entropy increment or that it is spread out over a rather broad temperature interval.

Values of C_p, S°, $H^\circ - H_0^\circ$ and $-(F^\circ - H_0^\circ)/T$ at selected temperatures are listed in Table II. The entropy and enthalpy increments were computed by numerical integration, using graphically interpolated values of heat capacity. The heat capacity values are considered to have a probable error of about 5% at 5°K., 1% at 10°K. and 0.1% above 25°K. Values below 5°K. were extrapolated with a T^3 function. The effects of nuclear spin and isotopic mixing are not included in the entropy and free energy functions and the values listed in Table II are therefore the conventional ones to be used in calculations of chemical equilibria. The estimated probable error in the thermodynamic functions is 0.1% above 100°K., but some of the values are given to an additional digit for comparison purposes.

The present measurements accord better with the data by Parks and Kelley[3] on specular hematite than on the finely divided powder but are 3% lower near 90°K. and within about 0.5% at higher temperatures, while they are 2 to 6% lower than those on the Kahlbaum sample. Inasmuch as even the specular hematite contained 0.5% H_2O and 0.5% SiO_2 and no attempt was made to correct for these impurities, the agreement must be considered satisfactory. Since Parks and Kelley[3] used the data on the specular crystals in calculating the entropy, 21.5 ± 0.5 e.u., the entropy increment over the common region (90 to 295°K.) agrees quite well with that found in the present investigation. Most of the difference of 0.6 e.u. is in the extrapolated portion as a consequence of the errors in their lowest temperature data.

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ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Heats and Entropies of Ionization of Phenol and Some Substituted Phenols

BY L. P. FERNANDEZ AND L. G. HEPLER

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Standard heats of ionization of aqueous phenol, *o*-chlorophenol, *p*-chlorophenol, *o*-nitrophenol and *p*-nitrophenol have been determined calorimetrically at 298°K. These heats of ionization have been used with free energies, obtained from ionization constants, to calculate standard entropies of ionization of these compounds in aqueous solution. A detailed quantitative interpretation of the thermodynamics of ionization of phenol and substituted phenols is impractical until more data are available but some interesting comparisons of entropies of ionization are discussed.

This investigation of the heats and entropies of ionization of aqueous phenol and some substituted phenols was undertaken as part of a program aimed at the accumulation of thermodynamic data on the ionization of certain selected organic acids in water. It is to be hoped and possibly expected that systematic accumulation of such data on selected acids, combined with similar data of other investigators, will lead to a detailed interpretation of the thermodynamics of aqueous acids in terms of the structure of the weak acids and their anions and of solute–solvent interactions.

Experimental

The solution calorimeter used in this investigation has been described in detail.[1,2] All of the calorimetric work reported in this paper was carried out with 950 ml. of water or solution in the calorimeter. All heats of reaction and solution were investigated at 25.0 ± 0.3°.

Baker C.P. phenol was distilled under reduced pressure with only the middle fraction saved for calorimetric experiments. Eastman Kodak Co. practical grade *o*-chlorophenol and *p*-chlorophenol also were purified by fractional distillation. The *o*-chlorophenol and *p*-chlorophenol for calorimetric experiments boiled at 173° and melted at 42.8–44.8°, respectively.

Sodium *o*-nitrophenoxide was prepared by adding *o*-nitrophenol (m.p. 45–46°) to a solution of NaOH in ethanol. The resulting phenoxide was recrystallized once from 95% ethanol and twice from absolute ethanol. It then was dried and stored for future analysis and use.

The *p*-nitrophenol (m.p. 112–114°) used for our calorimetric experiments was supplied by Eastman Organic Chemicals. Sodium *p*-nitrophenoxide dihydrate was prepared by adding some of this *p*-nitrophenol to a solution of NaOH in ethanol. The salt formed was recrystallized twice from ethanol–water mixtures and washed with ethanol before drying and storing for future analysis and use.

Sodium *o*-nitrophenoxide was analyzed by titration with aqueous HCl. The yellow *o*-nitrophenol formed as a product of the titration reaction partly precipitated out and partly remained in solution and tended to obscure the indicator color change at the end-point. To eliminate this difficulty, 10 ml. of CCl_4 was added to the solution to extract and dissolve the *o*-nitrophenol, thus leaving the water layer nearly colorless. Methyl red indicator then was added and the solution titrated to the indicator color change without removing the CCl_4 layer. The titrations required 100.8% of the theoretical amount of HCl.

Sodium *p*-nitrophenoxide dihydrate also was analyzed by titration with aqueous HCl. This compound could serve as its own indicator, but the addition of one drop of methyl red solution made the color change at the end-point easier to see. The titrations required 101.0% of the theoretical amount of HCl.

Results and Calculations

We have measured the heat of solution of phenol in water and the heat of neutralization of phenol

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(1) C. N. Muldrow and L. G. Hepler, THIS JOURNAL, **79**, 4045 (1957).

(2) R. L. Graham and L. G. Hepler, *ibid.*, **78**, 4846 (1956).

by 0.1039 *M* NaOH as in equations 1 and 2.

$$C_6H_5OH(c) = C_6H_5OH(aq) \qquad \Delta H_1 \quad (1)$$

$$C_6H_5OH(c) + OH^-(aq) = C_6H_5O^-(aq) + H_2O \quad \Delta H_2 \quad (2)$$

Standard heats of reactions 1 and 2, ΔH_1^0 and ΔH_2^0, were obtained from the experimental heats at finite concentrations (given in Tables I and II) by graphically extrapolating to infinite dilution. Heats so obtained were $\Delta H_1^0 = 3100 \pm 50$ and $\Delta H_2^0 = -4750 \pm 80$ cal./mole where ± indicates our estimate of the maximum total uncertainty.

TABLE I

HEATS OF SOLUTION OF PHENOL IN WATER

Moles C_6H_5OH/950 ml.	ΔH_1 (cal./mole)
0.005574	3091
.005919	3113
.01032	3164
.01082	3091
.01273	3016
.01431	3103

TABLE II

HEATS OF NEUTRALIZATION OF PHENOL BY 0.1039 *M* NaOH

Moles C_6H_5OH/950 ml.	ΔH_2 (cal./mole)
0.004370	−4728
.004909	−4752
.007862	−4765
.01048	−4713
.01522	−4702
.01735	−4733
.03337	−4716
.03662	−4732

The standard heat of ionization of aqueous phenol as in equation 3 has been calculated from ΔH_1^0, ΔH_2^0 and the heat of ionization of water, ΔH_w^0.[3]

$$C_6H_5OH(aq) = C_6H_5O^-(aq) + H^+(aq) \quad \Delta H_3^0 \qquad (3)$$

The relation $\Delta H_3^0 = \Delta H_2^0 - \Delta H_1^0 + \Delta H_w^0$ leads to $\Delta H_3^0 = 5650 \pm 100$ cal./mole. The estimated uncertainty for ΔH_3^0 is less than the sum (or the square root of the sum of the squares) of uncertainties in ΔH_1^0, ΔH_2^0 and ΔH_w^0 because ΔH_1^0 and ΔH_2^0 were determined under similar conditions in the same calorimeter so that systematic errors partly cancel each other.

The ionization constant of aqueous phenol at 25° has been investigated many times and we have chosen $K_3 = 1.05 \times 10^{-10}$. References 4–7 describe representative investigations of this ionization constant. We have calculated from K_3 that $\Delta F_3^0 = 13610$ cal./mole and have combined this free energy with ΔH_3^0 to obtain $\Delta S_3^0 = -26.7$ cal./deg. mole.

We have also measured heats of solution and neutralization of *o*-chlorophenol and *p*-chlorophenol. The calorimetric reactions were analogous to reactions 1 and 2 for phenol and the heats of these reactions have been designated $\Delta H_1'$, $\Delta H_2'$, $\Delta H_1''$ and $\Delta H_2''$ where ′ refers to *o*-chlorophenol and ″ to *p*-chlorophenol. Results of these calorimetric experiments are given in Tables III, IV, V and VI. Graphical extrapolations to infinite dilution have yielded $\Delta H_1^{0\prime} = -78 \pm 20$, $\Delta H_2^{0\prime} = -8950 \pm 80$, $\Delta H_1^{0\prime\prime} = 3825 \pm 60$ and $\Delta H_2^{0\prime\prime} = -3880 \pm 60$ cal./mole. Standard heats of ionization of aqueous *o*-chlorophenol and *p*-chlorophenol (analogous to ΔH_3^0 and designated $\Delta H_3^{0\prime}$ and $\Delta H_3^{0\prime\prime}$) have been calculated from these heats of solution and neutralization in the same way that ΔH_3^0 was calculated. We have found $\Delta H_3^{0\prime} = 4630 \pm 80$ and $\Delta H_3^{0\prime\prime} = 5800 \pm 90$ cal./mole for *o*-chlorophenol and *p*-chlorophenol, respectively.

TABLE III

HEATS OF SOLUTION OF *o*-CHLOROPHENOL

Moles *o*-ClC_6H_4OH/950 ml.	$\Delta H_1'$ (cal./mole)
0.009028	−67
.01346	−88
.05473	−79
.06043	−75

TABLE IV

HEATS OF NEUTRALIZATION OF *o*-CHLOROPHENOL BY 0.1279 *M* NaOH

Moles *o*-ClC_6H_4OH/950 ml.	$\Delta H_2'$ (cal./mole)
0.002116	−8915
.002496	−8900
.004804	−8979
.006606	−8940
.01821	−8851

TABLE V

HEATS OF SOLUTION OF *p*-CHLOROPHENOL

Moles *p*-ClC_6H_4OH/950 ml.	$\Delta H_1''$ (cal./mole)
0.006661	3849
.008469	3829
.009627	3860
.01444	3938
.02511	4000
.03140	3998
.04375	4045

TABLE VI

HEATS OF NEUTRALIZATION OF *p*-CHLOROPHENOL

Moles *p*-$ClC_6H_4OH \times 10^2$/950 ml.	NaOH, *M*	$\Delta H_2''$ (cal./mole)
1.1184	0.1279	−3888
1.229	.1170	−3874
1.428	.1170	−3885
1.796	.1279	−3876
2.292	.1407	−3858
2.587	.1599	−3924
3.476	.1279	−3928
4.058	.1727	−3872

Ionization constants at 25° for aqueous *o*-chlorophenol and *p*-chlorophenol have been determined by Judson and Kilpatrick who have also reviewed earlier investigations. We have calculated from the constants given by Judson and Kilpatrick that the standard free energies of ionization of aqueous *o*-chlorophenol and *p*-chlorophenol are 11570 and 12800 cal./mole, respectively. These free energies and our heats of ionization ($\Delta H_3^{0\prime}$ and $\Delta H_3^{0\prime\prime}$) have been used to calculate that the standard entropies of ionization of aqueous *o*-

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(3) H. M. Papee, W. J. Canady and K. J. Laidler, *Can. J. Chem.*, **34**, 1677 (1956).

(4) A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956).

(5) G. R. Sprengling and G. W. Lewis, THIS JOURNAL, **75**, 5709 (1953).

(6) C. M. Judson and M. Kilpatrick, *ibid.*, **71**, 3110 (1949).

(7) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952).

chlorophenol and *p*-chlorophenol are both −23.5 cal./deg. mole.

The small solubility and slow rate of solution of *o*-nitrophenol made the calorimetric determination of the heat of solution of this compound difficult. Therefore, a procedure different from that followed for phenol and the chlorophenols was used for calorimetric determination of the heat of ionization of aqueous *o*-nitrophenol. The heat of solution of the salt, sodium *o*-nitrophenoxide, was measured in dilute NaOH in order to prevent any appreciable hydrolysis of the anion. The calorimetric reaction is given by equation 4 and the experimental

$$o\text{-}NO_2C_6H_4ONa(c) = o\text{-}NO_2C_6H_4O^-(aq) + Na^+(aq) \quad \Delta H_4 \qquad (4)$$

results are in Table VII. We have extrapolated to infinite dilution to obtain $\Delta H_4{}^0 = 2130 \pm 60$ cal./mole.

TABLE VII

HEATS OF SOLUTION OF SODIUM *o*-NITROPHENOXIDE

Moles o-$NO_2C_6H_4ONa$/950 ml.	NaOH, $M \times 10^3$	ΔH_4 (cal./mole)
0.002674	3.823	2141
.006205	5.310	2187
.01042	2.655	2166

The heat of reaction of sodium *o*-nitrophenoxide with dilute HCl to form aqueous *o*-nitrophenol as in equation 5 also has been measured. We have

$$o\text{-}NO_2C_6H_4ONa(c) + H^+(aq) = o\text{-}NO_2C_6H_4OH(aq) + Na^+(aq) \quad \Delta H_5 \qquad (5)$$

extrapolated the results of these experiments (given in Table VIII) to infinite dilution to obtain $\Delta H_5{}^0 = -2525 \pm 50$ cal./mole. The heat of ionization of aqueous *o*-nitrophenol has been calculated as $\Delta H_4{}^0 - \Delta H_5{}^0$ and found to be 4655 ± 70 cal./mole.

TABLE VIII

HEATS OF REACTION OF SODIUM *o*-NITROPHENOXIDE WITH 0.02444 *M* HCl

Moles o-$NO_2C_6H_4ONa \times 10^3$/950 ml.	ΔH_5 (cal./mole)
3.423	−2526
6.596	−2513
9.229	−2527

Biggs[4] and Judson and Kilpatrick[6] have reported ionization constants of aqueous *o*-nitrophenol at 25° that are in good agreement with each other. The average of their values, 6.0×10^{-8}, has been used to calculate the standard free energy of ionization of aqueous *o*-nitrophenol to be 9850 cal./deg. From this free energy and our heat of ionization we have calculated that the standard entropy of ionization of *o*-nitrophenol is −17.4 cal./deg. mole.

Neither the solubility nor the rate of solution of *p*-nitrophenol causes undue difficulty in the calorimetric investigation of the heat of solution of *p*-nitrophenol. Therefore, we have determined the heat of ionization of aqueous *p*-nitrophenol in the same way that we investigated phenol and the chlorophenols. Results of our heat of solution and heat of neutralization experiments (designated $\Delta H_1'''$ and $\Delta H_2'''$) are given in Tables IX and X. We have extrapolated from these heats to obtain $\Delta H_1{}^{0'''} = 5400 \pm 100$ and $\Delta H_2{}^{0'''} = -3270 \pm 90$ cal./mole and have calculated $\Delta H_3{}^{0'''} = \Delta H_2{}^{0'''} - \Delta H_1{}^{0'''} + \Delta H_w{}^0 = 4830 \pm 130$ cal./mole for the heat of ionization of aqueous *p*-nitrophenol at 298°K.

TABLE IX

HEATS OF SOLUTION OF *p*-NITROPHENOL

Moles p-$NO_2C_6H_4OH$/950 ml.	$\Delta H_1'''$ (cal./mole)
0.006493	5385
0.01198	5423

TABLE X

HEATS OF NEUTRALIZATION OF *p*-NITROPHENOL IN 0.1170 *M* NaOH

Moles p-$NO_2C_6H_4OH$/950 ml.	$\Delta H_2'''$ (cal./mole)
0.005166	−3255
0.01009	−3235

The heat of ionization of aqueous *p*-nitrophenol also has been investigated by the method used for *o*-nitrophenol. Heats of solution of sodium *p*-nitrophenoxide dihydrate in dilute aqueous NaOH and in aqueous HCl (designated $\Delta H_4'$ and $\Delta H_5'$, respectively) have been measured and the results of these experiments are given in Tables XI and XII. We have extrapolated to infinite dilution to obtain $\Delta H_4{}^{0'} = 7750 \pm 180$ and $\Delta H_5{}^{0'} = 3150 \pm 120$ cal./mole and have calculated $\Delta H_3{}^{0'''} = \Delta H_4{}^{0'} - \Delta H_5{}^{0'} = 4600 \pm 210$ cal./mole. We have taken 4700 cal./mole as the best value for the heat of ionization of *p*-nitrophenol and this value has been used in calculating the entropy of ionization to be −16.9 cal./deg. mole. For this calculation we used a free energy of ionization of *p*-nitrophenol ($\Delta F^0 = 9750$ cal./mole) based on an average ionization constant ($K = 7.2 \times 10^{-8}$) taken from the results of Judson and Kilpatrick[6] and Robinson and Biggs.[8] It might be noted that had we used $\Delta H_w{}^0 = 13.36$ kcal./mole as found by Pitzer[9] and others, most of the difference between our two values for the heat of ionization of *p*-nitrophenol would disappear. Nevertheless, we have used $\Delta H_w{}^0 = 13.50$ kcal./mole because this recent calorimetric value is in accord with the heat calculated from the temperature coefficient of the ionization constant of water.[3]

TABLE XI

HEATS OF SOLUTION OF SODIUM *p*-NITROPHENOXIDE DIHYDRATE

Moles p-$NO_2C_6H_4ONa \cdot 2H_2O \times 10^3$/950 ml.	$\Delta H_4'$ (cal./mole)
2.751	7804
5.635	7675

TABLE XII

HEATS OF REACTION OF SODIUM *p*-NITROPHENOXIDE DIHYDRATE WITH 0.2444 *M* HCl

Moles p-$NO_2C_6H_4ONa \cdot 2H_2O \times 10^3$/950 ml.	$\Delta H_5'$ (cal./mole)
3.908	3216
7.327	3158

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[8] R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc.*, **51** 901 (1955).

[9] K. S. Pitzer, THIS JOURNAL, **59**, 2365 (1937).

For easy comparison we have gathered in Table XIII the ionization constants and heats and entropies of ionization at 25° of aqueous phenol and a number of substituted phenols. Included in Table XIII are data on *m*-nitrophenol. The heat of ionization of *m*-nitrophenol has been determined calorimetrically by Cottrell, *et al.*[10] We have calculated the free energy and entropy of ionization from the ionization constant reported by Judson and Kilpatrick[6] and the heat reported by Cottrell, *et al.*[10] It may also be noted that Cottrell, *et al.*,[10] have reported heats of ionization of *o*-chlorophenol and *p*-nitrophenol that are in good agreement with our heats of ionization of these compounds.

TABLE XIII

THERMODYNAMICS OF IONIZATION OF AQUEOUS PHENOLS

Substance	$K_{298} \times 10^{10}$	ΔH^0 (cal./mole)	ΔS^0 (cal./deg. mole)
Phenol	1.05	5650	−26.7
o-Chlorophenol	33.4	4630	−23.5
p-Chlorophenol	4.18	5800	−23.5
o-Nitrophenol	600	4655	−17.4
p-Nitrophenol	720	4700	−16.9
m-Nitrophenol	45.1	4705	−22.5

Discussion

The principal aim of the research reported in this paper has been to obtain experimental data that will further our attempts to deduce and make use of relations between acid strength and structure. The following discussion of our data is relevant to that end.

It may first be noted that substitution of a chlorine or nitro group for hydrogen in the *o*-, *m*- or *p*-position yields an acid that is stronger than phenol. Other more interesting observations concern the relative importance of the heat and entropy of ionization for the various phenols under consideration. Along these lines, these several observations are pertinent to the problem at hand: (i) the heat of ionization of *p*-chlorophenol is more endothermic than that of phenol but, in spite of this, the free energy of ionization of *p*-chlorophenol is less positive (greater *K*) than that of phenol because of the considerable difference in the entropies of ionization. (ii) We note that *m*-nitrophenol is a weaker acid than *p*-nitrophenol and *o*-nitrophenol because of a considerable difference in entropy of ionization and *not* because of a more endothermic heat of ionization. Further, about two-thirds of the increase in acid strength of *p*-nitrophenol and *o*-nitrophenol over phenol is an entropy effect.

Any attempt to calculate or correlate heats of ionization of a series of acids must take account of the energy changes that occur *within* the acid as a result of losing a proton and acquiring a net negative charge. This problem is usually approached from the point of view of resonance, inductance, etc., effects on the energy or sometimes free energy difference between the acid and its anion. An equally important problem is consideration of energy effects arising ***outside*** the acid and anion due to differences in the acid–solvent and anion–solvent interaction energies. This combination of problems makes theoretical investigation (or even correlation) of heats of ionization appear less promising at present than investigation of entropies of ionization.

When considering the entropy of ionization in detail, we must be concerned with entropy changes due to differences *within* the acid and its anion and also with entropy changes due to differences in solute–solvent interactions. In this case the first problem has been discussed by Pitzer[9] who has shown that for a series of acids the "internal" entropies of the anions are less than those of the corresponding acids by an amount that is very nearly constant. We conclude, therefore, that most of the differences in entropy of ionization for the acids in Table XIII are due to differences in solute–solvent interactions.

With this background in mind, it is interesting to consider specifically the entropies of ionization of the nitrophenols. We conclude from these entropies of ionization that the anion of *m*-nitrophenol (relative to undissociated *m*-nitrophenol) is more effective in orienting neighboring water molecules than the anions of *o*- or *p*-nitrophenol (relative to undissociated *o*- or *p*-nitrophenol). It seems likely that this extra orienting effectiveness of the *m*-nitrophenol anion results from a greater localization of negative charge on the phenolic oxygen as compared to anions of *o*- and *p*- nitrophenol. This argument is in agreement with conventional ideas about the small tendency of ***meta*** substituents, as compared to ***ortho*** or ***para*** substituents, to take part in resonance with the phenolic function.

In summary, it is well to emphasize that a satisfactory correlation of strengths and structures of organic acids in aqueous solutions must not be based solely on energy (or even free energy) changes or differences *within* the acid and its anion. It is equally important that differences in solute–solvent interaction be considered in as much detail as possible. These solute–solvent interactions are presently most easily considered in terms of entropy changes.

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[10] T. L. Cottrell, G. W. Drake, D. L. Levi, K. J. Tully and J. H. Wolfenden *J. Chem. Soc.* 1016 (1948).