Influence of Solvation Factors on Acidity. Volumes of Ionization ($\Delta \bar{V}_i°$) of the Meta and Para Isomers of Nitrophenol and Formylphenol in Water at 25°[1-4]

Sir:

Hepler[5,6] has reported that while the acidities of *m*- and *p*-nitrophenol differ by more than one pK_a unit, the enthalpies of ionization are almost identical (4.90 and 4.65 kcal/mol, respectively). The entropies of ionization for the meta and para isomers, however, are −21.8 and −17.1 cal/(deg mol), respectively. Following the reasoning suggested by other workers in the area,[6-9] Hepler attributes the difference in acidity to solvation suggesting that the entropy of ionization ($\Delta \bar{S}_i°$) qualitatively reflects the relative degree of solvent orientation around the solute species involved in the equilibrium. It is argued that *m*-nitrophenoxide is more effective in orienting solvent molecules since the negative charge is more localized on the oxygen than in the *p*-nitrophenoxide case where the negative charge may be delocalized over the entire molecule (electromeric interaction). The entropies of ionization of *m*- and *p*-cyanophenol (−21.8 and −20.0 cal/(deg mol), respectively) and *m*- and *p*-formylphenol[4,6] (−23.4 and −20.2 cal/(deg mol), respectively) are also consistent with the above interpretation based upon the assumption that solvation differences are more important for the ionized forms of the acids than for the un-ionized.[6] We wish to report data which bear on this explanation.

The volume changes on ionization ($\Delta \bar{V}_i°$) of *m*- and *p*-nitrophenol and *m*- and *p*-formylphenol have been determined in water at 25°. Table I contains the infinite dilution partial molar volumes of the un-ionized and ionized forms of the acids along with the $\Delta \bar{V}_i°$ values. The partial molar volumes were determined from high-precision density measurements by means of a magnetic float densitometer as described by Millero.[10] The apparent molar volumes of the un-ionized forms of the acids were corrected for ionization by the method of King[11] and extrapolated to infinite dilution. The apparent molar volumes of the sodium salts were determined in excess sodium hydroxide to prevent hydrolysis, the apparent molar volume data being corrected with the known NaOH values.[12] In dilute solution the apparent molar volumes varied with $I^{1/2}$ according to the Debye–Hückel limiting law for 1:1 electrolyte.[13]

Table I. Partial Molar Volume and Volumes of Ionization[a] in Water at 25°[b,c]

Acid	$\bar{V}°_{HA}$	$\bar{V}°_{Na^+A^-}$[d]	$\bar{V}°_{H^+A^-}$[e]	$\Delta \bar{V}°$
m-Nitrophenol	99.71	85.67	86.87	−12.84
p-Nitrophenol	98.23	85.71	86.91	−11.32
m-Formylphenol	97.87	83.32	84.52	−13.35
p-Formylphenol	96.94	83.53	84.73	−12.21

[a] Ionization process: $HA \rightleftarrows H^+ + A^-$. [b] All volumes are in units of milliliters/mole. [c] As an experimental check of the method and procedures, the $\Delta \bar{V}_i°$ of phenol was determined (−18.01 ± 0.20). This compares favorably with the literature value (−17.3 ± 1.0): S. D. Harmann and S. C. Lim, *Aust. J. Chem.*, 7, 329 (1954). [d] The difference between the lowest observed apparent molar volume for each salt and the $\bar{V}°$ was less than 0.1 ml/mol in all cases. [e] Found from the values in the previous column by adding $\bar{V}°_{H^+} - \bar{V}°_{Na^+} = +1.20$ ml/mol.[11]

Examination of Table I reveals that $\Delta \bar{V}_i°$ is more negative for *m*-nitrophenol and *m*-formylphenol as compared to their corresponding para isomers. This appears to be consistent with the qualitative explanation of the entropy data cited above, in that the more negative the $\Delta \bar{S}_i°$ the more electrostriction is expected in the ionization process. Indeed, this type of behavior is qualitatively what might be predicted in view of the general correlation between $\Delta \bar{S}°$ and $\Delta \bar{V}°$ reported by Hepler for the ionization in water of a wide variety of structurally different acids.[14] Quite surprisingly, the partial molar volumes of the isomeric sodium salts were found to be almost identical (within experimental error) indicating that *the origin of the $\Delta \bar{V}_i°$ difference lies exclusively with the un-ionized forms.* This appears to be in direct contradiction to the interpretation given above for the origin of the difference in entropy changes. Based upon the data presented in this communication, it appears that *the solvation contribution to differences in acidity of isomeric phenols may have their primary origin in solvation differences in the un-ionized forms.*

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(1) Part IV in the series, "Thermodynamics of Acid–Base Equilibria."

(2) Part III: C. L. Liotta, E. M. Perdue, and H. P. Hopkins, Jr., *J. Amer. Chem. Soc.*, in press.

(3) Part II: C. L. Liotta, D. F. Smith, Jr., H. P. Hopkins, Jr., and K. Rhodes, *J. Phys. Chem.*, 76, 1909 (1972).

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Charles L. Liotta,* A. Abidaud
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

H. P. Hopkins, Jr.
Department of Chemistry, Georgia State University
Atlanta, Georgia 30332

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On the Conformation of Derivatives of 2,2,5,5-Tetramethylcyclohexane-1,3-dione

Sir:

A knowledge of the conformational properties of cyclohexane derivatives with ring carbons sp^2 hybridized is fundamental in organic chemistry. While cyclohexanone exists in a chair conformation, some of its alkyl derivatives have been found to exist predominantly in a twist-boat form.[1] Furthermore, it has been recognized for some time that cyclohexane-1,4-

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