Coordination in Solutions. III. Acid Strengths of 5- and 7-Hydroxy-1-indanone and Nitro Derivatives. Hydrogen Bonding in o-Carbonyl Phenols[1,2]

BY LAWRENCE B. MAGNUSSON, CAROLYN A. CRAIG, AND CLARENCE POSTMUS, JR.

The pK values for acid dissociation, expressed in molar concentrations, of 5-hydroxy-1-indanone, 7-hydroxy-1-indanone, and three nitro derivatives of the latter (4-nitro-, 6-nitro-, and 4,6-dinitro-) are 7.53, 8.43, 5.27, 5.31, and 1.94, respectively, in aqueous 0.1 M sodium perchlorate solutions at 25.0°. Measurements of the n.m.r. of the hydroxylic proton and ultraviolet absorption shifts upon methylation indicate that the strength of the intramolecular hydrogen bond increases in the order 7-hydroxy-1-indanone < 2-hydroxylbenzaldehyde < 8-hydroxy-1-tetralone ≃ 2-hydroxyacetophenone. Entropy changes and isotopic hydrogen effects in nitrophenols show that there is little or no intramolecular bonding in o-nitrophenol in aqueous solution. Correlations of the pK values of the o-carbonyl phenols and nitro derivatives with those of the parent phenols indicate there is little or no intramolecular hydrogen bonding in the indanone acids in aqueous solution. The effect of the *ortho* substituent, in the absence of intramolecular bonding, appears to be about equal to the *para* effect.

Introduction

Further information on the role of the carbonyl oxygen in the bonding of protons is to be found in a comparison of the properties of 7-hydroxy-1-indanone with those of the previously measured o-carbonyl phenols: 2-hydroxybenzaldehyde, 2-hydroxyacetophenone, and 8-hydroxy-1-tetralone.[3] The five-membered ring in the indanone increases the separation of the two chelating oxygens. Otherwise the structures are similar in the series and one might expect the acid association constants to follow closely the order of strength of the intramolecular hydrogen bonding. Prior data do not adequately define an order, particularly the relation between the bicyclic molecules and the other two.[4-6] Evidence is accumulating that the n.m.r. of hydroxylic protons moves to lower fields with increasing strength of inter- and intramolecular hydrogen bonding.[2,7] This paper reports an order of intramolecular hydrogen bond strength for the four o-carbonyl phenols derived from n.m.r. measurements and shifts in the position of an optical absorption band (*ca.* 325 mμ) upon methylation.[2,4,8,9] Variations in anion properties are deduced from the acidities and intramolecular H-bond strengths.

Experimental

Materials.—The organic acids were synthesized by Kaye.[10] The methods used for the purification of the acids in this laboratory and the preparation of other materials have been reported.[3]

The methyl ethers of 2-hydroxyacetophenone, 8-hydroxy-1-tetralone, and 7-hydroxy-1-indanone were obtained by reaction of o-carbonyl phenols with dimethyl sulfate in an aqueous alkaline medium. 2-Methoxybenzaldehyde, obtained commercially, and 7-methoxy-1-indanone were purified by recrystallization from ethanol. The remaining two, liquids at room temperature, were isolated from the reaction mixture by extraction into carbon

tetrachloride, which, after several washes with 5 M potassium hydroxide, was removed by evaporation. The absence of unmethylated material was established by the identity of the ultraviolet spectra in acidic and basic solutions.

Measurements.—The acid dissociation constants were evaluated from the spectral absorption of aqueous solutions as a function of pH using the same procedures and instruments described previously.[3]

The n.m.r. spectra were obtained with tetramethylsilane as an internal standard in a Varian A-60 spectrometer operating at 60 Mc. The o-carbonyl phenols were measured at 25° in carbon tetrachloride at concentrations of 0.48, 0.37, 0.19, and 0.19 M for 2-hydroxybenzaldehyde, 2-hydroxyacetophenone, 7-hydroxy-1-indanone, and 8-hydroxy-1-tetralone, respectively. Each solution was diluted by a factor of two and was remeasured.

Calculations.—The acid dissociation constant is defined by eq. 1.

$$K = [H^+][L^-]/[HL]$$

where [X] is the molar concentration of species X; L^- and HL are the anion and acid forms, respectively, of the phenol. Since all constants in this paper are concentration constants, the subscript c, used in ref. 3, has been omitted. The value obtained directly from experimental measurements is K' which differs from K in that the $[H^+]$ in eq. 1 is replaced by a'_H, where a'_H is defined as antilog $(-pH)$. The constant, K', was evaluated from either eq. 4 or 5 of ref. 3 and converted to the concentration constant, K, using the empirical relationship found previously between a'_H and $[H^+]$ in 0.100 M sodium perchlorate solutions.[3]

Results

The hydroxylic p.m.r. was located downfield by 8.90, 10.83, 11.95, and 12.11 p.p.m. in 7-hydroxy-1-indanone, 2-hydroxybenzaldehyde, 2-hydroxyacetophenone, and 8-hydroxy-1-tetralone, respectively. The values for the benzaldehyde and acetophenone are about 0.08 p.p.m. smaller than those reported by Forsén and Åkermark.[6] Relative to the tetramethylsilane standard, the downfield shift for phenol is 4.4 p.p.m.[2] These carbonyl phenols are monomeric and intramolecularly hydrogen bonded in carbon tetrachloride since dilution had no effect on the proton resonance (<0.03 p.p.m.)[11] and no OH absorption could be found in the 1.4 μ region.

Shifts in ultraviolet absorption caused by methylation are listed in Table I for the four o-carbonyl phenols in various solvents. The shifts in water are not definitive for 2-hydroxybenzaldehyde and 7-hydroxy-1-indanone but the order in water is confirmed by the larger shifts observed in the organic solvents. The order of increasing shift in the absorption is 7-hydroxy-1-inda-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Part II: C. Postmus, Jr., I. A. Kaye, C. A. Craig, and R. S. Matthews, *J. Org. Chem.*, **29**, 2693 (1964).

(3) Part I: L. B. Magnusson, C. Postmus, Jr., and C. A. Craig, *J. Am. Chem. Soc.*, **85**, 1711 (1963).

(4) V. C. Farmer, N. F. Hayes, and R. H. Thompson, *J. Chem. Soc.*, 3600 (1956).

(5) A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, *J. Am. Chem. Soc.*, **82**, 5057 (1960).

(6) S. Forsén and B. Åkermark, *Acta Chem. Scand.*, **17**, 1907 (1963).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 404.

(8) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

(9) T. A. Geissman and J. B. Harborne, *J. Am. Chem. Soc.*, **78**, 832 (1956).

(10) I. A. Kaye, R. S. Matthews, and A. A. Scala, *J. Chem. Soc.*, in press.

(11) Contrary to our result, a small concentration dependence for 2-hydroxybenzaldehyde was reported by I. Yamaguchi, *Bull. Chem. Soc. Japan*, **34**, 353 (1961).

none, 2-hydroxybenzaldehyde, 8-hydroxy-1-tetralone, and 2-hydroxyacetophenone. If 25 mμ is added to the reported wave lengths in Fig. 1 of ref. 4 for 7-hydroxy-1-indanone and its methoxy derivative, the spectra agree with ours and with that of the parent reported by other investigators.[12,13]

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TABLE I

ULTRAVIOLET ABSORPTION SHIFTS UPON METHYLATION[a]

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Compounds	Water	95% ethanol	100% ethanol	Cyclohexane[b]
7-Hydroxy-1-indanone	1	3.5[c]	4.5	6–9
2-Hydroxybenzaldehyde	2	6[d]	7	11.5–19
8-Hydroxy-1-tetralone	12	16.5[e]	18	22–27
2-Hydroxyacetophenone	15	19[f]	19.5	27.5–33.5

[a] Shifts, accurate to about 1 mμ, are measured as the difference between the free hydroxyl compound and its methoxy derivative in mμ at the longest wave length peak. [b] The absorption appears to be a single band in the hydroxylic solvents but is resolved in cyclohexane so that two or more slightly separated peaks appear. The wave length range in this column spans the minimum and maximum shifts. [c] 0 mμ reported in ref. 4. [d] 6 mμ reported in ref. 8. [e] 30–40 mμ shifts are reported for substituted tetralones in ref. 4. [f] 22 mμ reported in ref. 8.

The acid dissociation constants, as pK values at 25.0° and μ of 0.100, are listed in Table II for 5- and 7-hydroxy-1-indanone and three nitro derivatives of the latter. The variation in the pK values of p-carbonyl phenols is relatively small (7.45, 7.53, 7.74, and 7.87 for 4-hydroxybenzaldehyde, 5-hydroxy-1-indanone, 6-hydroxy-1-tetralone, and 4-hydroxyacetophenone, respectively, at μ of 0.100[3]). The o-carbonyl phenols are weaker acids with a wide range in pK values (8.14, 8.43, 10.07, and 11.14 for 2-hydroxybenzaldehyde, 7-hydroxy-1-indanone, 2-hydroxyacetophenone, and 8-hydroxy-1-tetralone, respectively[3]).

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TABLE II

ACID DISSOCIATION CONSTANTS[a]

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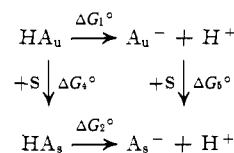| Substituted 1-indanone	pK
7-Hydroxy	8.43
6-Nitro-7-hydroxy	5.31
4-Nitro-7-hydroxy	5.27
4,6-Dinitro-7-hydroxy	1.94
5-Hydroxy	7.53

[a] Acid dissociation constants are given as pK values where $K = [H^+][L^-]/[HL]$ and all species are in concentrations, moles/l. Values are for 25.0° and μ = 0.100, maintained with sodium perchlorate.
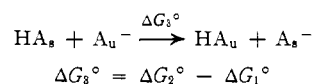
Discussion

Although none of the measurements in the present work is a direct determination of the hydrogen bond energy, a probable order of bond strength can be determined by assessing the effects of other variables. The relative intramolecular H-bond strength in 2-hydroxybenzaldehyde and 2-hydroxyacetophenone is well established[5,6] and is confirmed by the ultraviolet absorption shifts and the n.m.r. measurements. The measurements also show that the H-bond strength in 2-hydroxybenzaldehyde is stronger than in 7-hydroxy-1-indanone. The internuclear distances between the oxygen atoms, 2.48 Å. in the benzaldehyde and 2.94

Å. in the indanone,[14] are in the ranges for strong and weak bonds, respectively.[15] The ultraviolet and n.m.r. measurements indicate opposite orders for the relative bond strengths in the tetralone and the acetophenone. Two factors, the primary effect (the substituent acting upon the proton screening through the aromatic ring) and the intramolecular bond determine the position of the hydroxylic proton resonance.[2,5] The primary effect is assumed to increase in the o-carbonyl phenols in the order of decreasing pK values for the isomeric p-carbonyl phenols.[2] If the slightly larger n.m.r. shift in the tetralone were the result of the expected larger primary effect, the n.m.r. and ultraviolet shifts would indicate the same intramolecular bonding order for the tetralone and the acetophenone. The combined evidence from structure and the ultraviolet and n.m.r. shifts indicates that the intramolecular bond strength increases in the order 7-hydroxy-1-indanone, 2-hydroxybenzaldehyde, 8-hydroxy-1-tetralone, and 2-hydroxyacetophenone. The order of the last two is not certain, there being probably only a small difference in the bond strengths. Farmer, et al.,[4] noted that the frequencies of infrared absorption by the carbonyl group are about the same in 2-hydroxyacetophenone and 5,8-dihydroxy-1-tetralone.

Much of the ambiguity in the assignment of substituent effects to changes in the internal bonding of acid and anion has been removed by the work of Hepler[16,17] and O'Hara.[16] The substituent effect on the free energy of dissociation of phenol in aqueous solution can be expressed in terms of the following cycle

$$\begin{array}{ccc} HA_u & \xrightarrow{\Delta G_1°} & A_u^- + H^+ \\ +S \downarrow \Delta G_4° & & +S \downarrow \Delta G_5° \\ HA_s & \xrightarrow{\Delta G_2°} & A_s^- + H^+ \end{array}$$

where subscripts u and s refer to parent and derivative, +S symbolizes the addition of substituent group, and the ΔG are the free energy changes. The experimental, or total, enthalpy changes for reactions 1 and 2 include *internal* changes in bonding of acid and anion and *external* changes in reactions with the solvent. Subtracting reaction 1 from reaction 2 gives the symmetrical reaction 3 of Hepler and O'Hara[16]

$$HA_s + A_u^- \xrightarrow{\Delta G_3°} HA_u + A_s^-$$

$$\Delta G_3° = \Delta G_2° - \Delta G_1°$$

The free energy change, $\Delta G_3°$, turns out to be nearly equal to ΔH_{3int} provided the internal entropy changes from acid to anion are equal for reactions 1 and 2.[17] Since the sum of any one of the thermodynamic changes, internal or external, is zero around the cycle

$$\Delta G_3° = \Delta G_5° - \Delta G_4° = \Delta H_{5int} - \Delta H_{4int}$$

(12) J. D. Loudon and R. K. Razdan, J. Chem. Soc., 4299 (1954).

(13) R. Pasternack, L. H. Conover, A. Bavley, F. A. Hochstein, G. B. Hess, and K. J. Brunings, J. Am. Chem. Soc., **74**, 1928 (1952). In their Fig. 2, the wave lengths should be 250, 290, and 330 mμ.

(14) The internuclear distances were estimated from the following distances: C to C, 1.40 Å. in benzene and 1.46 Å. benzene to carbonyl; C to O, 1.36 Å. benzene to hydroxyl and 1.14 Å. in the carbonyl group. For 7-hydroxy-1-indanone, an interior angle of 108° (120° in 2-hydroxybenzaldehyde) between the carbonyl carbon to benzene bond and the benzene carbon to carbon bond was deduced by graphical closure of the five-membered ring with distances of 1.47, 1.53, and 1.50 Å. between the 1,2: 2,3; and 3 benzene carbons, respectively. In ref. 4, an estimate of 3 Å. is given for the internuclear distance between the oxygens.

(15) K. Nakamoto, M. Margoshes, and R. E. Rundle, J. Am. Chem. Soc., **77**, 6480 (1955).

(16) L. G. Hepler and W. F. O'Hara, J. Phys. Chem., **65**, 811 (1961).
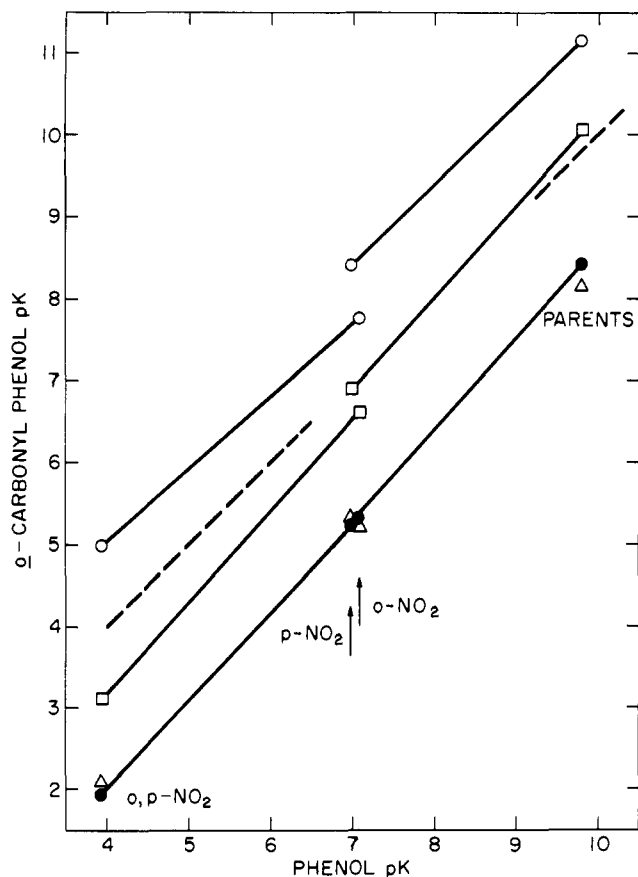
(17) L. G. Hepler, J. Am. Chem. Soc., **85**, 3089 (1963).

Fig. 1.—The pK values of the o-carbonyl phenols and nitro derivatives vs. the pK values of the phenol parents at ionic strength of 0.10: O, tetralones; □, acetophenones; ●, indanones; Δ, benzaldehydes. The dashed line, representing zero net substituent effect in the phenols as parents, has unit slope and intercepts the origin. The values are from ref. 3 and this work.

The free energy effect of a substituent, experimentally observed as a change in pK of the parent, may thus be equated to a change in the bonding of the substituent in the acid and anion. From the changes in pK for p-carbonyl substitution in phenol, the bonding energy of the substituent is larger in the anion as expected for charge transfer toward an electronegative substituent. The formation of an intramolecular H bond contributes a negative term to $\Delta H_{4\text{int}}$.

The pK values of the o-carbonyl phenols are plotted in Fig. 1 against the pK values of the parent phenols. The effect of the nitro substituent in an o-carbonyl phenol is the vertical decrease from the value for the parent acid. The solid lines connect an o-carbonyl phenol and its derivative containing a nitro group para to the hydroxyl group. The lines tend to be parallel (constant nitro substituent effect) except for those terminated by 5-nitro-8-hydroxy-1-tetralone and 5,7-dinitro-8-hydroxy-1-tetralone. The pK values of these acids appear to be anomalously large. A molecular model shows that one of the C–H orbitals of the adjacent methylene group may reduce the stabilities of the anions by interfering with the coplanarity of the 5-nitro group and the aromatic ring. The dashed line, representing zero effect for a carbonyl substituent in the phenols, has unit slope and intercepts the origin. The net effect of the carbonyl substituent in a phenol or nitrophenol is the vertical displacement from the

dashed line. The pK values appear above the line if the intramolecular H bonding to the carbonyl group is energetically dominant or below the line if the anion stabilization is dominant. Since the values for 2-hydroxyacetophenone and all the tetralone acids are above the dashed line, the intramolecular bond to the carbonyl group in these acids is stable in aqueous solution.

Before the substituent effects can be correlated, one must decide if there can be intramolecular H bonding to the nitro groups in aqueous solution. Although the o-substituent effect for the carbonyl group is less than the p-substituent effect, reflecting the formation of the intramolecular H bond, the o- and p-substituent effects on phenol for the nitro group are nearly the same.[3] This difference suggests that there can be little or no intramolecular bonding to the nitro group in aqueous solution and that the anion stabilization energies, $\Delta G_{5\text{int}}$, are about equal for o- and p-nitro substitution in phenol. These possibilities are supported by the following evidence.

The entropy change for the ionization of m-nitrophenol is 30% more negative than that for p-nitrophenol but the change for o-nitrophenol is only 3% more negative.[18] If there were a substantially larger anion stabilization (greater charge delocalization) for o-nitrophenol than for p-nitrophenol, one would expect to see a correspondingly less negative entropy change for the former.

There have been a few studies of the isotope effect in the dissociation of acids.[19,20] When the acid contains an intramolecular bond, the ratio of dissociation constants, K_H/K_D, is less than the ratio to be expected with no intramolecular bonding. The K_H/K_D ratio for o-nitrophenol is actually somewhat higher than expected for a "normal" acid,[19] so the dissociation constant ratio shows no evidence for an intramolecular bond.

When an intramolecular bond is formed, the ΔpK for carbonyl substitution, $pK_{\text{phenol}} - pK_{\text{carbonyl phenol}}$, is less negative (or more positive) for o-nitrophenol than p-nitrophenol (Fig. 1); i.e., the bond appears to be stronger in the isomer with the nitro group para to the hydroxyl group. Conversely, the existence of a positive difference between the ΔpK values for p- and o-nitrophenol is an empirical indication of the formation of an intramolecular bond. The difference is small for the nitro isomers of 2-hydroxybenzaldehyde and reverses sign for the indanones. One concludes that there is no significant bonding to the carbonyl group in the nitro derivatives of 7-hydroxy-1-indanone in aqueous solution. The absence of intramolecular bonding in the nitroindanones is consistent with the order of bond strength of the o-carbonyl phenols and the work of Brooks and Morman.[21] Extrapolation of the line through the points for the nitro derivatives in Fig. 1 suggests that the intramolecular bond in 7-hydroxy-1-indanone can contribute at most only a few tenths of a pK unit to the stability of the acid.

In addition to the enthalpy changes for the bonding of the substituent, the acidities of the o-carbonyl phenols depend on structural entropy and enthalpy changes. From dipole considerations, increases in the

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(19) A. C. McDougall and F. A. Long, J. Phys. Chem., 66, 429 (1962).
(20) J. E. Gordon and S. L. Johnson, ibid., 66, 534 (1962).
(21) C. J. W. Brooks and J. F. Morman, J. Chem. Soc., 3372 (1961).

energy release ($\Delta H_{5\text{int}}$) over those for the bicyclic anions may be expected for the formation of the anions of 2-hydroxybenzaldehyde and 2-hydroxyacetophenone because the carbonyl group is free to rotate away from the negative oxygen (flip effect). Evidence from n.m.r. proton couplings for the flipped conformation in anions of salicylaldehydes has recently been reported.[22] Furthermore, the internal entropy change for the dissociation of a substituted phenol with an intramolecular hydrogen bond will probably be more positive than that for the parent to an extent which depends on the frequencies of motion of the hydroxyl and substituted groups in the intramolecularly bonded acid and in the species, HA and $A_s{}^-$.[23,24] The free energy effect of the substituent will be larger than the difference in the enthalpy changes for the substituent bond-

(22) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963).

(23) W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Phys. Chem.*, **67**, 1933 (1963).

(24) Free internal rotation of the hydroxyl, formyl, and acetyl groups seems unlikely in aqueous solution, but the entropy of torsions in the non-intramolecularly H-bonded species, which may be low in frequency relative to those in 2-hydroxybenzaldehyde and 2-hydroxyacetophenone, could account for much of the free energy effect.

ing. In the present study the increase in entropy cannot be distinguished from a negative increment in $\Delta H_{5\text{int}}$; either, however, operates to increase the substituent effect.

The influence of the freedom of the carbonyl substituent may be seen in Fig. 1; the pK values of 2-hydroxyacetophenone, 2-hydroxybenzaldehyde, and their nitro derivatives are much lower relative to those of the bicyclic acids than might be expected from the order of intramolecular H-bond strength. The magnitude of the flip effect is about one pK unit for 2-hydroxyacetophenone if one assumes the same H-bond strength as for 8-hydroxy-1-tetralone. The repulsive energy in the anion of 7-hydroxy-1-indanone must be somewhat less than that in the anion of 8-hydroxy-1-tetralone because of the greater distance between the oxygen atoms; but, if the energy could be released and the small contribution from the intramolecular H-bond removed, the pK of the acid would be smaller and comparable to that of the *para* isomer, 5-hydroxy-1-indanone. The data for the indanone acids thus indicate, as for the nitrophenols, that the stabilization by charge transfer is about the same for *o*- and *p*-substitution.

New Complexes of Guanidinium Ion with Tetraphosphate Ion

By James I. Watters and Saburo Matsumoto

Received March 10, 1964

New complexes of guanidinium ion with tetraphosphate ion have been identified and their complexity constants have been evaluated on the basis of the pH lowering due to complex formation during the titration of tetraphosphate ion with hydrogen ion. The stability of these complexes which is similar to that of alkali metal ions with polyphosphates is probably due to at least three hydrogen bonds between amine nitrogen and phosphate oxygen atoms. The complexes and their over-all complexity constants at 25° with the ionic strength adjusted to unity with tetramethyammonium chloride are $C(NH_2)_3P_4O_{13}{}^{5-}$, $\beta_{GPq} = 10^{1.84}$; $[C(NH_2)_3]_2P_4O_{13}{}^{4-}$, $\beta_{G_2Pq} = 10^{2.76}$; $C(NH_2)_3HP_4O_{13}{}^{4-}$, $(GHPq) = 10^{1.16}$. A new method based on expressions for the mean number of bound hydrogen ions was used in evaluating these constants.

Introduction

Guanidine, the analog of urea in the ammonia system, is a compound of considerable biological and physiological significance. Since its protonated ion is one of the few cations forming a crystalline precipitate with the tetraphosphate ion, reactions between these two ions in solution are of practical importance. Since both amines and polyphosphates play important roles in the life process, the interaction of the type detected in the present study may have physiological effects.

The guanidinium ion is unique in that it contains one carbon bonded to three equivalent NH_2 groups. Resonance considerations indicate that a positive charge must be shared equally by the three equivalent NH_2 groups in a planar structure and that the proton should be strongly bound. This structure has been confirmed by X-ray,[1] Raman,[2] infrared,[3] and n.m.r. studies.[4] The ion has been compared to the alkali metal ions since its salts with anions of strong acids are essentially neutral and the solution of guanidine in

(1) W. Theilacker, *Z. Krist.*, **76**, 303 (1931); **90A**, 51, 256 (1934).

(2) J. Gupta, *J. Indian Chem. Soc.*, **13**, 575 (1936).

(3) C. L. Angell, N. Sheppard, A. Yamazuchi, T. Shimanouchi, T. Miyazawa, and S. Mizushima, *Trans. Faraday Soc.*, **53**, 589 (1957).

(4) A. Kotera, T. Morita, S. Aoyagi, Y. Kakiuchi, S. Nagakura, and K. Kume, *Nippon Kagaku Zasshi*, **82**, 302 (1961); *Chem. Abstr.*, **55**, 15,128e (1961).

water is a strong base. These properties are consistent with the exceedingly small acidic dissociation constant, $10^{-13.65}$ of quanidinium ion, reported by Hall and Sprinkle.[5]

The present study originated with the observation[6] that the pH was appreciably lowered during acidimetric titrations of tetraphosphate in the presence of the guanidinium ion introduced as the cation during the purification of the tetraphosphate by recrystallization.[7]

Applications of this effect in the evaluation of the complexity constants of polyphosphates have been made in this[8] and other laboratories.[9,10]

Theoretical

The association of the tetraphosphate ion with the first and second proton occurred with a barely perceptible break which vanished in the presence of

(5) N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

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(7) O. T. Quimby and F. P. Krause, *Inorg. Syn.*, **5**, 97 (1957); *J. Phys. Chem.*, **58**, 615 (1954).

(8) J. I. Watters, S. M. Lambert, and E. D. Loughran, *J. Am. Chem. Soc.*, **79**, 3651 (1957).

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