The Behavior Of Substituted Aromatic Acids In Selected Non-aqueous Solvents.

Mic 59-6965

MIRON, Roy Richardson Hurlbut. THE BEHAVIOR OF SUBSTITUTED AROMATIC ACIDS IN SELECTED NON-AQUEOUS SOLVENTS.

Lehigh University, Ph.D., 1959
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

THE BEHAVIOR OF SUBSTITUTED AROMATIC ACIDS IN SELECTED NON-AQUEOUS SOLVENTS

by

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A DISSERTATION

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

Lehigh University

1959

A CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Sept. 18, 1959
Date

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Accepted, Sept. 18, 1959
Date

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ACKNOWLEDGMENT

The author sincerely appreciates the advice and encouragement given by Assistant Professor David M. Hercules throughout the course of this investigation.

Thanks are also due to Mr. Richard M. King for his help in the repairing of the electronic components of the D. C. amplifier, and to Dr. Frederick A. Achey for his assistance in preparing the syringe.

The United States Steel Foundation of New York is to be thanked for their financial aid during the author's graduate studies.

To all of the above and especially to my wife, Doris, for her unselfish devotion and constant encouragement, I offer my deepest gratitude.

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INTRODUCTION

The history of analytical chemistry has shown that it has almost always depended upon the growth of the other branches of science. The rapid growth of organic chemistry required the development of organic analytical methods which were rapid, specific and accurate. These new methods were not developed immediately, but were gradually arrived at by attempts to modernize existing methods. An example of this is found in the investigation of non-aqueous solvents for quantative determination of organic compounds.

The most simple and dependable methods in analytical chemistry are those of acidimetry and alkalimetry, but it has been recognized only recently that the scope of these methods could be increased by the use of solvents other than water. Advances in the fundamental chemistry of the behavior of compounds in non-aqueous solutions were greatly hindered prior to 1900 because of the prevalent opinion that water was the only solvent in which one could carry out ionic and metathetical reactions. Although occasional fragmentary efforts had been made to study the behavior of typical salts when dissolved in non-aqueous solvents, unusual observations obtained from such experiments were considered special cases and water was considered the prototype for possible behavior of solutes in other systems.

Today, however, it is recognized that water is anomalous in many respects and that concepts defining the behavior of solutions can often be developed more readily on the basis of observations in non-aqueous solvents. A summary of the early observations dealing with solubilities and theoretical relationships in non-aqueous solvents is found in Walden's book (1). It was Walden and his co-workers who began the extensive investigation of the electro-chemistry of various electrolytes in sulfur dioxide, thionyl chloride, and other presumably inert organic and inorganic solvents. These investigations resulted in important modifications of the theory of acidimetry and alkalimetry which previously had been based on the Arrhenius concept (1884).

According to Arrhenius, acids were substances which yielded the hydrogen ion in solution, whereas bases produced the hydroxyl ion. Water was merely the solvent medium and served to bring about the dissociation of acid and base molecules into ions. Although this older generalization can still be regarded as having great practical value, it is limited specifically to water and cannot be applied to the multitude of other solvents which have been subjected to study since the turn of the century.

At least three other acid-base concepts have been advanced to include the work which is being done in non-aqueous solvent chemistry. Franklin (2) paved the way with his "solvent system concept" which was originally limited to water and ammonia but has since been

extended to other protonic and non-protonic media. The "protonic concept" advanced by Brönsted (3) and Lowry (4) in 1924 rejected the classical Arrhenius theory of electrolytic dissociation and advanced the idea that an acid was a substance which had a tendency to give up a proton while a base was a substance which could accept a proton. Each of these concepts proved to be too specific, with the result that Lewis (5) published his concept, based on the electronic theory of the structure of matter, to account for the behavior of acids and bases.

In 1903 Vorländer (6) titrated aniline by dissolving hydrogen chloride in benzene, followed by Folin, Wentworth, and Flanders (7, 8, 9) who published the results of their titrations of fatty acids with sodium ethoxide dissolved in benzene, chloroform, and carbon tetrachloride. The investigations of Hall, Conant, and Weaver in 1927 and 1928 (10, 11) were devoted to the dissociation of strong electrolytes in acetic anhydride and formic acid, and the effects of small quantities of water and alcohol on the dissociation. LaMer and Downs (12) were the first to use a potentiometric titration method in non-aqueous solvents. They employed two platinium electrodes and benzene saturated with tetra-isoamyl ammonium iodide to titrate diethylamine with trichloroacetic acid. Three years later Vorländer Fischer, and Felicitas (13, 14) published their work on the determination of amines and alkaloids.

Since 1935 there has been a tremendous quantity of work directed toward improving the methods of titrating compounds in a multitude of non-aqueous solvents. Notable among these are the following: Fritz et al (15, 16, 17, 18, 19, 20, 21), Riddick et al (22, 23, 24), and Wollish et al (25, 26, 27). The reader is referred to references (29) and (30) for the latest literature summary on acid-base titrations in non-aqueous solvents. The majority of these articles is an empirical collection of data with little or no attempt having been made to correlate these data with existing concepts of acid-base behavior.

Hammett (31) was the first to make an extensive study of the relationship between structure and acid strength in solution. Hammett's research had been the major work in this field, and until the work of Kolthoff and Bruckenstein (32) little research had been done to advance his concepts.

The present investigation was undertaken to further correlate the behavior of substituted aromatic acids in various non-aqueous solutions. It has been shown that it is possible to predict the behavior of these acids in non-aqueous solvents and consequently, to make an *a priori* prediction of their relative acidic strength in the solvent under investigation.

This study has shown that a definite correlation exists between the half neutralization potential of these substituted aromatic acids and their pKa in water, and that except for several notable exceptions,

the half neutralization potential is a function of Hammett's sigma value.

This investigation includes the study of the effect of solvent on ΔHNP. It was found that there was apparently no correlation of ΔHNP with a simple solvent property with the single exception of the meta-aminobenzoic acid derivative.

THEORY

Acid-Base Theory

The original Arrhenius definition limited acids to hydrogen compounds which gave the hydrogen ion in solution. Conversely, bases were compounds which gave the hydroxyl ion in solution. However, with the development of Franklin's (2) "solvent system concept" and its application both to protonic and to non-protonic solvents, it was soon realized that the number of acid and base types could be increased almost without limit. However, it was left to Brönsted (3) and Lowry (4) to present a unified concept of acid and base behavior. In presenting his proposal Brönsted stated:

"....if we seek with these considerations as a background (the fact that free hydrogen ions do not exist in solution and that there are many analogs of hydroxyl ions) a more general and a more precise definition of acid and base we recognize that such a definition must in the first place attribute characteristic acid-base properties to molecules of acids and bases themselves, that is, not to their solutions. Secondly, it must be a definition which relates the ideas of acid and base to each other in a more logical way than has hitherto been the case. It must further give an illuminating explanation of the peculiar character of these substances, and finally we may say that since acids and bases are found so universally in chemical systems, the definitions of these substances must be formulated independently of the solvent." (33)

At this point, it might be well to clarify a few terms which will appear throughout this discourse, namely:

1 Intrinsic acidity (or intrinsic basicity) of a substance represents its inherent tendency to lose(or gain) a proton. This characteristic is independent of the solvent and depends only upon the particular acid

or base under discussion.

2. Acidic character (or basic character) of a solute in a given solvent is defined as the tendency to lose a proton to (or to gain a proton from) the particular solvent in question. This, of course, will depend upon the relative affinity of solute and solvent for protons.

3. Strength of an electrolyte is characterized by the degree of dissociation and depends upon both the solute and solvent and especially upon the dielectric constant of the solvent.

Since the Brönsted-Lowry concept implies that an acid may only lose its proton when in the presence of a base acid-base reactions may be written as follows:

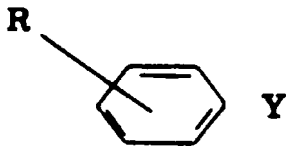
$$\underset{\text{acid}_1}{A_1} + \underset{\text{base}_2}{B_2} \rightleftharpoons \underset{\text{acid}_2}{A_2} + \underset{\text{base}_1}{B_1} \qquad \text{(I)}$$

Actually, according to this concept, neutralization is not considered to be an essential criterion for an acid-base reaction, and salt formation is purely incidental to the reaction between acids and bases in various media. It is this framework that will be used as the fundamental acid-base theory employed in this dissertation.

Chemical Structure And Reactivity

The correlation between the structure of compounds and their chemical reactivity has been one of the most interesting aspects of research in modern chemistry. Although certain qualitative theories

have existed for a long time, it has been only recently that the quantative aspects have been developed. In particular, the effects of substituents (R) on the reactivity of a functional group (Y) in compounds of Type I have received considerable attention.



Type I

At this point it might be well to review briefly some of the principles of the effect of structure on equilibra, as seen from a thermodynamic point of view.

A general equation for almost any type of reaction may be written as follows:

$$RY + Z \rightleftharpoons P \qquad (2)$$

where RY represents a reactant (R is a substituent group and Y is a functional group), Z is a reagent, and P, the products. If we write the equilibrium constant, K, for this reaction then for the same type of reaction involving R_0Y and the product P_0 we may write the equilibrium constant as K_0.

Thus, it is possible for a specific reaction series, by writing the equilibrium constants as K/K_0 for a reaction of the type shown in equation 3, to make a quantatative measure of the effect on the above equilibrium when the structure of the reactant is changed from R_0 to R.

$$RY + P_o \rightleftharpoons R_oY + P \qquad (3)$$

The effect of structure on equilibra must be discussed in terms of the changes in the relative standard free-energy, enthalpy, and entropy. The following equations acquired from the fundamental relations of statistical thermodynamics are applicable:

$$\Delta\Delta F^\circ = \Delta F^\circ - \Delta F_o^\circ = \Delta\Delta E_p^\circ - RT \ln(\Pi Q) \qquad (I)$$

$$\Delta\Delta F^\circ = -RT \ln(K/K_o) \qquad (II)$$

where $\Delta\Delta F_o^\circ$ = standard free energy change accompanying reaction 3, and $\Delta\Delta E_p^\circ$ = standard energy change accompanying reaction when both reactant and product states are completely deprived of all their energies of molecular motion. This energy may be regarded as the potential-energy change accompanying reaction 3.

$$(\Pi Q) = \frac{q_P \, q_{R_oY}}{q_{P_o} \, q_{RY}} \qquad (III)$$

where the q's are partition functions involving temperature-dependent kinetic energies of motion. These partition functions may be based upon the energy levels of all forms of motions, including solvent molecules involved in solvation and the motions at absolute zero (zero point vibrations). However, it may be considered that only rotation, bending, and stretching motions of the reactant and product molecules are the major contributors to (ΠQ). (35)

The following equations indicate the thermodynamic functions in terms of their experimental quantities:

$$\text{Enthalpy, } \Delta\Delta H^\circ = \frac{-R\left[\ln(K/K_o)_{T_2} - \ln(K/K_o)_{T_1}\right]}{1/T_2 - 1/T_1} \qquad \text{(IV)}$$

$$\text{Entropy of Activation, } \Delta\Delta S^\circ = \frac{RT\ln(K/K_o)_{T_2} - RT\ln(K/K_o)_{T_1}}{T_2 - T_1} \qquad \text{(V)}$$

It can be seen by equation I that the relative free energy, $\Delta\Delta F^\circ$, is a combination of a temperature-independent potential energy term and temperature-dependent term associated with kinetic energies of motion of the molecules. It is possible to separate $\Delta\Delta F^\circ$ into two terms providing certain thermodynamic values are known. The first term gives the value of $\Delta\Delta F^\circ$ at absolute zero, generally written as $\Delta\Delta E_o^\circ$. This value may be determined providing that heat capacities of products and reactants from absolute zero to the temperature under study are known. The second term is a kinetic energy term similar to $-RT\ln(\pi Q)$, but where the partition functions are based upon $\Delta\Delta E_o^\circ$ instead of $\Delta\Delta E_p^\circ$. Since the $\Delta\Delta E_o^\circ$ value is greater than the $\Delta\Delta E_p^\circ$ term in an amount equal to the zero-point vibrational energies of the products and reactants which may designated as $\Delta\Delta E_z^\circ$, we can evaluate $\Delta\Delta E_p^\circ$ as follows:

$$\Delta\Delta E_p^\circ = \Delta\Delta E_o^\circ - \Delta\Delta E_z^\circ \qquad \text{(VI)}$$

$\Delta\Delta E_z^\circ$ may be determined from spectroscopic data, however, values for $\Delta\Delta E_o^\circ$ are difficult to obtain since only the hydrocarbons have been investigated to the extent where a large number of values for ΔE_o°

are available (36).

Thus, it can be seen that it is very difficult to separate $\Delta\Delta F^{\circ}$ into its contributing factors without employing the use of extra thermodynamic methods, and that log K/K_0 is a combination of both potential and kinetic energy values.

There are several factors which affect molecular reactivity by contributing to the potential energy ($\Delta\Delta E_p^{\circ}$). These have been found to be:

1. polar effect
2. resonance effect
3. steric effect

These effects arise from the various interactions within the molecule however, there is no thermodynamic method, at present, to distinguish these individual terms from their over-all effect on the potential energy.

The polar effect may be considered to arise from coulombic forces between the substituent group R and the functional group Y. These forces are due to charge separation arising from differences in electronegativities between the two groups.

The resonance effect requires at least two different valence-bond structures for the groups. Several books (37, 38) have been written concerning this particular effect, and both of them deal with quantum-mechanical descriptions necessary for a clear understanding of this phenomena.

Van der Waals type forces are the basis for steric interaction between a functional group and the substituent group (39). Angle strain energies which are associated with a decrease in the binding energy between R and Y, because of a distortion of the normal bond angles in the R group, are generally classified as steric interactions. Thus, we can make the statement that all the factors contributing to the potential energy term $\Delta\Delta E_p^\circ$ are fundamentally electrical in nature.

Hammett Equation

By the mid 1930's it had been repeatedly noted that the effects of substituents on many reactions of benzene derivatives could be related to the acid strengths of the corresponding benzoic acids (40, 41, 42, 43). As a result of these data Hammett (44, 45) proposed his now famous equation which related a substituent R with the reactivity of the functional group Y. This equation may be written as follows:

$$\log (k/k_o) = \rho\sigma \qquad \text{(VII)}$$

where k is the rate or equilibrium constant (K) for reactions involving a substituted compound, and k_o the rate or equilibrium constant (K_o) for the parent compound.

The substituent constant, σ, is dependent only on the type and position of R, while the reaction constant, ρ, must be determined for each specific reaction series and depends upon the conditions under which the reaction takes place and the nature of the side chain, Y.

The equation is applicable only to derivatives of benzene with substituents in the meta and para positions, since reactivity is greatly complicated in reaction series in which substituents are introduced close to the reaction center such as found in the ortho substituted compounds. The equation was checked by Hammett in over fifty reaction series and found to have a mean deviation of about $\pm$ 15% Despite the fact that several attempts have been made to provide a theoretical background or derivation (46) for Hammett's equation it remains essentially an empirical relationship.

When the K's are equilibrium constants the expresion on the left hand side of equation (VII) is proportional to the difference between the free energies of reaction of the substituted and unsubstituted compounds. When the k's are rate constants then the expression is proportional to the difference between the energies of activation.

Hammett (31) has suggested that based on thermodynamic considerations the free energy change can be considered as the sum of three terms: the entropy change, and changes in the kinetic and potential energies. Therefore, all three terms must be considered in any correlation of structure with reactivity. However, as it has been shown previously it is difficult to evaluate change in entropy and kinetic energy. However, Hammett has shown that the mean value of the entropy difference for meta and para derivatives is only — O. 2

(cal/deg.) and that the probable error of any single value is 0.3. Since this is well within experimental error for determination of the entropies of activation, it may be said that the entropy term is not significally affected by a substituent in the meta or para position. Hammett states (31) :

".... it is clear that the effect of a para or meta substituent on the reactions of benzene derivatives is exerted solely or chiefly through the change in potential energy. The substituent has little or no effect upon the terms that involve the internal kinetic energies."

Thus, it is possible to discuss the validity of Hammett's equation in terms of the potential energy difference between the initial and final states, or in the case of reaction rates the difference between the ground and transition states. Since the reaction site can be considered to be insulated from the ring when there are one or more methylene groups between it and the substituent group, there will be little effect on the difference in the potential energy between the initial and final states. The substituent groups may then be considered to affect the energy of activation by the change they cause in the electron density of the reaction site. If, however, the reaction site is not insulated from the benzene ring, the effect of the substituent on the differences in potential energy between the initial and final states must also be considered. Since in all cases of the meta and para derivatives of benzoic acid this insulating group is not present the differences in resonance energy between the initial and final states must be considered.

However, it is possible to approximate this difference by assuming that the reactivity depends upon the electron distribution in the molecule.

Eyring (47) and Wheland (48) have shown that the reactivity of a molecule does depend upon the electron distribution within the molecule. Brown (49) has verified the predication of reactivities from electron density considerations paralleling those made from considerations of structure, or calculations involving the energy of the transition state.

Reaction Constants

Hammett has defined the reaction constant rho as:

$$\rho = \frac{B_1/\varepsilon + B_2}{RT\,d^2} \qquad \text{(VIII)}$$

where R = gas constant, T is the absolute temperature, ε the dielectric constant of the solvent, and d the distance from the substituent to the reaction site. He assumed that B_1 depended only on the electrostatic interaction between the reacting benzene derivative and the solvent. B_2 was considered to be a measure of the susceptibility of the reaction to changes in charge density at the reaction site.

The reaction constant (ρ) can then be considered to measure the effect on the reaction rate of the type of substituent present. The factors affecting the rate can be divided into three groups: (50)

1. transmission of electrical effects to the reaction site
2. effect on the reaction to changes in electron density at the

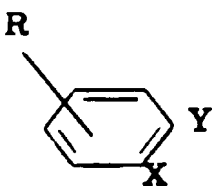
reaction site

3. the effect of reaction conditions

Transmission of electrical effects to the reaction site

Branch and Calvin (51) have shown that the validity of Hammett's equation is dependent upon the fact that sigma represents the electrical effect of the substituent. Consequently, rho must depend upon the effectiveness with which the side chain can transmit the electrical effects of the substituent to the reaction site. Hammett has indicated this relationship in equation VIII by introducing a value, d, for the distance between the substituent and the reaction site. However, this factor fails to compensate for the insulating property of a methylene group when it is present between the reaction site and the benzene ring. Experimental values obtained in these cases are smaller than those predicated by theory.

Jaffe (50) has also shown that the reaction constants will depend on the polarizability of the side chain. As the distance from the nucleus and the number of electrons increase the reactant constant decreases. He also indicates that for a series of compounds of Type II



Type II

where X is the same for the whole series, the reaction constants are

essentially independent of the nature of X.

Effect on the reaction to changes in electron density at the site of the reaction

Remick (52) has shown that a positive rho indicates the reaction is aided by a low electron density at the reaction site, and that a negative rho indicates a reaction favored by a high electron density.

Effect of reaction conditions

Jaffe (50) has demonstrated that ρ, as defined by equation VIII, is not completely independent of temperature conditions of the reaction but for the majority of cases the expression appears to represent the dependence adequately.

We can also see from equation VIII that as the dielectric constant of the solvent decreases the reaction constant (ρ) should increase. Jaffe (50) has shown this to be true in most cases tested. However reaction constants derived from rate data show a greater deviation in behavior when the solvent is changed. Brown (53) has even postulated a theory based on a change in mechanism due to a change in solvent. Also, cases have been found where the reaction constant changes sign with a change in solvent. In order to explain these phenomenon with respect to equation VIII it must be assumed that B_1 and B_2 may have opposite signs, and that either B_1/ϵ or B_2 may predominate (44). However, until the nature of B_1 and B_2 are better understood, the facts cannot be interpreted adequately.

SUBSTITUENT CONSTANTS

Hammett (31) originally defined the substituent constant as

$$\sigma \equiv \log (k/k_o) \qquad \text{(IX)}$$

where K and K^o were the dissociation constants of the substituted and unsubstituted benzoic acids respectively. The equation implies that the reaction constant for this series of acids is unity, and that sigma for benzoic acid is zero. On this basis it is possible to calculate sigma values for the other substituent groups. However, Hammett later discovered that these sigma values would not hold for the derivatives of phenol and aniline. This was particularly shown to be true for the case of the para nitro derivative. Hammett also suggested that special substituent constants might be necessary for substituents such as CN, COOH, and CHO. Roberts and McElhill(54) confirmed this to be the case for the para-cyano derivative. This apparently appears to hold true for most of the electron attracting groups in the para position. As a matter of fact, cases have been reported (31, 49) where it is necessary to have two distinct sigma values in order that the equation would describe the data.

Jaffe (49) has suggested that the substituent constant be redefined as "the value of sigma which best fits the entire body of experimental data". However, Jaffe himself has pointed out the shortcomings of his redefinition:

"....it makes substituent constants dependent on the body of knowledge available at the time of their evaluation, and implies that they should be revised at frequent intervals. Moreover, the evaluation of such substituent constants requires the formidable task of fitting the entire available data by some suitable statistical procedure. Such computation is not feasible without the use of electronic computing equipment".

McDaniel and Brown (55) have made note of this and have proposed that there should be a return to the use of dissociation constants as a basis for evaluating Hammett's sigma functions.

As it was brought out earlier in this discussion, the use of thermodynamic data provides little information as to the energy of activation of substituted benzoic acids, consequently, it would be of little practical value to discuss the substituent constants in this light. It would probably be more fruitful to look at them in the light of Hammett's suggestion; their effect on the electron densities at the reaction site. This approach was confirmed by Meal (56) who studied the effects of F^{19} and Cl^{35}, on the electron density in side chains by means of nuclear magnetic resonance.

Using the assumption that sigma is proportional to the change in electron density induced by the substituent, Jaffe (57, 58) has attempted to correlate sigma values with electron densities calculated by molecular orbital theory. Although the calculations are admittedly crude(due to difficulty in choosing the correct parameters) he has found that they can be used to predict roughly the magnitude of the substituent constants.

Additional work (59, 60) in this field definitely indicates that both inductive and resonant effects must be considered in looking for a basis for the theoretical predication of sigma values.

Since it has been shown by Jaffe (50) that at least 42, 000 rate and equilibrium reactions can be related to the Hammett equation(VIII) it may be considered that the Hammett equation is generally applicable to most reaction series. Therefore, we can say that the substituent constants must be essentially independent of the nature of the reacting side chain except in those cases previously noted.

This duality of substituent constants for electron-attracting groups apparently is related to a resonance phenomenon such as illustrated:

III IV

The substituent constants will then indicate the effect of R on the functional group Y depending, of course, on the predominance of III. Naturally, the importance of the resonant structure will depend on the type of side chain present.

Jaffe (49) has reported this to be the case where Y=SH. Although the sulfhydral group is similar to the hydroxyl group it apparently does not resonate as strongly with the benzene ring.

This duality of values for sigma may be interpreted as being due to a difference in the resonance stabilization between the initial and

product states. However, due to the difficulty of determining the energies of activation. little can be said about the actual extent of these differences.

Electronic theory in the English School(52) interprets the total effects of substituents in terms of the following effects:

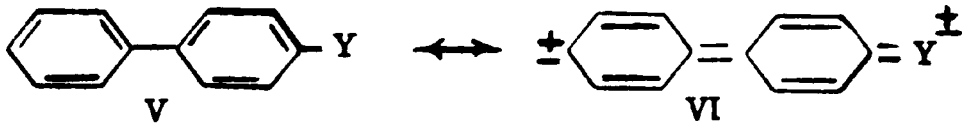
1. inductive
2. mesomeric
3. inductomeric
4. electromeric

The inductive effect, symbolized by I_s, signifies a "polarization effect" characteristic of a molecule in equilibrium with its environment. This effect is generally believed to be due to changes in the screening effect, with its magnitude related to the electron-attracting powers of the atom or group in question.

The mesomeric effect, **M**, is considered to represent the true state of a molecule if it is possible to write two or more different electronic structures for the molecule without changing the arrangement of the atoms or exceeding the number of electrons which can exist in any one atom.

The inductomeric and electromeric effects may be combined into a overall polarizability of effect, which in light of the possibility of dual substituent constituents, is the same as discussing the substituent groups in terms of their polarizability.

Polarizability effects play an important role in the behavior of meta and para substituted compounds. In the case of meta and para phenyl substituted benzene rings they result in a wide deviation from Hammett's equation. The reason is apparently that the following resonance equilibrium takes place:



V VI

Since only para substituted compounds are involved in electromeric effects, the substituent can either attract or repel electrons. The meta phenyl group has a large polarizability due to its inductomeric effect, which may operate in either direction. This may also explain why frequently rate and equilibrium constants for unsubstituted compounds deviate from a straight line. Jaffe (49) gives this as reason why the para fluoro and meta methoxy group sometimes appear to behave as electron donors, and the meta methyl group as an electron acceptor.

Of course, it must be realized that the substituent groups may interact with the solvent molecules. If this solvent interaction were the same for all substituents, it would not affect the substituent constants. However, this is not the case and substituent constants will not be independent of solvent effects in those cases where hydrogen bonding or other types of attractive forces come into play. This has

been found to be the case for the para-alkyl groups. Kloosterziel and Backer (61) have found that the sigma value for the para-alkyl substituted benzoic acid derivatives gradually become more positive in solvents of decreasing dielectric strength. In the case of the para-methyl substituent in n-hexane they reported a sigma value of —.08 and concluded that the sigma value depends upon the medium. This deviation from Hammett's value for the para-methyl group of —.17 is explained on the basis of hyperconjugation of the methyl group, since they found that in the series of para-methyl, para-ethyl, para-isopropyl, and para-tertiary butyl sigma gradually became more negative as the degree of hyperconjugation decreased. This particular interpretation appears to be open to question.

Koshi and Hammond (63) suggested that this anomalous behavior of the para-methyl derivatives was due to a decrease in the entropy of the molecule. They based this opinion on a study of the rate of hydrolysis for a series of benzyl tosylate derivatives.

Taft (35) makes note of the fact that since the Hammett equation (VII) holds, regardless of the resonance of the functional group with the benzene ring in the reactant, transition, or product states, the polar effect of the substituent must be independent of the resonance of the functional group with the ring. If this is the case, only polar effects will vary with the substituent. However, when resonance

is possible between the substituent and the functional group, the substitutent effect will then be a combination of both polar and resonance effects. As mentioned previously, these resonance effects are one of the principle causes for the duality of sigma values, or the failure of the Hammett equation.

Resonance effects apparently contribute a constant value to the total substituent effect, and Taft (35) has proposed an equation to correlate resonance effects with sigma and rho.

$$\log {}^{k}/_{k_o} = \sigma\rho + \gamma \qquad (X)$$

where γ is the resonance effect, and $\sigma\rho$ the polar effect. Taft then suggests that γ can be evaluated by:

"....finding the vertical displacement of the experimental point for the resonating para substituent from the correlation line at the position of the polar sigma values gives the value of γ".

Taft has extended his work to the aliphatic carboxylic acid series in an effort to separate the polar, steric, and resonance effects of various substituent groups on the molecule. By expanding previous work (64) he has proposed the following equation for calculating the polar effects of substituents on the rates of normal hydrolysis of carboxylic esters:

$$\sigma^* = \frac{1}{2.48} \left[\log \left({}^{k}/_{k_o}\right)_B - \log \left({}^{k}/_{k_o}\right)_A \right] \qquad (XI)$$

where σ^* is a substituent constant dependent only upon the net polar effect of the substituent, the standard acid being where $R=CH_3$. Taft states that σ^* is analogous to Hammett's σ. The constant 1/2.48 was introduced in order to put polar effects obtained from equation XI on the same scale as Hammett's sigma.

As we have seen, solvent effects play an important role in the behavior of acids in solution. McRae (66) has investigated the effects of dipole interactions on frequency shifts in solution, and he has derived a general expression involving contributions of the solvent from dispersive and static dipole interactions. Equation (XII) is a generalized form of McRae's equation which was derived by perturabation theory

$$R = B\left[\frac{n_D^2 - 1}{2n_D^2 + 1}\right] + C\left[\frac{(D - 1)}{(D + 2)} - \frac{(n_D^2 - 1)}{(n_D^2 + 2)}\right] \qquad \text{(XII)}$$

where B and C are constants and n_D represents the refractive index of the solvent and D the dielectric constant.

It was felt that since this equation is roughly similar to that for the total molar polarizability of a solvent which was found to be inadequate in many cases to describe the phenomenon occurring in solution, it would be more exact in relating the solvent behavior with intrinsic acidity of an acid in solution.

APPARATUS

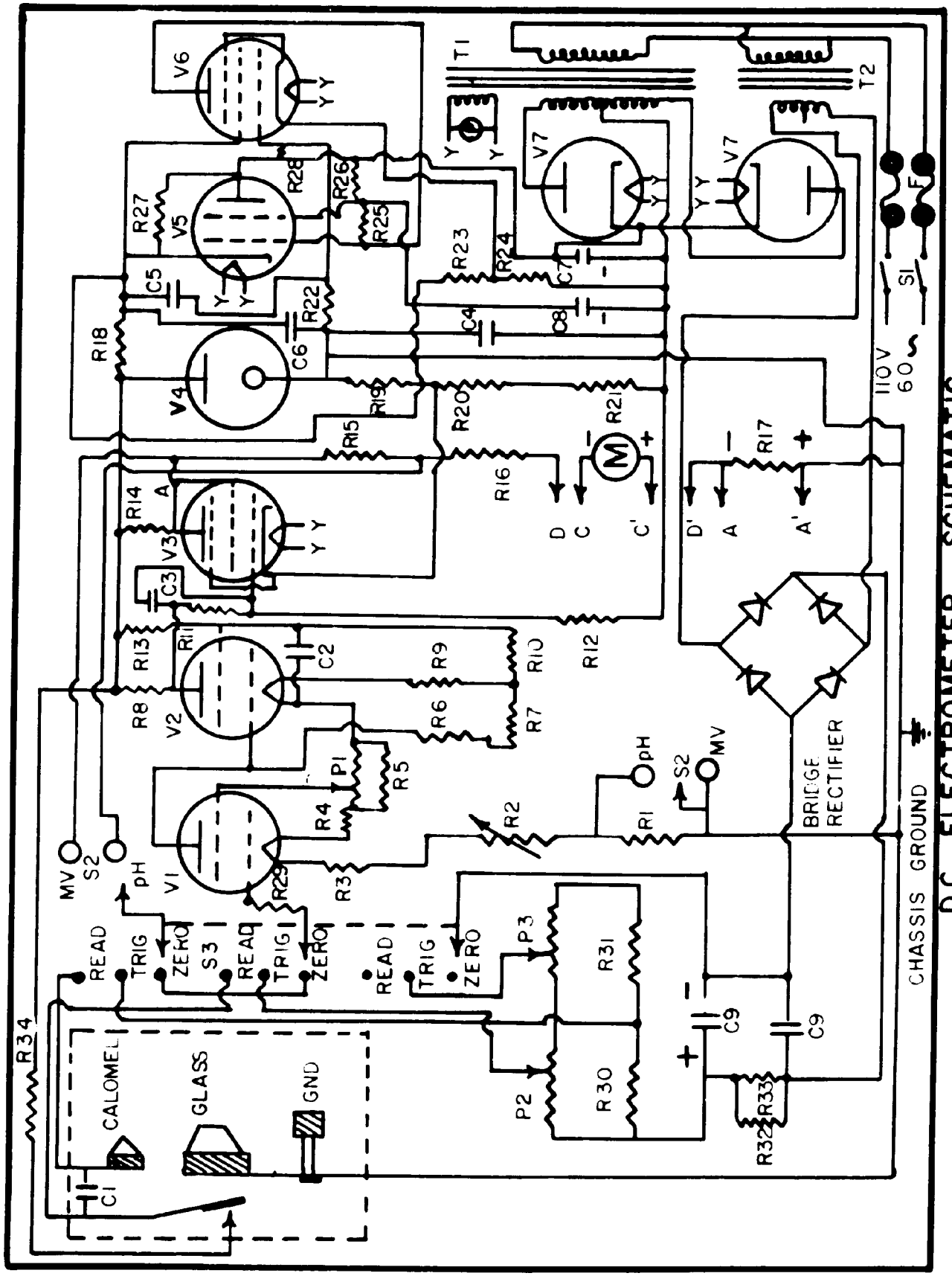
D. C. Electrometer

The use of a high impedance glass indicating electrode and a calomel reference electrode necessitated that the potential difference in solution be magnified by means of a suitable electronic apparatus.

The device employed in this investigation was a D. C. electrometer acquired from an apparatus designed by Professor E. J. Serfass (67). This apparatus was originally designed for aqueous titrations in the range of 2 to 12 pH units or from 0 to 1000 millivolts. However, since the most desirable range for non-aqueous titrations is from 0 to ± 1500 millivolts, the circuit was modified to meet these requirements. The output of the circuit was then checked against a calibrated Leeds and Northrup potentiometer. The average deviation of a single reading was found to vary by 1.2 millivolts over the entire ± 1500 millivolt range.

The schematic of the modified amplifier is shown in Figure 1. A parts list is found in the appendix. The following is a description of the design, the pertinent details of which were acquired from a report by Professor E. J. Serfass (67):

The electrometer incorporates a regulated power supply, with an inverse feedback, which powers a three stage direct coupled electrometer input, inverse feedback D. C. amplifier. This is similar in



D.C. ELECTROMETER SCHEMATIC
FIGURE 1

design to the model "H2" Beckman pH meter.

A three position switch (S-3) allows the amplifier to be adjusted for zero input by controlling potentiometer(P-1). The second position, "Read", of (S-3) is used during actual operation. The third position originally designed for a "trigger circuit" was not employed in this investigation. Switch (S-4) was used only in the M. V. (millivolt) position.

Switching Panel

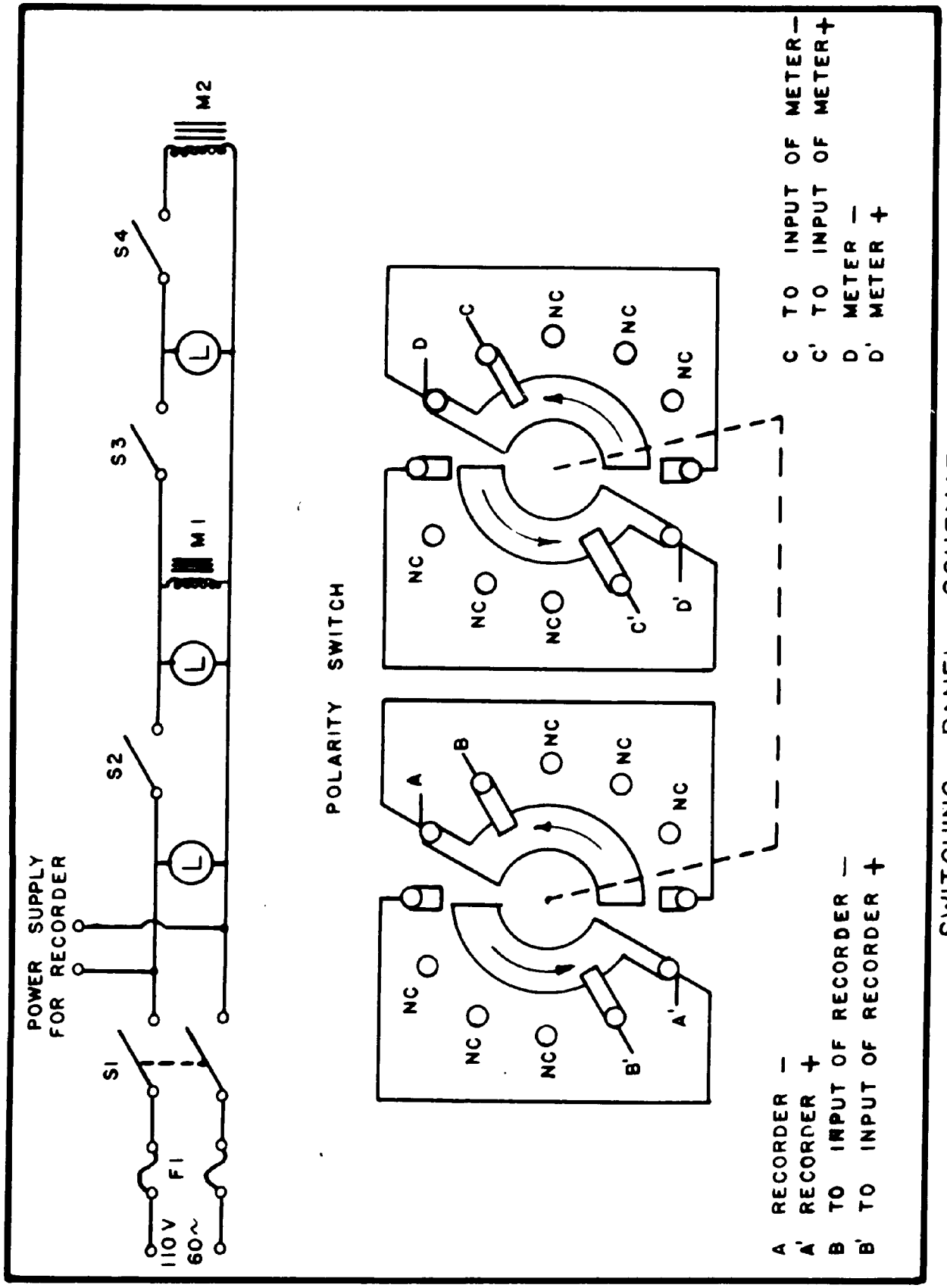
The output of the apparatus was fed into a switching panel(Figure 2), whose connectors led to a 4 pole, 5 position Steatite selector switch. This switch also connected the direct reading milliammeter with a high speed , low impedance , Brown recorder. This switch allowed both recorder and milliammeter to read a full range of $\pm$ 1500 millivolts.

The switches were arranged so that when the chart drive switch (S-2) was open the syringe drive would not operate. This allowed the chart drive motor (M-1) and the syringe motor (M-2) to be synchronized by closing one switch (S-2). The power for the entire switching panel was fed through one switch (S-1).

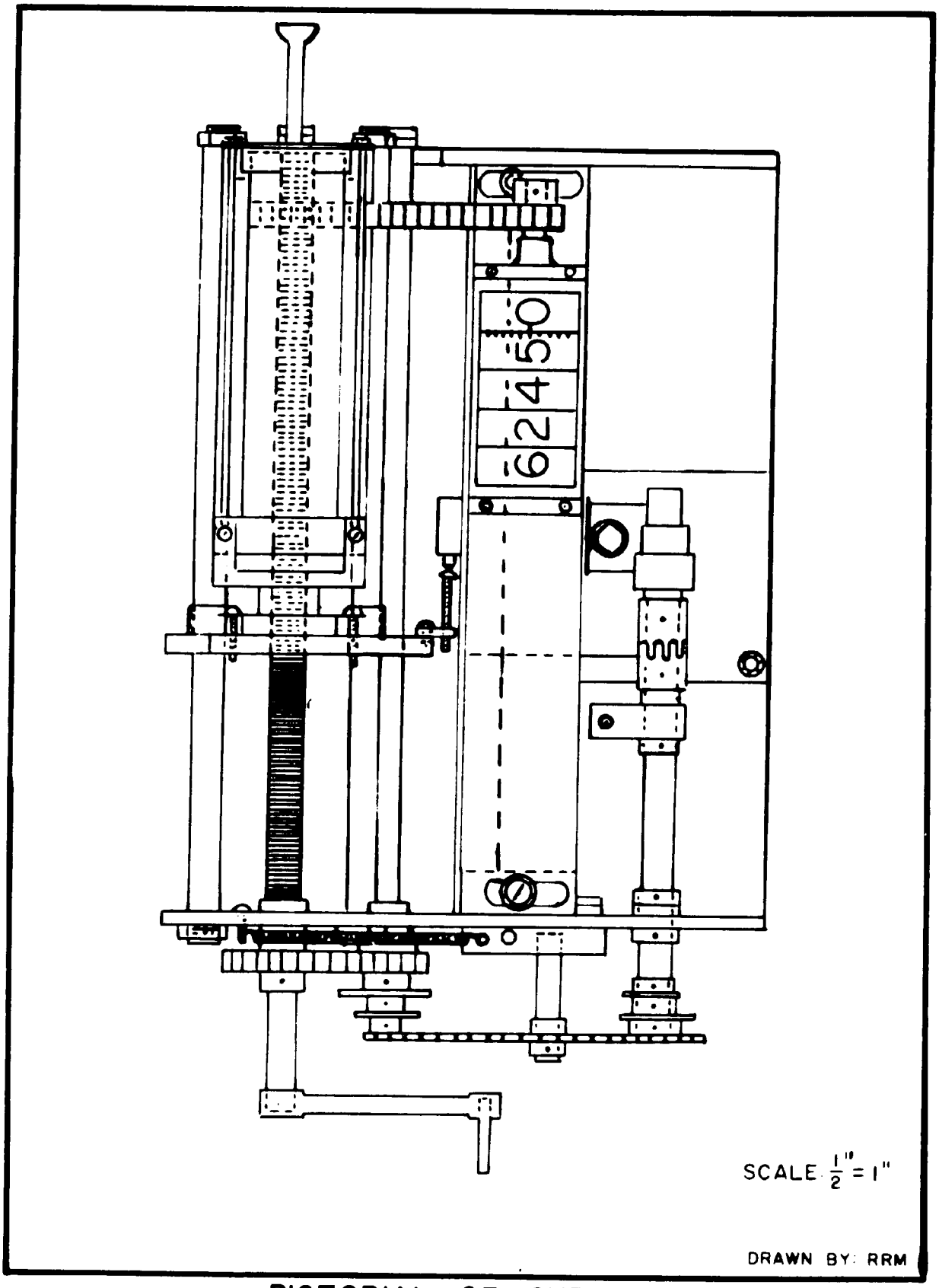
Syringe Drive

The syringe drive (Fig. 3) was based on a design by Lingane (68), modified to improve operation.

The drive mechanism was built on a framework of 3/16 inch steel



SWITCHING PANEL SCHEMATIC
FIGURE 2



PICTORIAL OF SYRINGE DRIVE

FIGURE 3

plate, to insure rigidity and stability. The brass platform for the syringe plunger was mounted on a 20 pitch 7/16 inch diameter lead screw turned down at the end to accept a 40 tooth drive gear. The guide bars were made from 3/8 inch steel rod stock. The drive gear was meshed with a 24 tooth spur gear mounted on a 3/8 inch shaft, step-cut to hold three sprocket gears of a size to give an approximate delivery rate of 0.5, 1, or 2 milliliters per minute. These sprocket gears were connected to their opposite number mounted on a step-cut 3/8 inch shaft. This shaft was coupled to a Bodine synchronous motor through a multi-jaw gear. These gears were connected by means of a 1/4 inch single pitch rollerless chain. A movable idler gear for the chain drive prevented slippage and facilitated removal of the chain.

The lead screw mounted a 20 tooth chain sprocket gear, connected to a 4 digit counter by means of a ladder chain. This mechanism was used for calibrating the rate of delivery, which was found to be 0.48, 0.95, and 1.90 milliliters per minute.

The syringe holder with adjustable slide bars firmly mounted on the steel framework was comprised of a slotted collar for the barrel end and a removal flange bar for the flange end of the syringe.

An adjustable screw mounted on the plunger platform engaged a normally closed micro-switch (S-4)(Figure 2), which stopped the drive motor when the syringe was empty.

The syringe was connected to a 1000 milliliter reservoir (Fig. 4), by means of a three-way stopcock. This allowed the syringe to be filled without disconnecting it from the drive. The use of the ball and socket joints facilitated the removal and cleaning of the delivery tubes. The reservoir was fitted with a drying tube containing Ascarite and $Mg(ClO_4)_2$ to increase the stability of the titrant.

Syringe

The syringe was constructed from a regular 50 milliliter hypodermic syringe by replacing the tip with a standard-taper 12/5 female ball joint, joined to the syringe barrel through a graded seal of uranium glass. The plunger was filled with lead shot for increased drive stability.

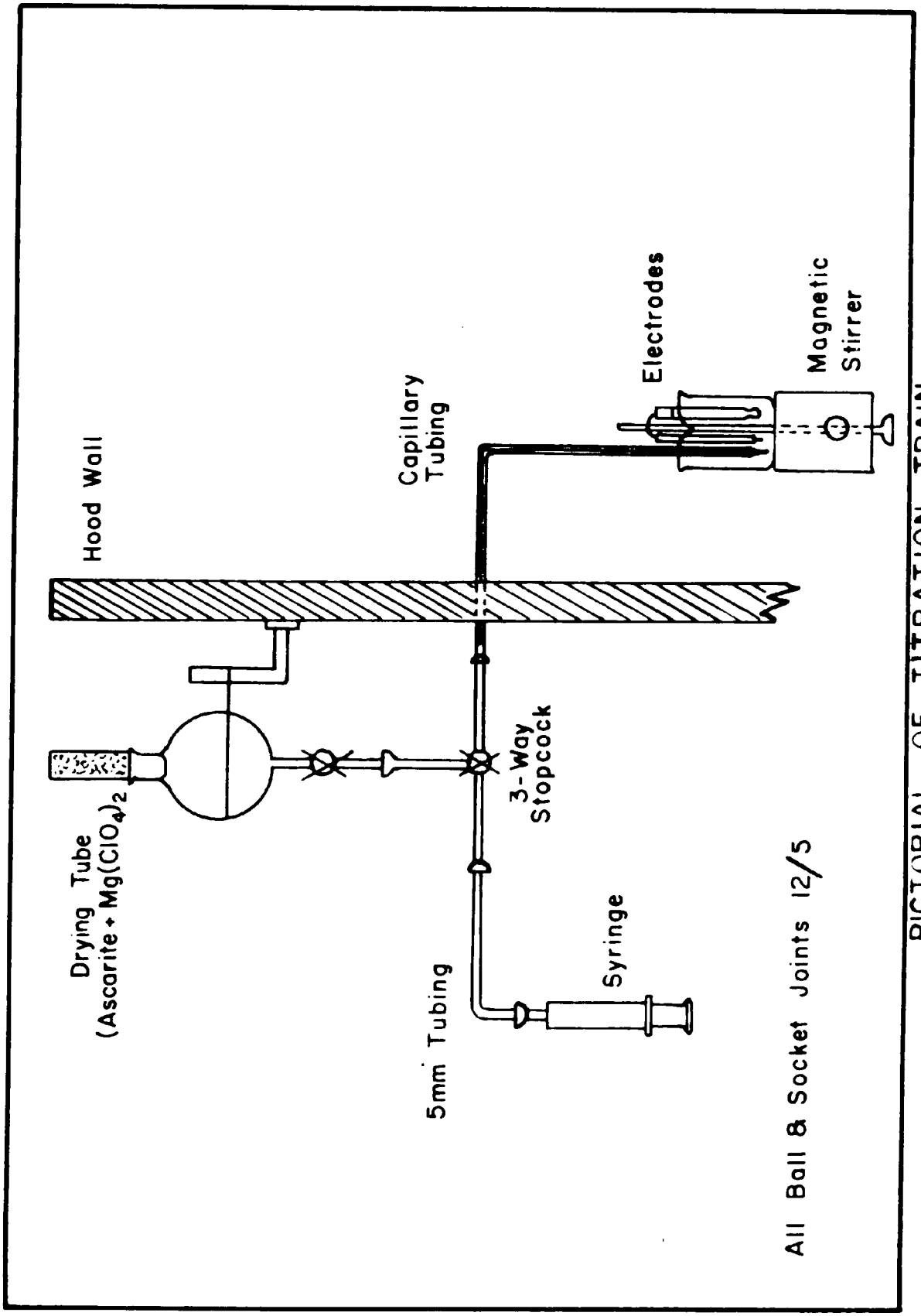
The syringe, which was mounted in a vertical position to facilitate the removal of air bubbles, was filled by removing the drive chain and turning the handle attached to the lead screw.

The syringe drive and micro-switch (S-4) were connected to the switching panel by means of a single 6 foot cable with a series 202 plug at each end. The syringe drive was grounded to prevent A. C. pick-up by the electrodes.

A parts list is included in the appendix.

Recorder

The chart speed was adjusted by installing the proper gears so that it would travel at the rate of one inch per minute; in this manner

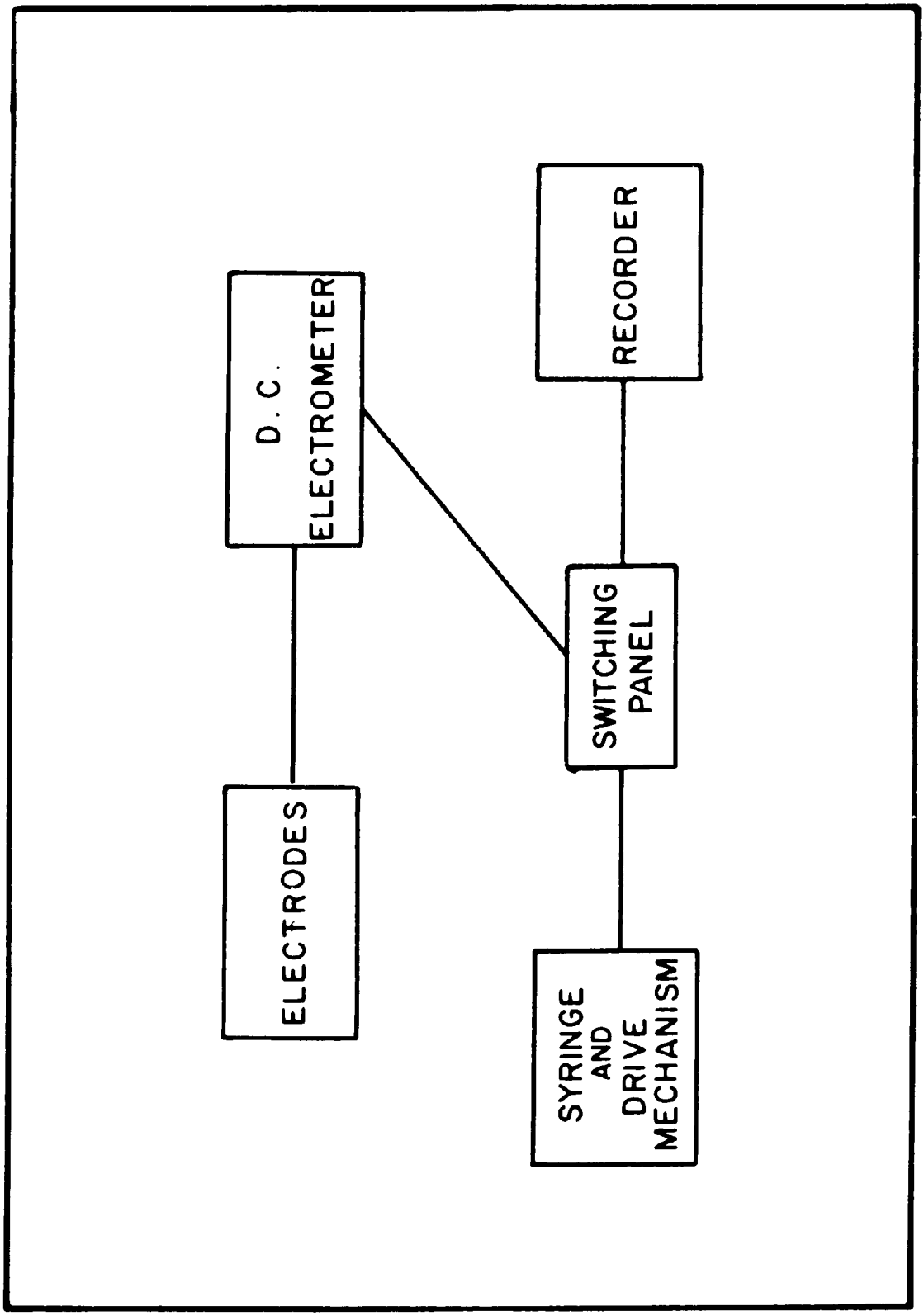


PICTORIAL OF TITRATION TRAIN
FIGURE 4

the quantity of titrant delivered was directly related to the calibrations on the chart paper. The chart paper was calibrated in one inch squares with ten sub-divisions to the inch.

The original recorder filament and chart drive switches were by-passed and wired directly to the switching panel through switches (S-1) and(S-2) respectively. In this manner, as mentioned previously, the chart drive switch was placed in series with the motor of the syringe drive, consequently, the syringe could not be turned on without first closing the chart drive switch.

A block diagram of the entire apparatus is shown in Figure 5.



BLOCK DIAGRAM OF APPARATUS
FIGURE 5

EXPERIMENTAL

An essential factor for the success of any potentiometric titration is the presence of a sufficiently steep potential rise in the titration curve at the equivalence point.

In order to be able to predict whether the titration of a certain acid or mixture of acids is feasible, and if so, to choose the most suitable solvent, one must know the relative positions of the half neutralization potentials (HNP) of these acids and the limiting potentials of the available solvents.

These potentials are determined by a large number of factors, and although the effect of each of these factors is known, the correlations, the interactions and their quantitative effect on the potentials has not been investigated to the extent where a suitable explanation of their behavior is possible.

The major factors which influence the HNP of an acid in a particular solvent are:

1. acidity or basicity of the solvent medium
2. intrinsic acidity of the titrated acid
3. tendency of the ions involved in the titration towards the formation of extraordinary stable complexes or insoluble salts.
4. liquid junction potentials occuring at the electrode boundaries

5. dielectric properties of the solvent medium

The acidity or basicity of the solvent medium determines the range of potentials which can be measured, since the limits of acidity and basicity are fixed by the acidity of the solvated proton (SH_2^+) and the basicity of the solvent anion (S^-), formed by the reaction of the dissolved acid (HA) with the solvent (SH).

$$HA + SH \rightleftharpoons A^- + SH_2^+ \quad (1)$$

$$B + SH \rightleftharpoons BH^+ + S^- \quad (2)$$

Thus, all acids above a certain strength will react with the solvent to an extent where the acidity is determined by the acidic nature of the SH_2^+ ion and the concentration of the dissolved acid. In such cases the acids will appear to have the same strength, consequently, the solvent is said to have had a "leveling effect" on the acids in solution.

On the other hand, the influence of the basicity of the solvent medium on the HNP of a dissolved acid would be expected to be small for an acid which is not "leveled". As a first approximation the tendency of the solvent to accept a proton from a dissolved acid will be inversely proportional to the tendency of the acid to donate the proton to the electrode. Thus, the fact that a particular acid is more highly dissociated in a strongly basic solvent, than a weaker acid of similar species, will exert little influence on the HNP of the acid, since the effect of the higher concentration of solvated protons formed in the

strongly basic solvent is cancelled by their lower acidity. This can be shown by means of the following equations:

$$HA + SH \rightleftharpoons A^- + SH_2^+ \quad (3)$$

$$SH_2^+ \rightleftharpoons SH + H^+ \quad (4)$$

In this manner, it can be seen that the "intrinsic acidity" of the titrated acid is a major factor influencing the measured HNP for all acids that are not leveled. Van der Heijde and Dahmen (69) have demonstrated this by showing that the HNP for benzoic acid and its derivatives is virtually independent of concentration over a concentration range of 3 to 30 milliequivalents per liter.

However, the above effect may be partially or completely overshadowed by the effect of the formation of very stable complexes or insoluble salts. If a stable salt, AX, is formed by the titration shown in equation 5 of the HNP of the acid will be determined primarily

$$AH + XOH \longrightarrow AX + H_2O \quad (5)$$

by the stability constant of the salt. If the salt is insoluble in the titration medium, the HNP will be largely determined by its solubility product.

This was shown to be the case when attempts to titrate several substituted benzoic acid derivatives with a mixture of lithium hydroxide in benzene were unsuccessful due to the formation of precipitates.

The electrical potential at any point in a circuit is defined as the work required to bring a unit positive charge from infinity to the

point where the potential is defined. Since this work is not the same on each side of an interface a difference in the potential will occur. The difference of electrical potential at the junction of the electrode and the solution is called a liquid junction potential and is reflected in the measurement of the total potential of the solution as shown in the following equation:

$$E = E_e + E_j \qquad (I)$$

where the e. m. f., E, is the sum of the potential differences at the electrodes, E_e, and the liquid junctions, E_j.

If we assume that the liquid junction potential remains reasonably constant for a given pair of electrodes in the same solution then we can calculate the difference in potential between two acids of the same species. In this manner it was possible to calculate the ΔHNP of a particular acid by using standard acid as a reference. Thus, the Δ HNP's of the acids under study were calculated by means of the following equation:

$$\Delta \text{ HNP} = \text{HNP}_2 - \text{HNP}_1 \qquad (II)$$

where HNP_2 represents the half neutralization potential of the acid under study and HNP_1 the half neutralization potential of the reference acid (benzoic acid).

The influence of the dielectric properties of the solvent medium on the dissociation of acids can be partially shown by examining a form of the Debye-Hückel equation (70). Equation III relates the

effect of changes of dielectric constant in the relationship between the activity coefficient and the ionic strength:

$$-\log f_i^* = \frac{(1.83 \times 10^6)\, z_i^2 \sqrt{\mu d^\circ}}{(\epsilon T)^{3/2}[1 + 50.29 (\epsilon T)^{-1/2} a_i (\mu d^\circ)^{1/2}]} \qquad \text{(III)}$$

a_i = ion-size parameter in Angstroms

d° = solvent density

T = Absolute temperature

z_i = valence of ionic species

ϵ = dielectric of solvent

f_i^* = activity coefficient of ionic species

μ = ionic strength

When a solution containing ions is diluted, work must be done to separate the ions of opposite charge. The above equation reflects the increased coulombic forces in media of lowered dielectric constant. A decrease in dielectric causes the activity coefficient to decrease more rapidly with increasing ionic strength than it does at higher values of the dielectric constant. The activity coefficient f_i^* expresses the departure from ideal behavior, and it becomes unity when a solution of ions is diluted without limit.

The primary effect of a decrease in the dielectric constant is to increase the attractive forces between ions of unlike charge. If opposite charged ions are created from neutral molecules in the dissociation of an acid as shown by reaction 6, the dissociation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (6)$$

constant will be considerably reduced by a lowering of the dielectric

constant, however, if the dissociation is an isoelectric process of the type

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad (7)$$

changes in dielectric will not have much effect on the point of equilibrium. Van der Heijde and Dahmen (69) have shown this to be the case.

Further investigations in the behavior of acids in some non-aqueous solvents by Streuli and Miron (71) proved that there was a definite relationship between the behavior of acids in water and their behavior in other solvents. With this as a background the present study was undertaken to find other relationships which could be correlated to give a better understanding of the phenomena occurring in solution.

Calibration of Apparatus

The titration apparatus was calibrated incrementally using a volumetric procedure. Table I on the following page shows the relation between the number of revolutions of the lead screw, duration of delivery, and the quantity of titrant delivered. A statistical analysis of these data showed that the within range delivery was not significant at the 95% level.

TABLE I

CALIBRATION OF SYRINGE

	Range			
Run 1	11-20	21-30	31-40	41-50
Revolutions	1695	1054	1096	1132
Duration (sec)	475.8	295.5	307.4	317.6
Milliliters	15.04	9.33	9.75	9.87
Rate (ml./min.	1.89	1.89	1.90	1.86
Run 2				
Revolutions	1029	1078	1100	1177
Duration (sec.)	288.6	302	308.4	330.5
Milliliters	9.20	9.52	9.78	10.41
Rate (ml./min.)	1.91	1.89	1.90	1.89
Run 3				
Revolutions	1078	1036	1071	1225
Duration (sec.)	302.1	290.2	300.3	343.8
Milliliters	9.60	9.20	9.50	10.81
Rate (ml./min.)	1.90	1.90	1.90	1.89

The value used was 1.90 milliliters per minute. Additional calibration showed that the other gear positions were .48 and .95 ml./min. respectively.

Experimental Procedure

The acids studied were in most cases Eastman Kodak White Label Grade. Table I shows the uncorrected melting points versus those recorded in the literature.

TABLE II

COMPARISON OF MELTING POINTS FOR COMPOUNDS INVESTIGATED

Compound	Melting Point (Literature)(72) °C	Melting Point (Found) °C
1. benzoic acid	122.4	121-122
2. m-chlorobenzoic acid	156-158	153.5-154
3. p-chlorobenzoic acid	240-242	239-240
4. m-bromobenzoic acid	156-158	152-153.5
5. p-bromobenzoic acid	256-258	254-256
6. m-iodobenzoic acid	185-187	187.5-188
7. p-iodobenzoic acid	269-270	267-269
8. m-aminobenzoic acid	172-173	169.8-172
9. p-aminobenzoic acid	188d	186d
10. m-methylbenzoic acid	109-112	109-111
11. p-methylbenzoic acid	178.5-180	180-181.5
12. m-nitrobenzoic acid	141-142	140.5-142
13. p-nitrobenzoic acid	240-242	239-240
14. m-methoxybenzoic acid	106-107.5	106-107

TABLE II - Continued

Compound	Melting Point (Literature) °C	Melting Point (Found) °C
15. p-methoxybenzoic acid	184-186	183.5-184.5
16. p-ethoxybenzoic acid	196-198	197-197.8
17. p-isopropylbenzoic acid	115-117	115-117
18. phenol	40.9	40-41
19. m-chlorophenol	32-33	Liq. at R. T.
20. p-chlorophenol	41-43	41-42
21. m-nitrophenol	96-97	94-95
22. p-nitrophenol	114	113-113.5
23. p-bromophenol	63.5	63-64

The solvents were obtained from various sources and were dried and redistilled as shown in Table II.

TABLE III

PURIFICATION OF SOLVENTS

Solvent	Source	Dried	B P. Range Collected °C
1. Pyridine	Baker Chemical	KOH	115-116
2. Acetonitrile	Matheson, Coleman and Bell	Activated Alumina	81-82
3. 4-Methyl-2-Pentanone	Matheson, Coleman and Bell	Anhydrous $MgSO_4$	115-117
4. 2-Nitropropane	Commercial Solvents	Anhydrous $MgSO_4$	118-120
5. o-Nitrotoluene	Eastman Kodak (White Label)	Anhydrous $MgSO_4$	220-221
6. Nitrobenzene	Lehigh Stock	Anhydrous $MgSO_4$	210-211
7. N, N'Dimethyl - formamide	Eastman Kodak (White Label)	Anhydrous $MgSO_4$	80(150mm)
8. Chlorobenzene	Matheson, Coleman and Bell	Activated Alumina	130.5-131.5
9 Bromobenzene	Matheson, Coleman and Bell	Activated Alumina	155-156.5

The requirements for a titrant are

1. a strong base in the titration medium

2. form soluble salts in the titration medium

3. should not effect the functioning of the electrodes

4. stable

The titrant which met the foregoing requirements was prepared from tetrabutyl ammonium iodide (Eastman Kodak White Label) by converting it to the hydroxide by the method suggested by Cundiff and Markunas (73). The excess titrant was stored under nitrogen to insure its long range stability.

In all cases where solubility permitted, 1 milliequivalent of the acid was weighed into a 150 millliliter beaker, and then 100 milliliters of the solvent was pipetted into the beaker.

In solvents of lower dielectric strength such as chlorobenzene and bromobenzene 0.5 milliequivalents were used. In some cases in these solvents it was necessary to use saturated solutions because of the low solubility. The solution was allowed to stir for periods ranging from 1 - 3 hours and then the excess acid was filtered and the volume brought to 100 milliliters. Generally, enough acid remained in solution to produce a suitable titration curve.

A Leeds and Northrup standard calomel electrode was modified by replacing the saturated aqueous KCl with a saturated methanol solution of KCl as described by Cundiff and Markunas (73). The potential of this electrode differed by .042 volts from the unmodified S. C. E. without taking into consideration the differences in the liquid junction potential between the two electrodes.

A Beckman general purpose glass indicating electrode was also

employed.

The following procedure was followed for the actual titration:

1. the amplifier was allowed to stabilize for one hour.
2. one milliequivalent of the acid was weighed in a 150 milliliter beaker, and then 100 milliliters of solvent were pipetted into the beaker. The mixture was allowed to stir until solution was complete, or until it was certain that the solution was saturated. The excess acid was filtered and the solution brought to a total volume of 100 milliliters.
3. the syringe was filled with titrant from the reservoir.
4. the syringe drive switch was turned on and the beaker placed on the magnetic stirrer.
5. the recorder was zeroed and the switch turned to the "Read" position.
6. the chart drive switch was turned on to start the titration.
7. after the titration the electrodes were washed with absolute methanol and wiped dry with tissue.

All solutions, reagents, and titrant were kept at constant temperature controlled at 22°C.

None of the solutions was protected from carbon dioxide, however, no perceptible titration blank for the solvents was noted since the solutions were generally titrated within ten minutes after they were prepared.

The titration curves were recorded automatically and the HNP was determined by finding the total number of milliliters to the equivalence point and then dividing this value by two. The potential equivalent to this value was determined from the titration curve and designated as the HNP for the acid.

Experimental Results

Because of the possibility of day to day shifts in the liquid junction potential, all the curves have been normalized against benzoic acid as a reference standard. Thus, the curves are in the correct relative relation to one another. The benzoic acid standard samples were run intermittently during the course of the titration and the average HNP value was used. It was found that a single determination rarely varied by more than $\pm$ 10 millivolts from the mean.

The results of these titrations are found in the following tables and graphs.

TABLE IV

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN PYRIDINE AND WATER

Number	Acid	Δ HNP	pKa (Lit.)	pKa (Calcd.)	Δ pKa
1	m-chlorobenzoic	- 49	3.83	3.84	0.01
2	m-bromobenzoic	- 63	3.81	3.73	-0.08
3	m-iodobenzoic	- 44	3.85	3.88	0.03
4	m-aminobenzoic	38	4.82	4.50	-0.32
5	m-methylbenzoic	16	4.27	4.34	0.07
6	m-nitrobenzoic	- 97	3.49	3.48	-0.01
7	m-methoxybenzoic	- 5	4.09	4.17	0.08
8	p-chlorobenzoic	- 25	3.98	4.02	0.04
9	p-bromobenzoic	- 30	3.97	3.98	0.01
10	p-iodobenzoic	- 24	4.02	4.03	0.01
11	p-aminobenzoic	105	4.92	5.00	0.08
12	p-methylbenzoic	3	4.37	4.23	-0.14
13	p-nitrobenzoic	- 92	3.42	3.52	0.10
14	p-methoxybenzoic	45	4.47	4.55	0.08
15	p-ethoxybenzoic	46	4.44	4.56	0.12
16	p-isopropylbenzoic	35	4.35	4.47	0.12
17	benzoic	0	4.20	4.21	0.01

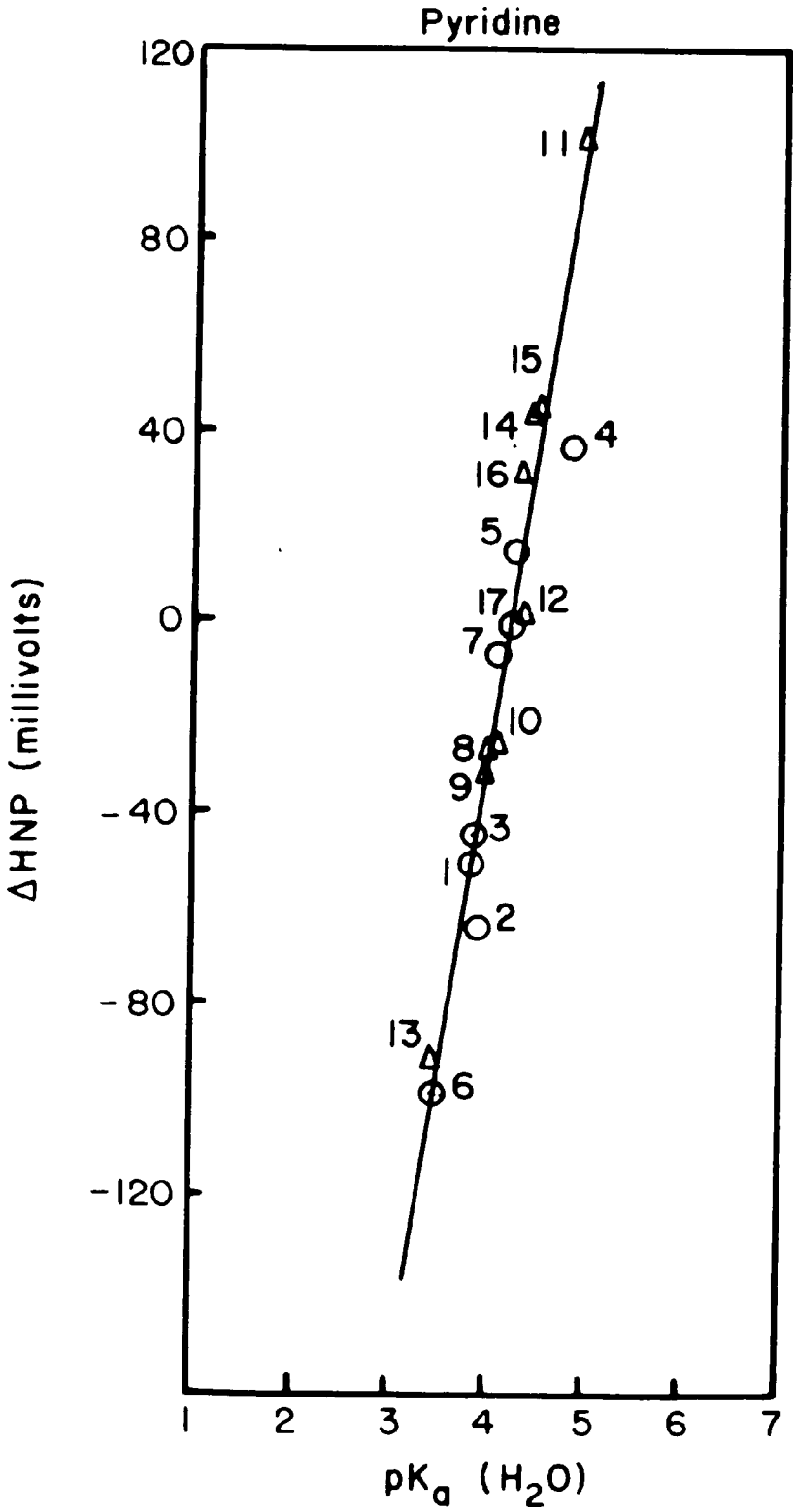

Pyridine
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
15
14
4
16
5
17
12
7
10
8
9
3
1
2
13
6

FIGURE 6

TABLE V

CORRELATION OF Δ HNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN PYRIDINE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	Δσ
1	m-chlorobenzoic	-49	.373	.385	.012
2	m-bromobenzoic	-63	.391	.480	.089
3	m-iodobenzoic	-44	.352	.351	-.001
4	m-aminobenzoic	38	-.160	-.204	-.044
5	m-methylbenzoic	16	-.069	-.055	.014
6	m-nitrobenzoic	-97	.710	.711	.001
7	m-methoxybenzoic	-5	.115	.087	-.028
8	p-chlorobenzoic	-25	.227	.222	-.005
9	p-bromobenzoic	-30	.232	.257	.025
10	p-iodobenzoic	-24	.18	.216	.036
11	p-aminobenzoic	105	-.66	-.658	.002
12	p-methylbenzoic	3	-.170	.033	.203
13	p-nitrobenzoic	-92	.778	.677	-.101
14	p-methoxybenzoic	45	-.268	-.251	.017
15	p-ethoxybenzoic	46	-.240	-.258	-.018
16	p-isopropylbenzoic	35	-.151	-.183	-.032
17	benzoic	0	0	.053	.053

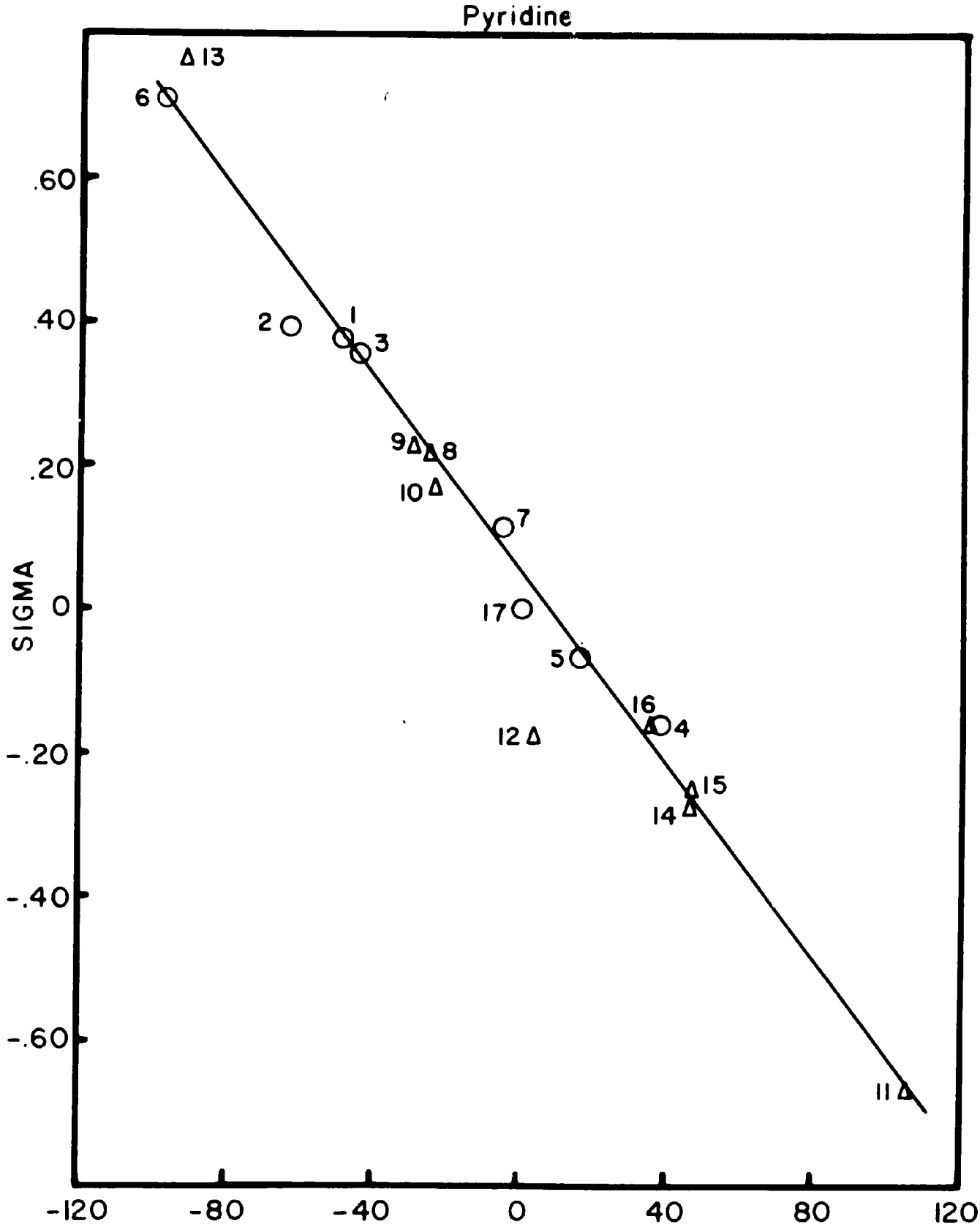

Pyridine
Δ13
6
.60
.40
2
1
3
9Δ
8
.20
10Δ
7
SIGMA
0
17
5
16
4
12Δ
-.20
15
14Δ
-.40
-.60
11Δ
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)

FIGURE 7

TABLE VI

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN ACETONITRILE AND WATER

Number	Acid	ΔHNP	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	m-chlorobenzoic	-54	3.83	3.83	0
2	m-bromobenzoic	-51	3.81	3.85	0.04
3	m-iodobenzoic	-68	3.85	3.74	-0.11
4	m-aminobenzoic	78	4.82	4.66	-0.16
5	m-methylbenzoic	8	4.27	4.22	-0.05
6	m-nitrobenzoic	-105	3.49	3.50	0.01
7	m-methoxybenzoic	9	4.09	4.23	0.14
8	p-chlorobenzoic	-39	3.98	3.92	-0.06
9	p-bromobenzoic	-17	3.97	4.06	0.09
10	p-iodobenzoic	-42	4.02	3.90	-0.12
11	p-aminobenzoic	118	4.92	4.92	0
12	p-methylbenzoic	17	4.37	4.28	-0.09
13	p-nitrobenzoic	-100	3.42	3.53	0.11
14	p-methoxybenzoic	64	4.47	4.58	0.11
15	p-ethoxybenzoic	59	4.44	4.55	0.11
16	p-isopropylbenzoic	42	4.35	4.43	0.08
17	benzoic	0	4.20	4.17	-0.03

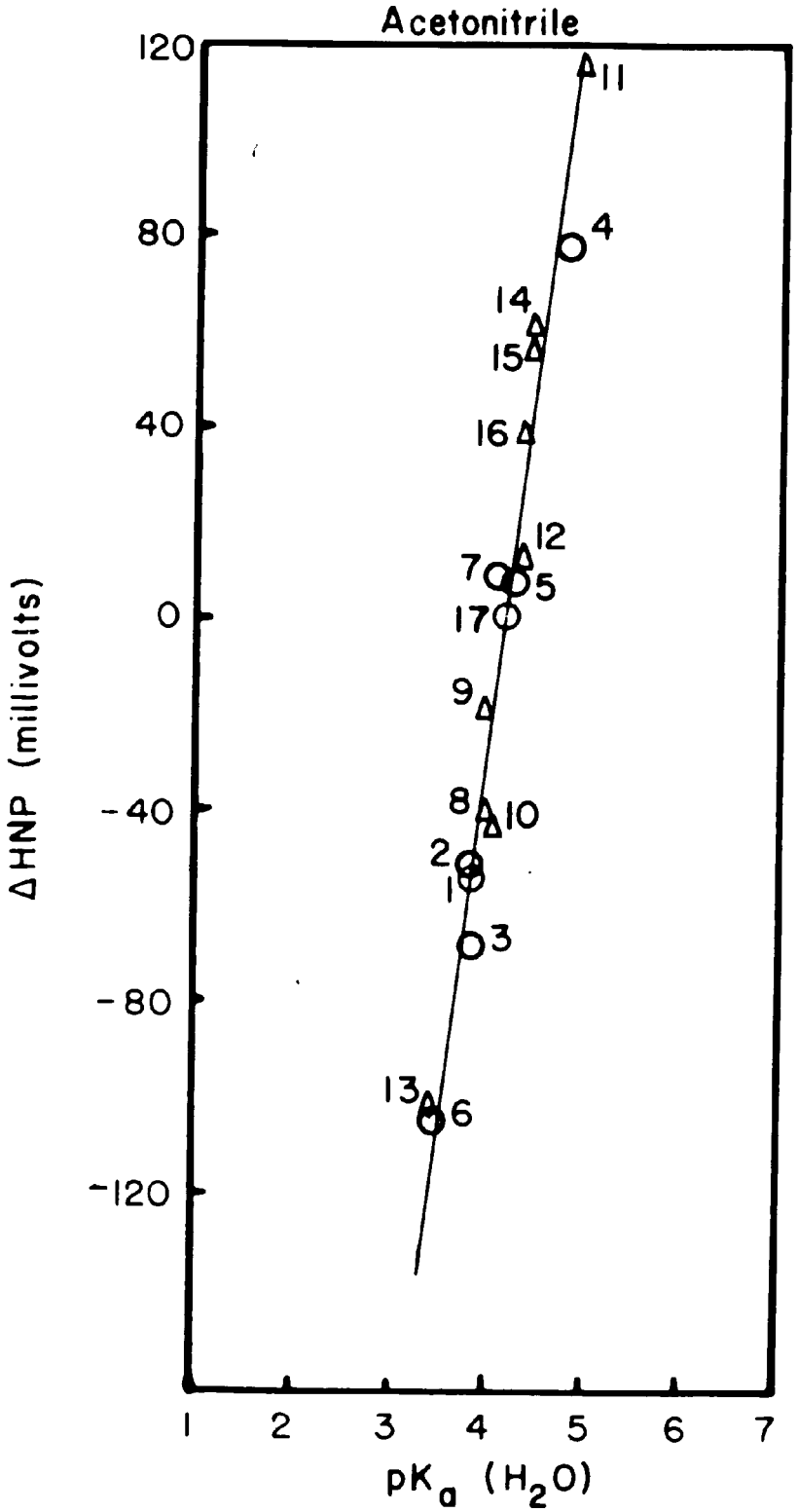

Acetonitrile
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
4
14
15
16
12
7
5
17
9
8
10
2
1
3
13
6

FIGURE 8

TABLE VII

CORRELATION OF Δ HNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN ACETONITRILE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-54	.373	.375	.002
2	m-bromobenzoic	-51	.391	.358	-.033
3	m-iodobenzoic	-68	.352	.454	.102
4	m-aminobenzoic	78	-.160	-.364	-.204
5	m-methylbenzoic	8	-.069	-.028	.041
6	m-nitrobenzoic	-105	.710	.661	-.049
7	m-methoxybenzoic	9	.115	.023	-.092
8	p-chlorobenzoic	-39	.227	.291	.064
9	p-bromobenzoic	-17	.232	.168	-.064
10	p-iodobenzoic	-42	.18	.308	.128
11	p-aminobenzoic	118	-.66	-.588	.072
12	p-methylbenzoic	17	-.170	-.022	.148
13	p-nitrobenzoic	-100	.778	.633	-.145
14	p-methoxybenzoic	64	-.268	-.285	-.017
15	p-ethoxybenzoic	59	-.240	-.257	-.017
16	p-isopropylbenzoic	42	-.151	-.162	-.011
17	benzoic	0	0	.073	.073

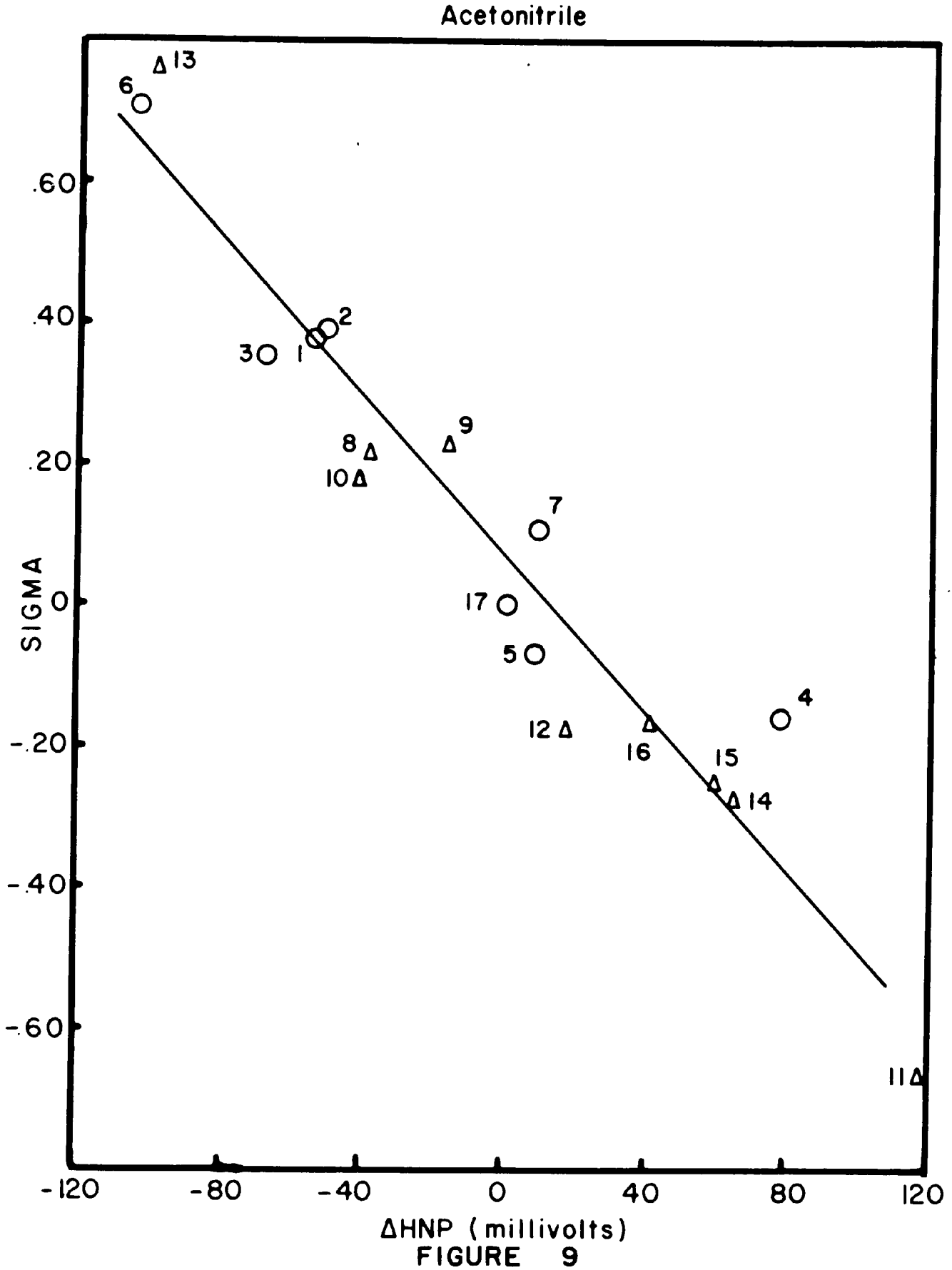

Acetonitrile
SIGMA
.60
.40
.20
0
-.20
-.40
-.60
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)
13
6
2
3
1
8
9
10
7
17
5
4
12
16
15
14
11

FIGURE 9

TABLE VIII

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN 4-METHYL-2-PENTANONE AND WATER

Number	Acid	Δ HNP	pKa (Lit.)	pKa (Calcd.)	Δ pKa
1	m-chlorobenzoic	-42	3.83	3.95	0.12
2	m-bromobenzoic	-55	3.81	3.86	0.05
3	m-iodobenzoic	-60	3.85	3.83	-0.02
4	m-aminobenzoic	26	4.82	4.42	-0.40
5	m-methylbenzoic	9	4.27	4.30	0.03
6	m-nitrobenzoic	-123	3.49	3.39	-0.10
7	m-methoxybenzoic	5	4.09	4.27	0 18
8	p-chlorobenzoic	-53	3.98	3.88	-0.10
9	p-bromobenzoic	-37	3.97	3.99	0.02
10	p-iodobenzoic	-26	4.02	4.06	0.04
11	p-aminobenzoic	107	4.92	4.98	0.06
12	p-methylbenzoic	0	4.37	4.24	-0.13
13	p-nitrobenzoic	-95	3.42	3.59	0.17
14	p-methoxybenzoic	38	4.47	4.50	0.03
15	p-ethoxybenzoic	51	4.44	4.59	0.15
16	p-isopropylbenzoic	25	4.35	4.41	0.06
17	benzoic	0	4.20	4.24	0.04

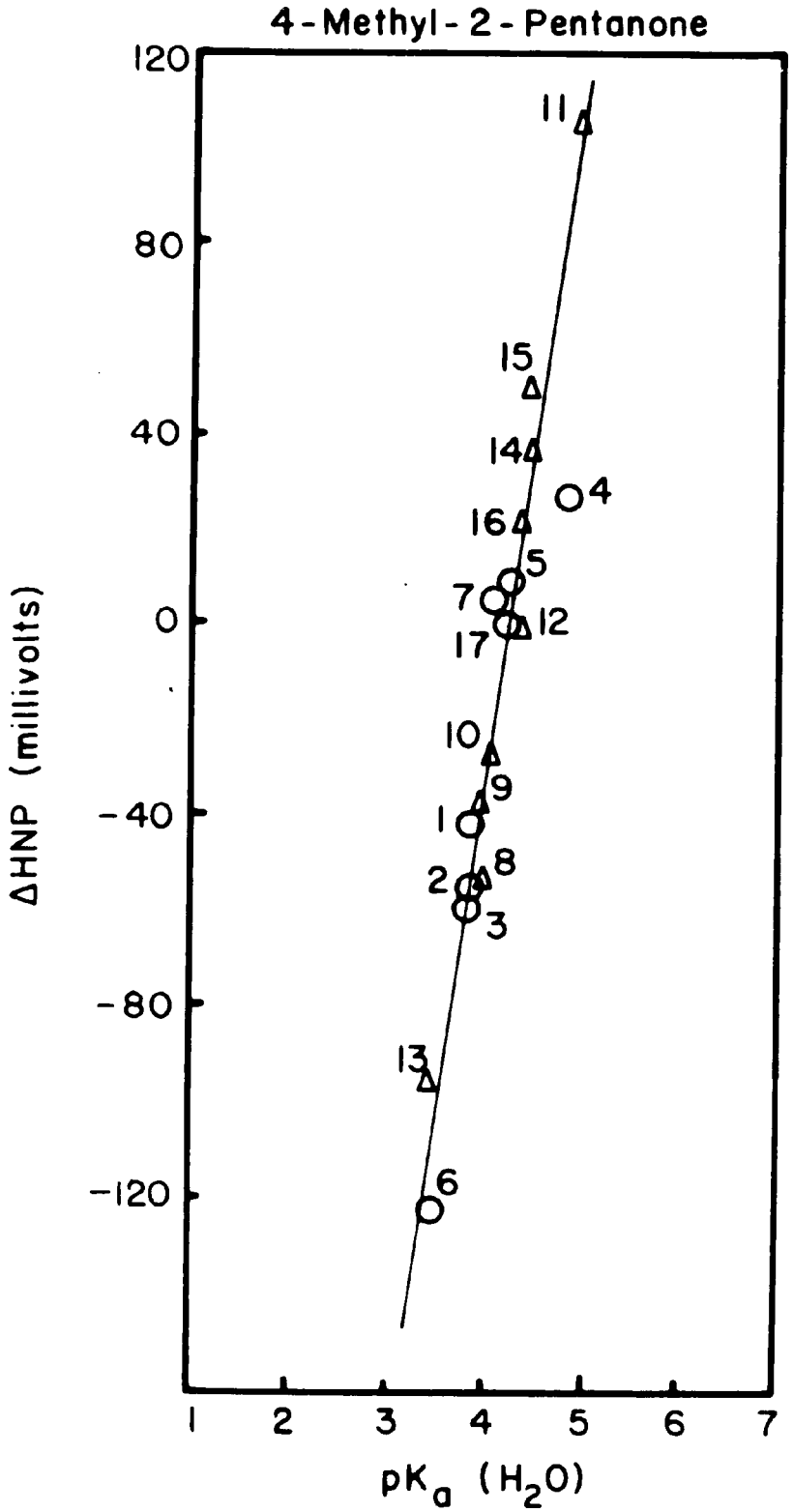

4-Methyl-2-Pentanone
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
15
14
4
16
5
7
12
17
10
9
1
8
2
3
13
6

FIGURE 10

TABLE IX

CORRELATION OF ΔHNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN 4-METHYL-2-PENTANONE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-42	.373	.289	-.084
2	m-bromobenzoic	-55	.391	.370	-.021
3	m-iodobenzoic	-60	.352	.401	.049
4	m-aminobenzoic	26	-.160	-.135	.025
5	m-methylbenzoic	9	-.069	-.029	.040
6	m-nitrobenzoic	-123	.710	.794	.084
7	m-methoxybenzoic	5	.115	.004	-.111
8	p-chlorobenzoic	-53	.227	.357	.130
9	p-bromobenzoic	-37	.232	.257	.025
10	p-iodobenzoic	-26	.18	.189	.009
11	p-aminobenzoic	107	-.66	-.640	.020
12	p-methylbenzoic	0	-.170	.027	.197
13	p-nitrobenzoic	-95	.778	.619	-.159
14	p-methoxybenzoic	38	-.268	-.210	.058
15	p-ethoxybenzoic	51	-.240	-.291	.051
16	p-isopropylbenzoic	25	-.151	-.129	.022
17	benzoic	0	0	.027	.027

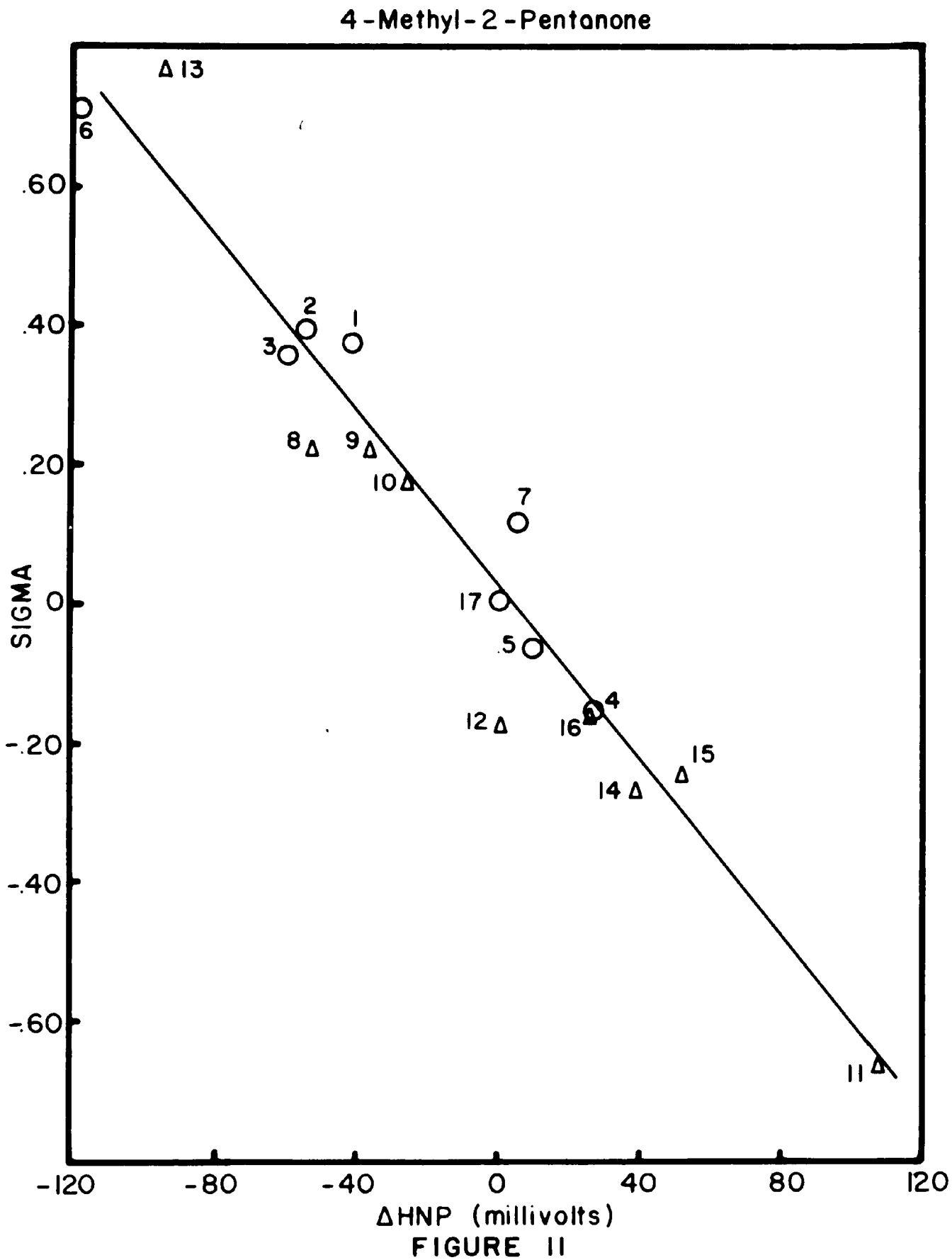

4-Methyl-2-Pentanone
Δ13
6
.60
.40
2
1
3
.20
8Δ
9Δ
10Δ
7
0
SIGMA
17
5
4
12Δ
16Δ
-.20
15
Δ
14Δ
-.40
-.60
11Δ
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)

FIGURE 11

TABLE X

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN 2-NITROPROPANE AND WATER

Number	Acid	Δ HNP	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	m-chlorobenzoic	-49	3.83	3.77	-0.06
2	m-bromobenzoic	-39	3.81	3.84	0.03
3	m-iodobenzoic	-46	3.85	3 79	-0.06
4	m-aminobenzoic	55	4.82	4.51	-0.31
5	m-methylbenzoic	34	4.27	4.36	0.09
6	m-nitrobenzoic	-104	3.49	3.37	-0.12
7	m-methoxybenzoic	21	4.09	4.27	0.18
8	p-chlorobenzoic	-8	3.98	4.06	0.08
9	p-bromobenzoic	4	3.97	4.15	0.18
10	p-iodobenzoic	8	4.02	4.18	0.16
11	p-aminobenzoic	86	4.92	4.74	-0.18
12	p-methylbenzoic	-19	4.37	3.98	-0.39
13	p-nitrobenzoic	-67	3.42	3.64	0.22
14	p-methoxybenzoic	61	4.47	4.55	0.08
15	p-ethoxybenzoic	64	4.44	4.58	0.14
16	p-isopropylbenzoic	30	4.35	4.34	-0.01
17	benzoic	0	4.20	4.12	-0.08

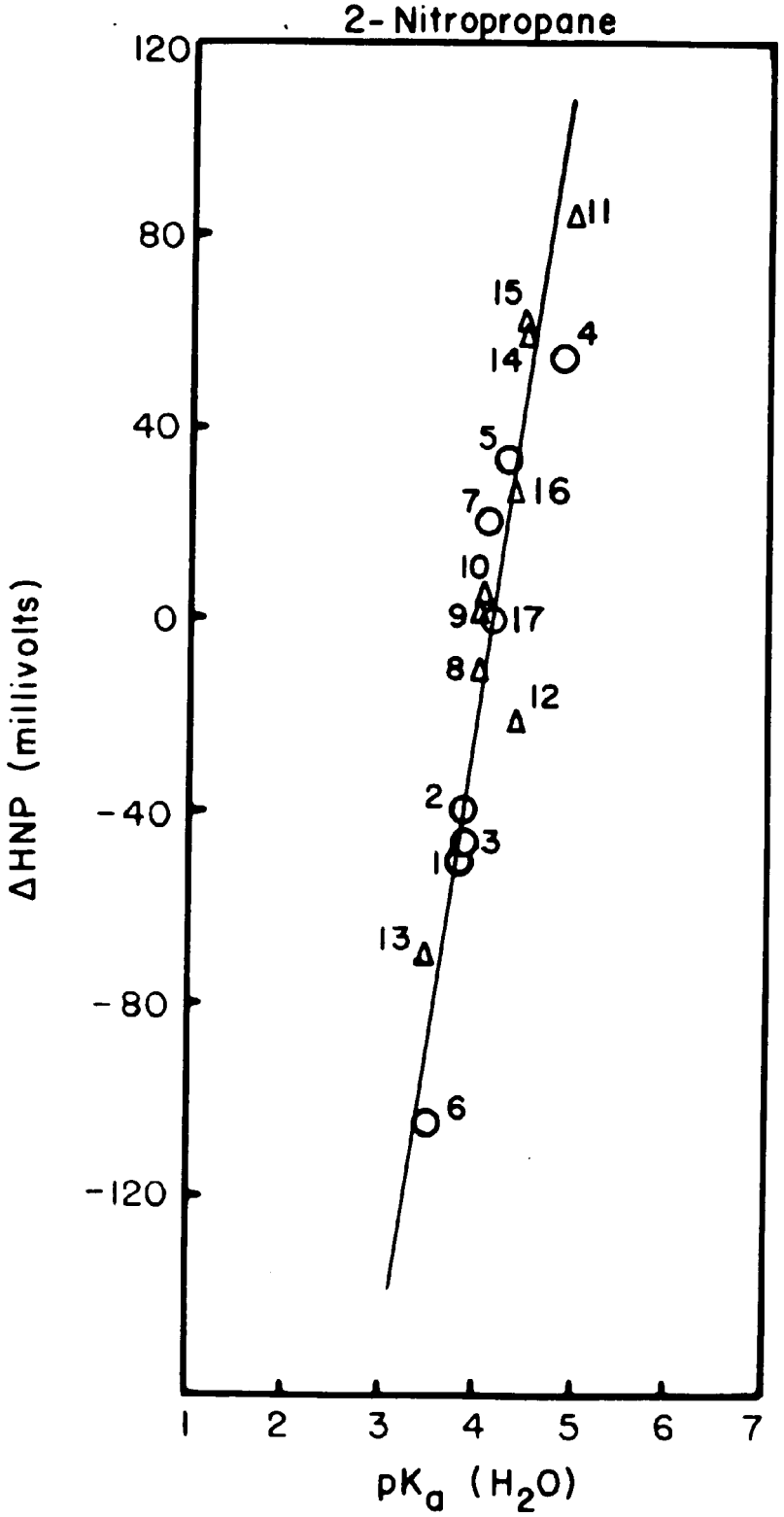

2-Nitropropane
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pKa (H2O)
Δ11
15
14
4
5
Δ16
7
10
9
17
8
12
2
3
1
13
6

FIGURE 12

TABLE XI

CORRELATION OF Δ HNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN 2-NITROPROPANE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-49	.373	.428	.055
2	m-bromobenzoic	-39	.391	.373	-.018
3	m-iodobenzoic	-46	.352	.412	.060
4	m-aminobenzoic	55	-.160	-.148	.012
5	m-methylbenzoic	34	-.069	-.031	.038
6	m-nitrobenzoic	-104	.710	.734	.024
7	m-methoxybenzoic	21	.115	.041	-.074
8	p-chlorobenzoic	-8	.227	.201	-.026
9	p-bromobenzoic	4	.232	.135	-.097
10	p-iodobenzoic	8	.18	.113	-.067
11	p-aminobenzic	86	-.66	-.320	.340
12	p-methylbenzoic	-19	-.170	.262	.432
13	p-nitrobenzoic	-67	.778	.528	-.250
14	p-methoxybenzoic	61	-.268	-.181	.087
15	p-ethoxybenzoic	64	-.240	-.198	.042
16	p-isopropylbenzoic	30	-.151	-.010	.141
17	benzoic	0	0	.157	.157

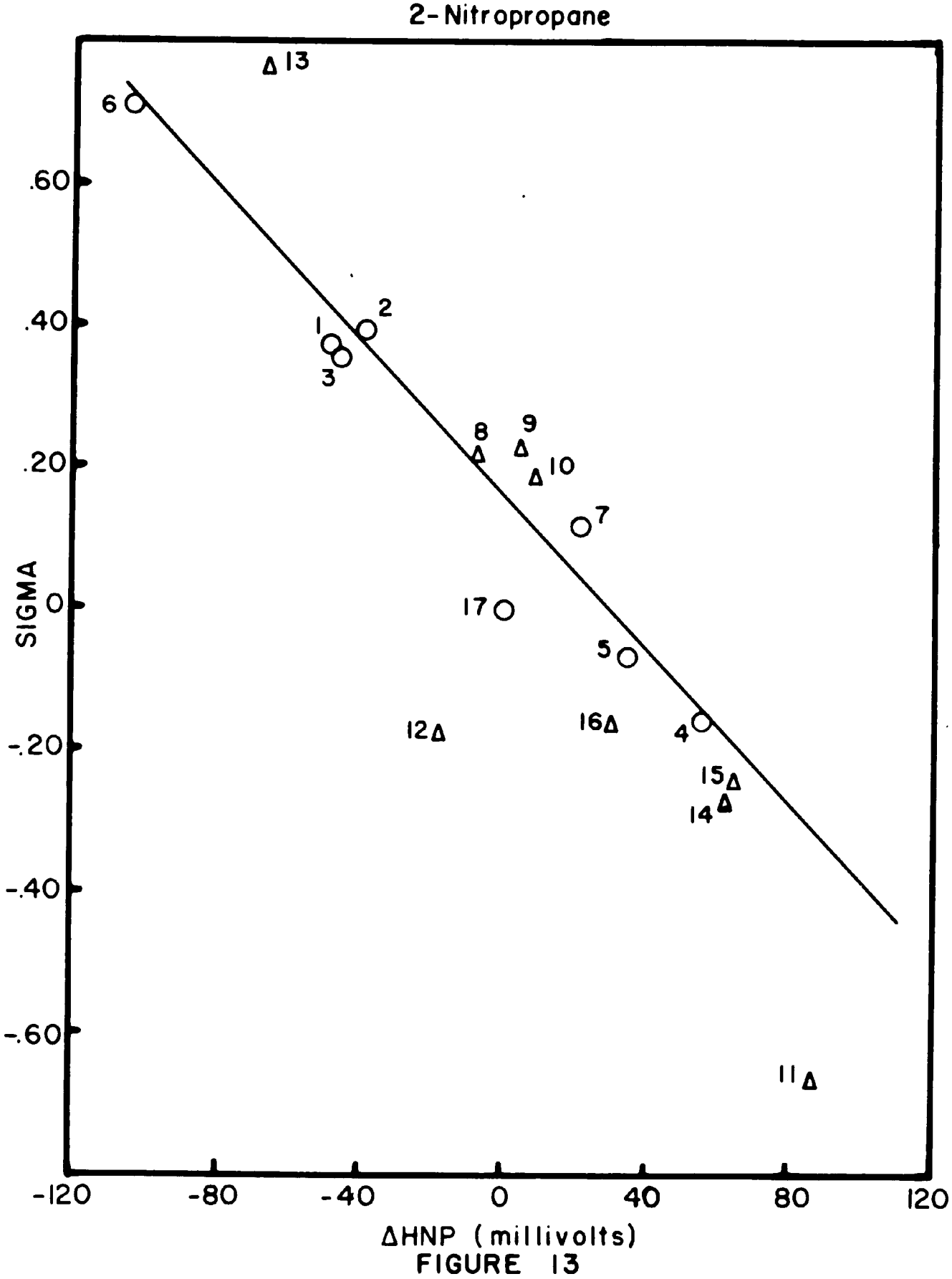

2-Nitropropane
Δ 13
6
.60
.40
1
2
3
8
9
Δ
Δ 10
.20
7
SIGMA
0
17
5
12Δ
16Δ
4
-.20
15Δ
14Δ
-.40
-.60
11Δ
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)

FIGURE 13

TABLE XII

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN O-NITROTOLUENE AND WATER

Number	Acid	ΔHNP	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	m-chlorobenzoic	-50	3.83	3.75	-0.08
2	m-bromobenzoic	-41	3.81	3.81	0
3	m-iodobenzoic	-46	3.85	3.77	-0.08
4	m-aminobenzoic	Insol.	4.82	~	~
5	m-methylbenzoic	36	4.27	4.34	0.07
6	m-nitrobenzoic	-89	3.49	3.48	-0.01
7	m-methoxybenzoic	16	4.09	4.20	0.11
8	p-chlorobenzoic	-24	3.98	3.93	-0.05
9	p-bromobenzoic	3	3.97	4.11	0.14
10	p-iodobenzoic	-3	4.02	4.07	0.05
11	p-aminobenzoic	94	4.92	4.73	-0.19
12	p-methylbenzoic	-14	4.37	3.99	-0.38
13	p-nitrobenzoic	-52	3.42	3.73	0.31
14	p-methoxybenzoic	68	4.47	4.56	0.09
15	p-ethoxybenzoic	67	4.44	4.55	0.11
16	p-isopropylbenzoic	45	4.35	4.40	0.05
17	benzoic	0	4.20	4.09	-0.11

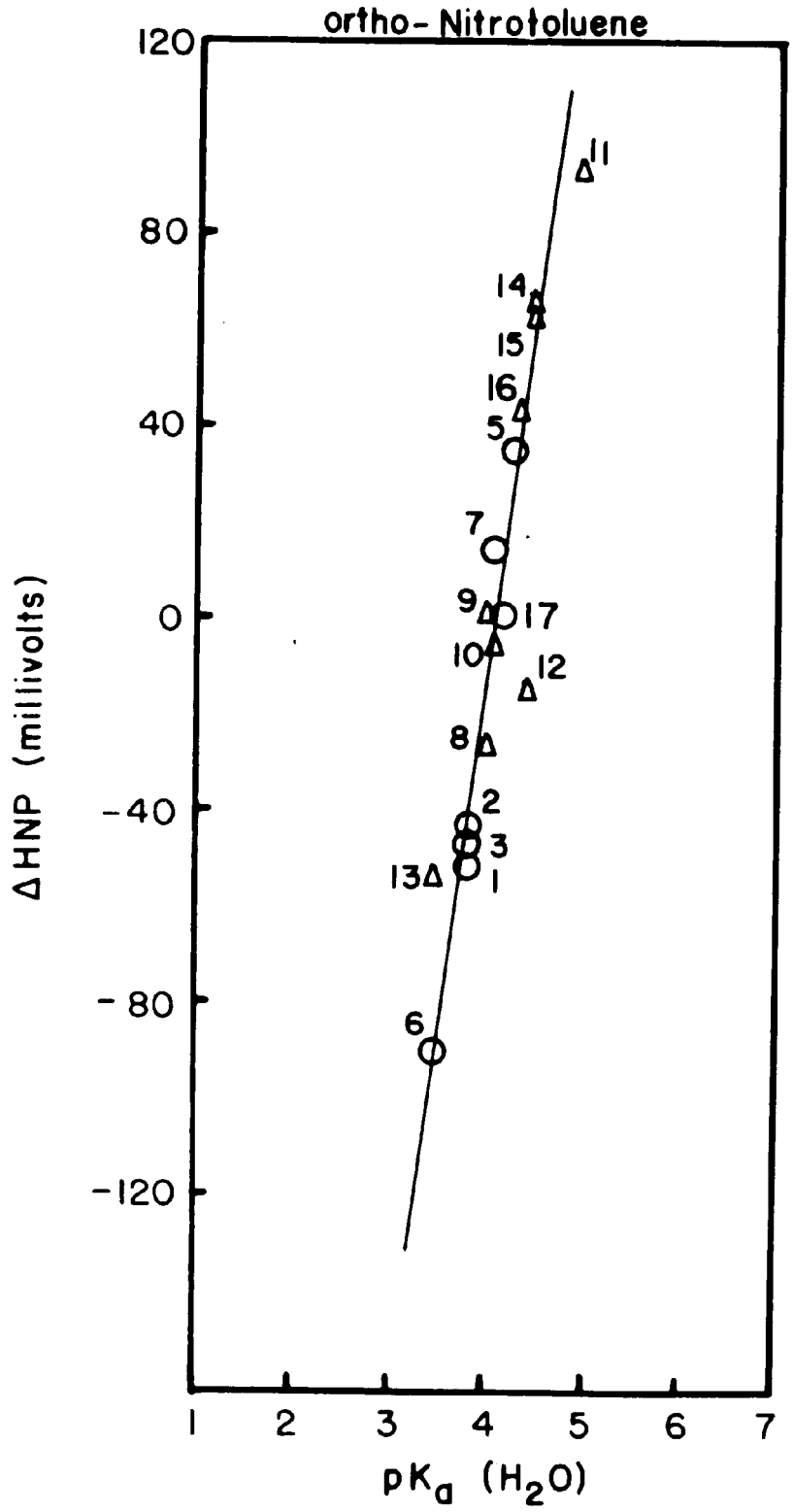

ortho-Nitrotoluene
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pKa (H2O)
11
14
15
16
5
7
9
17
10
12
8
2
3
13
1
6

FIGURE 14

TABLE XIII

CORRELATION OF Δ HNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN O-NITROTOLUENE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-50	.373	.499	.126
2	m-bromobenzoic	-41	.391	.448	.056
3	m-iodobenzoic	-46	.352	476	.124
4	m-aminobenzoic	Insol.	-.160	~	~
5	m-methylbenzoic	36	-.069	.011	.080
6	m-nitrobenzoic	-89	.710	.720	.010
7	m-methoxybenzoic	16	.115	.124	.009
8	p-chlorobenzoic	-24	.227	.351	.124
9	p-bromobenzoic	3	.232	198	-.034
10	p-iodobenzoic	-3	.18	.232	.052
11	p-aminobenzoic	94	-.66	-.319	.341
12	p-methylbenzoic	-14	-.170	.294	.464
13	p-nitrobenzoic	-52	.778	.510	-.268
14	p-methoxybenzoic	68	-.268	-.171	.097
15	p-ethoxybenzoic	67	-.240	-.165	.075
16	p-isopropylbenzoic	45	-.151	-.041	.110
17	benzoic	0	0	.215	.215

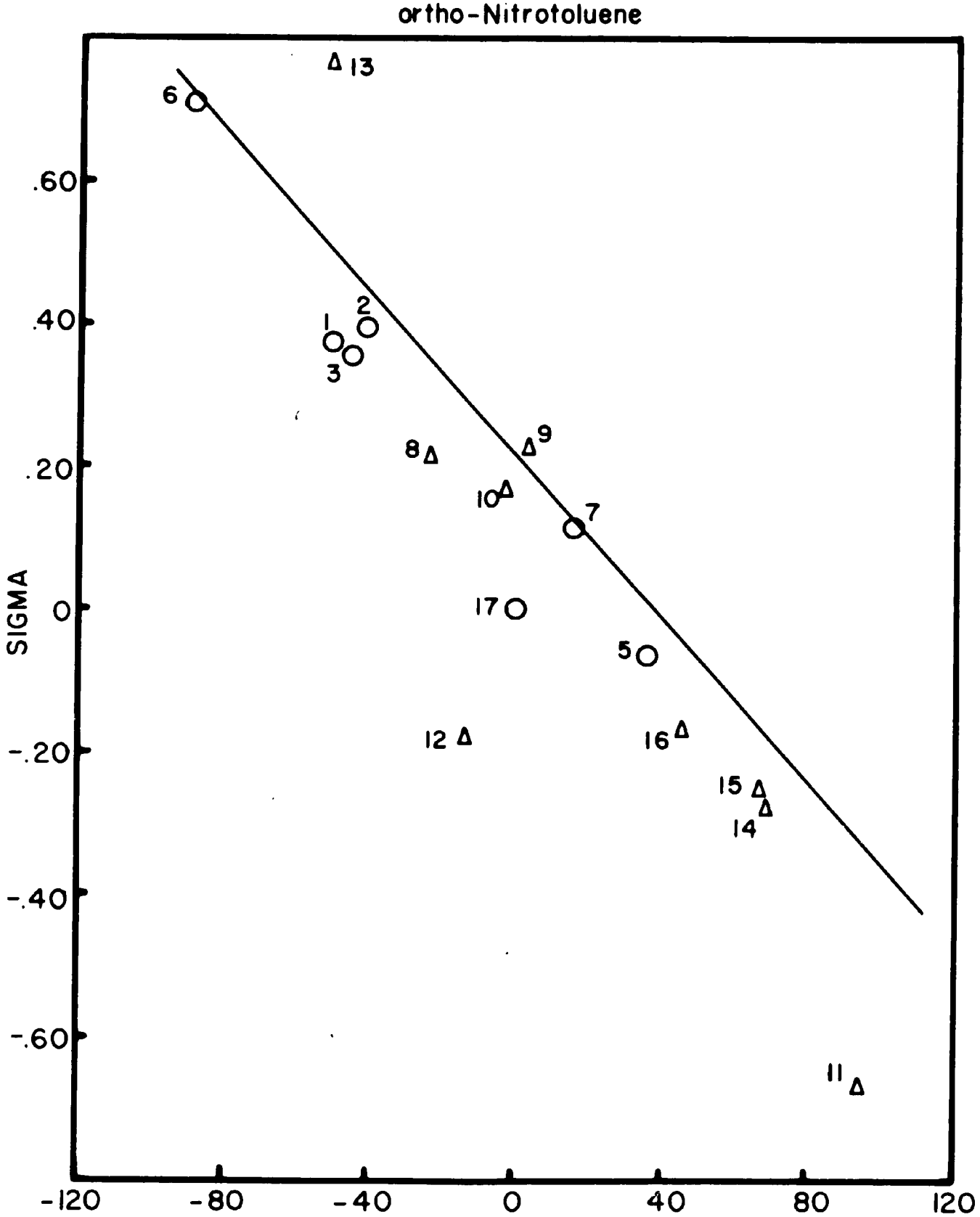

ortho-Nitrotoluene
SIGMA
.60
.40
.20
0
-.20
-.40
-.60
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)
1
2
3
5
6
7
8
9
10
11
12
13
14
15
16
17

FIGURE 15

TABLE XIV

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN NITROBENZENE AND WATER

Number	Acid	ΔHNP	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	m-chlorobenzoic	-54	3.83	3.81	-0.02
2	m-bromobenzoic	-53	3.81	3.82	0.01
3	m-iodobenzoic	-57	3.85	3.79	-0.06
4	m-aminobenzoic	78	4.82	4.68	-0.14
5	m-methylbenzoic	4	4.27	4.20	-0.07
6	m-nitrobenzoic	-122	3.49	3.37	-0.12
7	m-methoxybenzoic	-1	4.09	4.16	0.07
8	p-chlorobenzoic	-8	3.98	4.12	0.14
9	p-bromobenzoic	-12	3.97	4.09	0.12
10	p-iodobenzoic	-27	4.02	3.99	-0.03
11	p-aminobenzoic	90	4.92	4.76	-0.16
12	p-methylbenzoic	-20	4.37	4.04	-0.33
13	p-nitrobenzoic	-70	3.42	3.71	0.29
14	p-methoxybenzoic	69	4.47	4.62	0.15
15	p-ethoxybenzoic	63	4.44	4.58	0.14
16	p-isopropylbenzoic	50	4.35	4.50	0.15
17	benzoic	0	4.20	4.17	-0.03

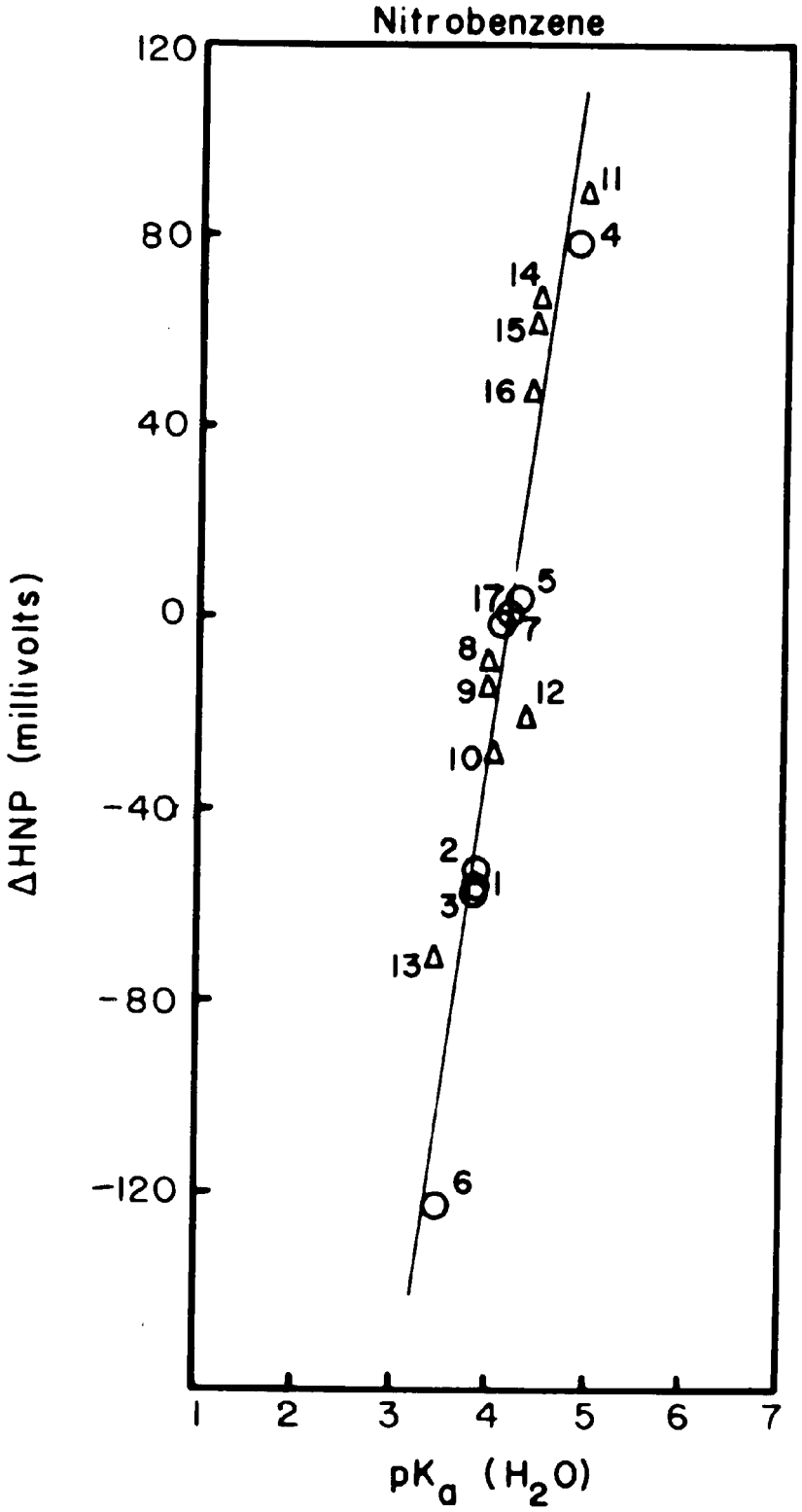

Nitrobenzene
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
4
14
15
16
17
5
7
8
9
12
10
2
1
3
13
6

FIGURE 16

TABLE XV

CORRELATION OF ΔHNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN NITROBENZENE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m - chlorobenzoic	-54	.373	.365	-.008
2	m-bromobenzoic	-53	.391	.360	-.031
3	m-iodobenzoic	-57	.352	.380	.028
4	m-aminobenzoic	78	-.160	-.307	-.147
5	m-methylbenzoic	4	-.069	.07	.139
6	m-nitrobenzoic	-122	.710	.712	.002
7	m-methoxybenzoic	-1	.115	.085	-.030
8	p-chlorobenzoic	-8	.227	.130	-.097
9	p-bromobenzoic	-12	.232	.151	-.081
10	p-iodobenzoic	-27	.18	.227	.047
11	p-aminobenzoic	90	-.66	-.369	.291
12	p-methylbenzoic	-20	-.170	.192	.362
13	p-nitrobenzoic	-70	.778	.447	-.331
14	p-methoxybenzoic	69	-.268	-.261	.007
15	p-ethoxybenzoic	63	-.240	-.231	.009
16	p-isopropylbenzoic	50	-.151	-.165	.014
17	benzoic	0	0	.090	.090

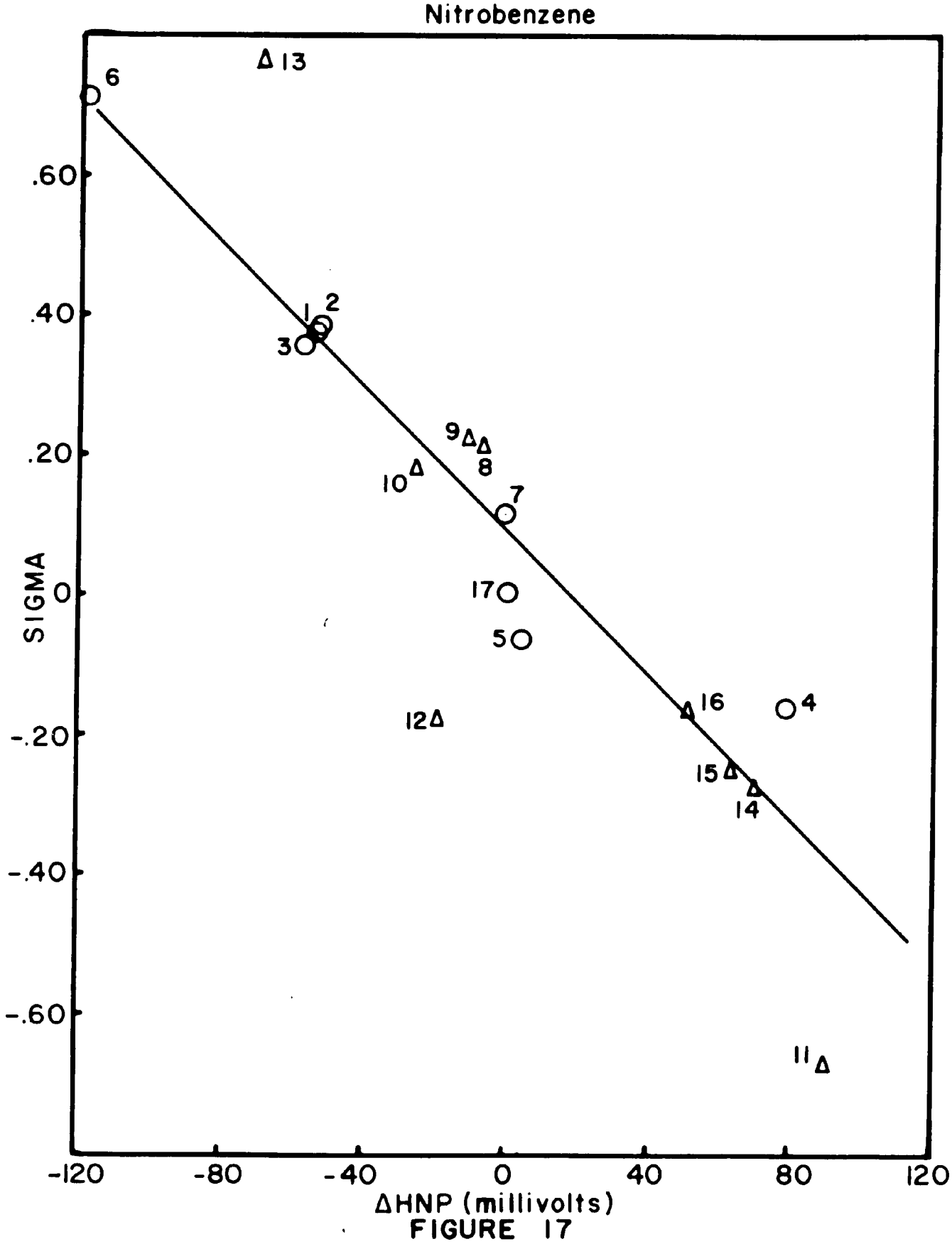

Nitrobenzene
Δ 13
6
.60
.40
1
2
3
9
Δ
Δ
8
.20
10
Δ
7
SIGMA
0
17
5
16
4
12
Δ
-.20
15
Δ
14
-.40
-.60
11
Δ
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)

FIGURE 17

TABLE XVI

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN N, N' DIMETHYLFORMAMIDE AND WATER

Number	Acid	ΔHNP	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	m-chlorobenzoic	-46	3.83	3.86	0.03
2	m-bromobenzoic	-68	3.81	3.71	-0.10
3	m-iodobenzoic	-42	3.85	3.89	0.04
4	m-aminobenzoic	48	4.82	4.51	-0.31
5	m-methylbenzoic	5	4.27	4.21	-0.06
6	m-nitrobenzoic	-110	3.49	3.42	-0.07
7	m-methoxybenzoic	2	4.09	4.19	0.10
8	p-chlorobenzoic	-28	3.98	3.99	0.01
9	p-bromobenzoic	-25	3.97	4.01	0.04
10	p-iodobenzoic	-24	4.02	4.01	-0.01
11	p-aminobenzoic	111	4.92	4.95	0.03
12	p-methylbenzoic	14	4.37	4.28	-0.09
13	p-nitrobenzoic	-89	3.42	3.56	0.14
14	p-methoxybenzoic	59	4.47	4.59	0.12
15	p-ethoxybenzoic	56	4.44	4.56	0.12
16	p-isopropylbenzoic	26	4.35	4.36	0.01
17	benzoic	0	4.20	4.18	-0.02

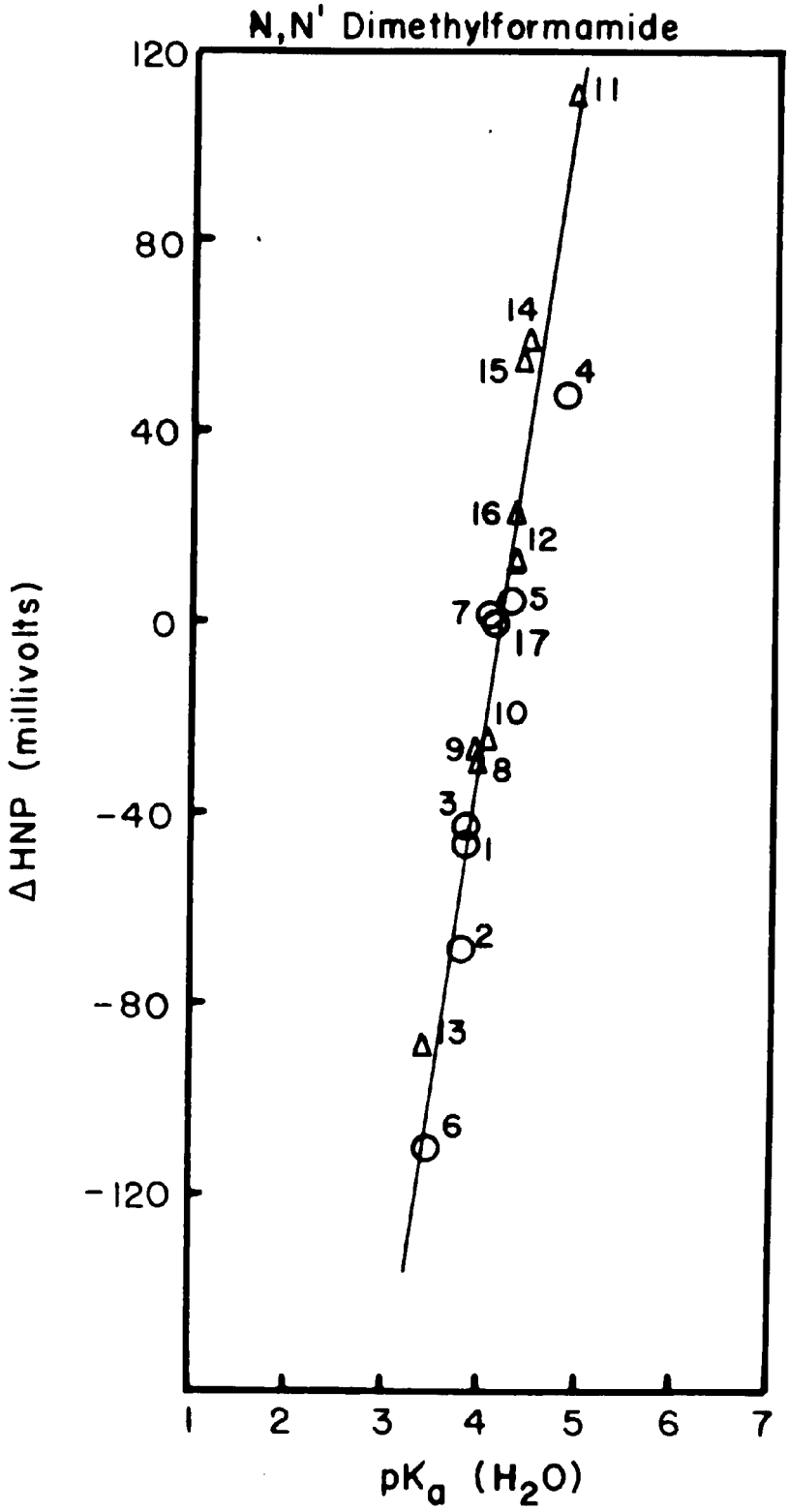

N,N' Dimethylformamide
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
14
15
4
16
12
5
7
17
10
9
8
3
1
2
13
6

FIGURE 18

TABLE XVII

CORRELATION OF ΔHNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN N, N' DIMETHYLFORMAMIDE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-46	.373	.389	.016
2	m-bromovenzoic	-68	.391	.526	.135
3	m-iodobenzoic	-42	.352	.364	.012
4	m- aminobenzoic	48	-.160	-.196	-.036
5	m-methylbenzoic	5	-.069	.072	.141
6	m-nitrobenzoic	-110	.710	.788	.078
7	m-methoxybenzoic	2	.115	.091	-.024
8	p-chlorobenzoic	-28	.227	.277	.050
9	p-bromobenzoic	-25	.232	.258	.026
10	p-iodobenzoic	-24	.18	.252	.072
11	p-aminobenzoic	111	-.66	-.588	.072
12	p-methylbenzoic	14	-.170	.016	.186
13	p-nitrobenzoic	-89	.778	.657	-.121
14	p-methoxybenzoic	59	-.268	-.264	.004
15	p-ethoxybenzoic	56	-.240	-.245	-.005
16	p-isopropylbenzoic	26	-.151	-.059	.092
17	benzoic	0	0	.10	.10

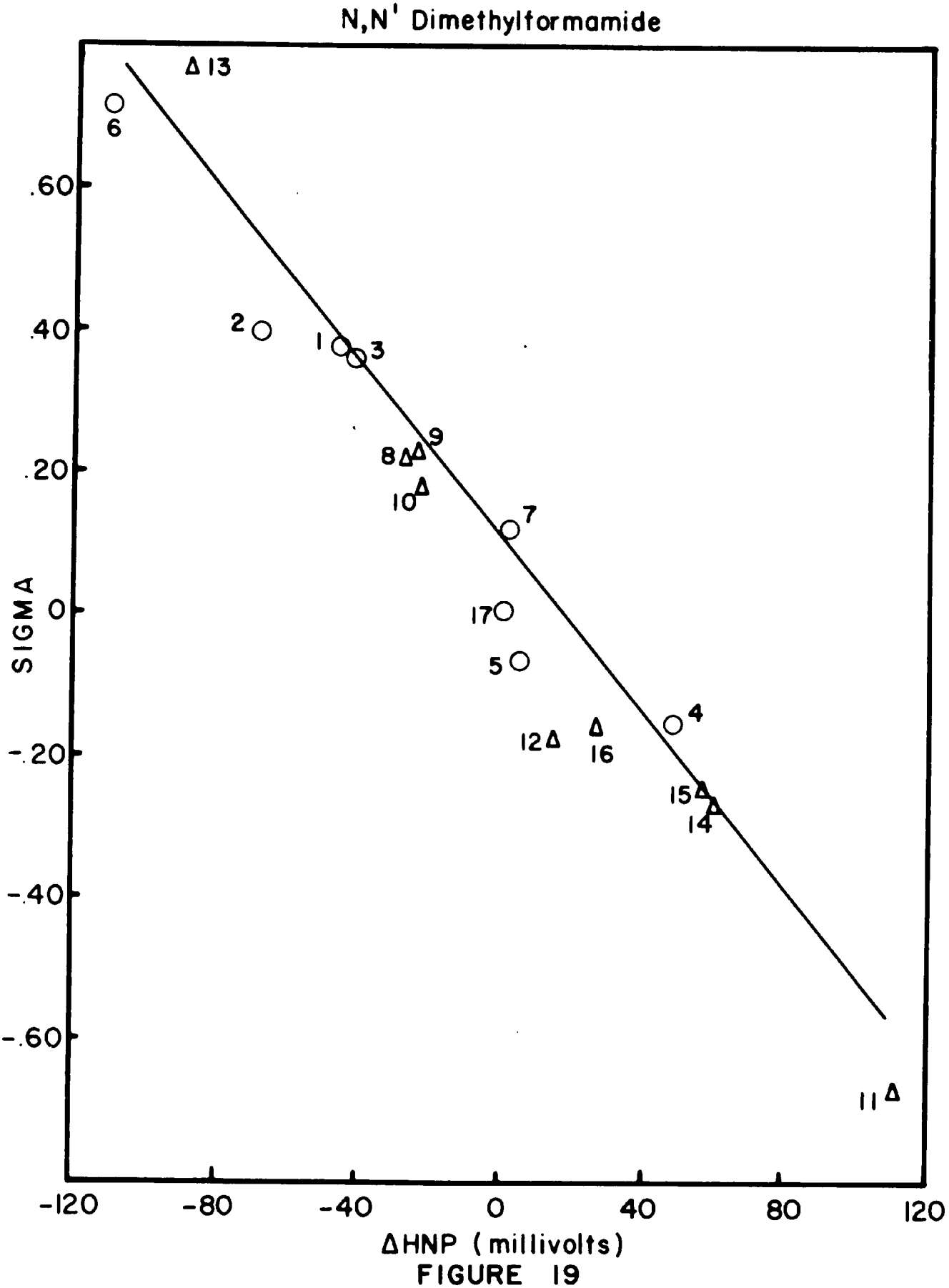

N,N' Dimethylformamide
Δ 13
6
.60
.40
2
1
3
.20
8Δ
9
10Δ
7
SIGMA
0
17
5
-.20
12Δ
Δ
16
4
15Δ
14
-.40
-.60
11Δ
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)

FIGURE 19

TABLE XVIII

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN CHLOROBENZENE AND WATER

Number	Acid	ΔHNP	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	m-chlorobenzoic	-36	3.83	3.85	0.03
2	m-bromobenzoic	-32	3.81	3.87	0.06
3	m-iodobenzoic	-41	3.85	3.81	-0.04
4	m-aminobenzoic	Insol.	4.82	~	~
5	m-methylbenzoic	17	4.27	4.22	-0.05
6	m-nitrobenzoic	-94	3.49	3.44	-0.05
7	m-methoxybenzoic	15	4.09	4.00	-0.09
8	p-chlorobenzoic	-51	3.98	3.74	-0.24
9	p-bromobenzoic	-61	3.97	3.67	-0.30
10	p-iodobenzoic	-24	4.02	3.93	-0.09
11	p-aminobenzoic	107	4.92	4.85	-0.07
12	p-methylbenzoic	38	4.37	4.37	0
13	p-nitrobenzoic	-55	3.42	3.71	0.29
14	p-methoxybenzoic	38	4.47	4.37	-0.10
15	p-ethoxybenzoic	31	4.44	4.32	-0.12
16	p-isopropylbenzoic	64	4.35	4.55	0.20
17	benzoic	0	4.20	4.10	-0.10

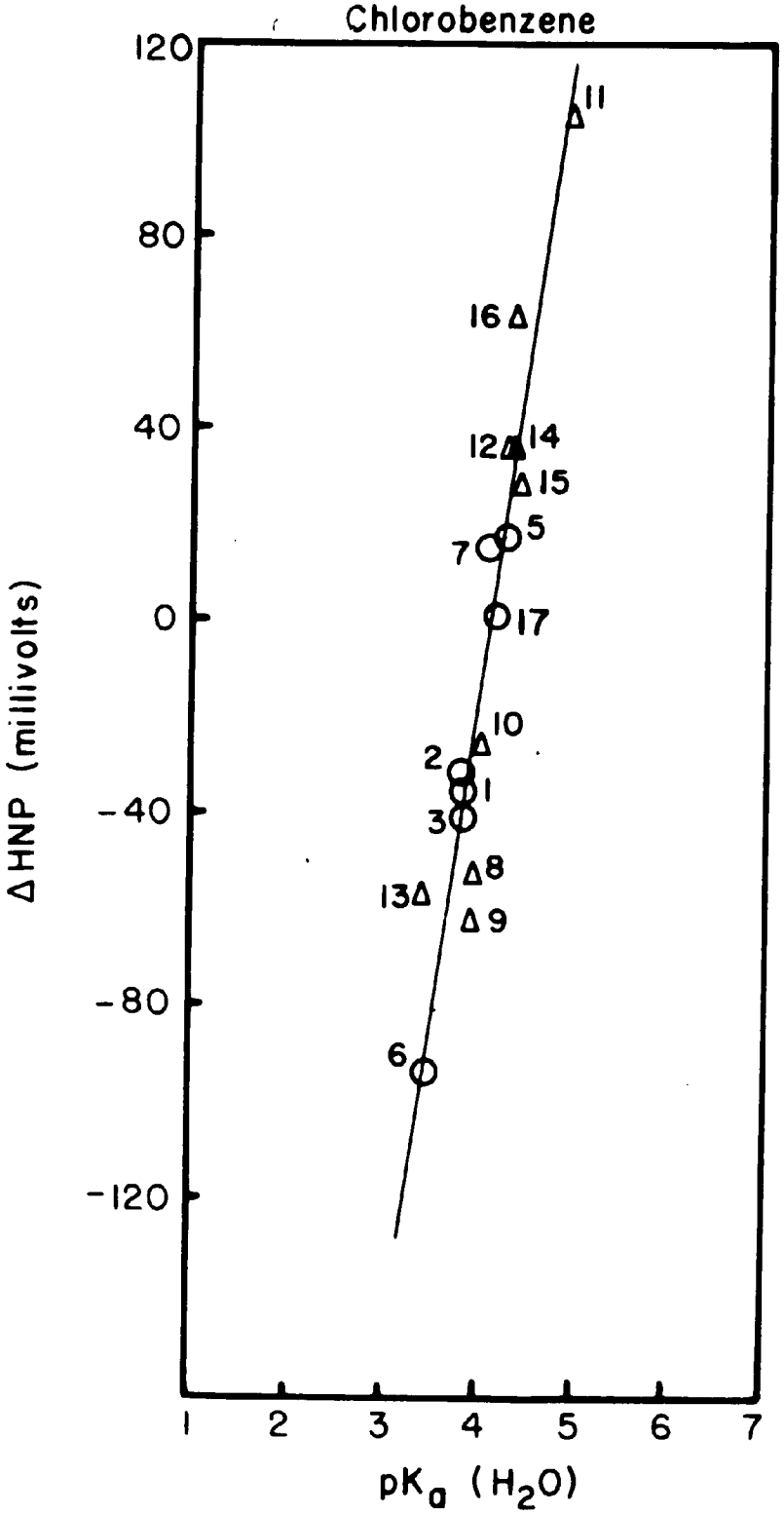

Chlorobenzene
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
16Δ
12Δ
14
Δ15
7
5
17
10
2
1
3
Δ8
13Δ
Δ9
6

FIGURE 20

TABLE XIX

CORRELATION OF ΔHNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN CHLOROBENZENE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-36	.373	.366	-.007
2	m-bromobenzoic	-32	.391	.340	-.051
3	m-iodobenzoic	-41	.352	.397	.045
4	m-aminobenzoic	Insol.	-.160	~	~
5	m-methylbenzoic	17	-.069	.027	.106
6	m-nitrobenzoic	-94	.710	.737	.027
7	m-methoxybenzoic	15	.115	.040	-.075
8	p-chlorobenzoic	-51	.227	.462	.235
9	p-bromobenzoic	-61	.232	.526	.294
10	p-iodobenzoic	-24	.18	.289	.109
11	p-aminobenzoic	107	-.66	-.547	.113
12	p-methylbenzoic	38	-.170	-.106	.064
13	p-nitrobenzoic	-55	.778	.487	-.291
14	p-methoxybenzoic	38	.268	-.106	.162
15	p-ethoxybenzoic	31	-.240	-.062	.178
16	p-isopropylbenzoic	64	-.151	-.272	-.121
17	benzoic	0	0	.136	.136

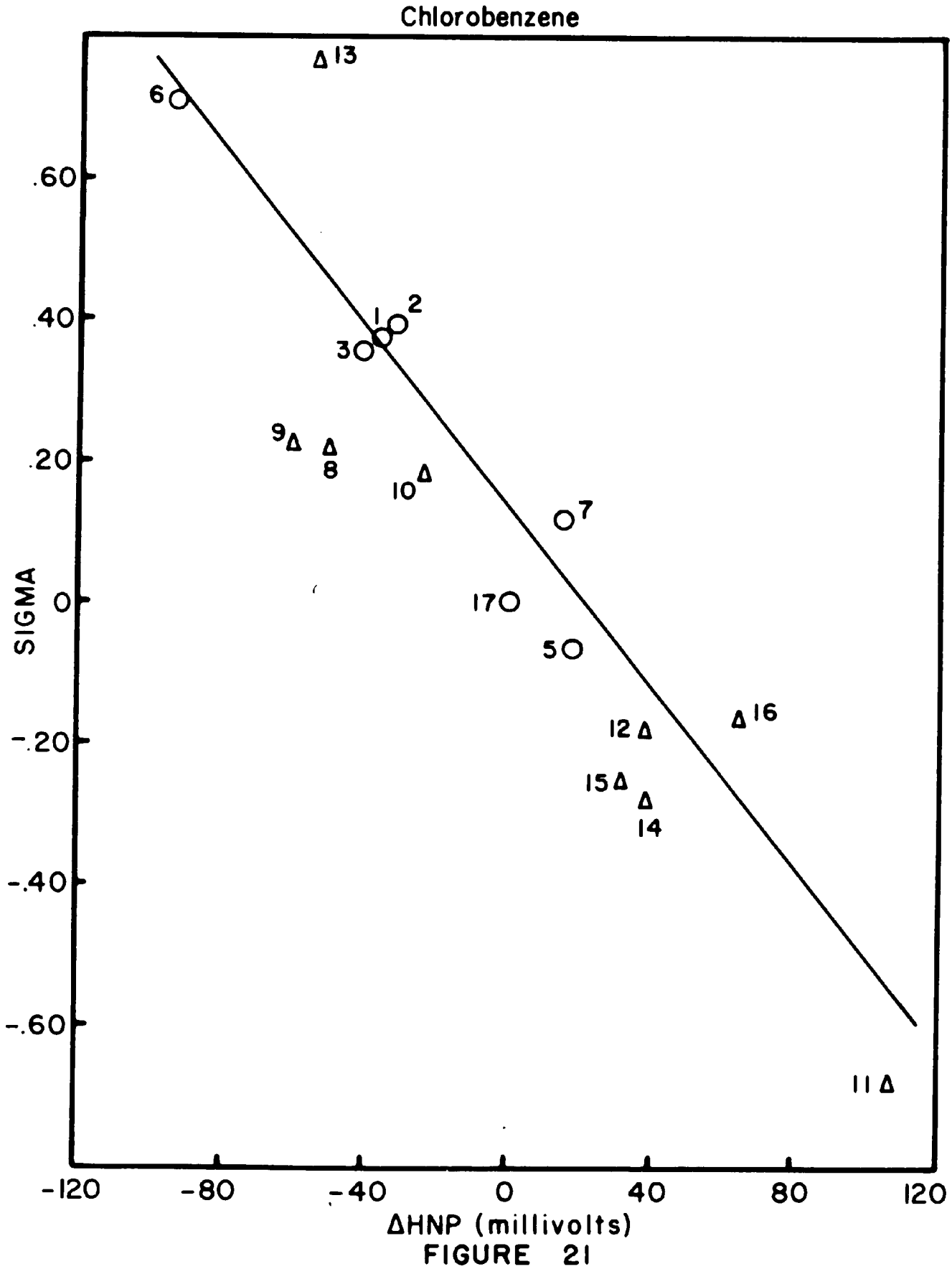

Chlorobenzene
SIGMA
.60
.40
.20
0
-.20
-.40
-.60
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)
13
6
1
2
3
9
8
10
7
17
5
16
12
15
14
11

FIGURE 21

TABLE XX

ACIDIC STRENGTH OF SUBSTITUTED BENZOIC ACIDS IN BROMOBENZENE AND WATER

Number	Acid	ΔHNP	pKa (Lit.)	pKa Calcd.)	ΔpKa
1	m-chlorobenzoic	-39	3.83	3.91	0.08
2	m-bromobenzoic	-64	3.81	3.75	-0.06
3	m-iodobenzoic	-32	3.85	3.95	0.10
4	m-aminobenzoic	Insol.	4.82	~	~
5	m-methylbenzoic	11	4.27	4.23	-0.04
6	m-nitrobenzoic	-103	3.49	3.50	0.01
7	m-methoxybenzoic	20	4.09	4.29	0.20
8	p-chlorobenzoic	-39	3.98	3.91	-0.07
9	p-bromobenzoic	-43	3.97	3.88	-0.09
10	p-iodobenzoic	-51	4.02	3.83	-0.19
11	p-aminobenzoic	104	4.92	4.82	-0.10
12	p-methylbenzoic	11	4.37	4.23	-0.14
13	p-nitrobenzoic	-94	3.42	3.56	0.14
14	p-methoxybenzoic	61	4.47	4.55	0.08
15	p-ethoxybenzoic	52	4.44	4.49	0.05
16	p-isopropylbenzoic	55	4.35	4.51	0.16
17	benzoic	0	4.20	4.16	-0.04

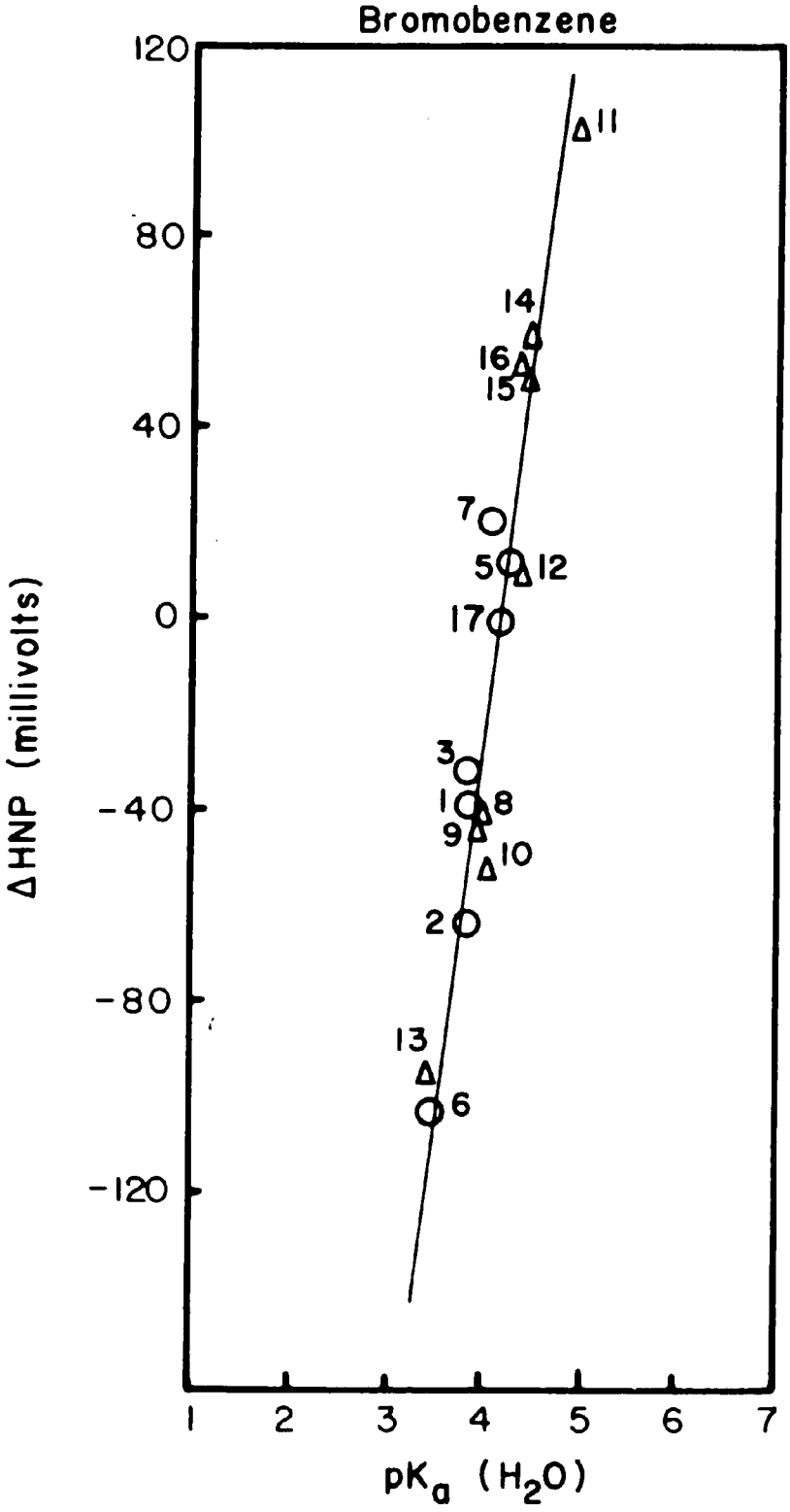

Bromobenzene
120
80
40
0
-40
-80
-120
ΔHNP (millivolts)
1
2
3
4
5
6
7
pK$_a$ (H$_2$O)
11
14
16
15
7
5
12
17
3
1
8
9
10
2
13
6

FIGURE 22

TABLE XXI

CORRELATION OF Δ HNP FOR SUBSTITUTED BENZOIC ACIDS WITH SIGMA IN BROMOBENZENE

Number	Acid	ΔHNP	σ (Lit.)	σ (Calcd.)	$\Delta\sigma$
1	m-chlorobenzoic	-39	.373	.376	.003
2	m-bromobenzoic	-64	.391	.527	.136
3	m-iodobenzoic	-32	.352	.334	-.018
4	m-aminobenzoic	Insol.	-.160	~	~
5	m-methylbanzoic	11	-.069	.076	.145
6	m-nitrobenzoic	-103	.710	.762	.052
7	m-methoxybenzoic	20	.115	.022	-.093
8	p-chlorobenzoic	-39	.227	.376	.149
9	p-bromobenzoic	-43	.232	.401	.169
10	p-iodobenzoic	-51	.18	.449	.269
11	p-aminobenzoic	104	-.66	-.484	.176
12	p-methylbenzoic	11	-.170	.076	.246
13	p-nitrobenzoic	-94	.778	.707	-.071
14	p-methoxybenzoic	61	-.268	-.225	.043
15	p-ethoxybenzoic	52	-.240	-.171	.069
16	p-isopropylbenzoic	55	-.151	-.189	.038
17	benzoic	0	0	.142	.142

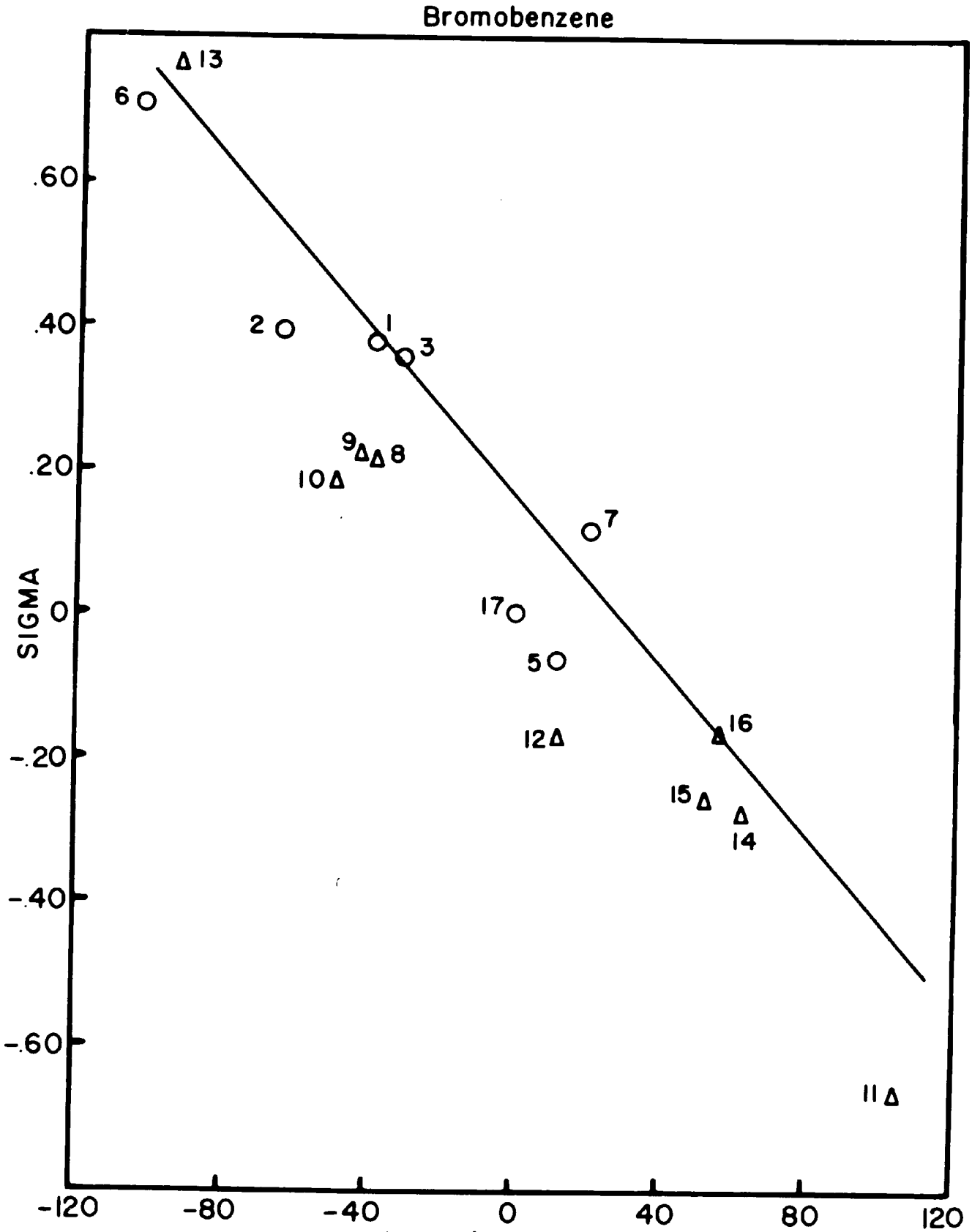

Bromobenzene
Δ 13
6 O
.60
.40
2 O
1
3
9 Δ Δ 8
10 Δ
.20
O 7
0
17 O
5 O
12 Δ
16
-.20
15 Δ
Δ
14
-.40
-.60
11 Δ
SIGMA
-120
-80
-40
0
40
80
120
ΔHNP (millivolts)

FIGURE 23

TABLE XXII

ACIDIC STRENGTH OF SUBSTITUTED PHENOLS IN 4-METHYL-2-PENTANONE AND WATER

Number	Acid	Δ^{HNP}	pKa (Lit.)	pKa (Calcd.)	ΔpKa
1	Phenol	320	9.94	10.04	.10
2	m-chlorophenol	180	9.02	8.90	-.12
3	m-nitrophenol	107	8.35	8.29	-.06
4	p-chlorophenol	214	9.38	9.18	-.20
5	p-nitrophenol	-18	7.14	7.27	.13
6	p-bromophenol	220	9.25	9.22	-.08

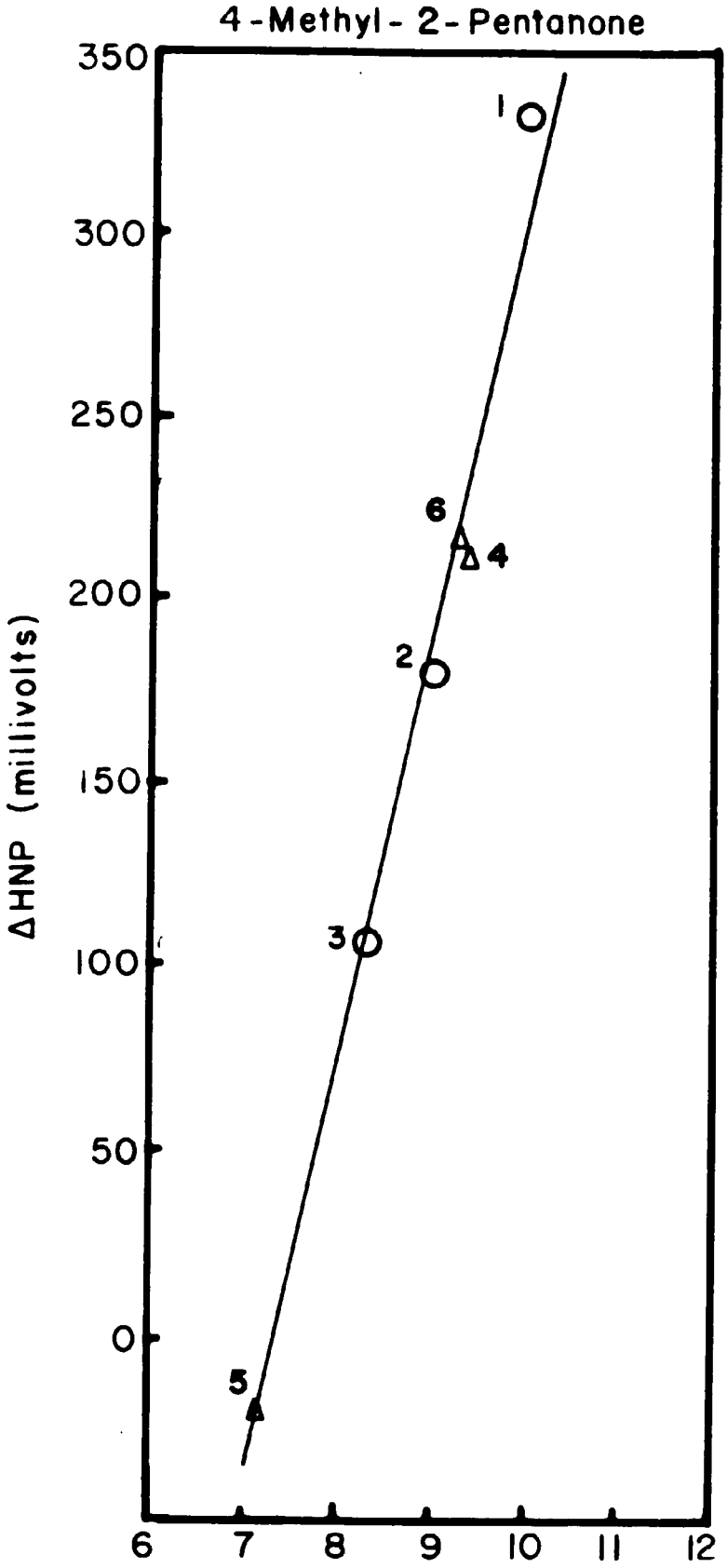

4-Methyl-2-Pentanone
350
300
250
200
150
100
50
0
ΔHNP (millivolts)
1
2
3
4
5
6
6
7
8
9
10
11
12
pK a (H2O)

FIGURE 24

TABLE XXIII

CORRELATION OF Δ HNP FOR SUBSTITUTED PHENOLS WITH SIGMA IN 4-METHYL-2-PENTANONE

Number	Acid	Δ HNP	σ (Lit.)	σ (Calcd.)	Δσ
1	Phenol	320	0	.096	.096
2	m-chlorophenol	180	.435	.464	.029
3	m-nitrophenol	107	.754	.756	.002
4	p-chlorophenol	214	.266	.328	.062
5	p-nitrophenol	-18	1.33	1.26	- .07
6	p-bromophenol	220	.328	.304	- .024

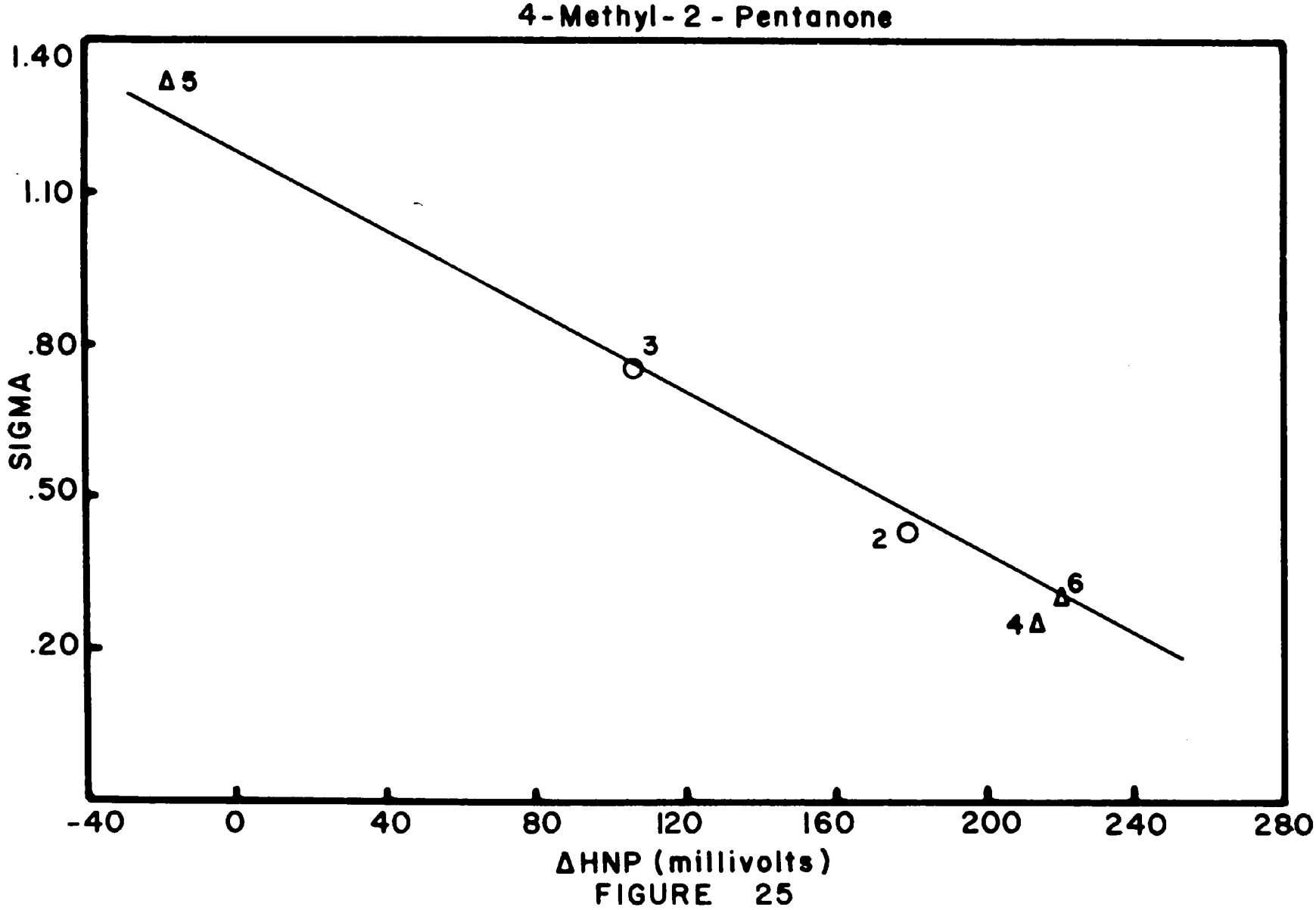

4-Methyl-2-Pentanone
1.40
1.10
.80
.50
.20
SIGMA
Δ5
3
2
6
4Δ
-40
0
40
80
120
160
200
240
280
ΔHNP (millivolts)

FIGURE 25

TABLE XXIV

ACIDIC STRENGTH OF SUBSTITUTED PHENOLS IN N, N' DIMETHYLFORMAMIDE AND WATER

Number	Acid	Δ HNP	pKa (Lit.)	pKa (Calcd.)	Δ pKa
1	phenol	180	9.94	9.99	.05
2	m-chlorophenol	141	9.02	8.96	-.06
3	m-nitrophenol	122	8.35	8.46	.09
4	p-chlorophenol	157	9.38	9.39	.01
5	p-nitrophenol	69	7.14	7.06	-.08
6	p-bromophenol	149	9.25	9.17	-.08

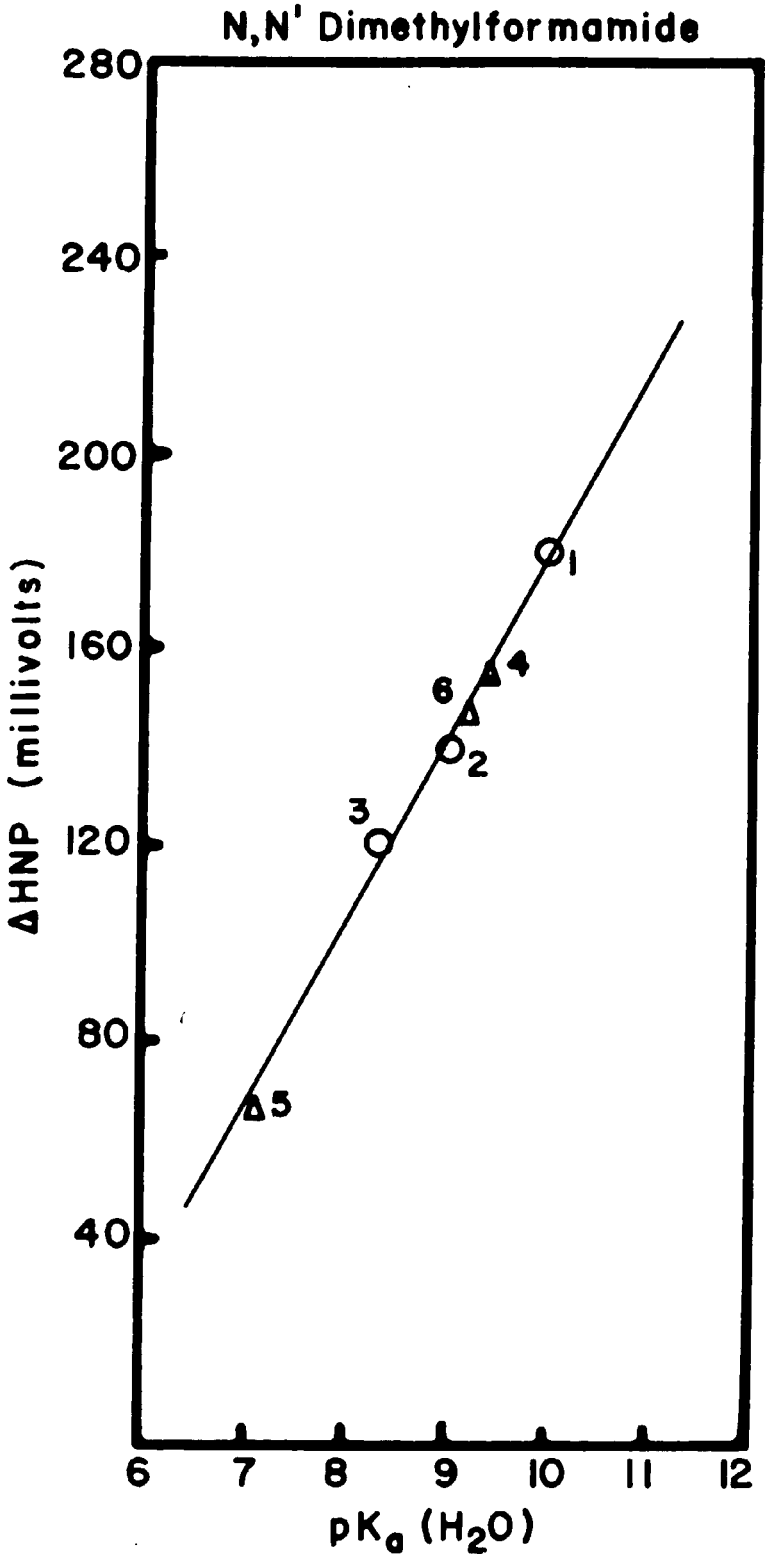

N,N' Dimethylformamide
280
240
200
160
120
80
40
ΔHNP (millivolts)
1
2
3
4
5
6
6
7
8
9
10
11
12
pKa (H2O)

FIGURE 26

TABLE XXV

CORRELATION OF Δ HNP FOR SUBSTITUTED PHENOLS WITH SIGMA IN N, N' DIMETHYLFORMAMIDE

Number	Acid	Δ HNP	σ (Lit.)	σ (Calcd.)	Δσ
1	phenol	180	0	.007	.007
2	m-chlorophenol	141	.435	.460	.026
3	m-nitrophenol	122	.754	689	.065
4	p-chlorophenol	157	.266	.269	.003
5	p-nitrophenol	69	1.33	1.33	0
6	p-bromophenol	149	.328	.365	.037

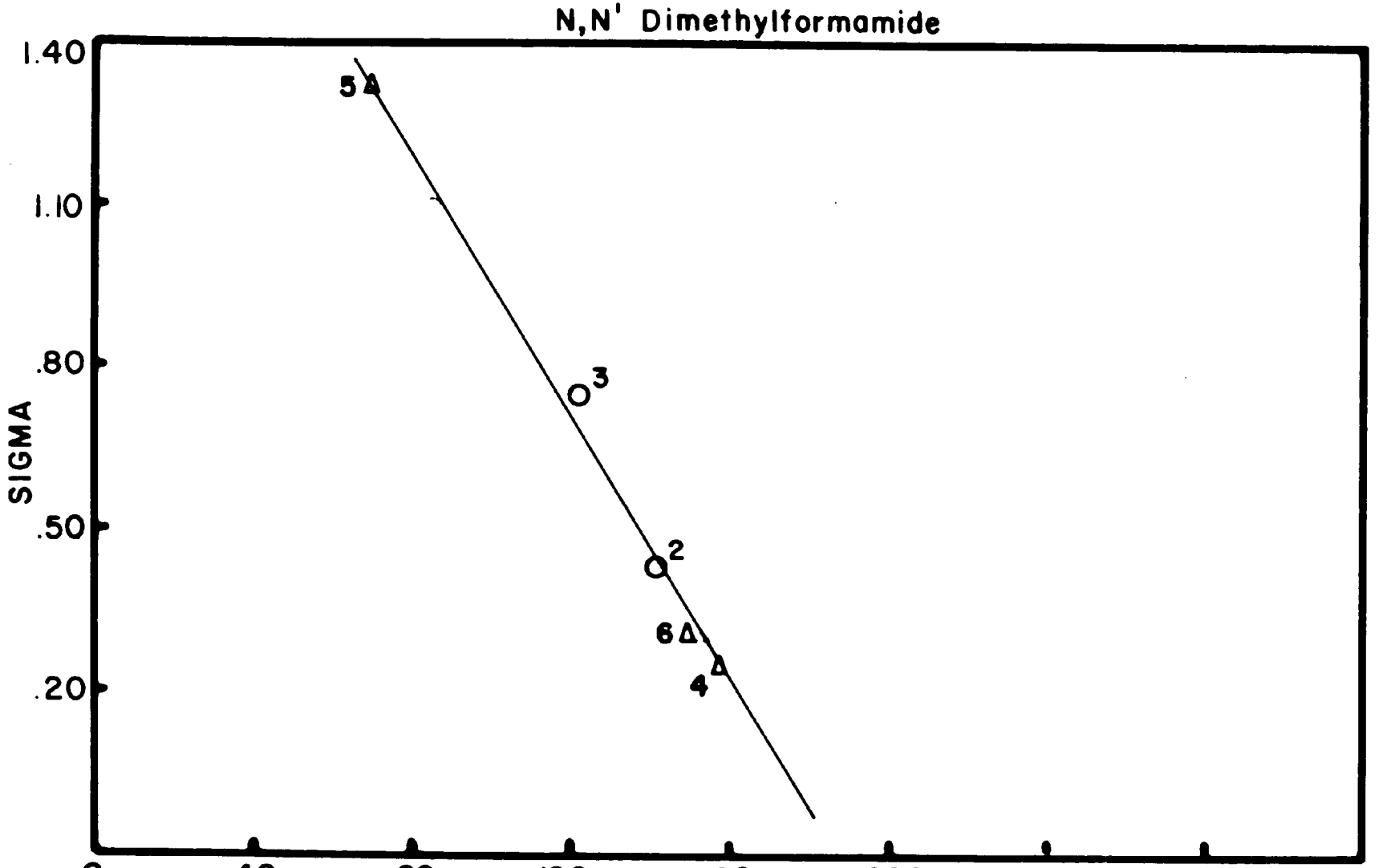

N,N' Dimethylformamide
1.40
1.10
.80
.50
.20
SIGMA
5
3
2
6
4
0
40
80
120
160
200
240
280
320
ΔHNP (millivolts)

FIGURE 27

TABLE XXVI

TITRATION RANGE OF SOLVENTS

Solvent	ϵ (74)	n_D (72)	Range in mv.
Nitrobenzene	34.8	1.5524	-120 to 670
o-nitrotoluene	27.4	1.5474	-20 to 620
Acetonitrile	37.5	1.3460	40 to 670
N, N'Dimethylformamide	26.6	1.4280	300 to 860
2-Nitropropane	25.5	1.3941	-410 to 420
Pyridine	12.3	1.5090	255 to 1050
4-Methyl-2-Pentanone	13.1	1.3960	180 to 880
Chlorobenzene	5.7	1.5251	-55 to 600
Bromobenzene	5.4	1.5604	-210 to 690

TABLE XXVII

SOLVENT PROPERTIES

Solvent	D	n_D	R	P_t	$1/P_t$
Bromobenzene	5.4	1.5604	5.154	62.4	.0160
Chlorobenzene	5.7	1.5251	5.384	62.1	.0161
Pyridine	12.3	1.5090	7.215	63.6	.0157
4-Methyl-2-Pentanone	13.1	1.3960	7.547	100.2	.0099
o-Nitrotoluene	27.4	1.5474	8.215	105.9	.0094
Nitrobenzene	34.8	1.5524	8.410	94.0	.0106
N, N'Dimethyl-formamide	26.6	1.4280	8.424	68.9	.0145
2-Nitropropane	25.5	1.3941	8.447	80.3	.0124
Acetonitrile	37.5	1.3460	8.866	48.4	.0206

TABLE XXVIII

AVERAGE DEVIATION OF ΔHNP VALUES FOR SUBSTITUTED BENZOIC ACID DERIVATIVES

Acid Derivative	Bromo-benzene ΔHNP*	Chloro-benzene ΔHNP*	Pyr-idine ΔHNP*	4-Methyl-2-Pentanone ΔHNP*	o-Nitro-toluene ΔHNP*	Nitro-benzene ΔHNP*
Meta-chlorobenzoic	-39	-36	-49	-42	-50	-54
Para-chlorobenzoic	-39	-51	-25	-53	-24	-8
Meta-bromobenzoic	-64	-32	-63	-55	-41	-53
Para-bromobenzoic	-43	-61	-30	-37	3	-12
Meta-iodobenzoic	-32	-41	-44	-60	-46	-57
Para-iodobenzoic	-51	-24	-24	-26	-3	-27
Meta-aminobenzoic	~	~	38	26	~	78
Para-aminobenzoic	104	107	105	107	94	90
Meta-methylbenzoic	11	17	16	9	36	4
Para-methylbenzoic	11	38	3	0	-14	-20
Meta-nitrobenzoic	-103	-94	-97	-123	-89	-122
Para-nitrobenzoic	-94	-55	-92	-95	-52	-70
Meta-methoxybenzoic	20	15	-5	5	16	-1
Para-methoxybenzoic	61	38	45	38	68	69
Para-ethoxybenzoic	52	31	46	51	67	63
Para-isopropylbenzoic	55	64	35	25	45	50

* = millivolts

TABLE XXVIII (CONTINUED)

AVERAGE DEVIATION OF Δ HNP VALUES FOR SUBSTITUTED BENZOIC ACID DERIVATIVES

Acid Derivative	N, N'Dimethyl-formamide ΔHNP *	2-Nitro-propane ΔHNP*	Acetoni-trile ΔHNP*	Average ΔHNP*	Average Deviation (millivolts)
Meta-chlorobenzoic	-46	-49	-54	-47	5
Para-chlorobenzoic	-28	-8	-39	-31	13
Meta-bromobenzoic	-68	-39	-51	-52	10
Para-bromobenzoic	-25	4	-17	-24	15
Meta-iodobenzoic	-42	-46	-68	-48	9
Para-iodobenzoic	-24	8	-42	-24	10
Meta-aminobenzoic	48	55	78	54	17
Para-aminobenzoic	111	86	118	102	8
Meta-methylbenzoic	5	34	8	16	9
Para-methylbenzoic	14	-19	17	3.3	13
Meta-nitrobenzoic	-110	-104	-105	-105	9
Para-nitrobenzoic	-89	-67	-100	-79	16
Meta-methoxybenzoic	2	21	9	9	7
Para-methoxybenzoic	59	61	64	56	10
Para-ethoxybenzoic	56	64	59	54	8
Para-isopropylbenzoic	26	30	42	41	11

* = millivolts

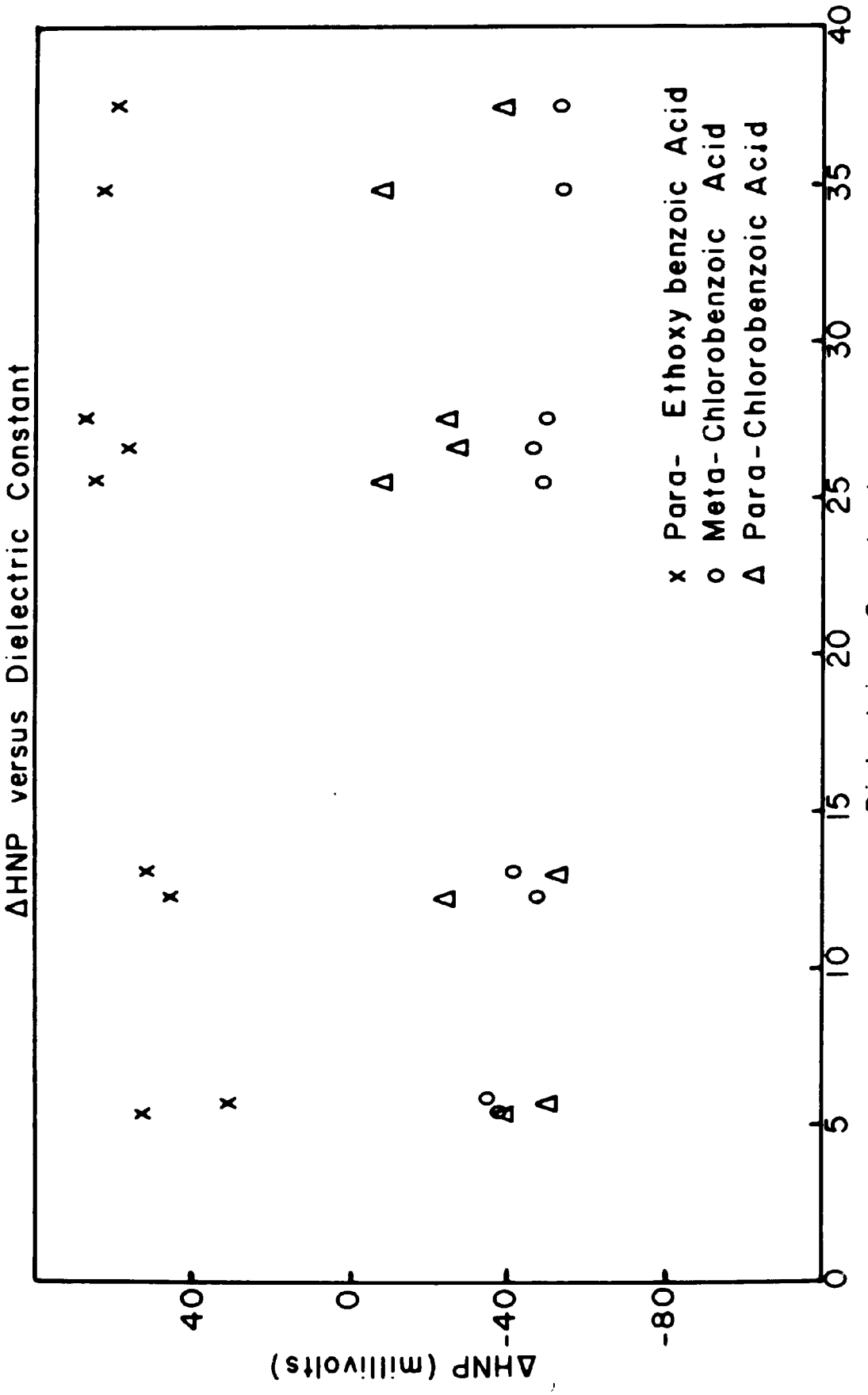

ΔHNP versus Dielectric Constant
ΔHNP (millivolts)
40
0
-40
-80
0
5
10
15
20
25
30
35
40
Dielectric Constant
x Para- Ethoxy benzoic Acid
o Meta-Chlorobenzoic Acid
Δ Para-Chlorobenzoic Acid

FIGURE 28

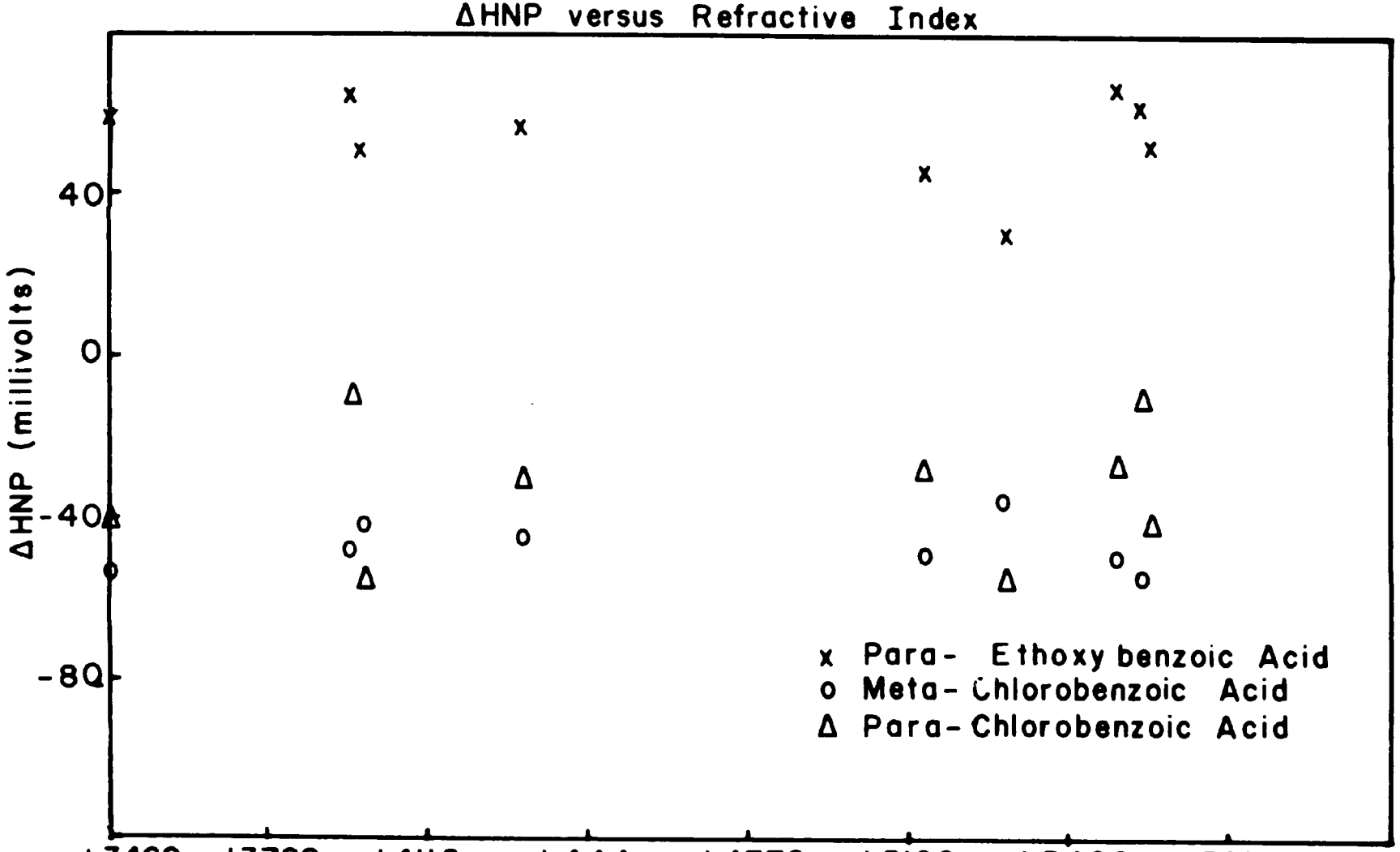

ΔHNP versus Refractive Index
ΔHNP (millivolts)
40
0
-40
-80
1.3460
1.3788
1.4116
1.444
1.4772
1.5100
1.5428
1.5756
Refractive Index
x Para- Ethoxy benzoic Acid
o Meta- Chlorobenzoic Acid
Δ Para- Chlorobenzoic Acid

FIGURE 29

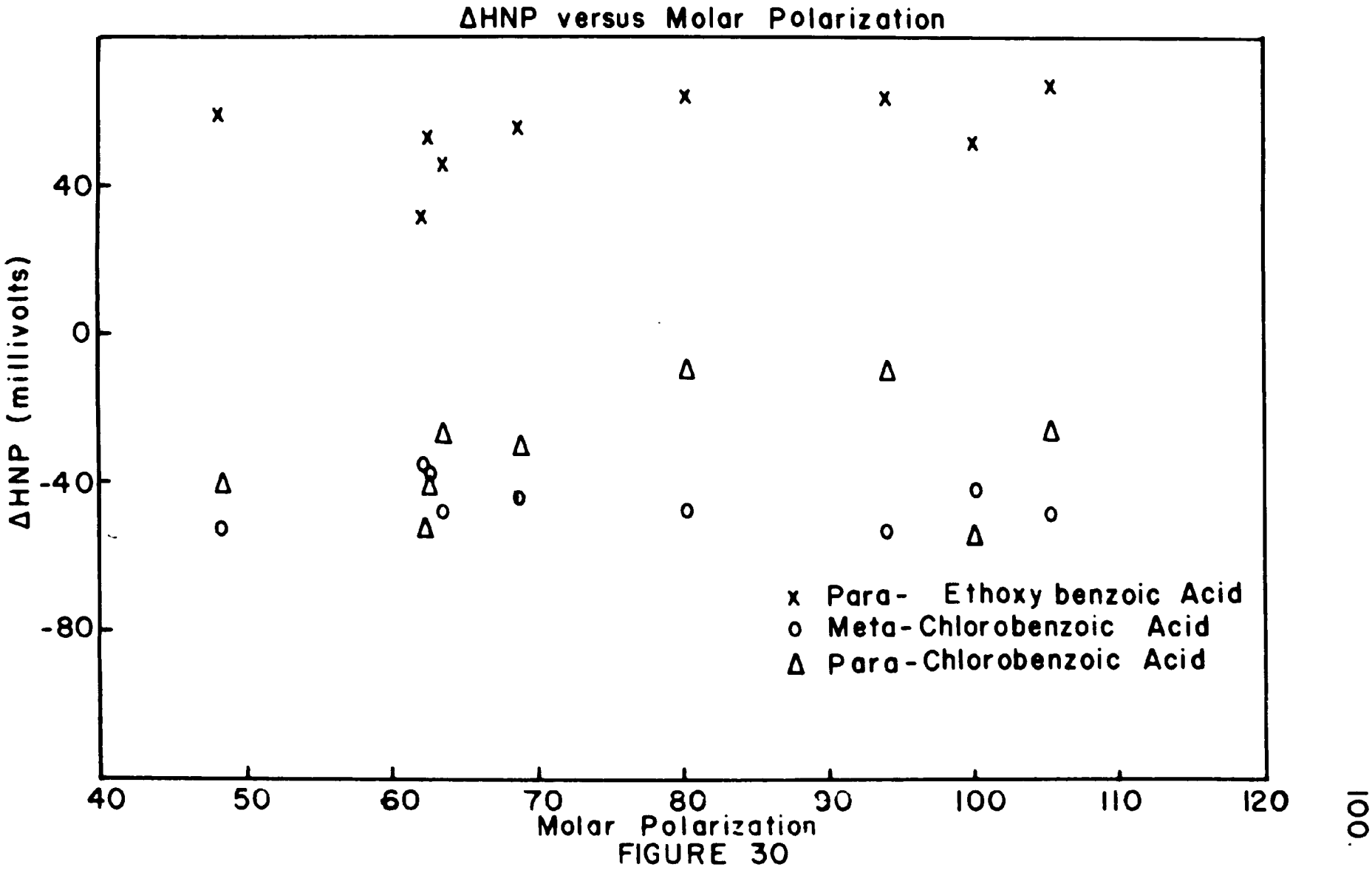

ΔHNP versus Molar Polarization
ΔHNP (millivolts)
40
0
-40
-80
40
50
60
70
80
90
100
110
120
Molar Polarization
x Para- Ethoxy benzoic Acid
o Meta-Chlorobenzoic Acid
Δ Para-Chlorobenzoic Acid

FIGURE 30

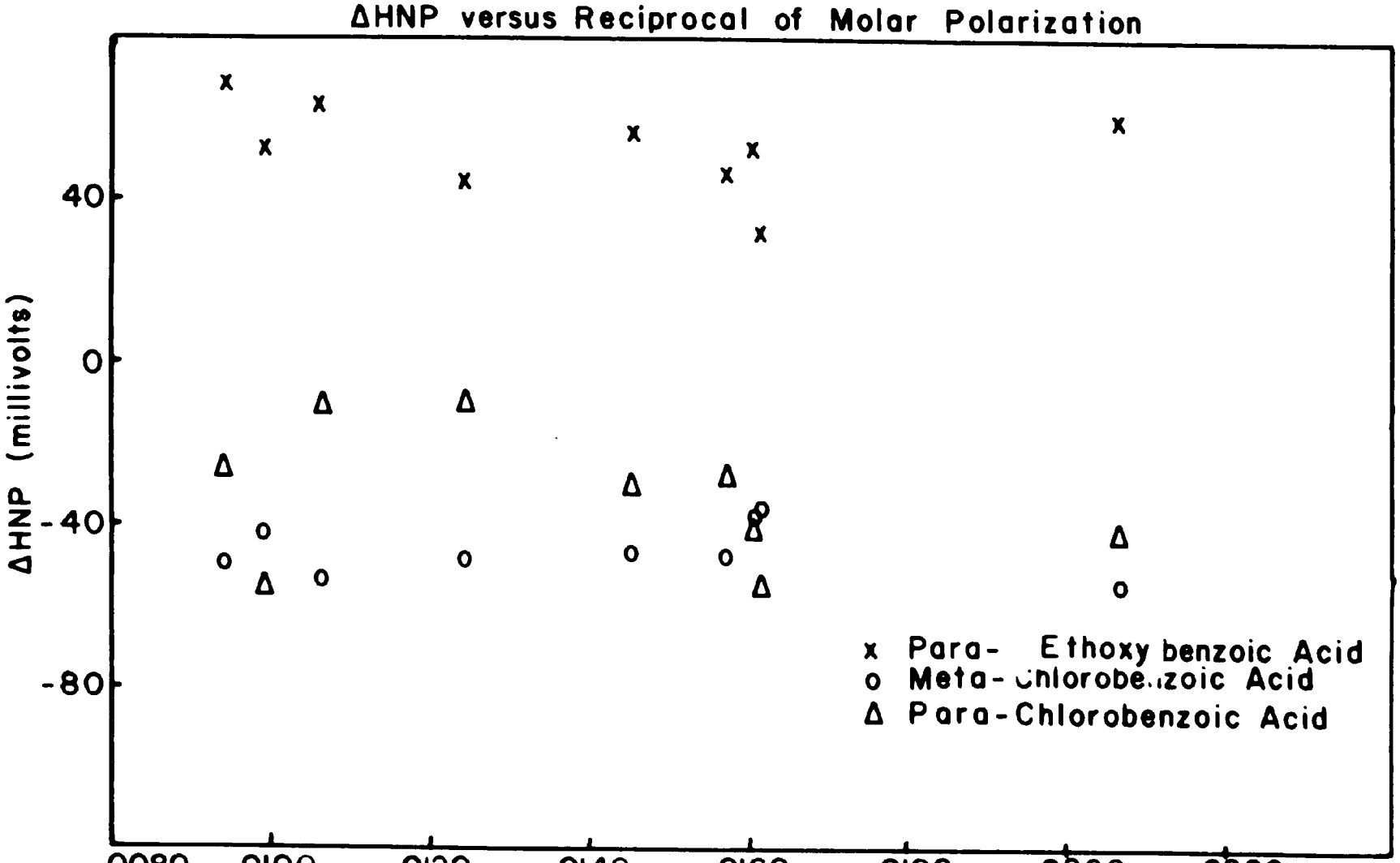

ΔHNP versus Reciprocal of Molar Polarization
ΔHNP (millivolts)
40
0
-40
-80
.0080
.0100
.0120
.0140
.0160
.0180
.0200
.0220
Reciprocal of Molar Polarization
x Para- Ethoxy benzoic Acid
o Meta-Chlorobenzoic Acid
Δ Para-Chlorobenzoic Acid

FIGURE 31

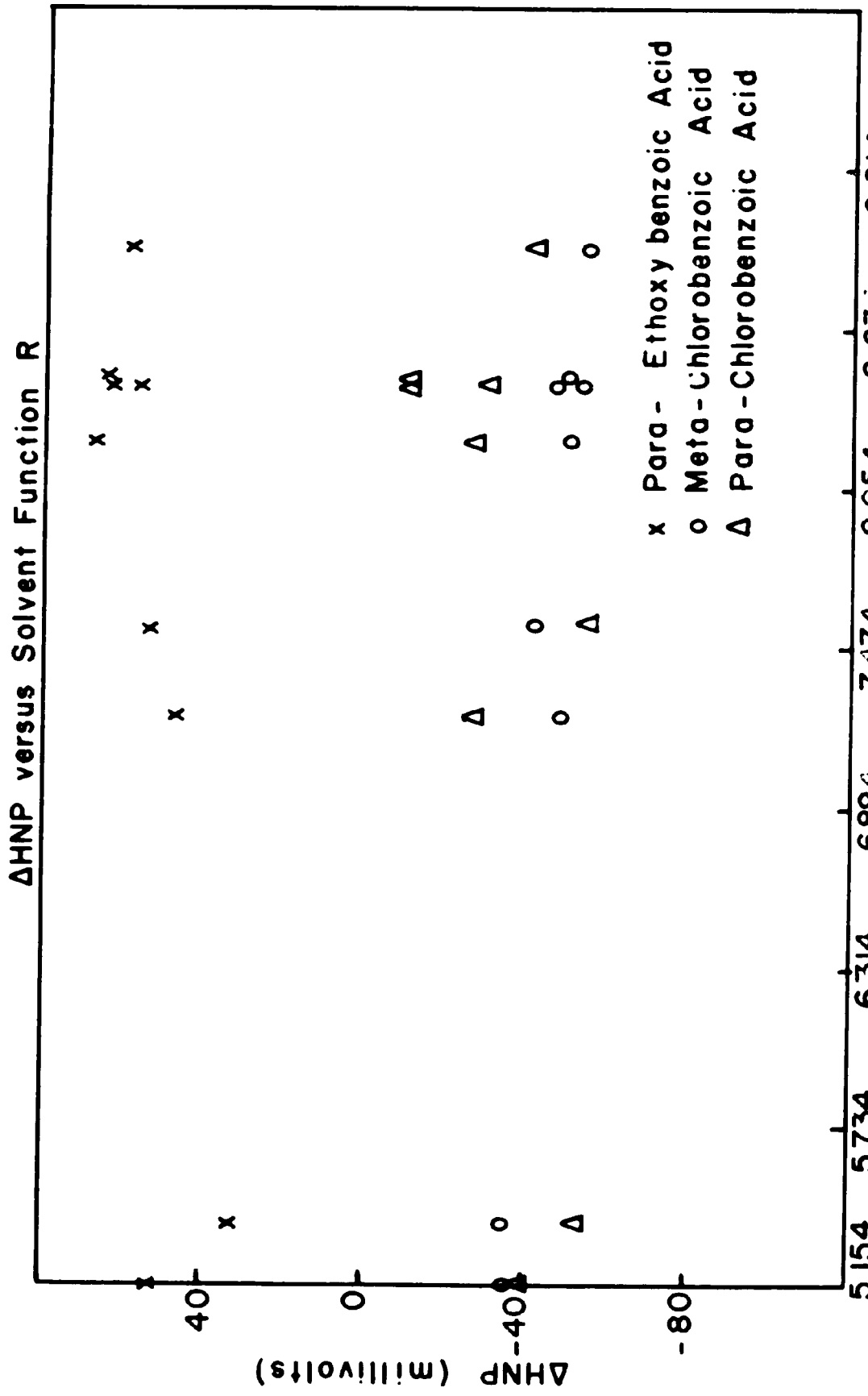

ΔHNP versus Solvent Function R
ΔHNP (millivolts)
40
0
-40
-80
5.154
5.734
6.314
6.894
7.474
8.054
8.634
9.214
R
x Para- Ethoxy benzoic Acid
o Meta-Chlorobenzoic Acid
Δ Para-Chlorobenzoic Acid

FIGURE 32

TABLE XXIX

CORRELATION OF AMINOBENZOIC ACID ΔHNP WITH SOLVENT FUNCTION R

Solvent	R	Graph Divisions	Meta Substituted Derivative		$\Delta\Delta$HNP	Para Substituted Derivative		$\Delta\Delta$HNP
			ΔHNP Exptl.	ΔHNP Calcd.		ΔHNP Exptl.	ΔHNP Calcd.	
Bromobenzene	5.154	0	~	~	~	104	100	4
Chlorobenzene	5.384	7.9	~	~	~	107	101	6
Pyridine	7.215	71.0	38	17	21	105	109	-4
4-Methyl-2-Pentanone	7.547	82.5	26	30	-4	107	110	-3
o-Nitrotoluene	8.215	105.5	~	~	~	94	112	-18
Nitrobenzene	8.410	112.3	78	63	15	90	114	-24
N, N'Dimethyl-formamide	8.424	112.8	48	63	-15	111	114	-3
2-Nitropropane	8.447	113.6	55	64	-9	86	114	-28
Acetonitrile	8.866	130.0	78	80	-2	118	116	2

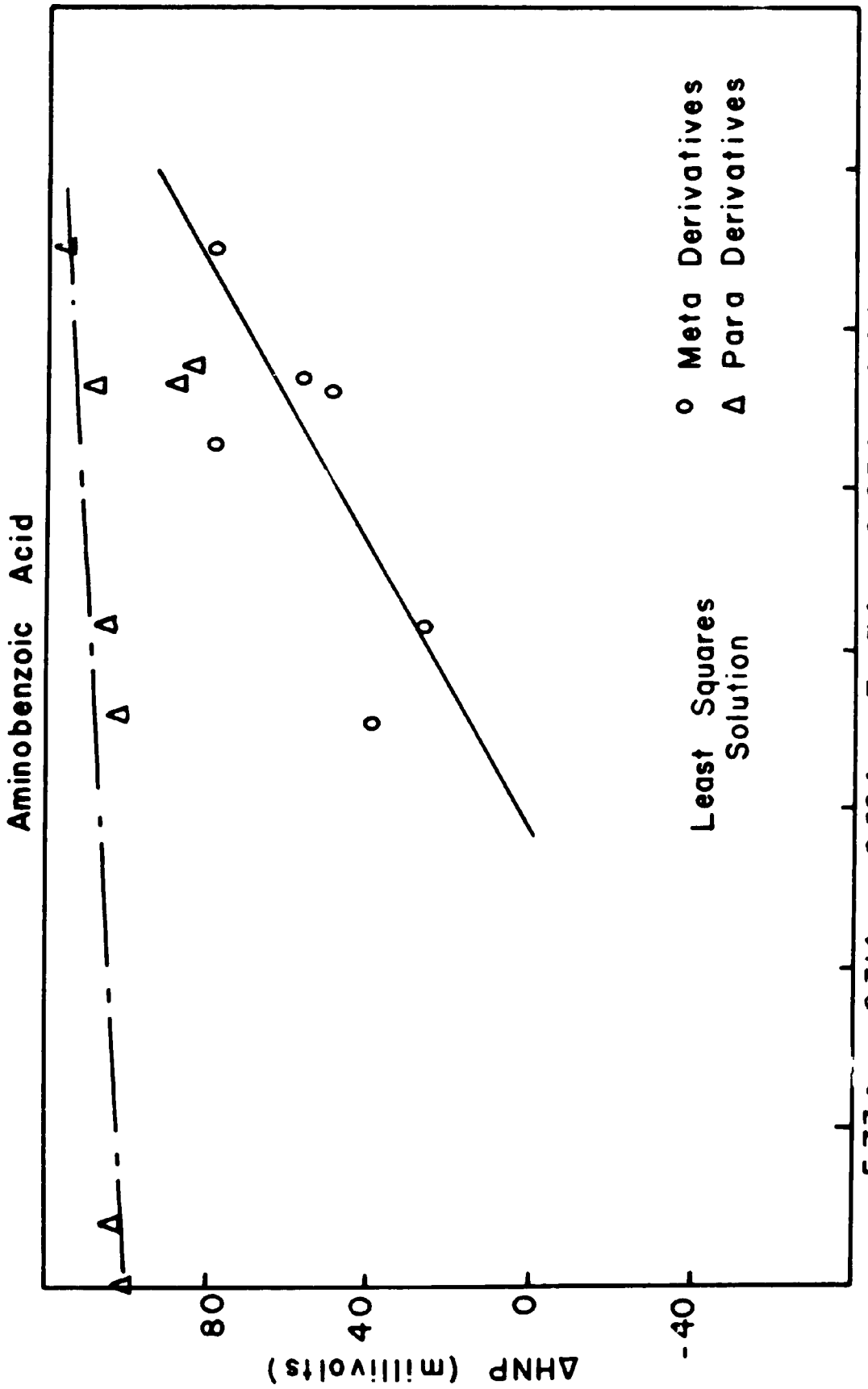

Aminobenzoic Acid
ΔHNP (millivolts)
80
40
0
-40
5.734
6.314
6.894
7.474
8.054
8.634
9.214
R
o Meta Derivatives
Δ Para Derivatives
Least Squares Solution

FIGURE 33

TABLE XXX

CORRELATION OF METHOXYBENZOIC ACID ΔHNP WITH SOLVENT FUNCTION R

Solvent	R	Graph Divisions	Meta Substituted Derivative		ΔΔHNP	Para Substituted Derivative		ΔΔHNP
			ΔHNP Exptl.	ΔHNP Calcd.		ΔHNP Exptl.	ΔHNP Calcd.	
Bromobenzene	5.154	0	20	18	2	61	16	45
Chlorobenzene	5.384	7.9	15	17	-2	38	19	19
Pyridine	7.215	71.0	-5	12	-17	45	46	-1
4-Methyl-2-Pentanone	7.547	82.5	5	12	-7	38	51	-13
o-Nitrotoluene	8.215	105.5	16	10	6	68	61	7
Nitrobenzene	8.410	112.3	-1	9	-10	69	64	5
N, N'Dimethyl-formamide	8.424	112.8	2	9	-7	59	64	-5
2-Nitropropane	8.447	113.6	21	9	12	61	64	-3
Acetonitrile	8.866	130.0	9	8	1	64	70	-6

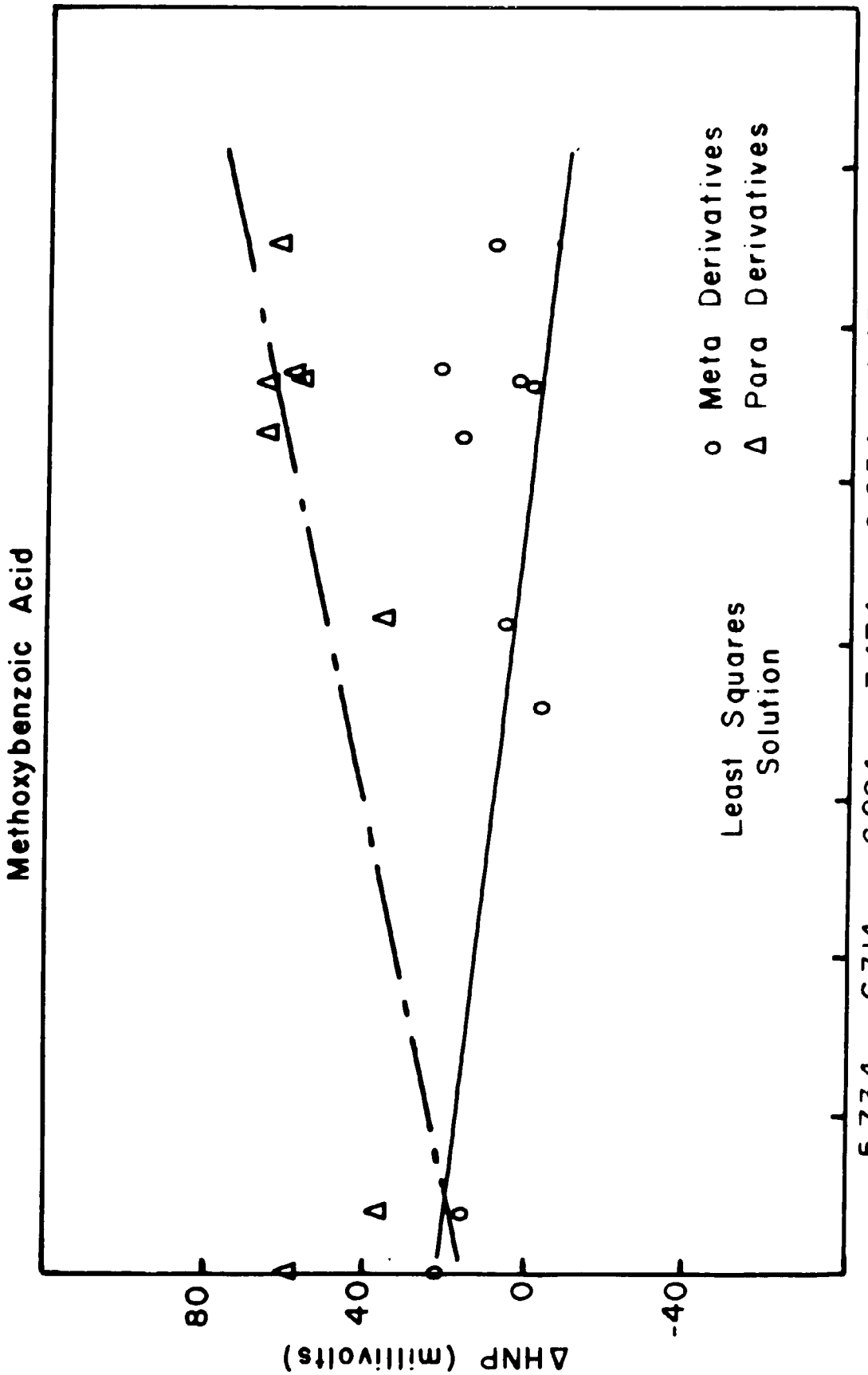

Methoxybenzoic Acid
ΔHNP (millivolts)
80
40
0
-40
5.734
6.314
6.894
7.474
8.054
8.634
9.214
R
o Meta Derivatives
Δ Para Derivatives
Least Squares Solution

FIGURE 34

DISCUSSION OF RESULTS

Substituted Benzoic Acids

The relative acidities of meta-and para-substituted benzoic acids in pyridine and in water are shown in Figure 6. The Δ HNP scale, previously described, where benzoic acid has a value of zero, is used for the non-aqueous solvent data and pKa values are used for the water scale. The data are listed in Table IV.

The linear relation between the solvents for the meta-and para-substituted benzoic acids is excellent (standard deviation is 0.11 pKa units). In pyridine the slope of the line is 130 mv/ pKa(H_2O). This span offers the possibility of separating acids which could not be distinguished from one another in water. The relation between pKa (H_2O) and HNP (pyridine) values is given by the equation

$$pKa = .00755 \Delta HNP + 4.21 \qquad (I)$$

The best fit of the data to a straight line was calculated by the least squares method. A statistical method, as illustrated by Davies (75), was employed to determine which points deviated significantly from the population of data under consideration. It was assumed that these data followed a normal distribution curve. Thus, if 2s is considered to be the value within which 95% of the data will fall, then values beyond 2s may be considered to be significantly different from

the universe of data under consideration.

The only value which is significantly different in pyridine is that for meta-aminobenzoic acid, (s = −.32) which is a stronger acid than is predicable by the equation. Infrared data (76) indicate the presence of NH_3^+ groups in the crystalline solid. If in solution the actual species titrated is NH_3^+, an enhancement in acidity would be expected, as the ionized form is less preferred in a low dielectric solvent. However, the fact that pyridine is a stronger base than aniline would seem to discount the presence of the zwitterion in solution. The more logical explanation in this case would seem to be that the basicity of pyridine tends to decrease the bond strength of the acidic hydrogen making it appear as a stronger acid.

If the line which describes the ratio of acidities in pyridine and in water for the meta-and para-substituted benzoid acids is taken as a normal criterion, all the points to the left of the line represent acids that are relatively weaker in pyridine than in water; all points to the right are drawn from acids that are relatively stronger in pyridine than in water.

In general it may be said that acids which can undergo internal hydrogen bonding or appear in charged form in a low dielectric solvent, will be stronger in that solvent than in water.

A correlation of Δ HNP in pyridine with Hammett's sigma values is found in Figure 7. The data are described in Table V

The linear relation between sigma and ΔHNP is given by the equation

$$\sigma = -.00678\,\Delta HNP + .053 \qquad (II)$$

The standard deviation, s, is 064. The only value which is not predicable within 2s is that for para-methyl benzoic acid (s = .203). This substituent should apparently have a sigma value which is more positive in nature than found by means of Hammett's equation. The general deviation of the para-alkyl group has been the subject of many investigations, with an equal number of concepts being arrived at to explain their anomalous behavior Baker, Dippy, and Page (77) determined the thermodynamic dissociation constants for a series of para-alkyl substituted benzoic acids. They found a partial inversion in the relative values of the dissociation constants, more than would be anticipated from inductive effects alone. They found that the para-ethyl and para-isopropyl derivatives were stronger acids than the methyl and tertiary-butyl compounds. Baker, however, postulated that in addition to hyperconjugation, heat capacity and entropy effects might be at least partly responsible for the observed order. Similar anomalous behavior, as has been mentioned previously, for the para-methyl derivatives wasfound by Kloosterziel and Backer (61) and Kochi and Hammond (63). Additional evidence in the support of the work of Kloosterziel and Backer was found during the course of this investigation when it was noticed that the para-isopropylbenzoic acid derivative behaves "normally". Of course, another explanation is possible, that

the sigma value derived from the dissociation constant of para-toluic acid is incorrect. This appears like a remote possibility in the light of work done by Dippy (77) on the determination of the dissociation constant of para-toluic by means of thermodynamic methods. Brieglieb and Bieber (78) checked Dippy's results when they arrived at a pKa (water) value of 4.34.

It is obvious that the behavior of this particular acid is anomalous, however, it is certain that the aqueous pKa values for the para-alkyl derivatives are not a real indication of the intrinsic acidity of the acid. If, at present, for the lack of some other logical explanation, we may examine the effect on ring resonance due to hyperconjugation in the light of the behavior of another electron contributing group, namely $-NH_2$, we may be able to get a clearer picture of what type of phenomenon is occurring in solution. However, for the moment let us examine the over-all picture in the light of specific deviations in the solvents investigated.

The relative acidities of the meta-and para-substituted benzoic acids in acetonitrile and water are shown in Figure 8. The linear agreementhere as shown by the standard deviation of .09 pKa units is excellent. The slope of the line was found to be 148 mv/pKa indicating that the resolving power of this solvent should be good. The equation for the line is represented by

$$pKa = .00637\,\Delta_{HNP} + 4.17 \qquad \text{(III)}$$

The data for this curve appears in Table VI.

Figure 9 illustrates the relationship between ΔHNP and sigma in acetonitrile represented by the equation

$$\sigma = -.00560 \Delta HNP + .073 \qquad (IV)$$

where the standard deviation is .095 sigma units. Here as in pyridine the meta-amino derivative of benzoic acid is significantly displaced from the "normal line" (s = .204).

Figure 10 illustrates the relative acidities of the substituted benzoic acid derivatives in 4-methyl-2-pentanone (methyl isobutyl-ketone). The equation for this relationship was found to be

$$pKa = .00688 \Delta HNP + 4.24 \qquad (V)$$

with a standard deviation, s, of .139 pKa units. The slope of the line is 136 mv/pKa.

Here as in the previously mentioned cases the meta-amino derivative is significantly (s = -.40) displaced from the line. However, in this solvent, methyl isobutyl ketone, it is possible for the zwitterion to exist because of the stronger acidic nature of the solvent. The data for the curve appear in Table VIII.

The correlation of sigma with ΔHNP in 4-methyl-2-pentanone is shown in Figure 11. The line is represented by the following equation

$$\sigma = .00624 \Delta HNP + .027 \qquad (VI)$$

with a standard deviation of .086 sigma units. As was the case in pyridine (ε = 12.3) with its low dielectric, so to in the case of

4-methyl-2-pentanone where the dielectric strength is 13.1, the para-methyl derivative is significantly (s = .197) displaced from the line.

The relationship between ΔHNP in 2-nitropropane and pKa(water) is shown in Figure 12. The equation for this line is represented by

$$pKa = .00719\,\Delta HNP + 4.12 \qquad \text{(VII)}$$

where the standard deviation is found to be .17 pKa units. The slope of the line is given as 134 mv/pKa. These data are found in Table X.

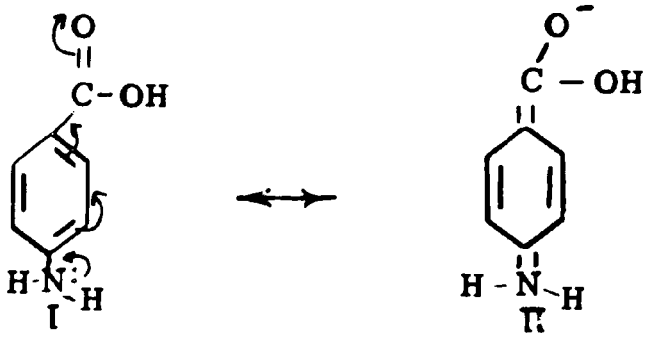
These data show that the para-methyl derivative is significantly displaced (s = .39) from the line, but in this solvent the deviation is much greater than in the previous solvents. The other acids do not deviate significantly from the normal line.

This deviation is shown also in Figure 13 where ΔHNP in 2-nitropropane is compared with sigma. The data appear in Table XI. The equation for the line was found to be

$$\sigma = -.00555\,\Delta HNP + .157 \qquad \text{(VIII)}$$

with a standard deviation of .177 sigma units. The para-methyl derivative shows its greatest deviation (s = .432) in this solvent, along with a deviation of s = .340 for the para-amino derivative.

The para-amino derivative of benzoic acid, which is apparently behaving as a stronger acid in this solvent has the following resonance configurations which decrease the strength of the acid .



Now, if in the case of an acidic solvent, the movement of the electron pair on the nitrogen should be inhibited by association with the solvent, the resonance of the carbonyl carbon with the ring would be affected. One result of this might be that the bond between the oxygen and hydrogen atoms would be weakened allowing the hydrogen to react more easily, thus resulting in an apparent increase in acidity of the molecule.

This deviation is not seen in the solvents ortho-nitrotoluene and nitrobenzene as shown in Figures 14, 15, 16, and 17 where the acidic nature of the solvent in less than that shown by 2-nitropropane. The equations for these lines are as follows

Figure 14

$$pKa = .00687 \Delta HNP + 4.09 \qquad (IX)$$

where s = .156 and the slope of the line is 146 mv/pKa.

Figure 15

$$\sigma = .00568 \Delta HNP + .215 \qquad (X)$$

where s = .189 sigma units.

Figure 16

$$pKa = .00659 \Delta HNP + 4.17 \qquad (XI)$$

where s = .151 pKa units and the slope of the line is 144 mv/pKa

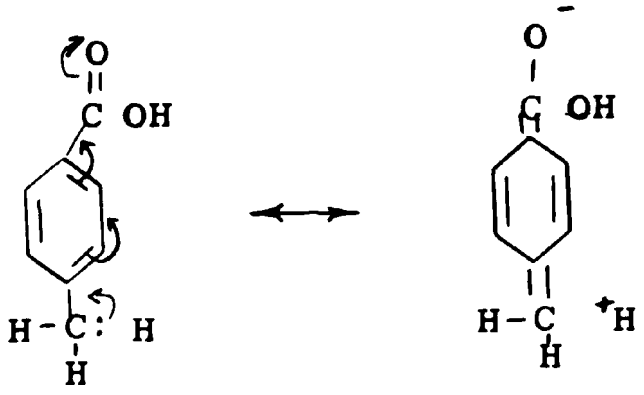
Figure 17

$$\sigma = -.0051 \Delta \text{HNP} + .0903 \qquad \text{(XII)}$$

where the standard deviation, s, is .157 sigma units. The data for these figures appear in Tables XII, XIII, XIV, and XV, respectively.

The para-methyl substituted benzoic acid also shows some of its greatest deviations in o-nitrotoluene and nitrobenzene. If we accept the possibility that the solvent association with the molecule will affect the resonant structure of the molecule, then using a similar explanation as that employed for para-aminobenzoic acid the following events might occur.

Considering the possibility of hyperconjugation which would ordinarily decrease the acidity of the molecule we may write the following resonant structures:



III IV

Essentially then, this is the same phenomenon occurring in the case of para-aminobenzoic acid. Conceivably then, it would be possible for the solvent to associate with the molecule in such a manner as to impede the movement of electrons toward the ring resulting in a comparatively stronger acid molecule.

Para-nitrobenzoic acid shows a deviation beyond 2s in the solvent nitrobenzene. In this solvent the substituted benzoic acid is acting as a weaker acid than in water. This is difficult to explain except on the basis of a possible interaction of the solvent with the resonanting molecule. Now it is well known that nitrobenzene will act as a base in the reaction with the Lewis acid $AlCl_3$. This presents the possibility that the nitrobenzene molecule is reacting in some manner with the nitro group of the substituted benzoic acid to reduce its electron withdrawing capacity, perhaps with the positively charged nitrogen.

In the solvent, N, N'dimethylformamide, as in pyridine, the behavior of the substituted benzoic acids is similar. In Figure 18, it is seen that once again the meta-amino group is significantly (s = −.31) displaced from the behavior of the other acids. Here also it is possible for the zwitterion to be stabilized, resulting in a stronger acid. The equation for this line is

$$pKa = .00695\Delta HNP + 4.18 \qquad \text{(XIII)}$$

where s = .108 and the line has a slope of 140 mv/pKa. These data appear in Table XVI.

The similarity of the solvents may again be seen when Figure 19, a plot of sigma versus Δ HNP in N, N'dimethylformamide is compared to Figure 7. In this solvent, as in pyridine, the para-methyl substituted derivative is displaced from the normal line in the direction of increasing acidity. Here the equation for the line is represented by the equation

$$\sigma = -.00623 \Delta \text{HNP} + .103 \qquad \text{(XIV)}$$

where s = .089. These data are tabulated in Table XVII.

This phenomenon implies that here also the solvent is reacting with the substituted benzoic acid molecule in such a manner as to reduce the activation energy of the molecule or effect the resonance structure resulting in an increase in acidity. However, the para-isopropyl derivative follows a more normal behavior.

The plot showing the relationship of pKa with ΔHNP for the meta- and para-substituted benzoic acids in chlorobenzene is shown in Figure 20. The least squares solution of the data for this line resulted in the equation

$$\text{pKa} = .00704 \Delta \text{HNP} + 4.10 \qquad \text{(XV)}$$

where s = .15 and the slope of the line is 136 mv/pKa.

Despite the low dielectric and the poor solvent properties the data show excellent correlation, since none of the values fell outside the normal distribution at the 95% level. These data are tabulated in Table XVIII.

The correlation of ΔHNP with sigma is shown in Figure 21. The equation for this line is

$$\sigma = -.00639\,\Delta\text{HNP} + .136 \qquad \text{(XVI)}$$

with a standard deviation of .156 sigma units. The data appear in Table XIX.

Figure 22 shows the relationship between ΔHNP and pKa in bromobenzene. The equation for this line is

$$\text{pKa} = .00644\,\Delta\text{HNP} + 4.16 \qquad \text{(XVII)}$$

where the slope is 152 mv/pKa and the standard deviation, s, is .110. The correlation in this solvent is excellent. These data appear in Table XX.

A plot of Δ HNP of the meta-and para-substituted benzoic acids versus sigma is shown in Figure 23. The equation for this line is

$$\sigma = -.00602\,\Delta\text{HNP} + .142 \qquad \text{(XVIII)}$$

with a standard deviation of .141. In consideration of the low dielectric of the solvent this also is excellent.

The equations mentioned in the preceeding discussion are summarized in the following table:

TABLE XXX!

TABULATION OF pKa AND SIGMA EQUATIONS FOR SUBSTITUTED BENZOIC ACID DERIVATIVES

Solvent	Relation with pKa	Relation with Sigma
Pyridine	pKa= 00755 △ HNP+4. 21	σ=-. 00678△HNP+. 053
Acetonitrile	pKa=. 00637 △ HNP+4. 17	σ=-. 00560△HNP+. 073
4-Methyl-2-Pentanone	pKa=. 00688 △HNP+4. 24	σ =-. 00624△HNP+. 027
2-Nitropropane	pKa=. 00719 △ HNP+4. 12	σ=-. 00555△HNP+. 157
o-Nitrotoluene	pKa=. 00687 △ HNP+4. 09	σ=-. 00568△HNP+. 215
Nitrobenzene	pKa=. 00659△ HNP+4. 17	σ=-. 0051 △ HNP+. 090
N, N'Dimethylformamide	pKa=. 00695 △HNP+4. 18	σ=-. 00623△HNP+ 103
Chlorobenzene	pKa=. 00704 △ HNP+4. 10	σ=-. 00639△HNP+. 136
Bromobenzene	pKa=. 00644 △ HNP+4. 16	σ=-. 00602△HNP+. 142

Substituted Phenols

During the course of this investigation it was thought that a brief study of the behavior of phenols might provide additional information as to the behavior of acids in solution. An attempt to correlate the sigma values for phenols with those of the substituted benzoic acids was unsuccessful. This is not surprising in the light of Hammett's (31) findings that the sigma values for phenol and aniline derivatives did not match those for the substituted benzoic acids.

Figure 24 illustrates the correlation between ΔHNP and pKa (water) in 4-methyl-2-pentanone. The equation for this line is

$$pKa = .0082\,\Delta HNP + 7.42 \qquad (XIX)$$

where the standard deviation is .146 pKa units. These data appear in Table XXII.

Figure 25 demonstrates the relationship between ΔHNP and sigma in 4-methyl-2-pentanone. The equation for the line was found to be

$$\sigma = -.004\,\Delta HNP + 1.184 \qquad (XX)$$

where the standard deviation was found to be .06 sigma units. These data appear in Table XXIII

The relationship between ΔHNP and sigma in the solvent N, N'dimethylformamide is shown in Figure 26. The equation for this line is

$$pKa = .0264\,\Delta HNP + 5.24 \qquad (XXI)$$

where the standard deviation is .07 pKa units and the slope of the

line is 36 mv/pKa. These data appear in Table XXIV

The comparison of Δ HNP with sigma is seen in Figure 27 The equation for this line is

$$\sigma = 0120\Delta HNP + 2\ 153 \qquad \text{(XXII)}$$

with a standard deviation of s = 06 sigma units

The equations mentioned in the preceeding section are summarized in Table XXXII.

TABLE XXXII

TABULATION OF pKa AND SIGMA EQUATIONS FOR SUBSTITUTED PHENOL DERIVATIVES

Solvent	Relation with pKa	Relation with Sigma
4-Methyl-2-Pentanone	pKa= 0082ΔHNP + 7 42	σ=-.004ΔHNP+1 184
N, N'Dimethylformamide	pKa= 0264ΔHNP + 5 24	σ=.0120ΔHNP+2 153

It is apparent then that although the relationship between sigma pKa and ΔHNP hold within the phenol family, it forms a distinct and separate relationship from that of the substituted benzoic acid derivatives.

Solvent Relationship

This investigation studied the possibility of relating the ΔHNP of a substituted benzoic acid derivative with a particular solvent

function which would allow the investigator to predict the value of ΔHNP in the solvent, this would enable him to determine whether or not an acid could be titrated in that particular solvent or whether or not it would be possible to resolve a particular acid pair. Previous investigators (71) have shown that it is possible to resolve an acid pair provided that their HNP's differ by at least 138 millivolts.

Figures 28 through 31 indicate the attempt to correlate the ΔHNP values with simple solvent properties such as dielectric constant, refractive index, and molar polarization. A wide scatter of points was obtained when these values were plotted against the ΔHNP of a particular acid in a variation of solvents. However, there was no statistical basis for assuming that these values were related to the solvent function being investigated. A further attempt (Figure 32) employing McRae's equation (66), mentioned in the theoretical section as Equation XII, provided very little additional information as to the ability to predict the value of Δ HNP through the use of easily obtainable solvent constants (see appendix for calculations). However, it was noticed that there was an apparent smaller degree of scatter when the R values were plotted against Δ HNP. There was one notable exception, that being the case of meta-aminobenzoic acid. Here the ΔHNP value appeared to be related to the solvent function R and an equation was derived from the least squares analysis of the points which appeared to predict the ΔHNP value fairly accurately. This equation was found

to be

$$R = .026\ \Delta HNP + 6.78 \qquad \text{(XXIII)}$$

Since it has been demonstrated (79) that the zwitterion species exists in water, a reasonable explanation for the increased acidity can be suggested on the basis of increased attraction between the zwitterion hydrogen and the negatively charged oxygen of the carboxyl group. The increased attractive force would tend to pull the hydrogen toward the oxygen, and since the distance between the two groups is too great to form a hydrogen bond, the electron density around the hydrogen would be decreased, consequently, the removal of the proton by the titrant would be easier, resulting in an apparent increase in acidity.

The para-amino derivative appeared to be insensitive to changes in the solvent function R.

It was noted during these attempts to correlate the solvent function R with Δ HNP that the Δ HNP's of the meta and para isomers of a particular acid (Figure 34) appear to show a divergence in solvents of increasing R value. Although statistically the values did not have a high degree of dependence, it indicated that further work in solvents having very high values of dielectric constant such as HCN or the substituted acetamides, should be investigated to see if the trend toward divergency continued. If it did, it would be a new method for separating acid isomers or acid mixtures.

No attempt was made to correlate the Δ HNP of phenols with the solvent function equation because of the lack of sufficient data to draw suitable conclusions about their behavior. It was felt that the indicated correlation between pKa and sigma with Δ HNP was sufficient to show the similarity in behavior between the derivatives of phenol and benzoic acid.

In general, the equations for the correlation of pKa and sigma may be written as follows:

$$pKa = A \Delta HNP + B \qquad \text{(XXIV)}$$

$$\sigma = C \Delta HNP + D \qquad \text{(XXV)}$$

CONCLUSIONS

This investigation of the behavior of substituted aromatic acids in non-aqueous solvents can be summarized by the following conclusions:

1. a correlation between ΔHNP and pKa (water), with appropriate equations, has been shown to exist in solvents other than pyridine.

2. a correlation between ΔHNP and Hammett's sigma value has been demonstrated. These results have been translated into equation form.

3. the substituted phenols have been shown to form their own family of curves rather than being related in a direct way with the substituted benzoic acid derivatives.

4. the use of the developed mathematical relationships will aid the analytical chemist in making predications about the ability to titrate two different acids in a particular solvent.

5. indicates a possible extension of this type of investigation to aromatic organic bases and aliphatic acids.

6. provides a foundation for future work on solvent correlations.

7. indicates that the comparative acidity of the substituted benzoic acid derivatives studied is reasonably constant, when compared to benzoic acid in the solvents investigated, with the notably exception of the meta-aminobenzoic acid derivative.

APPENDIX

Definitions

1. Differentiating and Leveling Solvents: Solvents in which typical electrolytes are equally strong are known as leveling solvents. Those in which differentiation in strength of electrolyte occurs are known as differentiating solvents.

2. Solvolysis: When the dissolved solute reacts with the solvent in such a way that the normal anion and cation concentrations of the solvent are changed, the solute is said to have undergone solvolysis.

3. Solvation Reactions: The process of solvation results in the attachment of the solvent molecule to the cation, anion, or a molecule of solute, either by coordination or by hydrogen bonding.

4. Basic Solvent: A solvent which will form the onium ion readily, or is able to denote a pair of electrons.

5. Acidic Solvent: A solvent which tends to dissociate the hydrogen ion readily, or is able to accept a pair of electrons.

6. Amphiprotic Solvent: Solvents capable of acting as electron pair donors, but will under the proper circumstances also dissociate the proton to a dissolved solute.

7. Aprotic Solvent: Solvents which have no affinity for the proton or which are incapable of the dissociating the proton.

PARTS LIST FOR D. C. ELECTROMETER

A. Tubes

V1, type 932 Electrometer

V2, type 1L4

V3, V6 type 6AK6

V4, type VR105

V5, type 6Y6G

V7, type 6X4

P, 110v type neon pilot light

B. Input Panel

1. special brass plus synthane machine parts

2. 1 binding post

C. Recorder Output

1. insulated banana jacks and plugs

D. Power Inlet

1. 6 ft. twin power cord

2. 1 male 110v plug

E. Condensers

C1, 250 mmfd-400v paper

C2, .005 mfd-postage stamp mica

C3, 10 mmfd - postage stamp mica

C4, 0.1 mfd - 600v paper

C5, .05 mfd - 400v paper

C6, .25 mfd - 400v paper

C7, C8 20-20 mfd-electrolytic dual 450v common negative can

C9, 1000-1000 mfd electrolytic dual 15v

F. Potentiometers

P1, 10,000 ohm wire wound

P2, 1000 ohm wire wound

P3, 100 ohm wire wound

G. Resistors

R1, 10 ohm 1 watt 5%

R2, 50 ohm 10 watt slider variable

R3, 20 ohm 1 watt 10%

R4, 430 ohm 2 watt 5%

R5, 82 ohm 1 watt 5%

R6, R7 22 megohm 1/2 watt 10%

R8, 2 megohm 1/2 watt 5%

R9, 430 ohm 2 watt 5%

R10, 820 ohm 2 watt 5%

R11, 22 megohm 1/2 watt 5%

R12, 5.6 megohm 1/2 watt 5%

R13, 1.2 K ohm 10 watt 5%

R14, 27 K ohm 2 watt 10%

R15, 408.5 ohm special wire wound precision shunt

R16, 506.5 ohm special wire wound precision shunt

R17, 10 ohm special wire wound precision shunt

R18, 20 ohm 1/2 watt 5%

R19, 1100 ohm 10 watt 5%

R20, 300 ohm 2 watt 5%

R21, 270 ohm 2 watt 5%

R22, 200 K ohm 1/2 watt 5%

R23, R24 18 K ohm 2 watt 10%

R25, 1 megohm 1/2 watt 10%

R26, 3000 ohm 1/2 watt 5%

R27, 4000 ohm 10 watt 10%

R28, 9.1 megohm 1/2 watt 5%

R29, 10 megohm 1/2 watt 10%

R30, R31, 100 ohm 1, 2 watt 10%

R32, R33, 500 ohm 1 watt 10%

R34, 10 megohm 1/2 watt 10%

H. Sockets

1. 2-octal amphenol

2. 4-minature 7 pin ceramic

3. 2-one inch pilot light assembly and jewel

4. 1-standard 4 prong plug for 932

I. Switches

S1, DPST toggle

S2, 2-pole, 2-position Central Lab No. 1405

S3, 4-pole, 4-position Central Lab No. 2515

J. Fuses

1. double little fuse holder (chassis mounting)

2. 2-2 ampere fuses

K. Transformers

1. T-1 Merritt P3148 (1 plate winding, 1-6.3v winding)

2. T-2 Thordarson T22-R32

L. Indicator

1. Weston voltmeter model 269(0-1 v in 0.01 v divisions and 1000 ohm resistance)

PARTS LIST FOR SWITCHING PANEL

A. Switches

S1, DPST toggle

S2, S3, SPST toggle

S4, Type Z microswitch

B. Sockets

1. 3-pilot lights 110 v

2. Series 202 plugs and sockets (Allied)

C. Input Panel

1. Insulated banana jacks and plugs

D. Fuses

1. 2-10 ampere fuses and holder

PARTS LIST FOR SYRINGE DRIVE

A. Spur Gears*

1. 1-40 tooth NA-40 20 pitch 3/8" face 2.000 Pitch Diameter
2. 1-24 tooth NA-24 20 pitch 3/8" face 1.200 Pitch Diameter

B. Sprocket Gears

1. 2-20 tooth K2520 3/8" hole diameter 1.60 Pitch Diameter
2. 2-15 tooth K2515 5/16" hole diameter 1.20 Pitch Diameter
3. 2-10 tooth K2510 1/4" hole diameter 0.81 Pitch Diameter
4. 1 idler gear K2515
5. 1-9 tooth ladder chain sprocket gear CA-9
6. 1-20 tooth ladder chain sprocket gear CA-20

C. Couplings

1. 1-FA 75 5/16" hole diameter 3/4" O.D.
2. 1-FA 75 3/8" hole diameter 3/4" O.D.

D. Chains

1. 1-1/4" single pitch rollerless chain
2. 1A ladder chain

E. Lead Screw

1. 1-20 Pitch 7/16" diameter turned to 3/8" to accept gears

F. Guide Bars

1. 2-smooth steel rods 3/8" diameter

G. Bushings

1. All bushings machined from solid brass stock

H. Motor

1. Bodine Type NSY-12R 115 volt AC .53 amperes, 1800 rpm, 1/150 HP Continuous duty

* All gears listed in Boston Gear Catalog No. 56

SAMPLE CALCULATION OF LEAST SQUARES METHOD OF ANALYSIS

HNP X	pKa Y
-49	3.83
-63	3.81
-44	3.85
38	4.82
16	4.27
-97	3.49
-5	4.09
-25	3.98
-30	3.97
-24	4.02
105	4.92
3	4.37
-92	3.42
45	4.47
46	4.44

$\Sigma X = -176$

$\bar{X} = 11.73$

$\Sigma X^2 = 45,180$

$(\Sigma x)^2 = 30,976$

$\frac{(\Sigma X)^2}{N} = 2065.06$

$\Sigma Y = 61.75$

$\bar{Y} = 4.116$

$\Sigma XY = -399.22$

$\bar{Y}\Sigma X = -725.12$

$\Sigma X^2 - (\Sigma x)^2/N =$

$= 45,180 - 2065.1$

$= 43,114.94$

$\Sigma XY - \bar{Y}\Sigma X =$

$= 399.22 - (-725.12)$

$= 325.90$

$b = \frac{325.90}{43,114.94} = .00755$

$Y = \bar{Y} + b(X - \bar{X})$

$pKa = 4.21 + .00755 \Delta HNP$

CALCULATION OF SOLVENT FUNCTION R

Cpd.	n_D	$\frac{n_p^2 - 1}{2n_s^2 + 1}$	$\frac{n_p^2 - 1}{n_s^2 + 2}$	D	$\frac{D-1}{D+2}$	$\left[\frac{D-1}{D+2} - \frac{n_s^2-1}{n_s^2+2}\right]$
C_6H_5Br	1.5604	.2444	.3235	5.4	.5945	.2710
C_6H_5Cl	1.5251	.2346	.3065	5.7	.6103	.3038
Pyridine	1.509	.2299	.2986	12.3	.7902	.4916
MIBK	1.396	.1937	.2403	13.1	.8013	.5610
o-Nitro-toluene	1.5474	.2409	.3173	27.4	.8979	.5806
$C_6H_5NO_2$	1.5524	.2423	.3197	34.8	.9184	.5987
N, N'DMF	1.4280	.2046	.2573	26.6	.8951	.6378
2-Nitro-propane	1.3941	.1931	.2393	25.5	.8909	.6516
CH_3CN	1.3460	.1756	.2129	37.5	.9240	.7110

$$R = B\left[\frac{n_s^2 - 1}{2n_s^2 + 1}\right] + C\left[\left(\frac{D - 1}{D + 2}\right) - \left(\frac{n_s^2 - 1}{n_s^2 + 2}\right)\right]$$

C_6H_5Br	10 (.2444) + 10 (.2710) = 5.154
C_6H_5Cl	10 (.2346) + 10 (.3038) = 5.384
Pyridine	10 (.2299) + 10 (.4916) = 7.215
MIBK	10 (.1937) + 10 (.5610) = 7.547
o-Nitro toluene	10 (.2409) + 10 (.5806) = 8.215
$C_6H_5NO_2$	10 (.2423) + 10 (.5987) = 8.410
N, N'DMF	10 (.2046) + 10 (.6378) = 8.424
2-Nitro propane	10 (.1931) + 10 (.6516) = 8.447
CH_3CN	10 (.1756) + 10 (.7110) = 8.866

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VITA

Roy Richardson Hurlbut Miron, son of Murray R. Miron and Myrtle E. (deceased) Miron, was born on February 22, 1928 in Philadelphia, Pennsylvania. During the early years of the depression he moved to Allentown, Pennsylvania and after attending public schools in Allentown, he entered Lehigh University in June, 1945. He attended Lehigh until February 1946 at which time he entered the United States Army.

He received his basic training at Camp Crowder, Missouri after which he was selected to attend radio school at Fort Monmouth, New Jersey in May 1946. He was sent to Hawaii in November of the same year where he served at the Helemano Radio Station until his discharge on August 7, 1947 at Fort Lewis, Washington. While awaiting to re-enter Lehigh University, he attended the Bethlehem Area College for veterans.

In the Fall of 1947 he entered Lehigh as a sophomore in the College of Arts and Sciences, majoring in Chemistry. The following year he married Miss Doris E. Krick of Lyndhurst, New Jersey. In 1951 he was graduated from Lehigh with the degree of Bachelor of Arts.

Immediately after graduating from Lehigh University, he entered Middlebury College, Middlebury, Vermont as a graduate assistant

in chemistry. During his graduate studies his marriage was blessed with the birth of a son, Bruce Richardson. The degree of Master of Science was awarded in 1953.

After receiving his M. S. in Chemistry he was employed by the American Cyanamid Company, as a trainee in the Plastics and Resins Division. In October 1954 he was promoted to technical salesman and assigned to the Cleveland, Ohio office. In this position he was required to give technical assistance to over 150 customers, some of which included companies such as Goodyear Aircraft, Firestone Tire and Rubber, General Electric, and Westinghouse. In February, 1955, another son, Craig William was born. When the opportunity for a postion which required a Ph. D. occurred in the Sales Development Group, he applied for an educational leave of absence in order to continue his studies. He entered Lehigh University in the Fall of 1956 as a candidate for the degree of Doctor of Philosophy. During this period he held a research grant from the United States Steel Foundation, and became the father of two girls, Kathy Lee and Sheila Bonnie.

Mr. Miron is co-author of a paper entitled "Relative Acidities Of Organic Acids In Pyridine And Water", and a co-owner of Patent Number 2, 822, 343, assigned to the American Cyanamid Company.