

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 85, NUMBER 12

JUNE 20, 1963

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Coördination in Solutions. I. Acid Strengths of Phenol Derivatives in Water¹

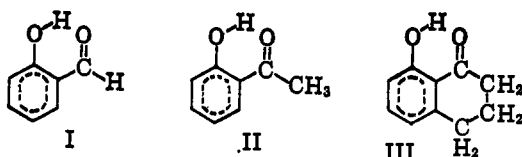
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RECEIVED DECEMBER 31, 1962

Acid dissociation constants were determined at 25° and ionic strengths 0.1 and 0.001 for 2-hydroxybenzaldehyde, 2-hydroxyacetophenone, 8-hydroxy-1-tetralone and three nitro derivatives of each with the nitro group *ortho* or *para* to the hydroxyl group or in both positions. Measurements were also made on 4-hydroxybenzaldehyde, 4-hydroxyacetophenone, 6-hydroxy-1-tetralone, phenol and the three nitrophenol derivatives. From the values determined at 0.001 ionic strength with a glass electrode and saturated KCl, calomel cell, thermodynamic pK values were calculated which agree with literature values. The substituent effects are discussed in terms of the relative stabilization of the parent acid and anion species by the substituent. The decrease in acid strength from the benzaldehyde to the acetophenone is consistent with the change in intramolecular hydrogen bonding observed in infrared spectra.

Introduction

As part of a survey of properties of chelating ligands, a consistent set of acid dissociation constants was measured for 2-hydroxybenzaldehyde (I), 2-hydroxyacetophenone (II), 8-hydroxy-1-tetralone (III) and the three nitro derivatives of each of these compounds



with the nitro group *ortho* or *para* to the hydroxyl group or in both positions. In the anions of I and II the carbonyl oxygen is free to rotate away from the hydroxyl oxygen to positions unfavorable for chelation. It appeared of interest to investigate the properties of III, which is similar to I and II except that the coördinating oxygens are restricted to the *cis* position required for chelation. In addition to the structural variation in the I, II, III series, the substituent effects of nitro groups were examined. In these compounds the hydrogen may be intramolecularly hydrogen bonded to the carbonyl oxygen, or, in the *o*-nitro derivatives, to one of the nitro oxygens. If the free energies for bonding to the two sites are not greatly different, measurable concentrations of each species will be present. To obtain information on the strengths of these bonds, measurements were made on phenol, its nitro derivatives and compounds similar to I, II and III with the hydroxyl group *para* to the carbonyl. Acid dissociation constants will be presented in this paper as measures of the relative strengths of proton chelation. The chelation of metal ions and comparisons with the proton bonding will be presented later.

Acid dissociation constants for water-dioxane solutions of I, some of its nitro derivatives and II have been reported.² Robinson and Kiang³ have deter-

mined a thermodynamic value for I in water. Equilibria in our work were measured at 25° in aqueous solutions of ionic strength of 0.100 and *ca.* 10⁻³. The quantities K' are in units of a'_H and are defined by eq. 1

$$K' = a'_H[L^-]/[HL] \quad (1)$$

where $[L^-]$ and $[HL]$ are the molar concentrations of the anion and acid, respectively, and a'_H is defined by eq. 2

$$a'_H = \text{antilog}(-pH) \quad (2)$$

where the pH is measured with a glass electrode. The quantity defined by eq. 1 has been called an apparent constant by Sager, *et al.*⁴ From calibration of the pH response of the cell to hydrogen ion concentration, the quantities K' are converted to concentration constants at 0.100 ionic strength. Dissociation constants at infinite dilution are obtained from the values at 10⁻³ ionic strength.

Experimental

Materials.—The organic acids, except for a few available commercially, were prepared by Kaye.⁵ Prior to use in our laboratory the acids were recrystallized, solvent extracted or redistilled. The criteria for purity were a straight line plot for the determination of K' (see final section) and constancy for the value of K' upon further purification. The inorganic acids and bases were standardized with potassium acid phthalate. Sodium and potassium perchlorates were prepared by recrystallization of commercial salts or by neutralization of the carbonate with perchloric acid followed by boiling to remove the carbon dioxide. Standardization was gravimetric on aliquots evaporated to dryness.

pH Measurement.—A Beckman model G pH meter was used in conjunction with a shielded Beckman general purpose glass electrode and a Beckman saturated KCl, calomel electrode. The glass electrode was suspended in an open test cup of 15-ml. capacity which was on the top of one arm of a Pyrex U-tube.

House, London, 1957; (b) J. G. Jones, J. B. Poole, J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

(3) R. A. Robinson and A. K. Kiang, *Trans. Faraday Soc.*, **52**, 327 (1956).

(4) E. E. Sager, M. R. Schooley, A. S. Carr and S. F. Acree, *J. Research Natl. Bur. Standards*, **55**, 521 (1945).

(5) The syntheses were undertaken by Prof. Irving A. Kaye of Brooklyn College with support from the Argonne National Laboratory (research and development subcontract No. 31-109-38-889). Information on syntheses will appear in separate publications by Prof. Kaye.

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

(2) (a) J. Bjerrum, G. Schwarzenbach and L. Sillén, "Stability Constants. Part I. Organic Ligands," The Chemical Society, Burlington

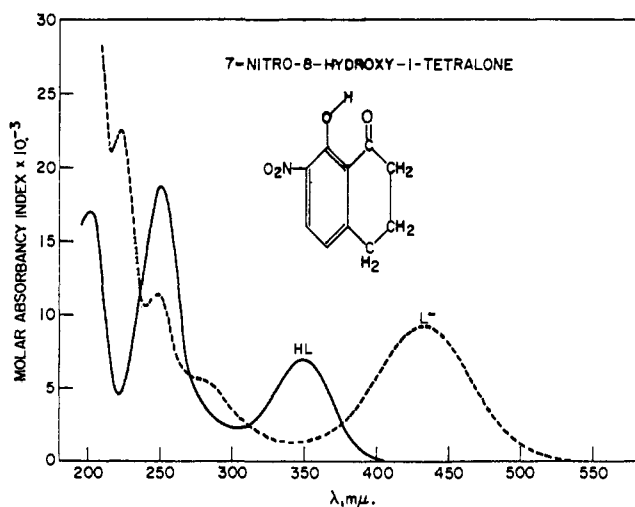


Fig. 1.—Spectra of the acid (—) and anion (---) of 7-nitro-8-hydroxy-1-tetralone.

The bottom of the cup was connected to the U-tube through a closed, ground glass stopcock which was sealed at both ends with Apiezon wax. The U-tube was filled with saturated KCl solution which was forced around the middle portion of the closed stopcock in a thin film. By immersing the calomel electrode into the KCl solution in the other arm of the U-tube, the normal position of the liquid junction at the wick of the calomel electrode was transferred to the saddle-shaped loop on the top of the plug formed by the opening at the bottom of the cup. The height of the KCl solution in the one arm of the U-tube was equal to or greater than that of the test solution to keep test solution out of the film about the plug. An essential requirement for this type of cell is that the ionic strength of the test solution is not changed significantly by leakage of KCl from the bridge. The stopcock was leak tested with a Ag-AgCl electrode (*vs.* the calomel electrode), stirrer and 10^{-4} M hydrochloric acid solution in the cup. With a well ground stopcock the leakage (or diffusion) of KCl during the time required for a pH measurement was negligible in contrast to the large amount which flows in when this type of reference electrode is inserted directly into the test solution. The U-tube assembly was immersed almost completely in a water-bath regulated at $25 \pm 0.03^\circ$.

Calibration of the pH Scale.⁶—The accuracy of the slide wire dial and temperature compensator of the pH meter was tested by applying known voltages from a Leeds and Northrup type K-2 potentiometer to the meter with a 90 megohm shielded resistor at the high impedance input. The errors in the slide-wire and compensator were within the uncertainty (0.01) of reading the dial.

The pH apparatus was standardized with National Bureau of Standards certified buffer samples of potassium tetroxalate, potassium hydrogen phthalate, equimolar potassium dihydrogen phosphate and disodium hydrogen phosphate, and sodium tetraborate. These were dissolved in distilled water which had been boiled in quartz to remove the carbon dioxide. A saturated solution of calcium hydroxide was prepared according to the procedure used at the National Bureau of Standards⁷ and was found by titration to have the correct normality. With the temperature compensator set at 25° all of these buffer solutions gave the recommended pH values⁸ within the limit of reading the dial. To relate the pH scale to hydrogen ion concentrations, measurements were made of solutions containing 10^{-4} to 10^{-1} M perchloric acid and sodium perchlorate at ionic strength 0.10. The difference between the measured pH and $-\log [H^+]$ was a constant (0.05 ± 0.01) for pH values 2 to 4. It is assumed that the difference would remain constant for higher pH values (up to about 12). At pH values less than 2, the difference was no longer constant but increased to 0.06, 0.07, 0.08 and 0.09 as the

(6) At various times during the course of this work Beckman buffer solutions were checked and found to give a pH scale different from that of the NBS. On the NBS scale the Beckman buffer with a nominal value of 4.00 was 4.07, the 7.00 was 7.00 and the 10.00 was 9.93. These results are averages for many different samples supplied by several chemical supply houses. Setting the temperature compensator to 18° forces the Beckman buffers to their nominal values and determines an operational pH scale which can be related to the NBS scale by the above measurements or the Nerst equation. Measurements have been made on the weak acids using both scales and the K values are in agreement if the Beckman scale is converted to the NBS scale.

(7) R. G. Bates, V. E. Bower and E. R. Smith, *J. Research Natl. Bur. Standards*, **66**, 305 (1956).

(8) R. G. Bates, *ibid.*, **66A**, 179 (1962).

pH was lowered to 1.8, 1.4, 1.2 and 1.1, respectively. A similar calibration of potassium perchlorate solutions gave a constant difference of 0.07 for pH values greater than 2.

Contrary to much of the experience noted in the literature, the glass electrode cell was remarkably stable and reproducible. The good stability probably resulted from a combination of the reproducible nature of the liquid junction and the practice of always keeping the bridge and electrodes at the constant temperature of the bath.

Measurements.—The anion and acid forms of these compounds have strong characteristic absorption spectra at wave lengths less than 5000 \AA . (see Fig. 1). The longest wave length bands are sufficiently separated for the spectrophotometric determination of the concentrations of the acid and base forms. Spectra were recorded with an Applied Physics Corp. (Cary) model 14 PM spectrophotometer equipped with a thermostated cell compartment. Nitrogen was passed through the optical compartments. The nitrogen for the cell compartment was passed through one-half of a double copper coil surrounded by a block of polystyrene foam mounted directly below the compartment. Water from the bath at 25° was pumped through the other half of the coil. The temperature of the nitrogen in the sample compartment was maintained at $25 \pm 0.05^\circ$ by pumping water through the walls of the cell compartment from an auxiliary bath. The spectra of the samples were measured in cylindrical, stoppered, silica cells usually of 2-cm. path length. The conventional V-shaped fingers for supporting the cells were replaced with copper troughs which had a radius matching that of the cells.

For measurement of K' at an ionic strength of 0.1, 10-ml. samples of HL were prepared containing various amounts of perchloric acid, sodium hydroxide and sodium perchlorate depending on the value of K' . For those acids having pK' values equal to or greater than 10, potassium rather than sodium perchlorate or hydroxide was used to eliminate sodium error in the glass electrode. The organic acids were added from ethanol stock solutions,⁹ except for I and its nitro derivatives which form acetals with ethanol; these were added from basic aqueous stocks. The volume of ethanol was normally 1% or less of the aqueous volume and had no measurable effect on the K' value by comparisons to runs which contained no ethanol. No ketal formation in ethanol stock solutions of II, III and their nitro derivatives was observed. The concentrations of the organic acids in the runs were 3×10^{-6} to 2×10^{-4} M. The spectrum of the solution was recorded at pH values sufficiently low and high to give the spectra of the acid and anion and at six to eight intermediate points. This was normally done on the same solution if the necessary change could be made in pH without changing the ionic strength and volume by more than 1%; otherwise two or more solutions were used. The pH of the solution was measured before and after recording the spectrum. The pH was changed by the addition of perchloric acid or sodium hydroxide. For pK' values in the range 6–9 the usual drift of the pH caused by atmospheric carbon dioxide was minimized by the addition of phosphate or borate at concentrations of *ca.* 10^{-3} M. The volatile acids (I, II, III, phenol and *o*-nitrophenol) were run somewhat differently in that separate portions of a larger stock were used for each pH. The optical cell was filled by pouring, the anion to acid ratio adjusted approximately to a desired value (monitored spectrophotometrically) by addition of acid or base directly to the cell, and the spectrum recorded. Small portions of the sample were used to rinse the pH cup and discarded. The pH was measured on each portion until successive readings agreed. A new anion to acid ratio was obtained on separate portions for at least six intermediate pH values plus those of the acid and anion. The measurements at low ionic strength were made in a way similar to that used for the volatile acids as an additional precaution against any increase in the ionic strength caused by KCl flowing in from the bridge. The criteria for accepting any set of data as reliable were that the standard buffer samples gave the same pH values before and after the run and that an invariant isosbestic point was obtained. Measurements were made at two different concentrations of the weak acid to check on possible dimerization of the weak acid. No dependence of the value of K' upon the concentration of the weak acid was found which indicates that dimerization is negligible.

Results and Discussion

At constant total HL concentration, cell length, and wave length equation (1) can be transformed to equations (3) and (4)¹⁰

$$A = A_{[L^-]} - a'_H(A - A_{[HL]})/K' \quad (3)$$

$$A = A_{[HL]} + K'(A_{[L^-]} - A)/a'_H \quad (4)$$

(9) Stock solutions of ethanol were used because of the limited water solubility of the acids. Basic aqueous stocks could have been used but decomposition of L^- becomes appreciable after a few days.

where A refers to the absorbance ($\log I^0/I$) of the solution and $A_{[X]}$ refers to the absorbance the solution would have if all of the HL were present in the form of species X. If K' is a constant,¹¹ a plot of A vs. $a'_H(A - A_{[HL]})$ would give a straight line (eq. 3) with the slope equal to the negative reciprocal of K' and the intercept equal to the absorbance of the solution if all the HL were present as the anion. Similarly, a plot of A vs. $(A_{[L^-]} - A)/a'_H$ would be linear (eq. 4) with the slope equal to K' and with the intercept equal to the absorbance of the solution if all the HL were present in the acid form. Calculations were normally carried out for three different wave lengths which were chosen to give large differences in absorbance between the acid and anion forms. Figure 2 shows typical results. Linearity was obtained consistently from the data for all the acids. The intercepts extrapolated from the lines agreed with the measured absorbances of the pure acid and anion. Agreement of K' values calculated at the various wave lengths, from both eq. 3 and 4, was good for any one run while the agreement of different runs was within the precision of calibrating and reading the pH meter. The average deviation in the values of K' was 0.01 log unit, with the maximum error believed to be about 0.02 unit. The results are given as pK_c values in Table I. The pK' values were converted to pK_c values by subtracting 0.05 for sodium perchlorate and 0.07 for potassium perchlorate solutions, the constant differences found between pH and $-\log [H^+]$ at $pH \geq 2$. The thermodynamic equilibrium constants were calculated from the pK' values at an ionic strength of *ca.* 10^{-3} by making a correction for the activity coefficient of the anion only. The activity coefficient was calculated using the Debye-Hückel limiting law, since this gave values within the desired accuracy of 0.005 log unit. The use of more extended forms, such as that proposed by Davies,¹² was unnecessary at these dilutions. The average difference between fifteen values (dinitro derivatives of II and III omitted) of pK_c at the ionic strength of 0.10 and our thermodynamic values is 0.18 with a mean deviation of 0.01. The equation of Davies gives 0.21 for $(-\log \gamma_{\pm}^2)$ at 0.10 ionic strength. Some lack of agreement may be expected since there is no term in the Davies equation for the activity coefficient of the undissociated acid. From the data of von Halban, Kortüm and Seiler¹³ $\log \gamma$ for 2,4-dinitrophenol is about -0.025 in sodium perchlorate solution. Assuming a similar value for $\log \gamma$ for all the acids in the present study, one may apply the Davies equation for the ionic activity coefficients plus the correction in $\log \gamma$ to the results at 0.10 ionic strength to secure thermodynamic values which agree well with those from the very dilute solutions. A value of 3.906 for the pK_c of 2,4-dinitrophenol in potassium perchlorate solution at 0.10 ionic

(10) Equations 3 and 4 have advantages over the more usual form given in eq. 5 for calculating K' from the experimental data

$$pK' = pH + \log (A_{[L^-]} - A)/(A - A_{[HL]}) \quad (5)$$

in that one can extrapolate the data for a single test solution to an absorbance for either the pure acid or anion when these have not been measured or are not obtainable experimentally under limitations imposed by the ionic strength on the concentrations of the hydrogen or hydroxide ions. As an example of the use of eq. 5 for a moderately strong acid, R. G. Bates and G. Schwarzenbach, *Experientia*, **10**, 482 (1954), used trial fitting of molar absorbance indices for the undissociated acid (picric) to achieve linearity in pK' .

(11) K' will be a constant if the product of a'_H/a_H and the ratio of the activity coefficients of HL and L⁻ is a constant. Since for most runs the change in medium is very small, this condition is expected to be fulfilled.

(12) C. W. Davies, "Ion Association," Butterworth, Inc., Washington, D. C., 1962, Chapter 3.

(13) H. von Halban, G. Kortüm and M. Seiler, *Z. physik. Chem.*, **A173**, 449 (1935). A plot of these data is reproduced in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3d Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 679.

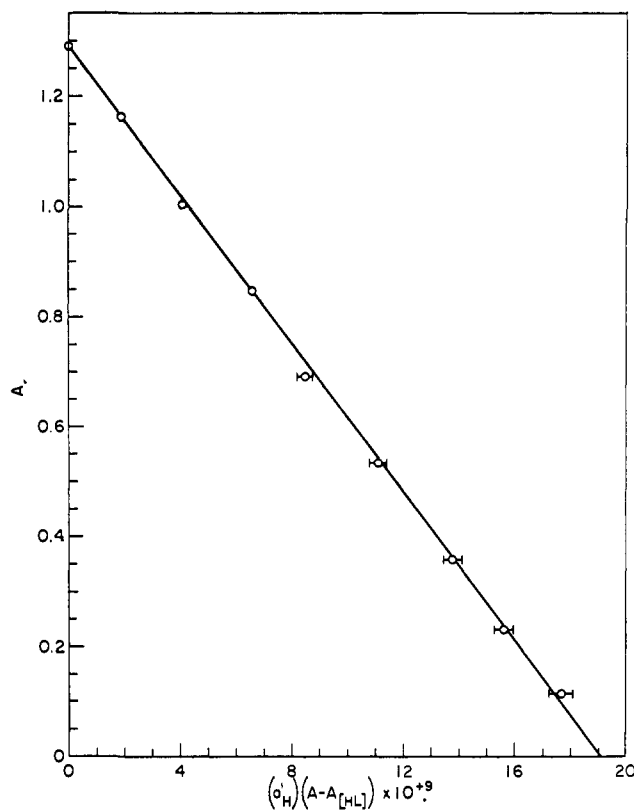


Fig. 2.—A typical plot of A vs. $(a'_H)(A - A_{[HL]})$. The data are for the evaluation of pK' for 7-nitro-8-hydroxy-1-tetralone at 4350 Å. and an ionic strength of 0.10. The value of K' as determined from the plot is equal to $19.05 \times 10^{-9}/1.290$ or 1.476×10^{-8} ; pK' 7.83. The line extrapolates to the experimentally measured anion density of 1.290. The horizontal bars are due to the experimental uncertainty in pH which has the greatest effect in the low pH region since (a) these are measured at pH values near 7 where CO_2 causes a drift, and (b) a given uncertainty in pH causes a greater absolute uncertainty in a'_H (ΔA) at low pH values than at higher pH values.

strength may be interpolated from the data of von Halban and Kortüm¹⁴ in fair agreement with our value for sodium perchlorate solution. The differences between the zero and 0.10 ionic strength pK_c values obtained by von Halban and Kortüm and by us agree very well, being 0.18 and 0.17, respectively.

On the reasonable assumption that the activity coefficient of HL is not significantly different from unity at 10^{-3} ionic strength, our values for the thermodynamic constants should differ from the true values by the proportionality factor between a'_H and the hydrogen ion activity. The good agreement of our values with constants given in the literature (Table I) indicates that at 10^{-3} ionic strength the proportionality factor is unity within an uncertainty of a few per cent. These results are contrary to the generally held opinion that potentials from cells containing saturated KCl liquid junctions may not be extrapolated to infinite dilution because of variations in the junction potential.¹⁵ In addition to the conclusion that a good approximation to the activity of hydrogen ion is obtained from the pH in very dilute solutions, our pH measurements on the standard tetroxalate buffer and calcium hydroxide solutions gave the recommended pH_s values and are not lower by 0.03 log unit as reported by Bates.⁸ An

(14) H. von Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 331 (1934).

(15) Reviews of the liquid junction problems are given by R. G. Bates, "Electrometric pH Determinations," J. Wiley and Sons, Inc., New York, N. Y., 1954, and G. Mattock, " pH Measurement and Titration," Heywood and Co. Ltd., London, 1961.

TABLE I

ACID DISSOCIATION CONSTANTS ^a AT 25°					
	Ionic strength ^b	Parent	<i>o</i> -Nitro ^c	<i>p</i> -Nitro ^c	<i>o,p</i> -Dinitro ^c
8-Hydroxy-1-tetralone	0.100	11.14 ^d	7.77	8.41	4.98
	0 ^e	11.31	7.95	8.59	5.12
2-Hydroxyacetophenone	0.100	10.07 ^f	6.59	6.88	3.11
	0 ^e	10.26	6.78	7.05	3.26
2-Hydroxybenzaldehyde	0.100	8.14	5.21	5.32	2.09
	0 ^e	8.34	5.41	5.51	2.27
	0	8.37 ^g			
Phenol	0.100	9.78 ^h	7.06	6.98	3.93
	0 ^e	9.98	7.25	7.16	4.10
	0	9.97-10.02 ⁱ	7.21-7.23 ^j	7.15 ^k	4.09-4.11 ^l
6-Hydroxy-1-tetralone	0.100	7.74			
4-Hydroxyacetophenone	0.100	7.87			
4-Hydroxybenzaldehyde	0.100	7.45			
	0 ^e	7.62			
	0	7.62 ^o			

^a As $pK_c = -\log [H^+][L^-]/[HL]$ where all species are in concentrations, moles liter⁻¹. ^b NaClO₄ except as noted in footnotes *d*, *f* and *h*. ^c Position of nitro group in respect to the hydroxyl group. ^d KClO₄, three runs which agreed. ^e Calculated from measurements at 10⁻³ ionic strength (see text). ^f KClO₄, six runs which agreed to 0.01; one run in NaClO₄ gave 10.06. ^g Ref. 3. ^h NaClO₄, three runs which agreed to 0.01; four runs which gave 9.78 to within 0.02 were made with KClO₄. ⁱ 9.998, A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956); 10.02, D. J. Y. Chen and K. J. Laidler, *ibid.*, **58**, 480 (1962), and E. F. G. Herington and W. Kynaston, *ibid.*, **53**, 138 (1957); 9.97, E. H. Binns, *ibid.*, **55**, 1900 (1959); 9.98 as the best average of lit. values, L. P. Fernandez and L. G. Hepler, *J. Am. Chem. Soc.*, **81**, 1783 (1959). ^j 7.234, C. M. Judson and M. Kilpatrick, *ibid.*, **71**, 3110 (1949); 7.23 ± 0.01, J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton, *J. Chem. Soc.*, 2995 (1956); 7.21, A. I. Biggs, footnote *e*. ^k 7.15, R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **37**, 1069 (1954); 7.14, Judson and Kilpatrick, footnote *j*; 7.15, R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc.*, **51**, 901 (1955). ^l 4.08, W. D. Bale and C. B. Monk, *ibid.*, **53**, 450 (1957); 4.11, R. G. Bates and G. Schwarzenbach, footnote *k*; 4.09, ref. 14.

experimental value lower than pH_s at the ends of the pH scale has been attributed to a change in junction potential as the concentration of either the highly mobile hydrogen or hydroxide ion becomes appreciable. Our pH values conform to the pH_s scale over wide ranges of pH and concentration; nevertheless, one should not conclude that junction potential is negligible or invariant because the scale is based on a non-thermodynamic description of the behavior of a single ion activity coefficient as a function of ionic strength.⁸ Bacarella, *et al.*,¹⁶ have recommended an equation relating e.m.f. and pH containing a term which is supposed to correct for the variation of junction potential with concentration of the test solution. If the pH_s calibration were adjusted by including this term, our thermodynamic pK values would be about 0.03 larger and in poorer agreement with the literature values. The conformance to the scale may be the result of our choice of method for forming the liquid junction. A similar type of junction was used by La Mer and Baker,¹⁷ but no dilution study was reported. The unique property of the junction, a very small cross section, and the validity of equating the a'_H value (at 10⁻³ ionic strength) from the liquid junction cell to the hydrogen ion activity merit further study with a potentiometer of higher precision.

The changes in acid strengths produced by substituent carbonyl and nitro groups are given in Table II.¹⁸ A comparison of *p*- and *m*-substitutions in phenol, which

TABLE II

SUBSTITUENT EFFECTS AS ΔpK VALUES ^a				
Substituent ^b	Phenol	I ^c	II ^c	III ^c
<i>m</i> -HCO	0.96 ^d			
<i>m</i> -CH ₃ CO	0.79 ^e			
<i>p</i> -HCO	2.36			
<i>p</i> -CH ₃ CO	1.94 ^f			
<i>p</i> -TCO	2.07 ^f			
<i>o</i> -HCO	1.64			
<i>o</i> -CH ₃ CO	-0.28			
<i>o</i> -TCO	-1.33			
<i>m</i> -NO ₂	1.59 ^g			
<i>p</i> -NO ₂	Parent	2.82	2.83	3.21
	<i>o</i> -NO ₂ ^h	3.15	3.14	3.52
<i>o</i> -NO ₂	Parent	2.73	2.93	3.48
	<i>p</i> -NO ₂ ^h	3.06	3.24	3.79

^a Difference, pK (of parent) - pK (of parent plus substituent). The pK values are from the present work calculated for zero ionic strength, with the exceptions noted in footnotes *d*, *e*, *f* and *g*. ^b *m*, *p* and *o* refer to the position of the substituent relative to the hydroxyl; T implies the closed ring of the tetralone structure. ^c (I) 2-hydroxybenzaldehyde, (II) 2-hydroxyacetophenone, (III) 8-hydroxy-1-tetralone. ^d The pK of 3-hydroxybenzaldehyde (9.016) is from ref. 3; the pK of phenol at infinite dilution was assumed to be 9.98. ^e The pK for 3-hydroxyacetophenone is from F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952). These authors do not give experimental concentrations and derive thermodynamic values by a questionable method, but the results for many phenol derivatives agree well with other literature values. Their value for the pK of phenol (9.98) was used for ΔpK . ^f The thermodynamic pK values for 4-hydroxyacetophenone and 6-hydroxy-1-tetralone were approximated by adding 0.17 to the pK_c values at ionic strength 0.10. ^g A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961); the pK of phenol was assumed to be 9.98. ^h Position, relative to hydroxyl group of nitro group already present.

are included for completeness, shows the well known enhancement from mesomeric interaction of *p*-groups. The effects important to this study are the interactions of groups *ortho* to each other and the effects of other substituents on these interactions. Organic theory is notably inadequate in the quantitative sense for correlating substituent effects and particularly so for *o*-substitution,¹⁹ which in the present study involves the formation of intramolecular hydrogen bonds. The complexity of the problem is apparent from a consideration of Table II. Whereas *p*-substitution of formyl, acetyl or the closed ring of the tetralone structure into phenol increases the acidity by about 2 pK units, the corresponding substituents in the *o*-position produce again three molecules of similar structure but with acid strengths both greater and less than that of phenol. A complete theoretical treatment of the effects of substituents on the acid dissociation equilibrium will require consideration of both the acid and anion.²⁰ In the acid, variation in the strength of intramolecular hydrogen bonding must be a major factor in the *o*-carbonyl substitution. Brooks and Morman have increased the information on hydrogen bond strengths in I and II and their nitro derivatives by infrared studies of the carbonyl and nitro vibrations in organic solvents.²¹ The bond strength increases from I to II, the bond in I appearing to be converted to an intermolecular bond with a basic solvent molecule.^{21,22} The bond in I is probably not broken by association with water since I, II and III were all similar in being more volatile from our test

(16) A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(17) V. K. La Mer and L. E. Baker, *J. Am. Chem. Soc.*, **44**, 1961 (1922).

(18) The substituent effects, except where noted in Table II, are given as the difference between the thermodynamic pK values of the parent and the substituted parent from the present work. If the pK_c values for 0.10 ionic strength had been used, the effects would be different by only a few hundredths.

(19) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter XIII; (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 2; (c) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3541, 3546, 3548 (1962).

(20) H. C. Brown, D. H. McDaniel and O. Hafziger in "Determination of Organic Structures by Physical Methods," ed. by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955, p. 572.

(21) C. J. W. Brooks and J. F. Morman, *J. Chem. Soc.*, 3372 (1961).

(22) P. Chiorboli and P. Mirone, *Ann. Chim. (Rome)*, **48**, 363 (1958).

solutions than were the isomers with no intramolecular bond.

Brooks and Morman observed specific effects on the intramolecular hydrogen bond in nitro derivatives of I and II.²¹ The bond appears to be weakened in the 5-nitro derivatives and, in the 3-nitro derivatives, the nitro group competes with the carbonyl group for the intramolecular hydrogen bond. Given these two intramolecularly bonded species, with equilibrium between them possibly altered by other substituents, and the amphiprotic nature of water solvent, the equilibrium situation in water is obviously complex and unpredictable.

There are two general features of interest in the nitro substituent effects. The first is that the effects are practically identical for *p* (to hydroxyl) nitro substitution in phenol, I and III. The second feature is that *p*-substitution in the acetophenone (II) and *o*-substitution in any of the carbonyl molecules causes larger effects than in phenol. A larger substituent effect for molecules with intramolecular hydrogen bonding might be expected from a consideration of the relative stabilization of the parent acid and anion species by the addition of a nitro group to each. If (1) the stabilization of the anions of phenol and one of the *o*-carbonyl acids, say II, is about the same and (2) the stabilization of the acid form of phenol is greater than that of II, the net result would be a larger substituent effect for the dissociation of the nitro derivative of II. One may argue in favor of the plausibility of both conditions. For (1), in addition to the C-N σ -bond formation, which should be about the same for acid and anion, the anion stabilization of phenol and II is formally the same for both, depending largely on the attraction between the polarizable and negatively

charged oxygen and the polarizable nitro dipole. The carbonyl and nitro dipole-dipole interaction (repulsive) may be assumed to be negligible. For (2), stabilization of phenol by the addition of the nitro group will depend on the shift of electron density from the hydroxyl group to the nitro group. The intramolecular hydrogen bond in II implies a larger polarization energy which would oppose shift of electron density toward the nitro group. Condition 2 would appear to be more plausible than 1.

The larger substituent effects in II as compared to I may be accounted for by the argument just given, based on the stronger hydrogen bond in II. The argument clearly does not explain the practically identical results for *p*-nitro substitution in phenol, I and III. It will not be attempted here, but one would examine the validity of condition 1 above with consideration being given to the effects of the orientation of the carbonyl groups. The behavior of the tetralone structure should be useful since the orientation is known in both acid and anion. The substituent effects for the tetralone structure are generally intermediate to those for I and II with the notable exception of the decrease in acidity in the series I, II and III. From the preceding discussion, a parallel increase in the strength of the intramolecular hydrogen bond does not necessarily follow from the decrease in acidity in the series. Information on the strengths of the intramolecular bond in III and its derivatives relative to those of I and II will be of value in estimating the acid and anion contributions to the substituent effects.

Acknowledgment.—The collaboration with Prof. Irving A. Kaye has been invaluable⁵ and we are grateful to Drs. William H. Kirchhoff and Robert E. Vandervenn for assistance with calculations.

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A Survey of C-H Groups as Proton Donors in Hydrogen Bonding¹

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RECEIVED NOVEMBER 21, 1962

The ability of C-H groups to act as proton donors in hydrogen bonding was surveyed by infrared spectroscopic techniques, using the strong proton acceptors, pyridine-*d*₅ and dimethyl sulfoxide-*d*₆, in CCl₄ solution. Pentachlorocyclopropane, pentachloroethane, Br₂CHCN, bromoform, iodoform and many other compounds gave larger C-H spectral shifts than chloroform, an accepted and well studied proton donor. The order of haloform spectral shifts was CHBr₃ > CHI₃ > CHCl₃; fluoroform gave inconclusive results. In a C-H compound capable of acting as a proton donor, replacement of Cl by CCl₃ and CN, as well as by Br and I, resulted in an enhancement of the spectral shifts to a common base. X-CH₂-Y compounds, where X, Y = Cl, Br, I and CN, showed evidence of hydrogen bonding to strong proton acceptors. *cis*- and *trans*-1,2-dichloroethylene also behaved as proton donors; the *trans* isomer gave the larger C-H spectral shifts. Other C(sp²)-H compounds giving evidence of proton-donating ability in hydrogen bonding were CHX=CX₂ (X = F, Cl, Br) and poly-substituted benzene derivatives with at least three strongly electron-withdrawing substituents. Aldehydic C-H bands did not give spectral shifts with strong bases; methyl compounds, CH₃X, also gave no evidence of proton donor ability. Assignment of C-H bands in more complicated spectra was facilitated by observing changes produced by deuterated bases.

That chloroform and acetone form a complex has been known for a long time; as early as 1914, attempts were made to calculate an association constant.⁴ In 1937, Glasstone⁵ proposed that such complexes of haloforms resulted from X₃CH...B hydrogen bonding.

(1) Paper X of a series on hydrogen bonding; paper IX, *J. Am. Chem. Soc.*, **85**, 866 (1963). This work was taken from the Ph.D. Thesis of Adam Allerhand, Princeton University, 1962.

(2) Merck Foundation Fellow, 1960-1961; Esso Foundation Fellow, 1961-1962.

(3) Alfred P. Sloan Research Fellow.

(4) E. Beckman and O. Faust, *Z. physik. Chem.*, **89**, 235, 247 (1914).

(5) S. Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937). Glasstone's proposal found reluctant acceptance. The discussion that followed the presentation of his paper is instructive in the history of the development of the concept of hydrogen bonding.

Since then extensive work has been carried out on the subject of C-H groups as proton donors in hydrogen bonding.⁶⁻¹³ Conclusive infrared and nuclear magnetic

(6) The question of hydrogen bonding involving the C-H group has been reviewed by C. G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Ch. 6, pp. 197-201. An extensive list of references is given therein.

(7) E. D. Becker, *Spectrochim. Acta*, **15**, 743 (1959); W. E. Thompson and G. C. Pimentel, *Z. Elektrochem.*, **64**, 748 (1960); D. G. Rea, *J. Chem. Phys.*, **33**, 1875 (1960); A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.*, **38**, 652 (1960); C. F. Jumper, M. T. Emerson and B. B. Howard, *J. Chem. Phys.*, **35**, 1911 (1961); D. K. Anderson and A. L. Babb, *J. Phys. Chem.*, **65**, 1281 (1961); E. R. Kearns, *ibid.*, **65**, 314 (1961); G. S. Denisov, *Optics and Spectry*, **11**, 232 (1961); K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, **18**, 329 (1962); C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962); W. G. Schneider in D. Hadzi, Ed., "Hydrogen Bonding,"