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THE IONIZATION CONSTANTS OF SOME SECONDARY AMINES IN METHANOL

by

Charles Louis Mehltretter

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Plant Chemistry

Approved

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In charge of Major Work

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INTRODUCTION AND HISTORICAL

It seems probable that the relative positivity or negativity of organic radicals can best be explained by the electron theory of valency and can be interpreted as the ability of the substituent radicals to share electrons with or transfer them to or from the atoms to which they are linked causing a change in the electronic configuration of the molecule which affects its ionization.

This influence of substituents on the magnitude of the ionization constants of organic acids was first observed by Ostwald (1), who found that the ionization constant changed by a definite factor when the substituent was placed in a certain position relative to the acid hydrogen of carboxylic acids. Wegscheider (2) investigated this "factor law" further and summarized the available data from which he compiled tables of factors representing the effect of the various substituents in the various positions on the ionization constants of organic acids. This "factor law" of Ostwald's, or the "Ostwald-Wegscheider Rule" as it is sometimes called, has been the basis of much experimental work and was used early by Walker (3) for determining the effect of introducing radicals into dibasic acids and esters and later by Chandler (4), Adams (5), and

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(1) Ostwald, J. prakt. Chem., 31, 433 (1885); Z. physik. Chem., 3, 170, 241 (1889).
(2) Wegscheider, Monatsh., 23, 287 (1902).
(3) Walker, J. Chem. Soc., 61, 715 (1892).
(4) Chandler, J. Am. Chem. Soc., 30, 694-713 (1908).
(5) Adams, J. Am. Chem. Soc., 38, 1503-10 (1916).

Bjerrum (6) who were interested in the ionization of dibasic acids. More recently Eucken (7) has treated the "Ostwald Law" from the point of view of dipole moments and has drawn the important conclusion that optical rotation, dissociation constants and Raman frequencies must be influenced in the same general way by substitution.

In an attempt to correlate electronegativity of organic radicals with degree of ionization of their compounds, Hixon and Johns (8) have demonstrated a mathematical relationship which places each organic radical attached to the same polar grouping in a definite position in a polarity series. The substituent groups, however, must not have polar linkages attached to them, nor must they rearrange to isomeric forms. Also, the electron-sharing ability appears to be dependent upon the mass and the potential of the atoms and the spatial configuration of the molecule. The latter is illustrated by the difference in ionization constants for maleic and fumaric acids and for the cis-trans crotonic acids (9).

The authors mentioned above (10) extended the electron-sharing ability concept to the organic derivatives of mercury and have investigated the equilibrium

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(6) Bjerrum, Z. physik. Chem., 106, 219 (1923).
(7) Eucken, Z. angew. Chem., 45, 202 (1932).
(8) Hixon and Johns, J. Am. Chem. Soc., 49, 1786 (1927).
(9) Ostwald, Z. physik. Chem., 3, 380 (1889).
(10) Johns with Hixon, J. Phys. Chem., 34, 2226 (1930).

$$2RHgX \rightleftharpoons R_2Hg + HgX_2$$

whereby they were able to place the organic radicals in positions in an electronegative series coinciding with the positions held by the same radicals in RNH_2 and RCOOH.

Allison and Hixon (11) observed that the polarity of the organic radicals varies from a range more positive than hydrogen to one more negative than chlorine. It has been found also that there are aliphatic radicals that are more negative as well as more positive than the typical aromatic groups as shown by the fact that in the order of relative electron-sharing ability the aromatic groups lie between the most positive and most negative aliphatic groups.

Osburn (12) and Ware (13) investigated the relationship of the electron-sharing ability of the substituted organic radicals attached to the arsonic acid grouping to the ionization constants of the acids by conductivity and e.m.f. methods, respectively, and obtained an order of electronegativity of radicals similar to that of Allison and Hixon.

Craig and Hixon (14) found that the ionization constants of the N-substituted and α-substituted pyrrolidines were a

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(11) Allison and Hixon, J. Am. Chem. Soc., 50, 168 (1928).
(12) Osburn, The Effect of the Electron-sharing ability of Organic Radicals on the Conductance and Toxicity of Certain Organic Arsenical Compounds. Unpublished Thesis, Library, Iowa State College, Ames, Iowa. 1930.
(13) Ware, The Electron-sharing Ability of Organic Radicals. Orthochlorobenzyl Radical. Unpublished Thesis, Library, Iowa State College, Ames, Iowa. 1930.
(14) Craig and Hixon, J. Am. Chem. Soc., 53, 4367 (1931).

function of the electronic effects of the substituent organic radicals. Craig (15), more recently, in an attempt to correlate toxicity with structure in a series of α-substituted N-methylpyrrolidines, found a relationship similar to the above in respect to basic strength and polarity.

At Harvard University, Bent and associates (16) have worked along somewhat similar lines and have determined electron affinities of free radicals in absolute values using the reversible reaction

$$(R)_3C \ + \ Na \rightleftarrows (R)_3C^- \ + \ Na^+$$

They have dealt only with the aromatic radicals phenyl, naphthyl and diphenyl substituted in $(C_6H_5)_2C\text{-}R$ and have not yet investigated other aromatic groups or the aliphatic groups.

Most of the work on ionization has been done in water and in the past the solvent effect has been more or less assumed to be constant for each compound measured. More recent investigators, particularly Conant (17), have emphasized the possible disturbing effect of the solvent on the values of the equilibrium constants; and this certainly is a factor to be considered when equilibria data in different media and even in the same medium are to be compared. However, there seem to be cases, as shown by Goodhue and Hixon (18)

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(15) Craig, J. Am. Chem. Soc., 55, 2543-50 (1933).
(16) Bent, J. Am. Chem. Soc., 52, 1498 (1930); 53, 1786 (1931).
(17) Conant, Ind. Eng. Chem., 24, 466-472 (1932).
(18) Goodhue and Hixon, J. Am. Chem. Soc., 56, 1329 (1934).

and Goldschmidt and co-workers (19), where the variations in the relative basicities of some compounds are approximately the same in different solvents. The former measured the ionization constants of a series of amines and organic acids in water, methanol and ethanol and on comparison of the values found the slopes of all three curves to be approximately the same, which indicates that each solvent changes the ionization constant of every compound in the series by a constant value. Bent (20) has found that the solvent has about the same effect on the free energy value of each of the radicals in a series investigated by him. Brønsted's (21) interpretations of the rôle of the solvent in dissociation have thus been substantiated to some degree, but more data are necessary for the proper elucidation of the problem.

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(19) Goldschmidt, Z. physik. Chem., 99, 116-154 (1921); 119, 439-473 (1926).
(20) Bent, J. Am. Chem. Soc., 53, 1794 (1931).
(21) Brønsted, Chem. Rev., 5, 291-312 (1928).

STATEMENT OF THE PROBLEM

Goldschmidt and Bader (22) were interested in obtaining a clearer relationship between substitution and degree of dissociation and in 1929 investigated the equilibrium between a series of α-aryl substituted β-benzoylhydrazyl radicals and their corresponding tetrazanes.

$$2(\text{aryl})_2\text{N-}\underset{|}{\text{N}}\text{COC}_6\text{H}_5 \rightleftharpoons [(\text{aryl})_2\text{N-NCOC}_6\text{H}_5]_2$$

They measured the dissociation constants of the substituted tetrazanes in toluene by a combination volumetric and spectral method. The tetrazanes varied only in the aryl groups substituted, the rest of the structure being unchanged, so that any difference in properties among the compounds would logically be due to these specific groups and their electronic effect on the rest of the molecule. It was felt that a correlation of the variations of the dissociation constants in a series of similarly substituted diphenylamines with those obtained by Goldschmidt and Bader would strengthen the evidence for the electronegativity series of organic radicals proposed by Hixon and Johns. Substituted diphenylamines were used, as thus the radicals under investigation were attached directly to nitrogen as Goldschmidt and Bader had them in their compounds. They kept one side of the molecule, $-\underset{|}{\text{N}}\text{COC}_6\text{H}_5$, constant throughout; in this work the hydrogen was always linked to nitrogen

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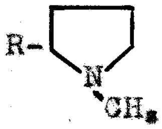
(22) Goldschmidt and Bader, Ann., <u>473</u>, 137 (1929).

so that the change in dissociation constants could be expected to be in the same direction in the series of compounds measured. Substituted hydrazines were not used, as they were too difficult to prepare and too unstable.

The ionization constants of the series of para substituted diphenylamines were measured by an e.m.f. method in absolute methanol (18) because of the insolubility of the compounds in water. Since the measurements were so satisfactory, it was decided to investigate several other series by this method in order to obtain further evidence for the electron-sharing ability concept and also to learn more about the effect of the solvent upon the electrical properties of organic compounds. The other series measured were $RNHC_2H_5$, $RNHCH_3$, $(R)_2NH$, and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The literature (23) has made available ionization data on several compounds of each of the above series in water which have been adapted to this concept and which have been plotted on a graph by the method of Johns and Hixon. All of the values used are satisfactory except that for α-naphthyl-N-methylamine in the $RNHCH_3$ series. The value of $pK_{b_{H_2O}}$ for this compound is higher than that predicted from the curve and since the values of the other members of the series fit the curve it

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(23) Hall and Sprinkle, J. Am. Chem. Soc., 54, 3469 (1932).

appears that it is erroneous, the low ionization probably being due to the extremely weak basicity and low solubility of the compound in water.

When the $pK_{b_{CH_3OH}}$ valuesof the $RNHCH_3$ series are measured in methanol and then plotted as ordinates against the electron-sharing ability of the substituted radicals as abscissas, a curve is obtained which should parallel that for the $pK_{b_{H_2O}}$ of the same series in water (18). When the curves are straight lines, the difference in pK_b between them has a constant value and can be used to calculate the pK_b of a compound in one solvent when its pK_b in the other solvent is known. The ionization constant of α-naphthyl-N-methylamine will be determined by the above method to test the validity of Hall and Sprinkle's measurement in water.

EXPERIMENTAL

Preparation of Compounds

Symmetrical Secondary Amine Series

p,p'-Dianisylamine.

This compound was prepared by the general method of Goldberg (24) with some modifications.

Forty grams of acetyl-p-anisidine prepared from 33.5 grams (0.3 mole) of p-anisidine and 28 grams (0.3 mole) of acetic anhydride were intimately mixed with 20 grams (0.15 mole) of powdered potassium carbonate and 1 gram of potassium iodide. This mixture was transferred to a 200 cc. three-necked flask fitted with a mercury seal mechanical stirrer and a Hopkins condenser and 100 grams (0.53 mole) of p-bromoanisole added. One gram of copper-bronze powder was then added and the whole refluxed for 24 hours. A dark brown oil was obtained. The excess p-bromoanisole was steam-distilled off and the residual oil extracted with ether and filtered. The ether was eliminated under diminished pressure and the oily residue allowed to crystallize. A mush was obtained which was refluxed 3 hours with alcoholic potassium hydroxide (70 cc. of 40 per cent KOH and 125 cc. of alcohol). The alcohol was distilled off and the oily residue separated from the water layer. An approximately 70 per cent solution of methanol was carefully added to the oil

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(24) Goldberg, Ber., 40, 4541 (1907).

and the whole allowed to stand overnight when a pale lavender crystalline mass formed which melted at 85-90°. The mass was filtered, washed with methanol and recrystallized three times from carefully diluted methanol. The melting point of the colorless, purified compound was 102°. Wieland (25) found the melting point to be 103° and other investigators (26) obtained 101-102°.

Anal. Calcd. for $C_{14}H_{15}O_2N$: N, 6.11 per cent. Found: N, 5.92 per cent.

p,p'-Ditolylamine.

An intimate mixture of 18 grams (0.12 mole) of acetyl-p-toluidine and 9 grams of potassium carbonate was placed in a 200 cc. three-necked flask to which was attached a Hopkins condenser and a mercury seal mechanical stirrer and then 30.5 grams (0.14 mole) of iodotoluene, 1 gram of potassium iodide and 1 gram of copper-bronze were added and the mixture refluxed for 22 hours with constant stirring. The excess iodotoluene was steam distilled off and the brown oily residue extracted with ether. The ether solution was filtered and the ether evaporated leaving a brown crystalline mass of melting point 78-80°. The crude acet-di-p-tolylamine was refluxed with alcoholic potassium hydroxide for three hours and the alcohol then distilled off leaving an oily residue which was separated

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(25) Wieland, Ber., 41, 3494 (1908).
(26) Meyer and Gottlieb-Billroth, Ber., 52, 1482 (1919).

from the water layer by extraction with ether. The ether solution was washed several times with distilled water and finally the ether was evaporated. A brown oil remained, which crystallized on cooling overnight. The crude product of melting point 68° was dried and fractionally distilled and the fraction boiling from 320-345° kept. The yield of 20 grams was again fractionated and the portion distilling over from 320-326° further purified by four crystallizations from slightly diluted ethanol. Colorless crystals that melted at 79° were obtained. The same compound prepared by a different method was found to have a melting point of 79° by Merz and Müller (27).

<u>Anal</u>. Calcd. for $C_{14}H_{15}N$: N, 7.10 per cent. Found: 6.83 per cent.

<u>Diphenylamine</u>.

This preparation, a c.p. grade, was distilled at 13 mm. pressure and the fraction boiling at 161.5° taken. This was recrystallized three times from ethanol and melted at 54°. Auwers and Kraul (28) reported the melting point as 54°.

The remaining compounds of this series were obtained from Eastman Kodak Company and were purified before use as indicated below for the respective preparations.

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(27) Merz and Müller, Ber., <u>20</u>, 546 (1887).
(28) Auwers and Kraul, Z. physik. Chem., <u>116</u>, 458 (1925).

Di-n-butylamine.

Purification of this compound was achieved by converting it to the hydrochloride and recrystallizing the latter from absolute ethanol. The amine was then liberated from its salt by means of concentrated potassium hydroxide solution, dried over stick potassium hydroxide and fractionally distilled. The compound boiled at 160° (29). When the amine was dried over potassium hydroxide and fractionally distilled without the above purification process of salt formation, no difference in the value of its ionization constant was obtained from that of the highly purified amine.

Anal. Calcd. for $(C_4H_9)_2NH$: neutral. equiv. 129.2. Found: 129.0.

Dibenzylamine.

The Eastman product was dried over potassium hydroxide and fractionally distilled. It boiled at 175-176°/12 mm.

Anal. Calcd. for $(C_6H_5CH_2)_2NH$: neutral. equiv. 197.1. Found: 197.1.

Di-(β-hydroxyethyl)-amine.

After being dried over solid potassium hydroxide, the colorless compound was distilled and the fraction boiling at 167-169°/15 mm. used. The literature gives the boiling point at 15 mm. as 167-169° (30).

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(29) Rossi, Ann., 158, 172 (1871).

(30) Preloz, Driza and Hanousek, Collect. Trav. Chim. Tchecoslovaquie, 3, 578-84 (December 1931); Centr. 1532 (1932).

Anal. Calcd. for $(HOC_2H_4)_2NH$: N, 13.33 per cent. Found: N, 13.16 per cent.

The N-Substituted Aniline Series

β-Hydroxyethylaniline.

Ninety grams (1 mole) of aniline and ninety grams (0.85 mole) of anhydrous sodium carbonate were put into a 500 cc. round-bottomed flask fitted with a Hopkins condenser and then 80.4 grams (1 mole) of ethylenechlorohydrin added. A reaction occurred immediately and the mixture was allowed to reflux gently for 3 hours. The contents of the flask were filtered and the residue washed several times with anhydrous ether. The filtrate and washings were fractionally distilled. The ether was removed and the first fraction 85-166°/19 mm. was discarded. The second portion 166-177° was refractionated and the part distilling over at 168-170°/19 mm. was kept. On redistillation of this fraction the portion boiling at 168-169°/19 mm. was considered to be sufficiently pure and was sealed in weighed ampules. The pure product is pale yellow and viscous and was obtained in 65 per cent of the theoretical yield.

The above procedure is essentially that of Rindfusz and Harnack (31). Adams and Segur (32) obtained better yields by a different method and the constants obtained above duplicate theirs.

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(31) Rindfusz and Harnack, J. Am. Chem. Soc., 42, 1725 (1920).
(32) Adams and Segur, J. Am. Chem. Soc., 45, 785 (1923).

p-Methoxydiphenylamine.

This compound could best be prepared by the Goldberg (24) method with some modifications.

To 36 grams (0.22 mole) of acetyl-p-anisidine, 18 grams of anhydrous potassium carbonate were added and this mixture covered with 250 grams (1.2 moles) of iodobenzene. To catalyze the reaction 1 gram of copper-bronze powder and 1 gram of potassium iodide were added. The whole was refluxed with stirring for 22 hours and the excess iodobenzene then steam-distilled off. The remaining dark red-brown oil was extracted with ether, the ether evaporated and the residue allowed to crystallize. The crude product was refluxed with alcoholic potassium hydroxide for 3 hours and then the alcohol distilled off. The purplish-brown solid residue was filtered, washed with water and dried. The yield of crude p-methoxydiphenylamine was 20 grams (46 per cent of the theoretical). When recrystallized four times from carefully diluted methanol it gave a constant melting point of 103° (uncorrected). The literature gives 105° (corrected)(33).

Anal. Calcd. for $C_{13}H_{13}ON$: N, 7.03 per cent. Found: N, 6.78 per cent.

p-Methyldiphenylamine.

Thirty-six grams (0.24 mole) of acetyl-p-toluidine were

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(33) Willstätter and Kubli, Ber., *42*, 4138 (1909).

intimately mixed with 18 grams of potassium carbonate and covered with 300 cc. of bromobenzene. About 1 gram of potassium iodide and 1 gram of copper-bronze powder were added and the whole refluxed for 20 hours. After the excess bromobenzene was removed by steam distillation, a thick red-brown oil was left which was the crude acetyl-p-methyldiphenylamine. This product was extracted with ether and after the removal of the ether by distillation was purified by crystallization from alcohol. Fine gray crystals were formed which melted at 51°. By saponification with alcoholic potassium hydroxide, 10 grams of p-methyldiphenylamine were obtained. The yield was 23 per cent of the theoretical. Goldberg (24) obtained 33 per cent. Three recrystallizations from alcohol gave a constant melting point of 87-88° which checks that in the literature (34).

Methylaniline.

The Eastman Kodak Company preparation was redistilled and the hydrochloride prepared and recrystallized several times from alcohol. The amine was liberated from its salt, dried over solid potassium hydroxide, and fractionally distilled to obtain the pure product. The boiling point was 190°.

Anal. Calcd. for C_7H_9N: N, 13.07 per cent. Found: N, 12.96 per cent.

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(34) Ullmann, Ann., 355, 325 (1907).

Benzylaniline.

The Eastman Kodak Company product was recrystallized three times from methanol and melted at 36-37°. The literature gives 37° (35).

Anal. Calcd. for $C_{13}H_{13}N$: N, 7.65 per cent. Found: N, 7.51 per cent.

Phenyl-α-naphthylamine.

This compound was purchased from the Eastman Kodak Company and was recrystallized twice from ethanol. It melted at 60.5° which value coincides with that in the literature (36).

Anal. Calcd. for $C_{16}H_{13}N$: N, 6.39 per cent. Found: N, 6.09 per cent.

The *N*-Substituted Methylamine Series

n-Butylmethylamine.

The procedure employed by Graymore (37) was used. Tri-n-butyltrimethylenetriamine was first made and then it was reduced to n-butylmethylamine.

To 20 grams of freshly distilled n-butylamine, 21 grams of 40 per cent formaldehyde solution were gradually added at 0°. The solution was made basic with an excess of sodium hydroxide and the top oily layer separated. This layer of tri-n-butyltrimethylenetriamine was dried over barium oxide for several

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(35) Tafel and Pfeffermann, Ber., **35**, 1513 (1902).
(36) Frie, Ber., **16**, 2077 (1883).
(37) Graymore, J. Chem. Soc., 1355 (1932).

days and distilled from the oxide. The first fraction up to 125° was discarded and the next one from 125-285° kept. About 20 grams were obtained which came over mostly at 275-285°.

Twenty grams of this base were dissolved in cold dilute hydrochloric acid and 20 grams of zinc powder added. About 100 cc. of 20 per cent hydrochloric acid were added and the whole allowed to stand overnight when all of the zinc had reacted and the reduction was complete. The solution was boiled for 3 hours to remove any excess formaldehyde. Sodium hydroxide was added until the solution was just neutralized when a heavy white precipitate of zinc hydroxide formed. This was filtered and the filtrate made extremely basic with a large excess of sodium hydroxide when the yellow oil of impure n-butyl methylamine separated out in the top layer. The yield was 11 grams. The secondary amine was purified through the nitroso compound. The amine was dissolved in about 1:1 hydrochloric acid, cooled in ice, and a concentrated solution of 18 grams of sodium nitrite added slowly. After standing a while the nitroso compound was liberated by an excess of sodium hydroxide solution and extracted with ether. The ether solution was evaporated in a vacuum and the oily nitroso amine refluxed several hours with alcoholic hydrogen chloride solution to form the amine salt. The base was liberated with sodium hydroxide solution after the alcohol was distilled off and was extracted with ether. The ether solution was dried over anhydrous potassium carbonate for several days and then the solvent distilled off and the amine also distilled and kept over solid sodium hydroxide for two days. The pure, dry amine was fractionated and the portion boiling at 90-91° sealed in ampules. The yield was about 5 grams.

Anal. Calcd. for $C_4H_9NHCH_3$: Neutral. equiv. 87.10. Found: 87.21.

β-Hydroxyethylmethylamine.

Fifteen grams (0.33 mole) of ethylene oxide and 41 grams of a 33 per cent water solution of methylamine (0.44 mole methylamine) were heated in a sealed tube at 100° for 12 hours. On cooling, the contents were poured into a 300 cc. flask and solid potassium hydroxide carefully added in excess. A pale yellow oil of strong amine odor came to the surface. The oily layer was separated, dried over potassium hydroxide and fractionally distilled. The first fraction boiling up to 130° was discarded; the second from 130-160° was refractionated. Most of the distillate came over in the 154-156° portion which was again distilled and the part boiling from 155-156° sealed in weighed ampules and used as the pure product. Schotte, Priewe and Roescheisen (38) prepared the compound by another method and found the boiling point to be 155-156°.

Anal. Calcd. for C_3H_9ON: N, 18.65 per cent. Found: N, 18.42 per cent.

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(38) Schotte, Priewe and Roescheisen, Z. physiol. Chem., 174, 119 (1928).

Benzylmethylamine.

Benzylidenemethylamine was first prepared according to Zaunschirm's method (39) and was reduced to the desired compound (40). To 113 grams (1.1 mole) of benzaldehyde, 100 grams of 33 per cent water solution of methylamine was added, and an immediate reaction occurred. The reaction mixture was extracted with ether, the latter dried over anhydrous potassium carbonate, filtered and then the ether evaporated. The residue was fractionally distilled and the fraction boiling at 176-180° taken. A yield of 25.5 grams (23 per cent of the theoretical) of the crude product was obtained. The crude benzylidenemethylamine was dissolved in 250 cc. of absolute ethanol and 10 grams of sodium gradually added. The solution was allowed to reflux until all the sodium had reacted, and on the cooling of the mixture a solid separated out. The reaction products were hydrolyzed with ice water, hydrochloric acid added until the mixture became acid, and then the alcohol distilled off. An excess of sodium hydroxide solution was added to the residue and a dark brown oil separated in the upper layer. The oil was made acid to form the hydrochloride and then extracted with ether to remove any benzaldehyde. The acidified water layer was treated with sodium hydroxide solution, and the dark brown oily amine that was liberated was separated and dried over

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(39) H. Zaunschirm, Ann., 245, 281-282 (1888).
(40) O. Emmerich, Ann., 241, 344 (1887).

stick potassium hydroxide. It was then filtered and fractionally distilled. The first distillate which boiled at 181-187° was further fractionated and the portion of boiling point 183-185°, which was colorless, sealed in weighed ampules as pure benzylmethylamine. Zaunschirm (40) gave the boiling point at 749 mm. as 184-185°.

Anal. Calcd. for $C_6H_5CH_2NHCH_3$: neutral. equiv. 121.1. Found: 121.0.

Methyl-p-anisidine.

The directions of Spaeth and Brunner (41) were followed for this synthesis. In a 200 cc. three-necked flask fitted with a reflux condenser and dropping funnel, 10 grams (0.8 mole) of p-anisidine were dissolved in 10 cc. of methanol and the flask cooled with ice while 9 cc. of dimethylsulfate were added dropwise. After the reaction had subsided the solution was refluxed on the water bath for one hour. The methanol was distilled off under diminished pressure and a brown oil remained, which crystallized to a bluish mass overnight. The product was dissolved in water, potassium hydroxide was added until the solution became alkaline, and the solution was then extracted with ether. The ether layer was dried over anhydrous sodium sulfate, filtered, and the ether removed from the filtrate by evaporation under diminished pressure. The residual brown oil

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(41) Spaeth and Brunner, Ber., 58, 522 (1925).

distilled over as a colorless liquid at 111-113/9 mm. The product was redistilled at 111-113/9 mm. and immediately sealed in weighed ampules. Seven grams of pure compound were obtained (63 per cent of the theoretical).

Methyl-α-naphthylamine.

The methyl-α-naphthylamine used in this study was obtained from the Eastman Kodak Company. It was dried over solid potassium hydroxide and purified by distilling under reduced pressure. It boiled at 144-145°/12 mm. When this colorless liquid is exposed to sunlight, it quickly turns brown.

Methyl-p-toluidine.

This compound was also purchased from the Eastman Kodak Company. The pale yellow oil was purified in the same manner as the preceding preparation and boiled at 208°. Thomsen (42) found the boiling point to be 208°.

α-Substituted-N-methylpyrrolidines

The compounds of this series were prepared by L. C. Craig (16) and kindly donated to us for further experimentation. Their purity was verified by means of their neutralization equivalents.

In the series of compounds used, all purified liquids were immediately sealed in weighed ampules. All crystalline

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(42) Thomsen, Ber., 10, 1584 (1877).

compounds, after purification, were dried in vacuo over calcium chloride for a day and then kept in a vacuum desiccator over phosphoric anhydride.

Measurement of Ionization Constants

Attempts have been made in the past to determine the e.m.f. of cells and also standard electrode potentials (43) in alcoholic solvents but these have usually been inconvenient because of the following difficulties:

1. The high resistance of the alcohol solutions which did not allow use of the ordinary potentiometer apparatus.

2. The lack of constant and reproduceable reference electrodes.

3. The use of electrodes, such as the quinhydrone electrode (44, 45) of dubious value because of their inconstancy of potential.

4. The use of calomel half-cells in water as reference electrodes where liquid junction potentials become an uncertainty and where there is the risk of contamination by water (46).

5. Insufficient purification of the solvent.

The work of Buckley and Hartley (45) and Goodhue and Hixon (18) has removed most of the above mentioned sources of error. The following explanation of procedure is taken primarily from the work of the latter authors.

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(43) Neustadt and Abegg, Z. physik. Chem., 69, 486 (1909); Isgarischew, Z. Elect., 18, 568 (1912); ibid., 19, 491 (1913); Neustadt, ibid., 16, 866 (1910); Carrara and Agostini, Gazz. chim. ital., 35, (I) 132 (1905).
(44) MacFarlane, J. Chem. Soc., 3212 (1931).
(45) Buckley and Hartley, Phil. Mag. (7) 8, 339 (1929).
(46) Ebert, Ber., 58, 175 (1925).

Goodhue, Schwarte and Fulmer (47) have devised a vacuum tube potentiometer apparatus for use with the highly electrically resistant glass electrode, and the first difficulty was removed by adapting it to the measurements of e.m.f.s in methanol solutions.

The second and fourth objectionable features were eliminated by the preparation of suitable alcoholic calomel half-cells. These were made in 0.1 formal sodium chloride solution of methanol and duplicated in appearance the type used for water measurements. To protect the methanol solutions from moisture, U tubes of concentrated sulfuric acid, phosphoric anhydride, and mercury were attached to the half-cells (fig. 1). Other reference electrodes could have been used but the above were satisfactory over short periods of time, and their potentials were checked periodically against silver-silver chloride electrodes freshly prepared by the method of Harned (type 2)(48). Two half-cells of e.m.f. 0.0449 volt and 0.0437 volt referred to the silver-silver chloride electrode were used. On restandardization of the first one after a month, the value 0.0454 volt was obtained.

The e.m.f. of the silver-silver chloride electrode referred to the normal hydrogen electrode in methanol was calculated to be 0.0711 volt by Buckley and Hartley (45) and

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(47) Goodhue, Schwarte and Fulmer, Iowa State Coll. J. Sci., 7, 111 (1933).
(48) Harned, J. Am. Chem. Soc., 51, 416 (1929).

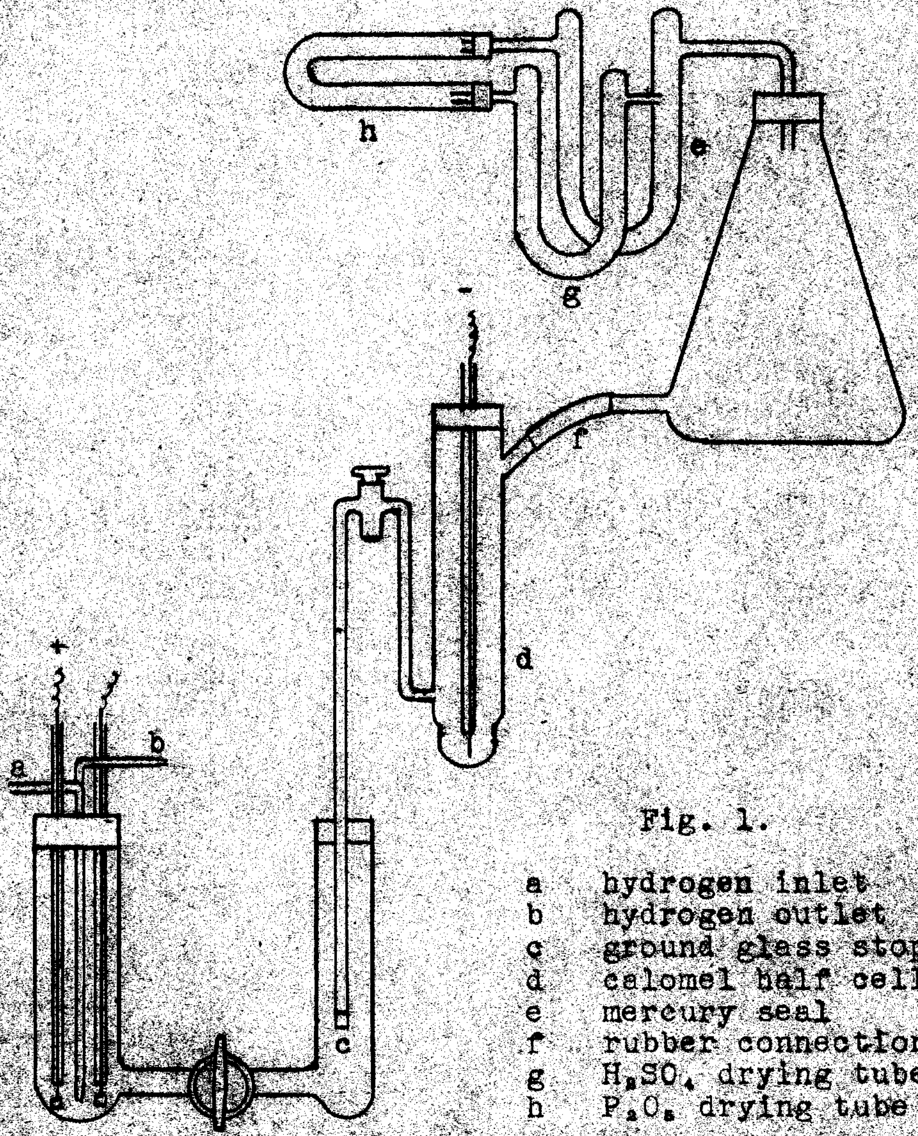

Fig. 1.

a	hydrogen inlet
b	hydrogen outlet
c	ground glass stopper
d	calomel half cell
e	mercury seal
f	rubber connection
g	H_2SO_4 drying tube
h	P_2O_5 drying tube

was added to the voltage of the calomel half-cell to refer the latter to the normal hydrogen electrode.

The measurements of the e.m.f.s of the methanol solutions were made in a U tube (fig. 1) both arms of which were connected by means of a closed ground glass stopcock. In this way no intermediate bridge was necessary as the current flowed through the ungreased and wet stopcock, and still enough of a seal was made to keep any calomel solution from getting through to poison the hydrogen electrodes in the opposite half of the cell. Various saturated salt solutions were tried by Buckley and Hartley (45) to eliminate the liquid junction potentials in the cell Ag, AgCl, HCl (0.1 f)//NaCl (0.1 f), AgCl, Ag but potassium iodide gave the best results (4.35 millivolts). Goodhue and Hixon (18) tried bridges of saturated solutions of potassium thiocyanate and sodium iodide respectively and found that the voltage of the cell did not change more than 1 millivolt from the value obtained without the bridges.

Ebert (46) claimed to have obtained satisfactory results using a quinhydrone electrode in the measurement of potentials of methanol cells, but Buckley and Hartley could not get steady values after considerable experimentation. In view of the work of the latter men, investigators in this laboratory decided to use the hydrogen electrode. At first some difficulty was encountered in obtaining a coating of platinum black which would not cause the electrode to become erratic almost immediately, but after numerous trials it was found that a thick layer was the most satisfactory.

The hydrogen electrodes used were smaller than the usual kind and were about 5 mm. square. They were prepared in duplicate and were platinized from a 3 per cent platinic chloride solution containing a trace of lead acetate with a current density of about 0.4 ampere for four minutes for both electrodes. After being washed with distilled water, they were electrolyzed at a moderate rate in very dilute sulfuric acid for five minutes and then washed with distilled water, 99 per cent methanol and finally absolute methanol to remove the last trace of water.

The two electrodes were kept together by a sulfur-free rubber stopper which was of a diameter such that it would fit snugly into the mouth of one side of a U tube having a ground glass stopcock between its arms (fig. 1). A third hole in the stopper held a piece of glass tubing which was drawn to a narrow tip and which extended downward to slightly below the level of the platinum flags so that hydrogen bubbling through would bathe them. A fourth hole contained a short exit tube for the hydrogen gas. This at first was submerged in methanol to keep out moisture, but later this seal was found to be unnecessary. The solution whose constant was to be measured was poured into the U tube and covered the platinum flags in one arm of the cell while the calomel half-cell dipped into the solution in the other arm. The glass stopcock was closed but moistened with the solution so that no dissolved calomel could get through to poison the hydrogen electrodes and still a current could flow through the cell. The calomel half-cell had a ground glass stopper in its tip to keep it from getting contaminated by the solution. The vertical side arm of the reference electrode was held in place in the U tube by a rubber stopper. These stoppers also served the purpose of keeping moisture out of the cell.

The hydrogen used was bubbled through absolute methanol before entering the cell. Its purity was determined by checking the e.m.f. of a palladium-black coated hydrogen electrode in a 0.05 molar potassium acid phthalate solution in water. A palladium coating was used to eliminate any reduction of the buffer which might occur with the more active platinum-black layer. The platinum-black electrodes did not reduce the buffer appreciably and were considered to be satisfactory if a pH of 3.97 was obtained.

The absolute methanol was prepared by the method of Hartley and Raikes (49) with several modifications. Instead of mercury seals for connecting the Hempel column with the distilling flask and thermometer, corks soaked in paraffin were used. To remove volatile impurities by refluxing over anhydrous copper sulfate, a current of dry hydrogen was passed through the alcohol, as a matter of convenience, rather than dry air. In subsequent runs no gas was used. The final

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(49) Hartley and Raikes, J. Chem. Soc., 127, 524 (1925).

distillation was done through an ordinary Liebig condenser and the distillate, considered pure enough for this work, preserved in Pyrex flasks with sulfur-free rubber stoppers. About 5 liters of solvent were prepared at a time. Several runs were made on the same compound with alcohol from different sources and similar values were obtained.

Sometimes traces of free mercury from the aluminum amalgam came over during the distillation of the alcohol, and when this occurred the alcohol was decanted and redistilled.

The method used for the measurement of the hydrogen ion activity of the methanol solutions is the same as that described by Carothers, Bickford and Hurwitz (50) for water solutions. The alcoholic amine solutions were half-neutralized by adding half of an equivalent amount of an alcoholic hydrogen chloride solution. The concentration of the latter was determined by titration with a standard alkali solution in water. All solutions of the amines were about 0.05 molal as indicated in table II, column 2.

Measurements were made on two solutions of each compound in an air thermostat at 25° ±0.1°, and each reading was checked with a duplicate hydrogen electrode. The electrodes were replatinized for the measurement of each compound to avoid poisoning errors. Occasionally poisoning occurred, and this was indicated by a fluctuation of the e.m.f. around the maximum

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(50) Carothers, Bickford and Hurwitz, J. Am. Chem. Soc., 49, 2908 (1927).

and then a gradual decrease in value. When the flow of hydrogen was stopped, the voltage rose again to its maximum.

All amine solutions were measured immediately after half-neutralization to avoid esterification errors (51). Also, all alcoholic hydrogen chloride solutions were used within three hours after preparation for the same reason.

The calculation of the $pK_{b_{CH_3OH}}$ values at 25° from the hydrogen ion activity is the same as that for $pK_{b_{H_2O}}$ for water solutions except for the substitution of the dissociation constant of the solvent, methanol (1.95×10^{-17}), for that of water. The equations used are

$$-\log a_H = \frac{E + E_{bar} - E_{cal}}{0.0591}$$

$$pK_{b_{CH_3OH}} = -\log K_{CH_3OH} - (-\log a_H)$$

$$pK_{b_{CH_3OH}} = 16.6990 - (-\log a_H)$$

E = observed e.m.f.

E_{bar} = e.m.f. correction for the barometric pressure.

E_{cal} = e.m.f. of the calomel half-cell.

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(51) Nonhebel and Hartley, Phil. Mag. [6], 50, 729 (1925).

Tabulation of Results

TABLE I.

Radical	$pK_{b_{CH_3OH}}$ $(R)_2NH$	pK^{*} $[(R)_2N\text{-}NCOC_6H_5]_2$
$(p\text{-}CH_3OC_6H_4)_2\text{-}$	13.45	highly dissociated
$(p\text{-}CH_3C_6H_4)_2\text{-}$	13.96	2.77
$\left.\begin{array}{r}p\text{-}CH_3OC_6H_4\\ C_6H_5\end{array}\right>$	14.15	2.46[a]
$\left.\begin{array}{r}p\text{-}CH_3C_6H_4\\ C_6H_5\end{array}\right>$	14.30	3.36
$(C_6H_5)_2\text{-}$	14.50	3.94
$\left.\begin{array}{r}p\text{-}BrC_6H_4\\ C_6H_5\end{array}\right>$	---	4.48
$\left.\begin{array}{r}p\text{-}NO_2C_6H_4\\ C_6H_5\end{array}\right>$	---	4.08[b]
$(p\text{-}BrC_6H_4)_2\text{-}$	---	4.84
$(p\text{-}NO_2C_6H_4)_2\text{-}$	---	6.22[b]

The constant recorded for each compound of the diphenylamine series is an average of two values agreeing within 0.05 of a pK unit.

The values of the constants for the tetrazanes were measured in toluene excepting those marked (a) and (b); (a) was measured in acetone and (b) in chloroform.

The last four compounds of the diphenylamine series were not basic enough to be measured by the method used.

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[*] These pK values were calculated from Goldschmidt and Bader's dissociation constants for the substituted tetrazane series.

TABLE II.

E.M.F. of Cells for a Series of N-Substituted Anilines in Methanol

Pt/H_2 (1 atm.), Amine salt // NaCl (0.1 f), Hg_2Cl_2/Hg

Compound	Total Concentration (molal)	E.M.F. corr. to: 760 mm.	pa_H	$pK_{b_{CH_3OH}}$
Methylaniline	0.0574	0.4539	5.71	10.98
	0.0656	0.4541	5.71	10.98
β-Hydroxyethylaniline	0.0556	0.4290	5.29	11.41
	0.0574	0.4297	5.30	11.40
Benzylaniline	0.0562	0.4080	4.93	11.70
	0.0620	0.4087	4.94	11.76
p-Methoxydiphenylamine	0.0624[a]	0.2665	2.57	14.13
	0.0600[a]	0.2636	2.52	14.18
p-Methyldiphenylamine	0.0518[a]	0.2562	2.39	14.31
	0.0646[a]	0.2568	2.40	14.30
Diphenylamine	0.0520[a]	0.2450	2.20	14.50
	0.0477[a]	0.2446	2.20	14.50
Phenyl-α-naphthylamine	0.0596	0.2274	1.88	14.82
	0.0621	0.2278	1.88	14.82

[a] The e.m.f. of the calomel half-cell used in the measurement of these compounds referred to the normal hydrogen electrode was 0.1148 volt. The other compounds were measured with a similar half-cell of 0.1165 volt.

TABLE III.

E.M.F. of Cells for a Series of N-Substituted Methylamines in Methanol.

Pt/H_2 (1 atm.), Amine // NaCl (0.1 f), Hg_2Cl_2/Hg
salt

Compound	Total Concentration (molal)	E.M.F. corr. to: 760 mm.	pa_H	$pK_{b_{CH_3OH}}$
Butylmethylamine	0.0572	0.8091	11.75	4.95
	0.0572	0.8096	11.74	4.94
β-Hydroxy-ethylmethylamine	0.0574	0.7690	11.04	5.66[a]
	0.0596	0.7714	11.08	5.62[a]
Benzylmethylamine	0.0574	0.7050	9.96	6.74
	0.0574	0.7017	9.90	6.80
Methyl-p-anisidine	0.0574	0.5187	6.81	9.89
	0.0572	0.5187	6.81	9.89
Methyl-p-toluidine	0.0576	0.4832	6.20	10.50
	0.0570	0.4832	6.20	10.50
Methylaniline	0.0574	0.4539	5.71	10.98
	0.0656	0.4541	5.71	10.98
Methyl-α-naphthylamine	0.0574	0.4022	4.83	11.87
	0.0571	0.4022	4.83	11.87

The calomel half-cell used referred to the normal hydrogen electrode had an e.m.f. of 0.1165 volt.

[a] These values are not very accurate, and the errors are probably due to a trace of water that could not be removed in the short period of drying.

TABLE IV.

E.M.F. of Cells for a Series of Alpha Substituted N-Methylpyrrolidines in Methanol.

Pt/H_2 (1 atm.) Amine // NaCl (0.1 f), Hg_2Cl_2/Hg
salt

Alpha Substituted Radical	Total Concentration (molal)	E.M.F. corr. to 760 mm.	pa_H	$pK_{b_{CH_3OH}}$
Methyl	0.0494	0.7344	10.46	6.24
	0.0590	0.7364	10.48	6.22
Ethyl	0.0522	0.7308	10.40	6.30
	0.0552	0.7300	10.39	6.31
n-Propyl	0.0552	0.7327	10.43	6.27
n-Butyl	0.0552	0.7309	10.40	6.30
	0.0540	0.7296	10.38	6.32
p-Methoxyphenyl	0.0552	0.6883	9.68	7.02
	0.0540	0.6878	9.68	7.02
Phenyl	0.0614	0.6693	9.36	7.34
p-Chlorophenyl	0.0577[a]	0.6450	9.05	7.65
	0.0598[a]	0.6440	9.03	7.67
β-Pyridyl (Nicotine)	0.0556[b]	0.5980	8.15	8.55
	0.0556[b]	0.5980	8.15	8.55

[a] The e.m.f. of the calomel half-cell referred to the normal hydrogen electrode was 0.1146 volts.

[b] The e.m.f. of the calomel half-cell was 0.1165 volt.

The other compounds of the series were measured with a half cell of 0.1160 volt.

TABLE V.

E.M.F. of Cells for a Series of Symmetrical Secondary Amines in Methanol.

Pt/H_2 (1 atm.) Amine // NaCl (0.1 f), Hg_2Cl_2/Hg
salt

Compound	Total Concentration (molal)	E.M.F. corr. to 760 mm.	pa_H	$pK_{b_{CH_3OH}}$
Di-n-butylamine	0.0590	0.7990	11.55	5.15
	0.0590	0.7990	11.55	5.15
Di-(β-hydroxy-ethyl)-amine	0.0562	0.7422	10.59	6.11[b]
	0.0596	0.7419	10.58	6.12[b]
Dibenzylamine	0.0656	0.6654	9.28	7.41
	0.0556	0.6690	9.35	7.35
p,p'-Dianisyl-amine	0.0646[a]	0.3058	3.23	13.47
	0.0400[a]	0.3073	3.26	13.44
p,p'-Ditolyl-amine	0.0500[a]	0.2763	2.73	13.97
	0.0518[a]	0.2757	2.72	13.98
Diphenylamine	0.0520[a]	0.2450	2.20	14.50
	0.0477[a]	0.2446	2.20	14.50

[a] These compounds were measured by a calomel half-cell having an e.m.f. of 0.1148 volt when referred to the normal hydrogen electrode. A calomel electrode of 0.1165 volt was used with the other compounds in the series.

[b] These values are not very accurate due to a trace of water that could not be removed readily from the compound.

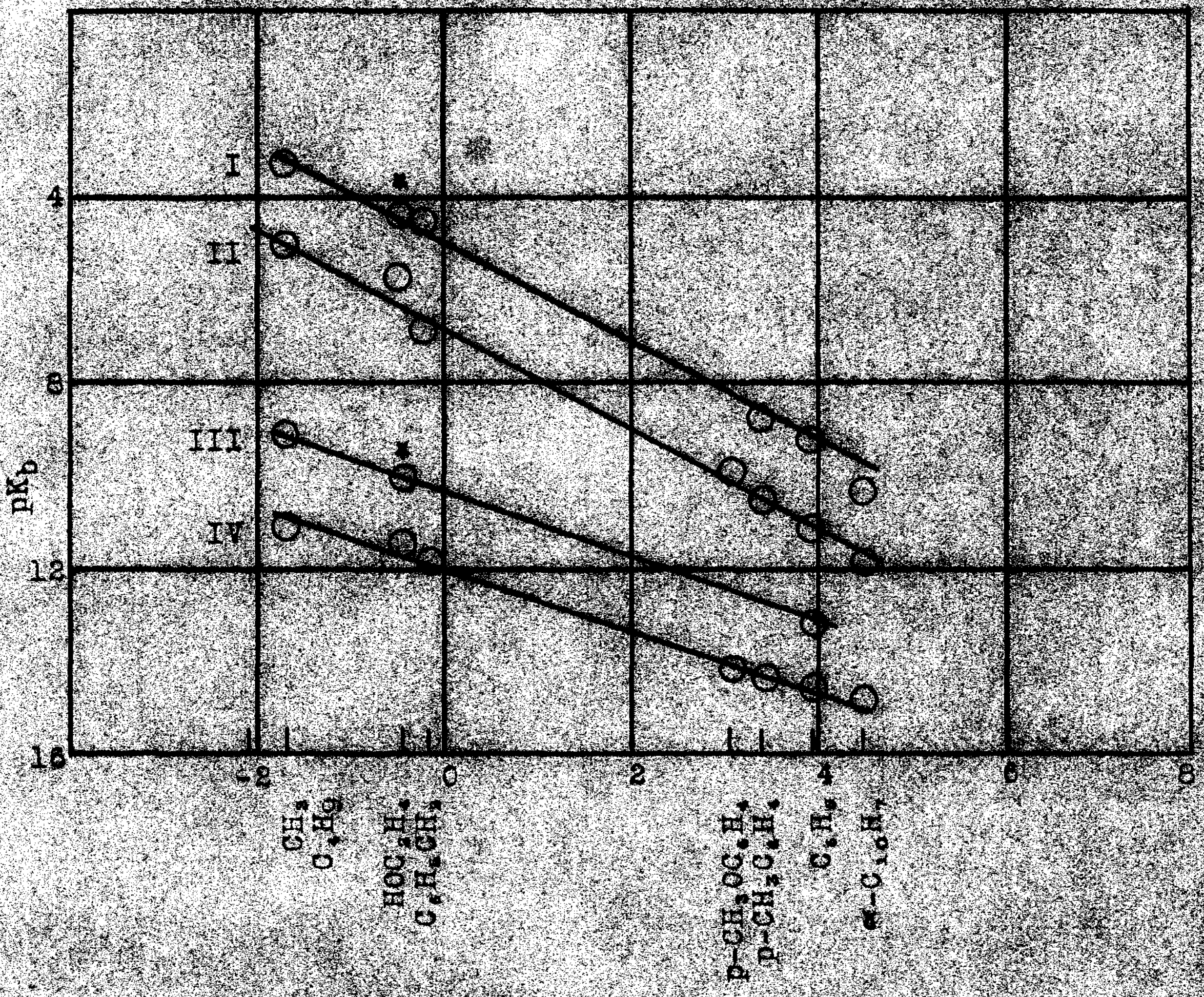

Fig. 2. The ionization constants of a series of N-substituted methylamines in water (I) and in methanol (II) and a series of N-substituted anilines in water (III) and in methanol (IV) plotted as functions of the electron-sharing ability of organic radicals.

*The pK_b value in water of β-hydroxyethylmethylamine was found to be 4.30 and of β-hydroxyethylaniline 9.93.

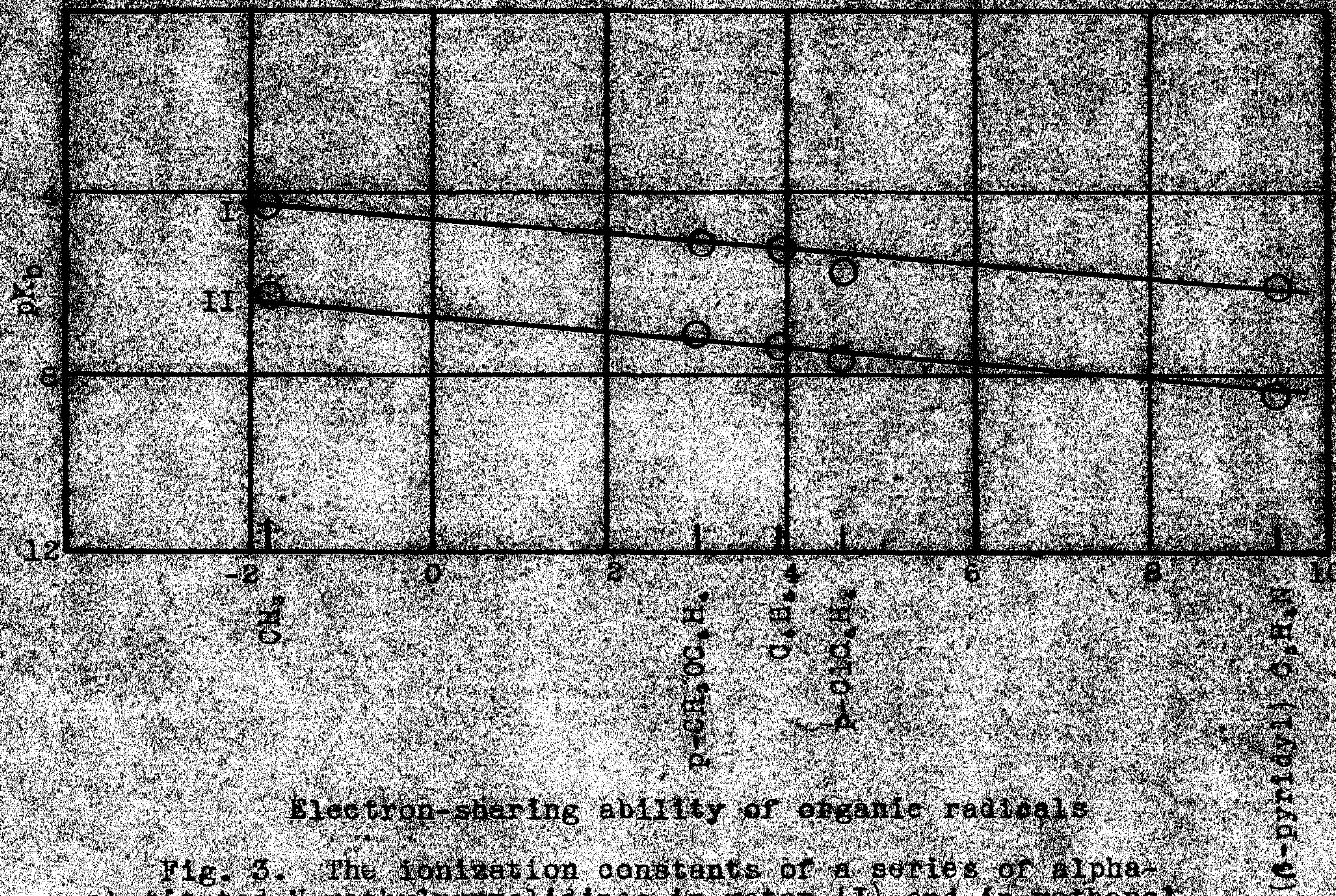

Fig. 3. The ionization constants of a series of alpha-substituted-N-methylpyrrolidines in water (I) and in methanol (II) plotted as functions of the electron-sharing ability of the organic radicals.

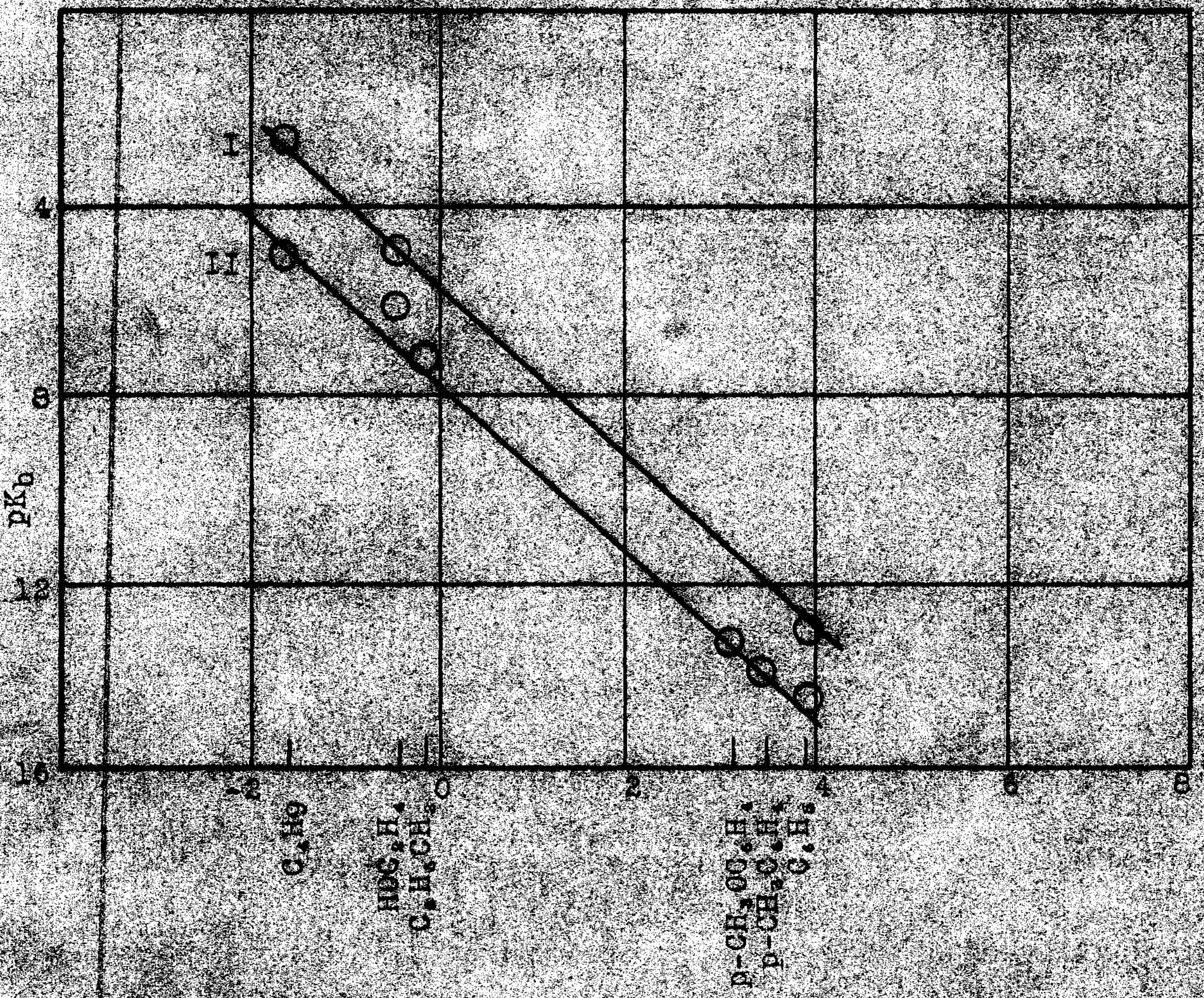

Fig. 4. The ionization constants of a series of symmetrical secondary amines in water (I) and in methanol (II) plotted as functions of the electron-sharing ability of organic radicals.

DISCUSSION OF RESULTS

Table I. shows a comparison of the constants of Goldschmidt and Bader's substituted tetrazanes with those of similarly substituted diphenylamines. The radicals are arranged in the order of increasing negativities (increasing pK_b of the compound). As no values could be obtained for the last four diphenylamine compounds, the p-bromo- and p-nitro- diphenylamines were placed in the order in which the radicals appear in the RNH_2 series. This is logical, as in the case of the diphenylamines the $C_6H_5\overset{|}{N}H_2^+$ is constant and in the primary amine series the $-NH_3^+$ is the same throughout so that the variations in the ionization constants should be in the same direction for each series. It is more difficult, however, to place the p,p'-dibromo- and p,p'-dinitrodiphenylamines, as here there are two radicals varying in each compound. These were placed in the order obtained by Goldschmidt and Bader.

The first substituted tetrazane in the third column could not be measured because of its high dissociation. The third compound in this series could not be measured in toluene, and Goldschmidt and Bader used acetone because of its similarity to toluene in its solvent effect. The change of solvent is undoubtedly the reason why this compound has a low pK and is out of place in the series. Measurements on the substituted tetrazanes in both acetone and toluene indicate that the pK value should be larger in the latter solvent. The p-nitrodiphenyl- substituted tetrazane is also in the wrong place in the series due to a change of solvent. Since it could not be measured in either toluene or acetone, chloroform was used. Previous work shows that the pK should be larger in toluene than in chloroform, and a greater value would tend to place the compound in the correct position.

In general, the results found confirm the order of electronegativity of radicals obtained by Goldschmidt and Bader in their work on the dissociation of α-aryl substituted β-benzoyltetrazanes.

A further verification of Brønsted's statement that the solvent influence is constant and additive for amines in water and methanol has been made by determining the ionization constants in methanol of seven N-substituted anilines (table II), seven N-substituted methylamines (table III), eight α-substituted N-methylpyrrolidines (table IV), six symmetrical secondary amines (table V), and comparing them with their water constants (fig. 2, 3, 4). The pyrrolidine series was used mainly to demonstrate that compounds having a structure quite different from the secondary amines are affected similarly by the solvent.

Ionization constants in water for the water soluble compounds of the series were known and differed widely enough to allow plotting of the values to form representative curves.

In figures II and IV the values of $pK_{b_{CH_3OH}}$ for β-hydroxyethylmethylamine and di-(β-hydroxyethyl)-amine, respectively, do not coincide with the curves and evidently are in error. The discrepancies are probably due to traces of water present in the compounds which could not be removed in the short period of drying. Both of the compounds are hygroscopic and the presence of water would increase the ionization in methanol as was observed. The fact that the pK_b value obtained for β-hydroxyethylmethylamine in water, in which it is very soluble, fits the water curve verifies the purity of the compound and further indicates that water is the cause of the error in the methanol measurement. The ionization constant for di-(β-hydroxyethyl)-amine in water has been obtained from the literature, and it also coincides with the water curve.

In contradistinction to the above, another ethanol derivative, β-hydroxyethylaniline, is only slightly soluble in water and easily dried and gives satisfactory pK_b values in both methanol and water (fig. II).

The remainder of the compounds of the symmetrical secondary amine series have ionization values coinciding fairly well with the smooth methanol curve. The combined electronic effects of the two similar radicals substituted in the compounds give ionization constants which place the combined radicals in a series of electronegativity similar to that for the individual radicals in the RNH_2 series.

There also seems to be a quantitative effect. The decrease of pKb_{CH_3OH} when a methyl group is substituted in diphenylamine in the para position is 0.19 unit, and when another methyl group is placed in the para prime position a further decrease of 0.34 unit is observed. The substitution of a methoxy group in the para position of diphenylamine lowers the pKb_{CH_3OH} value 0.35, and substitution of another methoxy group in the other para position further lowers the value 0.69 unit. It appears then that the introduction of two similar radicals in the para and para prime positions has about three times the effect on the pK value of diphenylamine of that of only one radical. Unfortunately it was not possible to obtain further data on this phenomenon as the constants of the bromo and nitro substituted diphenylamines could not be measured by the same method.

The slopes of the water curves for the α-substituted pyrrolines, α-substituted pyrrolidines, and α-substituted N-methylpyrrolidines and the methanol curves for the latter two are almost identical. The solvent and radical effects are therefore constant for each series and the differences in the positions of the curves on the chart are due to structural influences such as the introduction of one double bond in the pyrrolidine ring to form the pyrrolines and the substitution of a methyl group for a hydrogen atom attached to nitrogen in the pyrrolidines to form the N-methylpyrrolidines.

The water curves of the RNH_2 and $RNHCH_3$ series and also their methanol curves have the same slope and can be explained as above.

In the $RNHCH_3$ series it appears that the ionization constant for methyl-α-naphthylamine as found by Hall and Sprinkle (23) is in error as the pK_b value 10.30 does not fit the water curve.

A corrected value 9.87 has been calculated by subtracting the constant term 2, found for the difference in pK_b between the water and methanol curves as described on page nine, from the $pK_{b_{CH_3OH}}$ of the compound in methanol (11.87).

This error of 0.43 pK_b unit is probably due to the extremely weak basicity and low solubility of the compound in water.

SUMMARY

1. The ionization constants of eighteen secondary amines and eight alpha-substituted N-methylpyrrolidines have been measured in absolute methanol using the hydrogen electrode and a reference calomel half-cell containing 0.1 f. sodium chloride in methanol.

2. The results found confirm the order of electronegativity of organic radicals obtained from Goldschmidt and Bader's data on the dissociation of a series of α-aryl substituted β-benzoyltetrazanes.

3. The effect of substitution of organic radicals into the series $RNHCH_3$, $RNHC_6H_5$ and R- on the ionization constants of the compounds gives an order of electronegativity of radicals similar to that obtained by Hixon and Johns and co-workers.

4. The order of polarity of a series of $(R)_2$- radicals obtained from the ionization constants of $(R)_2NH$ compounds was found to be similar to that for the R- series.

5. Brønsted's opinion that the solvent influence is a constant and additive factor in the ionization of bases and acids in alcoholic solutions has been verified further for the case of bases in methanol.

6. The pK_b value of α-naphthyl-N-methylamine in water obtained by Hall and Spinkle has been corrected from ionization data in methanol.