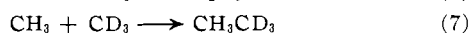
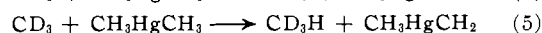
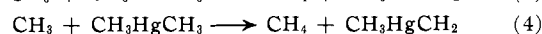
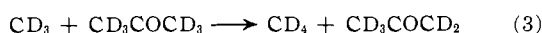
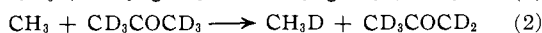
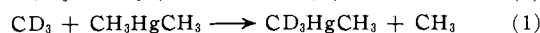
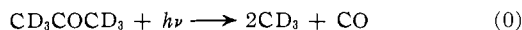


uct distribution and will be tentatively considered as the most likely mechanism by which CH_3 radicals are produced in this system. The occurrence of reaction 1 is substantiated by the results obtained in the liquid-phase photolysis of $\text{CH}_3\text{N}_2\text{CH}_3$ in the presence of CD_3HgCD_3 . The fact that, in these experiments, the ethane fraction consists exclusively of C_2H_6 demonstrates that reaction A does not occur in this system. On the other side, the appearance of CD_3H as a product can reasonably be accounted for by the occurrence of reaction 1. Furthermore, the absence of C_2D_6 in the ethane fraction indicates that the formation of CD_3H cannot be accounted for by a decomposition of an electronically excited dimethylmercury molecule because, in view of the existence of a cage effect, this should result in the formation of C_2D_6 as well.

Accepting the occurrence of reaction 1, the following reaction mechanism may be proposed to account for the products formed during the photolysis of $\text{CD}_3\text{-COCD}_3$ carried out in the presence of CH_3HgCH_3



If methane is formed only by reactions 2 to 5, then it follows that

$$\frac{R_{\text{CH}_4}}{R_{\text{CD}_3\text{H}}} = \frac{k_4}{k_5} \frac{[\text{CH}_3]}{[\text{CD}_3]} \text{ and } \frac{R_{\text{CH}_3\text{D}}}{R_{\text{CD}_4}} = \frac{k_2}{k_3} \frac{[\text{CH}_3]}{[\text{CD}_3]}$$

Also if ethane is formed only by reactions 6 to 8, then

$$\frac{R_{\text{CH}_3\text{CD}_3}}{R_{\text{C}_2\text{D}_6}} = \frac{k_7}{k_6} \frac{[\text{CH}_3]}{[\text{CD}_3]} \text{ and } \frac{R_{\text{C}_2\text{H}_6}}{R_{\text{CH}_3\text{CD}_3}} = \frac{k_8}{k_7} \frac{[\text{CH}_3]}{[\text{CD}_3]}$$

It has been shown in particular that $k_2 = k_3^{13}$ and it

may be expected that $k_4 = k_5$ and $k_7 = 2k_6 = 2k_8$. Thus, it follows that

$$\frac{R_{\text{CH}_4}}{R_{\text{CD}_3\text{H}}} = \frac{R_{\text{CH}_3\text{D}}}{R_{\text{CD}_4}} = \frac{R_{\text{CH}_3\text{CD}_3}}{2R_{\text{C}_2\text{D}_6}} = \frac{2R_{\text{C}_2\text{H}_6}}{R_{\text{CH}_3\text{CD}_3}} = \frac{[\text{CH}_3]}{[\text{CD}_3]}$$

Table IV substantiates the equality as well as the mechanism. Moreover, from the postulated mechanism, the rate of formation of CD_3 and CH_3 are given by the equations

$$R_{\text{CD}_3} = 2I_0\Phi + 2R_{\text{CO}}, \text{ and } R_{\text{CH}_3} = k_1[\text{CH}_3\text{HgCH}_3][\text{CD}_3]$$

Again, if CD_3 and CH_3 undergo the same reactions with the same rate constants, then the ratio of their rates of formation is equal to the ratio of their steady-state concentrations. Thus

$$\frac{R_{\text{CH}_3}}{R_{\text{CD}_3}} = \frac{[\text{CH}_3]}{[\text{CD}_3]} = \frac{k_1[\text{CH}_3\text{HgCH}_3][\text{CD}_3]}{2R_{\text{CO}}}$$

Any one of the four ratios, given before, can be used for $[\text{CH}_3]/[\text{CD}_3]$. However, the ratio $R_{\text{CH}_3\text{CD}_3}/2R_{\text{C}_2\text{D}_6}$ should be the most accurate. Thus this equation can be rearranged to

$$\frac{k_1}{k_6^{1/2}} = \frac{R_{\text{CH}_3\text{CD}_3}}{R_{\text{C}_2\text{D}_6}^{1/2}} \frac{R_{\text{CO}}}{[\text{CH}_3\text{HgCH}_3]}$$

The results (Table IV) show that $k_1/k_6^{1/2}$ is essentially independent of intensity (see experiments 14–17) and also relatively independent of pressure (see experiments 19–21). The accumulation of evidence is in favor of the postulated type mechanism and the Arrhenius plot gives an activation energy of 12.6 kcal./mole which may be assigned to reaction 1.

Finally it is to be noted that the temperature independence of the ratio $\text{CD}_4/\text{CD}_3\text{H}$ for equal amounts of CD_3COCD_3 and CH_3HgCH_3 means that the activation energy difference $E_3 - E_5$ is 0.0 ± 0.4 kcal./mole. This is in agreement with the reported values of $E_3 = 11.2$ kcal./mole¹³ and $E_5 = 10.8$ kcal./mole.¹

Acknowledgment.—This research was supported by a grant from the United States Public Health Service, Department of Health, Education and Welfare.

(13) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **76**, 1416 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNA.]

Effects of Substituents on Acidities of Organic Acids in Water: Thermodynamic Theory of the Hammett Equation

BY LOREN G. HEPLER

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Qualitative discussion of ΔH° and ΔS° of ionization of some organic acids in aqueous solution is followed by development of thermodynamic equations for reactions of the type $\text{HA}_s(\text{aq}) + \text{A}_u^-(\text{aq}) = \text{A}_s^-(\text{aq}) + \text{HA}_u(\text{aq})$, where subscripts *s* and *u* indicate substituted and unsubstituted acids. The resulting thermodynamic equations, which are based on the idea that ΔH° and ΔS° can be expressed as sums of external and internal contributions, are used in determining values of ΔH_{int} for various substituted acids transferring a proton to the anion of the unsubstituted acid. Combination of these thermodynamic equations with the Hammett equation leads to the prediction that the Hammett σ - and Taft σ^* -substituent constants should be proportional to ΔH_{int} . The equations also predict correctly the observed linear dependence of ρ on $1/T$.

Introduction

There are nearly as many theories and correlations of acid strengths as ionization data for organic acids. One of the reasons for developing another theory can be illustrated by considering the ionization of *p*-nitrophenol and *m*-nitrophenol in aqueous solution.

It has been stated many times that greater resonance stabilization of the anion of *p*-nitrophenol as compared to the anion of *m*-nitrophenol accounts for *p*-nitrophenol being a stronger acid than *m*-nitrophenol. If the resonance energy argument correctly describes the

only important factor contributing to a difference in ionization of these phenols, we should expect differences in ΔF° of ionization to be accounted for entirely by values of ΔH° of ionization. Earlier investigations¹ have yielded the data listed in Table I, which show that the difference in acidity of aqueous *p*-nitrophenol and *m*-nitrophenol is due to different ΔS° of ionization rather than different ΔH° of ionization. We conclude that interpretation of acid strengths solely in terms of

(1) L. P. Fernandez and L. G. Hepler, *J. Am. Chem. Soc.*, **81**, 1783 (1959).

TABLE I
THERMODYNAMICS OF IONIZATION OF AQUEOUS PHENOLS AT
298°K.

	<i>m</i> -Nitrophenol	<i>p</i> -Nitrophenol
$K \times 10^{10}$	45.1	720
ΔF° , cal./mole	11,400	9750
ΔH° , cal./mole	4,705	4700
ΔS° , cal./deg. mole	-22.5	-16.9

energies of molecules and ions is certainly incomplete in this instance and may be so for other acids.

Realistic models or theories designed to account for the thermodynamics of ionization of aqueous organic acids must be concerned with the properties of water and with solute-solvent interactions. We shall find it convenient to work out our theory in terms of ΔH_{int} , ΔH_{ext} , ΔS_{int} , and ΔS_{ext} . External contributions to the enthalpy and entropy are associated with solute-solvent interactions and internal contributions arise from differences in enthalpy and entropy within the acid molecule and its anion. Arguments concerning resonance stabilization of anions (as in *p*-nitrophenol) apply to ΔH_{int} , as do arguments involving inductive effects on bond dissociation energies.

Pitzer² has shown that the difference in internal entropy for an acid and its anion is nearly constant for a series of similar acids. Hence the difference in entropy of ionization of *p*-nitrophenol and *m*-nitrophenol is due to differences in solute-solvent interactions.

Although the data in Table I show that resonance energy arguments alone do not account for differences in thermodynamics of ionization of nitrophenols, these data may be shown to be in accord with conventional ideas about bonding and charge distribution in nitrophenols and their anions. According to the resonance picture, the negative charge on the anion of *p*-nitrophenol is spread over the phenolic oxygen and the two nitro oxygens while the negative charge on the anion of *m*-nitrophenol is more localized on the phenolic oxygen. The relatively concentrated negative charge on the anion of *m*-nitrophenol interacts more strongly with surrounding water than does the more diffuse charge on the resonance stabilized anion of *p*-nitrophenol. Hence we expect ΔS_{ext} (and ΔS° , since ΔS_{int} values are nearly the same for both acids) to be more negative for ionization of *m*-nitrophenol than for *p*-nitrophenol. Similarly, we expect ΔH_{ext} of ionization to be more negative (exothermic) for ionization of *m*-nitrophenol than for *p*-nitrophenol. On the basis of the resonance stabilization of the anion of *p*-nitrophenol, we expect ΔH_{int} to be smaller (less endothermic) for *p*-nitrophenol than for *m*-nitrophenol. It is only coincidence that the sum $\Delta H_{\text{int}} + \Delta H_{\text{ext}} = \Delta H^\circ$ equals 4.70 kcal./mole for both nitrophenols.

TABLE II¹
THERMODYNAMICS OF IONIZATION OF AQUEOUS PHENOL AND
p-CHLOROPHENOL AT 298°K.

	Phenol	<i>p</i> -Chlorophenol
$K \times 10^{10}$	1.05	4.18
ΔF° , cal./mole	13,610	12,800
ΔH° , cal./mole	5,650	5,800
ΔS° , cal./deg. mole	-26.7	-23.5

The suggestions that *p*-chlorophenol should be a stronger acid than phenol and that chloroacetic acid should be stronger than iodoacetic acid because (Cl) substituents make it "easier" to lose a proton than do (H) or (I) substituents are supported by the K and ΔF° values in Tables II and III but contradicted by the ΔH° values that are more relevant to energy arguments.

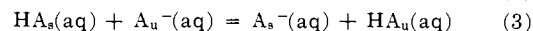
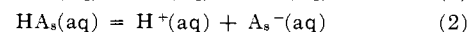
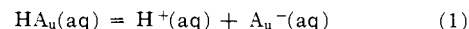
(2) K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

TABLE III³
THERMODYNAMICS OF IONIZATION OF AQUEOUS CHLOROACETIC
AND IODOACETIC ACIDS AT 298°K.

	Chloroacetic acid	Iodoacetic acid
$K \times 10^3$	1.36	0.67
ΔF° , cal./mole	+3920	+4330
ΔH° , cal./mole	-1120	-1420
ΔS° , cal./deg. mole	-16.9	-19.3

Heats and Entropies of Ionization

Since we are primarily interested in the effects of substituents on such parent acids as phenol and acetic acid, we begin by writing the equations⁴



Subscripts *u* and *s* refer to the unsubstituted parent acid and the substituted acid. Most of our reliable data are in the form of ΔF° , ΔH° , and ΔS° values for reactions of types 1 and 2, which can be combined according to $\Delta H_3^\circ = \Delta H_s^\circ - \Delta H_u^\circ$ and $\Delta S_3^\circ = \Delta S_s^\circ - \Delta S_u^\circ$ to give desired values for reactions of type 3. Our attention is first confined to ΔH_3° and ΔS_3° because we can calculate ΔF_3° , K_3 , $d\Delta F_3^\circ/dT$, and $d \ln K_3/dT$ from these quantities.

To indicate specifically that ΔH_3° and ΔS_3° are considered as sums of external and internal contributions, we write

$$\Delta H_3^\circ = \Delta H_{\text{int}} + \Delta H_{\text{ext}} \quad (4)$$

and

$$\Delta S_3^\circ = \Delta S_{\text{int}} + \Delta S_{\text{ext}} \quad (5)$$

Application of Pitzer's² method shows that ΔS_{int} for the symmetrical reaction 3 is nearly zero, giving

$$\Delta S_3^\circ = \Delta S_{\text{ext}} \quad (6)$$

Several models for ion-solvent interaction (Born⁵ and Powell-Latimer,⁶ for example) lead to the reasonable conclusion that ΔH_{ext} is proportional to ΔS_{ext} . Since most of the inadequacies of the various models cancel when applied to symmetrical reactions of type 3, we write

$$\Delta H_{\text{ext}} = \beta \Delta S_{\text{ext}} = \beta \Delta S_3^\circ \quad (7)$$

Theories of solute-solvent interactions are, unfortunately, inadequate for reliable calculation of this proportionality constant, so we regard β as a parameter that should be the same for all aqueous acids of the same charge type.

Combining eq. 4 and 7 gives

$$\Delta H_3^\circ = \Delta H_{\text{int}} + \beta \Delta S_3^\circ \quad (8)$$

When we apply 8 to a series of *n* substituted acids, we have *n* equations like 8, *n* unknown ΔH_{int} values, and the additional unknown β that is common to all the equations. Once β is known, experimental ΔH_3° and ΔS_3° data lead directly by 8 to values of ΔH_{int} for each substituent.

Because we have (*n* + 1) unknowns and only *n* equations, more information about β or ΔH_{int} is required. One approach may be patterned after that of Hepler and O'Hara,⁴ who applied 8 to methyl substituted phenols by relating the O-H stretching frequency to ΔH_{int} . It was suggested that ΔH_{int} should be proportional to $(\nu_s^2 - \nu_u^2)$. Since $(\nu_s^2 - \nu_u^2) = (\nu_s + \nu_u)(\nu_s - \nu_u)$ and $(\nu_s + \nu_u) \cong 2\nu_u$ for substituted phenols with O-H stretching frequencies near to that of unsubstituted phenol, ΔH_{int} might also have been

(3) D. J. G. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955).

(4) L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, **65**, 811 (1961).

(5) M. Born, *Z. Physik*, **1**, 45 (1920).

(6) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

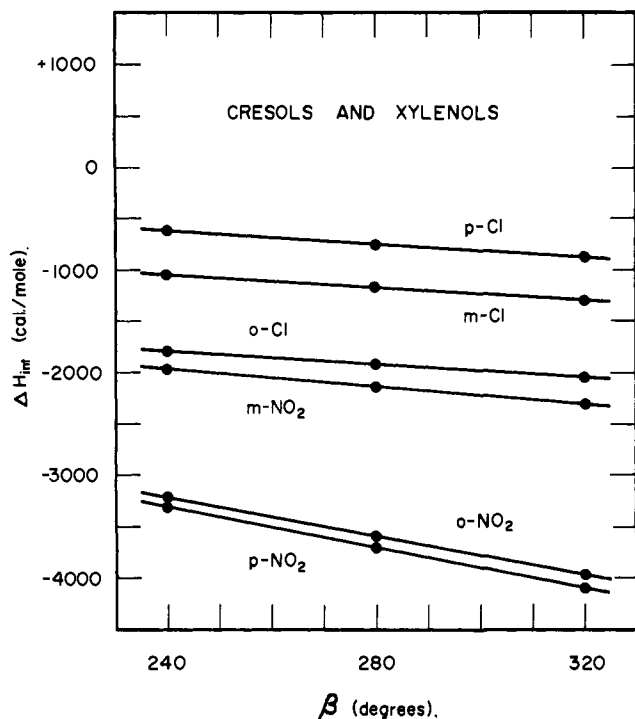


Fig. 1.—Graph of calculated ΔH_{int} values (from eq. 8) for substituted phenols in reaction 3 vs. assumed values of β . Lines for cresols and xylenols fall close together at the top of the graph.

taken proportional to $(\nu_s - \nu_u)$ with the same final result with respect to β . This method, which may be thought of as based on expressing ΔH_{int} as a power series in $(\nu_s - \nu_u)$ and then, considering only the first term, should be most nearly correct for substituents (such as $-\text{CH}_3$) that have little effect on the O-H bond.

Using thermodynamic data reported by Laidler and co-workers,⁷ Hepler and O'Hara⁴ calculated $\beta = 284^\circ$. Later calculations based on different data for the same acids, also reported by Laidler,⁸ suggest a smaller value of β . Since the ΔH° and ΔS° data of Chen and Laidler⁸ for *o*-chlorophenol are not in good agreement with results of other investigators,^{1,9} and the relation of ΔH_{int} to O-H stretching frequencies may be quantitatively inadequate, we are reluctant to base the value of β solely on methyl-substituted phenols.

Another approach to evaluating β and thence obtaining ΔH_{int} values involves use of qualitative knowledge of effects of various substituents on chemical properties. For instance, since considerable chemical evidence indicates that methyl groups are weakly electron releasing to the benzene ring, we expect ΔH_{int} values to be small and positive for methyl-substituted phenols. This expectation is in accord with the observation that $(\nu_s - \nu_u)$ is positive for methyl-substituted phenols. It is not entirely clear whether methyl and other alkyl groups substituted on acetic acid donate electrons to or withdraw electrons from the carboxyl group, as compared to hydrogen, but the effect is certainly small. ΔH_{int} should be near zero for alkyl-substituted acetic acids, where acetic acid is represented by HA_u in 3.

Various values of β (for instance, 240, 280, and 320°) have been assumed and used with ΔH_3° and ΔS_3° values in eq. 8 for calculation of corresponding values of ΔH_{int} for substituted phenols and acetic acids. Results of some of these calculations are shown in Fig. 1 and 2.

(7) H. M. Papee, W. J. Canaday, T. W. Zawidzki, and K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1734 (1959).

(8) D. T. Y. Chen and K. J. Laidler, *ibid.*, **58**, 480 (1962).

(9) T. L. Cottrell, G. W. Drake, D. L. Levi, K. J. Tully, and J. H. Wolfenden, *J. Chem. Soc.*, 1016 (1946).

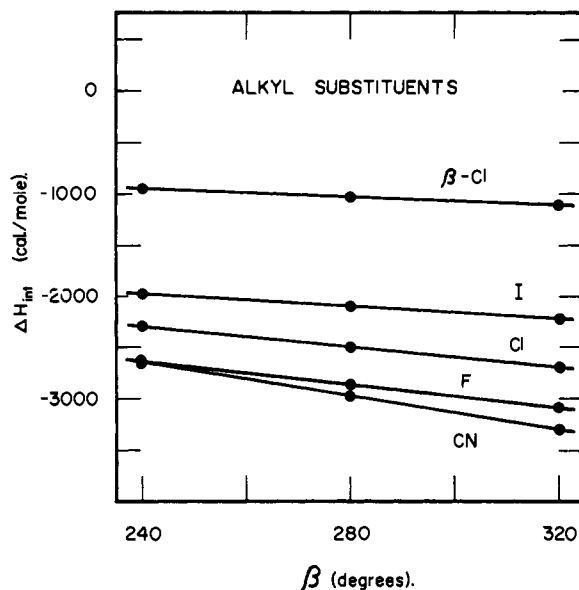


Fig. 2.—Graph of calculated ΔH_{int} values (from eq. 8) for substituted acetic acids in reaction 3 vs. assumed values of β . Lines for alkyl-substituted acetic acids fall close together at the top of the graph.

ΔH_{int} values corresponding to $\beta = 240^\circ$ and to $\beta = 280^\circ$ are small and positive for all cresols and xylenols. For $\beta = 320^\circ$ some of these ΔH_{int} values become negative. It should be expected that ΔH_{int} would be larger for 2,6-xyleneol than for any of the other xylenols or cresols. For values of β less than about 270°, ΔH_{int} for 2,4-xyleneol is larger than ΔH_{int} for 2,6-xyleneol. These calculations therefore indicate that $270^\circ < \beta < 320^\circ$.

Values of β from 240 to 320° yield corresponding ΔH_{int} values that are small, both positive and negative, for the alkyl-substituted acetic acids. These data are in agreement with the conclusion above that $270^\circ < \beta < 320^\circ$.

In recent investigations^{10,11} of linear enthalpy-entropy relations, Brown has found evidence that β is about 280° for ionization of organic acids in water.

We shall take $\beta = 280^\circ$ for purposes of further calculations and discussions. Fortunately, as shown by Fig. 1 and 2, calculated values of ΔH_{int} are changed, on the average, by only about 5 cal./mole per degree change in the chosen value of β , and relative ΔH_{int} values for different acids are changed even less.

Values of ΔH_{int} for various substituted phenols and acetic acids (calculated by means of eq. 8 with $\beta = 280^\circ$ for reactions of type 3) are listed in Tables IV^{1,8,12} and V.^{3,9,13-19}

The ΔH_{int} values listed in Tables IV and V resolve the difficulties discussed in the Introduction. First, ΔH_{int} values show that it is indeed "easier" (after correction for solute-solvent interactions) to transfer a proton from *p*-nitrophenol to phenoxide ion than from *m*-nitrophenol to phenoxide ion, confirming the prediction based on the idea of resonance stabilization of the anion of *p*-nitrophenol. Similarly, the ΔH_{int}

(10) R. F. Brown, *J. Org. Chem.*, **27**, 3015 (1962).

(11) R. F. Brown and H. C. Newson, *ibid.*, **27**, 3010 (1962).

(12) W. F. O'Hara and L. G. Hepler, *J. Phys. Chem.*, **65**, 2107 (1961).

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958.

(14) F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, 2798 (1956).

(15) D. H. Everett, D. A. Landsman, and B. R. W. Pinsent, *Proc. Roy. Soc. (London)*, **A215**, 403 (1952).

(16) A. W. Martin and H. V. Tartar, *J. Am. Chem. Soc.*, **59**, 2672 (1937).

(17) L. F. Nims, *ibid.*, **58**, 987 (1936).

(18) E. J. King, *ibid.*, **82**, 3575 (1960).

(19) L. F. Nims and P. K. Smith, *J. Biol. Chem.*, **113**, 145 (1936).

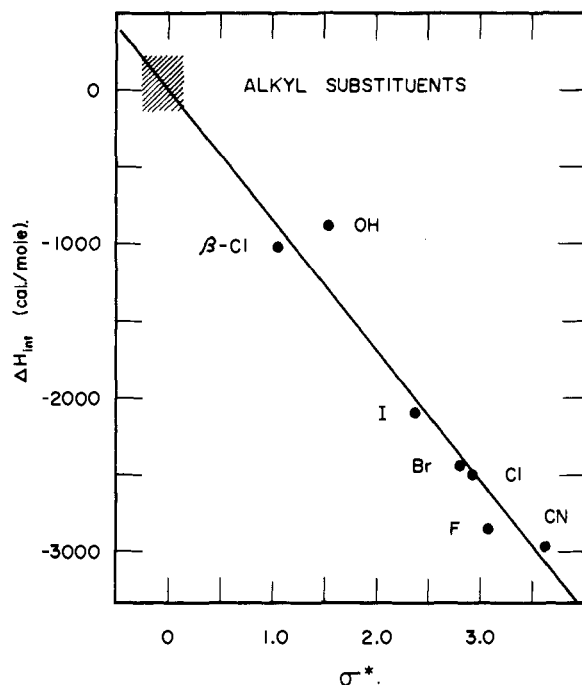


Fig. 3.—Graph of ΔH_{int} for substituted acetic acids in reaction 3 vs. Taft σ^*

value for *p*-chlorophenol in reaction 3 shows the effect expected on the basis of the greater electron-withdrawing power of chlorine as compared to hydrogen. In the same fashion ΔH_{int} values for chloroacetic and iodoacetic acids are in accord with qualitative predictions based on electronegativities, even though ΔH° values seem anomalous.

The ΔH_{int} values in Table IV show that the effect of a chlorine substitution in phenol decreases with increasing distance from the -OH position. Similarly, ΔH_{int} for β -chloropropionic acid is less exothermic than ΔH_{int} for chloroacetic acid.

Linear Free Energy and Enthalpy-Entropy Relations

Since the equations to be developed in this section are relevant to rates as well as proton transfers, superscripts will be omitted with the understanding that either $^\circ$ or * may be added.

Substituting eq. 8 in $\Delta F = \Delta H - T\Delta S$ and rearranging leads to

$$\frac{\Delta F_3}{\Delta H_{\text{int}}} = 1 + \frac{(\beta - T)\Delta S_3}{\Delta H_{\text{int}}} \quad (9)$$

for symmetrical reactions of type 3. Since $(\beta - T) \cdot \Delta S_3/\Delta H_{\text{int}}$ is much smaller than unity ($\Delta S_3/\Delta H_{\text{int}}$ ranges between 0.0017 and 0.0042 deg.⁻¹ for substituted phenols) for T not too far from β , eq. 9 may be simplified to

$$\Delta F_3 \cong \Delta H_{\text{int}} \quad (10)$$

TABLE IV

ΔH_{int} VALUES (REACTION 3) FOR SUBSTITUTED PHENOLS ($\beta = 280^\circ$)

Substituted phenol	ΔH_{int} , cal./mole	Substituted phenol	ΔH_{int} , cal./mole
<i>o</i> -Nitro-	-3600	<i>m</i> -Chloro-	-1170
<i>m</i> -Nitro-	-2130	<i>p</i> -Chloro-	-750
<i>p</i> -Nitro-	-3690	Cresols and xylenols	+80 to +780
<i>o</i> -Chloro-	-1920		

TABLE V

ΔH_{int} VALUES (REACTION 3) FOR SUBSTITUTED ACETIC ACIDS ($\beta = 280^\circ$)

Substituted acetic acid	ΔH_{int} , cal./mole	Substituted acetic acid	ΔH_{int} , cal./mole
Fluoroacetic	-2860	Cyanoacetic	-2970
Chloroacetic	-2500	Glycolic	-880
β -Chloropropionic	-1020	Lactic	-1160
Bromoacetic	-2460	Methoxyacetic	-1560
Iodoacetic	-2100	Alkyl-subst. acetic	-140 to +300

which is directly verified by the ΔH_{int} data already given and ΔF° of ionization data.

We write the Hammett equation (in terms of our $K_2/K_1 = K_3$ or the corresponding rate constants) as

$$\log K_3 = \rho\sigma \quad (11)$$

and combine with $\Delta F_3 = -RT \ln K_3$ and eq. 10 to obtain

$$\rho\sigma = -\frac{\Delta H_{\text{int}}}{2.303RT} = \left[\frac{C}{2.303RT} \right] \left[-\frac{\Delta H_{\text{int}}}{C} \right] \quad (12)$$

We identify $C/2.303RT$ with ρ and $-\Delta H_{\text{int}}/C$ with σ in the Hammett equation.

Jaffé²⁰ has summarized data relevant to the Hammett equation and has found that ρ is a linear function of $1/T$, as predicted by eq. 12. A graph of ΔH_{int} values from Table IV vs. σ gives a straight line through the origin as predicted by eq. 12 or by eq. 10 and the well known applicability of the Hammett equation to ionization of substituted phenols.

The treatment leading to eq. 12 did not distinguish between aromatic and aliphatic systems. We should, therefore, expect the ΔH_{int} values in Table V to be proportional to substituent constants for aliphatic systems. Taft²¹ has deduced and tabulated appropriate substituent constants (called σ^*), which are graphed in Fig. 3 vs. ΔH_{int} values from Table V.

Acknowledgments.—The author is grateful to the National Science Foundation for support of this research and to Allan Colter and E. M. Arnett for stimulating discussion.

(20) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(21) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.