

THE ACIDITIES OF ARYLAMINES AND ARYLAMMONIUM IONS

by

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B.Sc., University of British Columbia, 1962

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required standard

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DOUGLAS DOLMAN

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THE ACIDITIES OF ARYLAMINES AND ARYLAMMONIUM IONS

ABSTRACT

In order to study quantitatively the acidity of very weak acids and at the same time the effect of a polar aprotic solvent on the basicity of hydroxide ion a Hammett H_- acidity function based on the ionization of 24 substituted anilines and diphenylamines has been established in the system dimethylsulfoxide-water-tetramethylammonium hydroxide. The basicity of hydroxide ion is increased dramatically as the solvent is changed from water to dimethylsulfoxide. The H_- of a 0.011 molar solution of tetramethylammonium hydroxide ranges from 12 in water to 26 in 99.6 mole % dimethylsulfoxide-water, an increase in basicity of fourteen powers of ten. The increase in basicity is due to the increased activity of the hydroxide ion brought about by the reduction in its solvation in the poor anion-solvating solvent dimethylsulfoxide and indicates the extensive solvation enjoyed by the hydroxide ion in water.

The pK_{HA} values of the indicator acids vary from 13.84 for 2,4-dinitrodiphenylamine to 25.63 for 3-chloroaniline. From a plot of $\log K_{HA}$ versus Hammett substituent constants (σ) for six monosubstituted diphenylamines a rho (ρ) value of 4.07 is found. The magnitude of substituent effects on the acidity of aniline appears to be quite similar. The acidities of all the substituted diphenylamines do not follow the above mentioned correlation with Hammett σ constants; the pK_{HA} values of 4-amino-, 4-methoxy-, 4-methylsulfonyl-, and 4-nitrodiphenylamine are all less than expected from the Hammett σ constants for the substituents in these compounds. The 4-nitro substituent exerts a particularly large acid-strengthening effect on the acidities of aniline and diphenylamine; the decreases in pK_{HA} being approximately 8.4 and 6.8 pK units, respectively.

The pK_{HA} values of 17 compounds other than those indicators used to establish the H_- function have been determined with the aid of the H_- function. Most of these compounds are alkyl-substituted 4-nitroanilines. Alkyl groups ortho to the amino group of 4-nitroaniline cause a decrease in the pK_{HA} (an increase in acidity). Similarly, N-methyl-, N-ethyl-, and N-isopropyl-4-nitro-

aniline are all stronger acids than 4-nitroaniline itself. An explanation for the effects of alkyl substituents on the acidity of 4-nitroaniline in terms of the solvation of both the ionized and unionized amines is advanced.

A Hammett H_0 acidity function based on the protonation of 17 diphenylamines in 20 volume % ethanol-aqueous sulfuric acid has been established. The H_0 value for the most acidic solution studied is -6.97 for 11.2 molar sulfuric acid. This acidity function differs from that based on the protonation of azobenzenes in the same solvent system; the latter acidity function diverges to more negative H_0 values as the sulfuric acid concentration increases.

The pK_{BH^+} values for the protonation of the diphenylamines vary from 1.36 for 4-methoxydiphenylamine to -6.21 for 4,4'-dinitrodiphenylamine. A plot of $\log K_{BH^+}$ versus Hammett σ constants for five mono-substituted diphenylamines yields a ρ (ρ) value of 3.36. The pK_{BH^+} values for 4-methoxy-, 4-methyl-, 4-methylsulfonyl-, and 4-nitrodiphenylamine are all less (more negative) than expected from the Hammett substituent constants. Substituent effects on the basicities of aniline and diphenylamine are the same. This is evident from the fact that a plot of the pK_{BH^+} values of 11 diphenylamines versus the pK_{BH^+} values of the corresponding anilines yields a good straight line with slope 1.01.

The basicities of several nitro-substituted diphenylamines appear to vary regularly and do not reflect the presence of a strong interaction between the nitro group and sulfuric acid.

A plot of the acidity versus the basicity (pK_{HA} versus pK_{BH^+}) for nine diphenylamines yields a straight line with slope 1.30. In a similar plot for 33 substituted anilines and diphenylamines two types of behaviour are observed. Those anilines and diphenylamines without an ortho or para nitro group fall about the line with slope 1.30 while those amines with at least one nitro group in the ortho or para position fall on a different, curved line with a slope of less than unity.

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ABSTRACT

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INTRODUCTION

A. Definitions of Acid and Base

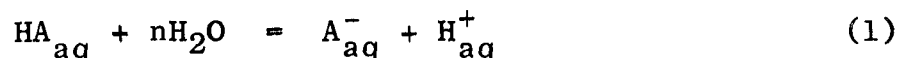
The existence of acids and bases has been recognized for a long time. The question of what exactly is an acid or a base has, however, received a variety of answers. Arrhenius^{1a} defined an acid as a substance that ionizes in aqueous solution to produce a hydrogen ion and a base as a substance that ionizes to produce a hydroxide ion. Bronsted² and Lowry³ defined an acid as a proton donor and a base as a proton acceptor. Lewis⁴ broadened the concept of an acid with his description of an acid as a molecule or ion capable of coordinating with the unshared electron pair of a base. Usanovitch⁵ defined an acid as any substance capable of giving up cations or of combining with anions, and a base as any substance capable of giving up anions or of combining with cations.

These descriptions vary considerably in scope. The definition of Arrhenius restricts acids and bases to aqueous solution, while that of Usanovitch is independent of solvent and covers a wide variety of substances. The latter definition has even been extended to oxidizing and reducing agents by also defining as acids those substances that combine with electrons and as bases those substances that give up electrons.

A Bronsted acid is a special type of Lewis acid since the proton from a proton donor coordinates with the electron pair of a base^{1a}. Bronsted acids have received by far the greatest attention since it is possible to describe these acids in quantitative thermodynamic terms.

B. The Acid Dissociation Constant

The acidity of a Bronsted acid in aqueous solution is expressed in terms of the equilibrium



where "aq" denotes that the species are hydrated. HA is an acid with any net charge and A⁻ is the base conjugate to HA with one unit less positive charge. The equilibrium is expressed by the relation*

$$K' = \frac{(\text{A}^-)(\text{H}^+)}{(\text{HA})(\text{H}_2\text{O})^n} \quad (2)$$

in which the subscript "aq" has been omitted. In dilute aqueous solution the quantity (H₂O) is almost constant and equal to unity so that the expression can be rewritten⁶

* The following symbols, [], (), and f will be used to refer to concentration, activity, and activity coefficient, respectively, on the molar scale. As usual, all activity coefficients tend to unity as the solvent composition tends toward that of the pure solvent^{7b}.

$$K_{HA} = K' (H_2O)^n = \frac{(A^-)(H^+)}{(HA)} \quad (3)$$

The constant K_{HA} is known as the acid dissociation constant^{7a}.

Because individual activities can be determined for uncharged species only, direct measurement of thermodynamic dissociation constants usually involves measuring the classical dissociation constant

$$K_c = \frac{[A^-][H^+]}{[HA]} \quad (4)$$

as a function of ionic strength and extrapolating to infinite dilution⁶.

Kortum, Vogel and Andrussow⁶ have surveyed methods of determining acid dissociation constants in aqueous solution.

For the sake of convenience acid dissociation constants are often expressed in terms of pK units, where

$$pK_{HA} = -\log K_{HA} \quad (5)$$

so that one pK unit corresponds to a change of one power of ten in K. The smaller the value of pK_{HA} , the stronger the acid. It should also be mentioned that the basicity of Bronsted bases is often expressed in terms of the pK_{HA} of their conjugate acids.

Since measurements of acid dissociation constants require extrapolation of K_c to infinite dilution, measurements must be made in solutions of low ionic strength. If equation (3) is rewritten as

$$pK_{HA} = \log \frac{(HA)}{(A^-)} - \log (H^+) \quad (6)$$

then it can be seen that there is a limit to the type of acid for which pK_{HA} can be determined accurately.

In equation (6) the last quantity is just the pH of the solution (or at least approximates the pH, since the definition of pH is now an operational one^{7c}). Now consider a very weak acid with a pK_{HA} of 20 in a solution with pH of 10. If the concentration of HA is 10^{-3} molar, then from equation (6) (and neglecting any difference between activity and concentration) the concentration of A^- is 10^{-13} molar. This is much too small to be measured and so the direct measurement of pK_{HA} for this acid is impossible.

There are many acids that do not show appreciable ionization in the usual pH range, and on which, therefore, it is impossible to make accurate measurements in dilute aqueous solution. Many of these acids ionize in either strongly acidic or strongly basic media, and it is of interest to use these observations to make estimates of the dissociation constants of the acids in aqueous solution. This also provides

some quantitative knowledge of the acidity of these media.

C. Hammett Acidity Functions

By far the most popular approach to this problem is that developed by Hammett and Deyrup^{8,9}. Equation (6) may be rewritten as

$$pK_{HA} = \log \frac{[HA]}{[A^-]} - \log (H^+) \frac{f_{A^-}}{f_{HA}} \quad (7)$$

and the following definition made

$$H = - \log (H^+) \frac{f_{A^-}}{f_{HA}} \quad (8)$$

For two acids, HA_1 and HA_2 , in the same solution

$$pK_{HA_1} - pK_{HA_2} = \log \frac{[HA_1]}{[A_1^-]} - \log \frac{[HA_2]}{[A_2^-]} + \log \frac{f_{HA_1} f_{A_2^-}}{f_{A_1^-} f_{HA_2}} \quad (9)$$

The success of the Hammett treatment depends on the last quantity in equation (9) being zero or, in other words, on the ratio f_{A^-}/f_{HA} in a given solution being independent of the indicator acid. In this case, the function H is also independent of the indicator. This has become known as the Hammett activity coefficient postulate^{10a}. In the event that this postulate holds, equation (9) reduces to

$$pK_{HA_1} - pK_{HA_2} = \log \frac{[HA_1]}{[A_1^-]} - \log \frac{[HA_2]}{[A_2^-]} \quad (10)$$

and the relative pK 's for two acids that are partially ionized in the same solution can be obtained by measuring the two quantities on the right side of equation (10). This is usually done spectrophotometrically so that concentrations of indicator acid, about 10^{-4} to 10^{-6} molar, that do not measurably change the medium can be used. If the Hammett postulate holds, then the relative pK 's obtained from equation (10) for two acids should be the same when measured in a series of solutions of varying acidity. Consequently, such constancy in the relative pK 's is generally taken as experimental proof that the quantity $\log \frac{f_{HA_1} f_{A_2^-}}{f_{A_1^-} f_{HA_2}}$ is actually zero.

Given the thermodynamic pK_{HA} for one of the indicators, then using the relative pK 's, the thermodynamic pK_{HA} for the second indicator can be obtained. The procedure can be applied to a third acid HA_3 if both HA_2 and HA_3 are partially ionized in the same solution. By a choice of indicator acids with suitably spaced pK 's the ionization constants of acids with a wide range of pK 's can be determined depending upon the range of solvent acidities available. It should be stressed that if the Hammett postulate holds rigorously the pK_{HA} 's determined using this procedure are the thermodynamic ones for ionization of the acids in aqueous solution.

From the same measurements of $[HA] / [A^-]$ that are used to determine the pK 's of the indicator acids, the Hammett acidity function, H , can be determined for the solutions in which the measurements were made. Thus from equations (7) and (8)

$$H = pK_{HA} - \log \frac{[HA]}{[A^-]} \quad (11)$$

For an acid that obeys the Hammett postulate it can be seen from equation (11) that the pK_{HA} of the acid is equal to the value of H for the solution in which it is half ionized. Also a plot of $\log [HA] / [A^-]$ versus H gives a straight line with unit slope.

As was mentioned earlier, H_A has been used to refer to acids of any charge type. The symbol for a Hammett acidity function is generally written with subscript indicating the charge on the base conjugate to the indicator acid used to determine the H function. Thus H_0 refers to the ionization of acids such as ammonium ions with one positive charge and H_- refers to the ionization of neutral acids such as acetic acid.

Much of the earlier work on acidity functions was done in strongly acidic media such as aqueous sulfuric acid^{9,11}. Paul and Long¹² have reviewed the work that had been done up to 1956 and Deno¹³ has published a bibliography of acidity

functions reported from 1957 to 1962. Arnett¹⁰ has reviewed the basicities of organic compounds obtained using acidity functions and other methods.

In recent years it has become quite obvious that the traditional H_O scale¹², derived largely using primary amine indicators, does not enjoy widespread quantitative applicability to the protonation of organic bases. This is shown by the fact that plots of $\log [BH^+]/[B]$ versus H_O for amides^{14,15} aliphatic ethers¹⁶, pyrroles¹⁷, indoles¹⁸, and azulenes¹⁹ do not have unit slope as is required by equation (11) for protonation equilibria governed by H_O . Instead, it appears that organic bases fall into many separate classes according to structural differences, the ionization equilibria of each class describing its own self-consistent acidity function. Thus, separate H_O acidity functions have been derived for the protonation of amides^{20,21,22}, primary amines²³, tertiary amines²⁴ and indoles¹⁸ in acid media.

The disparity between the H_O functions in sulfuric acid for primary²³ and tertiary²⁴ amines emphasizes the necessity of using indicators of only one structural type in developing a scale. Thus in 90% sulfuric acid, H_O based on the protonation of primary amines is -8.93^{23} , while H_O based on tertiary amines is -11.14^{24} . The difference between

the two scales decreases as the concentration of sulfuric acid decreases since eventually the two scales must become identical with pH in dilute aqueous solution (see equation (8)).

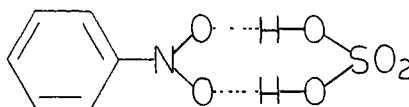
The differences among the H_o scales described by the various types of base stem from changes, depending on the structure of the base, in the activity coefficients of both the uncharged bases^{22,25,26,27} and their positively charged conjugate acids^{15,22,25,26,28,29,30} on passing from dilute aqueous solution to strong acid media.

In short, the prospect of there being only one H_o function for a given solvent system has not materialized and instead several H_o functions, each determined by the protonation equilibria of one narrow functional class of bases, have emerged. This does not, however, invalidate the usefulness of acidity functions if caution is exercised in their use, especially in interpretations of kinetic correlations^{31,32}.

One factor that can complicate the use of acidity functions in strongly acid media is the behaviour of unsaturated substituents such as the nitro and carboxyl groups. This is of particular importance for the H_o scales for primary²³ and tertiary²⁴ amines in which every indicator possesses at least one nitro substituent. Deno and Perrizzolo²⁷ have shown that the behaviour of the activity

coefficients of a variety of organic molecules including nitrobenzene and benzoic acid is similar from 0 to 60% sulfuric acid. Beyond 60% sulfuric acid the latter two compounds and others containing the same groups show markedly different behaviour from hydrocarbons such as benzene. The activity coefficients of compounds containing the nitro and carboxyl groups decrease rapidly as the medium approaches high (90%) sulfuric acid concentrations, in contrast to the behaviour of the activity coefficients of benzene and chlorobenzene. In fact, nitrobenzene dissolves to the extent of 98% in 96.7% sulfuric acid²⁷, as compared to a solubility of 0.0098 moles/1000 grams of solution in 35.8% sulfuric acid³³. This is in spite of the fact that nitrobenzene is less than 1% protonated in 97% sulfuric acid³⁴.

Deno and Perrizzolo²⁷ have suggested that the great increase in solubility of nitrobenzene at high sulfuric acid concentrations³³ is due to formation of a hydrogen bonded species such as (I). Haldna and co-workers^{35,36} have postulated the existence of a similar species for nitromethane in greater than 85% sulfuric acid. They also suggest that in mixtures of 35 to 85% sulfuric acid the nitromethane molecule exists as a hydrate of the protonated form.



I

Arnett and Anderson³⁷ have found that almost all weak bases bearing an unsaturated function exhibit behaviour similar to nitrobenzene and benzoic acid³³ in sulfuric acid solutions. Such interactions of substituents with acid media would preclude accurate estimation of the pK's of such compounds from measurements of their ionization equilibria in these solutions. Arnett and Mach²⁴ have suggested that nitroanilines might be such weak bases because "of the ability of the nitro group to be strongly solvated in medium strength acid".

Until recently, acidity functions in acidic media have occupied the attentions of most workers in this field. In the past five years, however, there has been a considerable amount of work done in basic media. This has accompanied an increased interest in the effects of polar aprotic solvents on reactions³⁸.

Basic solutions have been used to study the ionizations mainly of neutral acids. The appropriate acidity function for this type of equilibrium



is the H_- function where

$$H_- = pK_{\text{HA}} + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (13)$$

A review of H_- acidity functions in basic solutions is to be published in the near future³⁹.

There are, in general, three methods of producing solvent systems with continuously variable basicity, and H_- acidity functions have been determined for all three types.

The most obvious, and first studied, solvent system type is that consisting of a protic solvent and a salt of its conjugate base. The basicity of the system is varied by changing the concentration of the base. Some systems of this type that have been studied are lithium⁴⁰, sodium^{41,42}, potassium⁴¹, and benzyltrimethylammonium⁴⁰ hydroxide in water, and lithium⁴³, sodium^{43,44}, and potassium^{43,45} methoxide in methanol.

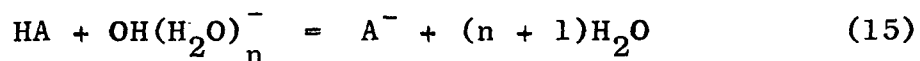
At low concentrations of base (less than 0.1 molar) there is a direct relationship^{42,46} between H_- and base

concentration of the form

$$H_- = B + \log [OR^-] \quad (14)$$

in which B is a constant and depends on the solvent. As the concentration of base continues to increase, however, the H_- increases beyond that expected from this simple relationship^{40,42,44}. This results from reduction of the amount of free solvent present to solvate an increasing amount of base. The thermodynamic activity of free hydroxide or alkoxide ions is probably very much greater than that of the solvated species.

The data of Schwarzenbach and Sulzberger⁴¹ for H_- in aqueous solutions of sodium and potassium hydroxide have been interpreted by Yagil and Anbar⁴⁷ in terms of the equilibrium



They derived equation (16) to express H_- as a function of the hydroxide and "free" water concentrations. This is based on the assumption that the ratio of activity coefficients, $f_A - f_{H_2O}^{(n+1)} / f_{HA} f_{OH^-}$ is zero.

$$H_- = pK_w + \log [OH^-] - (n + 1) \log [H_2O] \quad (16)$$

In the above equation pK_w refers to the ion product of water and the concentration of water is that not bound by the hydroxide ion ("free" water). Best agreement with the

experimental results was obtained for n equal to 3 or, in other words, for the assumption that hydroxide exists as a tri-hydrated species.

Previously, Edward and Wang⁴² in a similar treatment of their data on H_- in solutions of sodium hydroxide had calculated H_- as a function of base concentration and water activity rather than "free" water concentration. They proposed that the activity coefficient ratio $f_{HA}f_{OH^-}/f_{A^-}$ is a function of water activity such that

$$\log \frac{f_{HA}f_{OH^-}}{f_{A^-}} = r \log (H_2O) \quad (17)$$

Thus they used the equation

$$H_- = pK_w + \log [OH^-] - (-r+p+1) \log (H_2O) \quad (18)$$

to attempt to calculate H_- . In this case the quantity p , though analogous to n , is not necessarily the hydration number of the hydroxide ion but rather the difference in hydration numbers between the left and right sides of equation (15). Over the range of base concentrations measured (0 to 4.5 molar) good agreement between calculated and observed H_- values was obtained for $(-r+p+1)$ equal to 3.2.

Solutions of continuously variable basicity can also be produced with binary solvent systems in which one solvent is itself quite basic. Members of this type of

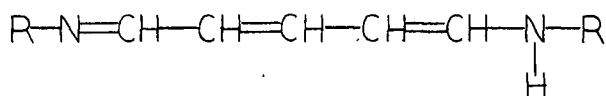
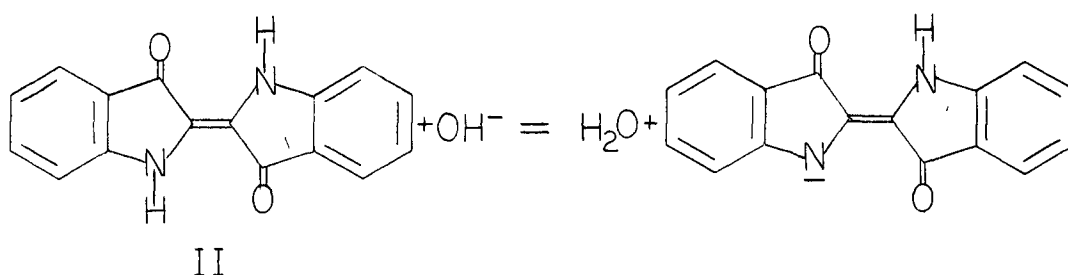
system that have been studied are aqueous solutions of hydrazine^{48,49}, ethylenediamine⁵⁰, and 2-aminoethanol⁵¹.

The third type of solvent system also uses a binary solvent system, one of the pair being a hydroxylic solvent such as water and the other being a polar aprotic solvent such as dimethylformamide. These solutions themselves are not particularly basic so that base must be added, generally as the conjugate base of the hydroxylic member. Although the basicity can be varied by changing the base concentration it can be varied just as effectively by changing the composition of the binary solvent pair. At constant base concentration, the basicity of this type of solvent system increases as the proportion of the polar aprotic component increases.

Studies of H_- functions have been made on aqueous tetramethylenesulfone (sulfolane) solutions containing tetramethylammonium hydroxide⁴⁰ and phenyltrimethylammonium hydroxide⁵², aqueous pyridine containing tetramethylammonium hydroxide⁴⁰, aqueous dimethylsulfoxide (DMSO) containing tetramethylammonium hydroxide⁴⁰, methanol-dimethylsulfoxide containing sodium methoxide⁵³, and ethanol-dimethylsulfoxide containing sodium ethoxide⁵⁴.

A variety of indicator acids have been used in studying H_- acidity functions. These have included acids

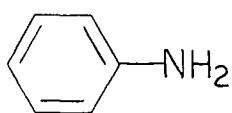
in which the acidic proton is attached to carbon, nitrogen and oxygen. Schwarzenbach and Sulzberger⁴¹ used indigo derivatives (II) as acids but obtained results suggesting a greater increase in basicity when substituted glutarcondialdehyde dianils (III) were used.



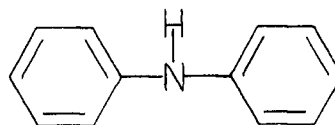
III

They suggested that the latter compounds ionized not by simple proton loss but rather by a process involving hydroxide addition. Edward and Wang⁴² suggested, however, that the difference in behaviour is due to differences in hydration of the two conjugate bases. Using thioacetamide as the indicator acid, these workers obtained results in sodium hydroxide solutions similar to those obtained using the indigo compounds.

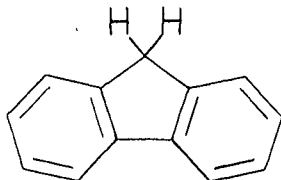
The majority of H_- studies have used substituted anilines (IV) and diphenylamines (V)^{40,44,48,51,52} and various carbon acids^{48,52,54} such as fluorene (VI) derivatives and substituted diphenyl- and triphenylmethanes (VII) as indicators.



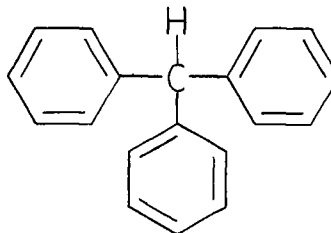
IV



V



VI

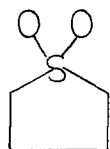


VII

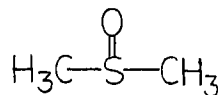
Rochester⁵⁵ has determined an H_- scale in solutions of sodium methoxide in methanol using hindered phenols as acids and has found that this scale does not rise as rapidly as the scale obtained by Ridd and More O'Ferrall⁴⁴ using substituted anilines and diphenylamines. Similar results have been obtained by Stewart and Buckley⁵⁶ in methanol-dimethylsulfoxide solutions containing sodium methoxide.

Until further work is done on the dependence of H_- on the structure of the indicators, and in view of the dependence of H_0 scales on indicator structures, it is advisable to use acids of only one type in determining an H_- scale.

As an indication of the basicities of the solutions that have been studied, the H_- values for the most basic solution in some of the systems will be mentioned. An aqueous solution of 10 molar potassium hydroxide has an H_- of 17.3⁴¹, 2.38 molar benzyltrimethylammonium hydroxide has an H_- of 16.2⁴⁰, and 4 molar sodium methoxide in methanol has an H_- of about 17.1⁴⁴. A solution of 95 mole % hydrazine in water has an H_- of 19⁴⁰. The effect of polar aprotic solvents on hydroxide ion basicity is very pronounced. The H_- of a 0.011 molar tetramethylammonium hydroxide solution is 19.2 in 95 mole % aqueous tetramethylene-sulfone (VIII)⁴⁰ and 18.6 in 70 mole % aqueous dimethylsulfoxide (IX)⁴⁰ as compared to approximately 12 in aqueous solution.



VIII



IX

In a recent communication⁵⁷, Steiner and Gilbert reported measurements made in dimethylsulfoxide containing small amounts of water or methanol. The base was added in the form of the potassium salt of the conjugate base of dimethylsulfoxide. The pK_{HA} values of a series of hydrocarbon acids, the weakest being triphenylmethane with a pK_{HA} of 27.2, were determined based on the value of 18.4 for the pK_{HA} of 4-nitroaniline obtained by Stewart and O'Donnell⁴⁰. It would appear that solutions with H_- of about 30 can be obtained in this system.

D. Other Methods of Measuring Acidities

Some of the earliest measurements of the acidities of very weak acids were made by Conant and Wheland⁵⁸ and by McEwen⁵⁹. They studied the equilibrium established between one weak acid and the potassium salt of another in ether solution. The position of the equilibrium was determined



colorimetrically. This technique has been used with modern spectrophotometers by Streitwieser and co-workers⁶⁰ and by Steiner and Gilbert⁵⁷.

Kinetic measurements of hydrogen isotope exchange have been used to compare the strengths of weak acids. For

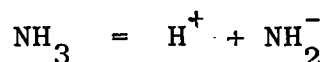
this approach to be valid it is essential that the rate of attainment of equilibrium is directly related to the position of equilibrium and that ionization is the rate-determining process in hydrogen exchange reactions⁶¹. Shatenshtein and co-workers⁶² have studied hydrogen isotope exchange of weak hydrocarbon acids in liquid ammonia with potassium amide. Streitwieser and his students^{60,61,63} have made similar studies in cyclohexylamine with lithium cyclohexylamide as base. They have shown⁶⁰ that the equilibrium acidities of a series of fluorene derivatives (VI) determined in this system by the method of Conant and Wheland⁵⁸ give a fair correlation with the relative rates of hydrogen-tritium exchange in methanol containing sodium methoxide⁶⁴.

It is necessary to be certain in interpreting isotope exchange rates that ionization of the proton actually determines the rate of its exchange. For the exchange of the methyl hydrogens of toluene in the cyclohexylamine solvent system there is a kinetic isotope effect, k_H/k_D , greater than 10^{63b} . Hydrogen exchange in this system obviously involves breaking of the carbon-hydrogen bond in the rate-determining step. On the other hand, in dimethylsulfoxide with potassium t-butoxide as base the kinetic isotope effect, k_D/k_T , is approximately unity and therefore, presumably, k_H/k_D is also approximately

unity⁶⁵. It appears that in this system the breaking of the carbon-hydrogen bond is not, or is only partially, rate-determining in exchange reactions. Consequently, relative rates of hydrogen exchange in this medium cannot readily be taken as a measure of acidity.

E. First and Second Dissociation Constants of Dibasic Acids

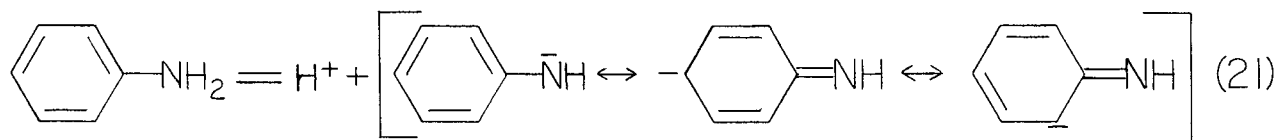
The present knowledge of first and second dissociation constants for acids of the type H-Z-H, in which both acidic protons are attached to one central atom, is limited. Some values that are known include pK_1 and pK_2 for H_2S , 7.1 and 13.1 respectively, and for H_2Se , 3.9 and 10.0 respectively⁶⁶. There is a difference of about 6 pK units between the pK's for the first and second dissociations of these two acids. The following processes



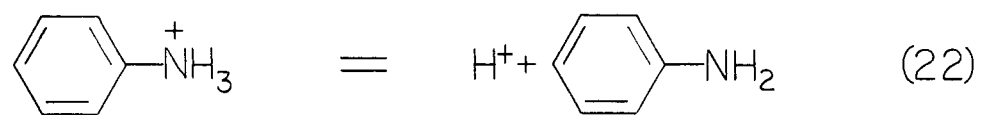
must also be considered as the first and second ionizations of an acid of the type H-Z-H. The pK_1 and pK_2 of the ammonium ion are 9.25⁶⁷ and an estimated 35⁶⁸ respectively. The difference here is about 25 pK units.

Stewart and O'Donnell⁴⁰ have determined the acid dissociation constants for a series of nitro-substituted

anilines and diphenylamines using Hammett H_{A} acidity functions in a variety of media. The dissociation constants for the corresponding ammonium ions of many of these compounds had been determined previously using the H_0 scale. A plot of pK_1 (as ordinate) versus pK_2 (as abscissa) for the ammonium ions gave a line with slope of about 0.6⁶⁹. This means that substituents have a larger effect on the acidity of ammonium ions than on the acidity of the corresponding neutral amines. Such an effect is surprising since the opposite might have been predicted. Ionization of the neutral amine produces an anion capable of dispersing its negative charge over an aromatic ring; this is not possible for the positive charge of the anilinium ion. It would be

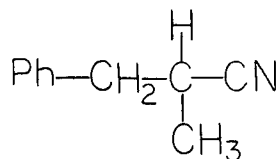


expected that substituents on the ring should have a considerable effect on the charge delocalization and consequently on the energy of the anion. One would expect this to be reflected in a greater effect of substituents on the equilibrium (21) than on equilibrium (22).



OBJECTS OF THE PRESENT RESEARCH

This work was undertaken to study solutions of greater basicity than had been previously studied using the method of Hammett. The binary solvent system water-dimethylsulfoxide containing tetramethylammonium hydroxide appeared to hold considerable promise for great basicity since it had been shown that a solution of 70 mole % dimethylsulfoxide has an H_- of 18.6⁴⁰. As the remaining 30 mole % of the water is removed the basicity would be expected to continue to rise. It had also been found that the rate of racemization of (+)-2-methyl-3-phenylpropionitrile (X) as catalysed by methoxide ion is accelerated by a factor of approximately 10^9 upon changing the solvent from methanol to dimethylsulfoxide⁷⁰. Its high dielectric constant, 48.9 at 20°, ⁷¹ and its ability to dissolve a wide variety of compounds⁷² also commend dimethylsulfoxide for such a study.



X

Furthermore, the dissociation constants of the anilines and diphenylamines used as indicators would be obtained from this study. It was hoped that this would

provide some information on substituent effects on the acidity of amines.

The determination of the dissociation constants of the conjugate acids of a series of diphenylamines as well as of the diphenylamines themselves was also undertaken to examine further the linear relationship between pK_1 and pK_2 of anilinium and diphenylammonium ions observed by Stewart and O'Donnell for the nitrated analogs⁶⁹.

METHODS OF APPROACH

The ionization of anilines and diphenylamines is accompanied by a marked change in electronic absorption spectra. The anions exhibit strong light absorption in the visible or near ultraviolet regions with maxima at wavelengths at which the unionized compounds transmit all, or almost all, the incident light. This provides a convenient means for following the ionization equilibria of these amines.

The ionization of these amines in strong acid media can also be studied this way, since, on protonation, the long wavelength absorption of these amines disappears.

All indicators used in this work showed virtually instantaneous spectral changes upon addition of base to their solutions in dimethylsulfoxide-water mixtures. The spectra of the unionized amines could be regained by neutralizing the base with acetic acid. These two observations, instantaneous and reversible spectral changes, were used as criteria of ionization by proton loss for all acids.

EXPERIMENTAL

A. Preparation and Purification of Indicators

Some of the compounds were obtained from commercial sources; the others were prepared by known methods. Information on their preparation and purification is to be found in the appendix A.

Melting points were determined in capillaries using a Buchi melting point apparatus and are uncorrected.

Sublimation proved to be a most useful technique both in purifying compounds and in recovering products from reaction mixtures. In several cases it was the only practicable method of product recovery since reaction conditions were so drastic as to produce large amounts of tarry materials. Sublimations were carried out at temperatures near the melting points of the compounds and under oil pump pressure.

B. Purification of Solvents

Dimethylsulfoxide (DMSO) was stirred in a closed vessel over powdered calcium hydride for at least two days and then distilled under reduced pressure. Fractions containing the first 15 to 20% and the last 10 to 15% of the distillate were discarded. Nitrogen gas was used in

the leak. A Perkin triangle was used to cut fractions allowing nitrogen to be introduced directly on top of the distilled DMSO in the collection vessels. These flasks were sealed with ground glass stoppers which were further sealed with masking tape and then transferred to a dry box with nitrogen atmosphere. In this way the DMSO was protected from atmospheric moisture and oxygen.

The DMSO obtained in this manner was shown to contain less than 0.01% water by titration with Karl Fischer reagent.

When the DMSO was to be used to make solutions containing more than 90 mole % DMSO it was further purified by a simplified zone freezing method⁷³. This consisted of cooling the vessel in an ice-water bath until 75 to 85% of the DMSO had frozen and then decanting the remaining liquid. The solid was melted and the procedure repeated. Decanting of the liquid was done in the dry box under nitrogen atmosphere.

Water that was used for preparing DMSO-water mixtures was distilled, boiled and then cooled with nitrogen bubbling through it.

Tetramethylammonium hydroxide was obtained from Eastman Organic Chemicals either as a 10% aqueous solution or as the crystalline pentahydrate and was used without further purification.

Sulfuric acid was Baker and Adamson Reagent grade material.

Constant boiling ethanol (95.6% ethanol) was prepared from commercial 100% ethanol by addition of the amount of water calculated to give the azeotropic composition followed by distillation. After a first fraction of approximately 5%, the next 60% was collected and used for measurements with sulfuric acid.

C. Preparation of Solutions

Stock solutions of DMSO-water were prepared and stored in ordinary liquid reagent bottles stoppered with rubber serum stoppers with a flap that could be bent down over the lip and neck of the bottle forming an airtight seal. The membrane of the serum stopper could be penetrated many times without losing its seal. Care was taken that the solutions did not splash against the rubber stoppers.

The bottle and stopper were weighed, transferred to the dry box and then a calculated amount of DMSO introduced into the bottle with a large syringe. The stoppered bottle was then removed from the dry box and weighed again. Finally, the required amount of water was added - again by syringe - and a third weighing made. From the three weighings the exact composition of the solvent could be calculated.

Solutions containing more than 97.5 mole % DMSO were prepared in a similar manner from DMSO and a solution of about 50 mole % DMSO.

Indicator measurements in the DMSO-water system were done using a constant concentration of base, 0.011 molar tetramethylammonium hydroxide. Introduction of the base in a 10% aqueous solution also introduces water into the system and thus produces an upper limit of approximately 97 mole % on the amount of DMSO present in the system. This upper limit can be extended to about 99.5 mole % DMSO by using tetramethylammonium hydroxide pentahydrate and in this case base was introduced into the DMSO-water mixtures by way of a stock solution of the latter compound in DMSO.

A sample of the tetramethylammonium hydroxide pentahydrate was ground in a mortar, weighed into a stoppered flask and an appropriate amount of DMSO added. The mixture was shaken and warmed to cause dissolution. There was always a small amount of undissolved material (possibly carbonate) and this was removed by filtration through a sintered-glass funnel. The clear solution was transferred to a glass reagent bottle and stoppered with a serum stopper. All the above operations, except the warming, were carried out in the dry box under nitrogen atmosphere.

Samples of the base solution were titrated with standardized hydrochloric acid using phenolphthalein indicator. A solution of about 0.12 molar base could be prepared in this way. The water content of the solution was determined by Karl Fischer titration in methanol - acetic acid. Correction was made for the water formed from neutralization of the base.

Solutions prepared in this manner were initially colorless but turned yellow after one or two weeks. After three weeks there was a slight drop of about 4% in base concentration, presumably due to decomposition caused by attack by hydroxide ion on the tetramethylammonium ion^{74,75}. Consequently, measurements using the solution were made within two weeks of its preparation. It is interesting that no etching of glass containers, syringes or absorption cells by solutions of hydroxide ion in DMSO was ever noticed during this work despite their great basicity.

D. Spectral Measurements in the Dimethylsulfoxide-Water System

All measurements of spectra were made in 1 cm silica cells using a Bausch and Lomb Model 502 recording spectrophotometer. The instrument was equipped with constant-temperature cell holder having a liquid capacity of 300 ml.

Water from a bath thermostated at 25°C was pumped through the cell holder.

Since many of the anions used in this work, especially the more basic ones, reacted readily with oxygen, the procedure developed previously by O'Donnell⁷⁶ was used to protect them from oxygen.

The solutions were prepared in 1 cm silica absorption cells fitted with a silicone rubber disc in the ground glass neck. The discs were of the type used as injection septums in gas chromatography. They could be pierced many times with small gauge syringe needles without leaking and were inert to DMSO. In preparing a solution, the cell was first fitted with a silicone disc and then two syringe needles inserted through this. Nitrogen was passed in through one of the needles so that the cell was flushed continuously with nitrogen. Next, 30 microliters of a solution of indicator acid ($2 - 25 \times 10^{-3}$ molar) in DMSO was added from a 50 microliter syringe fitted with a Chaney adapter. The concentration of stock solution was so chosen as to produce an absorbance near 0.7 to 0.8 in the final solution when the indicator was completely ionized. Approximately 2 ml of DMSO-water solution was then added with a 5 ml syringe also fitted with a Chaney adapter.

In the case of anions reactive with oxygen it proved profitable to bubble nitrogen through the solution for about two minutes at this point. This was simply accomplished by lowering the tip of the nitrogen inlet syringe needle below the liquid level.

The syringe needles were then removed from the silicone disc, the cell transferred to the cell compartment of the spectrophotometer and allowed to equilibrate for at least 10 minutes. Finally the base was added with a third syringe either as a 10% aqueous solution or as a 0.12 molar solution in DMSO; the amount added being sufficient to bring the concentration of tetramethylammonium hydroxide in the cell to 0.011 molar. The spectrum of the solution was taken immediately and retaken at least once after an interval of 3 or 4 minutes to insure that the indicator solution was stable. In the few cases where the anion appeared to react in some manner, the absorbance of the solution was obtained by extrapolation of the readings obtained at appropriate time intervals to the time of addition of the base. In general, however, the spectrum showed no change for at least 10 to 15 minutes.

Except for the addition of 30 microliters of indicator solution in DMSO, a blank solution was prepared in the same manner as described above using the same

DMSO-water stock solution. This solution was used in the reference beam of the spectrophotometer.

The final composition of the solution was calculated from the volumes of added components and their densities. The density data for the DMSO-water mixtures at 25°C were those of Cowie and Toporowski⁷⁷.

E. Spectral Measurements in 20% Ethanol-aqueous Sulfuric Acid

An attempt was made to determine the dissociation constants of the ammonium ions of substituted diphenylamines in aqueous sulfuric acid. Diphenylamine itself proved sufficiently soluble in water for spectral measurements in 1 cm cells. However several other diphenylamines, including the chloro-, trifluoromethyl, methylsulfonyl- and 3,4'-dinitro-substituted compounds, were so insoluble as to preclude measurements in 1 cm cells and, in several cases, in 10 cm cells. It was decided, therefore, to adopt the procedure of Jaffé and co-workers^{78,79} who studied the basicities of azobenzenes in "20% ethanol"-aqueous sulfuric acid solutions. The amines possessed sufficient solubility in this medium containing approximately 19 volume % ethanol.

The solutions were prepared in the following way. Two ml of a solution of an amine ($1 - 3 \times 10^{-4}$ molar) in constant boiling ethanol (95.6%) was pipetted into a 10 ml

volumetric flask which was then filled to the mark with aqueous sulphuric acid of the appropriate strength. The stoppered flask was then suspended in a water bath thermostated at 25°C for at least 10 minutes. At high acid concentrations heat was evolved on addition of the acid to the ethanol and the thermostated solutions had to be topped off with more acid due to the contraction of the volume of the solution on cooling. The solution was then transferred to a 1 cm silica cell and the spectrum of the solution taken after further equilibration in the cell holder. All spectra were invariant with time. A blank solution prepared in the same manner (except for the absence of amine in the ethanol) using the same acid stock solution was used in the reference beam.

The concentration of the acid in each solution was determined volumetrically by titration of a blank solution with 0.1 molar sodium hydroxide.

F. Treatment of the Spectral Data

In the DMSO-water system the longest wavelength absorption maxima for most of the anions showed solvent dependence; these generally shifted to longer wavelength as the fraction of DMSO increased. The shift for most of the anions of the anilines and diphenylamines was about 5m μ on passing from 10% to 90% ionization.

In the sulfuric acid media the position of the absorption maxima of the neutral diphenylamines shifted about 3 or 4 $m\mu$ on passing from 10% to 90% ionization for the nitrodiphenylamines and not at all for the others. The shift was to longer wavelength as the acid concentration increased.

The equations for H_o and H_- can be written as

$$H_o = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \quad (23)$$

and $H_- = pK_{HA} + \log \frac{[A^-]}{[HA]} \quad (24)$

respectively. Since there are such large changes in absorption spectra for anilines and diphenylamines on ionization the following expressions⁸⁰ can be used to calculate the ratios $[BH^+]/[B]$ and $[A^-]/[HA]$ from the spectral data

$$\frac{[BH^+]}{[B]} = \frac{\epsilon_B - \epsilon}{\epsilon - \epsilon_{BH^+}} \quad (25)$$

$$\frac{[A^-]}{[HA]} = \frac{\epsilon - \epsilon_{HA}}{\epsilon_{A^-} - \epsilon} \quad (26)$$

where ϵ_B is the molar absorptivity of the neutral amine at its wavelength of maximum absorption

ϵ_{BH^+} is the molar absorptivity of its conjugate base at the same wavelength

ϵ is the molar absorptivity, at the same wavelength, of a solution in which the indicator is partially ionized,

and ϵ_{A^-} is the molar absorptivity of the anion at its wavelength of maximum absorption

ϵ_{HA} is the molar absorptivity of the neutral amine at the same wavelength

ϵ is the molar absorptivity, at the same wavelength, of a solution in which the indicator is partially ionized.

Since, as was noted previously, the absorption maxima shifted with change in solvent composition ϵ_B , ϵ_{A^-} , and ϵ were measured at the absorption maximum for each solution. This method has been used by Jorgenson and Hartter²³ to correct for medium shifts. It was felt that this method would best correct for these shifts. Also, since for any given indicator all the measurements were made using the same concentration of indicator the absorbance (A) rather than the molar absorptivity (ϵ) was used.

The molar absorptivity (ϵ_{A^-}) of an anion was obtained in a solution the H_+ of which was a least 2 units higher than the pK_{HA} of the indicator. In the case of 3-chloro-, 3-trifluoromethyl- and 3-cyanoaniline it was necessary to use a solution of potassium t-butoxide in DMSO to obtain ϵ_{A^-} for the anions. The t-butoxide ion is known to be an extremely strong base in DMSO, since it appears to be in equilibrium with the conjugate base of DMSO itself^{81,82}.

For 3,4'-dinitro-, 4-nitro-3'-trifluoromethyl- and 4-nitrodiphenylamine the molar absorptivities of the anions varied with the solvent composition so that the extent of ionization was determined by measuring the disappearance of the peak due to the neutral amine rather than the appearance of the peak due to the anion. This was possible since the anions absorbed little at the wavelength of maximum absorption of the neutral amines.

Similarly, in the work in acid solutions, the molar absorptivity of a neutral amine (ϵ_B) was obtained in a solution the H_0 of which was at least 2 units above the pK_{BH^+} of the indicator. In the case of 4,4'-dinitrodiphenylamine the molar absorptivity (ϵ_B) changed slightly with acid concentration so that it was necessary to measure ϵ_B over a range of solutions of from 0 to 6.5 molar sulfuric acid and extrapolate to the region of ionization.

Appendix B contains spectral data for the amines in constant boiling ethanol and for their anions in DMSO-water mixtures.

Appendix C contains the ionization ratio data for the amines in the DMSO-water and 20% ethanol-water-sulfuric acid systems.

RESULTS

A. The System DMSO-Water-Tetramethylammonium Hydroxide

From spectral measurements on solutions of amine indicators in the mixtures of DMSO-water containing 0.011 molar tetramethylammonium hydroxide the ratios of the concentrations of ionized to unionized indicator ($I = [A^-] / [HA]$) are obtained as described in the previous section. From these ratios are then obtained the relative pK values of the amine indicators and the H_0 values for the solutions in which the measurements were made.

The relative pK values were obtained by Hammett's method⁹ of comparing ionization ratios of overlapping indicators in the same solution. The quantity $\log I$ was plotted against solvent composition for each indicator and a smooth curve drawn through the points for each plot. Values of $\log I$ between -1 and 1 corresponding to 10% and 90% ionization, respectively, were used in the plots. Where successive curves overlapped, differences were taken at regular intervals and the results averaged. These averages gave the differences between the pK values of the indicators.

The reference acid, the indicator for which the acid dissociation is known, was 2,4-dinitrodiphenylamine.

Stewart and O'Donnell⁴⁰ have determined values of 13.83, 13.83 and 13.85 in three solvent systems for its pK_{HA} . The value 13.84 for the pK_{HA} of this compound was then used with the relative pK values of the rest of the indicators to calculate their thermodynamic pK_{HA} values. Table I contains a list of the indicators used to establish the H_- scale along with their pK_{HA} values obtained in this work. Literature values of pK_{HA} are also presented for those compounds that have been used previously.

The H_- values for the DMSO-water mixtures were then calculated from the pK_{HA} values of the indicators listed in Table I and the values of $\log I$ obtained from the smoothed curves mentioned above. This was accomplished using equation (13).

$$H_- = pK_{HA} + \log \frac{[A^-]}{[HA]} \quad \left(I = \frac{[A^-]}{[HA]} \right) \quad (13)$$

For a given solution, H_- is generally an average of values obtained from two or more indicators.

Table II lists the average H_- values for the DMSO-water mixtures along with the average deviation of the individual values from the mean. Also, the indicators that were used to determine the H_- for a particular solution are given in the last column. The numbers in this column refer to the numbers of the indicators listed in Table I.

TABLE I

The pK_{HA} Values of the Indicators Used
to Establish the H_+ Acidity Function

	<u>Indicator</u>	<u>pK_{HA}</u>	<u>pK_{HA} reported</u>
<u>Diphenylamines</u>			
1	2,4-dinitro	(13.84)	(13.84) ^a
2	3,4'-dinitro	14.66	
3	4-nitro-3'-trifluoro- methyl	14.96	
4	4-nitro	15.67	15.90 ^a , 15.68 ^b
5	2-nitro	17.91	17.57 ^a
6	4-methylsulfonyl	18.80	
7	3-nitro	19.53	
8	3,4'-dichloro	19.73	
9	3-trifluoromethyl	20.48	
10	3-chloro	20.73	
11	4-chloro	21.33	
12	3-methoxy	22.22	
13	H	22.44	
14	4-methyl	22.95	
15	4-methoxy	23.22	
<u>Anilines</u>			
16	4-chloro-2-nitro	17.08	17.22 ^a , 17.13 ^b
17	2,3,5,6-tetrachloro	19.22	
18	4-cyano	22.68	
19	3,4,5-trichloro	22.86	
20	3,5-dichloro	23.59	
21	3,4-dichloro	24.60	
22	3-cyano	24.64	
23	3-trifluoromethyl	25.40	
24	3-chloro	25.63	

^a Stewart and O'Donnell, ref. 40

^b Langford and Burwell, ref. 52, as corrected in ref. 40

TABLE II

H₋ Values for the System

DMSO-Water-Tetramethylammonium Hydroxide (0.011 M)

Mole % DMSO	H ₋ Value	Ave. Dev. from Mean	Indicators ^a
10.32	13.17	-	1
15.20	13.88	0.04	1,2
20.18	14.49	.02	1,2,3
23.57	14.86	.01	2-4
26.95	15.22	.005	2-4
30.11	15.54	.005	2-4
33.42	15.87	.02	3,4
36.79	16.17	.005	4,16
39.86	16.48	.01	4,16
43.27	16.83	-	16
46.54	17.12	.02	5,16
49.59	17.42	.005	5,16
52.55	17.73	.01	5,16
55.95	18.08	.02	5,6,16
58.56	18.34	.02	5,6,17
62.27	18.72	.01	5,6,17
64.20	18.92	.005	6-8,17
69.09	19.41	.01	6-8,17
71.35	19.65	.01	6-9,17
73.69	19.90	.02	7-9,17
76.12	20.14	.005	7-9
78.36	20.38	.01	7-11
80.78	20.68	.005	9-11
83.14	20.97	.005	9-11
85.46	21.27	.01	9-11
88.79	21.61	.02	10-13
90.07	21.98	.005	12-14,18,19
92.47	22.45	.01	12-15,18,19
94.74	23.01	.01	13-15,18-20
95.77	23.32	.005	13-15,18-20
96.21	23.48	.01	14,15,18-20
97.13	23.88	.02	20-22
97.89	24.25	.005	20-22
98.29	24.50	.01	20-23
98.71	24.84	.01	21-24
99.14	25.30	.01	21-24
99.59	26.19	.05	23,24

^a Numbers refer to those in table I

Figure 1 is a plot of H_- versus composition of the DMSO-water-tetramethylammonium hydroxide system. The value of H_- for 0.011 molar tetramethylammonium hydroxide in water was calculated from the equation

$$H_- = pK_w + \log [\text{OH}^-] \quad (27)$$

This relationship was found to hold for solutions of sodium hydroxide of from 0.01 to 1 molar concentration by Edward and Wang⁴². If this relationship is assumed to hold for tetramethylammonium hydroxide and the value 14.00⁸³ used for pK_w then the H_- for 0.011 molar hydroxide ion is 12.04.

It is evident from equation (13) that a plot of $\log I$ versus H_- should give a straight line with unit slope and intercept equal to the pK_{HA} of the indicator. Figure 2 is such a plot of $\log I$ ($\log [A^-] / [HA]$) versus H_- for the indicators in Table I. Lines of unit slope with intercepts equal to the pK_{HA} values of the indicators have also been drawn. The fit of the experimental values of $\log I$ to these lines is a measure of the precision of the results and of the validity of the whole procedure.

The pK_{HA} values of a number of compounds were determined from the H_- scale using equation (13). These were acids that were not used in the establishment of the

FIGURE I H_- ACIDITY FUNCTION FOR THE SYSTEM: DMSO-WATER-TETRAMETHYLAMMONIUM HYDROXIDE (0.011 M)

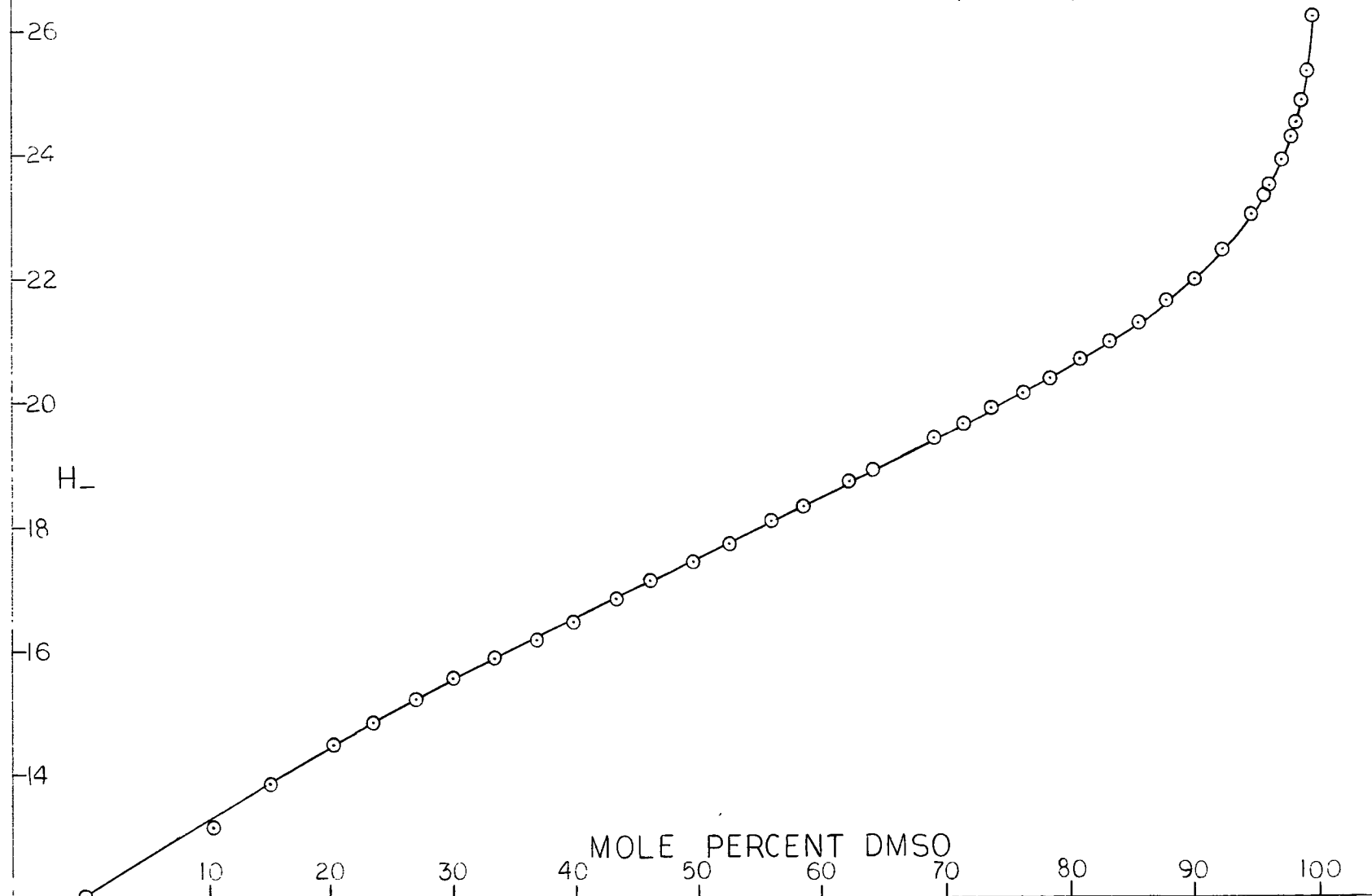


FIGURE 2 PLOT OF $\text{LOG } \frac{[A^-]}{[HA]}$ VERSUS H_L FOR THE INDICATORS USED TO ESTABLISH THE H_L SCALE

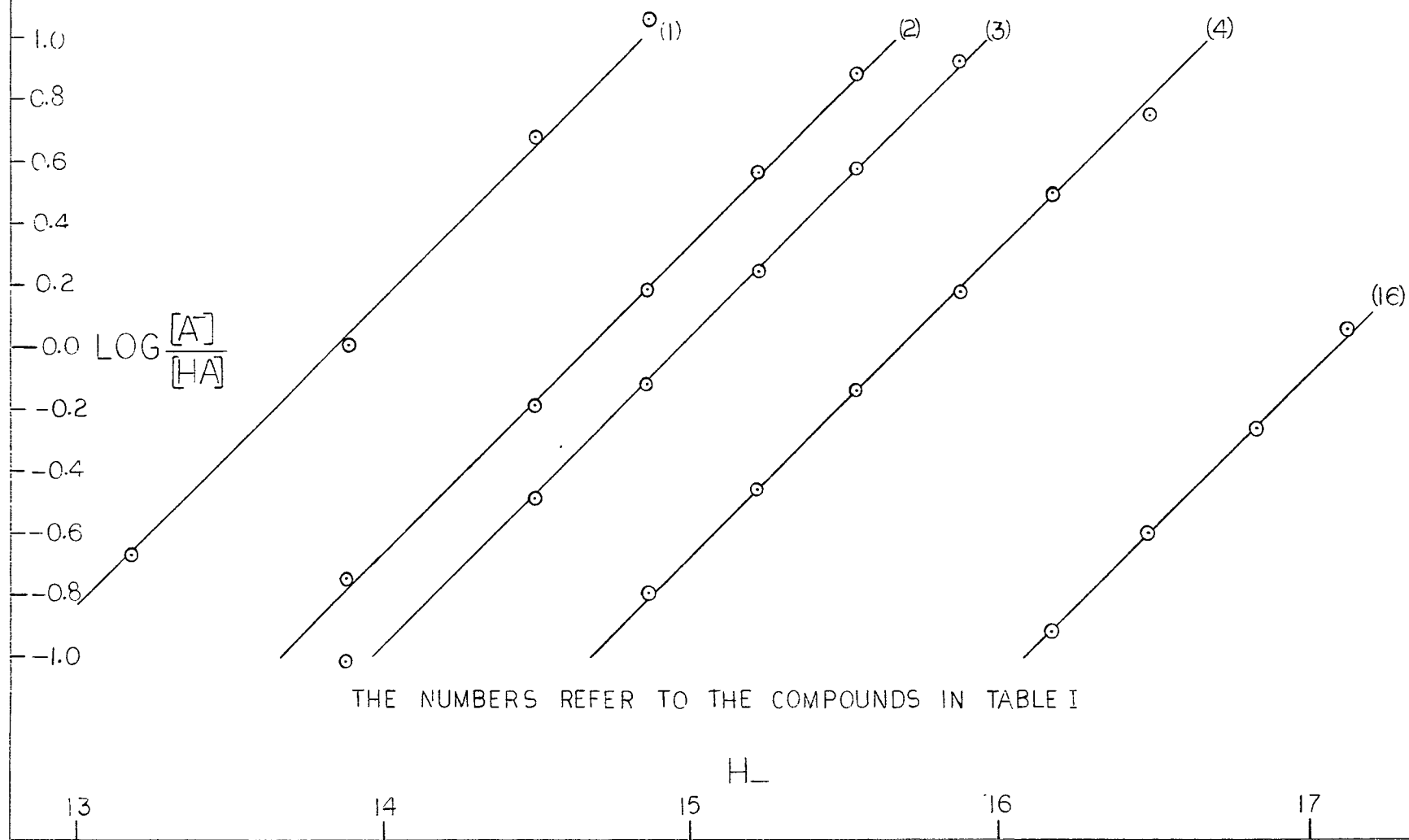


FIGURE 2 (CONT.)

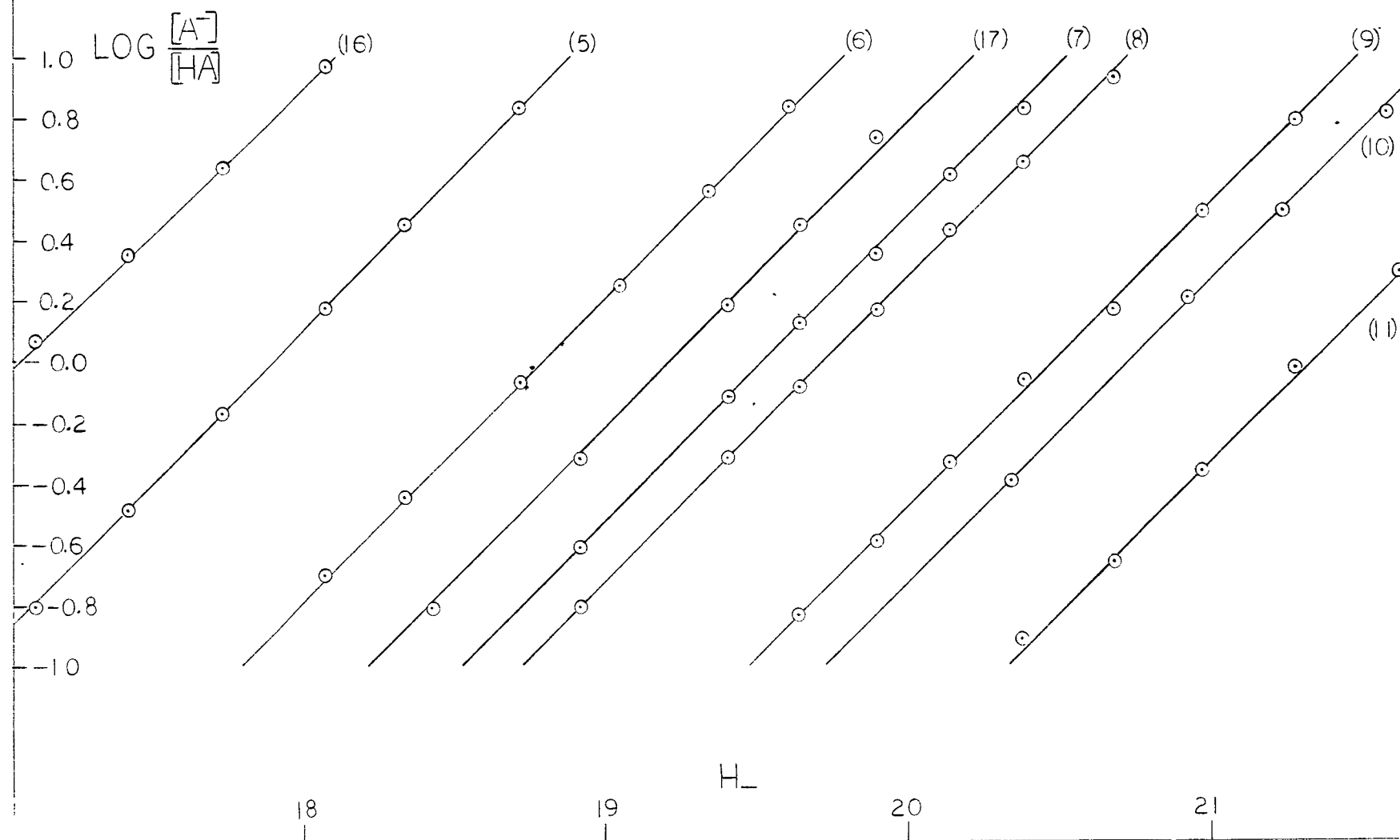
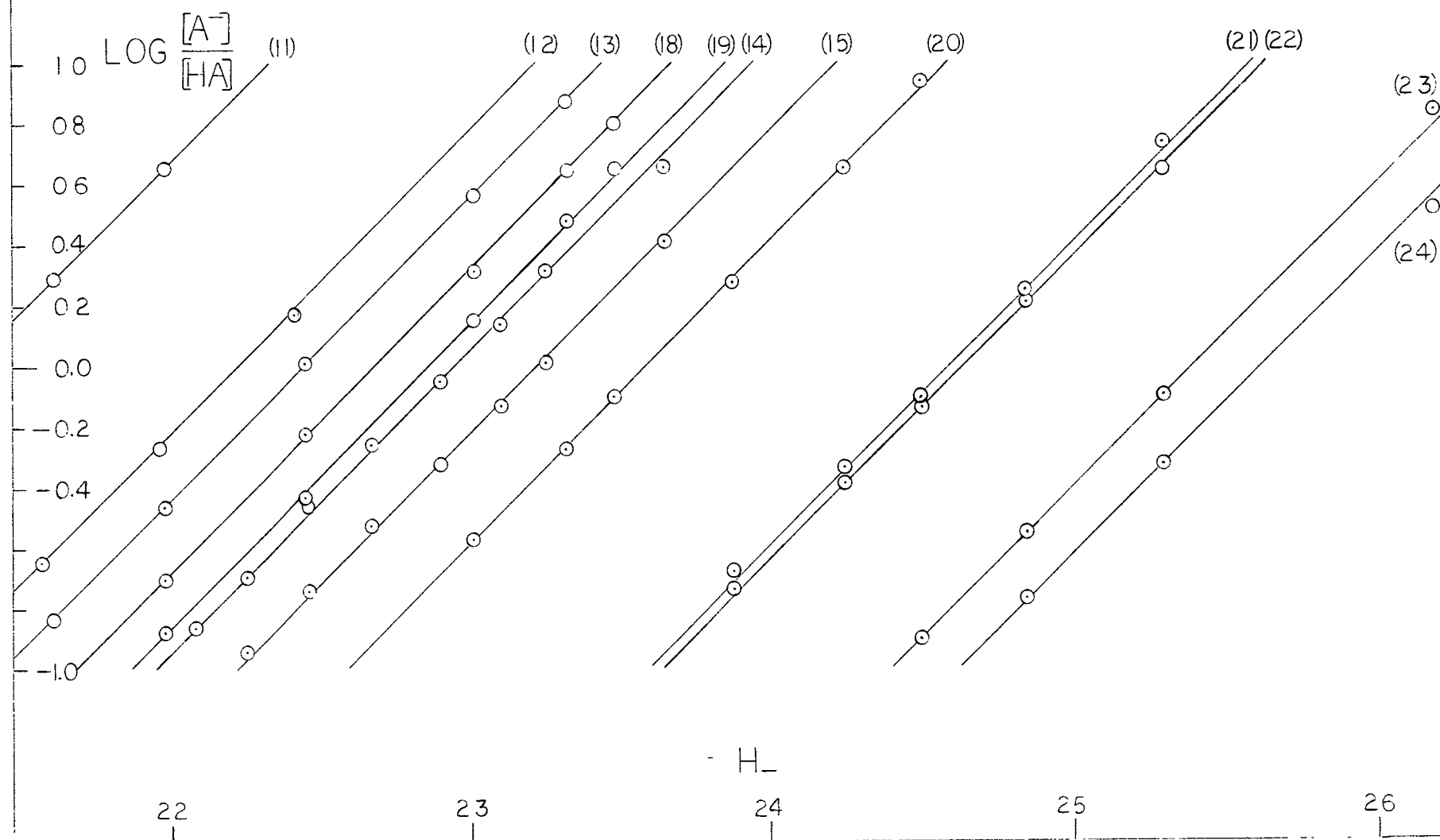


FIGURE 2 (CONT)



H₋ scale and consisted mainly of alkyl-substituted 4-nitroanilines. The pK_{HA} of an acid was taken as the intercept of a plot of $\log I$ versus H₋, that is, the H₋ of the solution in which the indicator is half ionized. These plots are not all of unit slope, especially for the substituted nitroanilines. However, for four dichloroanilines the slopes are, within experimental error, unity.

The acids, their pK_{HA} values and the slopes of the plots of $\log I$ ($\log [A^-] / [HA]$) versus H₋ are listed in Table III and the above mentioned plots are shown in Figure 3. The plot for 2,6-di-t-butyl-4-nitroaniline is not a straight line although it appears the points approach a line of unit slope for values of $\log I$ less than zero.

An estimate was made of the pK_{HA} of 4-aminodiphenylamine. An accurate measurement could not be made because of the difficulty in purifying this compound and its readiness to react with the slightest trace of oxygen in the basic media. A value of 24.2 was obtained from a comparison of its ionization ratios in three solutions with those of 4-methoxydiphenylamine.

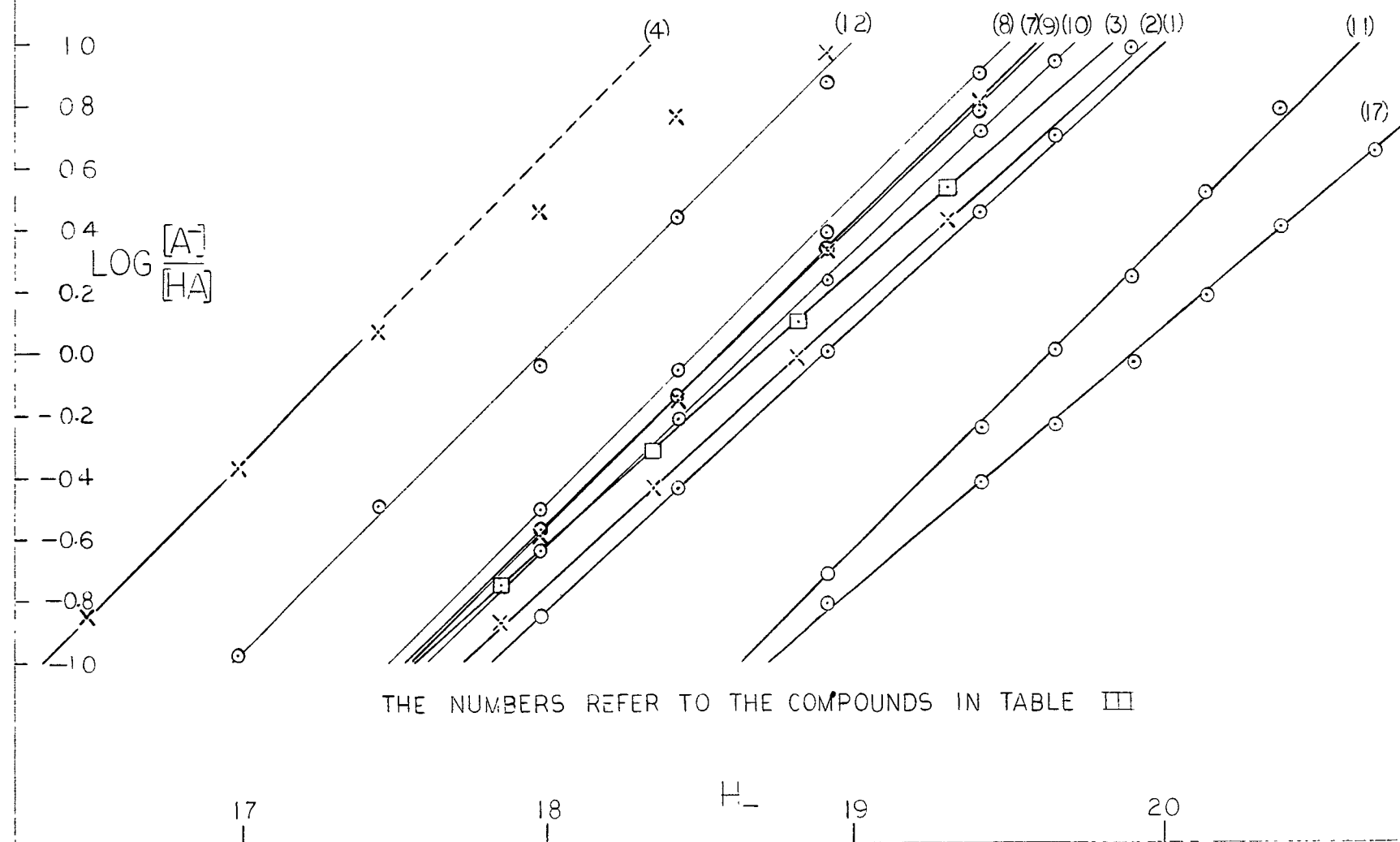
TABLE III

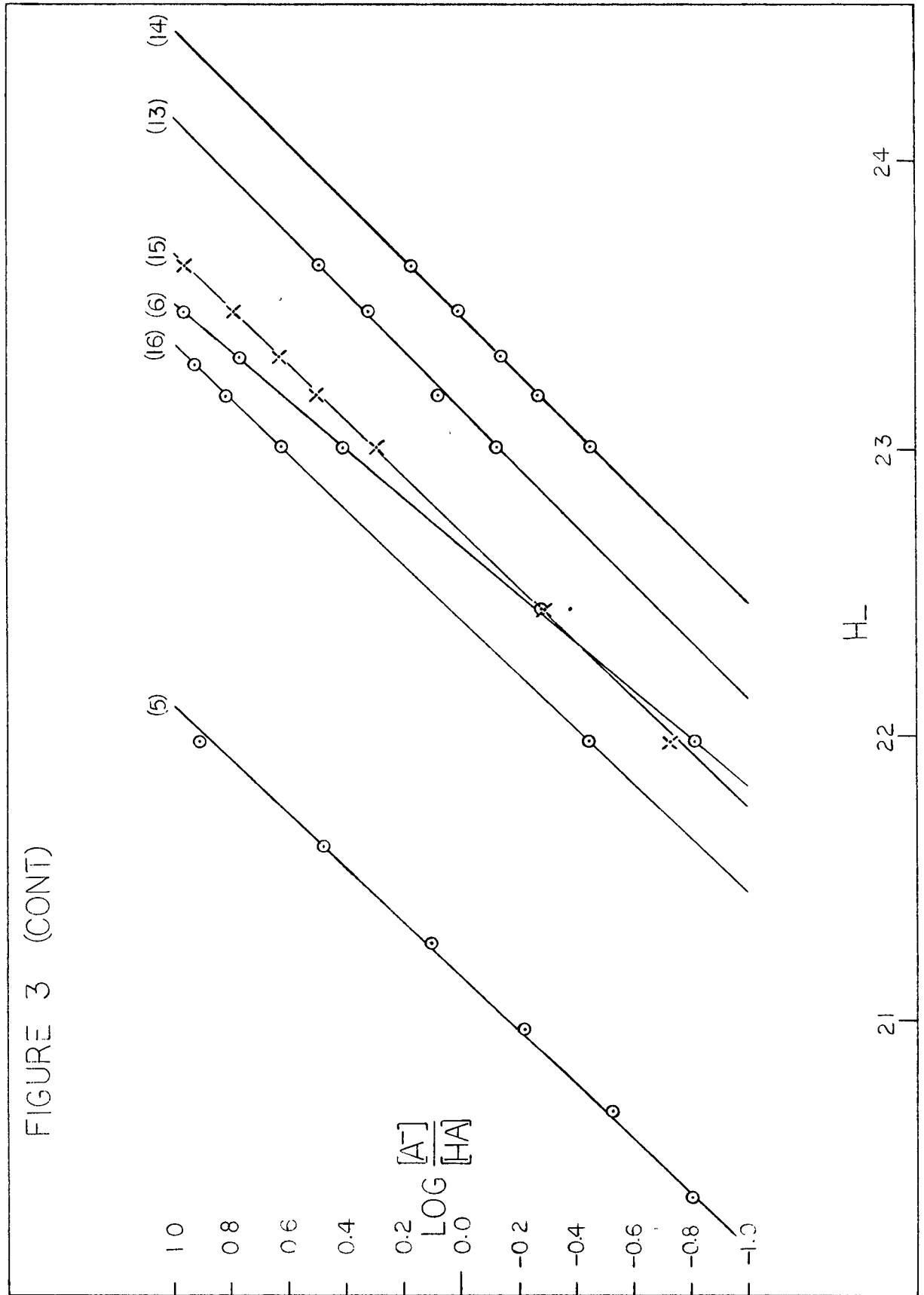
Summary of pK_{HA} Values of Various Amine Acids

	Compound	pK_{HA}^a	Slope of plot of log I vs H_-
1.	4-nitroaniline	18.91	0.92
2.	4-nitro-2-methylaniline	18.83	0.91
3.	4-nitro-2,6-dimethylaniline	18.71	0.89
4.	4-nitro-2,6-di-t-butylaniline	17.4	-
5.	4-nitro-3,5-dimethylaniline	21.16	1.05
6.	4-nitro-2,3,5,6-tetramethyl- aniline	22.66	1.18
7.	4-nitro-N,2-dimethylaniline	18.58	0.96
8.	4-nitro-N-methylaniline	18.49	0.99
9.	4-nitro-N-ethylaniline	18.58	0.95
10.	4-nitro-N-isopropylaniline	18.66	0.95
11.	4-nitro-N-t-butylaniline	19.64	1.02
12.	4-nitro-N-triphenylmethyl- aniline	17.98	0.99
13.	2,3-dichloroaniline	23.14	1.00
14.	2,4-dichloroaniline	23.46	1.00
15.	2,5-dichloroaniline	22.71	1.04
16.	2,6-dichloroaniline	22.40	1.02
17.	2,2'-dipyridylamine	19.91	0.85

^a pK_{HA} taken as the H_- at half ionization

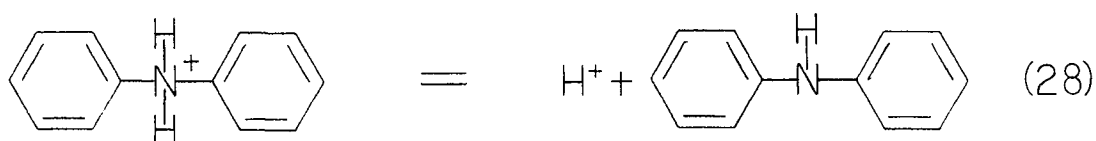
FIGURE 3 PLOT OF $\text{LOG } [A^-]/[HA]$ VERSUS H_L FOR VARIOUS AMINES





B. The System "20% Ethanol"-Aqueous Sulfuric Acid

The pK_{BH^+} values for the ionization of the diphenylammonium ions in this medium were obtained in the same way



as the pK_{HA} values for the ionization of the neutral amines in the basic medium. The reference base was diphenylamine. The pK_{BH^+} value of its conjugate acid was found to be 0.78 from a comparison of its ionization with that of the conjugate acid of 4-nitroaniline in aqueous solutions of hydrochloric acid. The following equation was used

$$pK_{BH^+}^A - pK_{BH^+}^D = \log I_A' - \log I_D' + \log \left(\frac{f_B}{f_{BH^+}} \right)_D \left(\frac{f_{BH^+}}{f_B} \right)_A \quad (29)$$

where the letters "A" and "D" refer to 4-nitroaniline and diphenylamine respectively, and I' refers to the ratio $[\text{BH}^+]/[\text{B}]$. Experimentally it was found that $\log I_A' - \log I_D'$ had a value of $0.217 \pm .004$ for seven solutions of hydrochloric acid varying in strength from 0.03 to 0.5 molar. There appeared no tendency of this quantity to vary, within experimental error, with acid concentration.

Since the last term in equation (29) must, by definition, be zero in dilute aqueous solution it is very probably zero in the hydrochloric acid solutions because of the constancy of the $\log I'_A - \log I'_D$ term. Thus the number 0.217 is the difference in pK_{BH^+} values for 4-nitroaniline and diphenylamine.

This difference combined with the pK_{BH^+} value of 1.00 for 4-nitroaniline^{84,85} gives a value of 0.78 for the pK_{BH^+} of diphenylamine. A value of 0.79 has been found by Paul⁸⁵, although it is recorded as 0.78 in the review of Paul and Long¹². The pK_{BH^+} values of all the substituted diphenylamines are based on a pK_{BH^+} value of 0.78 for diphenylamine.

Equation (23) was used to calculate H_O values for the various acid solutions. As before, two or more indicators were generally used to calculate H_O for

$$H_O = pK_{BH^+} - \log I' \dots \left(I' = \frac{[BH^+]}{[B]} \right) \quad (23)$$

each solution.

Table IV lists the diphenylamines and their pK_{BH^+} values used to calculate the H_O function in "20% ethanol"-aqueous sulfuric acid.

TABLE IV

Values of pK_{BH^+} for the Diphenylamines
used to Establish the H_0 Acidity Function

	Substituents	pK_{BH^+}
1	4-methoxy	1.36
2	4-methyl	1.20
3	none	(0.78) ^a
4	3-methoxy	0.40
5	4-chloro	0.01
6	3-chloro	-0.45
7	3-trifluoromethyl	-0.78
8	3,4'-dichloro	-1.19
9	3-nitro	-1.61
10	4-methylsulfonyl	-2.54
11	4-nitro-3'-methyl	-2.93
12	4-nitro	-3.13
13	2-nitro	-4.12
14	4-nitro-3'-chloro	-4.15
15	4-nitro-3'-trifluoromethyl	-4.47
16	3,4'-dinitro	-5.19
17	4,4'-dinitro	-6.21

^a This value determined in aqueous solutions of HCl

Table V lists the mean H_0 values determined for these solutions along with the average deviation of the individual values from the mean and also the identity of the indicators used to calculate H_0 for each solution.

Figure 4 is a plot of the data in Table V.

Figure 5 is a plot of the experimental values of $\log I' ([BH^+]/[B])$ versus H_0 . As before, lines of unit slope with intercepts equal to the pK_{BH^+} values of the indicators have also been drawn for comparison. The fit of the experimental points to the lines is a measure of the validity of the results.

C. Probable Error in H and pK Values

With all acidity functions it is difficult to estimate the uncertainty in H values and in the pK values of the indicators used to determine them. The further an acidity function is from the usual pH range the greater likelihood of errors because of the stepwise procedure used to establish it. For example, in strongly basic solutions any error encountered in determining the difference in pK_{HA} values between two overlapping indicators is incorporated in the pK_{HA} value of the less acidic one and also in the H_- values determined from its ionization ratios. Errors can be minimized by using a large number of overlapping

TABLE V

H₀ Values for the System "20% Ethanol"-Aqueous
Sulfuric Acid

Molarity of H ₂ SO ₄	H ₀ Value	Ave. Dev. from Mean	Indicators ^a
0.0163	1.86	0.01	1,2
0.0339	1.56	.01	1,2
0.0567	1.34	.00	1-4
0.0808	1.18	.005	1-4
0.163	0.87	.00	1-4
0.245	0.67	.01	1-4
0.406	0.41	.00	1-5
0.611	0.17	.01	3-6
0.763	0.03	.00	3-7
0.914	-0.10	.00	3-7
1.26	-0.35	.005	4-8
1.47	-0.48	.005	4-8
1.72	-0.63	.00	5-8
1.98	-0.78	.00	5-9
2.25	-0.93	.01	5-9
2.49	-1.07	.00	6-9
2.73	-1.20	.005	6-9
3.07	-1.40	.005	7,8
3.29	-1.53	.00	7-9
3.58	-1.70	.01	7-10
3.76	-1.81	.01	8-10
4.14	-2.03	.01	8-11
4.38	-2.17	.005	9-12
4.62	-2.32	.005	9-12
4.90	-2.51	.01	9-12
5.15	-2.65	.01	10-12
5.41	-2.81	.005	10-12
5.66	-2.97	.00	10-12
5.95	-3.18	.03	10-14
6.47	-3.52	.02	10-15
6.81	-3.75	.01	11-15
7.16	-3.99	.005	12-15
7.64	-4.33	.005	13-16
8.14	-4.69	.02	13-16
8.44	-4.91	.03	13-16
8.87	-5.20	.005	15-17
9.31	-5.54	.00	16,17
9.81	-5.91	.005	16,17
10.18	-6.19	.005	16,17
10.65	-6.54	-	17
11.22	-6.97	-	17

^a Numbers refer to those in Table IV

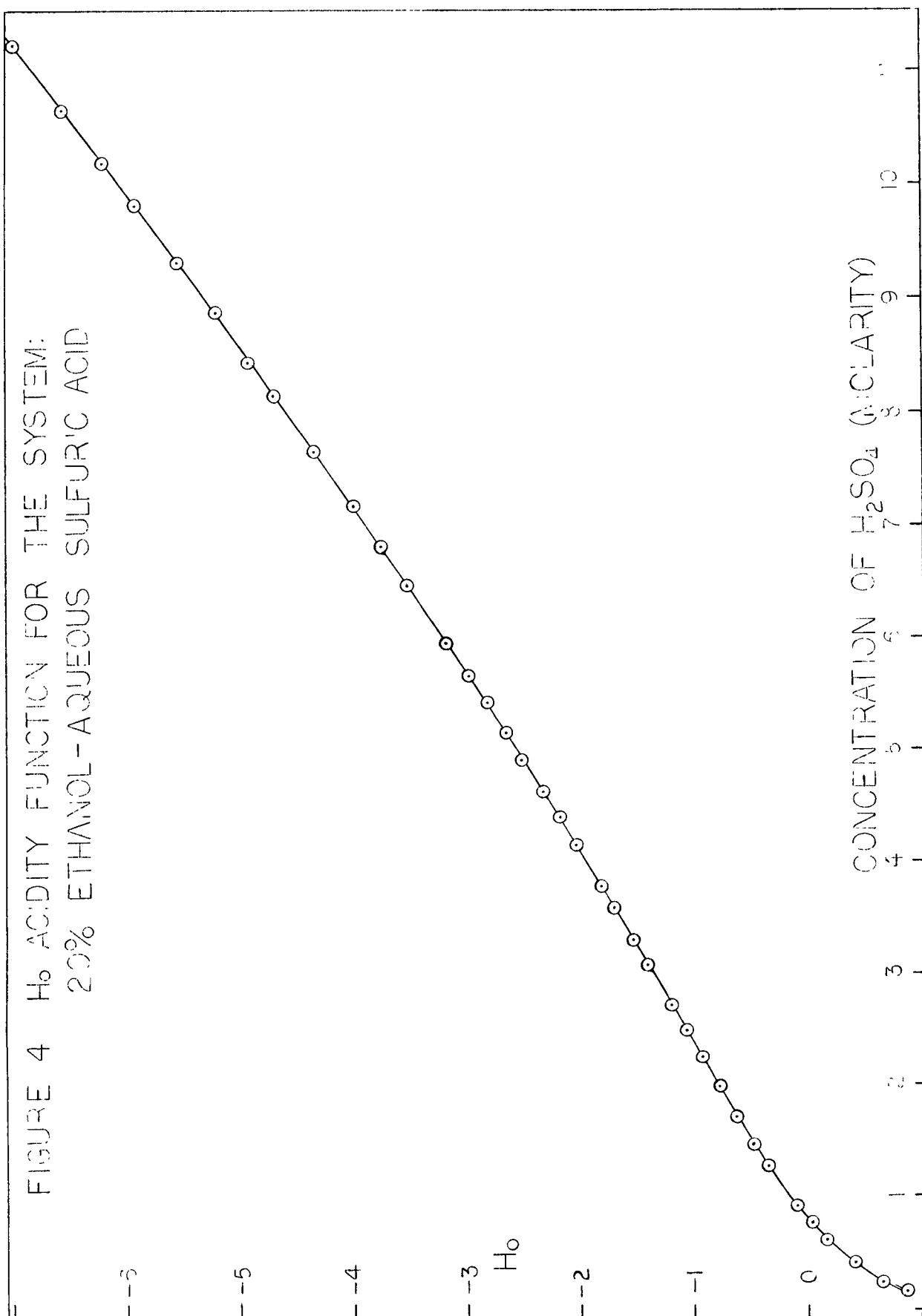


FIGURE 5 PLOT OF $\text{LOG} \frac{[\text{BH}^+]}{[\text{B}]}$ VERSUS H_0 FOR THE INDICATORS
USED TO ESTABLISH THE H_0 SCALE

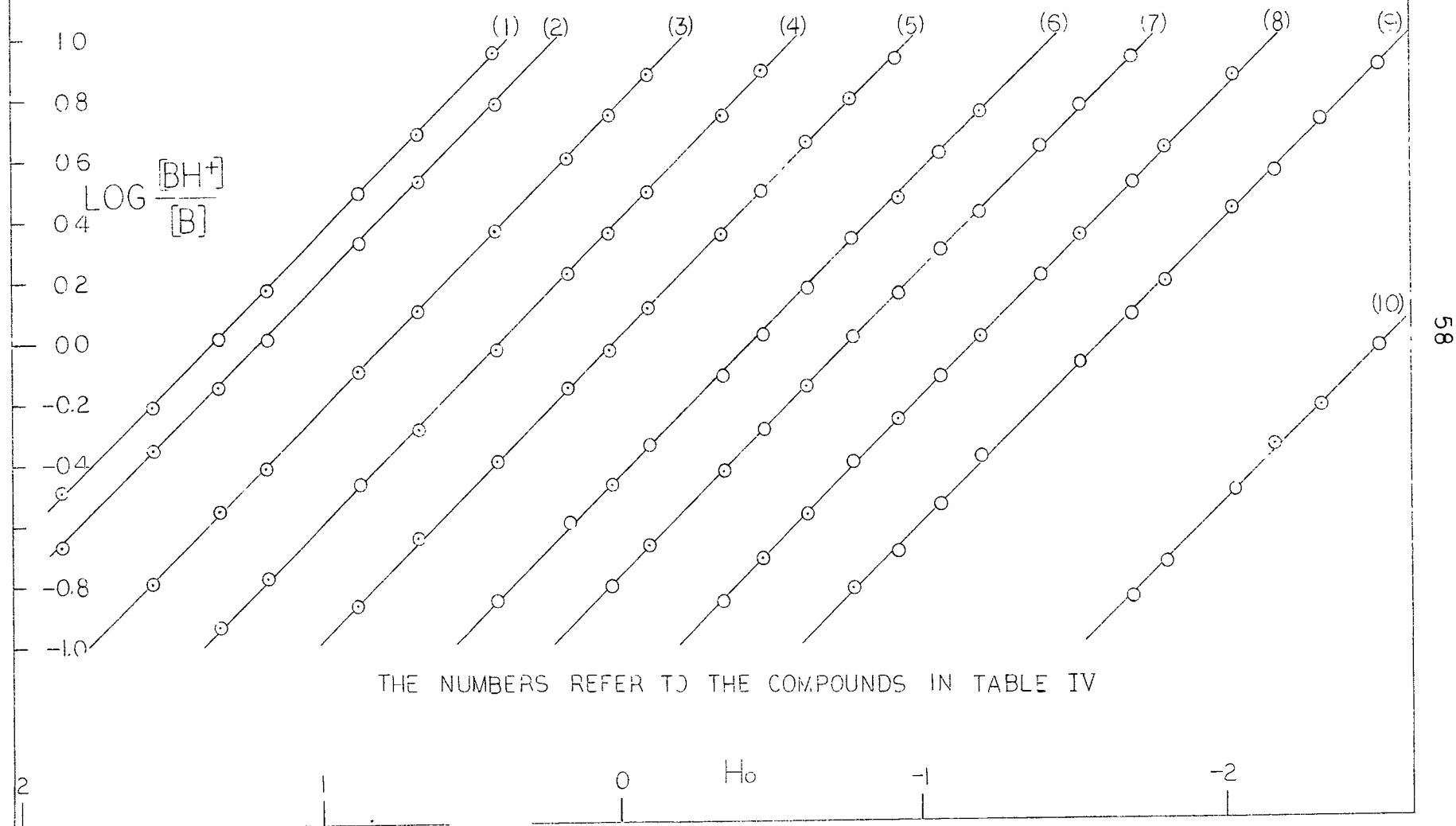
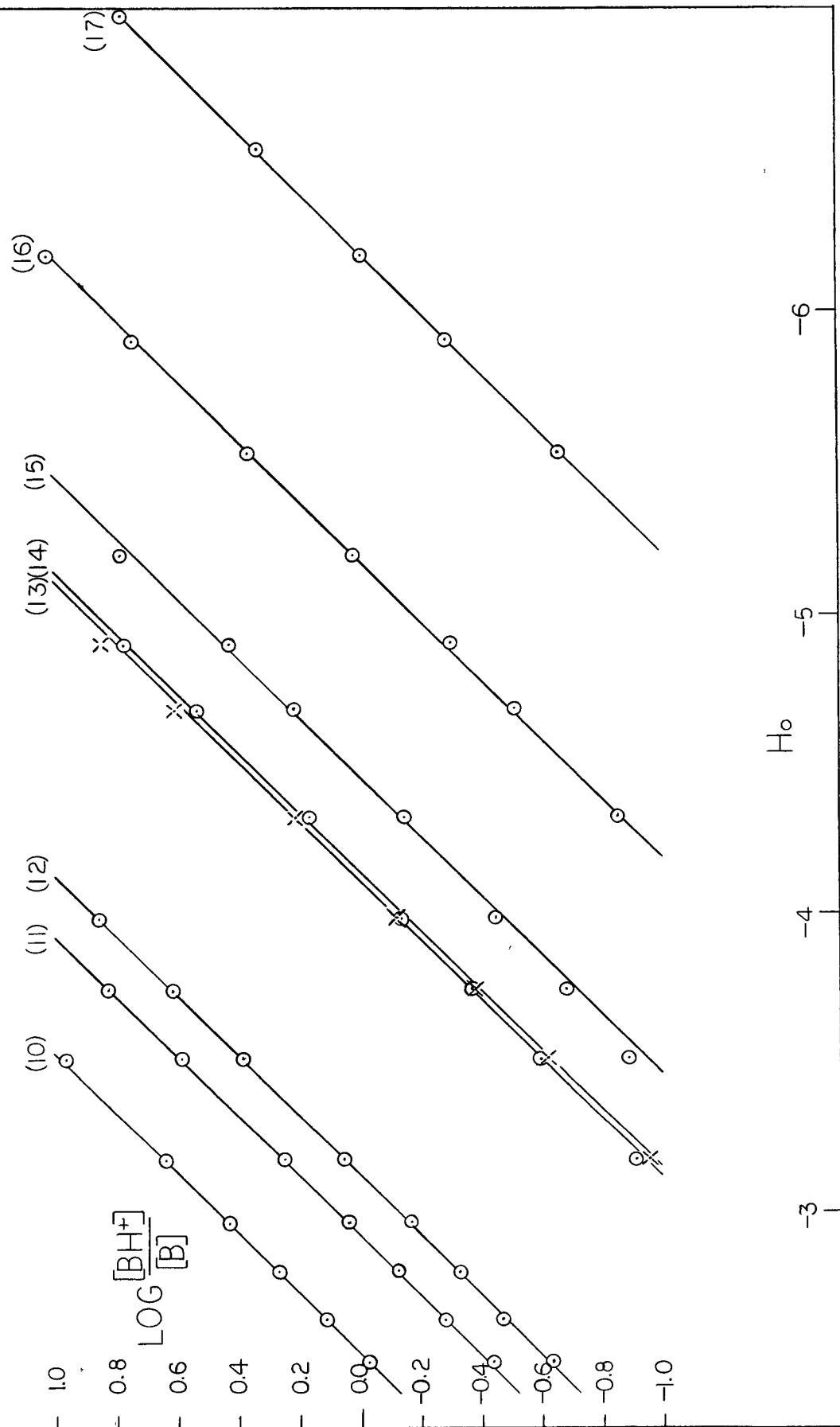


FIGURE 5 (CONT)



indicators so that the H value for a given solution is not dependent on the data for one indicator and by using indicators of the same structural type to ensure that the Hammett activity coefficient postulate is obeyed as closely as possible.

The pK values in this work are recorded to two decimal places. This is valid for the relative pK values of indicators that are not more than one or two pK units apart. The uncertainty in this case is probably $\pm .03$ to $\pm .05$ pK units. The uncertainty in the thermodynamic pK values, however, is likely greater than this and the figure in the second decimal place is of little significance. This is particularly true of very high pK_{HA} values and of large negative values of pK_{BH^+} .

DISCUSSION

A. Validity of the H_- Function

The use of the Hammett procedure to establish an H_- function for the ionization of aromatic amines in the DMSO-water system seems justified. This is evident in the fact that the plots of $\log I$ versus solvent composition gave parallel curves for overlapping indicators. It can also be seen in the good agreement in H_- values calculated using different indicators (Table II) and in the fit of the experimental points for $\log I$ to the lines of unit slope (Figure 2).

As shown in Table II and Figure 2, a number of indicators have in general been used to determine H_- for each solution. This procedure ensures that the H_- scale is not too dependent on any one indicator.

Both primary and secondary amines have been used in constructing the H_- scale and it appears that the ionization behaviour in the DMSO-water system of both types of amines is described by one acidity function. This fact is particularly evident in Figure 2 for the indicators ionizing in the region of H_- from 21.5 to 24.0. In this range there are seven closely spaced indicators of which three are primary amines and four are secondary amines.

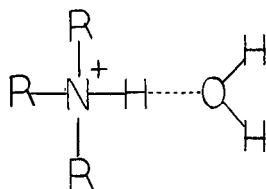
The plots of $\log I$ versus H_- for both types of indicator are parallel to one another indicating that the ionization of primary and secondary amines is governed by one H_- function.

The existence of only one H_- Scale for both primary and secondary amines contrasts with the fact that there are separate H_0 scales to describe the protonation of primary and tertiary^{23,24} and also, quite probably, secondary²⁸ amines in sulfuric acid mixtures. The different behaviour in acidic and basic media is not unreasonable in view of current ideas on the solvation of ammonium ions.

The fact that ionizations of the ammonium ions resulting from primary, secondary and tertiary amines are described by different H_0 functions is believed to stem, to a great extent, from differences in the solvation of these ammonium ions^{24,25,28}, which is reflected in the activity coefficient term f_{BH^+} of the expression

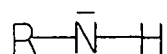
$$H_0 = -\log (H^+) \frac{f_B}{f_{BH^+}} \quad (30)$$

The differences in the solvation of the ammonium ions is in turn believed to be a result of specific solvation of these ions involving formation of strong hydrogen bonds between the hydrogen atoms on the nitrogen atom of an amine and the oxygen atom of a water molecule^{28,30,86}. The number of such interactions and hence the solvation of



the ammonium ion will depend on whether the amine is primary, secondary or tertiary.

Hydrogen bonding of this type in amine anions should be of little importance because of the negative charge on the nitrogen atom. For these ions hydrogen bonds



involving the electron pairs on the nitrogen atom would be more important. Since there are two pairs of unshared electrons on an amine anion regardless of whether it is primary or secondary it would be expected (neglecting steric effects) that the solvation of these ions would be quite similar. In view of this, the use of just one H_- function to describe the ionization of primary and secondary amines in basic solution is reasonable.

A test of the validity of H_- functions is the agreement among pK_{HA} values measured in different solvent systems. In Table I it can be seen that the agreement between the pK_{HA} values determined in this work and those determined in aqueous sulfolane by Langford and Burwell^{40,52} for 4-nitrodiphenylamine and 4-chloro-2-nitroaniline is very good (differences of .01 and .05 respectively). The agreement with the values of Stewart and O'Donnell⁴⁰ measured in the same solvent is not quite as good. A large discrepancy exists for the pK_{HA} value of 4-nitroaniline as observed in this work, 18.91, and by Stewart and O'Donnell⁴⁰, 18.37, and by Langford and Burwell^{40,52}, 18.39. It should be noted that 4-nitroaniline was not used in determining the H_- scale in this work and that the slope of the plot of $\log I$ versus H_- is 0.92 for this compound.

4-Nitroaniline was not used in determining the H_- scale since the plot of $\log I$ versus solvent composition for it was not parallel to similar plots for the indicators 4-methylsulfonyldiphenylamine and 2,3,5,6-tetrachloroaniline that ionize in the same range of solvent composition. Because of the behaviour of 4-nitroaniline, the alkyl derivatives of this compound were also not used to determine H_- . The slopes of the plots of $\log I$ versus H_- for most of these compounds (Table III) lie between 0.95 and 1.05

and it appears that the ionization of these compounds is governed at least approximately by H_- . However, for some others, such as 4-nitro-2,3,5,6-tetramethylaniline (slope = 1.18), the slopes of the plots vary considerably from unity indicating that the ionization of these compounds is not governed by H_- . The cause of this variance in the behaviour of the 4-nitroaniline derivatives is not known. The ionization of one non-nitro aromatic amine, 2,2'-dipyridylamine (slope = 0.85), is also not governed by H_- .

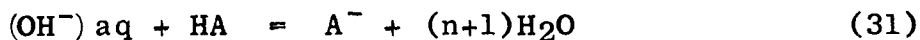
B. Interpretation of Solvent Basicity

The addition of dimethylsulfoxide to aqueous solutions of hydroxide ion has a great effect on the basicity of these solutions. Thus the H_- of 0.011 molar tetramethylammonium hydroxide rises from 12 in water to 26 in 99.5 mole % DMSO, an increase of 14 powers of ten in basicity (as measured by its effect on arylamine ionization). In Figure 1 it can be seen that the basicity increases steadily as the solvent composition proceeds from aqueous to 85 mole % DMSO. In this region the plot of H_- versus mole % DMSO is nearly linear with slope, $d(H_-)/d(\text{mole \% DMSO})$, of about 0.10. Above 85 mole % DMSO the slope increases and the basicity rises very quickly as the water concentration approaches zero. From 95 to 97.5 mole %

DMSO, H_- increases by almost one unit and from 97.5 to 99.0 mole % H_- increases again by one unit.

What are the causes for the great enhancement in basicity of hydroxide ion in DMSO solutions?

One approach to answering this question is to consider the equilibrium between hydroxide ion and indicator acid, HA,



in which the hydroxide ion is considered to be intimately solvated by a number of water molecules. The number n can be considered either as the hydration number of the hydroxide ion⁴⁷ or, if the indicator or its anion are also intimately solvated, as the difference in solvation numbers⁴² between the left and right sides of equation (31). The effect of adding DMSO to the system is to drive this equilibrium to the right, an effect that is interpreted as an increase in basicity of the hydroxide ion.

It is possible to derive the following expression for H_- in terms of the equilibrium in equation (31).

$$H_- = \log \frac{(\text{OH}^-)}{K_w} - (n + 1) \log (\text{H}_2\text{O}) - \log \frac{f_{\text{A}^-}}{f_{\text{HA}}} \quad (32)$$

On this basis the change in H_- with increasing concentration of DMSO can be attributed to changes in hydroxide ion activity, in water activity and in the activity coefficient ratio f_{A^-}/f_{HA} .

It is difficult to predict the effect upon the last term in equation (32) of changing the solvent from water to DMSO. Since such polar aprotic solvents as DMSO are poor at solvating anions³⁸ the activity coefficient f_{A^-} of an amine anion probably increases in the change from water to DMSO. This increase is not as large as that suffered by the hydroxide ion since anions larger than the chloride ion are not considered to be intimately hydrated^{87,88} in aqueous solution. At any rate, the term $\log f_{A^-}/f_{HA}$ probably increases as the amount of DMSO in the system increases and consequently will tend to decrease H_- .

The large increases in H_- upon the addition of DMSO to the system must be due to increases in the activity of the hydroxide ion and to decreases in the water activity. The decrease in water activity is not due just to a dilution effect but also to the ability of DMSO to complex with water by formation of strong hydrogen bonds^{89,90}. This fact is also evident from the large heats of mixing of DMSO and water⁷⁷. Data for the activity of water in DMSO-water mixtures at 25° are not available, however data are available

for 70°⁹¹. They show that as the water content decreases and the DMSO content increases not only does the activity of the water decrease but also the activity coefficient, f_{water} , steadily decreases.

The increase in H_- due to decrease of the water activity will depend on the state of hydration of the hydroxide ion and to a much lesser extent on the hydration of the indicator and its anion. As was mentioned above, large anions such as those of aniline and diphenylamine are not considered to be extensively hydrated. On the other hand, such small anions as the fluoride and hydroxide ions are strongly hydrated in aqueous solution^{87,88}. Estimates of the number of water molecules in the hydration shell of the hydroxide ion have been made. Yagil and Anbar⁴⁷ found that the H_- values for aqueous sodium and potassium hydroxides could be calculated assuming a hydration number of 3. Other estimates of the hydration number vary from 4⁸⁸ to 6^{92,93}. If the number n in equilibrium (31) and in equation (32) is identified with the hydration number of the hydroxide ion then the position of the equilibrium and therefore the basicity of the solution depend on at least the fourth power of the water activity.

This dependence of H_- on water activity must account for a part of the increase in H_- with increase in

DMSO content especially in the linear portion of the curve in Figure 1. However, it cannot account for all the increase in this region. For example, if the H_- is assumed to depend on the fourth power of the water activity and the activity data for DMSO-water at 70°⁹¹ is assumed to approximate that at 25° then the change of H_- for 0.011 molar hydroxide on passing from water to 50 mole % DMSO should be about 2 units. (This is the change due to the mass action effect and not due to the change in hydroxide activity.) Figure 1 shows that the actual change in H_- is 5.5 units. Thus, the increase in basicity upon adding DMSO to aqueous solutions of hydroxide ion is due partly to the reduction in water activity and its subsequent mass action effect on the equilibrium between hydroxide ion and acid and partly to the increased activity of the hydroxide ion.

The activity coefficient of the hydroxide must show large increases even at low DMSO concentrations since reasonable assumptions about water activity and hydration numbers do not account for the large increase in H_- in this region of solvent composition. It should be pointed out that only at compositions greater than 99 mole % DMSO does the water concentration become so low as to approach that of the hydroxide ion. In fact, in the most basic

solution studied, 99.59 mole % DMSO, the ratio of concentrations of water to hydroxide ion is slightly greater than 5.

An explanation of the increase in hydroxide ion activity at low DMSO concentrations may lie in the effect of DMSO on the structure of water. Liquid water is considered to retain much of the open structure of ice in which the water molecules are hydrogen bonded to four other water molecules in a tetrahedral array^{94a}. Small ions and multivalent ions increase the viscosity of water and are believed to promote formation of an ice-like structure in the water molecules beyond the nearest neighbour molecules. Such anions as F^- and OH^- belong to this class and are said to be structure-making ions^{94b}. Larger ions decrease the viscosity of water and are believed to break down the ice-like structure of water beyond the nearest neighbour molecules. This class is said to be structure-breaking and contains such anions as Cl^- , Br^- , I^- and NO_3^- ^{94b}. Some ions are intermediate in character and have little effect on the structure of liquid water.

Frank⁹⁵ has pointed out that ions of opposite character in the same solution bring about an increase in their activity coefficients over that to be expected if they were not structure-altering. Consider, for example, a structure-making cation and a structure-breaking anion. The

cation tends to produce more structure in the water and consequently creates a hostile environment for the anion, which in turn "wants" to break down the structured environment. The reverse argument also applies. The net result is that the ions tend to salt each other out of solution and thus produce an increase in their activity coefficients. These effects can be surprisingly large. Frank⁹⁵ has interpreted some e.m.f. measurements as indicating that the activity coefficient of the iodide ion in 0.03 molar tetrabutylammonium iodide is 8.65 times as large as the activity coefficient of the iodide ion in 0.03 molar potassium iodide. The iodide ion is structure-breaking, the tetrabutylammonium ion is strongly structure-making and the potassium ion is weakly structure altering. The increased activity of the iodide ion in the first solution is a result of the strongly opposed characters of the tetrabutylammonium and iodide ions.

As was mentioned above, the hydroxide ion is a structure-making ion. Consequently, anything that breaks down the structure of water will increase the activity coefficient of the hydroxide ion and, therefore, the basicity of the solution. The addition of DMSO to the solution may have this effect. The ability of DMSO to form strong hydrogen bonds with water molecules^{89,90} may permit it to break down the partial ice structure of water. This is

supported by the fact that the density of DMSO-water mixtures is greater than that expected from additivity⁷⁷. This would not be expected if the open, ice-like structure of water persisted. Further, the addition of DMSO to water causes the water proton magnetic resonance signal to shift to higher magnetic field⁹⁶, an effect that is generally interpreted as a reduction in hydrogen bonding⁹⁷. This is also consistent with a break-down of the water structure. All the evidence, however, is not consistent with this picture. The viscosity of DMSO-water mixtures is greater than would be expected from additivity whereas break-down of the hydrogen-bonded ice-like structure of water should be accompanied by an increased fluidity^{94b}.

It is possible, then, that the basicity of hydroxide ion solutions is increased at low DMSO concentrations due to breaking down of the water structure. This argument, however, has neglected the effects of these changes on the activities of the indicator and its anion. It is possible that the effects would be similar for both species because of the relatively small structural changes of the amines on ionization and the charge dispersal over one or two aromatic rings in the anion. In this case the effects on the equilibrium in equation (31) would cancel.

The cause of the rapid up-swing in H_- as the solvent changes from 80 to 100 mole % DMSO is most probably the break-down of the hydration shell of the hydroxide ion brought about by the efficiency with which the DMSO competes with the hydroxide ion for the water molecules. A decrease in the number of water molecules solvating the hydroxide ion brings about a great increase in its activity and therefore in the basicity of the solution. This is supported by the very low solubility of sodium hydroxide in DMSO (upper limit of 7.6×10^{-4} molar)⁹⁸.

It might be pointed out that DMSO possesses the ability not only to produce large changes in equilibrium processes, as observed in this work, but also in kinetic processes. The base catalyzed racemization of certain hydrocarbons⁷⁰, the saponification of esters^{90,99} and nucleophilic aromatic substitution¹⁰⁰ all show dramatic increases in rate when the solvent is changed from water or alcohol to DMSO or mixtures of these solvents with DMSO.

C. Validity of the H_O Function

The H_O scale in ethanol-aqueous sulfuric acid has been determined using indicators of one structural type, substituted diphenylamines. This is an important point, considering the sensitivity of H_O functions to the

structure of the basic center. Unfortunately, the measurements could not be made in completely aqueous sulfuric acid because of insufficient solubility of the diphenylamines. The introduction of ethanol into the solvent precludes any direct comparison of the results obtained in this work with the results obtained using primary²³ and tertiary²⁴ aromatic amines.

The introduction of ethanol into the solvent also makes it particularly important that indicators of one type be used. This can be illustrated by a result obtained with 4-nitroaniline and diphenylamine. First, equation (29) may be rearranged as follows:

$$\log I'_A - \log I'_D = pK_{BH^+}_A - pK_{BH^+}_D - \log \left(\frac{f_B}{f_{BH^+}} \right)_D \left(\frac{f_{BH^+}}{f_B} \right)_A \quad (33)$$

where "A" and "D" refer to 4-nitroaniline and diphenylamine, respectively, and I' refers to the ratio of the concentrations of ammonium ion to amine. It will be recalled that the quantity on the left side of equation (33) is equal to 0.22 and the last term is zero in aqueous solutions of hydrochloric acid. In solutions of sulfuric acid of 0.03 to 0.9 molar in 20 volume % ethanol-water the quantity on the left side of equation (33) is $0.07 \pm .01$. Since the difference between

the pK_{BH^+} values for the two amines is 0.22 the last term in the equation cannot be zero, that is, the Hammett activity coefficient postulate¹⁰ is not obeyed. Consequently, 4-nitroaniline cannot be used to anchor an H_O scale for secondary amines in 20 volume % ethanol-water.

The Hammett postulate appears to be obeyed in this solvent when amines of the same type are used. From preliminary measurements in aqueous dilute sulfuric acid the difference in the pK_{BH^+} values for 4-methoxydiphenylamine and diphenylamine was found to be 0.59. In 20 volume % ethanol the difference was found to be 0.58 (Table IV). The fact that the Hammett postulate is not obeyed when comparing the protonation of a primary with a secondary amine in 20 volume % ethanol-water is probably a result of the importance of hydrogen bonding in the solvation of their ammonium ions^{26,28,86} and the sensitivity of the solvation to solvent changes²⁵.

In Table V, it can be seen that the agreement among the H_O values calculated for a given solution using different indicators is generally very good. Figure V shows that for the most part closely spaced indicators with accurately parallel ionization slopes have been used.

The pK_{BH^+} values for almost all the diphenylamines used in this work have not been hitherto determined. Hammett and Deyrup⁸, in their original work in sulfuric acid, obtained a value of -2.50 for the pK_{BH^+} of 4-nitrodiphenylamine. This had been determined with reference to an H_0 scale constructed using aniline indicators. Taft²⁸ has shown that the ionization behaviour of this compound in sulfuric acid is anomalous when compared to the behaviour of the primary amines used by Hammett and Deyrup.

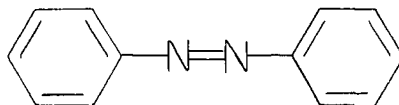
The H_0 value of 5.5 molar sulfuric acid is -2.50¹² determined using primary amines, and 4-nitrodiphenylamine is half ionized in this solution. Using the tertiary amine scale²⁴, the H_0 of 5.5 molar sulfuric acid is -3.58. Consequently, if the " pK_{BH^+} " value for this compound had been determined with reference to the second H_0 scale a value of -3.58 would have been obtained. Of course, the true pK_{BH^+} value for 4-nitrodiphenylamine cannot be obtained from either of these scales but must be determined with reference to an H_0 function for secondary amines.

There is no reason to believe that the H_0 of 5.5 molar sulfuric acid for secondary amines would not lie between the values for primary (-2.50) and tertiary (-3.58) amines. This also means that the pK_{BH^+} value for 4-nitrodiphenylamine

should also lie between the same limits. The pK_{BH^+} found in this work is -3.13 and lies near the middle of these extremes.

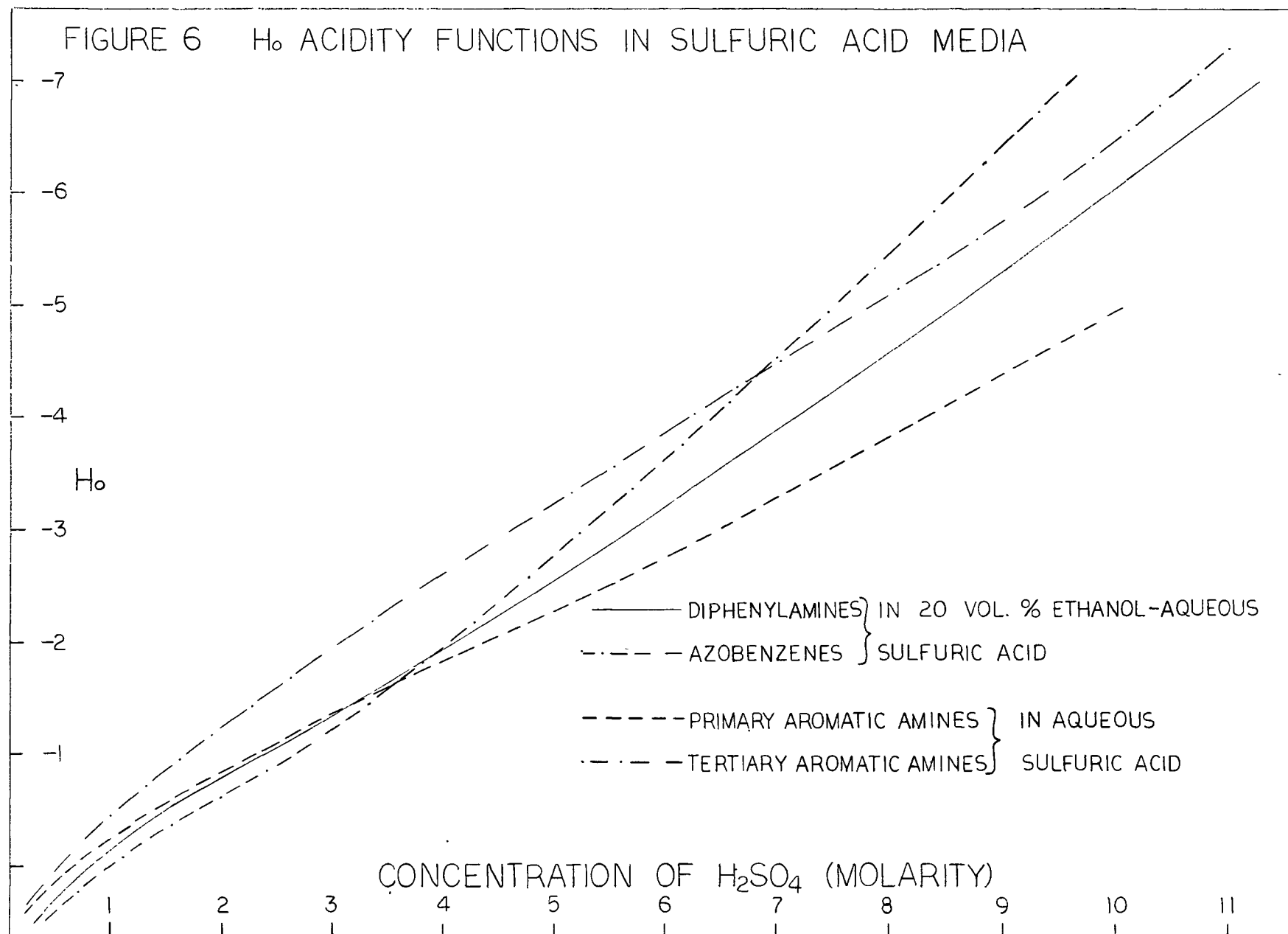
D. Comparison of the H_O Function for Diphenylamines with Other H_O Functions

As was mentioned before, the H_O scale obtained in this work is not directly comparable with those determined for primary and tertiary amines because of the use of ethanol in the solvent. Jaffé and co-workers^{78,79} have determined an H_O scale for the protonation of azobenzenes (XI) in the same solvent system that has been used in this work. Figure 6 is a plot of H_O versus molarity of sulfuric acid for: (i) azobenzenes in 20 volume % ethanol-aqueous sulfuric acid^{78,79}, (ii) diphenylamines in 20 volume % ethanol-aqueous sulfuric acid, (iii) anilines in aqueous sulfuric acid¹², and (iv) tertiary aromatic amines in aqueous sulfuric acid²⁴.



XI

FIGURE 6 H_0 ACIDITY FUNCTIONS IN SULFURIC ACID MEDIA



For purposes of discussion the scale for primary amines in aqueous sulfuric acid will be called H_O' , the scale for diphenylamines in 20 volume % ethanol-aqueous sulfuric acid will be called H_O'' , the scale for tertiary aromatic amines in aqueous sulfuric acid will be called H_O''' , and the scale for azobenzenes in 20 volume % ethanol-aqueous sulfuric acid will be called $H_O^{N=N}$.

First, it should be pointed out that it is possible that the $H_O^{N=N}$ scale of Yeh and Jaffé⁷⁹ should be shifted to more negative H_O values. This arises because of the manner in which their scale was anchored to the region of dilute acid. Azobenzenes of sufficient basicity to protonate in this region were not available and so 4- and 2-nitroaniline were used as indicators. It has just been shown that the Hammett postulate is not obeyed in 20 volume % ethanol-water when comparing the protonation of a primary and secondary amine. There is no reason to believe that it would be obeyed on comparing the protonation of a primary amine and an azobenzene. Azobenzene bears closest resemblance to a tertiary amine because of the lack of hydrogens attached to the nitrogen atoms. This would cause the discrepancy in the apparent pK values obtained in the comparison of an azobenzene with an aniline to be greater than that observed in the case of 4-nitroaniline and diphenylamine. The direction of this discrepancy is such that the $H_O^{N=N}$ scale

would be shifted to more negative values had it been based in the dilute acid region on the ionization of an azobenzene with known pK_{BH^+} . It is not possible to estimate the magnitude of this shift.

Figure 6 shows that at concentrations of acid less than 4 molar the $H_O^{N=N}$ scale is slightly more positive than the H_O'' scale but at greater concentrations the $H_O^{N=N}$ scale becomes progressively more negative than the H_O'' scale. Considering the discussion above, the relative positions of the two scales might actually be reversed in the low concentration range. At any rate, the divergence of the two scales at high acid concentration is not unexpected. It can be seen that the H_O' and H_O''' scales diverge as the acid concentration increases. If the cause of this divergence is the specific interaction of the ammonium ions of the primary and tertiary amines with solvent molecules^{25,28} then a divergence would also be expected for the H_O'' and $H_O^{N=N}$ scales. Azobenzenes resemble tertiary amines and consequently a difference in the H_O scales for azobenzenes and for diphenylamines (secondary amines) would be expected.

At acid concentrations of less than 3 molar both the H_O' and H_O''' scales in aqueous acid are more negative than the H_O'' scale in 20 volume % ethanol-aqueous acid. At higher concentrations of acid, however, the scale in 20

volume % ethanol decreases at a greater rate than either of the aqueous scales. The first observation is consistent with the fact that the addition of ethanol to aqueous solutions tends to increase the $\text{pH}^{79,101}$. Also Braude and Stern¹⁰² have shown that H_0 in 0.1 molar hydrochloric acid increases on proceeding from aqueous to 55 mole % ethanol-water solutions and then decreases until in ethanol H_0 is less (more acidic) than in water.

The second observation, that the H_0'' function in the ethanol-aqueous sulfuric acid mixtures decreases (becomes more acidic) at a greater rate than either the H_0' or H_0''' functions in aqueous acid at the higher acid concentrations, can be explained, as pointed out by Yeh and Jaffé⁷⁹, on the basis of two effects. The first is that at a constant molarity of acid the mole fraction of H_2SO_4 in 20 volume % ethanol-aqueous acid is greater than it is in aqueous solution due to the greater molecular weight and molar volume of the ethanol as compared to the water. At high acid concentrations this becomes important since there is less hydroxylic solvent present to solvate the protons in the ethanolic solutions than there is in the aqueous solutions. The second effect stems from the fact that ethanol is a weaker base than water¹⁰². This means that EtOH_2^+ is a stronger acid than H_3O^+ . As the molarity of sulfuric acid increases, the concentration of water decreases while the concentration

of ethanol remains constant in the ethanol-water-sulfuric acid system. This leads to an increasing amount of EtOH_2^+ as compared to the amount of H_3O^+ and consequently to a greater acidity for the solution because of the greater inherent acidity of EtOH_2^+ .

E. Correlation of Structure with Acidity

One of the important consequences of the great basicity of solutions of hydroxide ion in DMSO-water mixtures is that it has allowed the pK_{HA} values of aromatic amines that do not possess the nitro group as a substituent to be determined. Hammett acidity scales, in both strong acid and base media, using amine indicators, have all made exclusive use of nitro-substituted aromatic amines. This has resulted from necessity rather than choice. However, the extension of the H_- scale to values beyond 19 has allowed the study of the acidity of a series of diphenylamines with a wide variety of substituents whose effects on the acidity of diphenylamine are not dominated by the presence of a nitro substituent.

Inspection of Table I will show that the pK_{HA} of diphenylamine is very sensitive to substituent effects. The pK_{HA} values of all the monosubstituted diphenylamines do not correlate with the Hammett σ^- values nor with any one modification of them. However, if only diphenylamines with

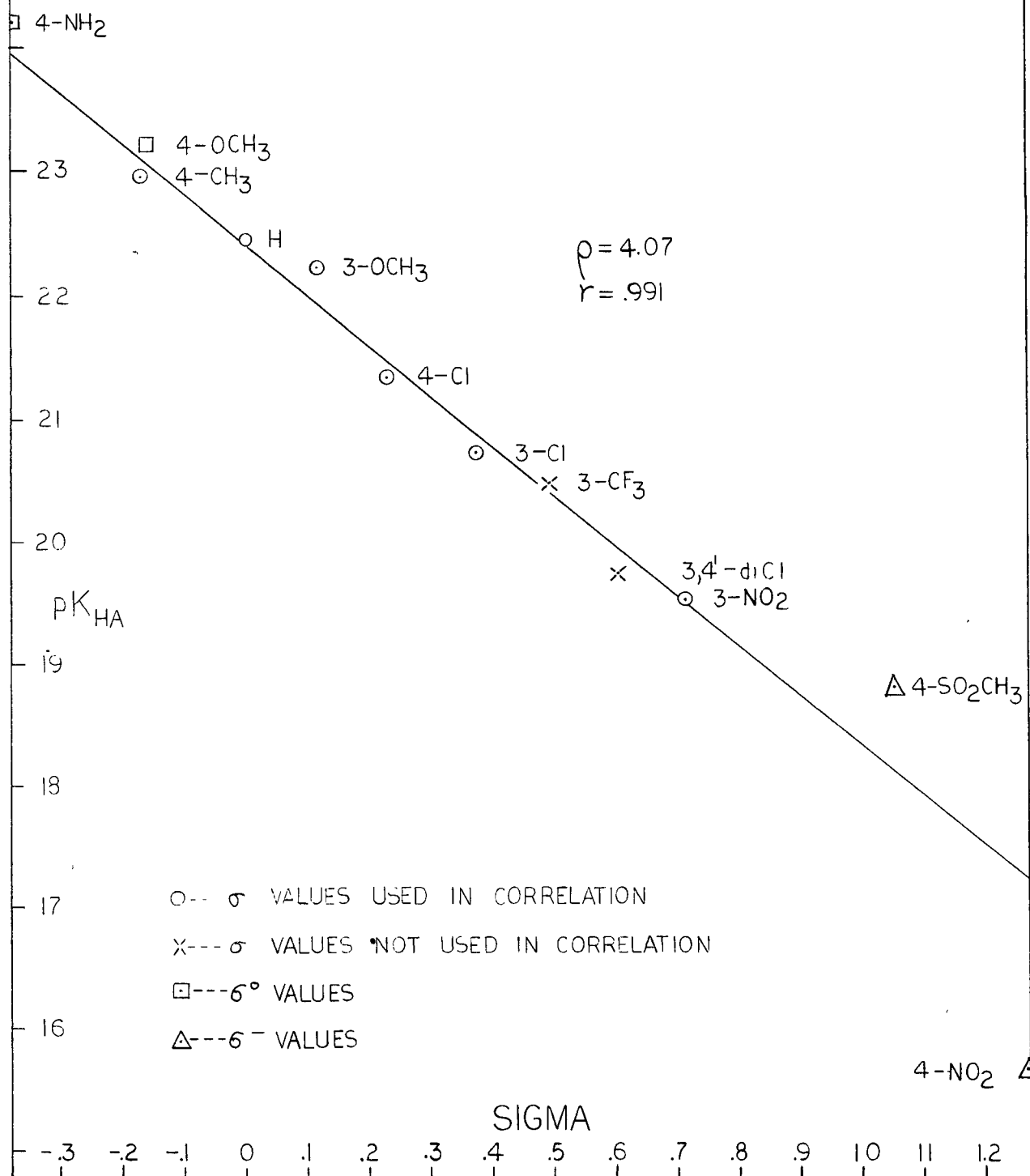
well-behaved substituents are considered, a good correlation is obtained between pK_{HA} and σ . From a plot of $\log K_{\text{HA}}$ versus σ^{103a} for the unsubstituted, 4-methyl, 3-methoxy, 4-chloro, 3-chloro, and 3-nitrodiphenylamines a ρ value of 4.07 is found*. The correlation coefficient, r ,¹⁰⁴ for this plot is 0.991. The plot is shown in Figure 7.

The magnitude of the ρ value is a measure of the sensitivity of the acid strength of diphenylamine to substituents. It should be compared to ρ values of 1.00 for benzoic acids¹⁰⁴, 2.23 for phenols¹⁰⁵, and 2.89 for anilinium ions¹⁰⁵ for aqueous systems at 25°. Thus the acidity of diphenylamine is more sensitive to substituent effects than are the acidities of benzoic acid, phenol or the anilinium ion.

The pK_{HA} values for 3,4'-dichloro and 3-trifluoromethyldiphenylamine were not used in the correlation in Figure 7; the first because the compound has two substituents in different rings and the second because the σ value of the substituent is not well established. If, however, the

* In this and subsequent correlations the method of least mean squares has been used to calculate the best straight line. The equations given by Jaffé¹⁰⁴ have been used for this purpose.

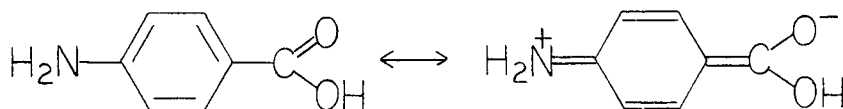
FIGURE 7 HAMMETT CORRELATION OF THE ACIDITY
OF SUSBSTITUTED DIPHENYLAMINES



sum of the σ values for the two chloro groups and the value of 0.49¹⁰⁶ for the 3-trifluoromethyl group, obtained from the ionization of anilinium ions, are used then the points for these two compounds fall near the line.

There are four compounds, 4-amino-, 4-methoxy, 4-methylsulfonyl, and 4-nitrodiphenylamine, for which the pK_{HA} values do not correlate with σ . This is not altogether surprising since the substituents in these compounds display variable resonance effects depending on the nature of the reaction site^{1b, 104}. The acidic site in diphenylamines is attached directly to the aromatic ring while it is not in benzoic acids (whose ionizations are used to determine σ values^{103a}). It might be expected, then, that the four substituents mentioned above would behave differently in the ionization of diphenylamines.

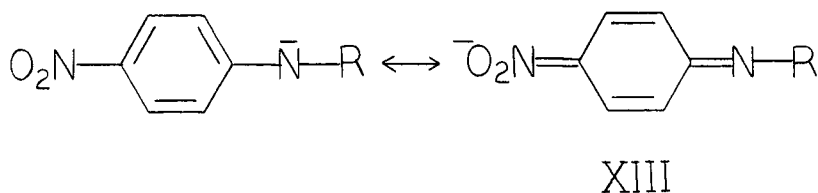
Thus for the 4-amino and 4-methoxy groups resonance interaction of the type, (XII), that is very probably of some importance in the benzoic acids^{1b} is of little importance in the diphenylamines. This is supported by the fact that



XII

the pK_{HA} values for these two compounds are fairly well correlated (figure 7) with σ° values (determined from reactions in which resonance effects are minimal^{103b}).

On the other hand, resonance interaction of the following type is of greater importance for the anion of

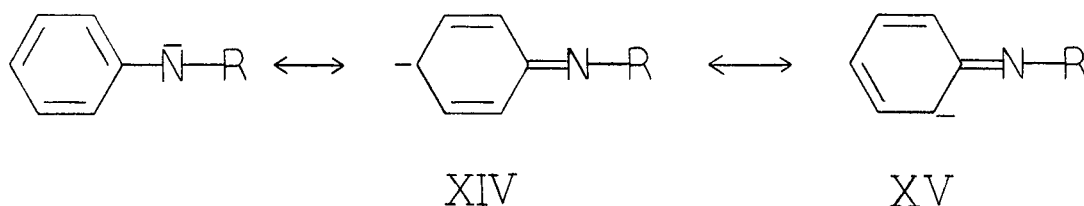


diphenylamine than for the anion of benzoic acid. The σ value for the 4-nitro group is 0.778 in the ionization of benzoic acids^{103a}, 1.27 in the ionization of phenols and anilinium ions^{103c} and must be assigned a value of 1.65 in the ionization of diphenylamines.

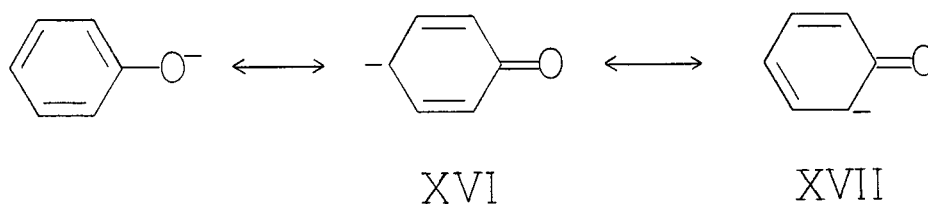
Comparison of substituent effects on the acidity of phenols and diphenylamines should be interesting since these compounds are quite similar. (Anilines would be better nitrogen analogs of phenols than are diphenylamines, however there is insufficient data for a good comparison.) The ρ value for ionization of diphenylamines is 1.8 times as large as the ρ for ionization of phenols; that is, the effects of substituents on the acidity of diphenylamine are 1.8 times as great as they are on the acidity of phenol. This is

probably a result of the greater importance of charge delocalization in the aromatic ring in the anion of diphenylamine than of phenol.

In terms of the resonance viewpoint, structures such as (XIV) and (XV) should contribute more to the



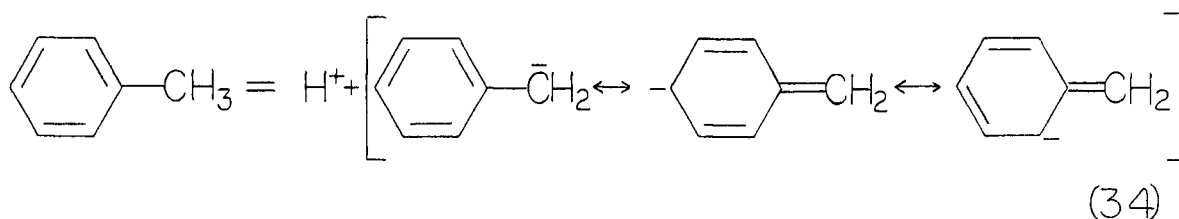
resonance hybrid of the diphenylamine anion than the corresponding structures, (XVI) and (XVII), to the



resonance hybrid of the phenoxide ion. This is because of the smaller difference in electronegativity between carbon (2.5) and nitrogen (3.0) than between carbon and oxygen (3.5)^{1c, 107}. Substituents on the ring should perturb the charge delocalization. This perturbation will therefore be greater for the anion of diphenylamine than the phenoxide ion. This in turn suggests that the acidity

of diphenylamine should be altered more by substituents in the aromatic ring than the acidity of phenol.

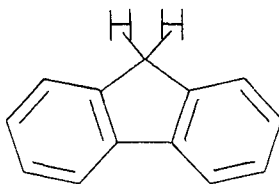
From these same arguments it would be expected that the acidity of toluene is even more sensitive to substituent effects than the acidity of diphenylamine or phenol. Although the equilibrium acidities of substituted



toluenes have not been determined, there is indirect evidence that the acidity of toluene is affected to a greater extent by substituents.

Streitwieser and Koch¹⁰⁸ have measured the relative rates of deuterium exchange of a series of substituted toluenes in cyclohexylamine with lithium and cesium cyclohexylamide as catalysts. A plot of log (relative exchange rate) versus Hammett σ values yields a line with ρ (slope) of 4. If the relationship between the relative rate of hydrogen-deuterium exchange and the equilibrium acidities of substituted toluenes were known then the ρ value for ionization of toluenes could be calculated. This relationship is not known; however, it is known for another series of carbon acids.

Andreades⁶⁴ has determined the relative rates of tritium exchange for a series of carbon acids with the fluorene structure (XVIII) in sodium methoxide-methanol. Streitwieser and co-workers⁶⁰ have determined the equilibrium acidities for these same acids in the cyclohexylamine system. A plot of log (relative exchange rate) versus pK for this series of acids gives a fairly good plot with slope of -0.4 ⁶⁰. If a similar relationship were to hold for the toluene series then the ρ value for toluene ionization would be approximately 10. There is a great deal of uncertainty in such an estimation;



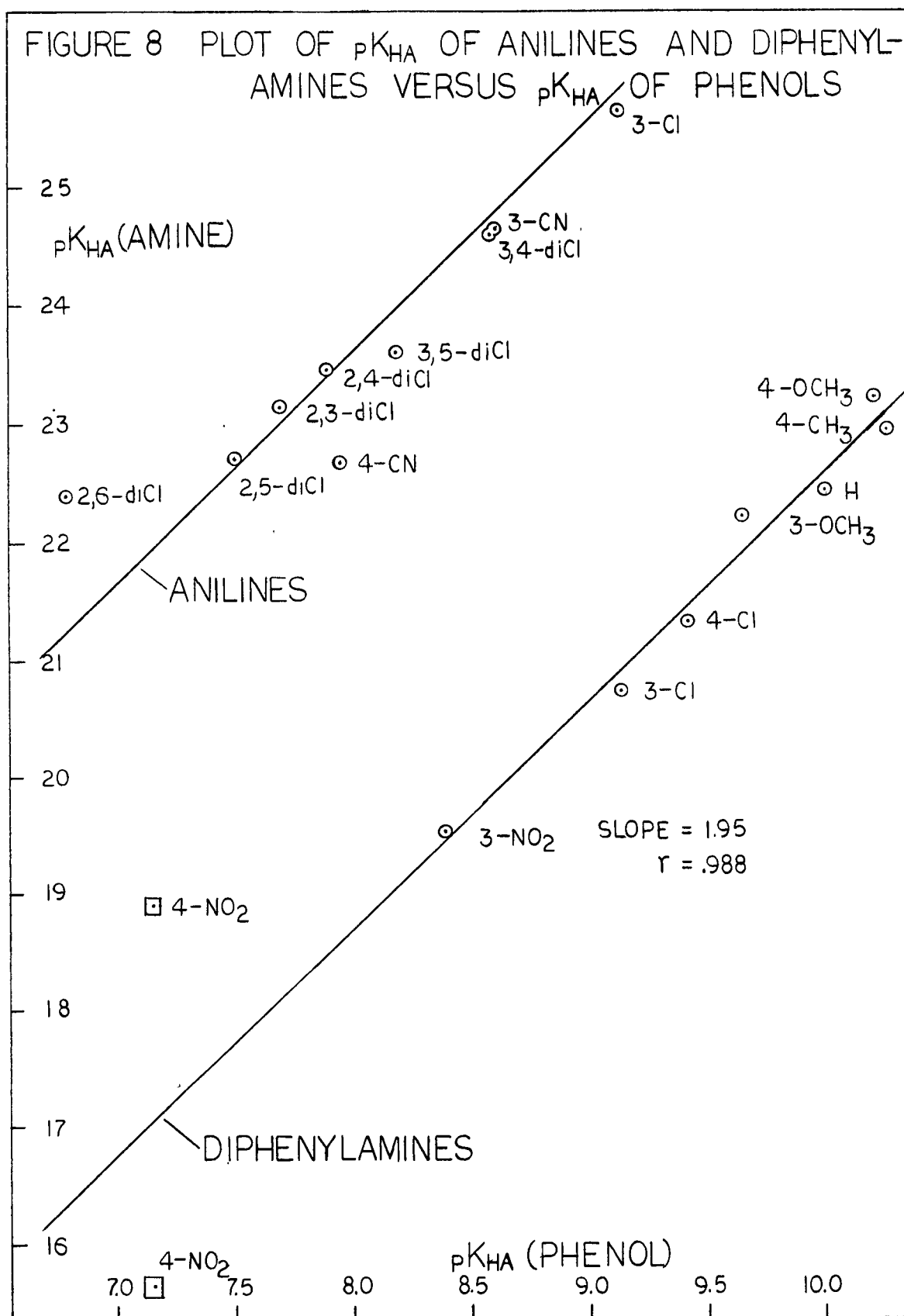
XVIII

however, it does indicate that the ρ for ionization of toluenes is greater than for the ionization of phenol or diphenylamine. This is in agreement with the prediction that the magnitude of substituent effects on acidities should increase in the series phenol, diphenylamine (aniline), toluene.

The data on the ionization of anilines is insufficient to attempt a Hammett plot or even to make a direct comparison with the data for diphenylamines. However, it is possible to make a comparison of the acidities of anilines and diphenylamines indirectly by comparing them both to a common quantity, the acidity of phenols. Thus, Figure 8 contains a plot of the pK_{HA} values of anilines and diphenylamines versus those of phenols. The pK_{HA} values of the monosubstituted phenols are from the data of Biggs and Robinson¹⁰⁵ and those for the dichlorophenols are from the data of Robinson¹⁰⁹.

The best straight line through the points for the diphenylamines is drawn. It was calculated omitting the points for the 4-nitro and 4-methyl-sulfonyl substituents and has slope $1.95 \pm .13$ and correlation coefficient, r , of 0.988. This slope is slightly higher than the ρ values for the ionization of diphenylamines and phenols would lead one to expect.

A line with the same slope is drawn through the points for the anilines. It can be seen to accomodate most of the points, suggesting that substituent effects in the ionization of anilines are the same as in diphenylamines. The difference along the ordinate between the two lines, 4.9 pK units, represents the difference in pK_{HA} values

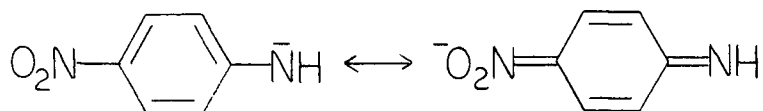


caused by replacing an amino hydrogen of aniline with a phenyl group. This can be used to calculate a pK_{HA} value of 27.3 for aniline from the value 22.44 of diphenylamine. This is in excellent agreement with the pK_{HA} value of 27 obtained by McEwen⁵⁹ thirty years ago. The agreement, however, must be considered largely fortuitous since his values were based on semi-quantitative measurements in a solvent of low dielectric and on an arbitrary value of 16 for the pK_{HA} of methanol.

It might be noted in Figure 8 that the points for the 4-nitro substituent for both the aniline and the diphenylamine fall well below the lines that correlate most of the data. This substituent, then, has a much greater effect on the acidity of aromatic amines than would be expected from its effect on the acidity of phenol. This was mentioned earlier in a different way when it was stated that the 4-nitro substituent has an apparent sigma value of 1.65 in the ionization of diphenylamines as compared to 1.27 in the ionization of phenol. On the other hand, the 3-nitro substituent behaves as would be expected since the point for it lies on the line correlating the pK_{HA} values of phenols and diphenylamines.

The difference in behaviour of the nitro group at the 3 (meta) and 4 (para) positions is no doubt due to

the large contribution made in the latter case by the structure (XIX) to the resonance hybrid of the anion of 4-nitroaniline and of 4-nitrodiphenylamine.



XIX

The study of a series of alkyl-substituted 4-nitroanilines produced some interesting results. The effect of alkyl substituents ortho to the amino group is to increase the acid strength (decrease the pK_{HA}) of 4-nitroaniline. Thus one ortho methyl group decreases the pK_{HA} of 4-nitroaniline by 0.08 units, two ortho methyl groups by 0.20 units and two t-butyl groups by more than 1.0 units. The effect of these groups is in the opposite direction to that which would be expected on the basis of simple inductive effects.

It is encouraging, at least with regard to the validity of the results, that similar trends are observed in the acidities of ortho-alkyl-4-nitro-phenols. The pK_{HA} values of these compounds have been measured in aqueous solution where it is not necessary to resort to the Hammett

technique to determine acid dissociation constants. The pK_{HA} values for these anilines and phenols are listed in Table VI.

The effect of alkyl substituents is better illustrated by the data in Table VI for phenols since they are more complete than for anilines. The pK_{HA} of 2,6-dimethylphenol is approximately 0.6 units greater than the pK_{HA} of phenol; that is, phenol is the stronger acid. It might be expected then that 4-nitrophenol would be about 0.6 pK units stronger as an acid than 2,6-dimethyl-4-nitrophenol. In fact it is not; the pK_{HA} values of the two compounds are roughly the same. With bulkier ortho groups the effect is even greater since 2,6-di-*t*-butyl-4-nitrophenol is 0.5 pK units stronger as an acid than 4-nitrophenol rather than being an expected 1.7 units weaker. The data for 4-nitroanilines, though limited, is similar in trend.

The explanation for the acid strengthening effects of ortho alkyl groups on the acidity of 4-nitroaniline and 4-nitrophenol is not at all obvious. Steric inhibition to solvation of the anions would be expected to bring about the opposite effect. That solvation is probably restricted for the anions with bulky ortho groups is evidenced by the fact that 2,6-di-*t*-butylphenol is too insoluble in

TABLE VI

The pK_{HA} Values of some Alkyl-Substituted
Anilines and Phenols

Substituents	pK_{HA} value of substituted aniline	pK_{HA} value of substituted phenol	Lit. ref.
none		10.00	105
2-methyl		10.29	113
4-methyl		10.26	113
4-t-butyl		10.23	110
2,6-dimethyl		10.59	114
3,5-dimethyl		10.14	114
2,6-di-t-butyl		11.70 ^b	110
4-nitro	18.91	7.15	105
2-methyl-4-nitro	18.83		
2,6-dimethyl-4-nitro	18.71	7.19	114
2,6-di-t-butyl-4-nitro	17.4 ^a	6.65	110
3,5-dimethyl-4-nitro	21.16	8.25	114
2,3,5,6-tetramethyl-4-nitro	22.66		

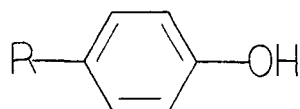
^a approximate value

^b estimated from a Hammett plot for 4-substituted-
2,6-di-t-butylphenols

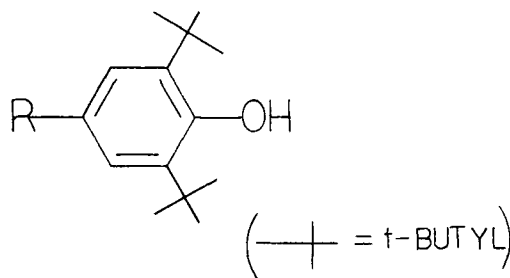
water at high pH to allow spectral measurements to be made on its ionization¹¹⁰. In fact it has been reported that 2,6-di-*t*-butyl-4-methylphenol is insoluble in aqueous alkali of any strength¹¹¹.

A possible explanation of these phenomena might lie in solvation effects on both the ionized and unionized species. In the anion of phenol the negative charge must reside primarily on the oxygen atom where it can be stabilized by solvation. The introduction of bulky alkyl groups ortho to the oxygen hinders solvation and consequently increases the energy of the anion. However, if a substituent such as the nitro group is placed at the 4-position of phenol a large portion of the ions negative charge will reside on this substituent which has no hindrance to solvation. Thus, the effect of substituents in the para position capable of supporting part of the negative charge in the phenoxide ion (or aniline anion) is to lessen the acid weakening effect of ortho alkyl groups.

The findings of Cohen and Jones¹¹⁰ support such an explanation. They measured the pK_{HA} values of two series of phenols of the type (XX) and (XXI) and found that the difference between the pK_{HA} values for members of the



XX



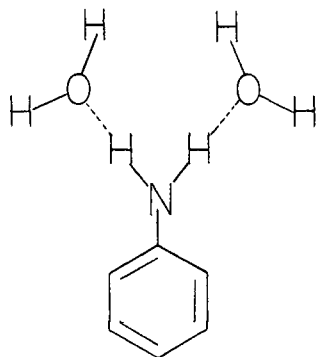
XXI

two series with a given substituent R decreases as the substituent becomes more electron withdrawing (as measured by the Hammett σ^- parameter).

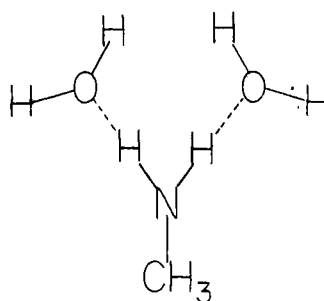
This explanation can account for a lessening of the acid weakening effect of ortho alkyl groups; however it cannot account for the apparent acid strengthening effect of these groups in 2,6-di-t-butyl-4-nitroaniline and the corresponding phenol. A further process is required to explain this and it is possible that it involves solvation of the amino and hydroxyl functions of the unionized anilines and phenols.

In a recent attempt to explain the basicities of aliphatic amines and of N-alkylanilines in terms of the hydration of the neutral amines and their ammonium ions, Condon^{26,86} was drawn to the conclusion that hydration of the free aniline or N-alkylaniline is base weakening by 1.6 pK units as compared to aliphatic amines. This increased

importance of hydration in the aniline bases as compared to the aliphatic amines was attributed to the greater importance of hydrogen bonding of the type (XXII) in aniline than in aliphatic amines (XXIII). This is reasonable since



XXII



XXIII

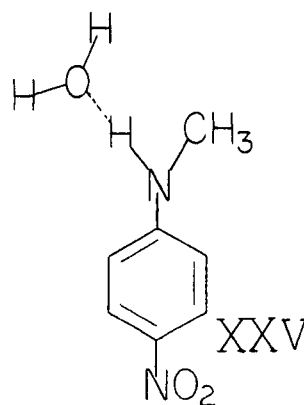
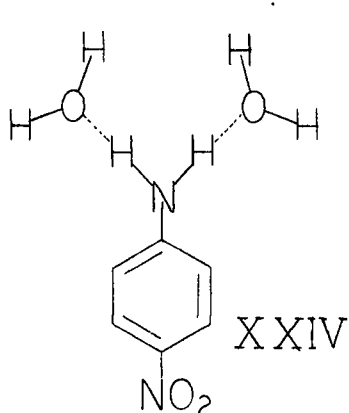
the nitrogen atom is at the positive end of the dipole in aniline^{107b} whereas it is probably at the negative end in aliphatic amines²⁶. Hydrogen bonding should be of similar or greater importance in phenols¹¹².

The presence of large groups ortho to the hydroxyl or amino function may weaken or eliminate hydrogen bond solvation and consequently raise the energy of the phenol or aniline. This would be an acid strengthening effect which in conjunction with the first explanation might result in 2,6-di-*t*-butyl-4-nitrophenol being a stronger acid than 4-nitro phenol and 2,6-di-*t*-butyl-4-nitroaniline being a stronger acid than 4-nitroaniline.

The importance of the nitro group in delocalizing the charge on the anions of 4-nitrophenol and 4-nitroaniline can be seen from the effect of putting alkyl groups ortho to the nitro group. Two methyl groups ortho to the nitro group twist it out of planarity with the ring, reducing the resonance interaction with the ring¹¹⁵. The result is a decrease of 1.1 pK units in the acidity of 4-nitrophenol and 2.2 pK units in the acidity of 4-nitroaniline. With methyl groups ortho to both the nitro and amino functions the pK_{HA} of 4-nitroaniline increases by 3.7 units; that is, it becomes a considerably weaker acid.

The pK_{HA} values of some 4-nitroanilines with alkyl substituents on the nitrogen, as with the other alkyl substituted 4-nitroanilines, showed some unexpected effects. The data are listed in Table III. The striking feature is that the pK_{HA} values of N-methyl, N-ethyl, and N-isopropyl-4-nitroaniline are less than that of 4-nitroaniline itself. As before, it would be expected on the basis of the usual inductive effects that the substitution of methyl for the hydrogen of the amino group would increase the pK_{HA} of 4-nitroaniline. The acidities of the N-alkyl-4-nitroanilines do fall in the order expected from their inductive effects as measured by Taft's σ^* parameters^{103d}; however, they do not show a linear correlation.

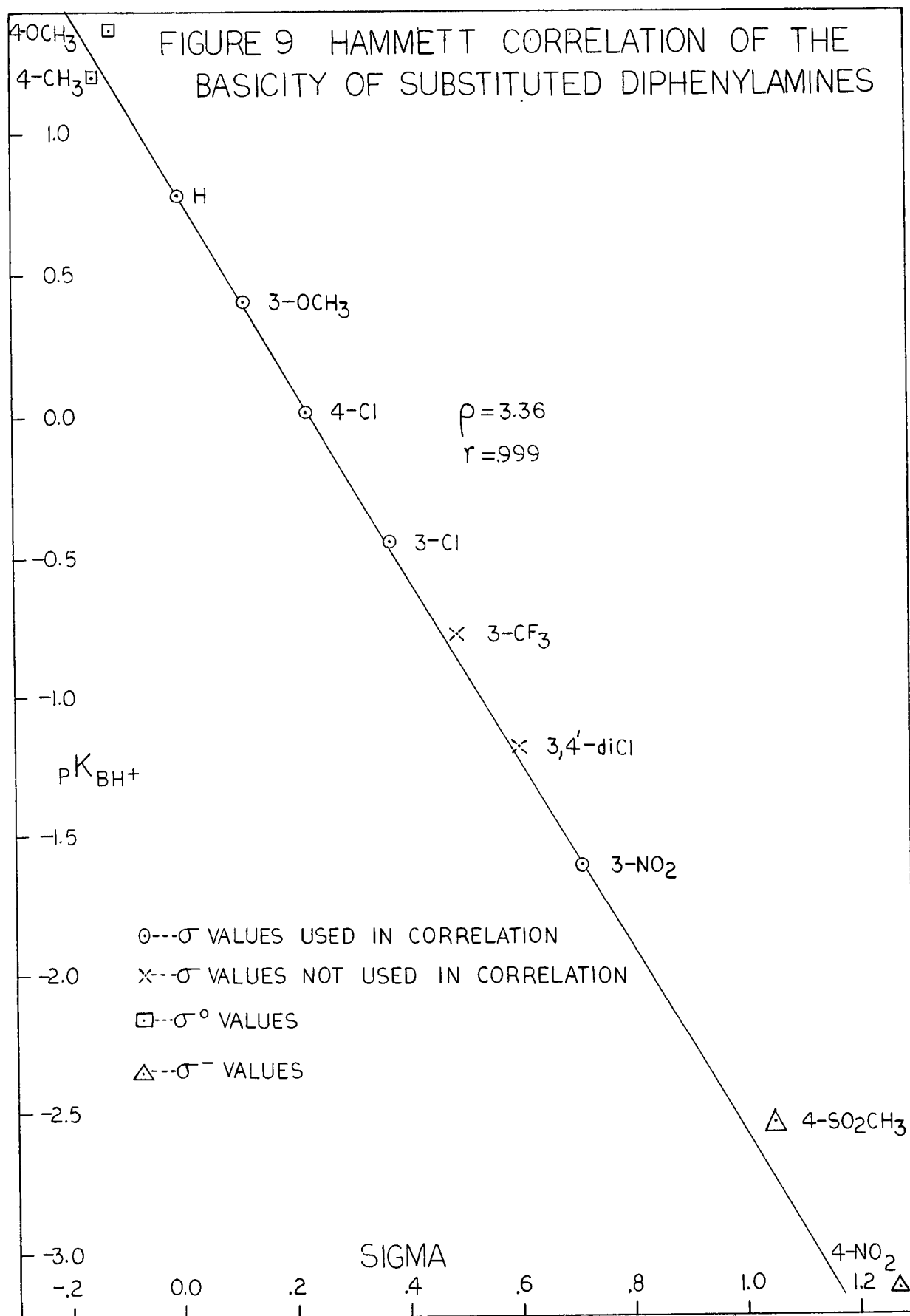
An explanation for the fact that N-methyl-4-nitroaniline is a stronger acid than 4-nitroaniline might lie in the solvation of the unionized amines. If, as suggested by Condon²⁶, these amines are solvated by formation of hydrogen bonds as shown, (XXIV) and (XXV), the substitution



of methyl for one of the hydrogen atoms on the nitrogen destroys the site of one of the hydrogen bonds. Since the measurements were made in DMSO-water mixtures it is possible that DMSO replaces water in this type of hydrogen bonding, particularly since DMSO forms strong hydrogen bonds with proton donors^{89,116}. The loss of solvation destabilizes N-methyl-4-nitroaniline with respect to 4-nitroaniline. It might be possible that this decrease in solvation energy is large enough to overcome the inductive effect of the methyl group causing N-methyl-4-nitroaniline to be a stronger acid than 4-nitroaniline.

The effect of substituents on the acidity of the diphenylammonium ion (the basicity of diphenylamine) is similar in trend to their effect on the acidity of diphenylamine. Again, no one set of Hammett substituent constants correlates the acidities of all the ammonium ions. Figure 9 contains a plot of pK_{BH^+} versus σ^{-103a} for the following diphenylamines: 3-methoxy, 4-chloro, 3-chloro and 3-nitrodiphenylamine and diphenylamine itself. The reaction constant ρ is $3.36 \pm .04$ with correlation coefficient r of 0.999. The points for 3-trifluoromethyldiphenylamine ($\sigma = .49^{106}$) and for 3,4'-dichlorodiphenylamine ($\sum\sigma = .600$) fall very close to the line. As before, the pK_{BH^+} values for the compounds with the 4-methoxy, 4-methyl, 4-methylsulfonyl, and 4-nitro substituents do not correlate with σ . The points for the electron-releasing substituents, 4-methoxy and 4-methyl, can be brought near the line by using σ^{-103b} instead of σ . For the strongly electron withdrawing substituents, 4-methylsulfonyl and 4-nitro, the use of σ^{-103c} rather than σ brings the points closer to the line.

There is considerably more data on the basicities of anilines than of diphenylamines since the protonation of the monosubstituted anilines takes place within the pH range. Biggs and Robinson¹⁰⁵ found that for twelve anilines with substituents ranging from 4-methyl ($\sigma = -.170^{103a}$) to

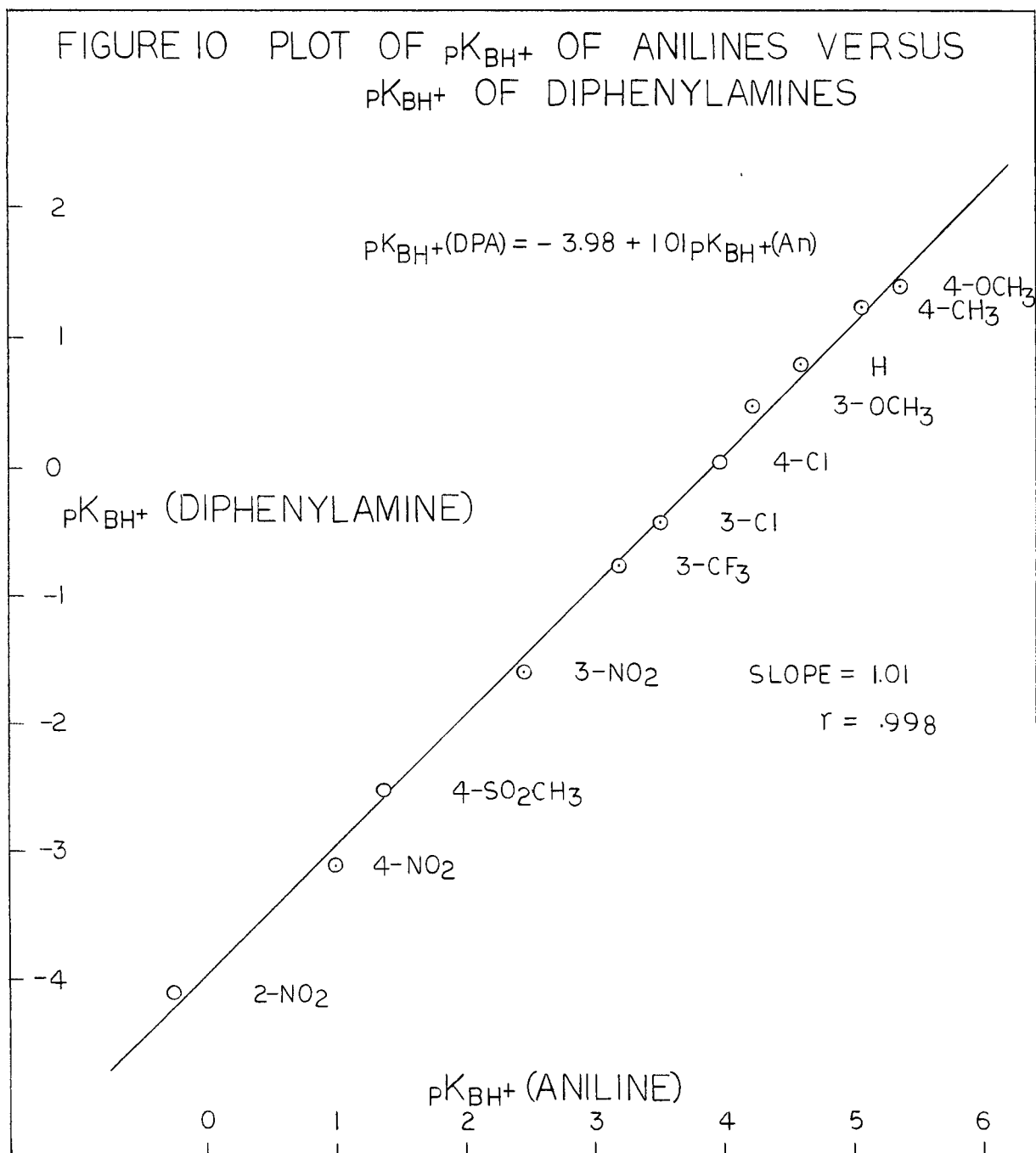


3-nitro ($\sigma = .710$ ^{103a}) there is a good correlation of pK_{BH^+} with σ . The reaction constant ρ is 2.89, although a value of 3.00 is obtained for ρ using the pK_{BH^+} values for the five anilines corresponding to the five diphenylamines used above in calculating ρ for the protonation of diphenylamines. Fickling and co-workers¹¹⁷ have found that the reaction constant ρ for the protonation of substituted N,N-dimethylanilines is 3.43. On this basis, substituent effects on the basicity of secondary and tertiary aromatic amines are slightly larger in magnitude than on primary aromatic amines.

A plot of the pK_{BH^+} values of diphenylamines versus the pK_{BH^+} values of the corresponding anilines, using a wider variety of substituents than those used to calculate ρ , gives a fairly good straight line with slope near unity. For eleven compounds whose basicities range over 5 pK units, the equation relating the pK_{BH^+} of a diphenylamine (DPA) to the pK_{BH^+} of the corresponding aniline (An) is

$$(pK_{BH^+})_{DPA} = -3.98 + 1.01 (pK_{BH^+})_{An} \quad (35)$$

Figure 10 is a plot of the data for this line which has correlation coefficient, r , of 0.998. The pK_{BH^+} values of the anilines are taken from the data of Biggs and Robinson¹⁰⁵



except for the values for 3-trifluoromethylaniline, given by Shephard¹⁰⁶, and 4-methylsulfonylaniline, from the compilation of Perrin¹¹⁸.

On the basis of the relationship expressed in equation (35) the magnitude of substituent effects on the basicities of aniline and diphenylamine are, on the average, the same. For the hypothetical aniline with pK_{BH^+} of zero the pK_{BH^+} of the corresponding diphenylamine is -4.0; that is, the replacement of a proton of the amino group of the aniline by a phenyl group decreases the basicity by 4.0 units. It will be recalled that the same replacement increases the acidity of aniline by 4.9 pK units. The difference in the basicities of an aniline and the corresponding diphenylamine is due not only to the different electronic effects of phenyl as compared to hydrogen but also to differences in the solvation energies of the primary and secondary amines and their conjugate acids^{26,86}.

F. Acid and Base Strengths of Nitro-substituted Aromatic Amines

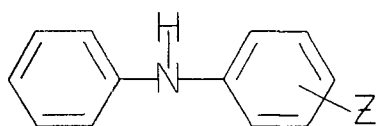
It was mentioned in the Introduction that there is a body of evidence to suggest that the nitro group takes part in some specific interaction with a component of concentrated acid solutions. The exact nature of this

interaction is not known. Hogfeldt and Leifer¹¹⁹ have interpreted the solubility data³³ for nitrobenzene in aqueous sulfuric acid in terms of complex formation between the nitro group and mono- and trihydrated protons. Deno and Perrizzolo²⁷ have suggested the existence of a hydrogen bonded complex between a molecule of nitrobenzene and another of sulfuric acid. The question then arises of how the basicities of nitro-substituted aromatic amines are affected in solutions of high acid concentration. It has been suggested³⁷ that nitroanilines are weak bases partly because of such interactions between the nitro group and the acidic media.

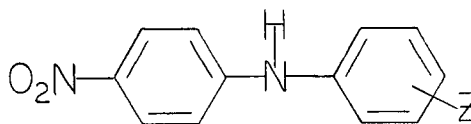
It was felt that some information might be gained about the effect of strongly acidic media on the basicity of nitro aromatic amines from measurement of the basicities of a series of substituted diphenylamines. Any peculiarity of the nitro substituent might show up in a Hammett σ_p plot or in a correlation of the basicities of substituted anilines with the corresponding diphenylamines. The protonation of 4-nitroaniline occurs in relatively dilute acid (approximately 0.1 N HCl) in which the nitro group should not be affected by the acid. On the other hand, 4-nitrodiphenylamine and 2-nitrodiphenylamine are half ionized in 5.9 and 7.3 molar aqueous-ethanolic sulfuric acid respectively.

It is obvious from Figures 9 and 10 that the behaviour of the nitro group as a substituent in sulfuric acid is very similar to its behaviour in aqueous solutions within the pH range. In terms of the Hammett substituent constant, the 4-nitro group has sigma value of 1.16 in the protonation of diphenylamines as compared to 1.27 for the protonation of anilines^{103c}. In view of the limited data (5 pK_{BH^+} values) used to calculate ρ for the protonation of diphenylamines and the change in structure between diphenylamine and aniline, the discrepancy in the sigma values for the 4-nitro substituent is not significant. In the correlation of the pK_{BH^+} values of anilines with those of the diphenylamines (Figure 10) the fit of the points for the 2- and 4-nitro substituents is as good as for the other substituents.

The basicities of the following two series of diphenylamines also correlate quite well with one another.

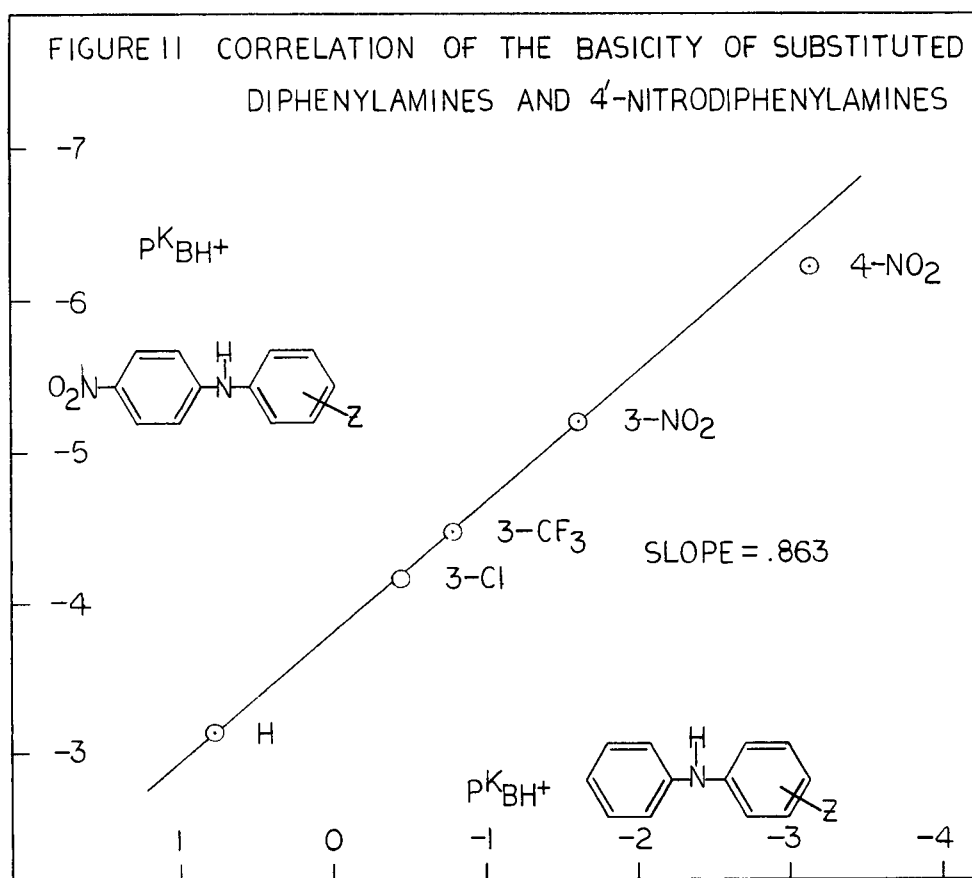


XXVI

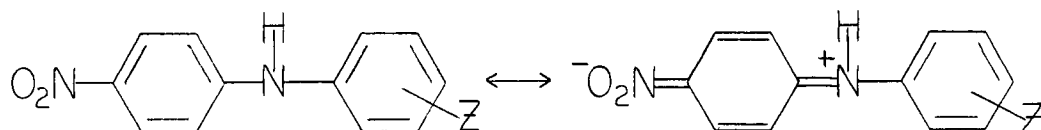


XXVII

Figure 11 is a plot of the pK_{BH^+} values of the mono-substituted diphenylamines (XXVI) versus the pK_{BH^+} values



of the correspondingly substituted 4-nitrodiphenylamines (XXVII). The slope of the line is 0.86 indicating that the effect of substituents on basicity is smaller in the second series than in the first. This is probably a result of the interaction of the amino group with the nitro group in one ring causing a decrease in its inter-



action with substituents in the other ring. The point for Z equal to 3-nitro falls on the plot with three non-nitro substituents while the point for Z equal to 4-nitro falls a little below the line.

It can be seen that the effect of the nitro group on the basicity of diphenylamines does not exhibit any observable change on proceeding from dilute to concentrated acid. This is not to say that the nitro group does not form a complex with some component of strongly acidic media since it may do so at higher acid concentrations than were used here (approximately 11 molar sulfuric acid) or it may be that the presence of such an interaction is not observable in such an indirect fashion as this.

It is interesting to consider the effect of the nitro group on the acidity of aromatic amines. The 4-nitro substituent increases the acidity of aniline and diphenylamine by approximately 8.4 and 6.8 pK units respectively. On the other hand the 3-nitro substituent increases the acidity of diphenylamine by only 2.9 pK units. The exalted acidity of 4-nitroaniline and 4-nitrodiphenylamine, in which the substituent is conjugated with the amino group, must surely be a result of the extensive delocalization of the charge in the anions of these acids.

The effect of two nitro groups on the acidity of an aromatic amine is not additive; the second nitro group causes a smaller increase than expected. This is illustrated in Table VII for diphenylamines where the calculated pK_{HA} values refer to the values expected from addition of the increments for the individual substituents. It is obvious that the substituent effects are not additive. In the case of phenols, the deviation from additivity is in the opposite direction. Thus, 2,4,6-trinitrophenol is a stronger acid (pK_{HA} of 0.22)⁶ by more than 1 pK unit than would be expected from the pK_{HA} values of phenol (10.00), 2-nitrophenol (7.21) and 4-nitrophenol (7.15)¹⁰⁵.

In Table VII the largest deviations from additivity occur in the compounds with nitro groups in both rings, as

TABLE VII

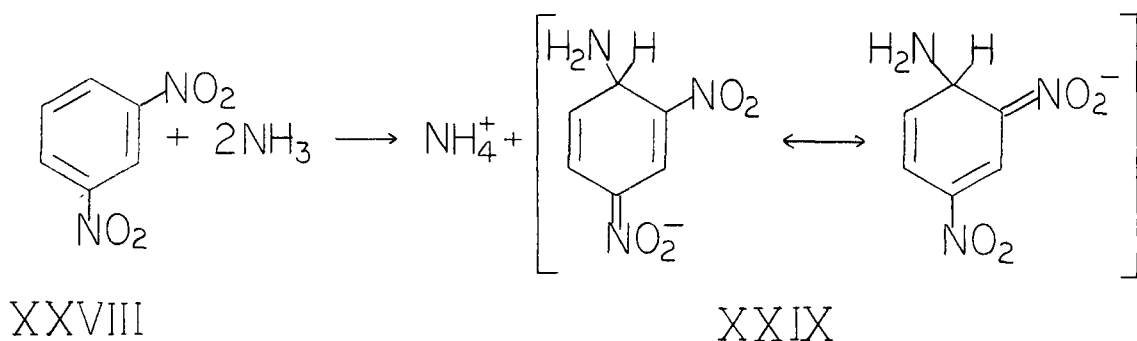
The pK_{HA} Values of Some Nitro-substituted
Diphenylamines

Substituents	Observed pK_{HA}	Calculated pK_{HA}
none	22.44	
2-nitro	17.91	
3-nitro	19.53	
4-nitro	15.67	
2,4-dinitro	13.84	11.14
3,4'-dinitro	14.66	12.76
4,4'-dinitro	14.08 ^a	8.90
2,4,6-trinitro	10.38 ^a	6.61
2,4,4'-trinitro	12.35 ^a	4.37

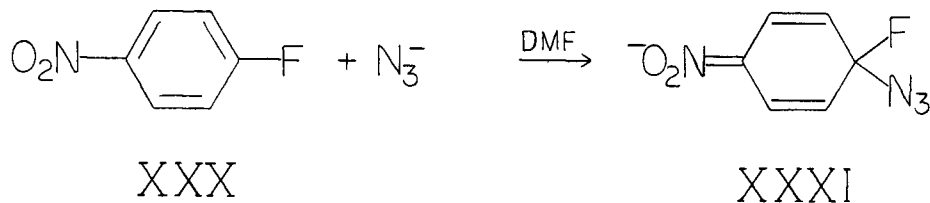
^a ref. 40

a result, no doubt, of the inability of both rings to attain, simultaneously, maximum overlap with the nitrogen atom.

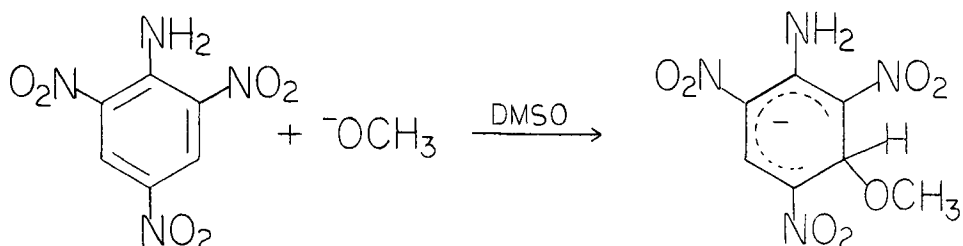
Not only does the nitro substituent produce large increases in the acidity of aromatic amines but it also produces large rate accelerations in the attack of nucleophiles on aromatic substrates¹²⁰. Farr, Bard and Wheland¹²¹ have observed that the dissolution of m-dinitrobenzene (XXVIII) in liquid ammonia yields a purple solution capable of conducting an electrical current probably due to the formation of the ion (XXIX). Similarly, Bolton, Miller and Parker¹²² found that 4-nitrofluorobenzene (XXX) reacts in dimethylformamide with azide ion without liberation of fluoride ion



to give a colored solution believed to be a result of the formation of the ion (XXXI).

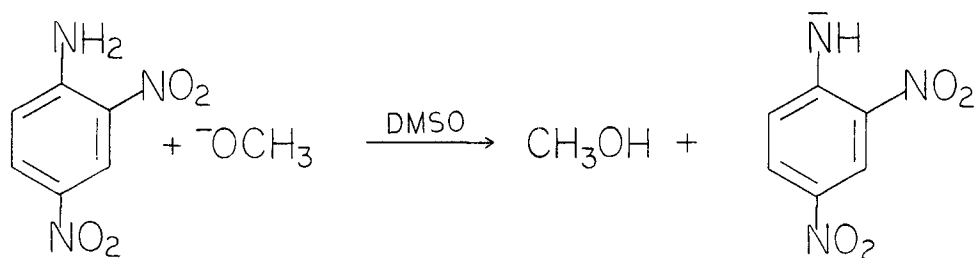


Such addition reactions are also possible with hydroxide or alkoxide ions. This means that addition of these ions to nitro aromatic amines may be a competing process with ionization by proton loss, particularly in the case of amines with more than two nitro substituents in one ring. Thus, Crampton and Gold¹²³ have shown, using nuclear magnetic resonance spectroscopy, that 2,4,6-trinitroaniline (XXXII) in DMSO reacts with sodium methoxide predominantly by methoxide ion addition rather than by proton dissociation.



XXXII

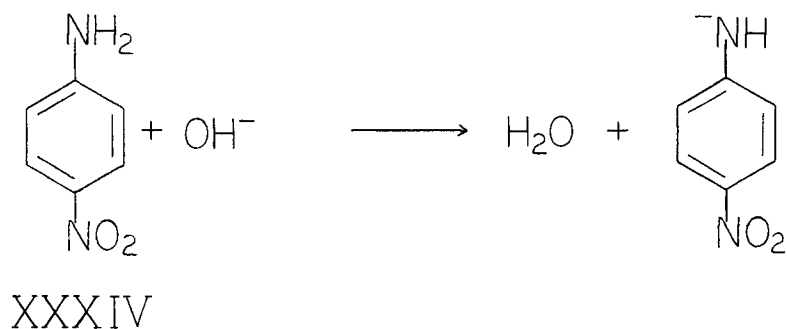
On the other hand, 2,4-dinitroaniline (XXXIII) and 2,4-dinitrodiphenylamine ionize by proton loss.



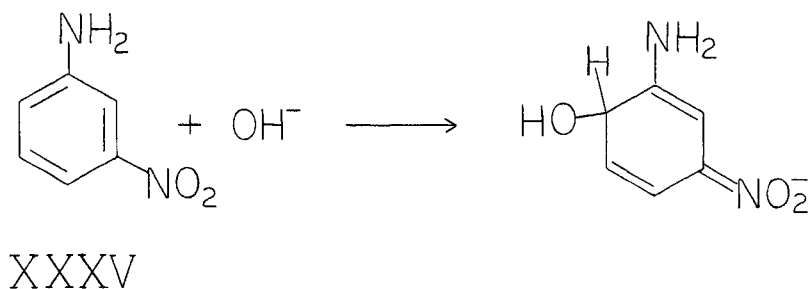
XXXIII

Hydroxide ion addition can compete with dissociation even in mono-nitroanilines. The nitro group is most effective at increasing acid strength when situated at the 2 or 4 position of aniline. Similarly the nitro group facilitates addition to aromatic compounds in the ortho and para positions.

In 4-nitroaniline (XXXIV) the nitro group exhibits a great acid strengthening effect so that this compound reacts with hydroxide ion by proton loss rather than hydroxide addition.

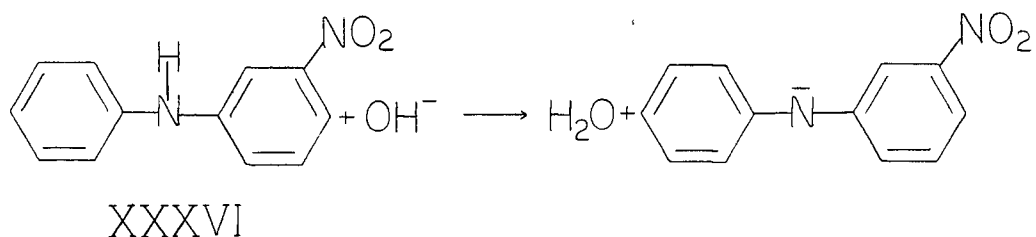


In 3-nitroaniline (XXXV) the nitro group displays its weakest acid strengthening effect whereas the compound is still susceptible to hydroxide ion addition at a position ortho or para to the nitro group.



Thus, in 97 mole % DMSO containing 0.011 molar hydroxide ion 3-nitroaniline does not undergo, as does

4-nitroaniline, a rapid spectral change characteristic of ionization by proton loss but rather produces a broad absorption in the region from 300 to 550 $m\mu$ that increases in intensity with time. In the same solution a similar spectral change occurs with nitrobenzene for which proton abstraction from the aromatic ring is improbable¹²⁴. It appears then that these two compounds react by hydroxide ion addition in strongly basic solutions. It is interesting that 3-nitrodiphenylamine (XXXVI) reacts by dissociation



rather than addition. This is due to the fact that the addition of the phenyl group to the amino group of 3-nitroaniline increases the acidity of the amino hydrogen by nearly 5 pK units whereas it produces only a secondary effect on the susceptibility of the aromatic ring to hydroxide ion addition.

Rochester¹²⁵, from a study of the ultraviolet absorption spectrum of 4-nitroaniline in aqueous sodium hydroxide (0 to 17 molar) has concluded that 4-nitroaniline takes part in two equilibria depending on the concentration

of the base. The first equilibrium predominates in the region from 0 to 8 molar sodium hydroxide, and is characterized by a shift in the long wavelength absorption maximum from 381 to 400 $m\mu$; the second equilibrium predominates from 8 to 17 molar base and is characterized by a further shift of the absorption maximum to 433 $m\mu$. Rochester has suggested that the first equilibrium is hydroxide ion addition to the 4-nitroaniline and the second is proton abstraction from this complex.

Others^{40,52} who have used 4-nitroaniline as an indicator in aqueous sulfolane with added base have not reported that it ionizes by other than simple proton loss. Similarly, the spectral changes observed in this work suggest only one equilibrium. It seems quite possible that the shift of absorption maximum observed by Rochester in 0 to 8 molar base is not the result of hydroxide ion addition to 4-nitroaniline but rather is a result of a change in the character of the medium. There must be a considerable change in the nature of the solvent in going from water to 8 molar sodium hydroxide since the concentration of free water (water not bound to the hydroxide ion) in 8 molar sodium hydroxide is reduced to one half of its value in water⁴⁷ . The effects of change in solvent on the position of the long wavelength absorption maximum of 4-nitroaniline

are large. Pearson¹²⁶ has observed shifts from 320 $m\mu$ in n-hexane to 380 $m\mu$ in dimethylformamide.

The possibility of the spectrum change being the result of a medium effect was tested by measuring the absorption spectrum of 4-nitroaniline in approximately 7 molar potassium fluoride solution. This showed that the long wavelength absorption maximum is shifted 8 to 10 $m\mu$ to the red with an increase of about 10 % in the molar absorptivity, ϵ , as compared to in water. A smaller shift of 4 to 6 $m\mu$ was observed in 8 molar sodium perchlorate. Rochester observed a shift of about 19 $m\mu$ in 8 molar sodium hydroxide with a small increase in molar absorptivity (the actual increase is not reported)¹²⁵.

It seems quite reasonable, then, to conclude that the absorption maximum of 4-nitroaniline is shifted to the red on passing from water to 8 molar sodium hydroxide due to a change in the solvent and its interaction with the 4-nitroaniline. The size of the shift depends on the added salt- probably on its ability to complex the water. This means that 4-nitroaniline does not react by hydroxide ion addition in 0 to 8 molar sodium hydroxide as suggested by Rochester¹²⁵.

G. Comparison of the Acidity and Basicity of Anilines
and Diphenylamines

Stewart and O'Donnell⁶⁹ have found that a plot of pK_{HA} (as ordinate) versus pK_{BH^+} (as abscissa) for a series of anilines and diphenylamines with nitro group substituents yields a line with slope of 0.6. Using some of the data obtained in this work, a similar plot for a series of seven monosubstituted diphenylamines, a dichlorodiphenylamine and diphenylamine itself also gives a straight line but with slope $1.30 \pm .05$ and with correlation coefficient r of 0.995. The plot is shown in Figure 12. The points for three mono-substituted derivatives - 4-methylsulfonyl, 2-nitro, and 4-nitrodiphenylamine - do not fall on this line.

The value of 0.6 for the slope found by Stewart and O'Donnell⁶⁹ indicates that substituents have a greater effect on basicity than on acidity for nitrated anilines and diphenylamines whereas the slope of 1.30 for the compounds in Figure 12 indicates that the opposite is true for diphenylamines with most other substituents, including the nitro group in the meta position.

Figure 13 is a plot similar to Figure 12 with most of the data at present available for anilines and diphenylamines. This includes the data in Figure 12 and

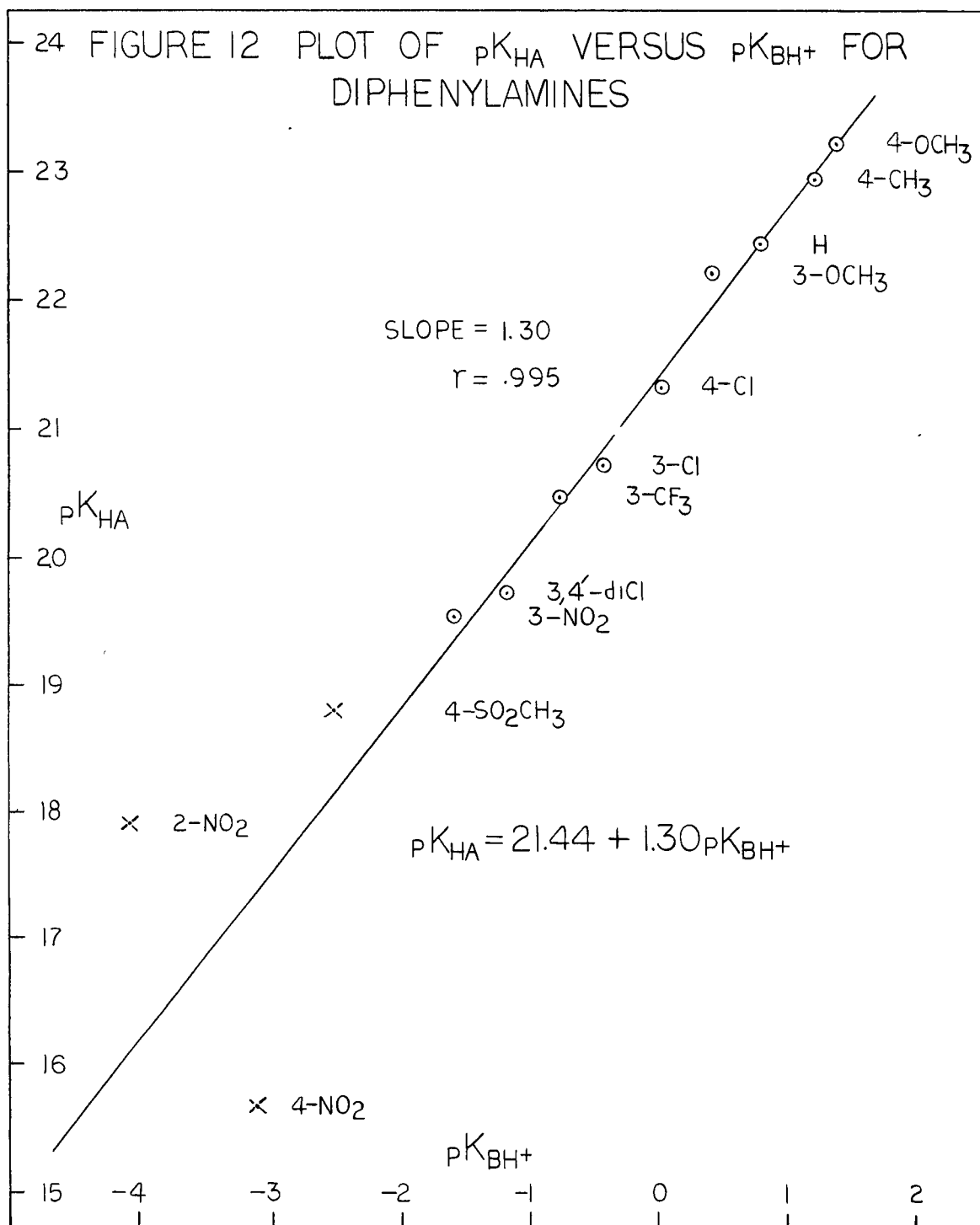
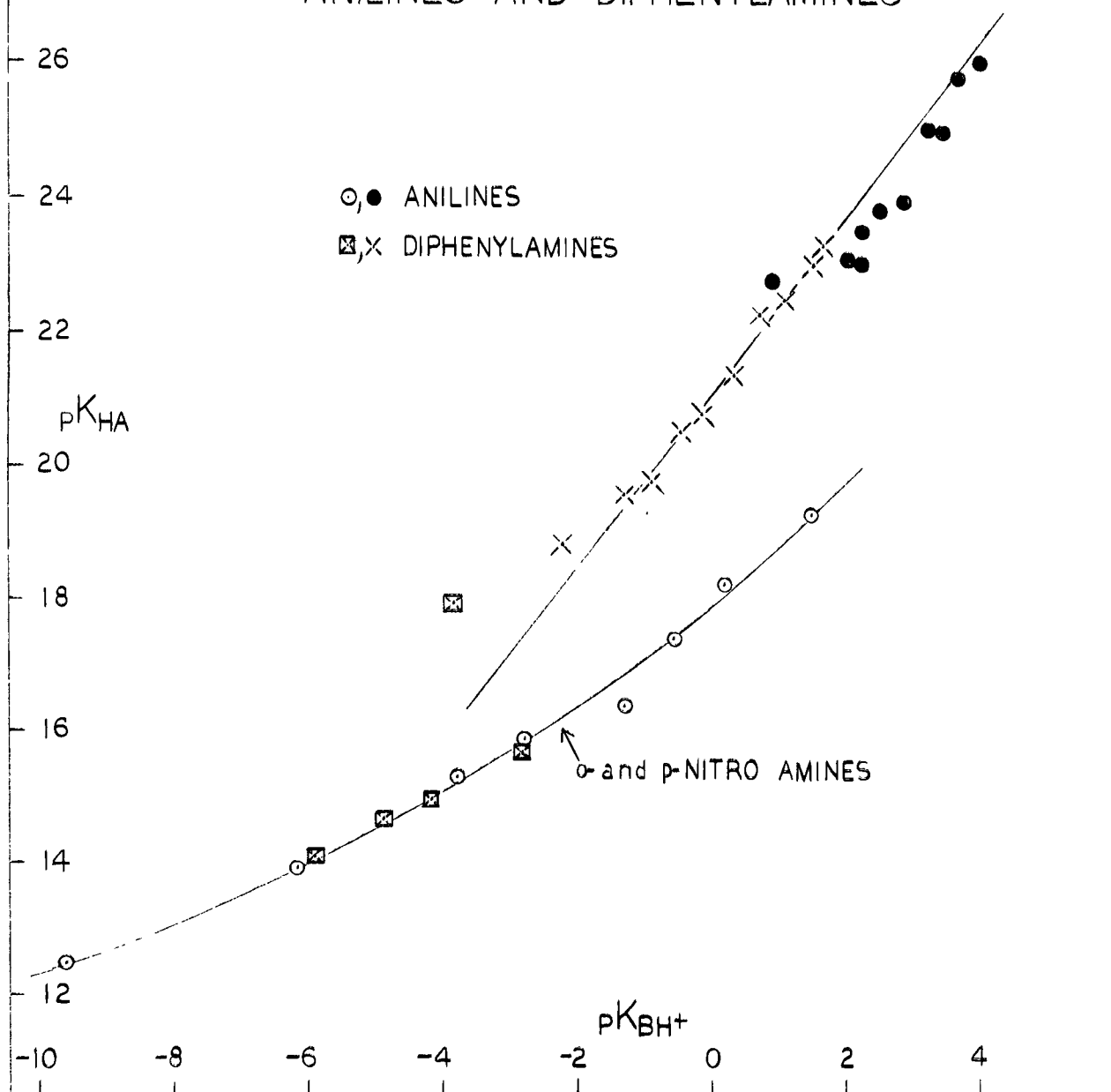


FIGURE 13 PLOT OF pK_{HA} VERSUS pK_{BH^+} FOR ANILINES AND DIPHENYLAMINES



also that of Stewart and O'Donnell⁶⁹ except that dissociation constants determined in this work were used where applicable. The pK_{BH^+} and pK_{HA} values are listed in Table VIII. Statistical corrections for the number of ionizable protons^{86,127} were applied to the pK values in Table VIII before plotting them in Figure 13. The corrections are: for the pK_{BH^+} of anilinium ions, add $\log 3$; for the pK_{HA} of anilines and the pK_{BH^+} of diphenylammonium ions, add $\log 2$; for the pK_{HA} of diphenylamines, no correction..

In Figure 13 it can be seen that the amines appear to fall into two classes. The anilines and diphenylamines without nitro groups form one class. The points for the anilines in this group fall slightly below the projection of the line for the diphenylamines but show a similar trend. The other class of amines is comprised of those anilines and diphenylamines containing at least one nitro group ortho or para to the acidic amino group. These amines fall on a slightly curved line of smaller slope.

The different behaviour of the nitrated anilines and diphenylamines as compared to the other substituted amines must be a result of the peculiar effect that the nitro group has on the acidity of aromatic amines. The effect of the nitro group on the basicity of aniline is quite

TABLE VIII

Values of pK_{BH^+} and pK_{HA} for

Anilines and Diphenylamines

Substituents	pK_{BH^+}	Lit. ref. ^a	pK_{HA}	Lit. Ref. ^a
Anilines				
3-chloro	3.52	105	25.63	
3-trifluoromethyl	3.20	106	25.40	
3-cyano	2.75	105	24.64	
4-cyano	1.74	118	22.68	
3,4-dichloro	2.97	109	24.60	
3,5-dichloro	2.38	109	23.59	
2,3-dichloro	1.76	109	23.14	
2,4-dichloro	2.02	109	23.46	
2,5-dichloro	1.53	109	22.71	
2,6-dichloro	0.42	109	22.40	
4-nitro	1.00	105	18.91	
2-nitro	- 0.26	105	17.88	40
2-nitro-4-chloro	- 1.07	128	17.08	
4-nitro-2,5-dichloro	- 1.78	23	16.05	40
4-nitro-2,6-dichloro	- 3.27	23	15.55	40
2,4-dinitro	- 4.26	128	15.00	40
2,4-dinitro-6-bromo	- 6.68	23	13.63	40
2,4,6-trinitro	-10.10	23	12.20	40
Diphenylamines				
4-methoxy	1.36		23.22	
4-methyl	1.20		22.95	
none	0.78		22.44	
3-methoxy	0.40		22.22	
4-chloro	0.01		21.33	
3-chloro	- 0.45		20.73	
3-trifluoromethyl	- 0.78		20.48	
3,4'-dichloro	- 1.19		19.73	
3-nitro	- 1.61		19.53	
4-methylsulfonyl	- 2.54		18.80	

Continued...

Table VIII - Continued..

Substituents	pK_{BH^+}	Lit. Ref. ^a	pK_{HA}	Lit. Ref. ^a
Diphenylamines				
2-nitro	- 4.12		17.91	
4-nitro	- 3.13		15.67	
4-nitro-3'- trifluoromethyl	- 4.47		14.96	
3,4'-dinitro	- 5.19		14.66	
4,4'-dinitro	- 6.21		14.08	40

a values without reference were determined in this work

regular. The pK_{BH^+} of 2,4,6-trinitroaniline would be expected to be -9.72 based on the pK_{BH^+} values of aniline (4.60), 2-nitroaniline (-0.26), and 4-nitroaniline (1.00)¹⁰⁵. It has been determined²³ to be -10.10. On the other hand, the effect of the nitro group on the acidity of aniline is quite irregular. The pK_{HA} value of 2,4,6-trinitroaniline would be expected to be 0.1 based on the pK_{HA} of aniline (estimated to be 27.3), 2-nitroaniline (17.88)⁴⁰, and 4-nitroaniline (18.91). It has been found⁴⁰ to be 12.20. Thus the first nitro group in the ortho or para position of aniline produces a great enhancement in acidity, however the effect on acidity of the second and subsequent substituents is dampened. On the other hand the basicities of anilines vary regularly with multiple substitution.

The equation for the line in Figure 12 relating the acidities to the basicities of diphenylamines is

$$pK_{HA} = 21.44 + 1.30(pK_{BH^+}) \quad (36)$$

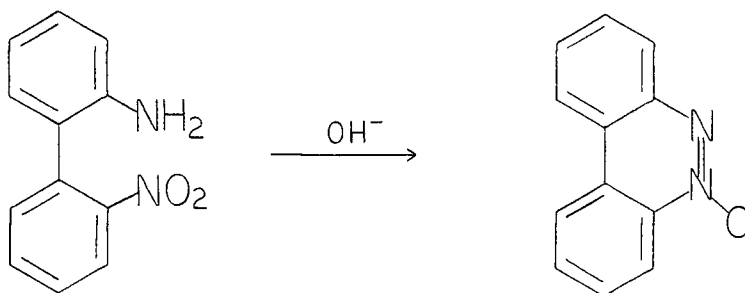
It is interesting to use this equation to estimate a value for the pK_{HA} of ammonia from its pK_{BH^+} . The pK_{BH^+} of ammonia is 9.25⁶⁷ but since there are four ionizable protons on the ammonium ion as compared to two on the diphenylammonium ion the factor $\log 2$ must be added to the pK_{BH^+} . Using the value 9.55 for the pK_{BH^+} of ammonia a value of 33.8 is

obtained for the pK_{HA} from equation (36). This in turn must be corrected for the fact that ammonia has three ionizable protons whereas diphenylamine has one so that the dissociation constant for the former compound should be three times as large as that given in equation (36). Thus the factor $\log 3$ must be subtracted from 33.8 to give a value of 33.3 for the pK_{HA} of ammonia. Bell⁶⁸ has estimated that the pK_{HA} of ammonia is 35.

SUGGESTIONS FOR FURTHER WORK

One of the potential applications of Hammett acidity functions is the elucidation of reaction mechanisms through the quantitative treatment of acid and base catalysis. Procedures have been outlined for use of correlations of reaction rates with H_0 ^{31,32} or H_- ¹²⁹ as a criterion of mechanism. Most correlations that have been made involved reactions of acids or bases of structural types different from those of the indicators that were used to determine H_- or H_0 . In order to draw valid conclusions about the reaction mechanism it is necessary that the ionization of the substrate involved in the reaction be governed by the acidity function used in the correlation. This has probably not been so in many cases.

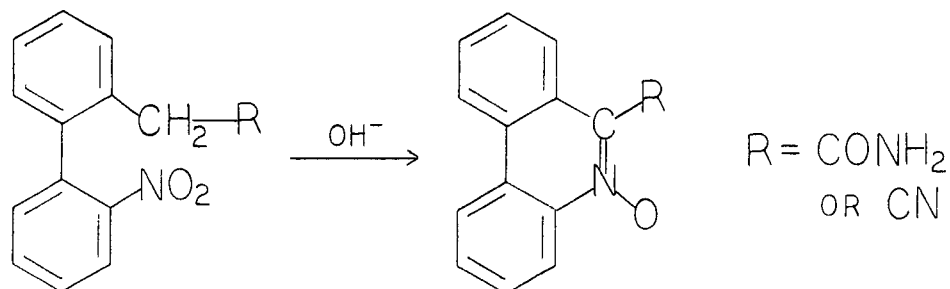
Since aromatic amines were used to establish the H_- scale in DMSO-water it would be preferable, in any investigation of correlations of rate with H_- in this system, to study the reaction of an aromatic amine substrate. One such reaction is the following base catalyzed intramolecular condensation of 2-amino-2'-nitrobiphenyl^{130,131}



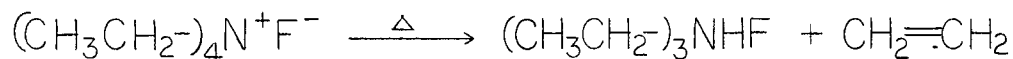
This reaction proceeds almost quantitatively in refluxing methanol containing sodium hydroxide¹³¹, probably by an aldol-type mechanism involving ionization of the amino group followed by attack of the anion on the nitrogen atom of the nitro group¹³². The ionization of the amino group should be governed by the H_- scale established in this work for DMSO-water mixtures.

It should be possible to modify the rate of the reaction by placing substituents in either ring. The kinetics could be followed conveniently by measuring the increase in light absorption due to the azoxy chromophore of the product.

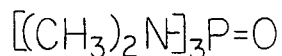
An interesting companion study would be the reaction^{130,131} in which the nucleophilic atom is carbon rather than nitrogen.



It would be interesting to study the basicity in polar aprotic solvents of such weak bases as phenoxide, benzoate, acetate, and fluoride ions since it is quite possible that some of these ions, when stripped of their solvating water molecules, would become quite basic. For example, the fluoride ion appears to be a strong base in aprotic solvents since tetraethylammonium fluoride when warmed in these solvents yields ethylene and triethylammonium fluoride¹³³. Such a study should provide information about the solvation of these ions in aqueous solution.



A solvent that has proven¹³⁴ to be useful in carrying out a great number of organic reactions involving anions is hexamethylphosphoramide (XXXVII).



XXXVII

It has a wide liquid range (4-232°) and a fairly large dielectric constant ($D = 30$ at 25°)¹³⁵. Because of the extremely weak acidity of its hydrogen atoms¹³⁵ hexamethylphosphoramidate does not react with such strong bases as the anion of cyclohexylamine, unlike DMSO. Since potassium hydroxide and *t*-butoxide appear to be very strong bases in hexamethylphosphoramidate¹³⁵ it might be possible to extend the H_- scale in this solvent.

Recently, Gordon¹³⁶ has made studies in molten quaternary ammonium salts and his results should stimulate interest in this field. The relatively low melting points of some of these salts should allow them to be studied using standard instrumentation. Gordon suggests^{136a} that the nucleophilic reactivity of anions is enhanced as the medium progresses from protic solvent to polar aprotic solvent to fused salt. The basicity of anions should also be enhanced in fused salts and deserves some study. Solubility should be no problem since nearly all types of organic compounds, with the exception of saturated hydrocarbons,

are miscible with the fused salts near their melting points^{136c}.

APPENDIX A: Preparation and Purification of Indicators

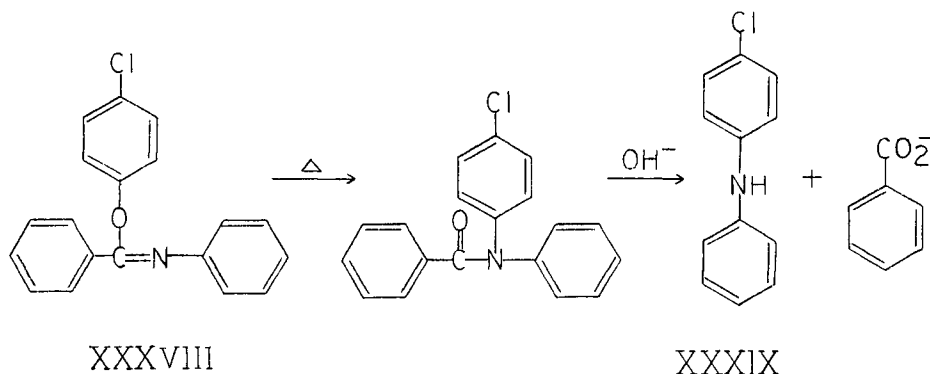
4-Methoxydiphenylamine: prepared by reaction of 4-hydroxydiphenylamine (Eastman Organic Chemicals) with dimethylsulfate in basic solution. The product melted at 104.5 - 105° after recrystallization three times from aqueous ethanol and once from petroleum ether (65-110°) followed by sublimation. Lit. m.p. 105° ¹³⁷.

4-Methyldiphenylamine: prepared from p-toluidine and bromobenzene by the same method used by Scardiglia and Roberts¹³⁸ to prepare 3-methyldiphenylamine. After several recrystallizations from petroleum ether (65 - 110°) followed by sublimation the product melted at 87.5 - 88°. Lit. m.p. 89° ¹³⁷.

Diphenylamine: obtained from Eastman Organic Chemicals was recrystallized from petroleum ether (30-60°) and sublimed, m.p. 53-53.5°. Lit. m.p. 54° ¹³⁷.

3-Methoxydiphenylamine: 3-hydroxydiphenylamine prepared from aniline and resorcinol by the method of Calm¹³⁹ was methylated in basic solution with dimethylsulfate. After sublimation followed by two recrystallizations from petroleum ether (65-110°) the product melted at 68.5-69°. Lit. m.p. 72° ¹⁴⁰.

4-Chlorodiphenylamine: prepared by the general method of Chapman^{143,144}. N-Phenylbenzimidino-4-chlorophenyl ether (XXXVIII), prepared from 4-chlorophenol and benzanilide by the same method used by Chapman^{143a} for the preparation of N-phenylbenzimidino-3-hydroxy-phenyl ether, was heated for two hours at 280-300° in a Woods' metal bath to yield a dark, viscous material that was hydrolyzed and the resulting 4-chlorodiphenylamine (XXXIX) isolated according to the method of Chapman^{143d}. After several recrystallizations from petroleum ether (65-110°) followed by sublimation, the product melted at 68.5-69°. Lit. m.p. 70.6°¹⁴⁵.



3,4'-Dichlorodiphenylamine: prepared by the same method used in the preparation of 4-chlorodiphenylamine. N-3-Chlorophenylbenzimidino-4-chloro-phenyl ether, prepared^{143a} from 4-chlorophenol and benz-3-chloroanilide, was heated for two hours at 290-300° and the resulting material refluxed in alcoholic potassium hydroxide for two hours^{143d}. After several recrystallizations from petroleum ether (65-110°) followed by sublimation the product, 3,4'-dichlorodiphenylamine, melted at 61-62°. Lit. m.p. 63-64°¹⁴⁶.

3-Trifluoromethyldiphenylamine: obtained from Aldrich Chemical Co. was distilled under reduced pressure, the middle cut dissolved in dry ether and hydrogen chloride gas bubbled through the solution. The precipitate was filtered off, washed with ether and recrystallized from dry benzene. It was then dissolved in aqueous sodium carbonate, extracted with ether, the ether solution dried, the ether removed and the amine distilled again, n_D^{20} 1.5675. Lit. n_D^{25} 1.5655¹⁴⁷.

3-Nitrodiphenylamine: prepared from 3-nitrobromobenzene and acetanilide by the method used by Hodgson and Dodgson¹⁴⁸ for the preparation of 3,3'-dinitrodiphenylamine. After three recrystallizations from aqueous ethanol, sublimation and another recrystallization from aqueous

ethanol the product melted at 110-111°. Lit. m.p. 112° 137°.

4-Methylsulfonyldiphenylamine: prepared from 4-bromophenyl-methylsulfone¹⁴⁹ and acetanilide by the method used by Nodiff and co-workers¹⁵⁰ for the preparation of 3-methylsulfonyldiphenylamine. The product was recrystallized from benzene, ethanol and ethylacetate, sublimed, passed down an alumina column with benzene-acetone (3:1) mixture and finally recrystallized from benzene-petroleum ether (65-110°), m.p. 168-168.5°.

Analysis:	C	H	N	S
calc.	63.13%	5.30%	5.66%	12.96%
found	63.20%	5.80%	5.45%	12.80%

4-Nitrodiphenylamine: had been prepared and purified previously⁷⁶ in this laboratory, m.p. 131-133°. Lit. m.p. 133° 141°.

2-Nitrodiphenylamine: obtained from Eastman Organic Chemicals was recrystallized twice from acetic acid, m.p. 73-74°. Lit. m.p. 75° 141°.

3-4'-Dinitrodiphenylamine: prepared from the sodium salt of 2-chloro-5-nitrobenzenesulfonic acid (Eastman Organic Chemicals) and 3-nitroaniline by the general method of Ullmann and Dahmen¹⁵¹. The product was recrystallized from aqueous acetic acid, passed down an alumina column

with benzene-acetone (1:1) mixture and recrystallized from benzene-petroleum ether (65-110°) pair, m.p. 215-216°. Lit. m.p. 217° ¹⁵².

4-Nitro-3'-methyldiphenylamine: prepared and purified by Dr. A. Buckley in this laboratory, m.p. 127-128°.

4-Nitro-3'-chlorodiphenylamine: prepared and purified by Dr. A. Buckley in this laboratory, m.p. 129-130°. Lit. m.p. 129° ¹⁵³.

4-Nitro-3'-trifluoromethyldiphenylamine: prepared and purified by Dr. A. Buckley in this laboratory, m.p. 137.5-138.5°.

2,4-Dinitrodiphenylamine: had been prepared and purified previously ⁷⁶ in this laboratory m.p. 155-156°. Lit. m.p. 155° ¹⁵⁴.

4,4'-Dinitrodiphenylamine: had been prepared and purified previously ⁷⁶ in this laboratory, m.p. 213-216°. Lit. m.p. 216° ¹⁵⁵.

3-Chloroaniline: obtained from Eastman Organic Chemicals was distilled from zinc dust and redistilled before use, n_D^{20} 1.5933. Lit. n_D^{20} 1.5931 ¹⁵³.

3-Trifluoromethylaniline: obtained from Matheson, Coleman and Bell was distilled twice, n_D^{20} 1.4795. Lit. n_D^{25}

1.4775 ¹⁵⁶.

3-Cyanoaniline: prepared from 3-bromoaniline and cuprous cyanide by the general method of Friedman and Schechter ¹⁵⁷. The product was sublimed, recrystallized from chloroform-petroleum ether (30-60°) pair, sublimed, recrystallized from cyclohexane-chloroform pair, and sublimed again, m.p. 52-53°. Lit. m.p. 52° ¹¹⁷.

4-Cyanoaniline: obtained from Eastman Organic Chemicals was sublimed, recrystallized three times from aqueous ethanol, sublimed, recrystallized from cyclohexane-chloroform pair and sublimed again, m.p. 85-86°. Lit. m.p. 86° ¹¹⁷.

2,3-Dichloroaniline: obtained from Aldrich Chemical Co. was distilled and recrystallized once from cyclohexane and twice from hexane, m.p. 26 - 26.5°. Lit. m.p. 23.5 - 24° ¹⁰⁹.

2,4-Dichloroaniline: obtained from Eastman Organic Chemicals was recrystallized twice from methanol and sublimed, m.p. 61.5 - 62.5°. Lit. m.p. 63° ¹⁰⁹.

2,5-Dichloroaniline: obtained from Aldrich Chemical Co. was recrystallized twice from cyclohexane and sublimed m.p. 49 - 50°. Lit. m.p. 50 - 50.5° ¹⁰⁹.

2,6-Dichloroaniline: obtained from Aldrich Chemical Co. was recrystallized from cyclohexane, distilled, and recrystallized from hexane, m.p. 37.5-38^o. Lit. m.p. 38.5-39^o ¹⁰⁹.

3,4-Dichloroaniline: prepared by the reduction of 3,4-dichloronitrobenzene (Columbia Organic Chemicals Co.) with stannous chloride by the method of Ferry and co-workers¹⁵⁸ used for the reduction of 4-nitro-4'-acetylaminodiphenylsulfone. After sublimation and two recrystallizations from cyclohexane the product melted at 71-72^o. Lit. m.p. 72^o ¹⁰⁹.

3,5-Dichloroaniline: prepared by first deaminating 2,6-dichloro-4-nitroaniline (Eastman Organic Chemicals) using the procedure of Vogel^{159a} for the deamination of 2,4,6-tribromoaniline and then reducing the resulting 3,5-dichloronitrobenzene in the same manner ¹⁵⁸ used for 3,4-dichloronitrobenzene. After sublimation, two recrystallizations from cyclohexane, and sublimation again the product melted at 49.5 - 51^o. Lit, m.p. 50 - 50.5^o ¹⁰⁹.

3,4,5-Trichloroaniline: prepared by the reduction of 3,4,5-trichloronitrobenzene (Columbia Organic Chemicals Co.) with stannous chloride by the same method¹⁵⁸ used in the reduction of 3,4-dichloronitrobenzene. After

recrystallization from ethanol and cyclohexane followed by sublimation the product melted at 97 - 97.5°. Lit. m.p. 89° ¹⁶⁰; 94-95° ¹⁶¹; 100° ¹⁶²; 101° ¹⁶³.

2,3,5,6-Tetrachloroaniline: prepared by reduction of the corresponding nitro compound. 2,3,5,6-Tetrachloronitrobenzene (Columbia Organic Chemicals Co.) (0.05 mole), 50 gram of zinc amalgam ^{159b} and 50 ml of concentrated hydrochloric acid were refluxed in 150 ml of ethanol for three hours. On cooling the reaction mixture the product crystallized out and was collected. After recrystallization twice from petroleum ether (65-110°), once from ethanol, and twice from aqueous acetic acid followed by sublimation the product melted at 106.5 - 107.5°. Lit. m.p. 107-108° ¹⁶⁴.

4-Nitroaniline: obtained from Eastman Organic Chemicals was recrystallized twice from aqueous ethanol, m.p. 147-148°. Lit. m.p. 148.5 - 149.5° ¹⁶⁵.

2-Methyl-4-nitroaniline: prepared by the method of Page and Heasman ¹⁶⁶. After two recrystallizations from methanol the product melted at 129.5 - 130.5°. Lit. m.p. 134 - 134.5° ¹⁶⁶; 131.5 - 132.5° ¹⁶⁷.

2,6-Dimethyl-4-nitroaniline: prepared by the method of Wepster¹⁶⁸. After two recrystallizations from aqueous ethanol the product melted at 161-162°. Lit. m.p. 163.5 - 164.5°¹⁶⁸.

2,6-Di-t-butyl-4-nitroaniline: 1,3,5-tri-t-butylbenzene was prepared from 1,4-di-t-butylbenzene (Eastman Organic Chemicals) and t-butylchloride by the method of Ross and co-workers¹⁶⁹. This compound was then nitrated and the nitro group reduced to yield 2,4,6-tri-t-butylaniline by the method of Burgers and co-workers¹⁷⁰. The latter compound was nitrated by the method of Burgers and co-workers¹⁷¹ to give the desired 2,6-di-t-butyl-4-nitroaniline, which, after recrystallization once from aqueous ethanol and twice from ethyl acetate-petroleum ether (65-110°) pair, melted at 259-260°. Lit. m.p. 257-258°¹⁷¹.

3,5-Dimethyl-4-nitroaniline: prepared by the method of Wepster and Verkade¹⁷². After two recrystallizations from ethanol followed by sublimation the compound melted at 130.5 - 131°. Lit. m.p. 131-132°¹⁷².

2,3,5,6-Tetramethyl-4-nitroaniline: 1,2,4,5-tetramethylbenzene (Eastman Organic Chemicals) was nitrated to give the dinitro derivative by the method of Smith and Dobrovolsky¹⁷³ which, in turn, was partially reduced.

by the method of Hampson and co-workers^{174,175} to give the desired product. After two sublimations and three recrystallizations from ethanol the compound melted at 160.5 - 161°. Lit. m.p. 161-162°¹⁷⁵.

N-Methyl-4-nitroaniline: prepared from 4-nitroacetanilide and methyl iodide by the method of Pachter and Kloetzel¹⁷⁶. After two recrystallizations from ethanol followed by sublimation the product melted at 150.5 - 151.5°. Lit. m.p. 153-154°¹⁷⁶.

N-Ethyl-4-nitroaniline: prepared from 4-nitroacetanilide and ethyl iodide by the same method¹⁷⁶ used for the N-methyl compound. After two recrystallizations from ethanol followed by sublimation the product melted at 94.5-95.5°. Lit. m.p. 95°¹⁷⁷.

N,2-Dimethyl-4-nitroaniline: prepared from 2-methyl-4-nitroaniline and methyl iodide by the same procedure¹⁷⁶ used in the preparation of N-methyl-4-nitroaniline. After recrystallization from aqueous ethanol, sublimation and two more recrystallizations from aqueous ethanol the product melted at 135.5 - 136.5°. Lit. m.p. 137°¹⁷⁸.

N-Isopropyl-4-nitroaniline: 4-nitroaniline (2 gm) was dissolved in 10 ml of DMSO and 1 gm of powdered potassium hydroxide added causing the solution to turn highly coloured. 2-Bromopropane (2 gm) was added, the mixture

stirred for ten minutes, and then heated on a steam bath for an hour, after which it was poured on to ice. A yellow solid material was sublimed from the resulting dark tarry product and on recrystallization from benzene-petroleum ether (65-110°) pair yielded a high melting product - probably unreacted 4-nitroaniline. Evaporation of the mother liquor gave about 0.5 gm of another yellow solid material that was passed down a silica gel column with benzene-ethylacetate (5:1) mixture. The first band off the column was collected and recrystallized from petroleum ether (65-110°), m.p. 83-84°.

Analysis:

	C	H	N
Calc.	59.99%	6.71%	15.55%
Found	59.85%	6.41%	15.59%

The NMR spectrum of the compound in carbon tetrachloride with internal TMS standard contains: a doublet centered at 2.03 τ and another at 3.55 τ both with relative area of two and splitting of about 9.3 c.p.s.; a broad absorption at about 5.19 τ with relative area of one; a highly structured absorption at about 6.35 τ with relative area of one; and a doublet centered at 8.79 τ with relative area of six and splitting of about 6.5 c.p.s.

N-t-Butyl-4-nitroaniline: prepared from the reaction of 4-nitroaniline and t-butyl alcohol in phosphoric acid by the method of Gleim¹⁷⁹. The product was passed down a silica gel column with benzene-ethyl acetate (10:1) mixture and the first band off the column was collected. This material was sublimed and recrystallized from ethyl acetate-petroleum ether (65-110°) pair, m.p. 68.5 - 69.5°. Lit. m.p. 68-69.5°¹⁸⁰.

Analysis:

	C	H	N
calc.	61.84%	7.27%	14.42%
found	61.95%	7.36%	14.42%

N-Triphenylmethyl-4-nitroaniline: prepared from triphenylmethyl chloride and 4-nitroaniline by the method of Verkade and co-workers¹⁸¹. After three recrystallizations from ethanol-chloroform pair the compound melted at 223-225°. Lit. m.p. 223-224°¹⁸¹.

2,2'-Dipyridylamine: obtained from Columbia Organic Chemicals Co. was recrystallized twice from aqueous ethanol and sublimed, m.p. 93 - 94°. Lit. m.p. 94-95°¹⁸².

4-Aminodiphenylamine: obtained from Matheson, Coleman and Bell was distilled, dissolved in a small amount of benzene and precipitated with petroleum ether (65-110°), recrystallized from benzene-petroleum ether (65-110°)

pair and then distilled again. The distillate was a pale yellow colour and solidified to give crystals melting at $72.5 - 74.5^{\circ}$. Lit. m.p. 75° 153.

APPENDIX B: Spectral Data for the Indicators

TABLE IX

Absorption Maxima and Molar Absorptivities
of the Indicators in 95.6% Ethanol

Substituent	Observed Values		Reported Values		ref.
	$\lambda_{\text{max.}}$ (m μ)	ϵ	$\lambda_{\text{max.}}$ (m μ)	ϵ	
diphenylamines					
4-methoxy	284	19,000			
4-methyl	286	21,400			
none	285	21,300	285	20,250 ^a	183
3-methoxy	283	18,500			
4-chloro	289	24,000			
3-chloro	286	21,300			
3-trifluoromethyl	286	21,600	285	11,200	184
3,4'-dichloro	290	25,300			
3-nitro	275	22,300			
	399	1,180			
4-methylsulfonyl	309	26,300			
4-nitro	392	21,700	390	21,200 ^a	183
2-nitro	426	6,710	422- 423	6,600 ^a	183
4-nitro-3'-methyl	394	22,300			
4-nitro-3'-chloro	385	22,700			
4-nitro-3'-trifluoro- methyl	381	19,200			
3,4'-dinitro	375	23,200			
4,4'-dinitro	403	34,100	402	37,600 ^a	183
2,4-dinitro	352	17,700	350- 351	17,000 ^a	183
anilines					
3-chloro	242	8,650			
	293	1,970			
3-trifluoromethyl	242	9,450			
	298	2,190			
3-cyano	251	7,320			
	320	4,040			

TABLE IX (Continued)

Substituent	Observed Values		Reported Values		ref.
	$\lambda_{\text{max.}}$ (m μ)	ϵ	$\lambda_{\text{max.}}$ (m μ)	ϵ	
anilines (Continued)					
4-cyano	275	23,600			
2,3-dichloro	243	6,670			
	297	2,830			
2,4-dichloro	245	11,500			
	306	2,510			
2,5-dichloro	244	8,520			
	300	3,260			
2,6-dichloro	239	6,780			
	296	3,490			
3,4-dichloro	248	11,600			
	305	2,040			
3,5-dichloro	249	9,360			
	300	2,320			
3,4,5-trichloro	249	12,200			
	311	2,430			
2,3,5,6-tetrachloro	309	4,070			
4-nitro	373	16,300	370	16,200	185
4-nitro-2-methyl	375	14,900	379	17,400	185
4-nitro-2,6-dimethyl	377	14,600	374	14,200	185
4-nitro-2,6-di-t-butyl	379	14,400			
4-nitro-3,5-dimethyl	382	4,970	386	5,000	185
4-nitro-2,3,5,6-tetramethyl	394	1,590	391	1,500	185
4-nitro-N-methyl	386	18,400	391	18,400	185
4-nitro-N-ethyl	388	19,800	386	18,900 ^a	183
4-nitro-N-isopropyl	389	20,800			
4-nitro-N-t-butyl	389	20,100			
4-nitro-N-triphenyl-methyl	376	19,000			
4-nitro-N,2-dimethyl	388	17,900	383	15,300	185
2,2'-dipyridylamine	264	22,200			
	312	14,700			

a in absolute ethanol

TABLE X

Absorption Maxima and Molar Absorptivities
of Diphenylamines in 20% Ethanol

Substituents	$\lambda_{\text{max.}}$ (m μ)	ϵ
4-methoxy	280	14,500
4-methyl	282	15,900
none	282	16,400
3-methoxy	282	14,800
4-chloro	286	18,600
3-chloro	284	16,900
3-trifluoromethyl	284	17,300
3,4'-dichloro	288	20,700
3-nitro	280	22,000
4-methylsulfonyl	309	25,200
4-nitro	409-	
	410	20,500
2-nitro	444	6,550
4-nitro-3'-methyl	411	20,500
4-nitro-3'-chloro	403	20,600
4-nitro-3'-trifluoro-		
methyl ^a	400	17,400
3,4'-dinitro ^a	396	20,200
4,4'-dinitro ^b	422	32,300

a 20% ethanol containing 2.25 molar sulfuric acid

b 20% ethanol containing 2.50 molar sulfuric acid

TABLE XI

Absorption Maxima and Molar Absorptivities
of Indicator Anions in DMSO-Water

Substituent	Observed Values			Reported Values		
	$\lambda_{\max.}$ (m μ)	ϵ	Mole % DMSO ^a	$\lambda_{\max.}$ (m μ)	ϵ	ref.
diphenylamines						
4-methoxy	370	28,100	99.8			
4-methyl	375	29,700	99.5			
4-amino	372	23,900	99.8			
none	376	28,500	99.5			
3-methoxy	380	25,800	99.0			
4-chloro	374	30,200	97.1			
3-chloro	370	26,900	97.1			
3-trifluoromethyl	368	28,800	97.1			
3-nitro	375	14,800	99.5			
3,4'-dichloro	376	30,600	97.1			
4-methylsulfonyl	383	29,400	83.1			
2-nitro	548	9,220	83.1	545	9,170 ^c	76
2,4-dinitro	434	19,000	46.5	432	21,800 ^d	76
anilines						
3-chloro	386	2,710	100 ^b			
3-trifluoromethyl	404	2,500	100 ^b			
3-cyano	447	2,530	100 ^b			
4-cyano	337	37,100	99.5			
2,3-dichloro	381	3,550	99.8			
2,4-dichloro	399	3,030	99.8			
2,5-dichloro	385	3,640	99.5			
2,6-dichloro	380	4,500	98.7			
3,4-dichloro	400	2,450	99.8			
3,5-dichloro	386	2,820	99.8			
3,4,5-trichloro	397	2,610	99.5			
2,3,5,6-tetrachloro	380	4,480	92.5			
4-nitro	467	30,800	87.8	467	32,300 ^c	76
4-nitro-2-methyl	471	31,900	92.3			
4-nitro-2,6-dimethyl	474	33,300	92.3			
4-nitro-2,6-di-t-butyl	470	29,300	95.3			
4-nitro-3,5-dimethyl	466	23,600	97.1			

TABLE XI (Continued)

Substituent	Observed Values			Reported Values		
	$\lambda_{\text{max.}} (\text{m}\mu)$	ϵ	Mole % DMSO ^a	$\lambda_{\text{max.}} (\text{m}\mu)$	ϵ	ref.
anilines						
4-nitro-2,3,5,6-tetramethyl	507	17,000	99.5			
4-nitro-N-methyl	483	31,200	97.1			
4-nitro-N-ethyl	482	31,300	97.1			
4-nitro-N isopropyl	480	32,000	97.1			
4-nitro-N-t-butyl	480	32,000	97.1			
4-nitro-N-triphenyl-methyl	490	38,600	92.5			
4-nitro-N,2-dimethyl	485	31,500	97.1			
2-nitro-4-chloro	495	8,440	78.4			
	520	8,440	78.4	516	6,900 ^c	76
2,2'-dipyridylamine	370	16,200	92.5			

a DMSO-water mixtures containing 0.011 molar tetramethylammonium hydroxide

b DMSO containing potassium t-butoxide as base

c 95 mole % sulfolane-water-0.011 molar tetramethylammonium hydroxide

d pyridine containing 0.011 molar tetramethylammonium hydroxide

APPENDIX C: Ionization Ratio Data

TABLE XII

Experimental Values of $\text{Log } [A^-] / [HA]$ for the Indicators
Used to Determine the H_L Values in DMSO-Water-
Tetramethylammonium Hydroxide (0.011 M.)

Indicator Mole % DMSO	2, 4-(NO ₂) ₂ DPA	3, 4'-(NO ₂) ₂ DPA	4-NO ₂ -3'-CF ₃ DPA	4-NO ₂ DPA	4-Cl-2-NO ₂ An	2-NO ₂ DPA	4-CH ₃ SO ₂ DPA	2, 3, 5, 6-(Cl) ₄ An
10.32	- .674							
15.20	.009	-.741	-1.012					
20.18	.683	-.185	-.483					
23.57	1.067	.195	-.117	-.788				
26.95		.571	.252	-.452				
30.11		.891	.585	-.135				
33.42			.933	.183				
36.79				.503	-.913			
39.86				.757	-.597			
43.27					-.253			
46.54					.068	-.808		
49.59					.356	-.489		
52.55					.639	-.170		
55.95					.962	.179	-.700	
58.56						.447	-.444	
59.38								-.808
62.27						.833	-.071	

TABLE XII (Continued)

Indicator Mole % DMSO	4-CH ₃ SO ₂ DPA	2, 3, 5, 6-(Cl) ₄ An	3-NO ₂ DPA	3, 4'-(Cl) ₂ DPA	3-CF ₃ DPA	3-ClDPA	4-ClDPA	3-CH ₃ ODPA
64.20		-.319	-.609	-.805				
65.48	.247							
68.51	.558							
69.09		.182	-.117	-.314				
71.12	.833							
71.35		.442	.128	-.083	-.838			
73.69		.730	.354	.167	-.594			
76.12			.609	.428	-.330			
78.01						-.397		
78.36			.827	.653	-.062		-.918	
80.78					.176		-.660	
82.75						.207		
83.14					.489		-.361	
85.17						.496		
85.46					.789		-.021	
87.51						.810		-.644
87.79							.294	
89.92								-.269
90.07							.658	
92.29								.172

TABLE XII (Continued)

Indicator Mole % DMSO	DPA	4-CNAn	3,4,5-(Cl) ₃ An	4-CH ₃ DPA	4-CH ₃ ODPA	3,5-(Cl) ₂ An	3,4-(Cl) ₂ An	3-CNAn
87.79	-.836							
90.07	-.465	-.703	-.882					
90.56				-.860				
91.48				-.693	-.945			
92.47	.012	-.229	-.434					
92.52				-.463	-.741			
93.47				-.261	-.524			
94.34				-.058	-.330			
94.74	.562	.310	.156			-.577		
95.04				.133	-.133			
95.55				.311	.009			
95.77	.874	.644	.479			-.280		
96.21		.799	.644			-.103		
96.64				.650	.407			
97.13						.274	-.688	-.740
97.31						.358		
97.89						.653	-.345	-.396

TABLE XII (Continued)

Indicator Mole % DMSO	3,5-(Cl) ₂ An	3,4-(Cl) ₂ An	3-CNAn	3-CF ₃ An	3-ClAn
98.29	.935	-.111	-.140	-.906	
98.71		.244	.203	-.558	-.777
99.14		.730	.640	-.105	-.336
99.59				.837	.510

NOTE DPA is diphenylamine

 An is aniline

TABLE XIII

Experimental Values of Log $[A^-]/[HA]$ for Various Indicators in DMSO-Water-Tetramethylammonium Hydroxide (0.011 M)

[illegible]

TABLE XIII (Continued)

Indicator	4-NO ₂ -N-t-butylAn	2,2'-dipyridylamine	4-NO ₂ -3,5-(CH ₃) ₂ An	2,6-(Cl) ₂ An	4-NO ₂ -2,3,5,6-(NO ₂) ₄ An	2,5-(Cl) ₂ An	2,3-(Cl) ₂ An	2,4-(Cl) ₂ An
Mole % DMSO								
64.20	-.714	-.802						
69.09	-.240	-.419						
71.35	.006	-.228						
73.69	.248	-.030						
76.12	.519	.188						
78.36	.788	.402	-.801					
80.78		.652	-.529					
83.14		.907	-.218					
85.46			.104					
87.79			.481					
90.07			.913	-.425	-.807	-.721		
92.47					-.276	-.282		
94.74				.629	.417	.299	-.122	-.445
95.34				.822		.506	.083	-.264
95.77				.930	.775	.635		-.135
96.21					.969	.798	.323	.012
96.66						.966	.499	.178

NOTE An is aniline
trityl is triphenylmethyl

TABLE XIV

Experimental Values of $\text{Log } [\text{BH}^+]/[\text{B}]$ for
the Substituted Diphenylamines Used to
Determine the H_0 Values in 20 Volume Percent
Ethanol-Aqueous Sulfuric Acid

Substituent	4-CH ₃ O-	4-CH ₃ -	none	3-CH ₃ O-	4-Cl-	3-Cl-	3-CF ₃ -	3,4'-(Cl) ₂ -
Molarity H ₂ SO ₄								
.0163	-.487	-.665						
.0339	-.202	-.350	-.792					
.0567	.017	-.141	-.555	-.937				
.0808	.175	.011	-.409	-.778				
.163	.490	.330	-.098	-.467	-.863			
.245	.682	.531	.102	-.286	-.642			
.406	.955	.788	.365	-.023	-.397	-.855		
.611			.602	.227	-.151	-.599		
.763			.741	.359	-.028	-.473	-.806	
.914			.869	.494	.105	-.344	-.676	
1.26				.741	.356	-.115	-.436	-.855
1.47				.890	.492	.020	-.296	-.715
1.72					.658	.175	-.155	-.572
1.98					.797	.337	.005	-.400
2.25					.932	.470	.152	-.261
2.49						.615	.293	-.120
2.73						.753	.420	.009

TABLE XIV (Continued)

Substituent Molarity H_2SO_4	3-CF ₃ -	3,4'-(Cl) ₂ -	3-NO ₂ -	4-CH ₃ SO ₂ -	4-NO ₂ -3'-CH ₃ -	4-NO ₂ -	2-NO ₂ -	4-NO ₂ -3'-Cl-
1.98	.005	-.400	-.818					
2.25	.152	-.261	-.693					
2.49	.293	-.120	-.540					
2.73	.420	.009	-.385					
3.07	.637	.212						
3.29	.771	.348	-.072					
3.58	.928	.516	.080	-.850				
3.76		.632	.192	-.735				
4.14		.863	.432	-.500	-.907			
4.38			.555	-.357	-.780	-.954		
4.62			.722	-.220	-.626	-.789		
4.90			.900	-.023	-.435	-.633		
5.15				.114	-.280	-.465		
5.41				.268	-.122	-.324		
5.66				.429	.036	-.165		
5.95				.638	.245	.048	-.957	-.914
6.47				.964	.585	.381	-.621	-.602

TABLE XIV (Continued)

Substituents	4-NO ₂ -3'-CH ₃ -	4-NO ₂ -	2-NO ₂ -	4-NO ₂ -3'-Cl-	4-NO ₂ 3'-CF ₃ -	3,4'-(NO ₂) ₂ -	4,4'-(NO ₂) ₂ -
Molarity H ₂ SO ₄							
6.47	.585	.381	-.621	-.602	-.888		
6.81	.825	.612	-.385	-.385	-.688		
7.16		.858	-.128	-.144	-.455		
7.64			.204	.160	-.156	-.857	
8.14			.601	.523	.207	-.516	
8.44			.840	.766	.420	-.306	
8.86					.780	.012	-1.026
9.10						.357	-.662
9.59						.735	-.298
9.95							-.017
10.40							.320
10.96							.762

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