or tetrabutylammonium chloride was present.

The observation<sup>1</sup> that tetrabutylammonium iodotetrachloride (tetrabutylammonium tetrachloroiodate [III]) chlorinated itself when il-

(1) R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **76**, 3716 (1954).

luminated to yield the (1-chlorobutyl)tributylammonium ion has led to the consideration of this salt as a source of chlorine for small scale chlorinations. In the present investigation tetrabutylammonium iodotetrachloride has been tried for