than on two lines is under 0.5%, and it may therefore be accepted that the −M and +M groups of substituents show distinctive properties in their $\Delta pK_a - \sigma_m$ relationships.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GA.]

Polar Effects on Rates and Equilibria. III[1]

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It is shown that the Hammett equation can be derived by the assumption that substituents add to the free energy content of a molecule or ion a term, called the free energy of polar interaction of substituents, that is proportional to the product of their polar substituent constants. By use of an analogous assumption for the calculation of the extra resonance energy of interaction between *para* groups, equations are developed that may be used to calculate 99 log (K/K_0) values in four different reaction series with an average deviation of 0.057. The derivation of equations to correlate equilibrium constants for the isomerization of m-XC_6H_4Y to p-XC_6H_4Y, the disproportionation of C_6H_5X to C_6H_6 and $C_6H_4X_2$'s and other reactions is also described, as is an expression for the ratio of the σ-constants for two substituents in terms only of the activity coefficients of certain aromatic compounds.

Introduction

It has been shown previously[2] that within the limits of applicability of the Hammett equation[3] or even a less restrictive but more general Hammett-type equation in which the reaction constants for *m*- and *p*-substituted compounds need not be identical, the reaction constant for an equilibrium process is proportional to the difference in the substituent constants for the two groups being equilibrated. Thus, for example, in the case of these equilibria for two related compounds

$$m\text{-}X_1C_6H_4Y_1 \underset{}{\overset{K_{m-X_1}{}^y}{\rightleftarrows}} m\text{-}X_1C_6H_4Y_2 \qquad (1)$$

$$m\text{-}X_2C_6H_4Y_1 \underset{}{\overset{K_{m-X_2}{}^y}{\rightleftarrows}} m\text{-}X_2C_6H_4Y_2 \qquad (2)$$

we may write

$$\log \frac{K_{m-X_1}{}^y}{K_{m-X_2}{}^y} = \tau_m(\sigma_{m-X_1} - \sigma_{m-X_2})(\sigma_{m-Y_1} - \sigma_{m-Y_2}) \qquad (3)$$

where $K_{m-X_1}{}^y$ and $K_{m-X_2}{}^y$ are the respective equilibrium constants, τ_m is a proportionality constant whose value depends only on the nature of the organic radical (*m*-phenylene in this eq.) to which the substituents are attached, the nature of the reaction medium and temperature, and the σ's are polar substituent constants. A more fundamental but to date perhaps less useful approach to the problem of the effect of structure on rate and equilibrium was initiated by Bjerrum[4] and culminated in the work of Kirkwood and Westheimer.[5] For application to reactions 1 and 2 the Kirkwood–Westheimer equations may be written in the form

$$\log (K_{m-X_1}{}^y/K_{m-X_2}{}^y) = C(\mu_{X_1} - \mu_{X_2})(\mu_{Y_1} - \mu_{Y_2}) \qquad (4)$$

where the μ's are the dipole moments (or the electrical charges in the case of charged groups) and C (whose evaluation was the goal of most of the earlier work) is a constant whose value depends only on the nature of the reaction medium and temperature (which determine the external dielectric constant) and the nature of the organic radical to which the groups are attached (which determines the distance and angle between the groups and the extent and dielectric constant of that part of the molecule between the groups).

Results and Discussion

Development of Equations.—The similarity in form between eq. 3 and 4 suggests a similarity in derivation. Kirkwood and Westheimer have used the accepted physical laws to calculate the contribution to the free energy content of various species due to the interactions of the dipoles and/or electrical charges of substituent groups. I shall assume that from the total free energy of a molecule or ion there may be separated a part to be called the *free energy of polar interaction*, whose magnitude may be calculated from certain properties of the substituent groups called their *polar substituent constants*. Thus, for m-$X_1C_6H_4Y_1$ the free energy of polar interaction of the substituent groups ($F_{\text{p.i.}}$) is assumed to be represented

$$F_{\text{p.i.}}{}^{m\text{-}X_1C_6H_4Y_1} = 2.3RT\tau_m\sigma_{m-X_1}\sigma_{m-Y_1} \qquad (5)$$

where the σ_m's are polar substituent constants characteristic of the interaction of the substituents with other substituents *meta* to them, τ_m is a proportionality constant describing the efficiency of such *meta* interactions in the solvent and at the temperature under consideration, and the $2.3RT$ has been inserted for convenience in the subsequent use of equilibrium constants. It is assumed that most of the contributions to the total free energy of m-$X_1C_6H_4Y_1$ (the energy of the aromatic ring, the four C–H bond energies, the energy of the group X_1 and of its interaction with the ring) are the same for m-$X_1C_6H_4Y_2$. Hence the free energy change for reaction 1 will include only the differences in free energies of polar interaction

$$F_{\text{p.i.}}{}^{m-X_1C_6H_4Y_1} - F_{\text{p.i.}}{}^{m-X_1C_6H_4Y_2} = 2.3RT\tau_m\sigma_{m-X_1}(\sigma_{m-Y_2} - \sigma_{m-Y_2})$$

and the differences between the free energy of the Y_1 and Y_2 groups and of their interactions with the ring. Assuming that this latter term will also be the only contributor, aside from the $\Delta F_{\text{p.i.}}$ term, to the free energy of reaction 2, it follows that

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[1] For parts I and II see ref. 2 and J. Hine and W. C. Bailey, Jr., THIS JOURNAL, **81**, 2075 (1959).

[2] J. Hine, *ibid.*, **81**, 1126 (1959).

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

[4] N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

[5] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

$$\begin{aligned}\Delta F_{1,2} &= -2.3RT\log\,(K_{m-\mathrm{X}_1}{}^{y}/K_{m-\mathrm{X}_2}{}^{y}) \\ &= F_{\mathrm{p.i.}}{}^{m-\mathrm{X}_1\mathrm{C}_6\mathrm{H}_4\mathrm{Y}_1} + F_{\mathrm{p.i.}}{}^{m-\mathrm{X}_2\mathrm{C}_6\mathrm{H}_4\mathrm{Y}_2} - \\ &\qquad F_{\mathrm{p.i.}}{}^{m-\mathrm{X}_1\mathrm{C}_6\mathrm{H}_4\mathrm{Y}_2} - F_{\mathrm{p.i.}}{}^{m-\mathrm{X}_2\mathrm{C}_6\mathrm{H}_4\mathrm{Y}_1} \\ &= 2.3RT\tau_m(\sigma_{m-\mathrm{X}_1} - \sigma_{m-\mathrm{X}_2})(\sigma_{m-\mathrm{Y}_2} - \sigma_{m-\mathrm{Y}_1})\end{aligned}$$

which leads to eq. 2, or in the case of the unsubstituted compound ($X_2 = H$), to the form

$$\log\,(K_{m-\mathrm{X}_1}{}^{y}/K_0{}^{y}) = \tau_m\sigma_{m-\mathrm{X}_1}(\sigma_{m-\mathrm{Y}_1} - \sigma_{m-\mathrm{Y}_2}) \quad (6)$$

since hydrogen is the standard substituent, all of whose σ's are defined as zero. Such an equation also could be derived for *p*-substituted compounds, but we have found that such a set of equations, like the simple Hammett equation with unique σ-values for the substituents, is not capable of satisfactorily correlating the data on processes in which the reaction center changes its resonance interaction with the ring sharply during the reaction. Hence, a resonance term will be introduced into the equation for free energy of polar interaction of *p*-compounds thus

$$F_{\mathrm{p.i.}}{}^{p-\mathrm{X}_1\mathrm{C}_6\mathrm{H}_4\mathrm{Y}_1} = 2.3RT\tau_p(\sigma_{p-\mathrm{X}_1}\sigma_{p-\mathrm{Y}_1} + \sigma_{\mathrm{X}_1}{}^{\mathrm{R}}\sigma_{\mathrm{Y}_1}{}^{\mathrm{R}}) \quad (7)$$

where the σ^{R}'s are the resonance substituent constants and $\sigma_{\mathrm{X}_1}{}^{\mathrm{R}}\sigma_{\mathrm{Y}_1}{}^{\mathrm{R}}$ is defined as zero unless $\sigma_{\mathrm{X}_1}{}^{\mathrm{R}}$ and $\sigma_{\mathrm{Y}_1}{}^{\mathrm{R}}$ are of opposite sign, that is, resonance electron-donors can interact only with resonance electron-withdrawers; and the other terms are defined analogously to those in eq. 5. From eq. 7 and assumptions like those used previously, the expression (8) results

$$\log\,(K_{p-\mathrm{X}_1}{}^{y}/K_0{}^{y}) = \tau_p[\sigma_{p-\mathrm{X}_1}(\sigma_{p-\mathrm{Y}_1} - \sigma_{p-\mathrm{Y}_2}) + \sigma_{\mathrm{X}_1}{}^{\mathrm{R}}\sigma_{\mathrm{Y}_1}{}^{\mathrm{R}} - \sigma_{\mathrm{X}_1}{}^{\mathrm{R}}\sigma_{\mathrm{Y}_2}{}^{\mathrm{R}}] \quad (8)$$

where $K_0{}^{y}$ is the equilibrium constant for the unsubstituted compound and the $\sigma^{\mathrm{R}}\sigma^{\mathrm{R}}$ terms are defined as zero if the individual σ^{R}'s are of like algebraic sign.[6]

Correlation of Data.—The linear free energy relationship consisting of eq. 6 and 8 was tested by application to specific organic reactions. Unless data are used in which the two "reaction center groups" Y_1 and Y_2 are also, in certain cases, substituent groups, eq. 6 is simply a dual-ρ form of the Hammett equation with the ρ's expressed as $\tau(\sigma_{\mathrm{Y}_1} - \sigma_{\mathrm{Y}_2})$. Therefore the acidities of benzoic acids, phenols and anilinium ions, the only reactions for which such data exist, have been correlated. In order to learn whether the treatment of resonance expressed in eq. 8 was applicable to reactions involving powerful resonance-electron-withdrawal at the reaction center, data on the solvolysis of *t*-cumyl chlorides[7] also was included in the correlation (Table I). For the *t*-cumyl chloride hydrolysis, the values of $\tau_m(\sigma_{m-\mathrm{Y}_1} - \sigma_{m-\mathrm{Y}_2})$, $\tau_p(\sigma_{p-\mathrm{Y}_1} - \sigma_{p-\mathrm{Y}_2})$ and $\tau_p(\sigma_{\mathrm{Y}_1}{}^{\mathrm{R}} - \sigma_{\mathrm{Y}_2}{}^{\mathrm{R}})$ were treated as three adjustable parameters designated as ρ_m, ρ_p and ρ_{R}, respectively.[8]

Data for the $-CO_2H$, $-CO_2^-$, $-OH$, $-O^-$, $-NH_3^+$ and $-NH_2$ substituents and the other

TABLE I

EXPERIMENTAL AND CALCULATED (FROM EQ. 6 AND 8) VALUES OF LOG (K/K_0)

	ArCO₂H's[a]				ArOH's[b]				ArNH₃⁺'s[c]				ArCClMe₂ solvolyses[d]			
	meta		para		meta		para		meta		para		meta		para	
	Calcd.	Expd.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
NO_2	0.700	0.710	0.780	0.778	1.587	1.600	2.618	2.810	2.100	2.134^{m}	3.841	3.604^{m}	−3.150	−3.060	−3.588	−3.590
CO_2Et	.370	.370	.460	.450			1.508	1.450	1.110	1.076^{n}	2.214	2.256^{h}	−1.665	−1.664	−2.116	−2.188
SO_2Me	.650	.600	.720	.720	1.474	1.550^{h}	2.142	2.120	1.950	1.956^{h}	3.150	3.156^{h}				
MeO	.100	.115	− .328	− .268	0.227	0.300	−0.357	− 0.250	0.300	0.426^{o}	−0.530	−0.670^{c}	−0.450	−0.213	3.512	3.530
Br	.390	.391	.224	.232	.884	.840	.525	.610	1.170	1.126^{o}	.779	.726^{o}	−1.755	−1.840	−0.690	−0.682
F	.350	.337	.004	.062	.793	.670	.063	.141^{l}	1.050	1.204^{m}	.093	.064^{m}	−1.575	−1.600	.322	.330
Cl	.410	.373	.213	.227	.929	.930	.525	.570	1.230	1.258^{m}	.779	.772^{m}	−1.815	−1.810	− .506	− .516
Me	− .060	− .069	− .177	− .170	− .136	− .130	− .273	− .240	−0.180	−0.092^{n}	− .405	− .434^{p}	0.270	0.301	1.426	1.410
O^-	− .470	− *.510*^{e}	−1.282	−*1.280*^{e}	−1.065	−1.070^{g,i}	−1.701	−1.790^{g,i}	−1.410	−*1.410*^{e}	−2.523	−*2.504*^{e}				
OH	.165	.121	−0.120	0.370	0.374	0.500^{g,i}	−0.411	−0.260^{g,i}	0.495	0.466^{b}	−0.654	−0.864^{h}				
NH_2	.020	*.013*^{e}	− .647	− *.620*^{e}	0.045	0.080^{j}	−0.609	−0.350^{j}	0.060	0.057^{g,q}	−0.903	−1.143^{g,q}				
NH_3^+	.860	*.950*^{e}	.600	*.647*^{e}	1.950	*1.956*^{e}	1.260	*1.290*^{e}	2.580	2.455^{g,q}	1.869	1.805^{g,q}				
CO_2^-	.020	− .101^{f,g}	.114	.015^{f,g}	0.045	0.010^{k}	0.607	0.560^{k}	0.060	*0.018*^{e}	0.881	*0.923*^{e}		^{r}		^{r}
CO_2H	.300	.279^{f,g}	.400	.361^{f,g}	0.680	*0.641*^{e}	1.470	*1.470*^{e}	0.900	*0.925*^{e}	2.153	*2.190*^{e}	−1.350	−1.463	−1.840	−1.907

[a] From D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958), defined as the σ's in their Table VII, unless otherwise noted. [b] *K* values from H. C. Brown, D. H. McDaniel and O. Häfliger in E. A. Braude and F. C. Nachod, Ed., "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, pp. 589, 590, unless otherwise noted. [c] *K* for anilinium ion and its *p*-methoxy derivative from B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 559 (1953); others as noted. [d] Ref. 7. [e] Value adjusted to fit a relation of the type of eq. 9 and, if applicable, eq. 10, exactly, and the correlation equations as well as possible. *K*'s for aminobenzoic acids from P. O. Lumme, *Suomen Kemistilehti*, **30B**, 168 (1957) [f] B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56**, 225 (1952). [g] Statistically corrected. [h] As corrected by F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058, 6317 (1952). [i] C. T. Abichandani and S. K. K. Jatkar, *Proc. Indian Inst. Sci.*, **21A**, 417 (1938); *C. A.*, **33**, 3662^{5} (1939); at 30°. [j] At 21–22°. [k] At 20°. [l] C. M. Judson and M. Kilpatrick, THIS JOURNAL, **71**, 3110 (1949). [m] log (K/K_0) from M. Kilpatrick and C. A. Avenberg, *ibid.*, **75**, 3812 (1953). [n] Assumed the same as the methyl ester quoted in ref. *b*. [o] N. F. Hall, THIS JOURNAL, **52**, 5115 (1930). [p] N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932). [q] R. Kuhn and F. Zumstein, *Ber.*, **59B**, 488 (1926), corrected as indicated by R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 3 (1928). [r] Since this reaction was not run in water, the only solvent for which the σ's for electrically-charged groups are claimed to be applicable, this point was omitted from the correlation.

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[6] This treatment must be modified for application to groups (like phenyl) that are capable of resonance electron donation *and* withdrawal.

[7] H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957); **80**, 4976 (1958); Y. Okamoto, T. Inukai and H. C. Brown, *ibid.*, **80**, 4969, 4972 (1958).

[8] In this case Y_1 is the 2-chloro-2-propyl substituent and Y_2 is the same group with the partial carbonium ion character and stretched C–Cl bond characteristic of the transition state in its solvolysis.

eight substituents for which the most data were available, were used. For obvious reasons many of the data, such as the acidity constant for the phenol group in *p*-hydroxybenzoic acid, are unavailable. However, this acidity constant is related to the likewise unknown acidity constant of *p*-$HO_2CC_6H_4O^-$ through the two known acidity constants of *p*-hydroxybenzoic acid as

$$K_{\mathit{H}\mathrm{OPhCO_2H}} \times K^{-}{}_{\mathrm{OPhCO_2}\mathit{H}} = K_{\mathrm{HOPhCO_2}\mathit{H}} \times K_{\mathit{H}\mathrm{OPhCO_2^-}} \quad (9)$$

where the *K*'s refer to the acidity of the italicized hydrogen atom. Thus the correlation of benzoic acid *K*'s provides not only a prediction of $K^{-}{}_{\mathrm{OPhCO_2}\mathit{H}}$, but also, through eq. 9, a prediction of $K_{\mathit{H}\mathrm{OPhCO_2H}}$. Since the correlation of *K*'s for phenols also provides predictions of these two *K*'s, a comparison of the two predictions serves as an additional test of eq. 6 and 8. $K_{\mathit{H}\mathrm{OPhCO_2H}}$ and $K^{-}{}_{\mathrm{OPhCO_2}\mathit{H}}$ (and other analogous *K*'s) have therefore been treated as parameters that are required to fit eq. 9 exactly but that are adjusted to give an optimum fit to the correlation equations. While the nature of the equilibria involved in the ionizations of the aminophenols and hydroxybenzoic acids is clear enough, in the case of the aminobenzoic acids it was necessary to make the added condition

$$K_{\mathrm{H_3\overset{+}{N}PhCO_2H}} = K_{\mathit{H}_3\mathrm{\overset{+}{N}PhCO_2H}} + K_{\mathrm{H_3\overset{+}{N}PhCO_2}\mathit{H}} \quad (10)$$

where $K_{\mathrm{H_3\overset{+}{N}PhCO_2H}}$ is the total first acidity constant of the carboxyanilinium ion.

As in the Hammett equation the functions that serve as the ρ-constants for the ionization of benzoic acids, namely, the *meta* and *para* $\tau(\sigma_{CO_2H} - \sigma_{CO_2^-})$ values, were defined as 1.000 in aqueous solution at 25°. The initial estimates of the "ρ"-values were made from plots of carboxylic acid *pK*'s *vs.* phenol and anilinium ion *pK*'s and cumyl chloride log *k*'s, with allowance in the *para* plots for resonance effects. Initial values of τ's then were obtained from the initial ρ's and estimates of the σ's for the $-CO_2H$, $-NH_2$, etc., groups with the assumption that the NH_3^+ group has no resonance effect. The various parameters then were adjusted by trial and error[9] to give an optimum fit. The values of the parameters obtained and those of certain derived parameters are listed in Table II.

TABLE II

SIGMA AND DERIVED PARAMETERS FOR EQ. 6 AND 8

Substituent	σ_m	σ_p	σ_R
NO_2	0.70	0.78	0.56
CO_2Et	.37	.46	.31
SO_2Me	.65	.72	.36
OMe	.10	− .17	− .30
Br	.39	.25	− .05
F	.35	.03	− .05
Cl	.41	.25	− .07
Me	− .06	− .13	− .09
O^-	− .47	− .81	− .90
OH	.165	− .21	− .40
NH_2	.02	− .29	− .72
NH_3^+	.86	.60	.00
CO_2^-	.02	.114	.21
CO_2H	.30	.41	.36

τ_m	3.57	$\sigma_{ArNH_3^+}{}^m$	3.000
τ_p	3.50	$\rho_{ArNH_3^+}{}^p$	3.115
$\rho_{ArCO_2H}{}^R$	−0.525	$\rho_{ArNH_3^+}{}^R$	2.52
$\rho_{ArOH}{}^m$	2.267	$\rho_{ArCClMe_2}{}^m$	−4.50
$\rho_{ArOH}{}^p$	2.100	$\rho_{ArCClMe_2}{}^p$	−4.60
$\rho_{ArOH}{}^R$	1.750	$\rho_{ArCClMe_2}{}^R$	−9.20

The average deviation of the calculated values were: from the 83 experimental values, 0.060; from the 16 log (K/K_0) values used as disposable parameters, 0.030; and from the 20 data on compounds in which the substituent was one that was also in some cases a reaction center, 0.086. While these average deviations are probably in the vicinity of the average uncertainty in the experimental values, the larger deviations range up to 0.26 and some probably are significant. A number of possible explanations for these deviations are apparent. The *m*-methoxycumyl chloride is more reactive than calculated, perhaps because there is some "extra" resonance even with *m*-derivatives. Equations like 6 and 8 take no account of saturation effects, although Deno, Jaruzelski and Schriesheim, for example, found that in general the effect that a given electron-donating substituent has on the stability of a diphenylmethyl or triphenylmethyl cation decreases with increasing stability of the cation.[10] Saturation effects also appear to be important in the rates of carbanion-formation of haloform,[11] and elsewhere.[12] The major cause of the present deviations, however, may be the use of σ-constants for charged groups in the same manner as those for uncharged groups. While changes in the extent of solvation of these groups are minimized by our restriction of the σ's for charged groups to a common solvent,[13] the fact that charge–dipole interactions change with distance and orientation in a different manner from charge–charge interactions also is not taken into account by eq. 6 and 8. While these and other complicating factors could be taken into account by extended forms of eq. 6 and 8, the resultant increase in the number of parameters might make it doubtful whether the extended correlation could really be tested on the basis of existing data. The correlation shown in Table I was accomplished with 45 independent parameters,[15] about the same number that would be required for satisfactory correlation by standard "modified Hammett equation" methods since practically all substituents that did not require a special σ (when *para*) for anilines and phenols would require one for the cumyl chloride solvolysis correlation. Furthermore, without any additional parameters, eq. 6 and 8 and the parameters

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(9) The use of a least-square method is made inconvenient by the fact that many of the 45 simultaneous equations that would have to be solved are of higher than the first order.

(10) N. R. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955); N. R. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

(11) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(12) *Cf.* G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, sec. 25.

(13) It is obvious that the σ's for charged groups must change with the solvent if we assume that σ's for uncharged groups are solvent-independent. Thus the observed changes in ρ that accompany changes in solvent in equilibria involving ionic species[14] must be due to changes either in τ or in the appropriate $(\sigma_{Y_1} - \sigma_{Y_2})$ term. If all of the changes were due to τ's, all of the ρ's would change in the same manner. Since they do not at least some of the σ's must change.

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

(15) The τ-values in water at 25° are defined as the reciprocals of the $(\sigma_{CO_2H} - \sigma_{CO_2^-})$ values.

in Table II can be used to predict 1,232 other log (K/K_0) values for such reactions as

$$\mathrm{ArNO_2} \rightleftarrows \mathrm{ArCl}, \text{ etc.}$$

in water at 25° (although with an unknown reliability).

The correlation also was attempted with the use of a smaller number of parameters, an inductive and a resonance σ for each substituent, with the *m*- and *p*-σ's being calculated from these by the method of Taft.[16a] While the average deviation in the best correlation obtained was just under 0.08, individual deviations were as large as 0.40. The somewhat poorer character of this correlation may not be inherent in the method of separation of σ's into inductive and resonance contributions but may stem from the use of σ's for charged groups. It would be valuable to have a large amount of data on equilibria not involving ions in order to investigate this point.

Other Applications.—The concept in the derivation of eq. 6 and 8 has been used in the derivation of several interesting new relationships which permit the prediction of many additional types of experimental results and which may lead to new methods of assessing the basic validity of the Hammett and related equations. Equilibria between *m*- and *p*-substituted benzene derivatives may be treated. Thus for the reaction

$$m\text{-}\mathrm{XC_6H_4Y} \overset{K_{\mathrm{mp}}}{\rightleftarrows} p\text{-}\mathrm{XC_6H_4Y} \qquad (11)$$

relation (12) may be derived

$$\log 2K_{mp} = \tau_m\sigma_{m-\mathrm{X}}\sigma_{m-\mathrm{Y}} - \tau_p(\sigma_{p-\mathrm{X}}\sigma_{p-\mathrm{Y}} + \sigma_{\mathrm{X}}{}^{\mathrm{R}}\sigma_{\mathrm{Y}}{}^{\mathrm{R}}) \qquad (12)$$

The τ's used must refer to the solvent in which K_{mp} is determined, and the factor "2" is made necessary by the greater statistical degeneracy of the *meta* compound.[17] For the disproportionation reaction in solvent A

$$2\mathrm{C_6H_5X} \overset{K_{\mathrm{d}}{}^{\mathrm{A}}}{\rightleftarrows} \mathrm{C_6H_6} + p\text{-}\mathrm{C_6H_4X_2} \qquad (13)$$

$$\log 6K_{\mathrm{d}}{}^{\mathrm{A}} = \tau_p{}^{\mathrm{A}}(\sigma_{p-\mathrm{X}})^2 \qquad (14)$$

where $\tau_{\mathrm{p}}{}^{\mathrm{A}}$ is the value of τ_{p} in the solvent A and "6" is a statistical correction.[17] While the neglect of extra resonance should be justified for most X's, it probably is not for such amphipolar substituents as phenyl and vinyl.

If $K_{\mathrm{d}}{}^{\mathrm{A}}$ is determined in sufficiently dilute solution and if activity coefficients are defined as unity in the pure solvent A, then $K_{\mathrm{d}}{}^{\mathrm{A}}$ becomes the thermodynamic equilibrium constant. In these terms the equilibrium constant $K_{\mathrm{d}}{}^{\mathrm{B}}$ determined in solvent B is equal to $K_{\mathrm{d}}{}^{\mathrm{A}}$ multiplied by the appropriate activity coefficient ratio. Expressing $K_{\mathrm{d}}{}^{\mathrm{A}}$ in terms of eq. 14 and $K_{\mathrm{d}}{}^{\mathrm{B}}$ in terms of the analogous expression for solvent B, and subtracting the first equation from the second

$$\log \frac{f_{\mathrm{PhH}}{}^{\mathrm{B}} f_{p-\mathrm{PhX_2}}{}^{\mathrm{B}}}{(f_{\mathrm{PhX}}{}^{\mathrm{B}})^2} = (\tau_p{}^{\mathrm{A}} - \tau_p{}^{\mathrm{B}})(\sigma_{p-\mathrm{X}})^2 \qquad (15)$$

where the f^{B} terms are activity coefficients in the solvent B referred to the standard solvent A. Since it is assumed that $\sigma_{p-\mathrm{X}}$ is solvent-independent, the group X probably could not be electrically charged. An expression like eq. 15 may be derived for the substituent Y, and the elimination of $\tau_p{}^{\mathrm{B}} - \tau_p{}^{\mathrm{A}}$ between the two relations gives

$$\frac{\sigma_{p-\mathrm{X}}}{\sigma_{p-\mathrm{Y}}} = \sqrt{\frac{\log\,[f_{\mathrm{PhH}}{}^{\mathrm{B}} f_{p-\mathrm{PhX_2}}{}^{\mathrm{B}}/(f_{\mathrm{PhX}}{}^{\mathrm{B}})^2]}{\log\,[f_{\mathrm{PhH}}{}^{\mathrm{B}} f_{p-\mathrm{PhY_2}}{}^{\mathrm{B}}/(f_{\mathrm{PhY}}{}^{\mathrm{B}})^2]}} \qquad (16)$$

from which the relative values of the polar substituent constants may be found by determination of the activity coefficients of five species. Relations analogous to eq. 12, 14 and 16 can be derived for other cases (some aliphatic) in which steric effects do not change greatly during the reaction.

In order to contribute to our understanding of the basic problem in the prediction of rate and equilibrium, the effect of substituent groups on the free energy content of a molecule, it is planned to apply eq. 12, 14 and 16 and analogous expressions to measurements on suitably chosen compounds in order to learn the range and degree of applicability of the equations. Since eq. 14 and 16 can be derived simply by assumption of the general applicability of the Hammett equation (with unique σ's for every substituent), or a dual-ρ modification of the Hammett equation, to all equilibria of *m*- and *p*-substituted derivatives, a test of these equations is a test of the dual-ρ Hammett equation. To avoid the intrusion of any more complications than necessary it is planned, in the initial experiments, to minimize the factors to which deviations from the Hammett equation are most commonly attributed: namely, (1) resonance interactions between substituent groups and reaction centers, (2) solvation of electrically charged groups, (3) hydrogen bonding and (4) complications peculiar to rate processes, such as changes in reaction mechanisms.

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[16] R. W. Taft, Jr., in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956; (a) pp. 594–597, (b) p. 606.

[17] Statistical corrections have been made by the method of S. W. Benson, THIS JOURNAL, **80**, 5151 (1958).