Acid–Base Properties of Mono- and Dinitrophenols in Acetonitrile[1]

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Abstract: Conductometric titrations of *o*-, *m*-, *p*-nitro-, 2,4-, 2,6-, 3,5-dinitro-, and 2,6-di-*t*-butyl-4-nitrophenols and picric acid with triethylamine are presented and interpreted in terms of the ionic dissociation constant K^{d}_{HA} of the acids, their homoconjugation constant $K^{f}_{HA_2^-}$, and ionic dissociation constant of the salts K^{d}_{BHA}. Values of $K^{f}_{HA_2^-}$ have been calculated from potentiometric pa_H measurements in mixtures of the acids and their tetraethylammonium salts, from spectrophotometric measurements, and in some instances from solubility data. Some heteroconjugation constants have been determined. Results are summarized in Tables V and VI. No simple relation between $(pK^{d}_{HA})_{water}$ and $(pK^{d}_{HA})_{AN}$ is found. Striking differences in K^{d}_{NaA}, $(K_{sp})_{NaA}$, $K^{f}_{HA_2^-}$, and $K^{f}_{AHR^-}$ (HR is *p*-bromophenol, A being *o*- or *p*-nitrophenolate ion) indicate greater stability in AN of *p*-nitrophenolate than of the *o*-nitrophenolate ion. Of the nitrophenols studied, only 2,6-dinitro- and 2,6-di-*t*-butyl-4-nitrophenol and picric acid are suitable as acid–base indicators.

In connection with a study of acid–base indicators to be used in the spectrophotometric determination of pa_H in acetonitrile, an investigation was made of the dissociation and conjugation constants of mono- and dinitrophenols. Methods used include the determination of conductometric titration curves of the phenols with a weak base,[2] potentiometric pa_H measurements in mixtures of the phenols with their tetraethylammonium salts,[3] and calculation of homo- and heteroconjugation constants from solubility and/or spectrophotometric methods[4] and from pa_H of mixtures of the phenols and their tetraalkylammonium salt.[3] It is shown in this paper that from the appearance of the conductometric titration curves with triethylamine no qualitative conclusions can be drawn regarding the acid strength, the homoconjugation constant, and the ionic dissociation constant, K^{d}_{BHA}, of the salt. Provided homoconjugation constants are known and certain conditions are fulfilled, the formation constant and the dissociation constant of the salts can be derived from the location of the maximum on the curves and the conductance at the maximum, respectively.[2]

Caution must be observed in the use of acid–base indicators for the spectrophotometric determinations of pa_H in acetonitrile and other aprotic solvents. In this paper we deal only with indicators which are uncharged in the acid form and univalent anions in the alkaline form. In general, homoconjugation ($HI + I^- \rightleftarrows HI_2^-$) can be neglected, as the indicator concentration is very small and of the order of 10^{-5} *M*. For example, when $K^{f}_{HI_2^-}$ is 10^3 and $[HI] = [I^-] = 10^{-5}$, $[HI_2^-] = 10^{-7}$. On the other hand, it is shown in this paper that heteroconjugation of the acid and basic forms of the indicator with the basic and acid constituents in a mixture of unknown pa_H makes the indicator

$$HI + A^- \rightleftharpoons AHI^-$$

$$I^- + HA \rightleftharpoons IAH^-$$

unsuitable for the pH measurement unless the heteroconjugate constants are negligibly small.

Dissociation constants and solubility products of a number of salts have been determined, and the interrelation between the various constants, including conjugation constants, has been interpreted on the basis of resonance in the anions and intramolecular hydrogen bonding in the acids.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[5] Perchloric acid (0.489 *M* in anhydrous acetic acid) was prepared as previously described.[6] The following compounds were used previously: benzoic[7] and salicylic[7] acids and their tetraethylammonium salts,[7] picric acid,[3] potassium picrate,[3] *p*-bromophenol,[8] triethylamine,[2] N,N-dimethylbenzylamine,[2] and dibromothymolbenzein.[9] The following were prepared and purified as described by Coetzee and Padmanabhan:[10] *o*-nitrophenol, mp 45°, lit.[11] 45°; *p*-nitrophenol, mp 115°, lit.[11] 114°; and their tetraethylammonium salts, *m*-nitrophenol, mp 97°, lit.[11] 96°, and 2,4-dinitrophenol, mp 114–116°, lit.[11] 111–114°.

2,6-Dinitrophenol, Eastman Kodak White Label, was recrystallized from water and dried *in vacuo* at 50°, mp 61, lit.[11] 63°. **3,5-Dinitrophenol** was prepared from City Chemical Corp. 3,5-dinitroanisole, mp 106–107°, as described by Hantzsch,[12] recrystallized from 0.1 *M* aqueous hydrochloric acid solution, and dried *in vacuo* at 70°, mp 112°, lit.[12] 122°.

2,6-Di-*t*-butyl-4-nitrophenol was prepared by nitration of Eastman Kodak Technical Grade 2,6-di-*t*-butylphenol according to the procedure of Stroh, *et al.*,[13] recrystallized from ethanol–petroleum ether "B" mixture, and dried at 80° *in vacuo*, mp 158–159°, lit.[13] 156°. The tetraethylammonium salts of 2,6-dinitrophenol, 3,5-dinitrophenol, and 2,6-di-*t*-butyl-4-nitrophenol were prepared by titrating potentiometrically with the glass electrode a solution of the phenol in ethanol with a 1 *M* aqueous tetraethylammonium hydroxide solution almost to the equivalence point, evaporating to dryness, washing the residue with several portions of Merck Reagent

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(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-65.

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Table I. Conductivity of Salts

Concn, M	Equivalent conductance, Λ						
	Et$_4$N o-nitrophenolate		Na o-nitrophenolate			Et$_4$N p-nitrophenolate	
		+0.140 M o-nitrophenol		+0.208 M o-nitrophenol	+0.10 M p-bromophenol		+0.057 M p-nitrophenol
1.0×10^{-4}	...	...	77.0	...		...	...
2.0×10^{-4}	171	159	58.0	154.5		170.0	138
3.0×10^{-4}	167	157	48	152.5		168	135.5
4.0×10^{-4}	164.5	156	43	150.5	83	166	133
6.0×10^{-4}	160	153	35.0	147	82	163	129
8.0×10^{-4}	156	150.5	31	143	81	160.5	125.5
1.2×10^{-3}	149	146.5	...	137.5	80	156.5	119
1.6×10^{-3}	142.5	142	...	133	78	153.5	115
2.0×10^{-3}	137	138	...	127	77	151	111.5
2.4×10^{-3}	132.5	134.0	...	126	76	148.5	107.5
3.0×10^{-3}	129	128	...	122.5	74	146	102.0
4.0×10^{-3}	...	122	...	117.5	72	141.5	94
5.0×10^{-3}	...	117.5	...	...	70	139	88.0
Slope of Λ *vs.* $\sqrt{C}$ plot	942	765	...[a]	860	...	500	683
Onsager's slope	363	350	352	347	...	338	336
$\Lambda_{0_{MA}}$ or $\Lambda_{0_{MHA_2}}$	182	163	(166)[b]	159	143	175	144
$\lambda_{0_{A^-}}$ or $\lambda_{0_{HA_2^-}}$	96	77	(80)[b]	73	73	89	58
K^d_{MA} or $K^d_{MHA_2}$	5.2×10^{-3}	6.3×10^{-3}	3.1×10^{-5}	7.7×10^{-4}	1.5×10^{-3}	...[c]	...[c]

Concn, M	Na p-nitrophenolate	K 2,4-dinitrophenolate	Et$_4$N 3,5-dinitrophenolate	Et$_4$N 3,5-dinitrophenolate + 0.022 M 3,5-dinitrophenol	Et$_3$NH$^+$ 2,6-di-t-butyl-4-nitrophenolate	N,N-Dimethylbenzylammonium 2,6-dinitrophenolate
1.0×10^{-4}	...	...	...	...	...	
2.0×10^{-4}	142.5	166.5	173.5	148	...	
3.0×10^{-4}	137.5	162	170	145	...	
4.0×10^{-4}	133	157.5	167.5	142	...	67
6.0×10^{-4}	125	150	163.5	137.5	...	56
8.0×10^{-4}	120	144.5	160.5	134.5	...	47
1.2×10^{-3}	113	136.5	155	130	53	39.5
1.6×10^{-3}	107	131	151	126	52	35
2.0×10^{-3}	102.5	126	148	123.5	50.5	32
2.4×10^{-3}	98	122	145	121	50	29.5
3.0×10^{-3}	93	116	141.5	118	48.5	27
4.0×10^{-3}	...	108	136	112	47	23.5
5.0×10^{-3}	...	101	134	105	45.5	21
Slope of Λ *vs.* $\sqrt{C}$ plot	530	122	690	750		
Onsager's slope	342	363	363	344		
$\Lambda_{0_{MA}}$ or $\Lambda_{0_{MHA_2}}$	152	181	182	156	175	148
$\lambda_{0_{A^-}}$ or $\lambda_{0_{HA_2^-}}$	82	95	96	70	89	78
K^d_{MA} OR $K^d_{MHA_2}$	3.1×10^{-3}	2.9×10^{-3}	1.0×10^{-2}	...[c]	1.8×10^{-3}	1.5×10^{-4}

[a] Accurate value of slope of Λ *vs.* $\sqrt{C}$ plot could not be obtained, as salt is poorly dissociated. [b] Value uncertain. [c] Salt extensively dissociated.

Grade anhydrous ether to remove excess phenol, recrystallizing from ethyl acetate–petroleum ether "B" mixture, and drying *in vacuo* at 70°. Assay of the latter two salts by visual titration in AN with 0.5 M perchloric acid in acetic acid, with 5×10^{-6} M dibromothymolbenzein as indicator,[9] gave 98% for both. **Sodium *p*-nitrophenolate,** Eastman Kodak White Label, was recrystallized from ethanol and dried at 100° *in vacuo*. **Sodium *o*-nitrophenolate** and **potassium 2,4-dinitrophenolate** were prepared as described above for tetraethylammonium 2,6-dinitrophenolate. The salts were recrystallized from methanol and dried at 70°.

Experimental Techniques. All experiments were carried out at 25.0°. Potentiometric measurements with the glass electrode, conductometric measurements, and solubility determinations of salts were carried out as described previously.[2,3] The solubilities of *o*- and *p*-nitrophenol in AN and sodium *o*-nitrophenolate in water were determined by saturating the solutions by shaking overnight, filtering, and weighing the residues. The end point in the titration of the saturated solutions of sodium *o*-nitrophenolate and potassium 2,4-dinitrophenolate in AN in the absence and presence of free phenol with perchloric acid (in glacial acetic acid) was found visually using dibromothymolbenzein as indicator.[9] The glass electrode was calibrated every day in a picrate buffer. For our electrode $pa_H = (821 - E)/59.1$ at 25°.[3]

Spectrophotometric measurements in *p*-nitrophenolate and 2,6-dinitrophenolate systems were carried out in a 1.8-cm glass-stoppered cylindrical Pyrex cell,[3] while those in 2,6-di-*t*-butyl-4-nitrophenolate and 3,5-dinitrophenolate systems were made in 1.00- and 10.00-cm, glass-stoppered silica cells. All spectra were run on a Cary Model 15 spectrophotometer. In addition, absorbance measurements in 3,5-dinitrophenolate solutions containing the parent acid or *p*-bromophenol were made in a Beckman DU spectrophotometer.

Results

Ionic Mobilities and Dissociation Constant of Salts. Table I, which lists the equivalent conductance of salts at concentrations from 1×10^{-4} to 1×10^{-2} M, was constructed from Λ *vs.* $\sqrt{C}$ plots of the following

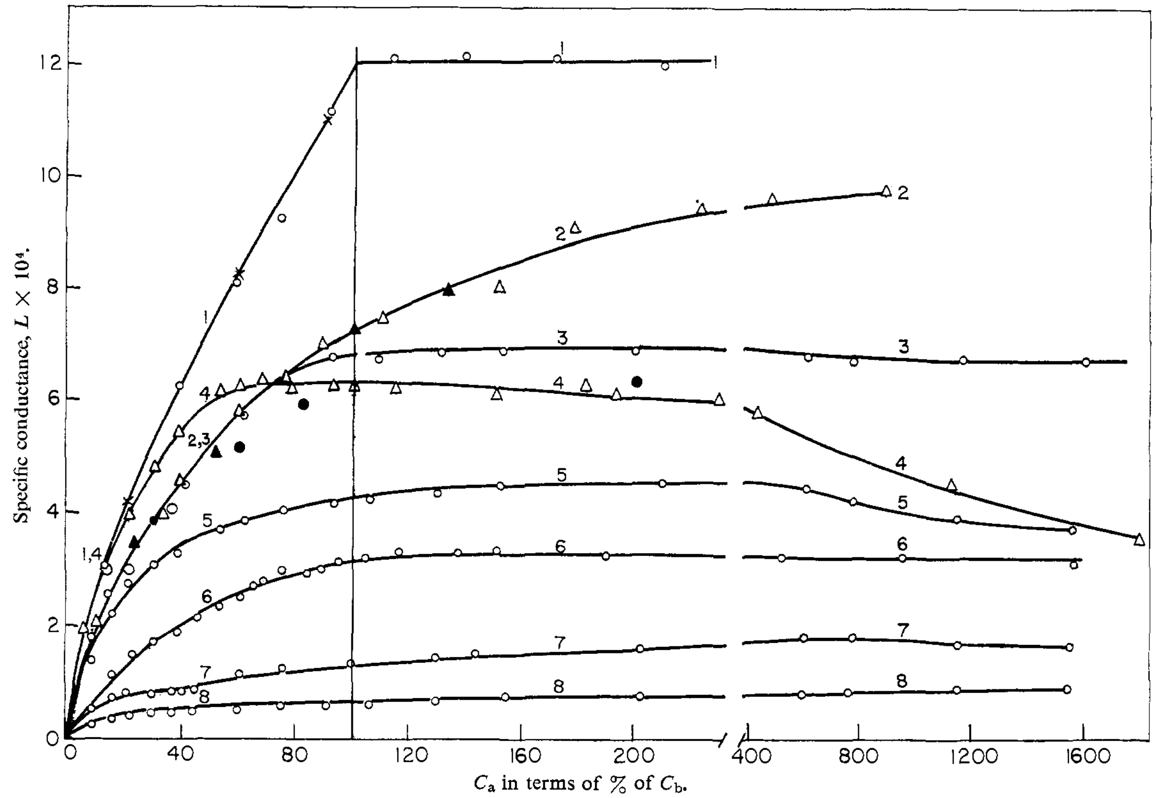

Figure 1. Conductometric titration curves of 1.87×10^{-2} *M* nitrophenols with triethylamine: (1) picric acid, (2) 2,6-di-*t*-butyl-4-nitrophenol, (3) 2,4-dinitrophenol, (4) 3,5-dinitrophenol, (5) *p*-nitrophenol, (6) 2,6-dinitrophenol, (7) *m*-nitrophenol, and (8) *o*-nitrophenol (calculated points for 2,6-di-*t*-butyl-4-nitrophenol, ▲; for 2,4-dinitrophenol, ●; for picric acid, ×).

electrolytes: tetraethylammonium *o*-nitrophenolate, *p*-nitrophenolate, and 3,5-dinitrophenolate; sodium *o*-nitrophenolate and *p*-nitrophenolate; and potassium 2,4-dinitrophenolate. Conductivity data of the above tetraethylammonium salts and of sodium *o*-nitrophenolate in presence of 0.02 to 0.21 *M* solutions of the parent acid and the latter salt in presence of 0.10 *M* *p*-bromophenol are also entered in Table I. The viscosity of the solutions used was practically the same as that of pure solvent with the exception of solutions which were 0.140 *M* in *p*-nitrophenol, 0.208 *M* in *o*-nitrophenol, and 0.10 *M* in *p*-bromophenol. At the high concentrations of hydrogen bond donors the anions are present practically entirely as the conjugates. Whenever the salt is sufficiently dissociated so as to yield a linear Λ *vs.* $\sqrt{C}$ plot in the concentration range studied, the observed and calculated Onsager slopes are given in Table I. In Table I the mobility of the anions of the above salts were calculated using Walden's value of $\lambda_{0\text{Na}^+} = 70$,[14] $\lambda_{0\text{K}^+} = \lambda_{0\text{Et}_4\text{N}^+} = \lambda_{0\text{Et}_3\text{NH}^+} = 86$.[14] From the data in Table I, tetraethylammonium *p*-nitrophenolate and its homoconjugate and the homoconjugate of tetraethylammonium 3,5-dinitrophenolate are found to be essentially completely dissociated at concentrations of 5×10^{-3} *M*. For all the other electrolytes the dissociation constants $K^d{}_{\text{MA}}$, $K^d{}_{\text{MHA}_2}$, or $K^d{}_{\text{MAHR}}$ ($\text{M}^+ = \text{K}^+, \text{Na}^+$, or Et_4N^+ and HR = *p*-bromophenol) where

$$K^d{}_{\text{MA}} = [\text{M}^+][\text{A}^-]f^2/[\text{MA}] \qquad (1)$$

$$K^d{}_{\text{MHA}_2} = [\text{M}^+][\text{HA}_2^-]f^2/[\text{MHA}_2] \qquad (2)$$

$$K^d{}_{\text{MAHR}} = [\text{M}^+][\text{AHR}^-]f^2/[\text{MAHR}] \qquad (3)$$

$$f_{\text{M}^+} = f_{\text{A}^-}, f_{\text{HA}_2^-}, f_{\text{AHR}^-}$$

(given in Table I) were calculated from the Fuoss and Kraus plot of the conductance data in Table I. In this paper all activity coefficients were calculated from the limiting Debye–Hückel expression. At the higher ionic strength these values undoubtedly are too large.

For the salts, triethylammonium 2,6-di-*t*-butyl-4-nitrophenolate and N,N-dimethylbenzylammonium 2,6-dinitrophenolate, $\Lambda_{0\text{BHA}}$ was taken equal to 176 and 148, respectively, assuming $\lambda_{0(2,6\text{-di-}t\text{-butyl-4-nitrophenolate})} = \lambda_{0(p\text{-nitrophenolate})} = 89$ (Table I), and $\lambda_{0(2,6\text{-dinitrophenolate})} = \lambda_{0(\text{Pi}^-)} = 78$.[14] $\lambda_{0(\text{N,N-dimethylbenzylammonium})}$ was reported as 70.[2]

Since these two salts exhibit appreciable molecular acid–base dissociation but negligible homoconjugation (*vide infra*), values of $K^d{}_{\text{BHA}}$ (*cf.* eq 1 where $\text{BH}^+ = \text{M}^+$) were calculated from the slope, $1/K^d{}_{\text{BHA}}\Lambda^2{}_{0(\text{BHA})}$, of the $1/\Lambda$ *vs.* *c* plots,[15] while the product $K^d{}_{\text{BHA}}K^f{}_{\text{BHA}}$ was

$$K^f{}_{\text{BHA}} = [\text{BHA}]/[\text{B}][\text{HA}] \qquad (4)$$

calculated from the intercept $[1 + 1/\sqrt{K^d{}_{\text{BHA}}K^f{}_{\text{BHA}}}]/\Lambda_{0(\text{BHA})}$ of the same plot. For the two above salts, values of the slope were 1.8×10^{-2} and 3.0×10^{-1}, yielding values of $K^d{}_{\text{BHA}}$ equal to 1.8×10^{-3} and 1.5×10^{-4}, respectively. From values of the intercept, 1.8×10^{-2} and 1.45×10^{-3}, $K^d{}_{\text{BHA}}K^f{}_{\text{BHA}}$ was found equal to 0.21 and 0.76, yielding values of $K^f{}_{\text{BHA}}$ equal to 1.2×10^2 and 5.1×10^3, respectively.

Introducing the values of $-(\text{p}K^f{}_{\text{BHA}})_{\text{AN}}$ equal to 18.46

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[14] P. Walden and E. J. Birr, *Z. Physik. Chem.*, 144, 269 (1929).

[15] M. Elliott and R. Fuoss, *J. Am. Chem. Soc.*, 61, 294 (1939).

for triethylammonium ion[10] and 16.0 for N,N-dimethylbenzylammonium ion[2] into the relation[2]

$$(\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HA}})_{\mathrm{AN}} = \mathrm{p}(K^{\mathrm{d}}{}_{\mathrm{BHA}}K^{\mathrm{f}}{}_{\mathrm{BHA}})_{\mathrm{AN}} - (\mathrm{p}K^{\mathrm{f}}{}_{\mathrm{BH^+}})_{\mathrm{AN}} \quad (5)$$

$\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HA}}$ of 2,6-di-*t*-butyl-4-nitrophenol and 2,6-dinitrophenol were found equal to 19.1 and 16.0, respectively.

Conductometric Titrations. In Figure 1 are presented conductometric titration curves with triethylamine of 1.87×10^{-2} *M* solutions of the following nitrophenols: *o*-nitro-, *p*-nitro-, 2,6-di-*t*-butyl-4-nitro-, *m*-nitro-, 2,4-dinitro-, 2,6-dinitro-, and 3,5-dinitrophenol and picric acid.

Since no maximum occurs in the curves of picric acid, 2,6-dinitrophenol, and 2,6-di-*t*-butyl-4-nitrophenol, homoconjugation is considered negligible. This is substantiated by an analysis of the curves presenting $\mathrm{p}a_{\mathrm{H}}$ values in mixtures of the phenols and their tetraethylammonium salts (*vide infra*).

In the titration of picric acid with triethylamine, molecular acid–base dissociation of the picrate salt is negligible, the break occurring at 100% titrated. $K^{\mathrm{f}}{}_{\mathrm{BHA}}$ has been calculated to be 6.4×10^9, using $\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HPi}} = 11.0$,[3] $\mathrm{p}K^{\mathrm{f}}{}_{\mathrm{BH^+}} = 18.46$,[10] and $\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{BHA}}$[14] $= 2.35$ in eq 5. The conductometric titration curve of picric acid was calculated, only considering dissociation of the normal picrate salt, taking $C_{\mathrm{s}} = [\mathrm{BH^+}] + [\mathrm{BHA}]$. Activity coefficient and Onsager ion atmosphere corrections were taken into account.

In the titration of 2,6-di-*t*-butyl-4-nitrophenol with triethylamine, where acid–base dissociation of the salt BHA is appreciable, the titration curve was calculated as described by Coetzee and Cunningham[16] taking $K^{\mathrm{f}}{}_{\mathrm{BHA}} = 1.2 \times 10^2$ and $K^{\mathrm{d}}{}_{\mathrm{BHA}} = 1.8 \times 10^3$ as found from a plot of $1/\Lambda$ *vs.* $c\Lambda$ of equimolar mixtures of acid and base.

The evaluation of $\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{BHA}}$ from the initial portion and from the maximum of the titration curves of 1.87×10^{-2} and 5.10×10^{-2} *M* *p*-nitrophenol and of 2.16×10^{-3} and 4.32×10^{-3} *M* 3,5-dinitrophenol with triethylamine was carried out as described in a previous publication,[2] and the pertinent data are summarized in Table VI.

Considerable scattering was found of the points of the plots of $L/[\mathrm{HA}]$ *vs.* $\sqrt{[\mathrm{B}]}$ on the initial portion of the titration curve; values of $L/[\mathrm{HA}]$ were accurate to only within 50%. In these calculations the value of $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$ of *p*-nitrophenol was derived from solubility data and that of 3,5-dinitrophenol from potentiometric data.

In the titration of 2,4-dinitrophenol and *o*-nitrophenol homoconjugation occurs to such a slight extent that the titration curves exhibit at best an ill-defined maximum. In addition, acid–base dissociation of triethylammonium 2,4-dinitrophenolate is so slight that $K^{\mathrm{d}}{}_{\mathrm{BHA}}$ could be calculated from the conductance at 2000% titrated, the average value being 5.6×10^{-4}. In conjunction with the potentiometric value of $\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HA}}$ of 16.0,[10] $K^{\mathrm{f}}{}_{\mathrm{BHA}}$ was calculated to be 4.5×10^5, using eq 5.

The conductometric titration curve of 1.87×10^{-2} *M* 2,4-dinitrophenol presented in Figure 1 was calculated according to the procedure described previously,[2] using the above values of $K^{\mathrm{f}}{}_{\mathrm{BHA}}$ and $K^{\mathrm{d}}{}_{\mathrm{BHA}}$, and the value of 1.2×10^2 for $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$ derived from solubility data. Calculation of the conductometric titration curves of *m*- and *o*-nitrophenol with triethylamine are involved, since $K^{\mathrm{d}}{}_{\mathrm{BHA}}$ cannot be obtained directly from the maximum or from the conductance in the presence of excess base, as acid–base dissociation of the normal salt is extensive in both instances.

Potentiometric Measurements. In mixtures of a tetraalkylammonium salt, MA, and its parent acid, HA, which dissociates simply, the following relation holds

$$\mathrm{p}a_{\mathrm{H}} = \mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HA}} - \log C_{\mathrm{a}}/C_{\mathrm{s}} + \log f \quad (6)$$

provided MA is completely dissociated, no acid–base dissociation of MA occurs, and HA is a sufficiently weak acid such that $[\mathrm{H^+}] \ll C_{\mathrm{s}}$. In eq 6 C_{a} and C_{s} refer to the analytical acid and salt concentrations, respectively. Under these conditions plots of $\mathrm{p}a_{\mathrm{H}}$ *vs.* $\log C_{\mathrm{a}}/C_{\mathrm{s}}$ are linear, with a slope of -1. At the midpoint of the potentiometric titration curve $C_{\mathrm{a}} = C_{\mathrm{s}}$ and from eq 6

$$\mathrm{p}a_{\mathrm{H}_{1/2}} = \mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HA}} + \log f \quad (6\mathrm{a})$$

the subscript $1/2$ denoting the midpoint. Hence at a constant ionic strength the half-neutralization point (HNP) is independent of concentration of acid and salt.

In the above mixtures when homoconjugation occurs, the following relation between C_{a}, C_{s}, and $a_{\mathrm{H^+}}$ has been derived.[3]

$$f^2C_{\mathrm{s}}a_{\mathrm{H^+}}{}^2 - fa_{\mathrm{H^+}}K^{\mathrm{d}}{}_{\mathrm{HA}}\{(C_{\mathrm{a}} + C_{\mathrm{s}}) + K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}(C_{\mathrm{s}} - C_{\mathrm{a}})^2\} + K^{\mathrm{d}}{}_{\mathrm{HA}}C_{\mathrm{a}} = 0 \quad (7)$$

From the HNP and the potential on any point on the potentiometric titration curve, $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$ has been calculated from the following relation, derived previously[3]

$$C_{\mathrm{s}}r^2 - r\{(C_{\mathrm{a}} + C_{\mathrm{s}}) + K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}(C_{\mathrm{s}} - C_{\mathrm{a}})^2\} + C_{\mathrm{a}} = 0 \quad (8)$$

where $r = a_{\mathrm{H^+}}/a_{\mathrm{H^+}_{1/2}}$.

When MA, but not $\mathrm{MHA_2}$, is incompletely dissociated, HNP no longer occurs when $\log C_{\mathrm{a}}/C_{\mathrm{s}} - \log f = 0$ in eq 6, thereby making the calculation of $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$ from eq 7 involved. To calculate $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$, HNP is located and as a first approximation $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$ evaluated as described above assuming MA completely dissociated. Next, C_{s} is eq 8 is corrected for undissociated MA by the following procedure. At a given point on the titration curve $[\mathrm{A^-}]$ is calculated from eq 9.

$$f^2K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}[\mathrm{A^-}]^3 + \{f^2 + (K^{\mathrm{d}}{}_{\mathrm{MA}} + C_{\mathrm{a}})K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}\}[\mathrm{A^-}]^2 + K^{\mathrm{d}}{}_{\mathrm{MA}}\{1 + K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}(C_{\mathrm{a}} - C_{\mathrm{s}})\}[\mathrm{A^-}] - C_{\mathrm{s}}K^{\mathrm{d}}{}_{\mathrm{MA}} = 0 \quad (9)$$

which is derived by combining eq 1, 10, and 11.

$$C_{\mathrm{a}} = [\mathrm{HA}] + [\mathrm{HA_2^-}] \quad (10)$$

$$C_{\mathrm{s}} = [\mathrm{M^+}] + [\mathrm{MA}] = [\mathrm{A^-}] + [\mathrm{HA_2^-}] + [\mathrm{MA}] \quad (11)$$

$$K^{\mathrm{f}}{}_{\mathrm{HA_2^-}} = [\mathrm{HA_2^-}]/[\mathrm{HA}][\mathrm{A^-}]$$

Next, $[\mathrm{M^+}]$ is evaluated from eq 12 (*cf.* eq 1 and 11) and

$$[\mathrm{M^+}] = C_{\mathrm{s}}K^{\mathrm{d}}{}_{\mathrm{MA}}/\{K^{\mathrm{d}}{}_{\mathrm{MA}} + f^2[\mathrm{A^-}]\} \quad (12)$$

substituted for C_{s} in eq 12 to calculate a better value for $K^{\mathrm{f}}{}_{\mathrm{HA_2^-}}$. If necessary the cycle is repeated. The

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(16) J. F. Coetzee and G. Cunningham, *J. Am. Chem. Soc.*, 87, 2534 (1965).

Table II. Calculation of $K^{f}_{HA_2^-}$ of 3,5-Dinitrophenol from Potentiometric Data (HNP_{cor} = −390,[a] $K^{d}_{Et_4NA}$ = 1.0 × 10^{-2})

C_a, $M \times 10^3$	C_s, $M \times 10^3$	$-E$, mv	pa_H[b]	$[A^-]$, $M \times 10^3$	$[HA_2^-]$, $M \times 10^3$	$[Et_4N^+]$, $M \times 10^3$	$[Et_4NA]$, $M \times 10^3$	$K^{f}_{HA_2^-}$ $\times 10^{-4}$
0.907	5.32	552	23.3	3.45	0.97	4.42	0.90	4.1
1.78	5.27	523	22.8	2.66	1.98	4.64	0.62	3.8
3.51	5.17	466	21.8	1.12	3.74	4.86	0.31	3.7
5.18	5.10	365	20.1	0.062	5.04	4.92	∼0	...
8.40	4.92	268	18.4	∼0	4.92	4.70	∼0	4.6
12.7	4.70	221	17.65	∼0	4.70	4.70	∼0	5.4
24.0	4.70	170	16.8	∼0	4.70	4.70	∼0	6.8
0.191	2.81	563	23.4	2.30	0.13	2.43	0.38	3.3
0.380	2.80	546	23.1	2.08	0.37	2.45	0.35	3.8
0.945	2.79	506	22.5	1.51	1.01	2.52	0.27	3.4
1.50	2.78	478	22.0	1.13	1.45	2.58	0.20	4.0
2.05	2.77	440	21.3	0.56	2.20	2.76	0.010	...
2.78	2.74	371	20.2	0.21	2.52	2.73	0.004	...
3.67	2.71	303	19.1	∼0	2.71	2.71	∼0	5.5
5.41	2.66	266	18.4	∼0	2.66	2.66	∼0	4.0
7.09	2.61	239	17.9	∼0	2.61	2.61	∼0	4.75
15.5	2.61	184	17.0	∼0	2.61	2.61	∼0	4.9
29.4	2.61	137	16.2	∼0	2.61	2.61	∼0	7.2
								Av 4.4 × 10^4

[a] Value of HNP corresponding to log C_a/C_s − log f = 0. [b] pa_H = (821 − E)/59.1.

entire procedure is performed taking several values for the corrected HNP. The corrected HNP is the value corresponding to log C_a/C_s − log f = 0 and gives the least drift in $K^{f}_{HA_2^-}$ calculated. As an example, for 3,5-dinitrophenol, C_a = 1.78 × 10^{-3}, C_s = 5.27 × 10^{-3}, E = −523 mv, K^{d}_{MA} = 1.0 × 10^{-2} (Table I), and f_2 = 0.59. Assuming [MA] = 0, $K^{f}_{HA_2^-}$ = 5.5 × 10^4 from eq 8 using the experimental value of HNP = −378 mv. With the above values of $K^{f}_{HA_2^-}$, K^{d}_{MA}, C_a, and C_s is eq 9, $[A^-]$ = 2.7 × 10^{-3} and from eq 12 $[M^+]$ = 4.64 × 10^{-3}. Substituting this value for $[M^+]$ into eq 8, $K^{f}_{HA_2^-}$ = 3.8 × 10^4, using the corrected HNP of −390 mv as the value giving the least drift in $K^{f}_{HA_2^-}$. Another cycle yields practically the same values. In all nitrophenol buffers C_s varied from 2 × 10^{-3} to 5 × 10^{-3} M and C_a from 2 × 10^{-4} to 5 × 10^{-2} M. Plots of pa_H *vs.* log C_a/C_s are presented in Figure 2 for the following nitrophenols and their tetraethylammonium salts: *o*-nitro-, *p*-nitro-, 2,6-di-*t*-butyl-4-nitro-, 2,6-dinitro-, and 3,5-dinitrophenol. The plots of pa_H *vs.* log C_a/C_s of 2,6-dinitrophenol and 2,6-di-*t*-butyl-4-nitrophenol in Figure 2 are linear, with a slope of unity, as found earlier with picric acid,[3] indicating simple acid dissociation. Plots of pa_H *vs.* log C_a/C_s of the other nitrophenols are not linear and also steeper, indicating homoconjugation.

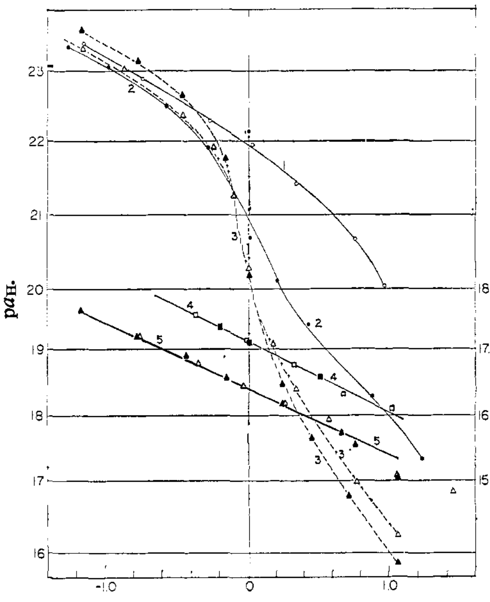

Figure 2. Plots of pa_H *vs.* log C_a/C_s from potentiometric measurements in nitrophenol–tetraethylammonium nitrophenolate mixtures: (1) ○, 4.76 × 10^3 M *o*-nitrophenolate; (2) ●, 3.53 × 10^{-3} M *p*-nitrophenolate; (3) ▲, 5.37 × 10^{-3} M, △, 2.8 × 10^{-3} M 3,5-dinitrophenolate; (4) ■, 6.21 × 10^{-3} M, □, 3.4 × 10^{-3} M 2,6-di-*t*-butyl-4-nitrophenolate; (5) ▲, 5.21 × 10^{-3} M, △, 2.00 × 10^{-3} M, 2,6-dinitrophenol (right-hand scale, 2,6-dinitrophenol; all others, left-hand scale).

As with the benzoic acids[7] a maximum deviation of $pa_{H_{1/2}}$ corresponding to ±4 mv in the HNP was found from the plots in Figure 2. Values of pK^{d}_{HA} calculated from the average value of $pa_{H_{1/2}}$ are entered in Table VI, and those of $K^{f}_{HA_2^-}$ calculated according to eq 8 are entered in Table V. In Table II are summarized the results of calculation of $K^{f}_{HA_2^-}$ for 3,5-dinitrophenol where MA is incompletely dissociated, K^{d}_{MA} being 1.0 × 10^{-2}. In an equimolar solution of 4.76 × 10^{-3} M *o*-nitrophenol and its tetraethylammonium salt, $(HNP)_{obsd}$ = −472 mv, $[A^-]$ = 2.50 × 10^{-3} M, $[HA_2^-]$ = 2.26 × 10^{-3} M, $[Et_4N^+]$ = 3.70 × 10^{-3} M, and $[Et_4NA]$ = 1.06 × 10^{-3} M, using the values of K^{d}_{MA} = 5.2 × 10^{-3} (Table I) and $K^{f}_{HA_2^-}$ = 1.0 × 10^2.[10] A corrected value of HNP of −492 mv was evaluated by the above method.

Homoconjugation and Heteroconjugation Constants of Nitrophenols from Solubility Data. The homoconjugation constants of *p*-nitro-, *o*-nitro-, and 2,4-dinitrophenol and the heteroconjugation constants of *p*-nitro- and *o*-nitrophenol and picric acid with *p*-bromophenol (HR) were estimated from the solubility of sodium *p*-nitrophenolate and *o*-nitrophenolate and potassium 2,4-dinitrophenolate and picrate in presence of parent acid or *p*-bromophenol.

Conductance data of solutions of sodium *p*-nitrophenolate, sodium *o*-nitrophenolate, and potassium 2,4-dinitrophenolate entered in Table I yield the following values of $\Lambda_{0(MA)}$ (K^{d}_{MA}): 152 (3.1 × 10^{-3}),

Table III. Conjugation Constants of Nitrophenols from Solubility Data

Phenol	C_{HA} or C_{HR}, $M \times 10^2$	Total solubility, S_t, $M \times 10^3$	$[M^+]$ $\{(S_t - [MA] - [MHA_2]\}$, $M \times 10^3$	f^2	[HA] or [HR] $\{C_a - S_t + [MA]\}$, $M \times 10^2$	$[MHA_2]$ or [MAHR], $M \times 10^4$	$K^f_{HA_2^-}$ or $K^f_{HAR^-} \times 10^{-3}$
Na *p*-nitrophenolate, $K_{sp} = 3.8 \times 10^{-6}$, $K^d_{NaA} = 3.2 \times 10^{-3}$, [NaA] $= 1.1 \times 10^{-3}$, $K^d_{NaHA_2}$, $K^d_{NaAHR} = \infty$							
p-Nitro-	0	3.42	2.32	0.71	0	0	...
	0.936	8.30	7.20	0.54	0.216	0	2.9
	1.91	15.6	14.5	0.43	0.46	0	4.9
	4.55	27.9	26.8	0.32	1.87	0	3.2
	9.00	47.8	46.7	0.22	4.33	0	2.9
							Av 3×10^3
p-Bromo-	0.913	6.55	5.46	0.60	4.84	0	0.76
	1.61	8.54	7.45	0.55	9.60	0	0.73
	3.29	12.2	11.1	0.48	22.7	0	0.65
							Av 7×10^2
Na *o*-nitrophenolate, $K_{sp} = 2.1 \times 10^{-3}$, $K^d_{NaA} = 3.1 \times 10^{-5}$, [NaA] $= 6.8 \times 10^{-4}$, $K^d_{NaHA_2} = 7.65 \times 10^{-4}$, $K^d_{NaAHR} = 1.5 \times 10^{-3}$							
o-Nitro-	0	0.83	0.15	0.92	0	0	...
	2.10	1.10	0.33_5	0.88	2.1	0.85	0.18
	5.18	1.40	0.49	0.83	5.1	2.3	0.17
	8.61	1.61	0.59	0.81	8.5	3.3_6	0.15
	13.3	1.76	0.68	0.80	13.1	4.0	0.13
							Av 1.6×10^2
p-Bromo-	4.23	2.69	1.6	0.70	4.03	4.4	2.0
	10.7	5.62	2.7	0.59	10.0	29	2.1
	20.2	9.29	3.9_4	0.51	19.4	47	1.9
	42.5	20.1	6.6	0.46	41.0	132	2.3
							Av 2.1×10^3
K 2,4-dinitrophenolate, $K_{sp} = 9.5 \times 10^{-6}$, $K^d_{KA} = 2.9 \times 10^{-3}$, [KA] $= 3.3 \times 10^{-3}$, $K^d_{KHA_2} = \infty$							
2,4-Dinitro-	0	7.1	3.8	0.66	0	0	
	2.02	10.5	7.1	0.55	1.55	0	0.13
	4.03	13.1	9.8	0.50	3.26	0	0.12
	7.60	17.2	13.9	0.43	6.36	0	0.12
	15.5	24.0	20.7	0.37	13.5	0	0.12
							Av 1.2×10^2
K picrate, $K_{sp} = 2.8 \times 10^{-5}$, $K^d_{KA} = 6.7 \times 10^{-3}$, [KA] $= 0.44 \times 10^{-2}$, $K^d_{KAHR} = 0$							
p-Bromo-	0	11.9	7.5	0.51	0	0	...
	24.3	13.2	8.8	0.51	24.2	0	1.7
	50	14.5	10.1	0.50	50	0	1.6
							Av 1.65

166 (3.1×10^{-5}), 181 (2.9×10^{-3}), respectively. From these values of K^d_{MA} and the total solubility of the above salts in absence of hydrogen bond donor phenol, found to be 3.42×10^{-3}, 0.83×10^{-3}, and 7.13×10^{-3} *M*, respectively (Table III), the following values of the ionic solubility, $[M^+]$, and K_{sp} ($=[M^+][A^-]f^2$; $f_{M^+} = f_{A^-} = f$) are calculated: 2.32×10^{-3}, 3.8×10^{-6}; 1.5×10^{-4}, 2.1×10^{-8}; 3.8×10^{-3}, 9.5×10^{-6}, respectively. The following values of K^d_{MA} and K_{sp} of potassium picrate were found previously,[3] 6.7×10^{-3} and 2.8×10^{-5}, respectively.

The homoconjugate and *p*-bromophenol heteroconjugate salts of sodium *p*-nitrophenolate and potassium 2,4-dinitrophenolate and picrate are assumed to be completely dissociated. From conductance data of sodium *o*-nitrophenolate in presence of 0.208 *M* *o*-nitrophenol, $\Lambda_{0(MHA_2)}$ and $K^d_{MHA_2}$ were found equal to 159 and 7.7×10^{-4}, respectively, while the corresponding values of $\Lambda_{0(MAHR)}$ and K^d_{MAHR} in presence of 0.10 *M* *p*-bromophenol are 143 and 1.5×10^{-3}, respectively.

Table III reports the solubility of the above salts in the presence of parent acid or *p*-bromophenol. Using the procedure described previously.[3] the following average values of $K^f_{HA_2^-}$ and $K^f_{AHR^-}$, respectively, were calculated: *p*-nitrophenol, 3×10^3, 7×10^2; *o*-nitrophenol, 1.6×10^2, 2×10^3; 2,4-dinitrophenol, 1.2×10^2; and picric acid 1.65 ($K^f_{AHR^-}$).

Spectrophotometric Determination of Homo- and Heteroconjugation Constants. Spectral Characteristics of Simple Nitrophenols and Their Anions. Absorption spectra of 1.85×10^{-5} *M* *p*-nitrophenol (presented in Figure 3), 2.6-di-*t*-butyl-4-nitrophenol, and 1.12×10^{-4} *M* 3,5-dinitrophenol (Figure 4) are in pure solution. In these solutions the nitrophenols are present entirely as undissociated acid. Beer's law was found to hold for all nitrophenols to at least 7×10^{-5} *M*. For *p*-nitro, 2,6-di-*t*-butyl-4-nitro-, and 3,5-dinitrophenol the absorbance indices at the maximum absorptivity, 306, 318, and 336 mμ, respectively, were 1.1×10^4, 0.98×10^4, and 3.3×10^3.

Spectra of the simple nitrophenolate ions were obtained in 5×10^{-6} to 3×10^{-5} *M* solutions of the tetraethylammonium salts of *p*-nitro-, 2,6-dinitro-, 2,6-di-*t*-butyl-4-nitro-, and 3,5-dinitrophenol. The absorbances at the maximum, at 415 mμ, of 1.89×10^{-5} *M* *p*-nitrophenol in 2×10^{-3} *M* tetrabutylammonium hydroxide (diluted with AN from *ca.* 0.7 *M* stock solution of the hydroxide in 9:1 benzene–methanol)[17] in Figure 3 and of 2.8×10^{-5} *M* 2,6-dinitrophenol in 2×10^{-3} *M* hydroxide, were approximately 2% greater than those observed with 2×10^{-3} *M* tetraethylammonium salts, indicating the presence of approximately 2% of free

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[17] R. Cundiff and P. Markunas, *Anal. Chem.*, 28, 792 (1956).

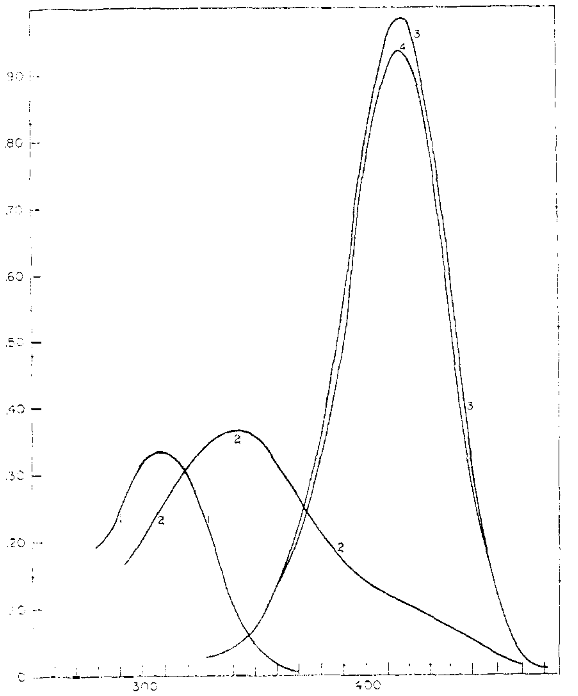

Figure 3. Spectra of 1.85 × 10^{-5} M p-nitrophenol in various media: (1) in pure solution; (2) in 3.10 × 10^{-3} M benzoic acid–3.10 × 10^{-3} M tetraethylammonium benzoate buffer; (3) in 0.070 M tetrabutylammonium hydroxide; and (4) 1.85 × 10^{-5} M tetraethylammonium p-nitrophenolate in pure solution (cell path length 1.73 cm).

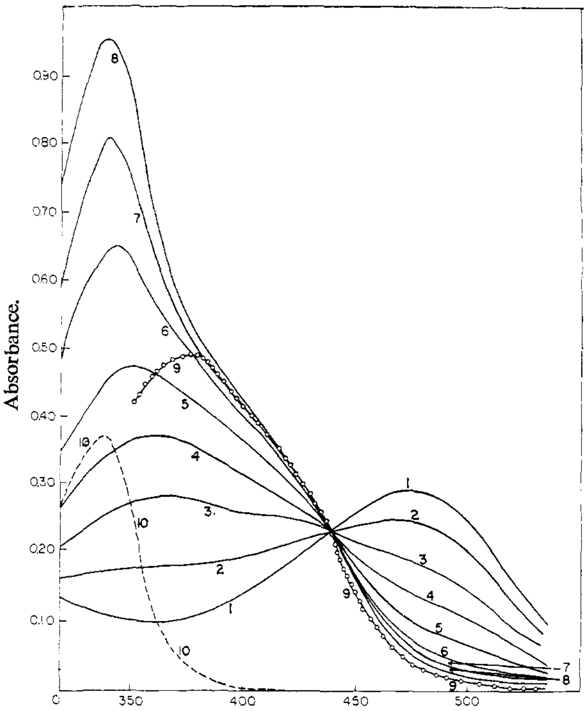

Figure 4. Spectra of 1.12 × 10^{-4} M tetraethylammonium 3,5-dinitrophenolate in the presence of 3,5-dinitrophenol at 25°: (1) 1.12 × 10^{-4} tetraethylammonium 3,5-dinitrophenolate alone; in presence of 3,5-dinitrophenol; (2) 2.05 × 10^{-5} M; (3) 5.14 × 10^{-5} M; (4) 1.23 × 10^{-4} M; (5) 1.84 × 10^{-4} M; (6) 2.36 × 10^{-4} M; (7) 2.87 × 10^{-4} M; (8) 4.10 ×10^{-4} M; and (9) 1.67 × 10^{-3} M; (10) 1.12 × 10^{-4} M 3,5-dinitrophenol alone (1.67 × 10^{-3} M 3,5-dinitrophenol in reference cell in 9, all others acetonitrile; cell path length 1.00 cm).

nitrophenol in the salts. The absorbance indices at the maximum absorptivity for p-nitro-, 2,6-dinitro-, 2,6-di-t-butyl-4-nitro-, and 3,5-dinitrophenolate at 415, 463, 452, and 475 mμ are 3.0 × 10^4, 1.2 × 10^4, 3.7 × 10^4, and 2.35 × 10^3, respectively.

Homoconjugation. A spectral shift of o-nitrophenolate ion in the presence of the free phenol, as a result of homoconjugation, was reported by Coetzee, *et al.*[10] A striking visual effect of homoconjugation is observed with 3,5-dinitrophenolate ion. The simple ion has a red color in AN, while that of the homoconjugate is yellow. Since the spectral maxima of A^- and HA_2^- of the 3,5-dinitrophenolate system are separated by 88 mμ (Figure 4), a reliable estimate of $K^f_{HA_2^-}$ could be made spectrophotometrically. Spectra of 1.12 × 10^{-4} M tetraethylammonium 3,5-dinitrophenolate alone and in the presence of 2.05 × 10^{-5} to 1.67 × 10^{-3} M 3,5-dinitrophenol are reproduced in Figure 4. Spectra of the homoconjugate ion were taken in 1.67 × 10^{-3} M 3,5-dinitrophenol solutions in which $[HA_2^-] \gg [A^-]$. A single maximum was observed at 375 mμ, with an absorbance index of 4.3 × 10^3. Beer's law is obeyed to at least 7 × 10^{-4} M. In mixtures of 3,5-dinitrophenolate and 3,5-dinitrophenol an isosbestic point occurs at 433 mμ, indicating that A^- and HA_2^- are in equilibrium. At 510 and 560 mμ, respectively, the absorbance indices of the homoconjugate and of the p-bromophenol heteroconjugate of 3,5-dinitrophenol are approximately 7 and 4, respectively, thereby allowing the spectrophotometric determination of the simple 3,5-dinitrophenolate ion in presence of its conjugates at these wavelengths. At the above wavelengths the absorbance indices of the 3,5-dinitrophenolate ion are 1.7_5 × 10^3 and 2.4 × 10^2, respectively. In Table IV absorbances at 510 or 560 mμ have been corrected for that of the conjugate following the same precedure as described in a previous publication[7] for correction for the concentration of the alkaline form of p,p'-dimethylaminoazobenzene in salicylate buffers.

Table IV. Spectrophotometric Determination of Conjugation Constants of 3,5-Dinitrophenolate Ion with 3,5-Dinitrophenol (HA) and p-Bromophenol (HR)

C_s, M × 10^4	C_{HA}, M × 10^4	$[A^-]$,[a] M × 10^5	$K^f_{HA_2^-}$ × 10^{-4}
0.195	0.100	1.43	7.6
	0.150	1.22	7.8
	0.250	0.89_5	8.1
	0.400	0.66	7.1
	0.700	0.43	6.5
2.18	1.95	5.6_3	8.7
	2.18	4.9	7.1
	2.36	4.0	9.8
19.3[b]	19.3	16.8	6.1
			Av 7.6 × 10^4

C_s, M × 10^4	C_{HR}, M × 10^4	$[A^-]$,[a] M × 10^6	$K^f_{AHR^-}$ × 10^{-4}
19.1	12.1	118	0.13
19.1	16.6	98	0.13
19.0	21.0	83	0.13
18.9	24.8	71	0.13
18.8	33.9	51	0.13
			Av 1.3 × 10^3

[a] Absorbances measured at 510 mμ for 1.95 × 10^{-5} M salt–3,5-dinitrophenol mxitures; all others at 560 mμ. [b] Cell path length, 1.00 cm for p-bromophenol and 1.93 × 10^{-3} M 3,5-dinitrophenol runs; all others, 10.0-cm cell.

In 1.9×10^{-5} to 1.9×10^{-3} *M* tetraethylammonium 3,5-dinitrophenolate solutions containing from 1.0×10^{-5} to 2×10^{-3} *M* 3,5-dinitrophenol or from 1×10^{-4} to 3.4×10^{-3} *M* *p*-bromophenol, $[A^-]$ was calculated from the absorbance at 510 or 560 mμ. Concentrations of the free phenol, conjugate ions, and the conjugation constant were calculated as described by Coetzee, *et al.*,[10] and $[A^-]$ and $K^f_{HA_2^-}$ are listed in Table IV. Spectra of 4.5×10^{-5} *M* tetraethylammonium 2,6-dinitrophenolate in absence and in presence of 2×10^{-2} *M* parent acid were found to be identical as were those of 2.2×10^{-5} *M* tetraethylammonium 2,6-di-*t*-butyl-4-nitrophenolate in absence and in presence of 2.2×10^{-2} *M* parent acid. Apparently these phenols do not homoconjugate.

Heteroconjugation. Any substance which can heteroconjugate with the 3,5-dinitrophenolate ion obliterates the red color of the solution. In the presence of sufficient *p*-bromophenol (<0.1 *M*), water, or methanol the solutions become yellow.

As a result of heteroconjugation the maximum absorbance of 1×10^{-5} to 2.2×10^{-5} *M* solutions of tetraethylammonium 2,6-di-*t*-butyl-4-nitrophenolate in the presence of 1.0×10^{-2} to 2.1×10^{-2} *M* *p*-bromophenol occurs at 446 mμ with an absorbance index of 2.6×10^4 instead of at 452 mμ (3.7×10^4), respectively, for the pure salt.

Nitrophenols as Acid–Base Indicators. Nitrophenols whose homo- and heteroconjugation constants are negligibly small are useful for the spectrophotometric determination of pa_H. Values of $[HI]/[I^-]$ were determined spectrophotometrically by measuring the absorption of I^- at 463 mμ in solutions of 1.75×10^{-3} *M* tetraethylammonium salicylate containing from 1.05×10^{-5} to 4.7×10^{-3} *M* salicylic acid with 3.58×10^{-5} *M* 2,6-dinitrophenol as indicator and also at 452 mμ in solutions of 7.7×10^{-4} *M* tetraethylammonium benzoate containing from 9.24×10^{-4} to 6.94×10^{-3} *M* benzoic acid with 1.1×10^{-5} *M* 2,6-di-*t*-butyl-4-nitrophenol as indicator. In both systems the absorption of HI and the buffer components are negligible at the wavelengths used. The pa_H of each buffer mixture was calculated according to eq 6, taking pK_{HA} equal to 16.8 and 20.7 (potentiometric values) for salicylic[7] and benzoic[7] acids, respectively, and $K^f_{HA_2^-}$ equal to $1.9 \times 10^{3,7}$ and $4.0 \times 10^{3,7}$ respectively. Plots of pa_H *vs.* log $[HI]/[I^-]f$ are given in Figure 5. Without homoconjugation the slopes of the plots should be 1.00, as compared to the slopes in Figure 5 of 1.00 and 1.06, respectively. Hence, the above nitrophenols function as simple acid–base indicators. When log $[HI]/[I^-]f = 0$ in the plots in Figure 5 (see eq 6a), pK^d_{HA} was found equal to 16.3 and 19.0 for 2,6-dinitro- and 2,6-di-*t*-butyl-4-nitrophenol, respectively. Nitrophenols and their anions which are subject to heteroconjugation are not suitable for pa_H measurements. As an example, we consider the spectral characteristics of *p*-nitrophenol in benzoate buffers. In 6.0×10^{-3} *M* benzoic acid–6.0×10^{-3} *M* tetraethylammonium benzoate buffer (pa_H = 20.3), the maximum in absorbance of 2.0×10^{-5} to 3.5×10^{-5} *M* tetraethylammonium *p*-nitrophenolate occurs at 340 mμ with an absorbance index of 1.2×10^4 instead of at 415 mμ and 3.0×10^4, respectively, for the pure phenolate (Figure 3). The change is due to heteroconjugation between *p*-nitrophenolate and benzoic acid and between *p*-nitrophenol and benzoate.

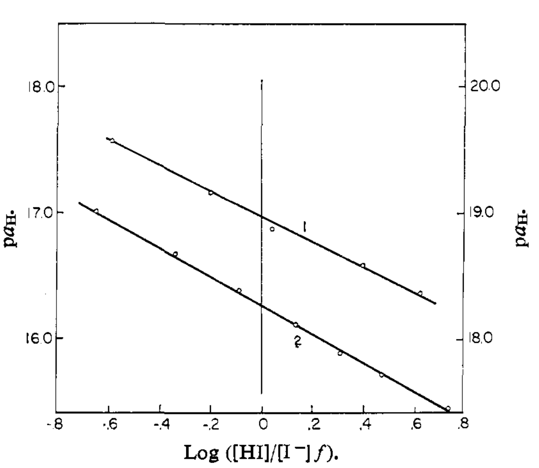

Figure 5. Plots of pa_H *vs.* log ($[HI]/[I^-]f$) of nitrophenols with $K^f_{HA_2^-} = 0$ in buffers of carboxylic acids: (1) 1.1×10^{-5} *M* 2,6-di-*t*-butyl-4-nitrophenol in benzoic acid–tetraethylammonium benzoate mixture at 452 mμ, $C_s = 7.7 \times 10^{-4}$ *M*, $C_a = 9.24 \times 10^{-4}$ to 6.94×10^{-3} *M;* (2) 3.58×10^{-5} *M* 2,6-dinitrophenol in salicylic acid–tetraethylammonium salicylate mixtures at 463 mμ, $C_s = 1.75 \times 10^{-3}$ *M*, $C_a = 1.05 \times 10^{-3}$ to 4.78×10^{-2} *M*. Slopes: (1) 1.00; (2) 1.06. pK^d_{HA}: (1) 19.0; (2) 16.3 (right-hand ordinate for 1 and left-hand ordinate for 2).

Discussion

Qualitatively, few conclusions can be drawn from the shape of conductometric titration of the nitrophenols, with triethylamine (Figure 1) regarding the ionic dissociation constants of the salts formed and of the acids and their homoconjugation constants. Evidently the homoconjugation constants of picric acid (curve 1) and of 2,6-dinitrophenol (curve 6) are negligibly small, and picric acid is a considerably stronger acid than 2,6-dinitrophenol. There is no distinct maximum in the titration curve of 2,4-dinitrophenol (curve 3). The small homoconjugation constant of 100 combined with the relatively large ionic dissociation constant of the triethylammonium salt and the relatively small concentration of acid titrated are responsible for the apparent absence of a maximum. From a comparison of curve 3 for 2,4-dinitrophenol with curve 6 of 2,6-dinitrophenol, one might erroneously conclude that the former is a considerably stronger acid than the latter. Actually the dissociation constants of both acids are of the same order of magnitude (Table VI). Also, from a comparison of curve 5 of *p*-nitrophenol with curve 6, it might be erroneously concluded that *p*-nitrophenol is a stronger acid than 2,6-dinitrophenol. Actually, the dissociation constant of the latter is about 10^5 times greater than that of the former. Even for a qualitative interpretation of most of the curves it is necessary to know the ionic dissociation constants of the triethylammonium salts, the homoconjugation and dissociation constants of the acids, and the ion mobilities.

From Table VI it appears that there is no simple relation between the dissociation constant K^d_{HA} of a nitrophenol in water and in AN. For example, K^d_{HA} in water of *o*-nitrophenol is virtually the same as that of *p*-nitrophenol, but in acetonitrile the constant of the latter is more than ten times as large as that of the *ortho*

Table V. Homo- and Heteroconjugation Constants of Nitrophenols

		Solubility method					Spectrophotometric method	
Phenolate	Potentiometric titration, $K^{f}_{\mathrm{HA_2^-}}$	Cation of sparingly soluble salt, M^+	K_{sp}	K^{d}_{MA}	$K^{f}_{\mathrm{HA_2^-}}$	$K^{f}_{\mathrm{AHR^-}}$	$K^{f}_{\mathrm{AHR^-}}$	$K^{f}_{\mathrm{AHR^-}}$
o-Nitro-	1.0×10^{2}[a]	Na^+	2.1×10^{-8}	3.1×10^{-5}[c]	1.6×10^{2}	2.1×10^{3}	1.0×10^{2}[a]	
p-Nitro-	4.7×10^{3} 1.4×10^{3}[a]	Na^+	3.8×10^{-6}	3.2×10^{-3}	3.3×10^{3}	7.1×10^{2}		
3,5-Dinitro-	4.4×10^{4}[b]	. . .[d]	. . .	. . .	. . .	. . .	7.6×10^{4}	1.3×10^{3}
2,4-Dinitro-	1.0×10^{2}[a]	K^+	9.5×10^{-6}	2.9×10^{-3}	1.2×10^{2}	. . .	. . .	. . .

[a] Value of $K^{f}_{\mathrm{HA_2^-}}$ reported by Coetzee, *et al.*[10] [b] Incomplete dissociation of Et_4NA taken into account in calculation of $K_{\mathrm{HA_2^-}}$; $K_{\mathrm{Et_4NA}} = 1.0 \times 10^{-2}$. [c] Incomplete dissociation of MHA_2 also taken into account; $K^{d}_{\mathrm{MHA_2}} = 7.6 \times 10^{-4}$. [d] $K^{f}_{\mathrm{HA_2^-}}$ too large to estimate from solubility method.

Table VI. pK^{d}_{HA} of Nitrophenols

	Conductometric titration with Et_3N										
		From maximum					Initial portion of titration curve		Potentiometric titration[g]		
Phenol	Concn of phenol, $M \times 10^{2}$	Location of max, $C_{\mathrm{b}m}/C_{\mathrm{a}}$	$[BH^+]_{\mathrm{max}}$, $M \times 10^{3}$	pK^{d}_{BHA}	$-pK^{f}_{\mathrm{BHA}}$	pK^{d}_{HA}	$p(K^{d}_{\mathrm{BHA}} \times K^{f}_{\mathrm{BHA}})$	pK^{d}_{HA}	pK^{d}_{HA}	$(pK^{d}_{\mathrm{HA}})_{\mathrm{w}}$	pK^{d}_{HA}[i]
o-Nitro-									22.0	7.23	15.0
									22.2		
p-Nitro-	1.87	3.0	3.9	3.8	1.3	20.9	2.6_5	21.1	20.7	7.15	13.9
	5.10	1.1	11.3	3.5	1.5	21.4	2.6_5	21.1	21.0		
m-Nitro-[a]	1.87	6.5	13	5.08	0.95	22.6	. . .	. . .	. . .	8.0	14.6
3,5-Dinitro-	0.216	6.0	0.66	4.2_4	1.9	20.8	2.5	20.9	20.5	6.7	14.0
	0.432	3.3	1.2	4.4	1.9	20.9	2.6_5	21.1			
2,4-Dinitro-	1.87			3.2[b]	5.7[c]	. . .	. . .	. . .	16.0[h]	4.0	12.0
	5.05			3.3	5.6						
2,6-Dinitro-	*d*, *e*			3.8_4[f]	3.8[f]	16.0	. . .	. . .	16.4_5	3.5_4	12.8
	1.87			3.66[b]	5.6_6[c]					3.7[j]	
2,6-Di-*t*-butyl-4-nitro	*e*			2.7_4[f]	2.1[f]	19.1	. . .	. . .	19.0	7.2	11.8
Picric acid	1.87			2.35[b]	9.8[c]		. . .	. . .	11.0	0.3	10.7

[a] $K^{f}_{\mathrm{HA_2^-}}$ for *m*-nitrophenol assumed same as for *p*-nitrophenol, *i.e.*, 3×10^{3}. [b] From conductivity at 1000–2000% titrated (Figure 1; see text). [c] Calculated from potentiometric value of pK^{d}_{HA}, $(pK^{d}_{\mathrm{BH^+}})_{\mathrm{AN}} = 18.46$,[10] and from pK^{d}_{BHA} in column 5 (see text). [d] N,N-Dimethylbenzylamine used as titrant base. [e] Equimolar mixtures of nitrophenol and base taken; concentration range 2×10^{-4} to 1×10^{-2} *M*. [f] Calculated from $1/\Lambda$ *vs.* $C\Lambda$ plot (see text). [g] pa_{H} mixtures of nitrophenol and its tetraethylammonium salt. [h] Value reported by Coetzee, *et al.*[10] [i] $(pK^{d}_{\mathrm{HA}})_{\mathrm{AN}} - (pK^{d}_{\mathrm{HA}})_{\mathrm{w}}$. [j] Value reported by G. Kortüm and K. Koch, *Z. Elektrochem.*, **69**, 677 (1965).

compound. One reason is that in AN the relative stability (related to water) of *o*-nitrophenol is greater than that of the *para* compound. In water the solubilities of the *ortho*[18] and *para*[19] phenols are 0.01 and 0.11 *M*, respectively, while the values in AN as determined in this laboratory are 6.8 and 5.3 *M*, respectively; hence in the latter solvent the activities are of the same order of magnitude. The relatively greater stability in AN of the *ortho* acid (due at least in part to the intramolecular hydrogen bonding) tends to make it a weaker acid than the *para* phenol in AN. Another factor which contributes to the magnitude of K^{d}_{HA} is the stability of the anion. From the results of the experimental work in this paper it is clear that the *p*-nitrophenolate in AN is more stable than the *ortho* ion. The dissociation constant of sodium *p*-nitrophenolate is 100 times that of the *ortho* salt (Table V). Because of the resonance between the phenolate oxygen and the oxygens in the neighboring nitro group in the *ortho* ion, the electrostatic force between the sodium and the anion is much greater than in the *para* ion. Resonance through the ring in the *para* ion favors a quinoid structure[20] and tends to stabilize the ion. Owing to the symmetrical location of the nitro groups in the *ortho* and *para* positions, the resonance effect is very pronounced in the picrate ion; consequently the dissociation constants of sodium and triethylammoniun picrates are much greater than that of the *p*-nitrophenolate.

Also, the dissociation constant of triethylammonium 2,4-dinitrophenolate is of the same order of magnitude, but twice as large as that of the *p*-nitrophenolate. In both salts the negative charge is more delocalized than in the *o*-nitrophenolate salt.[21]

Roughly paralleling the dissociation constants are the solubility products of sodium *o*- and *p*-nitrophenolate, the value for the *para* salt being 200 times as large as that for the *ortho* salt. In water the solubilities of the *ortho* (present investigation) and *para*[22] salts are 1.47 and 0.35 *M*, respectively, again indicating the greater stability in AN of the *para* ion as compared to the *ortho* ion.

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In spite of the greater stability of the *p*- than of the *o*-nitrophenolate ion in AN, the homoconjugation constant of *p*-nitrophenol is 20 times as large as that of *o*-nitrophenol (Table V). This is due to the intramolecular hydrogen bonding in *o*-nitrophenol. In line with the greater stability of the *p*-nitrophenolate ion it is found that the heteroconjugation constant with *p*-bromophenol of *o*-nitrophenolate is three times as large as that of the *para* ion (Table V). The heteroconjugation constant in AN of the stable picrate ion is more than $^1/_{1000}$th as large as that of *o*-nitrophenolate (Table III).

The homoconjugation constant of 2,6-di-*t*-butyl-4-nitrophenol is too small to be measured. This is caused by the blocking effect of the 2,6-di-*t*-butyl groups which hinder the homoconjugation. This acid has the same dissociation constant in water as *o*-nitrophenol, but in AN the constant of the blocked phenol is 1000 times as large as that of *o*-nitrophenol. The steric hindrance effect on homoconjugation of two methyl groups adjacent to the OH group has been observed in the conductometric titration of 2,4,6-trimethylphenol with sodium ethoxide in pyridine.[23]

Of the nitrophenols investigated, 2,6-dinitro- and 2,6-di-*t*-butyl-4-nitrophenol and picric acid have negligibly small homoconjugation constants and their anions negligibly small heteroconjugation constants. These three nitrophenols are suitable for the spectrophotometric determination of pa_H in AN.

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A Nuclear Magnetic Resonance Method for the Determination of Relative Acidities of Weak Acids in Liquid Ammonia

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Abstract: An nmr method for the establishment of a scale of acidities of weak acids in liquid ammonia is described. A p*K* range of 6.6 units has been covered using substituted anilines. The relative values fit a Hammett σ_p plot with $\rho = -5.3$. A new σ value for 4-fluorine of -0.05 is proposed for these systems.

In recent years there has been an increasing interest in strongly basic systems and in the determination of the acidities of very weak acids.[1-5] The acidities studied cover an enormous range of about 30 p*K* units, and no one solvent system has been used in their determination. In general, as an acid becomes weaker, the solvent system must become more basic in order to achieve a measurable ionization. The solvent systems used include aqueous hydroxide, pyridine,[1] dimethyl sulfoxide–alcohol mixtures,[2] cyclohexylamine,[3] and liquid ammonia,[5,6] to mention just a few. The principal disadvantage of most of these solvent systems is that they only cover a limited range of 5 or 6 pH units.[1] However, the high basicity and low ionization constant of liquid ammonia (10^{-27} at 25°)[7] indicate that this would be a suitable solvent in which to study acid dissociation. Recently a study of acid dissociation in liquid ammonia has been reported by Lagowski and co-workers,[6] who used a spectrophotometric technique.

The high volatility of ammonia makes it necessary either to work at low temperatures, as did Lagowski,[6] or to study the solutions under pressure, as we have chosen to do. Nmr is ideally suited for determining the concentrations of protonic species in sealed tubes, and we have used this technique to determine the relative acidities of some anilines covering a range of 6.6 p*K* units. Evidence will be presented to show that this method can be used to extend this range by at least 5 p*K* units at the weaker end of the scale. However, extension to the more acidic region where some direct measurements have been made[6] seems unlikely because of the tendency of the stronger acids to form complexes.[8]

The principal disadvantages of the spectrophotometric method are the complicated apparatus needed for the determinations and the fact that amide ion absorbs strongly at 350 mμ and so obscures bands in this region.[6] Solvent absorption has also been found to be troublesome in the determination of the acidities of anilines in dimethyl sulfoxide solutions.[9]

Experimental Section

Chemicals. All of the substituted anilines except 4-cyanoaniline were obtained commercially; 4-cyanoaniline was kindly donated by Dr. R. Stewart of the University of British Columbia. The anilines were purified by recrystallization from suitable solvents, or by drying followed by distillation, until the literature melting or boiling points were obtained.

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