Acidity in Nonaqueous Solvents. II. Picolinium Ions in Dimethylformamide Solution[1,2]

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Abstract: Free energies, enthalpies, and entropies of ionization for a series of α-substituted 4-picolinium ions in anhydrous dimethylformamide solution have been determined by the differential potentiometric method. The data are compared to corresponding data in methanol solution which have been previously reported. Use of a calibrated electrode system has allowed us to measure the acidity constants for several phenols in dimethylformamide also. The data obtained for these acids are in poor agreement with previous data, and attention is called to the large errors that may result from measurements made in solvent which has not been rigorously purified.

Dimethylformamide has been extensively used as a solvent in various fields of chemistry. The moderately high dielectric constant, 36.7 at 25°,[3] and aprotic nature make it particularly useful for acid–base studies,[4] and for a wide range of organic reactions.[5]

The increased interest in dipolar aprotic solvents, of which dimethylformamide is an example, has strongly focused attention on the question of the nature of solvent effects on reactivities in solution. This question is of fundamental importance in nearly all fields of chemistry. Although a great deal of data have been obtained in nonaqueous solvents in attempts to partially answer this question, virtually nothing is known about enthalpies and entropies in such solvents. Since this type of data has played such an important role in discussions of aqueous solutions,[6] we have directed our attention to obtaining thermodynamic data for the ionizations of several different types of acids in pure nonaqueous solvents.

In the first paper of this series,[1a] we reported data for the ionizations of a series of picolinium ions in anhydrous methanol. The present paper concerns measurements on the same series of acids in anhydrous dimethylformamide solution. Data for a series of carboxylic acids in methanol are reported in an accompanying paper.[7]

We have also carried out some preliminary measurements on several phenols in dimethylformamide at a single temperature, and report those measurements now.

Results

Measurements of ionization constants in solvents having lower dielectric constants than water are difficult primarily because of the low concentrations which must be employed to avoid ion pairing and acid–conjugate base association.[8]

In the present study, we have employed concentrations of approximately 10^{-3} M of the picolines, and less than 10^{-4} M of the phenoxides. These low concentrations require solvent of extremely high purity. The purification method detailed in the Experimental Section produces a solvent which contains less than 5×10^{-6} M acidic or basic impurities, and less than 10 ppm of water. Since dimethylformamide hydrolyzes at a relatively fast rate in the presence of acids or bases, we have been particularly careful to avoid contamination of the solvent by atmospheric moisture. All of the present experiments have been carried out under a purified nitrogen or argon atmosphere.

The titrations reported below have been carried out with dilute solutions of picric acid in dimethylformamide. Spectrophotometric studies of the acid solutions have shown that picric acid is completely dissociated at concentrations up to 10^{-3} M. Electrode calibrations with picric acid have indicated complete dissociation at concentrations of 10^{-2} M. Some preliminary measurements indicate that fluorosulfonic acid can also serve as the strong acid in such studies as the present, but we prefer picric acid because of the greater ease in purification and preparation of solutions.

Modified glass and calomel electrodes have been used in this study. The theoretical behavior of the electrodes has been shown by several methods. The response of the electrode system to dilute solutions of picric acid is linear in the log of the concentration of acid with the theoretical slope of 59 mv, and we have obtained linear plots with the theoretical slope for the quantity $\log (P/(1 - P))$ *vs.* mv, where P is the fraction of base titrated, in the titration of a large number of bases. Even more convincing, very good agreement in measurements of the ionization constant of 4-hydroxymethylpyridine by partial neutralization, employing an electrode calibrated with dilute solutions of picric acid, and by the differential potentiometric method, which does not depend on the electrode calibration, has been obtained. Values determined by the two methods at two different temperatures are shown in Table I.

(1) (a) For part I of this series, see: C. D. Ritchie and P. D. Heffley, *J. Am. Chem. Soc.*, **87**, 5402 (1965). (b) Taken in part from a thesis submitted to the Graduate School, State University of New York at Buffalo, by G. H. Megerle in partial fulfillment of the requirements for the Ph.D. degree, Feb 1967.

(2) This work was supported by Grant No. GP-2635 from the National Science Foundation.

(3) DMF Product Information Bulletin, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., 1962.

(4) G. D. Guerin and J. R. Lambling, *Bull. Soc. Chim. France*, 3277 (1964).

(5) R. S. Kittila, "A Review of Catalytic and Synthetic Applications for DMF and DMAC," E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., 1962.

(6) *Cf.* R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter V.

(7) C. D. Ritchie and G. H. Megerle, *J. Am. Chem. Soc.*, **89**, 1452 (1967).

(8) J. Coetzee and G. Padmanabhan, *J. Phys. Chem.*, **66**, 1708 (1962).

Table I. Agreement of Values Obtained for the pK of 4-Hydroxymethylpyridine by Two Methods

Temp, °C	pK Partial neutralization	pK Differential potent
15.0	4.573; 4.545	4.537; 4.541
25.0	4.238	4.243; 4.223

In the use of the partial neutralization method, it is necessary to calibrate the electrode system immediately preceding or following the titration since the modified calomel electrode deteriorates slowly. (We have not investigated the cause of deterioration.) The differential potentiometric method, which depends only on reversible electrode behavior in the end-point region, avoids this problem and is, therefore, the preferred method where both techniques are applicable.

The differential potentiometric method was employed in measurements of ionization constants for all of the picolines except those with the α-cyano and ammonio substituents. The latter two compounds were studied by the partial neutralization method because of the small slope of the titration curves at the end points.

The data obtained for the picolinium ions are summarized in Table II. All values are referred to a standard state of *ca.* 10^{-3} M in dimethylformamide solution.

Table II. Thermodynamic Data for the Reaction $4\text{-}XCH_2C_5N_4NH^+ \rightleftarrows 4\text{-}XCH_2C_5H_4N + H^+$ in Dimethylformamide Solution[a]

X	pK 15.0°	pK 35.0°	$\Delta G°$, 25.0° kcal/mole	$\Delta H°$, 25.0° kcal/mole	$\Delta S°$, eu 25.0°
H	4.963	4.819	6.896	2.93	−13.3
CH_3	4.981	4.831	6.917	3.05	−13.0
C_2H_5	5.009	4.831	6.937	3.62	−11.1
OH	4.528	4.235	6.178	5.96	−7.3
C_6H_5	4.768	4.625	6.622	2.91	−12.5
CN	3.609	3.571	5.062	0.77	−14.4
NH_3^+	3.901	3.617	5.300	5.78	+1.60

[a] The standard state is defined as infinite dilution in dimethylformamide solution.

Under the assumptions of Debye–Hückel theory, no correction is necessary for reference to infinitely dilute solution in dimethylformamide.

Duplicate determinations of the ionization constants by the differential potentiometric method show maximum deviations of 0.02 pK unit. From this, we estimate an uncertainty of *ca.* ± 0.5 kcal/mole in the values reported for $\Delta H°$ and ±1.5 eu for $\Delta S°$. Since most of the ionization constants are in the ideal range for the differential method, the accuracy should be comparable to the precision.

In the titrations of the phenoxides with picric acid in dimethylformamide, a "break" in the titration curves of about 500 mv (*ca.* 8.5 pH units) is observed at the end point. This extremely sharp break precludes the use of the differential method, and we have had to rely on the partial neutralization method. The maximum deviations in duplicate determinations of the pK values of the phenols was 0.05 for the chloro- and nitro-substituted phenols. The *m*-trifluoromethylphenol showed deviations as large as 0.1 pK unit. The data obtained at 25.0° for these compounds are shown in Table III.

Table III. pK Values for XC_6H_4OH in Dimethylformamide at 25.0°

X	*p*-NO_2	*m*-NO_2	*m*-CF_3	*m*-Cl	*p*-Cl
pK	12.34	15.43	15.7	16.29	16.78

We have not corrected these values for ionic strength since the corrections are no larger than the experimental uncertainty.

The pK of *p*-nitrophenol in dimethylformamide solvent has been reported as 10.9[9] and as 11.8[10] by other workers. The value of 10.9 obtained by Parker in a spectrophotometric study depends on a measurement of the extent of dissociation of 2,4-dinitrophenol in dilute sulfuric acid solutions and an overlapping of indicators. Measurements of extent of dissociation of this sort have caused a great deal of trouble in acetonitrile solvent,[11] and the problem of gross errors owing to small amounts of solvent impurities is equally likely in dimethylformamide. Juillard, who reported the value of 11.81, was aware of complications from acid–conjugate base association at the concentrations which he employed in the measurements.[10] This type of association would cause the measured pK to be lower than the true value.

In attempts to titrate more basic phenoxides than those reported in Table III, we encountered apparent irreversible behavior of the electrodes. We can estimate, however, that phenol has a pK of >18.0. This value is much higher than previously estimated.[9]

Discussion

It is interesting to compare the data in Table II for the thermodynamic parameters in dimethylformamide to the previously reported data for the same compounds in methanol.[1a] Three general facts are immediately obvious: (1) the pK values are about 1.4 units *lower* in dimethylformamide, (2) the entropies of ionization are *more negative* in dimethylformamide, (3) the enthalpies of ionization are *more positive in methanol.*

The lower pK values in dimethylformamide are probably due primarily to the greater basicity of dimethylformamide than that of methanol. Arnett[12] has reported pK values of the protonated solvents as −2.2 for methanol and −0.01 for dimethylformamide. Thus, the effect of basicity alone would be expected to change the pK values in dimethylformamide to 2.2 units lower than those in methanol. A naive view including the concentration of solvent would correct this figure to 1.9 units.

The greater basicity of dimethylformamide probably also causes a stronger hydrogen bond between the picolinium ions and solvent than is present in methanol. Another factor contributing to the difference in pK values in the two solvents is hydrogen bonding to the picolines by solvent. This latter type of interaction probably occurs in methanol, but, of course, would not be expected in dimethylformamide. Both types of hydrogen bonding would tend to suppress the ionization in dimethylformamide relative to that in methanol. In a given solution, hydrogen bonding of either type

(9) A. J. Parker, *et al.*, *J. Am. Chem. Soc.*, **88**, 1911 (1966).
(10) J. Juillard, *Compt. Rend.*, **260**, 1923 (1965).
(11) I. M. Kolthoff and M. K. Chantooni, *J. Am. Chem. Soc.*, **87**, 4428 (1965).
(12) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

would be expected to decrease the differences in the pK values of any two members of the series (*i.e.*, both types of hydrogen bonding tend to make reactants and products more alike in charge distribution). Since the difference in pK between the α-H and α-cyano compound is nearly the same in both solvents, the assumption of greater hydrogen bonding of the conjugate acid in dimethylformamide is necessary to counteract the effect of hydrogen bonding of methanol to the base.

The near constant values for the entropies of ionization (with the exceptions of the α-hydroxy- and ammonio-substituted compounds)[13] and the considerably more negative values than those found in methanol are worthy of note. In methanol solution, the entropies of ionization varied from +1.0 eu for the α-CN compound to −5.2 eu for 4-picolinium ion. In dimethylformamide, the entropies are all close to −13.0 eu. As we have pointed out earlier,[14] variations in entropy among a series such as the present are expected in cases where weak solvent–solute interactions are involved. The most likely source of these weak interactions in the present case is hydrogen bonding of solvent to the conjugate base. Hydrogen bonding of conjugate acid to solvent is expected to be considerably stronger, and the entropy of interaction should show less variation over the series. If these considerations are correct, the large negative values of the entropy in dimethylformamide must be due to an extremely large negative entropy of solvation of the proton. This large negative entropy should be associated with a large negative enthalpy, which can account for the smaller values of enthalpies of ionization in dimethylformamide than those in methanol.

It will be interesting to see how these ideas apply to the thermodynamics of ionization of carboxylic acids in the two solvents. In these cases, the strongest hydrogen bonding is expected to occur between the conjugate base and the solvent. We would predict that carboxylic acids in dimethylformamide should show more negative entropies of ionization than do the picolinium ions, and that the entropies of ionization for a similar series, such as benzoic acids, will show some variation among the series. Furthermore the entropies of ionization in dimethylformamide should *not* be much more than those in methanol, and may be even less negative.

In the above discussion, we have deferred the question of the data for the α-hydroxy- and ammonio-substituted compounds to the accompanying paper.[13] Both substituents have commonly shown deviations in Hammett-type correlations. We believe that these deviations are due to solvent–substituent interactions. The unusual behavior of the entropy of ionization in the present study of these compounds is also found in methanol solution. In aqueous solution, the entropy of ionization of 1,2-diammonioethane has been reported to be 10.9 eu more positive than that for the monoprotonated diamine.[15]

The ionization of phenols would also provide an interesting series with which to test some of the above ideas. Unfortunately we have not yet been able to attain the precision needed for a study of entropy and enthalpy of ionization for the phenols in dimethylformamide. Some conclusions may, however, be drawn from the pK values reported in Table III. These values are much greater than the corresponding values in water, although the pK of *p*-nitrophenol is only 1.1 units greater than the value found in methanol solution.[7,9] The differences of pK's among the series are much greater than those found in water also. These observations are most reasonable, explained in terms of hydrogen bonding of the hydroxylic solvent to the phenoxides being the primary contributing factor.[9] It will be interesting to obtain the pK values in methanol, a solvent of similar dielectric properties to dimethylformamide, in order to more fully understand this factor.[16]

As more data are obtained for various acid types in different solvents, we hope that interpretations can become quantitative. Unfortunately, accurate data are very difficult to obtain in nonaqueous solvents, and it will be some time yet before confidence can be gained in even semiquantitative interpretations.

Experimental Section

Materials. The α-substituted, 4-picolines were available in pure form from a previous study.[1a] The compounds were stored in an argon atmosphere at −20°. The ammonio-substituted compound was generated *in situ* during each measurement by the addition of an equivalent amount of the titrating acid to 4-aminomethylpyridine.

Baker and Adamson picric acid was recrystallized twice from acetone and dried under vacuum at 55°. The acid was then sublimed on the steam bath and stored under dry nitrogen or argon (mp 122°, lit.[17] 121°).

Recrystallized picric acid was titrated to a potentiometric end point in distilled water with standard sodium hydroxide solution. The solvent was evaporated under vacuum, and the resulting sodium picrate was recrystallized from 95% ethanol. The salt was vacuum dried at 40° and stored under nitrogen.

Linde Molecular Sieves, type AW-500, in $^1/_{16}$-in. pellet form, were washed with distilled water and reactivated before use.

Mallinckrodt USP analytical reagent phenol was vacuum sublimed and stored under nitrogen (mp 40.9°, lit.[17] 41.0°). The salt was prepared from the sublimed phenol by potentiometric titration with potassium hydroxide in ethanol solution, followed by solvent evaporation under vacuum and recrystallization from dioxane. The salt was dried in a vacuum desiccator for 48 hr over 3A Molecular Sieves and stored under nitrogen.

Pierce Chemical Co. *m*-trifluoromethylphenol was vacuum distilled at 65°, 4.9-mm pressure, and stored under nitrogen. The phenol was titrated in distilled water with potassium hydroxide using an external phenol red indicator followed by evaporation of solvent. The potassium salt was dried at 53° over phosphorus pentoxide for 24 hr. Separate samples of *ca.* 2 mg were sealed in vacuum capillary tubes.

Eastman White Label *m*-nitrophenol was vacuum sublimed at room temperature and stored under nitrogen (mp 96.0°, lit.[17] mp 96.0°). The phenol was titrated with potassium hydroxide to a potentiometric end point in distilled water. After evaporation of the solvent, the salt was vacuum dried for 48 hr at 53° over anhydrous magnesium perchlorate and stored under nitrogen.

Fisher reagent grade *p*-nitrophenol was recrystallized from distilled water, dried over AW-500 Molecular Sieves, and sublimed at 100° (mp 114.1°, lit.[17] mp 114.0°). The preparation and drying of the potassium salt followed the procedure given above for *m*-nitrophenol.

Eastman *m*-chlorophenol was fractionally frozen twice and stored under nitrogen. The potassium salt was prepared by titra-

(13) We believe that the unusual values of entropy of ionization for these compounds have a different source than the weak solvent–solute interactions discussed here. This source is discussed in ref 7.

(14) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 323 (1964).

(15) Reference 6, p 65.

(16) Reference 9 contains a discussion of the influence of hydrogen bonding on the pK values of a variety of acids.

(17) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio.

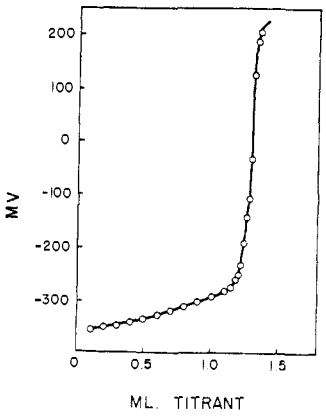

Figure 1. Titration of *m*-nitrophenoxide with picric acid in anhydrous dimethylformamide. Data from Table V.

tion of the phenol in distilled water using an external phenol red indicator. After vacuum evaporation of the solvent, the salt was dried under vacuum over phosphorus pentoxide and stored under nitrogen.

Eastman White Label *p*-chlorophenol was vacuum sublimed at room temperature and stored under nitrogen (mp 32.5°, lit. mp 32.8°). The potassium salt was prepared and dried in the same manner as that of *m*-chlorophenol. Separate samples of *ca.* 2 mg were sealed in vacuum capillary tubes.

Baker Analyzed reagent grade dimethylformamide was treated with Linde AW-500 Molecular Sieves for a minimum of 48 hr. This type of sieve was found to impart the least amount of additional impurities to the solvent and yet effectively dry it. The sieve drying efficiency (Table IV) was tested with 90 g of Molecular Sieve in 400 ml of solvent.

Table IV. Sieve Drying Efficiency

Drying time, hr	0	2	6	10	27
Water anal., ppm	160	152	56	32	<18

The sieve-dried solvent was purified by vacuum distillation from phosphorus pentoxide. The distillation apparatus consisted of a 3-necked, 600-ml flask fitted with a 20-cm Vigreux column, condenser, vacuum adapter, and receiving flask fitted with a capillary pressure bleed. A slurry of 25–30 g of phosphorus pentoxide and 400 ml of dimethylformamide was placed in the nitrogen-flushed distilling flask and stirred by means of a Teflon-covered magnetic stirrer. The pressure in the apparatus was maintained constant between 2.5 and 8.0 mm by means of the nitrogen capillary bleed in the receiving flask. This corresponds to a distillation temperature of 33–49°. The first fraction of the distillate, containing about 10^{-5} *M* basic impurities and a volume of 75–100 ml, was discarded. The second fraction of 75–200 ml was collected and stored under a nitrogen atmosphere at −20° in a freezer.

The purified solvent contains no detectable water and less than 4×10^{-6} *M* acidic or basic impurities. The purified solvent was used within 48 hr following preparation. The specific conductivity of a batch of this solvent was 3×10^{-7} mho-cm^{-1} at 25.0°.

Apparatus. All water analyses reported have been determined on 10-ml samples utilizing a Beckman Model KF3 Aquameter. Water determinations in solids utilized no less than 250-mg samples. The lower limit of reliable detectability was about 10 ppm.

Melting points were determined by use of a Mel-temp apparatus. All melting points are corrected, and boiling points uncorrected.

A Bronwill constant-temperature circulator or a Forma Scientific Refrigerated bath were employed in the constant-temperature work.

Visible and ultraviolet spectral data were obtained on a Cary Model 14 recording spectrophotometer. High purity nitrogen or argon gas was dried before use by passage through a train containing 3A Molecular Sieves and magnesium perchlorate.

Conductivity data were obtained on a Jones AC Conductivity Bridge, Leeds and Northrup No. 1631098, equipped with oscilloscopic output.

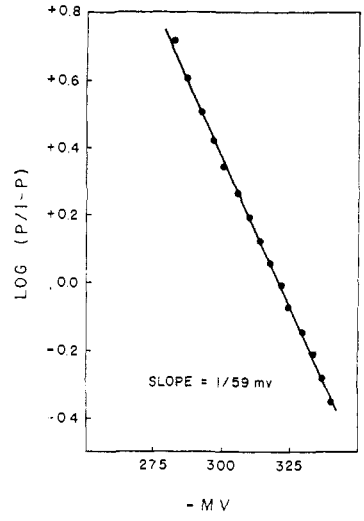

Figure 2. Plot illustrating the theoretical response of the glass electrode in the titration of *m*-nitrophenoxide with picric acid. Data from Table VI.

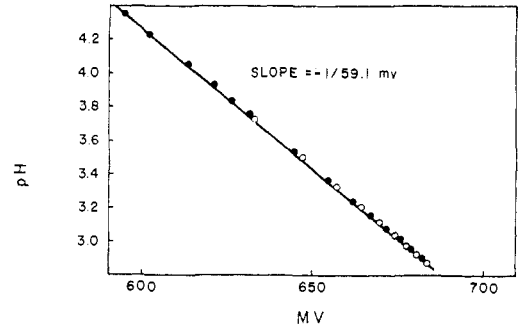

Figure 3. Calibration of the glass electrode with dilute solutions of picric acid in dimethylformamide. Data from Table VII.

Weighings of oxygen-sensitive or hygroscopic samples up to 1 g were made in an argon- or nitrogen-filled glove bag on a Cahn Gram Electrobalance. Liquid samples were weighed in small Teflon boats designed for use with the electrobalance. A Mettler Type H6 balance was used to weigh samples of 0.1 g or larger if the samples were not sensitive to oxygen or moisture.

Picric Acid in Dimethylformamide. Picric acid was shown to be completely dissociated in purified dimethylformamide to a concentration of about 10^{-3} *M* by spectrophotometric analysis. Calibrations of the electrode system described below indicated complete dissociation of the picric acid at concentrations of 10^{-2} *M* or greater. Solutions of the acid were prepared under a nitrogen atmosphere.

Electrode System. A Beckman 8990-90 glass electrode was dismantled and etched in a 20% aqueous solution of ammonium bifluoride for 3 min. The internal reference solution was replaced with a dimethylformamide solution containing *ca.* 10^{-3} *M* silver perchlorate, picric acid, and tetraethylammonium perchlorate. A silver wire internal reference element completed the electrode which was sealed with a rubber serum bottle cap.

A Leeds and Northrup Model 16251 calomel electrode was fitted with a side arm and filled with a saturated solution of potassium chloride in dimethylformamide.[18] This electrode was used with the glass electrode described above, or with a modified Beckman Type E-2 glass electrode. This latter electrode was prepared by replacing the internal aqueous buffer in the commercial electrode with elemental mercury.

The electrodes were stored in either pure solvent or in solvent containing about 10^{-3} *M* picric acid.

Determination of p*K*. The p*K* values of the various picolinium ions were determined in dimethylformamide by means of the differential potentiometric method.[19] Titrations of *ca.* 10^{-3} *M*

(18) M. Breant and N. VanKiet, *Bull. Soc. Chim. France*, 3638 (1965).
(19) E. Grunwald, *J. Am. Chem. Soc.*, 73, 4934 (1951).

Table V. Data for the Titration of Potassium 3-Nitrophenoxide in Dimethylformamide Solution[a]

ml	−mv	ml	−mv
0.10	354.6	1.05	287.1
0.20	350.9	1.10	282.1
0.30	346.6	1.16	268.9
0.35	344.4	1.18	260.4
0.40	339.0	1.20	250.4
0.45	336.2	1.22	231.8
0.50	333.4	1.24	191.0
0.55	329.5	1.26	143.4
0.60	326.2	1.27	124.2
0.65	321.8	1.28	107.0
0.70	317.3	1.29	77.6
0.75	314.2	1.30	32.7
0.80	310.4	1.31	−63.4
0.85	305.0	1.32	−123.4
0.90	300.7	1.33	−163.4
0.95	296.3	1.34	−187.5
1.00	292.1	1.35	−207.5

[a] These data are plotted in Figure 1.

Table VI. Calculation of pK_a from the Data in Table V[a]

ml	−mv	Log $(P/(1-P))$	pK_a
0.40	339.0	−0.357	15.42
0.45	336.2	−0.281	15.44
0.50	333.4	−0.210	15.40
0.55	329.5	−0.141	15.41
0.60	326.2	−0.073	15.41
0.65	321.8	−0.007	15.40
0.70	317.3	0.060	15.39
0.75	314.2	0.127	15.40
0.80	310.4	0.196	15.41
0.85	305.0	0.267	15.39
0.90	300.7	0.341	15.39
0.95	296.3	0.421	15.39
1.00	292.1	0.509	15.41
1.05	287.1	0.606	15.42

[a] A plot of mv *vs.* log $(P/(1-P))$ of these data is presented in Figure 2.

Table VII. Data for the Calibration of the Beckman Modified Glass and Leeds and Northrup Calomel Electrodes in Dimethylformamide[a]

ml	mv[b]	pH[b]	mv[c]	pH[c]
0.15	594.8	4.357		
0.20	602.4	4.232		
0.30	613.6	4.057		
0.40	621.1	3.933		
0.50	626.3	3.837		
0.60	631.9	3.759	633.2	3.719
1.00	644.5	3.540	647.0	3.500
1.50	654.7	3.368	657.2	3.329
2.00	661.8	3.248	664.5	3.208
2.50	667.3	3.155	669.7	3.115
3.00	671.7	3.080	674.4	3.040
3.50	675.6	3.017	677.8	2.977
4.00	678.8	2.963	680.9	2.923
4.50	681.7	2.916	683.6	2.876

[a] These data are shown plotted in Figure 3. [b] Determined with 1.470×10^{-2} *N* picric acid. [c] Determined with 1.611×10^{-2} *N* picric acid.

solutions of the picolines with 10^{-2} *M* solutions of picric acid utilized a precision micrometer microburet. All titrations were carried out under a dry argon atmosphere.

The p*K* values of the phenols were determined from partial neutralization data. The solutions were of 25–50-ml volume. Samples sealed in glass tubes were not weighed, but concentrations were calculated from the observed end points in the titrations. The tubes were broken in a clean titration vessel, and the solvent was added under a nitrogen atmosphere. Titration was then carried out with a solution of picric acid in dimethylformamide.

Data for the titration of *m*-nitrophenoxide and for the calculation of the p*K* are given in Tables V and VI. The data are shown graphically in Figures 1 and 2.

Electrode calibrations were determined after each titration. This was accomplished by the titration of purified solvent with a solution of picric acid. Data for a typical calibration are shown in Table VII, and graphically in Figure 3.

In all titrations, the electrodes reached stable potentials within 5 min of an incremental addition of titrant. Calibrations were virtually identical for up to 24 hr.

All potential readings were obtained with a Beckman Model 1019 research pH meter.