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Effect of Heteroconjugation on Acid-Base Conductometric Titration Curves of 3,5-Dinitrobenzoic Acid in Acetonitrile¹

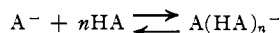
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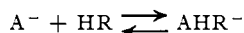
Heteroconjugation is defined as the conjugation of an anion A^- with a hydrogen bond donor HR : $A^- + nHR \rightleftharpoons A(HR)_n^-$. In a solvent which is a non-hydrogen bonder and has a dielectric constant of 40 or less, like acetonitrile, the degree of dissociation of a salt BH^+A^- is greatly increased by addition of HR . As a result of heteroconjugation the maximum in conductance between 50 and 100% neutralization in the conductometric titration with an amine of an incompletely dissociated acid HA , which has no intramolecular hydrogen bonds, can be eliminated in the presence of HR . Conductometric titration curves in acetonitrile of sulfuric acid with pyridine in the presence of various concentrations of resorcinol and of 3,5-dinitrobenzoic acid with triethylamine in the presence of resorcinol or *p*-bromophenol illustrate this effect of heteroconjugation. In order to calculate the conductometric titration curves it is necessary to know the stability constants of $A(HR)_n^-$ and the dissociation constants of the conjugate salts $BH^+A(HR)_n^-$. From solubility determinations at 25° in acetonitrile of potassium 3,5-dinitrobenzoate in the presence of resorcinol or of *p*-bromophenol it appeared that two conjugates are formed, AHR^- and $A(HR)_2^-$, with stability constants of 3.4×10^2 and 5.1×10^3 , respectively, HR being resorcinol, and of 3.6×10^2 and 3.9×10^3 , respectively, HR being *p*-bromophenol. The calculated conductances on the titration curves of 3,5-dinitrobenzoic acid with triethylamine in the presence of various concentrations of resorcinol were found to be in satisfactory agreement with the experimental data. Infrared spectra of solutions in acetonitrile of tetraethylammonium 3,5-dinitrobenzoate in the presence of varying concentrations of resorcinol or *p*-bromophenol substantiate the conclusion that heteroconjugation occurs by hydrogen bonding. In the presence of an excess of dinitrobenzoate over resorcinol it is concluded that a heteroconjugate $A_2(HR)_2^{2-}$ is formed. Structures for the various heteroconjugates are postulated.

Introduction

Homoconjugation is defined as the association of an anion A^- with its conjugate acid, HA , the equilibrium being characterized by the reaction



n being usually equal to 1 in acetonitrile.² Heteroconjugation is defined as the conjugation of an anion A^- with a hydrogen bond donor, HR , which is different from HA , *e.g.*

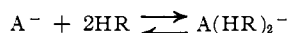


with a heteroconjugation constant

$$K_{AHR^-} = [AHR^-]/[A^-][HR] \quad (1)$$

$$f_{AHR^-} = f_{A^-}$$

and



with a heteroconjugation constant

$$K_{A(HR)_2^-} = [A(HR)_2^-]/[A^-][HR]^2 \quad (2)$$

$$f_{A(HR)_2^-} = f_{A^-}$$

In solvents lacking hydrogen bonding properties and with dielectric constants of the order of 40 or less, salts of the type BH^+A^- are incompletely dissociated



Conjugation reactions stabilize the anion A^- and increase the degree of dissociation of salts of the type

BH^+A^- . Homoconjugation accounts for the fact that in the conductometric titration of incompletely dissociated acids, which have no intramolecular hydrogen bonds, with aliphatic amines a maximum conductance is observed between 50 and 100% neutralization.³⁻⁵

Knowing the homoconjugation constant and dissociation constants of the normal and the conjugate salts, we have calculated the conductance during the titration of sulfuric acid (as a monobasic acid) and of 3,5-dinitrobenzoic acid with aliphatic amines.⁶ The calculated data are in good agreement with the experimental values.

The degree of dissociation of a salt BH^+A^- is increased by both homo- and heteroconjugation. Thus, when an acid HR , which is a much weaker acid than HA , is added to a solution of HA , the maximum in the titration curve can be made to disappear as a result of stabilization of A^- by heteroconjugation.

In the present paper are presented conductometric titration curves in acetonitrile of 3,5-dinitrobenzoic acid with triethylamine in the presence of various concentrations of the hydrogen bonders resorcinol or *p*-bromophenol. In order to calculate the titration curves it was necessary to determine the stability constants of the heteroconjugates $A(HR)_n^-$, A^- denoting the 3,5-dinitrobenzoate ion, and HR , resorcinol or *p*-bromophenol. From solubility measurements of potassium 3,5-dinitrobenzoate in solutions of varying concentrations of resorcinol or *p*-bromophenol it could be de-

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-63-0636 and Contract AF 49(638)-519.

(2) I. M. Kolthoff, S. Bruckenstein and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

(3) A. A. Maryott, *J. Research Natl. Bur. Standards*, **38**, 527 (1947).

(4) P. R. Bryant and A. W. Wardrup, *J. Chem. Soc.*, 895 (1957).

(5) G. Harlow and D. Bruss, *Anal. Chem.*, **30**, 1836 (1958).

(6) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **85**, 426 (1963).

rived that heteroconjugates AHR^- and $A(HR)_2^-$ are formed. The calculation of the stability constants of these conjugates from solubility data is described in the next section. Conductometric titration curves of 3,5-dinitrobenzoic acid in the presence of resorcinol were found to be almost identical with those obtained in the presence of the same concentrations of *p*-bromophenol. For this reason only conductometric titration curves in the presence of resorcinol are presented in this paper.

In order to calculate the titration curves it is also necessary to estimate the dissociation constants of the conjugate salts BH^+AHR^- and $BH^+A(HR)_2^-$, BH^+ denoting the triethylammonium ion.

Infrared spectra have been determined of solutions in acetonitrile of tetraethylammonium 3,5-dinitrobenzoate in the presence of varying concentrations of resorcinol or *p*-bromophenol. These studies provided further evidence that heteroconjugation occurs by hydrogen bonding and also gave further insight into the structure of these complexes.

Calculation of Stability Constants of $A(HR)_n^-$ from Solubility Measurements of Potassium 3,5-Dinitrobenzoate, K^+A^- , in the Presence of HR.—In these solutions, saturated with K^+A^- , the electroneutrality rule states

$$[K^+] = [A^-] + [AHR^-] + [A(HR)_2^-] \quad (3)$$

The solubility product of K^+A^- is

$$K_{sp} = [K^+][A^-]f^2 \quad (4)$$

$$f_{K^+} = f_{A^-} = f$$

K^+A^- is incompletely dissociated and $[K^+]$ is calculated from the total solubility, s ,⁷ using the relation

$$[K^+] = s - [K^+A^-] \quad (5)$$

In a previous paper, values for the dissociation constant and the solubility product of K^+A^- at 25° were reported to be 2.6×10^{-4} and 5.3×10^{-8} , respectively,^{6,7} from which a value of $0.49 \times 10^{-4} M$ for $[K^+A^-]$ in systems saturated with the salt is calculated. Because of heteroconjugation, the degree of dissociation of $K^+A(HR)_n^-$ is much greater than that of K^+A^- . In the concentration range used, $K^+A(HR)_n^-$ is considered to be completely dissociated.

Substituting eq. 1, 2, 4 and 5 into eq. 3 yields

$$f^2 \{s - [K^+A^-]\}^2 = K_{sp} \{1 + K_{AHR^-}[HR] + K_{A(HR)_2^-}[HR]^2\} \quad (6)$$

The equilibrium concentration of HR in saturated solutions of K^+A^- containing HR is

$$[HR] = a - \bar{n}[K^+] \quad (7)$$

where a denotes the analytical concentration of HR, and \bar{n} denotes the average number of HR molecules bound per A^- anion,⁸ *i.e.*

$$\bar{n} = \frac{[AHR^-] + 2[A(HR)_2^-]}{[A^-] + [AHR^-] + [A(HR)_2^-]} \quad (8)$$

Substituting eq. 1 and 2 into eq. 8 yields

$$\bar{n} = \frac{K_{AHR^-}[HR] + 2K_{A(HR)_2^-}[HR]^2}{1 + K_{AHR^-}[HR] + K_{A(HR)_2^-}[HR]^2} \quad (9)$$

An estimated value of \bar{n} is first taken and $[HR]$ calculated from eq. 7. Using these estimated values of $[HR]$ for solubility data at two different concentrations of HR, K_{AHR^-} and $K_{A(HR)_2^-}$ are calculated from a set of simultaneous equations (eq. 6). Better values of \bar{n} are then calculated from eq. 9 and the cycle repeated until the \bar{n} values no longer change appreciably. Values of \bar{n} , K_{AHR^-} and $K_{A(HR)_2^-}$ thus obtained are presented in Table II. All activity coefficients were calculated from the limiting Debye-Hückel expression.

(7) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962).

(8) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

Calculation of Conductometric Titration Curves of 3,5-Dinitrobenzoic Acid with Triethylamine in the Presence of Resorcinol (HR).—Making the justifiable assumption that $[A^-]$ is negligible, the electroneutrality rule in mixtures of a monobasic weak acid, HA, and its salts in the presence of a much weaker acid, HR (HR not reacting with the base B), from 0 to 100% neutralization yields

$$[BH^+] = [AHA^-] + [AHR^-] + [A(HR)_2^-] \quad (10)$$

Introducing eq. 1, 2 and the dissociation constant of the homoconjugate salt $K_{BH^+AHA^-}$ (eq. 11)

$$K_{BH^+AHA^-} = ([BH^+][AHA^-]/[BH^+AHA^-])f^2 \quad (11)$$

$$f_{BH^+} = f_{AHA^-} = f$$

and of the heteroconjugate salt $K_{BH^+A(HR)_2^-}$ (eq. 12)

$$K_{BH^+A(HR)_2^-} = ([BH^+][A(HR)_2^-]/[BH^+A(HR)_2^-])f^2 \quad (12)$$

$$f_{BH^+} = f_{A(HR)_2^-} = f$$

into eq. 10 gives

$$[BH^+] = \frac{1}{f} \sqrt{K_{BH^+AHA^-}[BH^+AHA^-] + qK_{BH^+A(HR)_2^-}[BH^+A(HR)_2^-]} \quad (13)$$

where $q = 1 + (K_{AHR^-}/K_{A(HR)_2^-}[HR])$

The sum of the concentration of all the salt species, c_s , is

$$c_s = [BH^+] + [BH^+A^-] + [BH^+AHA^-] + [BH^+AHR^-] + [BH^+A(HR)_2^-] \quad (14)$$

Introducing eq. 14 and 15

$$K_{BH^+AHR^-} = ([BH^+][AHR^-]/[BH^+AHR^-])f^2 \quad (15)$$

$$f_{BH^+} = f_{AHR^-} = f$$

into eq. 13 and upon simplification eq. 16 is obtained

$$[BH^+] = \frac{-K_{BH^+AHA^-} \pm \sqrt{K_{BH^+AHA^-}^2 + 4f^2\{K_{BH^+AHA^-}(c_s - [BH^+A^-]) + (qK_{BH^+A(HR)_2^-} - rK_{BH^+AHA^-})[BH^+A(HR)_2^-]\}}}{2f^2} \quad (16)$$

where

$$r = 1 + \frac{K_{BH^+A(HR)_2^-}K_{AHR^-}}{K_{BH^+AHR^-}K_{A(HR)_2^-}[HR]}$$

In order to calculate $[AHA^-]$, $[AHR^-]$ and $[BH^+AHR^-]$, $[HA]$ must be known. The concentration of the sum of the free and neutralized acid, c_a , is

$$c_a = [HA] + [BH^+A^-] + 2[BH^+AHA^-] + [BH^+AHR^-] + [BH^+A(HR)_2^-] + 2[AHA^-] + [AHR^-] + [A(HR)_2^-] \quad (17)$$

neglecting $[A^-]$.

Combining eq. 10, 14, 17 and 18, and simplifying, eq. 19 results

$$K_{AHA^-} = [AHA^-]/[HA][A^-] \quad (18)$$

$$f_{A^-} = f_{AHA^-}$$

$$[HA] = \frac{\{u[HR] + K_{AHA^-}v\} \pm \sqrt{\{u[HR] + K_{AHA^-}v\}^2 + 4K_{AHA^-}u[HR]([BH^+] - v)}}{2K_{AHA^-}} \quad (19)$$

where

$$u = K_{AHR^-} + K_{A(HR)_2^-}[HR]$$

$$v = 2c_a - c_a - [BH^+A^-] - r[BH^+A(HR)_2^-]$$

r being previously defined.

In the calculation of the titration curves, q , r and u are calculated, taking $[HR]$ equal to the analytical resorcinol concentration, as it is in large excess. A reasonable estimate of $[BH^+A(HR)_2^-]$ is made and $[BH^+A^-]$ calculated from the relation

$$[BH^+A^-] = \frac{[BH^+A(HR)_2^-]K_{BH^+A(HR)_2^-}}{K_{A(HR)_2^-}K_{BH^+A^-}[HR]^2}$$

obtained by combining eq. 2, 12 and 20

$$K_{\text{BH}^+\text{A}^-} = [\text{BH}^+][\text{A}^-]f^2/[\text{BH}^+\text{A}^-] \quad (20)$$

$$f_{\text{BH}^+} = f_{\text{A}^-} = f$$

Values of $[\text{BH}^+\text{A}(\text{HR})_2^-]$, $[\text{BH}^+\text{A}^-]$, q and r are introduced into eq. 16 to calculate $[\text{BH}^+]$. For the calculation of r , $K_{\text{BH}^+\text{AHR}^-}$ is taken equal to $K_{\text{BH}^+\text{A}(\text{HR})_2^-}$. Next, the values of u and v , calculated from the above relationships and $[\text{BH}^+]$ are introduced in eq. 19 to calculate $[\text{HA}]$. Once $[\text{HA}]$ is known, $[\text{AHA}^-]$, $[\text{AHR}^-]$ and $[\text{A}(\text{HR})_2^-]$ are calculated from the following relations, both easily derived

$$[\text{AHA}^-] = \frac{[\text{BH}^+][\text{HA}]K_{\text{AHA}^-}}{u[\text{HR}] + K_{\text{AHA}^-}[\text{HA}]}$$

$$[\text{AHR}^-] = \{[\text{BH}^+] - [\text{AHA}^-]\}K_{\text{AHR}^-}/u$$

Substituting the values of $[\text{BH}^+]$, $[\text{AHA}^-]$ and $[\text{AHR}^-]$ into eq. 10 yields a value of $[\text{A}(\text{HR})_2^-]$. The value of $[\text{BH}^+\text{AHA}^-]$ is then evaluated directly from the dissociation constant, $K_{\text{BH}^+\text{AHA}^-}$ (eq. 11); $[\text{BH}^+\text{AHR}^-]$ is evaluated, using the following relation which is easily derived

$$[\text{BH}^+\text{AHR}^-] = (r - 1)[\text{BH}^+\text{A}(\text{HR})_2^-]$$

When the correct value of $[\text{BH}^+\text{A}(\text{HR})_2^-]$ is taken in eq. 16, the summation of the concentration of the free acid and neutralized acid equals the analytical acid concentration (eq. 17) and the summation of all the salt species equals the analytical salt concentration (eq. 14).

In all cases, ionic mobilities were calculated from those at infinite dilution using the Onsager relation.⁹ Values of the homoconjugation constant (eq. 18), the mobility of the AHA^- ion and the dissociation constants of the simple salt BH^+A^- and the homoconjugation salt BH^+AHA^- have been determined previously.⁶

Values of the heteroconjugation constants K_{AHR^-} and $K_{\text{A}(\text{HR})_2^-}$ have been derived in the present paper from the solubility of potassium 3,5-dinitrobenzoate in the presence of resorcinol (HR). The value of the dissociation constant of the heteroconjugate salt $K_{\text{BH}^+\text{A}(\text{HR})_2^-}$ which yields the best agreement between calculated and experimental conductance values (corrected for viscosity effect) of triethylammonium 3,5-dinitrobenzoate in 0.5 M or more concentrated resorcinol solutions was used. In these solutions $\text{A}(\text{HR})_2^-$ is the predominant anionic species.

For the calculation of titration curves in more dilute resorcinol solutions in which appreciable amounts of AHR^- are present, $K_{\text{BH}^+\text{AHR}^-}$ was assumed equal to $K_{\text{BH}^+\text{A}(\text{HR})_2^-}$.

Experimental

Chemicals. Acetonitrile was purified and dispensed as previously described.² The purified solvent had a specific conductance of $1-2 \times 10^{-7}$ ohm⁻¹ cm.⁻¹ and a water content of 2×10^{-3} M . The ammonia content was 2×10^{-6} M as determined from spectrophotometric titration with picric acid.²

Triethylamine, *n*-butylamine, sulfuric acid, 3,5-dinitrobenzoic acid, tetraethylammonium 3,5-dinitrobenzoate and potassium 3,5-dinitrobenzoate were prepared and purified as described elsewhere.⁶

Pyridine was purified in the same way as the other bases.⁶

Resorcinol, an Eastman Kodak Co., White Label product, was used without further purification; dried at 80° *in vacuo* for 10 hours, m.p. 111°, literature¹⁰ value 110°.

***p*-Bromophenol**, an Eastman Kodak Co. White Label product, was recrystallized from water, then dried at 70° *in vacuo* for 2 hr.; m.p. 63°, literature¹⁰ value 63.50°.

Conductivity Measurements at 25°.—The 1RC-1B conductivity bridge, conductivity cell (cell constant equal to 0.224) and thermostat were the same as previously used.⁶ For the procedure for the conductometric titration reference is made to a previous paper.⁶

(9) L. Onsager, *Physik Z.*, **27**, 388 (1926); **28**, 277 (1927).

(10) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

Determination of Solubility of Potassium 3,5-Dinitrobenzoate in Presence of Resorcinol or *p*-Bromophenol at 25°.—The procedure for the preparation of saturated solutions of potassium 3,5-dinitrobenzoate in the presence of 3,5-dinitrobenzoic acid has been described previously.⁶ In the present work solid resorcinol or solid *p*-bromophenol was substituted for solid 3,5-dinitrobenzoic acid. A 1- to 5-ml. aliquot of the saturated solution was pipetted into the above conductance cell and made up to a 5.18-ml. mark with pure acetonitrile. The 3,5-dinitrobenzoate ion was titrated conductometrically with 0.485 M perchloric acid in anhydrous acetic acid, as described elsewhere.⁶

Infrared Spectra.—All infrared spectra were recorded by a Perkin-Elmer model 421 infrared spectrophotometer. The following settings were used: slit program 10, gain 5, attenuator speed 11, suppression 5, scale 1 and a source current of 0.35 amp. Sodium chloride cells of path length 34 and 97 μ and a 105- μ potassium bromide cell were used which were calibrated from interference patterns in air in the infrared.

In all cases the spectrum of a solution 0.15 M in resorcinol (or *p*-bromophenol) containing a large excess of tetraethylammonium 3,5-dinitrobenzoate (>0.30 M) served as the baseline. This baseline is 0.030 absorbance unit greater than that of pure solvent and 0.026 absorbance unit greater than that of a 0.15 M $\text{Et}_4\text{N}^+\text{DNB}^-$ solution in a 97- μ cell at 3400 cm.⁻¹. At 2750 cm.⁻¹ the spectra of the two above solutions and solvents coincide.

Experimental Results

Ionic Mobilities.—A value of 46 for $\lambda_{\text{ODNB}^-\text{HDNB}^-}$ at 25° has been reported previously⁶ ($\text{DNB}^- = 3,5$ -dinitrobenzoate). From a Λ vs. \sqrt{c} plot of the conductance data of solutions 2.4×10^{-3} to 1.67×10^{-3} M in tetraethylammonium 3,5-dinitrobenzoate and 0.371 M in resorcinol, corrected for viscosity effects, given in Table I, and Walden's value of $\lambda_{\text{OEt}_4\text{N}^+} = 86$,¹¹ $\lambda_{\text{ODNB}(\text{HR})_2^-}$ was found to be 42.

The experimental Onsager slope was 750 compared to the calculated value of 325, indicating slight association. For comparison, the experimental Onsager slope of 3300 was obtained in tetraethylammonium 3,5-dinitrobenzoate solutions in the absence of resorcinol.⁶ For simplicity in the calculation of conductometric titration curves, $\lambda_{\text{ODNB}^-\text{HDNB}^-} = \lambda_{\text{ODNB}(\text{HR})_2^-} = \lambda_{\text{ODNB}(\text{HR})_2^-} = 42$, and Walden's value of $\lambda_{\text{OEt}_4\text{N}^+} = 87$ were used.

TABLE I

CONDUCTANCE OF TETRAETHYLAMMONIUM 3,5-DINITROBENZOATE IN PRESENCE OF 0.371 M RESORCINOL

Concn., $M \times 10^4$, $\text{Et}_4\text{N}^+ 3,5\text{-DNB}^-$	Λ^a (cor. for viscosity)
0.238	125.0
.594	124.3
1.19	121.3
2.38	118.4
4.75	115.8
8.34	114.3
11.90	110.0
16.66	105.3

$\Lambda_0 = 129$

^a Viscosity is 0.383 cp. Onsager slope: calcd. 305, exptl. 750.

Heteroconjugation Constants, K_{AHR^-} and $K_{\text{A}(\text{HR})_2^-}$.—Solubility data of potassium 3,5-dinitrobenzoate in solutions of resorcinol and in solutions of *p*-bromophenol are given in Table II. The previously determined values of 2.6×10^{-4} and 5.3×10^{-8} of the dissociation constant and solubility product, respectively, of potassium 3,5-dinitrobenzoate⁶ was used in the calculation of heteroconjugation constants. Activity coefficients were calculated from the Debye-Hückel limiting law.

The salt $\text{K}^+\text{DNB}(\text{HR})^-$ has been found to be virtually completely dissociated at concentrations up to 8×10^{-3} M . The equivalent conductances of the saturated solutions of potassium 3,5-dinitrobenzoate in the presence of 0.137 and 0.344 M resorcinol were 112 and 91, respectively. Using $\lambda_{\text{ODNB}(\text{HR})_2^-} = 42$ and

(11) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

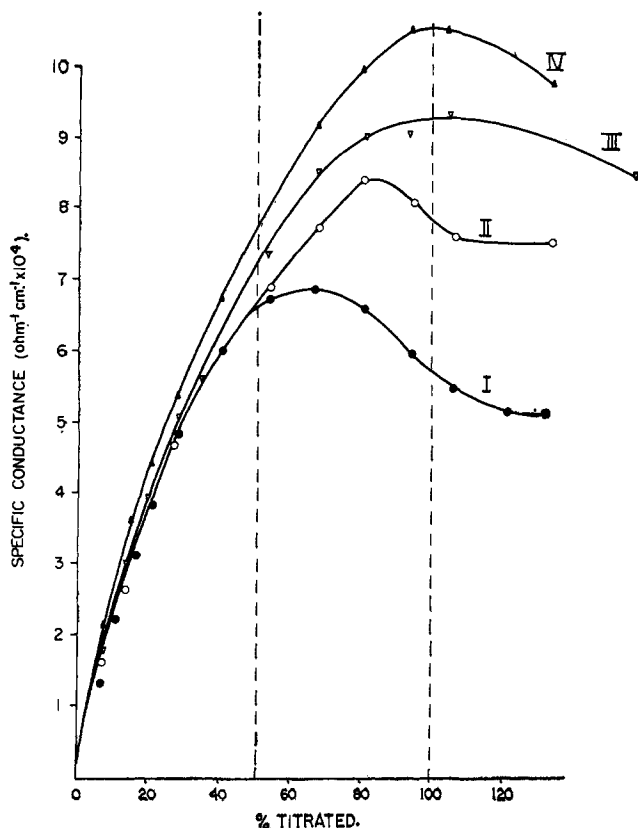


Fig. 1.—Conductometric titration of 0.0187 *M* sulfuric acid with pyridine in presence of resorcinol: I, no resorcinol added; II, 0.214 *M*; III, 0.384 *M*; IV, 0.745 *M* resorcinol present.

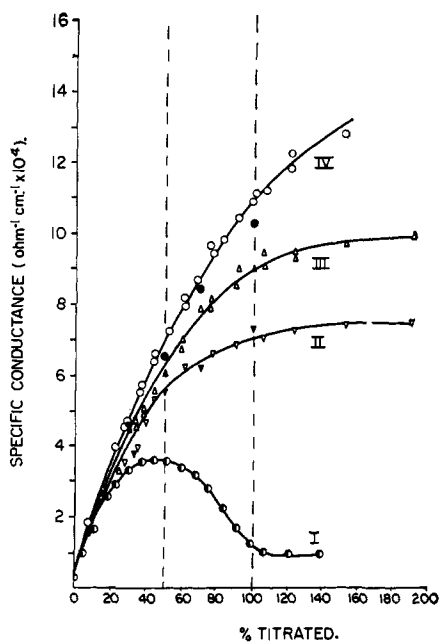


Fig. 2.—Conductometric titrations of 0.0187 *M* 3,5-dinitrobenzoic acid with triethylamine in the presence of resorcinol: curve I, no resorcinol present; II, 0.286 *M* in resorcinol; —▽—, experimental points, —▼—, calculated; III, 0.532 *M* in resorcinol; —△—, experimental points, —▲—, calculated; IV, 0.750 *M* in resorcinol; —○—, experimental points, —●—, calculated. Viscosity correction applied to all experimental values.

Walden's¹¹ value of $\lambda_{0K^+} = 87$, we calculate degrees of dissociation of 1.0 and 0.92, respectively, in the above saturated solutions. In all instances, viscosity and Onsager ion atmosphere corrections were applied. The salt $K^+DNB(HR)^-$, HR being *p*-bromophenol,

TABLE II
SOLUBILITY OF POTASSIUM 3,5-DINITROBENZOATE IN SOLUTIONS OF RESORCINOL OR *p*-BROMOPHENOL

Anal. concn. of HR, <i>M</i>	Solubility, <i>M</i> × 10 ⁴	<i>f</i> ²	\bar{n}	$K_{AHR^-} \times 10^{-2}$	$K_{A(HR)_2^-} \times 10^{-2}$
HR = resorcinol					
0	0.314	0.930
0.0136	.710	.847	0.936	3.5	4.9
.0248	.965	.811	1.08, 1.18	3.3	6.0
.053	1.56	.780	1.42, 1.30	3.8	5.4
.139	3.47	.652	1.56, 1.43	5.3	4.4
.344	8.21	.535	1.74, 1.85	3.1	5.1
.699	19.0	.381	1.93		
			Av.	3.4	5.1
HR = <i>p</i> -bromophenol					
0.0567	1.56	0.780	1.31	3.6	3.6
.0985	2.35	.720	1.48, 1.55	3.1	4.3
.223	4.89	.616	1.74, 1.65	4.2	3.9
.571	12.7	.455	1.83		
			Av.	3.6	3.9

could be considered to be completely dissociated up to concentrations of 1.9×10^{-2} *M*.

The average values of K_{AHR^-} and $K_{A(HR)_2^-}$ calculated from solubility data of potassium 3,5-dinitrobenzoate according to eq. 6 are 3.4×10^2 and 5.1×10^3 , respectively, with HR being resorcinol, and 3.6×10^2 and 3.9×10^3 with HR being *p*-bromophenol. The homoconjugation constant, K_{AHA^-} , has been reported⁶ to be 1.7×10^4 .

Dissociation Constants of Salts.—The values of $K_{Et_3NH^+DNB^-}$ and $K_{Et_3NH^+DNB^-HDNB^-}$ were found previously to be equal to 1.2×10^{-5} and 3.0×10^{-2} , respectively.⁶ Agreement between the experimental and calculated conductance values of 0.0187 *M* $Et_3N \cdot H^+DNB^-$ (at 100% titrated) in the presence of 0.75 *M* resorcinol is obtained when $K_{Et_3NH^+DNB(HR)_2^-}$ is taken equal to 1.0×10^{-2} . The value of $K_{Et_3NH^+DNB(HR)_2^-}$ was assumed equal to $K_{Et_3NH^+DNB(HR)_2^-}$ in the calculation of conductometric titration curves.

Conductometric Titration Curves Involving Heteroconjugate Ion Formation.—As an illustration of the effect of heteroconjugate ion formation upon the conductometric titration curve of an uncharged acid with a very weak base, titration curves of 0.187 *M* sulfuric acid with pyridine in the presence of 0.214 *M*, 0.384 *M* and 0.745 *M* resorcinol, respectively, are given in Fig. 1. The specific conductance of a mixture 0.785 *M* in resorcinol and 0.0187 *M* in pyridine is only 2.3×10^{-6} $ohm^{-1} cm^{-1}$. Therefore, no correction for the pyridine-resorcinol titration "blank" needs to be applied.

Calculated and Experimental Titration Curves of 3,5-Dinitrobenzoic Acid with Triethylamine in the Presence of Resorcinol.—The titration curves of 0.0187 *M* 3,5-dinitrobenzoic acid with triethylamine in the presence of 0.286, 0.532 and 0.750 *M* resorcinol are presented in Fig. 2.

Experimental conductances were corrected for viscosity effect, the viscosity of the above solutions being 0.373, 0.400 and 0.428 cp., respectively. From Fig. 2 it is evident that there is satisfactory agreement between experimental and calculated values of the conductance during the neutralization. Calculated values of the concentration of the various species in the titration of 0.0187 *M* 3,5-dinitrobenzoic acid in 0.75 *M*, 0.532 *M* and 0.286 *M* resorcinol are presented in Table III.

Calculated and Observed Infrared Spectra of Mixtures of Resorcinol or *p*-Bromophenol with Tetraethylammonium 3,5-Dinitrobenzoate ($Et_4N^+DNB^-$).—Infrared spectra of 0.15 *M* solutions of resorcinol in acetoni-

TABLE III

CALCULATED TITRATION CURVES OF 0.0187 M 3,5-DINITROBENZOIC ACID WITH TRIETHYLAMINE IN PRESENCE OF RESORCINOL

%	titrated	f^2	[BH ⁺].	[BHA].	[HA].	[BH ⁺ A- HA ⁻].	[AHA ⁻].	[BH ⁺ A- HR ⁻].	[AHR ⁻].	[BH ⁺ A- (HR) ₂ ⁻].	[A(HR) ₂ ⁻].	A	Specific conductance, ohm ⁻¹ cm. ⁻¹ × 10 ³	
			M × 10 ²	M × 10 ²	M × 10 ²	M × 10 ⁴	M × 10 ³	M × 10 ⁴	M × 10 ³	M × 10 ³	M × 10 ³		M × 10 ²	Calcd.
0.286 M resorcinol														
30	0.66	0.333	0.14	1.185	7.0	0.936	1.63	0.452	0.70	0.194	111.2	0.37	0.42	
50	.60	.507	.26	0.775	1.06	1.04	3.70	.772	1.30	.327	106.9	.55	.58	
70	.56	.571	.50	0.474	0.82	0.771	5.80	.90	2.50	.401	105.0	.60	.66	
100	.55	.720	.74	~0	~0	~0	8.60	1.36	3.70	.584	102.5	.74	.72	
0.532 M resorcinol														
30	0.64	0.422	0.054	1.268	0.45	0.495	1.10	0.416	0.90	0.331	109.0	0.46	0.47	
50	.57	.574	.131	0.871	.53	.482	2.75	.586	2.20	.467	106.0	.61	.63	
70	.53	.784	.178	0.476	.36	.262	3.80	.844	3.00	.674	101.2	.79	.77	
100	.515	.930	.336	~0	~0	~0	7.25	1.036	5.80	.83	98.9	.92	.91	
0.750 M resorcinol														
30	0.62	0.445	0.029	1.263	0.31	0.340	0.90	0.404	1.00	0.373	108.4	0.48	0.50	
50	.55	.655	.058	0.898	.46	.385	1.78	.605	2.00	.588	104.5	.66	.71	
70	.52	.845	.096	0.471	.39	.257	2.70	.818	3.30	.751	101.3	.85	.89	
100	.48	1.084	.169	~0	~0	~0	5.16	1.067	5.80	.977	96.0	1.04	1.11	

^a Corrected for viscosity.

trile in the presence of varying amounts of Et₃N⁺DNB⁻ are reproduced in Fig. 3. Similar spectra have been determined in 0.15 M solutions of *p*-bromophenol. Qualitatively, these spectra are very similar to those of resorcinol and are not reproduced in this paper.

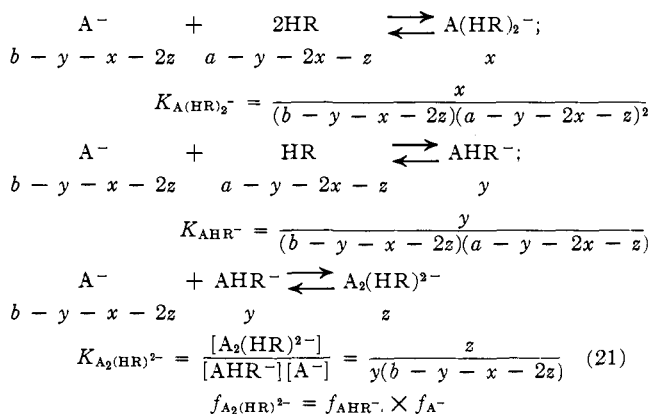
Resorcinol exhibits an -OH stretching band with a maximum at 3400 cm.⁻¹. The maximum for *p*-bromophenol was found at 3380 cm.⁻¹, while Tsubomura¹² reports a maximum of 3410 cm.⁻¹ for solutions of phenol in acetonitrile. In *n*-heptane he found a maximum at 3617 cm.⁻¹ and he attributes the difference to an association of the monomeric form of phenol with acetonitrile, no association occurring in *n*-heptane. He also found that solutions of phenol in acetonitrile up to a concentration of 3.2 × 10⁻² M obey Beer's law, the absorbance index at 3410 cm.⁻¹ being equal to 1.80 × 10². Assuming Beer's law to hold for solutions of resorcinol and *p*-bromophenol in acetonitrile to at least 0.15 M, we find absorbance indices for resorcinol at 3400 cm.⁻¹ and *p*-bromophenol at 3380 cm.⁻¹ of 3.57 × 10² and 1.90 × 10², respectively. It is to be noted that the absorbance index per OH group is practically the same in the three compounds, and that both hydroxyl groups in resorcinol contribute equally to the absorbance. No significant change in frequency (<10 cm.⁻¹) of the free OH band in resorcinol or *p*-bromophenol has been observed upon the addition of Et₃N⁺DNB⁻.

Formation of strongly hydrogen bonded species between resorcinol or *p*-bromophenol with 3,5-dinitrobenzoate in acetonitrile is indicated by the decreasing absorption at 3400 cm.⁻¹ of the free hydroxyl band with increasing dinitrobenzoate concentration and increasing absorption at frequencies between 2650 and 3150 cm.⁻¹ upon addition of Et₃N⁺DNB⁻ to either a 0.15 M resorcinol (Fig. 3) or *p*-bromophenol solution.

It has been shown that in solutions saturated with potassium 3,5-dinitrobenzoate the only heteroconjugates formed are AHR⁻ and A(HR)₂⁻, HR denoting resorcinol or *p*-bromophenol. When the concentration of dinitrobenzoate becomes in excess over the concentration of resorcinol (Fig. 3), there is indication of the formation of an additional heteroconjugate A₂(HR)₂²⁻ (see Discussion). No such conjugate can be formed with *p*-bromophenol.

In the calculation of the absorbance of mixtures of 3,5-dinitrobenzoate with resorcinol or *p*-bromophenol at 3400 and 3380 cm.⁻¹, respectively, the equilibrium

concentrations of A⁻, AHR⁻, A(HR)₂⁻, A₂(HR)₂²⁻ (the latter only in resorcinol solutions) and HR are calculated from the formation constants K_{AHR⁻}, K_{A(HR)₂⁻} and K_{A₂(HR)₂²⁻} (eq. 1, 2 and 21); viz.



where *a* and *b* denote the analytical resorcinol (or *p*-bromophenol) and tetraethylammonium 3,5-dinitrobenzoate concentrations, respectively. The various species of tetraethylammonium salts are considered to be completely dissociated. Values of *x*, *y* and *z* are chosen such that the values of K_{AHR⁻} and K_{A(HR)₂⁻} agree with the values found from solubility measurements of potassium 3,5-dinitrobenzoate, the value of K_{A₂(HR)₂²⁻} being taken equal to 5.0 × 10² (see Discussion).

To calculate the total absorbance of a mixture the concentrations of HR, AHR⁻, A(HR)₂⁻ and A₂(HR)₂²⁻ are multiplied by the product of the cell path length and appropriate absorbance index and summed. The calculated and observed absorbances at 3400 cm.⁻¹ in 0.15 M resorcinol and at 3380 cm.⁻¹ in 0.15 M *p*-bromophenol solutions at various analytical concentrations of tetraethylammonium 3,5-dinitrobenzoate together with the calculated concentrations of the various ionic species and of free phenol are given in Table IV.

Discussion

From the analytical viewpoint the presence of a hydrogen bond HR which eliminates the maximum in the conductometric titration curve near 50% neutralization (Fig. 2) is undesirable, because it also obviates the break at the equivalence point.

At a given fraction of neutralization in acetonitrile of a weak uncharged acid HA (without intramolecular

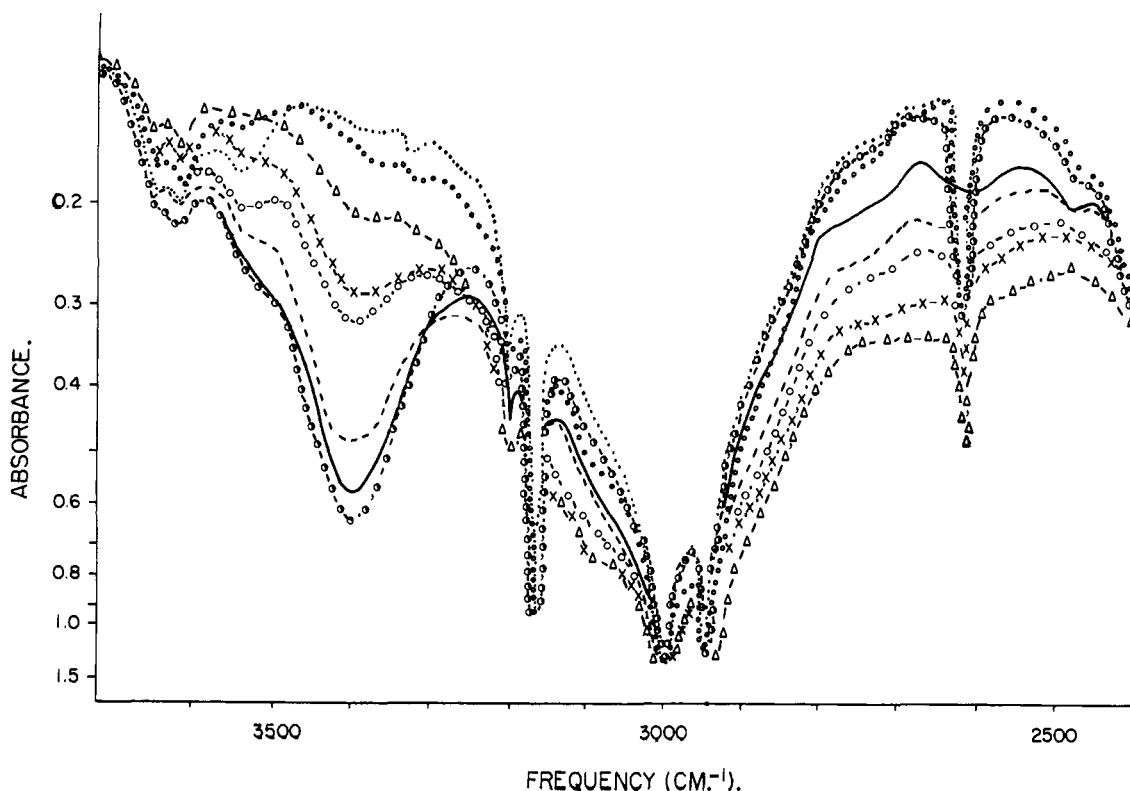


Fig. 3.—Infrared spectra in 97- μ NaCl cell of mixtures of resorcinol with tetraethylammonium 3,5-dinitrobenzoate in the region of OH absorption: —●—, 0.15 M resorcinol; 0.15 M resorcinol in the presence of: —, 0.0402 M ; - - - - , 0.0755 M ; —○—, 0.015 M ; —x—, 0.203 M ; and — Δ —, 0.312 M $\text{Et}_4\text{N}^+\text{DNB}^-$; , pure solvent; ○○○○○, 0.15 M $\text{Et}_4\text{N}^+\text{DNB}^-$

TABLE IV
ABSORBANCE OF THE —OH STRETCHING BAND OF *p*-BROMOPHENOL OR RESORCINOL IN MIXTURES WITH TETRAETHYLAMMONIUM 3,5-DINITROBENZOATE

0.15 M <i>p</i> -bromophenol, 3380 cm^{-1} , 105- μ KBr cell						
Concentration	[A- (HR) $_2^-$], M $\times 10^2$	[AHR $^-$], M $\times 10^2$	[A $^-$], M $\times 10^2$	[HR], $M \times 10^2$	A_{3380}	
Et $_4\text{N}^+$ DNB $^-$					Calcd.	Obsd.
0	15.0	0.275	0.275
0.020	1.30	0.68	0.02	11.7	.215	.209
.040	2.40	1.53	.07	8.35	.153	.150
.060	3.30	2.55	.15	5.85	.107	.100
.090	3.40	4.90	.70	3.30	.060	.057
.140	1.50	10.50	2.0	1.50	.028	.030
.209010
.290007

0.15 M resorcinol, 3400 cm^{-1} , 97- μ NaCl cell						
Concentration	[(HR)- A $_2^{2-}$], M $\times 10^2$	[(HR)- A $_2^{2-}$], M $\times 10^2$	[(HR)- A $_2^{2-}$], M $\times 10^2$	[(HR)- A $_2^{2-}$], M $\times 10^2$	A_{3400}	
					Calcd.	Obsd.
0	15.0	0.520	0.520
0.040	2.50	1.42	~ 0	8.58	.391	.420
.060	3.8	2.0	~ 0	5.4	.355	.370
.080	3.3	2.6	0.9	4.9	.326	.332
.110	2.4	5.3	1.5	3.4	.290	.263
.140	2.0	5.6	2.9	2.5	.249	.205
.200	0.9	5.0	6.6	1.4	.164	.140
.300	0.6	4.0	9.4	0.4	.102	.072

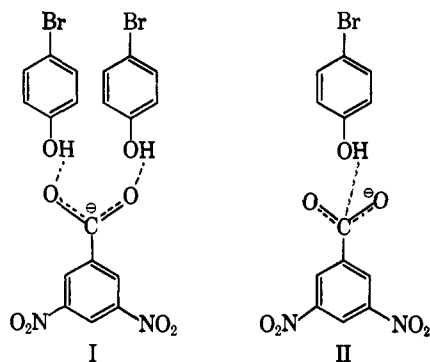
hydrogen bonding) with an amine, addition of a large excess of a hydrogen bond donor HR results in a relatively small increase in the equilibrium concentration of HA up to 50% neutralization and thereafter a decrease and in a marked decrease in [AHA $^-$] over the entire titration. For example, in the titration of 0.0187 M

3,5-dinitrobenzoic acid with triethylamine at 50% neutralization the values of [HA] and [AHA $^-$] are 5.9×10^{-3} and 3.2×10^{-3} M , respectively, in the absence of resorcinol and 9.0×10^{-3} and 0.39×10^{-3} M , respectively, in the presence of 0.75 M resorcinol. The corresponding figures at 30% neutralization are 11.0×10^{-3} and 3.0×10^{-3} M , respectively, in the absence and 12.6×10^{-3} and 0.34×10^{-3} M in the presence of 0.75 M resorcinol.

From Table III it appears that even when the acid is only 30% neutralized the sum of concentrations of all heteroconjugate species is considerably greater than that of the homoconjugate species, the difference becoming greater with increasing concentration of HR and with increasing fraction of acid neutralized. For example, in 0.532 M resorcinol at 30% neutralization of 0.0187 M 3,5-dinitrobenzoic acid the sum of the concentrations of the heteroconjugate species is 4.8×10^{-3} M and that of the homoconjugate species is 0.54×10^{-3} M , or a ratio of 9. At 70% neutralization these values are 11.0×10^{-3} M and 0.3×10^{-3} M , respectively, or a ratio of 37.

From the close similarity of the titration curves up to 50% neutralization in Fig. 2 it is apparent that the total concentration of the ionic species at a given fraction, titrated up to 50% neutralized, increases only slightly with increasing concentration of HR.

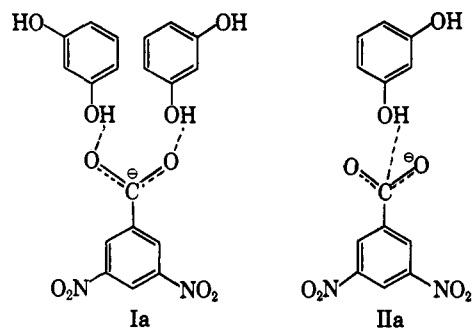
The infrared spectra of mixtures of 3,5-dinitrobenzoate with *p*-bromophenol are accounted for by formation of 2:1 and 1:1 hydrogen bonded complexes between *p*-bromophenol and DNB $^-$, represented by I (see also ref. 4) and II, respectively. In structure II (and IIa and V) the hydrogen bond resonates between the two oxygens of the carboxylate group, no evidence being found that hydrogen bonding takes place with the nitro groups.



In a mixture which is equimolar (0.15 *M*) in *p*-bromophenol and 3,5-dinitrobenzoate, species II is predominant and its concentration is much greater than that of I, while the concentration of free HR is even smaller than that of I.

The good agreement between calculated and observed absorbances at 3380 cm^{-1} in mixtures 0.15 *M* in *p*-bromophenol and various amounts of 3,5-dinitrobenzoate (Table IV) is further proof that the values of the heteroconjugation constants of AHR^- and A(HR)_2^- reported in this paper are of the right order of magnitude. It should be noted that the calculated values are only approximate since the activity coefficients of the various ionic species at the higher ionic strength are not known.

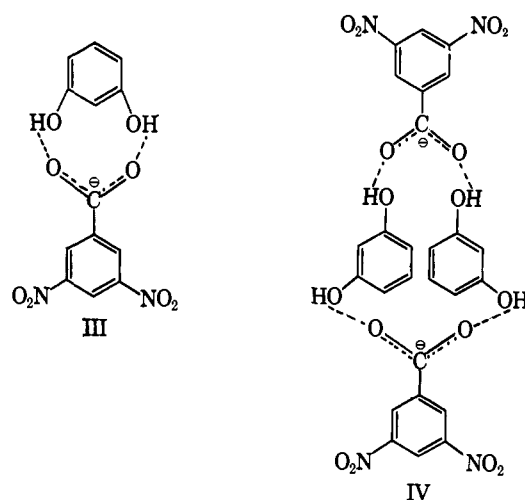
The large absorbance at 3400 cm^{-1} of a mixture 0.15 *M* in both resorcinol and 3,5-dinitrobenzoate (Fig. 3) as compared to the small absorbance of a similar mixture with *p*-bromophenol instead of resorcinol (Table IV) indicates the presence of free hydroxyl groups in the resorcinol heteroconjugates A(HR)_2^- and AHR^- with the suggested structures



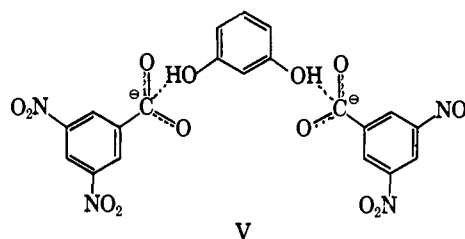
Structures Ia and IIa are similar to I and II, the stability constants of I and Ia and also of II and IIa being practically the same (Table III).

Fair agreement between calculated and observed absorbances is obtained in mixtures 0.15 *M* in resorcinol and containing up to 0.10 *M* $\text{Et}_4\text{N}^+\text{DNB}^-$. At higher concentrations of $\text{Et}_4\text{N}^+\text{DNB}^-$ the calculated absorbances are considerably higher than the observed ones. Even when 1:1 complexes of the structures III or IV, which have no free -OH groups, are postulated, the calculated absorbances are still considerably higher than the observed values.

To account for the low observed free -OH absorbances in mixtures 0.15 *M* in resorcinol and 0.15 to 0.3 *M*



in $\text{Et}_4\text{N}^+\text{DNB}^-$, a complex consisting of a dinitrobenzoate ion hydrogen bonded to each of the hydroxyl groups of a resorcinol molecule is proposed (structure V)



Structure V has no free hydroxyl group and hence does not absorb at 3400 cm^{-1} . With the estimated stability constant $K_{\text{A}_2(\text{HR})_2^-}$ of 5×10^2 the calculated concentration of $\text{A}_2(\text{HR})_2^-$ is small at 3,5-dinitrobenzoate concentrations less than 0.10 *M*, when the agreement between calculated and observed absorbances is fair (Table IV).

In both resorcinol and *p*-bromophenol solutions the formation constants K_{AHR^-} and $K_{\text{A(HR)}_2^-}$ are too small to permit a photometric titration of the free -OH band of the phenol with $\text{Et}_4\text{N}^+\text{DNB}^-$.

Hydrogen Bonded -OH Bands at 2650–3150 Cm^{-1} .

Upon addition of $\text{Et}_4\text{N}^+\text{DNB}^-$ to a 0.15 *M* *p*-bromophenol solution the absorbance of the very broad hydrogen bonded -OH band from 2650–3150 cm^{-1} increases and becomes practically constant when the 3,5-dinitrobenzoate concentration is equal to or greater than 0.20 *M*. Under these conditions virtually all the *p*-bromophenol is hydrogen bonded (Table III) mainly in the form of structure II.

The absorbance of the corresponding hydrogen bonded -OH bands in mixtures 0.15 *M* in resorcinol increases steadily with increasing concentration of $\text{Et}_4\text{N}^+\text{DNB}^-$ at least up to 0.30 *M* (Fig. 3), indicating that a complex is formed in which both -OH groups in resorcinol are hydrogen bonded as in structure V. In fact, the hydrogen bonded absorbance of a solution 0.15 *M* in resorcinol and 0.32 *M* in $\text{Et}_4\text{N}^+\text{DNB}^-$ is nearly twice that of a 0.15 *M* *p*-bromophenol solution which is 0.3 *M* in 3,5-dinitrobenzoate.