Ionization of Substituted Phenols in Aqueous Solution

BY H. C. KO, W. F. O'HARA,[1] T. HU, AND L. G. HEPLER

Ionization constants and heats of ionization have been determined for 2,4,6-, 3,4,5-, 2,4,5-, and 2,3,5-trimethylphenols, m- and p-cyanophenols, and m- and p-hydroxyphenyltrimethylammonium chlorides in aqueous solution at 25°. It is found that differences in acidities of several of these compounds are due to entropy effects. Effects of substituents on acidity are discussed in terms of ΔH_{int}, which refers to the part of $\Delta H°$ that is not due to solute–solvent interactions.

Introduction

Ionization constants and heats of ionization of a number of substituted phenols in aqueous solution have been determined at 25°. The results of these determinations have been used for calculation of $\Delta F°$, $\Delta H°$, and $\Delta S°$ of ionization of these acids. Substituent effects on acidity are discussed.

Experimental

Thermodynamic ionization constants were determined as previously described.[2] Heats of ionization at $25.0 \pm 0.2°$ were determined calorimetrically in apparatus also previously described.[3,4] All calorimetric measurements were made with 950 ml. of water or solution in the dewar.

All trimethyl- and cyanophenols were obtained from Aldrich Chemical Co. All trimethylphenols were recrystallized from alcohol–water mixtures and had the following melting points: 2,4,6-trimethylphenol, 218–220°, 3,4,5-trimethylphenol, 108–110°, 2,4,5-trimethylphenol, 228–231°, 2,3,5-trimethylphenol, 93–94°. Both m- and p-cyanophenols were recrystallized from carbon tetrachloride and melted at 112–113° and 111–112°, respectively. All melting points were in fine agreement with literature values.

Both m- and p-hydroxyphenyltrimethylammonium iodides were prepared according to the procedure of Hunig.[5] The iodides were converted to the chlorides by dissolving them in water and treating the solution with an excess of solid AgCl. The resulting chlorides were purified by dissolving them in hot alcohol and adding ether to precipitate the desired crystals. The compounds were analyzed gravimetrically for Cl⁻. The m-HOC₆H₄N(CH₃)₃⁺Cl⁻ and p-HOC₆H₄N(CH₃)₃⁺ Cl⁻ were found to contain 18.50 and 18.75% Cl⁻, respectively, as compared to the calculated value of 18.89%.

Results

The results of the determinations of the ionization constants of the various phenols in aqueous solution at 25° are given in Table I.

TABLE I

THERMODYNAMIC IONIZATION CONSTANTS OF SUBSTITUTED PHENOLS IN AQUEOUS SOLUTION AT 25°

Acid	pK	Acid	pK
Phenol	10.00	m-Cyanophenol	8.57
2,4,6-Trimethylphenol	10.89	p-Cyanophenol	7.97
3,4,5-Trimethylphenol	10.25	m-HOC₆H₄N(CH₃)₃⁺Cl	8.06
2,4,5-Trimethylphenol	10.57	p-HOC₆H₄N(CH₃)₃⁺Cl	8.35
2,3,5-Trimethylphenol	10.67		

Heats of ionization were all determined by measuring the heats of neutralization of substituted phenol solutions by aqueous sodium hydroxide. Ten-ml. aliquots of aqueous NaOH (4.980 M for some measurements and 4.535 M for the others) were caused to react with 950 ml. of solution containing a known amount of substituted phenol. A general reaction for this process is
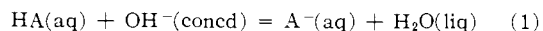
$$HA(aq) + OH^-(concd) = A^-(aq) + H_2O(liq) \quad (1)$$

Separate determination of the total heat effect associated with breaking the bulb containing the NaOH and dilution of the NaOH permitted us to calculate ΔH_2 for the reaction

$$HA(aq) + OH^-(aq) = A^-(aq) = H_2O(liq) \quad (2)$$

from the Q (calorimetric) for the process represented by eq. 1. The values of ΔH_2 for the various substituted phenols were extrapolated to infinite dilution yielding the values of $\Delta H_2°$ listed in Table II. Also listed in Table II are values for $\Delta H_{ion}°$ for reactions of the type

$$HA(aq) = H^+(aq) + A^-(aq)$$
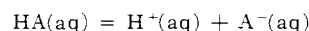
These values were calculated according to $\Delta H_{ion}° = \Delta H_W° + \Delta H_2°$, where $\Delta H_W° = 13.50$ kcal./mole for the ionization of water.[6] Standard free energies of ionization, $\Delta F_{ion}°$, have been calculated from the pK data in Table I and are also listed in Table II. Entropies of ionization have been calculated from

$$\Delta S_{ion}° = (\Delta H_{ion}° - \Delta F_{ion}°)/298$$

TABLE II

THERMODYNAMICS OF IONIZATION OF SUBSTITUTED PHENOLS IN AQUEOUS SOLUTION AT 298K.

Acid	$\Delta H_2°$ [a]	$\Delta H_{ion}°$ [a]	$\Delta F_{ion}°$ [a]	$\Delta S_{ion}°$ [a]
Phenol[7]		5.65	13.64	−26.8
2,4,6-Trimethylphenol	−8.06	5.44	14.85	−31.6
3,4,5-Trimethylphenol	−7.82	5.68	13.98	−27.9
2,4,5-Trimethylphenol	−7.10	6.40	14.41	−26.9
2,3,5-Trimethylphenol	−7.50	6.00	14.45	−28.7
m-Cyanophenol	−8.30	5.20	11.69	−21.8
p-Cyanophenol	−8.58	4.92	10.87	−20.0
m-HOC₆H₄N(CH₃)₃⁺Cl⁻	−7.41	6.09	10.99	−16.4
p-HOC₆H₄N(CH₃)₃⁺Cl⁻	−8.04	5.46	11.39	−19.9

[a] $\Delta H°$ and $\Delta F°$ in kcal./mole and $\Delta S°$ in cal./deg. mole.

Discussion

Sprengling and Lewis[8] have reported pK 10.88 for 2,4,6-trimethylphenol, in good agreement with our value. O'Hara[9] reported pK 10.87 for this compound, determined by spectrophotometry. Wheland, Brownell, and Mayo[10] reported the pK for p-cyanophenol to be 7.95. Fickling, et al.,[11] report pK values for m- and p-cyanophenols to be 8.68 and 7.97, respectively, in agreement with our values.

Oae and Price[12] report pK for m- and p-hydroxyphenyltrimethylammonium iodide to be 8.03 and 8.21, in fair agreement with our values for the chloride salt.

It is useful to discuss the effects of substituents on the thermodynamics of ionization of phenols in terms of reactions of the type shown in eq. 3

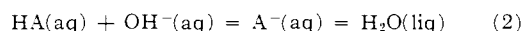(1) Chemistry Department, College of the Holy Cross, Worcester, Mass.

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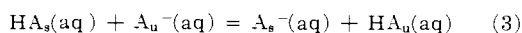(7) L. P. Fernandez and L. G. Hepler, J. Am. Chem. Soc., 81, 1783 (1959).

(8) G. R. Sprengling and C. W. Lewis, ibid., 75, 5709 (1953).

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(10) G. W. Wheland, R. M. Brownell, and E. C. Mayo, J. Am. Chem. Soc., 70, 2492 (1948).

(11) M. M. Fickling, A. Fishcher, B. R. Mann, J. Packer, and J. Vaughn, ibid., 81, 4226 (1959).

(12) S. Oae and C. C. Price, ibid., 80, 3425 (1958).

$$HA_s(aq) + A_u^-(aq) = A_s^-(aq) + HA_u(aq) \quad (3)$$

where subscripts s and u indicate substituted and unsubstituted phenol. Previous investigations[13,14] have shown that $\Delta H_3°$ may be expressed as the sum of two terms representing solute–solvent interactions (ΔH_{ext}) and "internal" effects. These considerations have led to the equation

$$\Delta H_3° = \Delta H_{int} + \beta \Delta S_3° \quad (\beta = 280°) \quad (4)$$

for reactions of type 3. Experimental enthalpy and entropy changes are represented by $\Delta H_3°$ and $\Delta S_3°$ while ΔH_{int} represents the part of the total $\Delta H_3°$ that is associated with breaking and forming O–H bonds as affected by resonance, inductive effects, etc. Combination of 4 with $\Delta F_3° = \Delta H_3° - T\Delta S_3°$ leads to

$$\frac{\Delta F_3°}{\Delta H_{int}} = 1 + \frac{(\beta - T)\Delta S_3°}{\Delta H_{int}} \quad (5)$$

and then, because $\dfrac{(\beta - T)\Delta S_3°}{\Delta H_{int}} \ll 1$, to

$$\Delta F_3° \cong \Delta H_{int} \quad (6)$$

Values of $\Delta H_3°$ and $\Delta S_3°$ used in eq. 4 have been calculated from the values of $\Delta H_{ion}°$ and $\Delta S_{ion}°$ in Table II and are listed in Table III along with values of ΔH_{int} and $\Delta F_3°$ ($\Delta \Delta F°$).

TABLE III

THERMODYNAMICS OF PROTON TRANSFER (REACTION 3) FOR SUBSTITUTED PHENOLS

HA$_s$	$\Delta S°{}^a$	$\Delta H_3°{}^a$	$\Delta H_{int}{}^a$	$\Delta F_3°{}^a$
2,4,6-Trimethylphenol	−4.8	−0.21	+1.13	+1.21
3,4,5-Trimethylphenol	−1.1	+ .03	+0.34	+0.34
2,4,5-Trimethylphenol	−0.1	+ .75	+ .78	+ .77
2,3,5-Trimethylphenol	−1.9	+ .35	+ .88	− .81
m-Cyanophenol	+5.0	− .45	−1.85	−1.95
p-Cyanophenol	+6.8	− .73	−2.63	−2.77
m-HOC$_6$H$_4$N(CH$_3$)$_3{}^+$	+10.2	+ .44	−2.42	−2.65
p-HOC$_6$H$_4$N(CH$_3$)$_3{}^+$	+6.9	− .19	−2.12	−2.25

^{a} ΔH and $\Delta F°$ in kcal./mole, $\Delta S°$ in cal./deg. mole.

The physical meaning of eq. 4, with β close to T, is that the effects of solute–solvent interactions on

(13) L. G. Hepler and W. F. O'Hara, J. Phys. Chem., **65**, 811 (1961).
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$\Delta H_3°$ and $T\Delta S_3°$ are nearly equal and hence contribute so little to $\Delta F_3°$ that $\Delta F_3° \cong \Delta H_{int}$.

A traditional explanation of the cyanophenols as compared to phenol and each other is that both are stronger acids than phenol because of the electron-withdrawing effect of the cyano group (partly due to resonance) and that p-cyanophenol is a stronger acid than m-cyanophenol because of resonance stabilization of the anion of p-cyanophenol. It can be seen that this explanation is in accord with the pK values. Since experimental $\Delta H°$ values include contributions from the solute–solvent interactions, it should not be surprising that $\Delta H_3°$ values are not simply related to either the pK values or the traditional explanation. Although the contribution of $\Delta H_{external}$ to $\Delta H_3°$ is important, eq. 4–6 and the accompanying discussion show that the net effect of solute–solvent interactions on $\Delta F_3°$ and thence ΔpK is small so that ΔH_{int} (to which resonance and inductive arguments apply) largely determines acidity.

Similar arguments apply to the other phenols.[13,15] For instance, both HOC$_6$H$_4$N(CH$_3$)$_3{}^+$ compounds are stronger acids than phenol. A simple explanation is that the positively charged substituent makes it "easier" to remove a proton from these compounds than from phenol. On the basis, the m-compound should be a stronger acid than the p-compound because the m-substituent is closer to the phenolic hydrogen than is the p-substituent. This explanation is supported by the pK and ΔH_{int} values, but the $\Delta H_3°$ and $\Delta S_3°$ values (which are affected importantly by solute–solvent interactions) are not simply related to the above explanation.

(15) L. P. Fernandez and L. G. Hepler, ibid., **81**, 1783 (1959).

[CONTRIBUTION FROM THE INTERNATIONAL BUSINESS MACHINES CORP., THOMAS J. WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

Stark Effect of Phenol Blue (Electrochromism)

BY J. C. POWERS, JR., W. R. HELLER, J. KUMAMOTO, AND W. E. DONATH

The effect of an external electric field on the absorption spectrum of phenol blue in an inert, transparent rigid matrix of high dielectric strength (polystyrene) has been studied. A net band shift to the red is observed. The results may be explained by assuming that a Stark shift occurs. A shift of 12 cm.$^{-1}$ at 9×10^5 v./cm. is observed on the band edge at 6500 Å., and this corresponds to an actual shift of 15 cm.$^{-1}$ when an intensity change correction is applied. A method for treating data to determine true band shifts in the presence of a simultaneous change in intensity is derived.

Phenol blue (I) has been of interest for some time because of the sensitivity of the position of its absorption

I

II
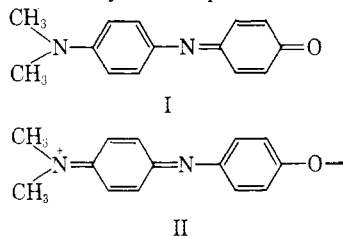
maximum to the polarity of a solvent. Brooker[1] found the maximum to be at 5520 Å. in cyclohexane and 6680 Å. in water. He rationalized this effect as due to a lowering of energy of the charged resonance forms, II, in a more polar solvent resulting in increased resonance stabilization of the molecule. Bayliss and McRae[2] and Platt[3] have used this concept of solvent–

(1) L. G. S. Brooker and R. H. Sprague, J. Am. Chem. Soc., **63**, 3214 (1941).
(2) N. S. Bayliss and E. G. McRae, J. Phys. Chem., **58**, 1002 (1954).
(3) J. R. Platt, J. Chem. Phys., **25**, 80 (1956).