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STRONGLY BASIC SYSTEMS

by

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# ABSTRACT

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In the last decade there has been considerable interest in strongly basic solutions and Hammett  $H_-$  acidity functions have been defined for various solvent systems. However some doubts still remain about the ionization modes of certain indicators which were used to determine these  $H_-$  functions, and the  $pK_a$  values assigned to weak carbon acids.

A careful anchoring of the  $H_-$  scale for the system dimethylsulfoxide-water-0.011 molar tetramethylammonium hydroxide with 2,4,4'-trinitrodiphenylamine was undertaken. The lower region of this scale correlates well with the recently published  $H_-$  function for the more basic regions.

To study the dependence of  $H_-$  functions on indicator structure, the ionization of nitrogen and oxygen acids were compared in strongly basic systems. The solvent systems used in the study were dimethylsulfoxide-methanol-0.01 molar sodium methoxide and dimethylsulfoxide-ethanol-0.01 molar sodium ethoxide. The shallow rise of the  $H_-^O$  function for phenols as compared to that of the  $H_-^N$  for diphenylamine is believed to be caused by the smaller degree of

charge delocalization in the phenolate anions than in the amide ions.

The dissociation constants of 15 substituted nitrodiphenylamines were determined in the two previously mentioned alcoholic dimethylsulfoxide systems, and in the aqueous dimethylsulfoxide system. The "similar colour indicator" postulate was elaborated on the observation that the relative acidity of Hammett-type indicators remains constant through changes in solvent environment only if their spectral characteristics are similar.

Linear free energy relationships between the  $pK$  values of 30 substituted diphenylamines and the substituent constant,  $\sigma^0$ , were drawn. The  $\rho$  value in excess of 4 for monosubstituted diphenylamines compared with  $\rho$  values of the order of 2 for nitrosubstituted diphenylamines, results from the low degree of conjugation between the central N atom and the ring substituent whenever a nitro group is present in the other ring.

The base-catalyzed rates of detritiation of various hydrocarbons were determined in dimethylsulfoxide mixtures. The logarithm of these rates were correlated with the thermodynamic basicity of the medium as measured by the  $H_-^N$  function and gave excellent straight lines with slopes around 0.8. The theoretical basis of such correlations is discussed, and it was concluded that the logarithm of the rates should be correlated with  $H_- + \log a_{ROH}$ . In the case of methanolic dimethylsulfoxide the activity of methanol has been determined, giving corrected correlations with slopes around 0.9.



The qualitative limitation due to the use of  $H_-^N$  instead of  $H_-^C$  functions is also discussed.

The activation parameters for these detritiations have been determined. The enthalpies of activation were found to increase with decreasing acidity of the hydrocarbon. These variations in enthalpy of activation, coupled with variation in the kinetic isotope effect and the observed Bronsted relationship have been interpreted in terms of a mechanism involving a rate-determining pre-equilibrium step with a transition state of increasing asymmetry.

A critical examination of the  $H_-^C$  scale for carbon acids in dimethylsulfoxide-ethanol-0.01 molar sodium ethoxide was made. The failure of the scale probably results from the fact that, for a number of indicators, proton abstraction is followed by a reaction between the carbanion and the neutral molecule to give a radical and radical anion. The carbanions of three nitrophenylmethanes were prepared in hexamethylphosphoramide and unequivocally identified by high resolution nuclear magnetic resonance. The spectral characteristics of the carbanions were recorded and compared with previously published values. The radical anions of these nitrophenylmethanes were generated electrochemically and their e.s.r. spectra measured. The variation in  $^{14}N$  hyperfine coupling constant ( $a_N$ ) of these radical anions indicated a large solvent shift in the absorption maxima.

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## INTRODUCTION

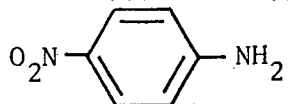
In a recently published review<sup>1</sup> on H<sub>+</sub> acidity functions, strongly basic systems have been arbitrarily defined as those solutions which ionize acids with an ability equal to or greater than 0.1 M aqueous alkali metal hydroxide solutions.

There are several methods of producing strongly basic systems. Of the two most common, the first consists of preparing a solution of a protic solvent and a salt of its conjugate base (e.g., sodium hydroxide-water), the basicity of the system increasing with increase of the base concentration. The second one, which produces startling effects, makes use of a binary solvent system: a protic and a polar aprotic solvent with a small concentration of the conjugate base of the protic partner. In this case the ability of the base to remove a proton from a weak acid is increased by increasing the concentration of the polar aprotic solvent. Indeed there have been cases reported in the literature<sup>2</sup> in which these methods were coupled, i.e. increasing the base concentration in a system consisting of a fixed percent polar solvent in a protic one.

The increase in ability of hydroxide ions to remove a proton from a weak acid by addition of a polar aprotic solvent like dimethylsulfoxide (DMSO) can be illustrated by the data in Table I which shows the effect of DMSO on the degree of ionization of three aromatic amines in solution each 0.01 M in hydroxide ion.

TABLE I\*

Degree of Ionization of Weak Acids, HA, in 0.01 M OH<sup>-</sup> Solutions

HA	Water	92 mole % DMSO	99.6 mole % DMSO
	undetectable	complete	complete
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH	undetectable	half	complete
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	undetectable	undetectable	one-tenth

Effectively there is a 10<sup>14</sup> fold increase in the basicity of the system toward aromatic amines by replacing water by DMSO. Table II shows how the degree of ionization of aniline (pK<sub>a</sub> = 27.3) varies with solvent enrichment in DMSO.

TABLE II\*

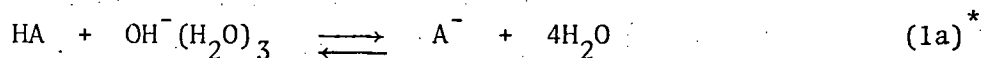
Degree of Ionization of Aniline, pK<sub>a</sub> = 27.3 in aqueous

DMSO, [OH<sup>-</sup>] = 0.01

wt - % DMSO	mole- % DMSO	H <sub>-</sub>	$\frac{[C_6H_5NH^-]}{[C_6H_5NH_2]}$
0	0	12.0	10 <sup>-15</sup>
20	5.45	12.6	10 <sup>-15</sup>
40	13.4	13.6	10 <sup>-14</sup>
†— 60	25.7	15.1	10 <sup>-12</sup>
80	48.0	17.3	10 <sup>-10</sup>
90	67.6	19.2	10 <sup>-8</sup>
95	81.5	20.8	10 <sup>-7</sup>
99.9	99.6	26.2	0.1
† in 66 wt % DMSO [C <sub>6</sub> H <sub>5</sub> NH <sup>-</sup> ] = [C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup> ]			

\* Table I and II are taken from reference (3).

This increase in basicity has been rationalized<sup>3,4</sup> by considering the effect of addition of DMSO on the equilibrium shown in equation (1a)



By addition of DMSO the activity of water will be lowered<sup>6</sup>. This lowering in the activity of the protic partner by increasing the concentration of the aprotic solvent was also noted in the sulfolane-water system<sup>7</sup> and in the DMSO-methanol system.<sup>8</sup> But this lowering in the activity of water cannot account for all the increase in basicity when DMSO is added to aqueous solutions of hydroxide ion.

Another factor of importance is the state of solvation of the species  $\text{OH}^-$  and  $\text{A}^-$  in equation (1a) as we go from aqueous solutions to DMSO. In water a small ion like hydroxide ion is surrounded by water molecules and is stabilized by strong hydrogen bonds while in DMSO the hydroxide ion is weakly solvated and thus its activity will increase with increasing DMSO content. This argument is based on the premise that an unsolvated ion will be more reactive than a solvated one which must be snatched from its sheath of solvent molecules before a reaction can occur. Until recently, it was widely accepted that large delocalized anions like amide ions or carbanions were more solvated in DMSO than in a protic solvent,<sup>9</sup> but this premise was recently challenged. Fuchs et al.<sup>10</sup> measured enthalpies of solution of lithium and potassium halides in DMSO and found that the order of solvation of halide ions in DMSO

---

\* The species  $\text{H}_7\text{O}_4^-$  in equation (1a) corresponds to the secondary hydrate complex  $\text{H}_9\text{O}_4^+$  in acid solutions.<sup>5</sup>

is the same as in water. They therefore postulated that differences of solvation between ions, whether large or small, in DMSO is minimal. The main effect of adding DMSO to the system shown in equation (1a) seems to be to desolvate  $\text{OH}^-$ .

Besides these two large effects, there are several minor ones. Lowering the concentration of water in the system will tend to shift the equilibrium to the right. DMSO itself is coordinated to two water molecules,<sup>11</sup> thus addition of DMSO further lowers the water concentration by complex formation. A fair estimate of the increase in  $H_-$  up to about 50 wt percent DMSO (20 mole percent) can be made<sup>12</sup> by considering only the effect of DMSO on the concentration of the individual species in equation (1a). With further increase of the DMSO content, the variation in the activity of water will be the predominant factor, and at very high DMSO content greater than 95 percent the desolvation of the hydroxide ion will have a dramatic effect on  $H_-$  values. All these factors will tend to shift the equilibrium (1a) to the right as DMSO replaces water as a solvent.

On the other hand, the activity coefficient of the neutral acid HA will tend to fall as water is replaced by DMSO as indicated by the generally higher solubility of aromatic amines and hydrocarbons in DMSO than in water. This is the only factor which will tend to shift the equilibrium to the left.

#### I. The $H_-$ acidity function

The  $H_-$  acidity function describes the proton-abstracting ability of a solution. The following equilibrium exists between an acid

uncharged and its conjugate base  $A^-$  in aqueous solution of a base;



The thermodynamic equilibrium constant for equation (1b) can be expressed as:

$$K_{HA} = \frac{a_{H^+} a_{A^-}}{a_{HA}} = \frac{[A^-]}{[HA]} \cdot \frac{f_{A^-}}{f_{AH}} a_{H^+} \quad (2)$$

or in a logarithmic form as

$$\log \frac{[A^-]}{[AH]} = \log K_{HA} - \log \frac{f_{A^-}}{f_{AH}} a_{H^+} \quad (3)$$

The symbols  $[ ]$ ,  $a$ ,  $f$ , refer to concentration, activity and activity coefficient respectively; and are related by the equation  $a_i = f_i[i]$ .

In very dilute solutions when the activity coefficients approach unity this equation reduces to

$$\log \frac{[A^-]}{[AH]} = \log K_{AH} - \log [H^+] \quad (4)$$

Since the simple term  $-\log [H^+]$  or pH measures the proton abstracting power in dilute aqueous solution, then the equivalent term in equation (3) can be used in strongly basic media, and thus defines the function

---

\* All these species are hydrated but are not so denoted, for the sake of simplicity.



$$H_- = -\log \frac{f_{A^-}}{f_{AH}} a_{H^+} \quad (5)$$

Hammett's activity coefficient postulate states that for  $H_-$  to define the acidity of the medium,  $\frac{f_{A^-}}{f_{AH}}$  should be independent of the structure of the indicator and only dependent on the solvent composition.

Substituting (5) into (3) and rewriting we get:

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

The Hammett indicator-overlap or stepwise technique of determining this acidity function  $H_-$  has been used by a number of workers in the past years. It involves the comparison of basicity of indicators in different media starting in the water region.

First let us consider an acid HA whose  $pK_a$  can be determined in aqueous buffer solutions. We can rewrite equation (2) as

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

Similarly for another acid HB, another equation can be written:\*

$$pK_{HB} = \log \frac{[BH]}{[B^-]} - \log a_{H^+} \frac{f_{B^-}}{f_{HB}} \quad (8)$$

Subtracting (8) from (7) gives the following equation:

---

\*  $pK_{HA}$ ,  $pK_{HB}$  are the  $pK_a$  values of the acids HA and HB respectively

$$pK_{HA} - pK_{HB} = \log \frac{[HA]}{[A^-]} - \log \frac{[HB]}{[B^-]} + \log \frac{f_{HA} f_{B^-}}{f_{HB} f_{A^-}} \quad (9)$$

Now if, and only if, the last term in equation (9) is equal to zero (Hammett's activity coefficient postulate) equation (9) becomes:

$$pK_{HA} - pK_{HB} = \log \frac{[HA]}{[A^-]} - \log \frac{[HB]}{[B^-]} \quad (10)$$

Hence, to establish an  $H_-$  scale referred to a standard state of infinite dilution in water, an acid indicator HA is required whose  $pK_a$  can be determined in aqueous buffers and whose ionization range spans the upper end of the pH scale and the beginning of the  $H_-$  scale. This indicator is then used to determine the  $H_-$  value for several different solutions e.g., DMSO-water where the solvent character changes from aqueous to non-aqueous. It is then possible to determine in the same solutions the fraction of an indicator HB that is ionized and by use of equation (10) determine its  $pK_a$ . If the Hammett postulate holds there should be a constant difference in the  $pK_a$ 's obtained from equation (10), for two acids in a series of solutions of different basicity.

This procedure can be applied repeatedly for successive indicators, and  $pK_a$ 's assigned to these indicators. These individual  $pK_a$  values are then used to calculate  $H_-$  values for each solution in which the indicator's ionization ratio can be measured with reasonable accuracy,  $\frac{[A^-]}{[HA]}$  between 0.1 and 10. This procedure results in several measured  $H_-$  values for each solution and these values are then averaged.

It is evident from equation (6) that a plot of  $\log \frac{[A^-]}{[HA]}$  versus  $H_-$  should give a straight line of unit slope and intercept equal to the  $pK_a$  of the indicator. The advantage of using a water-anchored  $H_-$  function, where  $H_- = pH$  in dilute aqueous solutions, is that the proton-abstracting power of any medium is then always expressed on the same scale. If it were possible to determine experimentally a very small amount of ionization, one should find values similar to those in Table II for the degree of ionization of aniline (of the order of  $10^{-15}$  in pure water with  $[OH^-] = 0.01$ ).

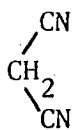
The validity of this treatment relies heavily on Hammett's assumption that the activity coefficient ratio of a base and its conjugate acid depends only on the solvent composition and is independent of the nature of the acid indicator. This assumption has been proven quite reliable in determining  $H$  functions in the acid region, although it has broken down in certain cases. One of the limitations which has arisen is that the indicators must be of similar structure. It is difficult to define the degree of similarity required but it is known that even primary and tertiary amines produce different  $H_o$  scales.

Bowden's review of acidity functions for strongly basic solutions<sup>1</sup> lists the  $H_-$  data for 29 different solvent systems. But in view of the dependence of  $H_o$  functions on indicator structure it is advisable to distinguish between  $H_-$  acidity functions determined with diverse indicator types. The ionization behaviour in basic solutions of each of the following type of indicators will be compared: neutral carbon ( $H_-^C$ ), nitrogen ( $H_-^N$ ) and oxygen ( $H_-^O$ ) acids.

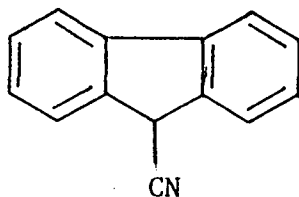
## II. Carbon Acids

Although carbon acids and their conjugate bases, carbanions, undoubtedly occupy a position of prime importance in organic chemistry, it is only recently that a monograph<sup>16</sup> has been written on the subject of carbanion chemistry, with a detailed discussion on thermodynamic and kinetic acidities of hydrocarbons.

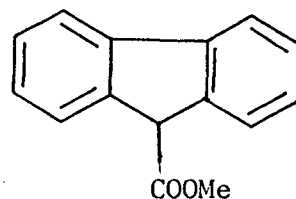
Bowden and Stewart<sup>17</sup> published in 1965 an  $H_-^C$  acidity function based solely on the ionization of carbon acids. The main difficulty in establishing a  $H_-^C$  scale is that most hydrocarbons are insoluble in water, even at spectroscopic concentrations ( $\sim 10^{-5}$  M), and thus the anchoring of the scale in dilute aqueous solutions is impossible. These authors circumvented this obstacle by first measuring the  $pK_a$  of malononitrile in aqueous solution ( $pK_a = 11.14$ ) and then in dilute solutions of ethanolic sodium ethoxide. They then proceeded to measure the  $pK_a$  of two other carbon acids, 9-cyanofluorene and methyl fluorene-9-carboxylate, in solutions of various concentration of sodium ethoxide in ethanol.



malononitrile

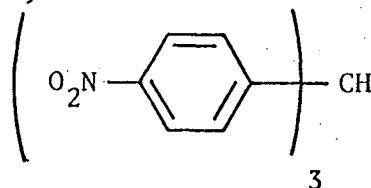


9-cyanofluorene



methyl fluorene-9-carboxylate

Finally they anchored the scale in 0.01 M sodium ethoxide with tris(p-nitrophenyl)methane



Subsequent work in this laboratory, much of which is described in this thesis, revealed that for some of these carbon acids the carbanion undergoes an unusually large spectral shift ( $\sim 100 \text{ m}\mu$ ) as the degree of ionization rises. Indeed, this behaviour was noticed by the original authors for tris(p-nitrophenyl)methane.

Kroeger and Stewart<sup>18</sup> in attempting to set up an  $H_-^C$  scale for comparison to their  $H_R$ - scale found cases where distinctly non-parallel ionization slopes occurred.

Independently, Ritchie and Uschold<sup>19</sup> suggested the existence of flaws in the  $H_-^C$  scale. By use of the glass electrode they measured the acidities of a number of weak acids in DMSO solutions relative to a standard state in the same solvent. They essentially titrated potentiometrically these acids with dimsyl cesium solutions,\* after having standardized the glass electrode with dilute p-toluenesulfonic acid solutions. The  $pK_a$ 's of fluorene (20.5) and triphenylmethane (28.8) thus measured were in agreement with values measured by Steiner and Gilbert,<sup>20</sup> by a stepwise method with 4-nitroaniline\*\* as an anchor. They measured the  $pK_a$ 's of four of Bowden and Stewart indicators (Table III) and concluded that the overlap of indicators used by Bowden and Stewart was not valid; though it is not obvious how they arrived at this conclusion.

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\* Dimsyl cesium is the cesium salt of the conjugate base of DMSO.

\*\* 4-Nitroaniline was found by Dolman and Stewart<sup>4</sup> to be a non-Hammett indicator slope of  $\log I$  vs  $H_-$  0.92,  $pK_a = 18.9$ .

TABLE III

$pK_a$  of carbon acids in ethanolic DMSO<sup>17</sup> and in DMSO<sup>19</sup>

Acid	$pK_a^a$	solvent	$pK_a^b$	solvent
malononitrile	11.14	water	11.0	DMSO
tris-(p-nitrophenyl)methane	14.32	DMSO-EtOH	12.0	"
9-phenylfluorene	18.59	"	16.4	"
fluorene	22.1 <sup>c</sup>	DMSO-H <sub>2</sub> O	20.5	"

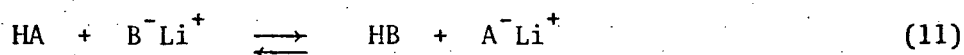
<sup>a</sup> Bowden and Stewart ref. 17.

<sup>b</sup> Ritchie and Uschold ref. 19.

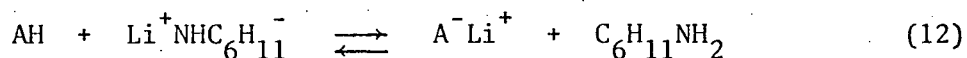
<sup>c</sup> Bowden and Cockerill ref. 23.

Relative acidities of a number of compounds are reversed by the change of solvent from water to DMSO. The  $pK_a$ 's of acetic acid and hydrazoic acid for example, are 11.6 and 7.9 respectively, while in water they both have a  $pK_a$  of 4.8. On the other hand the  $pK_a$  of p-nitrophenol is 10.4 in DMSO and 7.1 in water.

Strietwieser et al.<sup>21</sup> determined equilibrium acidities of various hydrocarbons toward lithium and cesium cyclohexylamide in cyclohexylamine. They measured the equilibrium constants between two hydrocarbons in cyclohexylamine when treated with an insufficient amount of lithium or cesium cyclohexylamide to produce the equilibrium shown in Equation (11) where HA and HB are two hydrocarbons.



Since all the hydrocarbons studied were more acidic than cyclohexylamine equilibrium (12) lay far to the right and the spectrum



of each hydrocarbon salt could be measured. The ultraviolet and visible spectra of the mixture (11) can then be compared with the spectra of the lithium salts of the two hydrocarbons in equation (12) and knowing the initial concentrations, the equilibrium constants determined. The main drawback of this procedure is that the conjugate bases involved are actually cesium carbanide ion pairs (contact) or lithium carbanide solvent-separated ion pairs. Streitwieser et al.<sup>21</sup> chose 9-phenylfluorene ( $\text{pK}_a$  18.59) as their anchor, although they subsequently<sup>22</sup> reduced their values uniformly by 2.3 units to conform to those of Ritchie and Uschold.<sup>19</sup>

Steiner and Gilbert<sup>20a</sup> have used a similar method to determine the acidity of a few hydrocarbons in both methanolic and aqueous DMSO. Their anchor was 4-nitroaniline  $\text{pK}_a$  18.4 (cf. footnote page 10). They later re-examined their  $\text{pK}_a$  values<sup>20b</sup> and added 1.6  $\text{pK}$  units to all the indicators less acidic than fluorene. Although the literature is in a state of some confusion as to the absolute  $\text{pK}_a$  to be assigned to these hydrocarbons, it seems that a certain consensus has lately been reached<sup>22</sup> between the four different group of workers. Table IV lists the different  $\text{pK}_a$  values published and also the "best values". All these values are based on a  $\text{pK}_a$  value of 16.4 for 9-phenylfluorene except for Steiner's values which are based on 4-nitroaniline  $\text{pK}_a$  = 18.4.

Kuhn and Rewicki<sup>24</sup> determined an  $\text{H}^{\text{C}}$  scale for DMSO-glacial acetic acid - 0.01 M sodium acetate, with various olefinic hydrocarbons

TABLE IV

$pK_a$  values of hydrocarbons and "best values"

Compound	Experimental $pK_a$							best value h
	a	b	c	d	e	f	g	
9-phenylfluorene			16.4	18.5	18.5	16.2	18.59	16.4
Indene	18.2	18.2	18.5	20.24	19.93	17.6		
4,5-methylphenanthrene	>19.5	>19.5	20.0	22.60	22.63	20.3	21.19	
2,3-benzofluorene	>19.5	>19.5			23.17	20.9		20.1
fluorene	20.5	20.5	20.5	22.83	22.74	20.4	22.10	20.5
9-phenylxanthene	24.3	25.9			28.5	26.2		26.0
triphenylmethane	27.2	28.8	28.0		31.48	29.2		29.0
diphenylmethane	28.6	30.2			33.1	30.8		30.5

- <sup>a</sup> Steiner and Gilbert, ref. 20a, used as anchor 4-NO<sub>2</sub>An.,  $pK_a$  18.4, from Stewart and O'Donnell ref. 13.
- <sup>b</sup> Steiner and Gilbert, ref. 20b, increased all values above fluorene by 1.6, as they found an error in the relative acidities of 9-phenylxanthene and fluorene.
- <sup>c</sup> Ritchie and Uschold, ref. 19, the validity of this scale is based on the agreement with:
1. Steiner<sup>20</sup> and Stewart<sup>13</sup> on the  $pK_a$  value of 2,4-dinitroaniline, 14.7.
  2. Steiner<sup>20</sup> on the  $pK_a$  value of fluorene.
- <sup>d</sup> Streitwieser et al., ref. 21, solvent separated ion pairs. The  $pK_a$  values were determined with lithiumcyclohexylamide in cyclohexylamine.
- <sup>e</sup> Streitwieser et al., ref. 21, contact ion pairs. The  $pK_a$  values were determined with cesium cyclohexylamide in cyclohexylamine.
- <sup>f</sup>  $pK_a$  values presented by Streitwieser et al., at the symposium in San Francisco ref. 22.
- <sup>g</sup> Bowden and Cockerill, ref. 23. The  $pK_a$  values were determined in aqueous DMSO.
- <sup>h</sup> The author's judgement.

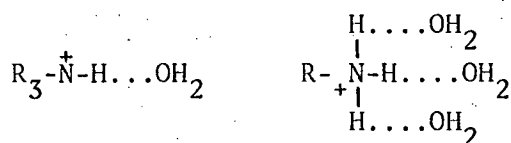


as indicators. The  $H_-$  values of the medium decrease with increase in acetic acid content of the solution. They<sup>25</sup> also measured the  $pK_a$  of a number of other olefinic hydrocarbons in the above mentioned system, and also in the systems DMSO-tri-n-propylamine, and hexamethylphosphoramide-tri-n-propylamine. The major drawback of their technique<sup>25</sup> is that the equilibrium between carbanions and hydrocarbon is not instantaneous. Kuhn and Rewicki chose 9-cyanofluorene, whose  $pK_a$  (11.4) was determined in ethanol<sup>17</sup> by direct overlap with malononitrile. Kuhn and Rewicki<sup>24</sup> determined a  $pK_a$  of 19.6 for 9-phenylfluorene based on a  $pK_a$  value of 11.4 for 9-cyanofluorene in DMSO-tri-n-propylamine, which is irreconcilable with the Ritchie and Uschold results. Indeed fluorene itself is half ionized in a 90 mole percent DMSO-water-0.01 M TMAOH solution, which gives a  $pK_a$  value of 22.0 if the  $H_-^N$  scale resembles the  $H_-^C$  scale,<sup>23</sup> and since the relative acidities of tris-p-nitrophenylmethane, 9-phenylfluorene, and fluorene are the same whether measured potentiometrically or spectrophotometrically (stepwise), it is not at all evident that the  $pK_a$  assignment by Bowden and Stewart is erroneous. Though this does not mean that their (Bowden and Stewart)  $pK_a$  values are correct, since the various substituted CH-acids are not really similar to the various fluorenes. The nitrophenylmethane anions are much more delocalized than the fluorenes. Moreover, it should be noted that Bowden and Stewart's extinction coefficients for 9-phenylfluorene, fluorene and tris-(p-nitrophenyl)methane anions do not agree with other reported values. It is thus of prime importance to determine the ionization behaviour of these

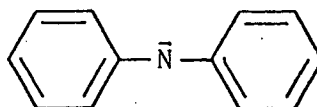
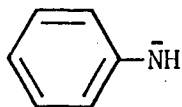
carbon-acids, and hopefully to find a series of hydrocarbons which ionize to give solely carbanions.

### III. Nitrogen Acids

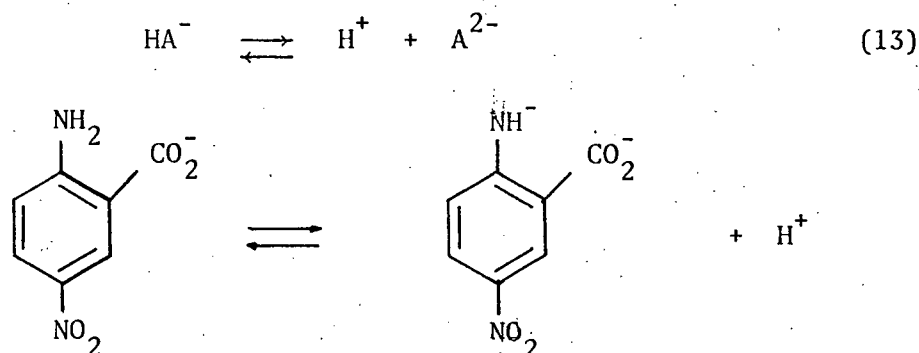
An  $H_-$  function has been determined for both primary and secondary amines in aqueous dimethylsulfoxide containing 0.01 M TMAOH (tetramethylammonium hydroxide) by Dolman and Stewart<sup>4</sup>. This scale starts at 10 percent DMSO-water with 2,4-dinitrodiphenylamine as the reference indicator, the  $pK_a$  of which was measured using the stepwise method by O'Donnell<sup>13</sup> and taken as 13.84. It appears that a single acidity function will describe the ionization behaviour for both types of amines. The existence of only one  $H_-$  scale contrasts with the fact that separate  $H_0$  scales are required for primary, and tertiary amines in sulfuric acid water mixtures. This is not surprising, if the cause of the latter effect is, as suspected, hydrogen bonding between the protons on cationic nitrogen and water.<sup>14</sup>



Hydrogen bonding of this type in amide ions should be of little importance because of the negative charge on the nitrogen atom. Solvation will occur on the nitrogen atom because of its negative charge.



An  $H_{2-}^N$  scale has also been established by Bowden, Buckley and Stewart<sup>15</sup> using anionic acids such as diphenylamine carboxylic or sulfonic acids, or aminobenzoic acids which ionize as follows:



$H_{2-}^N$  is defined in the following way

$$H_{2-}^N = pK_{HA} + \log \frac{[A^{2-}]}{[AH^-]} \quad (15)$$

This  $H_{2-}$  scale appears to rise slightly less rapidly than the previously evaluated  $H_-$  scale. In 97 mole percent dimethylsulfoxide-water-0.01 M TMAOH the  $H_-$  value is some two powers of ten higher than the corresponding  $H_{2-}$  value. This may be caused by the higher solvation requirement of the dianion with respect to the single ion reflecting a relatively large increase in the activity coefficient of the dianion.

#### IV. Oxygen Acids

The only oxygen acids that are sufficiently weak to be incompletely ionized in strongly basic media are alcohols and stereochemically hindered phenols. The spectrophotometric method is unsuitable for  $pK_a$  determination of alcohols, as they do not undergo significant

spectral shifts on ionization.

Coggeshall and Glessner<sup>28</sup> studied the ionization of several phenols in ethanol-water solutions containing sodium hydroxide and found that those phenols with t-butyl groups in the ortho position required the highest base concentration to produce complete ionization. This is presumably due to steric inhibition to the solvation of the phenoxide anions.

They pointed out that the difference of energy of transition between the ground and first excited state for the neutral molecule and the phenolate ion depends upon the type of phenols.

phenols	$\Delta(1/\lambda)^*$
unhindered	2100 cm <sup>-1</sup>
partially hindered (2-t-butyl-)	2300 cm <sup>-1</sup>
hindered (2,6-di-t-butyl)	3200 cm <sup>-1</sup>

They tentatively explained this phenomenon by considering the energy of polarization of the large ortho groups.

Cohen and Jones<sup>29</sup> measured the dissociation constants for a series of 4-substituted phenols and the corresponding 2,6-di-t-butyl-4-substituted phenols and found that the reaction constant  $\rho$  in water for the hindered phenols is 57% greater than for the unhindered phenols. Cohen and Jones suggested that the extremely weak acidity of hindered phenols may be attributed to the confinement of solvation on the phenolate oxygen, due to the concentration of negative charge on this atom. Cohen and Jones also correlated the ultraviolet spectral data of the 4-substituted and 2,6-di-t-butyl-4-substituted phenols and their

corresponding anions with substituent parameters. Since  $\rho$  (ultraviolet

\*  $\Delta(1/\lambda)$  is the difference in frequency of maximum absorption between the molecules and the phenolate ion in each series expressed in wavenumbers.

spectral shift) for the 2,6-di-*t*-butyl series is only slightly greater than  $\rho$  for the hindered phenols they concluded that the phenolic O-H bond is coplanar with the aromatic ring.

Further proof for the inhibition to solvation by ortho substituents was provided by Fischer et al.<sup>30</sup> who measured the dissociation constants of 4-substituted-2,6-dichloro and 2,6-dimethyl phenols in aqueous solutions. Since the chloro- and methyl-substituents are of similar size (van der Waals radii are 2.0 and 1.8 Å respectively) but have opposite inductive effects simple steric inhibition to solvation of the phenoxide anion should give similar reaction constants  $\rho$  for both series<sup>30b</sup> if the ortho substituents exhibits no, or very little, polar effect. Fischer et al. found a  $\rho$  value of the same order of magnitude for both series and higher than for unhindered phenols. The order of decreasing values is 2,6-di-*t*-butyl 3.50, 2,6-dimethyl 2.70, 2,6-dichloro 2.61, phenols 2.24, which is consistent with the expected magnitude for purely steric effects, thus confirming the suggestion that inhibition to solvation and not the polar effect of the alkyl group is the cause for the acid-weakening effect of ortho substituents in hindered phenols.

Rochester<sup>31</sup> has recently studied the ionization of six *t*-butyl substituted phenols in methanolic sodium methoxide solutions, and found the results to be consistent with an acidity function which differs from that obtained using anilines and diphenylamines. Indeed, he suggests that a small difference exists between the functions governing the ionization of partially hindered and hindered phenols. Rochester used the method of O'Ferrall and Ridd<sup>\*32</sup> and obtained  $pK_a$  values based on

\* plotting  $\log (I - [OMe^-])$  vs  $[OMe^-]$  and extrapolation to zero concentration of sodium methoxide.

methanol as the standard state. The  $H_-^O$  function differs by up to 0.5 unit in 3 M sodium methoxide from the  $H_-^N$  function, the latter being the greater. It would thus be interesting to compare the  $H_-$  acidity functions for amines and phenols. The most appropriate solvent system to use in this study would be methanolic and/or ethanolic DMSO since most phenols are completely ionized in 0.01 M aqueous base.

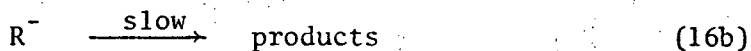
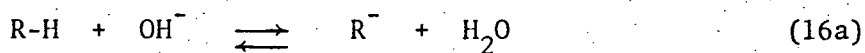
V. Application of the  $H_-$  Function to Kinetics and Mechanisms of Base Catalysis

As in the case of the  $H_0$  function, the main purpose of establishing an  $H_-$  function, besides equilibrium measurements of weak acids, is its possible correlation with rates of base-catalyzed reactions. These correlations are indeed a powerful tool in the elucidation of reaction mechanisms. Few such correlations have appeared in the literature and they in general involve breaking of a C-H bond in the rate determining step. The rate of racemization of (+)-2-methyl-3-phenylpropionitrile<sup>33</sup> in dimethylsulfoxide containing sodium methoxide has been correlated with the  $H_-^N$  function of the medium. A log k vs  $H_-$  plot is approximately linear with a slope of 0.87 over a range of rates greater than six powers of ten. A correlation<sup>34</sup> is also obtained between the logarithm of the rates for the methanolysis of chlorinated hydrocarbons and the  $H_-$  function of methanolic sodium methoxide solutions. A reasonable straight line is obtained with a mean slope of 0.8. It was suggested however, that this correlation<sup>35</sup> was fortuitous because of ion association in concentrated solutions of sodium methoxide in methanol.

Jones and Stewart<sup>36</sup> have reported a correlation between the logarithm of the ionization rate constant of ( $\alpha$ -<sup>3</sup>H) acetophenone and the  $H_-$  of the medium. The systems studied were: DMSO-water-0.01 M TMAOH, DMSO-methanol-0.01 M sodium methoxide, DMSO-ethanol-0.01 M sodium ethoxide. The slopes of these correlations though are only  $\sim 0.5$  but this might be accounted for by the fact that the  $H_-$  function for the ionization of a ketone must be quite different from the ionization of an amine. Keto-enol tautomerism should render an  $H_-$  function more sensitive to DMSO addition than a hydrocarbon or an amine. Jones and Stewart<sup>37</sup> correlated also the logarithm of the rate of ionization of DMSO in a DMSO-water-0.01 M TMAOH solutions with the  $H_-^N$  of the medium. They observed a linear relationship with a slope of 0.9.

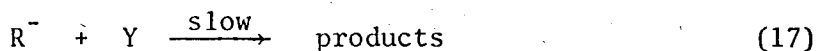
Anbar et al.<sup>38</sup> derived equations which correlate the rate constants of various base-catalyzed reactions with the  $H_-$  value of the medium. If the first step of the reaction is a proton abstraction, Anbar et al differentiate between the following cases:

a) A rapid preequilibrium is established between the base and the substrate followed by a first order rate determining step to give the products



In this case the logarithm of the rate constant correlates with the  $H_-$ . The above mentioned alkaline decomposition of chloroform is an example of such a case.

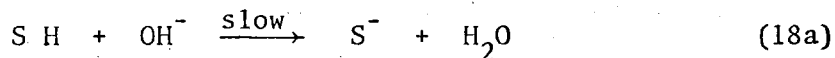
b) A rapid preequilibrium is also established as in case a) but it is followed by a second order rate determining reaction with another reactant Y



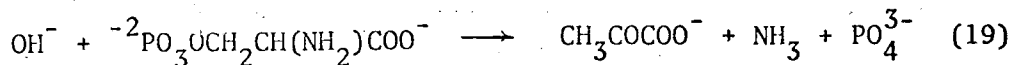
Here also there exists a linear relationship between the logarithm of the rate constant and the  $H_-$ . The reaction between chloramide and ammonia in aqueous solutions to form hydrazine is an example of such a correlation and has a slope of 0.9.

b') If Y is a solvent molecule and thus the reaction is pseudo first order, the logarithm of the rate constant should correlate with  $H_- + \log C_{H_2O}$ .

c) In the case where the proton abstraction is the slow step, followed by a fast reaction to give the products, Anbar et al suggested that the rate constants will also correlate with  $H_- + \log C_{H_2O}$ .



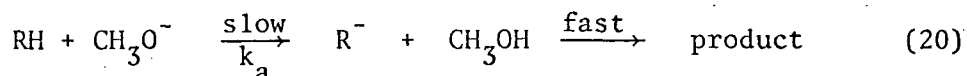
This similarity in rate correlation between case b') and c) is not surprising since the transition states in both of these cases should be similar. The decomposition of dl-serine phosphate to form pyruvate phosphate and ammonia is an example of such a reaction type.



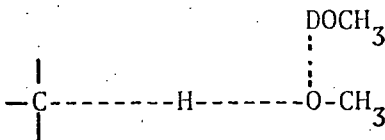


A plot of  $\log k$  against  $H_- + \log C_{H_2O}$  for this decomposition has a slope of 0.98. More recently Cram and Kollmeyer<sup>2</sup> have correlated the logarithm of the rates of potassium methoxide catalyzed isotopic exchange of carbon acids with the  $H_-$  of the medium. They proposed two mechanisms to account for the linear relationship observed.

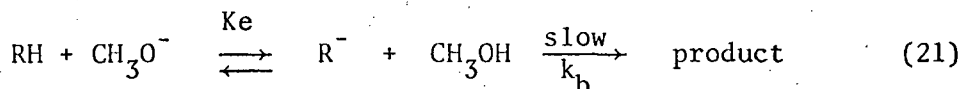
(a) The first one involves a slow ionization step



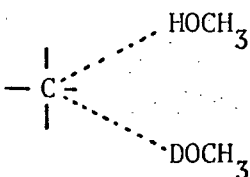
This mechanism occurs when  $\Delta pK$  ( $pK_{\text{hydrocarbon}} - pK_{\text{methanol}}$ ) has a low positive value. The transition state in this case can be represented by



(b) The second mechanism involves a rapid preequilibrium followed by a rate-limiting reaction with the solvent



This mechanism occurs when  $\Delta pK$  is large and the transition state in this case resembles



For both of these reaction paths Cram et al. suggested that there is a linear relationship between  $\log k_{\text{obs}}$  and  $H_-$ . The  $H_-$  functions used in these correlations<sup>2,32,33,35,36,37</sup> have been derived using diphenylamine and aniline indicators, and thus reflect the effect of changing medium on nitrogen acids rather than on carbon acids. This is reflected in the fact that the slope  $\theta$  of the correlation was always found to be lower than unity.

Kresge<sup>39</sup> suggests that kinetic acidity dependence is a property of the substrate and should not be interpreted as a mechanistic criterion. He believes that such correlations can be used to provide an insight into transition state structure in reactions of known mechanism, rather than to provide evidence useful in choosing between two or more possible mechanisms.

#### A. Kinetic-Thermodynamic relationships

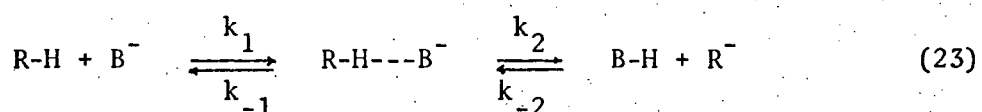
The rate of proton transfer in the ionization of carbon acids has been looked upon as a measure of the kinetic acidity of these acids. The kinetic acidity is defined as the forward rate of exchange, on a relative logarithmic scale



but until recently no systematic study of kinetic-thermodynamic relationships had been made for simple hydrocarbons. This is because they are much too weak as acids to ionize in common basic aqueous solutions. Special experimental techniques<sup>43</sup> had to be developed in order to study isotope exchange rates of hydrocarbons in liquid ammonia and it is only

in the last decade that the use of non-aqueous solvents as reaction media has gained a certain popularity.

Following Eigen's treatment, it is advantageous to consider that an intermediate (hydrogen-bonded) complex is formed between the acid and the base as in equation (23):



Normally the concentration of the complex  $\text{R-H} \cdots \text{B}^-$  is very small compared with the concentration of either reactants or products. Using the steady-state assumption the forward ( $k_f$ ) and reverse ( $k_r$ ) rate constants can be expressed as follows:

$$k_f = \frac{k_1 k_2}{k_{-1} + k_2} \quad k_r = \frac{k_{-2} k_{-1}}{k_{-1} + k_2}$$

The equilibrium acidity is related to the ratio of forward and reverse rate constants, usually as the negative logarithm, or

$$\log k_f - \log k_r = \text{pK}_{\text{RH}} - \text{pK}_{\text{BH}} = \Delta(\text{pK}) \quad (24)$$

The well-known Bronsted equation relates the kinetic and equilibrium acidities. In its simplest form it is written:

$$\log k_A = \log G_A - \alpha \log K_a \quad (25)$$

where  $k_A$  is the rate constant for acid catalysed reaction and  $K_a$  the

equilibrium acidity of the acid A, or of the conjugate acid of the base B.  $G_A$  and  $\alpha$  are constants. Considering equation (24), one may rewrite the simple Bronsted relation (25) in the following form<sup>40</sup>

$$\frac{d \log k_f}{d \Delta (pK)} = \alpha \quad (26)$$

where  $\alpha$  is the Bronsted slope. It is evident from equation (26) that  $\alpha$  is zero if  $\Delta (pK)$  has a large positive value and unity if  $\Delta (pK)$  is large negative. In the transition region between these extremes where  $\Delta (pK) \approx 0$ ,  $\alpha$  has an intermediate value between 0 and 1.\*

The integrated form of the Bronsted equation (equation 25) was proposed in 1924 to correlate the catalysed decomposition of nitramide as shown in equation (27). Bronsted<sup>41</sup> emphasized the fact that his equation is limited to a study of reactions catalysed by a small number of compounds



with comparable acid strength. Indeed Eigen<sup>5</sup> pointed out that the decomposition of nitramide shows a continuous variation of the coefficient  $\alpha$  if studied over a wide range of reactivities.

Even in the classical case of the base-catalysed halogenation of ketones<sup>42</sup>, Eigen showed that in a wider pK range  $\alpha$  is not constant and that all the curves can be constructed on the basis of the generalized relationship (26).

At high  $\Delta (pK)$  value - whether negative or positive - the rate of proton transfer is diffusion controlled. In the vicinity of  $\Delta (pK) \approx 0$

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\* Bordwell et al.<sup>55</sup> recently measured Bronsted coefficients larger than unity and smaller than zero for proton abstraction of nitroalkanes.

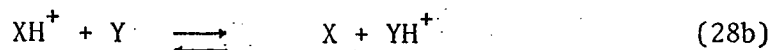
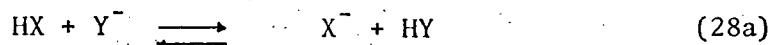
there is a transition where  $\log k$  is linearly related to  $\Delta$  (pK) and takes a value between 0 and 1. Normal acid-base systems are those which show a sharp narrow transition region. Such acids are usually of the OH- (phenols), NH- (aniline), NH- (pyridinium ion) type, whose  $pK_a$  values lie in the range -1 to 15.

CH-acids (or pseudo-acids) and some normal acids with special structural characteristics (internal hydrogen bonding for example) have broad transition regions. This transition from  $\alpha = 0$  to  $\alpha = 1$  will occur gradually so that  $\alpha$  might appear to have a constant value.

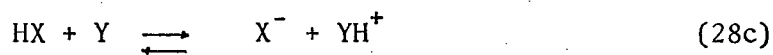
Carbon-acids show wide transition regions because usually deprotonation is associated with resonance stabilization and the recombination rate may therefore be relatively low. Many examples of curvature of  $\log k$  -  $\Delta$  pK relationships have been found and it is now a well accepted fact that Bronsted plots are usually non linear if a wide enough range of reactivities is examined. The  $\log k$  -  $\Delta$  pK relation approaches ideal behavior when:

- (i) both donor and acceptor belong to the classical hydrogen bond formers (O- and N-type).
- (ii) the electronic and spatial configurations of the acids and their conjugate bases are similar. If the limiting values of  $k$  are identical (the extrapolated straight lines at  $\alpha = 0$  and  $\alpha = 1$  intersect at  $\Delta$  pK = 0) then the slope of  $\log k$  -  $\Delta$  pK plot at  $\Delta$  pK = 0 is often close to 0.5. If however, the limiting values of  $k$  differ, then the center of symmetry--point of intersection of the straight line  $\alpha = 0$  and  $\alpha = 1$  --is displaced along the  $\Delta$  pK axis by the difference of the logarithms of these limiting value. The closer the value of  $k$  at  $\Delta$  pK = 0 is to the limiting value, the narrower is the transition region, where  $\alpha$  appears to be constant. This

symmetric behavior with respect to  $\Delta pK = 0$  is only valid for reactions of symmetric charge type.



However if the reaction shows an asymmetry of charge, the  $\log k$ - $\Delta pK$  curve becomes asymmetric with respect to  $\Delta pK = 0$ .



Recently Streitwieser et al.<sup>22</sup> measured the kinetic acidities of a series of hydrocarbons by hydrogen isotope exchange in methanolic sodium methoxide. The thermodynamic acidity of these same hydrocarbons have already been measured in cyclohexylamine by him, (cf. p. 12-13). A Bronsted plot of  $\log k_2$  (second order rate constant) vs.  $pK_a$  in cyclohexylamine showed distinct curvature with  $\alpha$  varying from about 0.4 near the fluorenes to 0.8 for di- and tri-arylmethanes.

Cram and Kollmeyer also published a kinetic-thermodynamic acidity correlation of carbon acids. Rate constants and activation parameters for potassium methoxide catalyzed exchange of a few hydrocarbons in methanol- $O$ - $d$ -dimethyl- $d_6$ -sulfoxide (~ 15 mole percent) were measured. These kinetic acidities varied by a rate factor of seven powers of ten, and the thermodynamic acidities by a factor of ten powers of ten. The Bronsted plot was also curved. The slope of the  $\log k$  vs.  $pK_a$  curve was ~ 0.5 for the strongest acids ( $pK_a = 23 \pm 3$ ) and unity for the three weakest acids ( $pK_a = 28 \pm 2$ ).

Shatenshtein et al.<sup>44</sup> have studied extensively isotopic exchange reactions of hydrocarbons in non-aqueous solvents, at first mainly in liquid ammonia<sup>43</sup>, but later also in cyclohexylamine, dimethylsulfoxide and others<sup>44,45,46</sup>. Shatenshtein<sup>44</sup> proposed a two-step mechanism similar to the one shown in equation (23). The first stage of this reaction is the limiting stage, and thus  $k_{\text{obs}} = k_1$ , i.e. the observed rate constants of the reaction is equal to the rate constant for the ionization of the R-H bond. It is only in this case that the kinetics of hydrogen exchange can characterise the acidity of this C-H bond.

Shatenshtein<sup>44</sup> suggested that there is no direct relation between the observed rate constant of the exchange reaction and the ionization rate constant, in the case where the second step in equation (23) is rate determining; since  $k_{\text{obs}} = \frac{k_1}{k_{-1}} k_2 = K k_2$ .

Shatenshtein<sup>44,45</sup> also pointed out that the relative kinetic acidities can vary with change in the solvent medium. Very large differences in relative kinetic acidities were found in comparing the kinetics of deuterium exchange in DMSO and in ammonia. For example the rate constants for the exchange of deuterium in the methyl group and in the ring of toluene in DMSO differ by a factor of  $10^6$  while they differ only by a factor of  $10^2$  in ammonia. He differentiates between C-H bonds in aromatic or heteroaromatic rings and those in methyl groups attached to aromatic rings, when plotting relative strengths of carbon acids in one solvent against the relative strength of the same acids in another solvent. Shatenshtein<sup>44</sup> found that there is no differentiating effect when the solvents belong to the same category (aprotic or protic), for example DMSO vs. methyl-bismethoxymethyl-phosphine oxide,  $(\text{CH}_3\text{OCH}_2)_2\text{PO}\cdot\text{CH}_3$ , or ammonia vs. cyclohexylamine. He found<sup>45</sup> though, that if the solvents

do not belong to the same group, DMSO vs. t-butanol or DMSO vs. ammonia, the points for the alkyl groups in alkylbenzenes lie on one line while those for benzene derivatives containing ring deuterium lie on another line.

Shatenshtein concludes that the differentiating action of solvents on the kinetic acidity of carbon acids depends on the structure and the solvation of the transition states formed during the isotopic exchange reactions. He also points out that the problem of determining acidities (thermodynamic and kinetic) of hydrocarbons is still quite complicated due to our limited knowledge of solvent effects.

#### B. Isotope effects

Primary kinetic isotope effects for the base catalysed proton abstraction from aromatic hydrocarbons have been measured by many workers. Streitwieser et al.<sup>47</sup> have measured the kinetic isotope effect  $k_H/k_D$  for the exchange of the methyl hydrogens of toluene in the cyclohexylamine, cyclohexylamide system. They found values greater than 10 for  $k_H/k_D$ , while in the DMSO - potassium-t-butoxide system Hofmann et al.<sup>48</sup> measured a  $k_D/k_T$  slightly less than unity. Hofmann et al believed that their results showed that the rate determining step was not initial ionization of the C-H bond, but the formation of a tight complex between the incipient carbanion and the alcohol.

This view was challenged by J.R. Jones<sup>49</sup>. Both theory<sup>50</sup> and experiment<sup>51,52,53</sup> indicate that the isotope effect for proton transfer between acid-base systems has a maximum value when the  $\Delta pK_a$  value between the two acids is equal to zero. In Streitwieser's case the  $pK_a$  of t-butanol is  $\sim 20$ , while the  $pK_a$  of toluene is  $\sim 40$ . Thus, we should expect to have a high isotope effect in cyclohexylamine, and a negligible



one in dimethylsulfoxide.

Kinetic isotope effects for proton abstraction reactions have been measured for other hydrocarbons<sup>2,22</sup> but these will be discussed later in this thesis.

#### SCOPE OF THE PRESENT RESEARCH

As emphasized in the introduction, the indicators used to determine  $H_-$  functions can be differentiated into oxygen, nitrogen and carbon acids. Part of this work was undertaken to determine the degree of divergence of acidity functions caused by variation in indicator structure. The ionization behaviour of diphenylamines ( $H_-^N$ ) and phenols ( $H_-^O$ ) were therefore determined in dimethylsulfoxide-methanol containing 0.01 molar sodium methoxide and dimethylsulfoxide-ethanol containing 0.01 molar sodium ethoxide. These weak acids exhibit a strong bathochromic shift on ionization, and this provides a simple way of determining the position of their ionization equilibria.

A redetermination of the  $H_-^N$  function in low percentage dimethylsulfoxide in water was also considered necessary as some doubts were raised on the ionization mode of the previously used anchor, 2,4,6-trinitroaniline.

Preliminary results indicated that the p-nitro substituent had an overwhelming effect. It was thus important to study the effect of substitution on the acidity of diphenylamines in the presence of the nitro group in the other ring. The main purpose in establishing an  $H_-$  function, apart from its use in equilibrium measurements of weak

acids, is its possible correlation with rates of base-catalyzed reactions.

Base-catalyzed rates of detritiation of various hydrocarbons were determined in dimethylsulfoxide mixtures. These rates (on a logarithmic scale) were then correlated with the thermodynamic basicity of the medium as measured by the  $H_-$  function. The shape of these correlations would then give us information on the applicability of these  $H_-$  functions, and on the structure of the transition state in base-catalyzed proton abstraction reactions. Hopefully a kinetic-thermodynamic relationship might also be derived from these rate measurements.

In view of the disparity between published  $pK_a$  and relative  $pK_a$  values of carbon acids, and the disagreements on spectral characteristics of their carbanions formed on ionization, a close examination of the ionization behaviour should be undertaken. It was of prime importance to prepare and characterize the carbanions of these nitrophenylmethanes and determine their spectral characteristics. One could then decide whether these carbon acids had ionized by proton abstraction in previously reported work. Also, the cause of the dependence of spectral characteristics on the solvent should be investigated.

## EXPERIMENTAL

Most of the handling techniques pertaining to the determination of the  $H_{-}$  functions are described in full detail elsewhere.<sup>4b</sup> An outline of these procedures is given below.

### I. Purification of solvents

DMSO was stirred in a closed vessel over powdered calcium hydride for at least two days and then distilled in a stream of nitrogen<sup>\*</sup> at reduced pressure. A Perkin triangle was used to cut fractions, and the first and last 20% of the distillate were discarded. The DMSO was stored in glass stoppered flasks over molecular sieves 4A and under nitrogen. The water content of the DMSO was measured prior to its use, by the Karl-Fischer method, and was shown to be less than 0.01%.

Hexamethylphosphoramide (HMPT) was fractionally distilled twice from molecular sieves 13X. The first and last 20% of the distillate were discarded each time. As HMPT dissolves most commercial vacuum greases, a distillation apparatus with "clear-fit" joints was used. The distilled HMPT was stored in stoppered bottles over molecular sieves 4A.

Carbonate-free water was prepared by boiling distilled water and then bubbling nitrogen through as it cooled.

<sup>\*</sup> The nitrogen gas used throughout was grade "L" (Liquid Air) as grade "G" contains small amounts of oxygen.

"Super dry" methanol and ethanol were prepared according to standard procedures in Vogel<sup>54</sup> and were stored over molecular sieves 3A and under nitrogen. Dryness was checked prior to use by Karl-Fischer titration.

Toluene was Baker analyzed reagent grade and was distilled before use.

## II. Base

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

Sodium methoxide and ethoxide were prepared from the required amount of sodium and the corresponding alcohol to produce a 1 M solution. This was done in a rubber stoppered bottle under a stream of nitrogen. After the reaction was complete aliquots of the stock solutions were titrated against standard acid. The stock solutions were kept under nitrogen and stored in the freezer compartment of a refrigerator. No solution older than 1 month was ever used.

## III. Preparation of solutions

The DMSO-protic solvent ( $H_2O$ , MeOH, EtOH) stock solutions were made up according to weight at approximately 5 mole percent intervals from 0 to 100 percent DMSO. Dry NO-SOL-VIT bottles with well fitting rubber stoppers - sleeve type - were weighed. Into each of these was syringed the required volume of DMSO, and the bottles were

reweighed to give the weight of DMSO. To this was syringed the appropriate amount of protic solvent and the bottles weighed for the final time to give the weight of the solvent. Nitrogen was then bubbled through these solutions for 3 minutes and they were then stored in a desiccator over Drierite. It was found that the amount of moisture which was picked up by the solvents during preparation was very small and did not warrant the extra precaution of using a drybox.

#### IV. Spectral measurements

Indicator measurements were made with a constant concentration of base (0.011 M tetramethylammonium hydroxide or 0.01 M sodium alkoxide). All measurements of spectra were made on a Bausch and Lomb model 502 recording spectrophotometer, with the cells thermostated at 25° by means of a constant temperature cell holder. The procedure developed previously by O'Donnell<sup>13</sup> and used since then in these laboratories to protect the system from oxygen was followed. This involves the use of silicone rubber disks to seal absorption cells and syringes to introduce the indicators and the base. Dry nitrogen was bubbled through the solution for about 2 minutes. None of the indicator anions used seemed to react in any way for at least 15 minutes, as their spectra showed no change during this lapse of time.

#### V. Treatment of data and calculations

From the spectral measurements on solutions of indicators in the aprotic-protic-base system, the ratios of the concentrations of ionized to unionized indicator ( $I = (A^-)/(HA)$ ) are obtained. From these

ratios are then obtained the relative  $pK_a$  values of the amine indicators and the  $H_-$  values for the solutions in which the measurements were made.

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

The  $H_-$  values were then calculated from the  $pK_a$  values of the indicators and the values of  $\log I$  obtained from the smoothed curves mentioned above. This was accomplished by using equation (6).

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

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

#### VI. Probable error in $H_-$ and $pK_a$ values

With all acidity functions it is difficult to estimate the uncertainty in the  $H$  values and in the  $pK$  values of the indicators used to determine them. The further the acidity function is from the usual pH range, the greater the likelihood of errors because of the

stepwise procedure used to establish it. The errors can be minimized by using a large number of overlapping indicators so that the  $H_{\text{c}}$  value for a given solution is not dependent on the data from any one indicator, and by using indicators of the same structural type to ensure that the Hammett activity coefficient postulate is obeyed as closely as possible. The previous estimate<sup>4</sup> of the uncertainty as 0.05 pK unit appears to be on the low side. A more reasonable estimate would be around  $\pm 0.2$ -0.3.

It is to be noted that the precision of the UV measurement far exceeds the method's overall accuracy. A change in absorbance of 0.02 alters  $\log I$  by only  $\sim 0.04$  if  $-0.5 < \log I < +0.5$  and by 0.08 if  $-0.5 > \log I > +0.5$ .

It was also noticed that solutions of indicators can be kept for an extended period of time (12 months) without any damage.

## VII. Kinetic measurements

### A. Hydrocarbon exchange

A weighed amount (10-30 mg) of tritiated hydrocarbon was weighed in a 125 ml erlenmeyer with a B24 stopper, and 100 ml of the appropriate mole percent DMSO-alcohol solution was introduced into the flask. After complete dissolution of the hydrocarbon was assured, the flask was immersed in a well-stirred thermostated bath. After sufficient time was allowed for temperature equilibration, 1.0 ml of a 1 M solution of sodium ethoxide in ethanol was added. Aliquots were withdrawn at fixed time intervals and introduced into a 125 ml separatory funnel containing 50 ml of cold water (to stop the reaction) and 15 ml of liquid scintillator (3.5 gm of 2,5-diphenyloxazole per



litre of toluene). The funnel was shaken by hand and the aqueous layer run off. The toluene solution was dried over anhydrous magnesium sulfate. An aliquot (10 ml) of the dried toluene was transferred into a counting vial. The latter was stored for 20 min. then counted in a Nuclear Chicago Mark I model 6860 liquid scintillation counter. The counting efficiency was roughly determined for each sample by the external standard technique utilizing the built-in barium-133 gamma source. All vials which did not have the average efficiency were discarded. The usual count at time zero was around 500,000 counts per minute. In general the reaction was taken to ~ 70% completion. However for each hydrocarbon, at least one run was allowed to proceed to greater than 90% completion. The base concentration was determined by simple titration against standard acid using phenolphthalein indicator.

The tritiated hydrocarbons were prepared (cf. preparation of compounds for details) by one of the following methods:

1. quenching of an ethereal solution of the sodium salt of the hydrocarbon with HTO,
2. catalytic exchange between the hydrocarbon and HTO<sup>55</sup>.

B. DMSO exchange

Solutions (~ 30 mls) of appropriate mole percent DMSO-protic solvent were prepared as previously described and 0.1 ml of tritiated DMSO or protic solvent, as the basicity of the medium warrants, was added. After thermal equilibration 0.3 ml of 1 M base solution was added. If the reaction was fast the base concentration was determined

by simple titration. Aliquots (3 mls) were withdrawn and injected into tubes containing 7 ml of methanol. The  $\text{CH}_3\text{OT}$  thus formed was separated from the DMSO by fractional distillation, dried and then added to 7 ml of the liquid scintillator, cooled and counted. If the reaction was slow 3 ml aliquots were withdrawn into vials and sealed under nitrogen and kept in the constant temperature bath. At appropriate time intervals, the vial was broken and 7 mls of MeOH was added and the same routine followed.

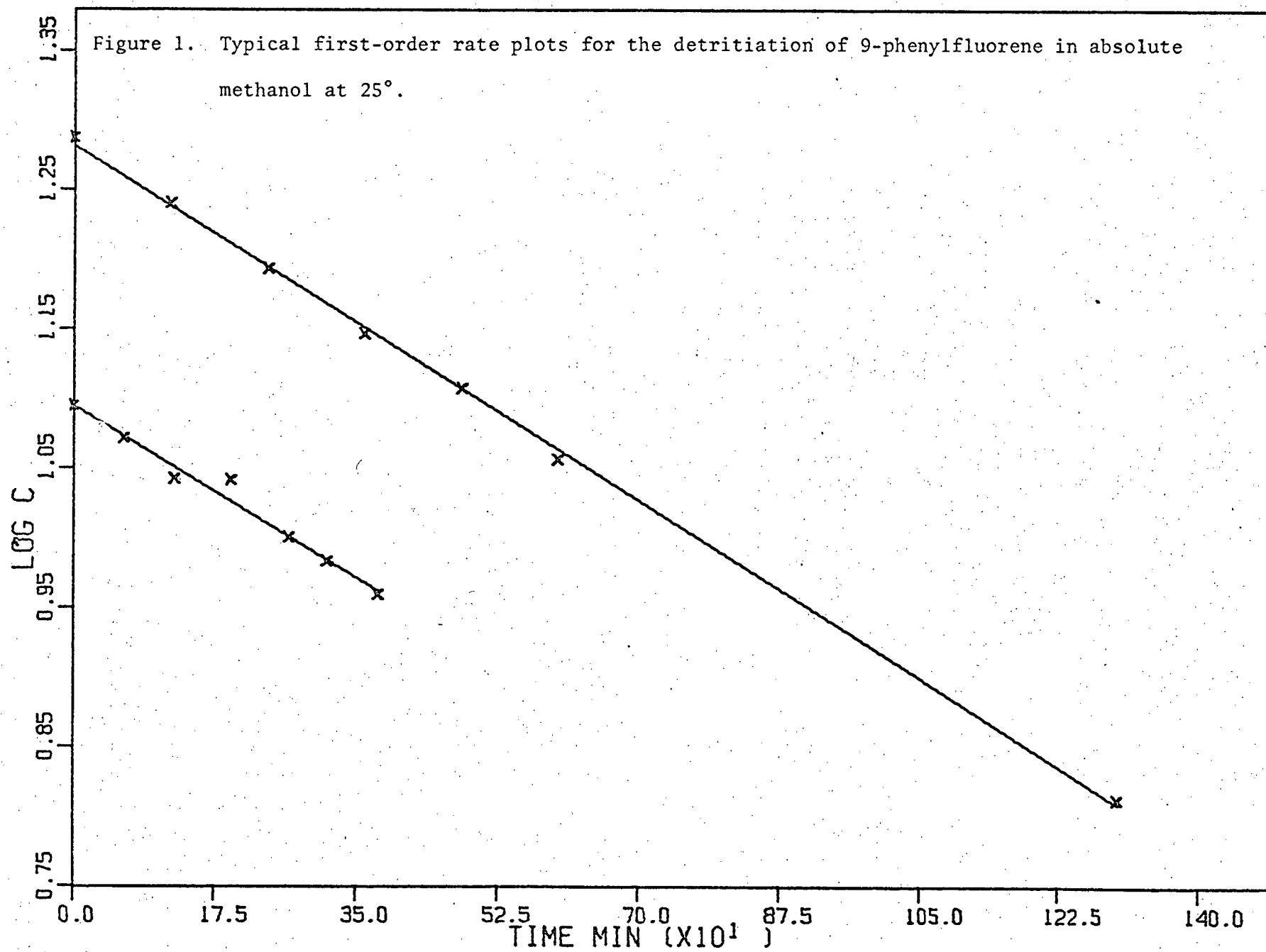
Tritiated DMSO was prepared by allowing 20 gm of DMSO to equilibrate with 0.1 ml of HTO (100 mcuries/ml) in the presence of a pellet of sodium hydroxide for 6 hours. The contents were neutralized with hydrochloric acid and 10 ml of methanol was added. The solution was dried, the methanol was removed by distillation and the DMSO was purified by vacuum distillation. Tritiated methanol and ethanol were prepared by allowing 10 ml of alcohol to equilibrate with 1 ml of HTO (4 mcurie/ml) for a half hour. The alcohol was then fractionally distilled and dried.

#### VIII. Treatment of the kinetic data

The pseudo first order rates for the detritiation of hydrocarbon are described by equation 29.

$$k = \frac{2.303}{[\text{OR}^-]_t} \log [C] \quad (29)$$

where the  $[C]$  terms refer to the radioactivity of the hydrocarbons at various time intervals. No infinity correction was made as the hydrocarbon



loses almost all of its activity to the solvent sink. An infinity point showed an activity of  $\sim 1000$  c/min which is negligible with respect to the average activity of 200,000 c/min. Eight points were obtained from each run and  $k$  was determined from the slope of the plot of  $\log C$  against  $t$ . Duplicate runs showed the rate constants to be in agreement within  $\pm 5\%$ . A representative plot of a duplicate detritiation measurement - 9-phenylfluorene in absolute methanol - is shown in figure 1.

In the case of the DMSO exchange the equations are:

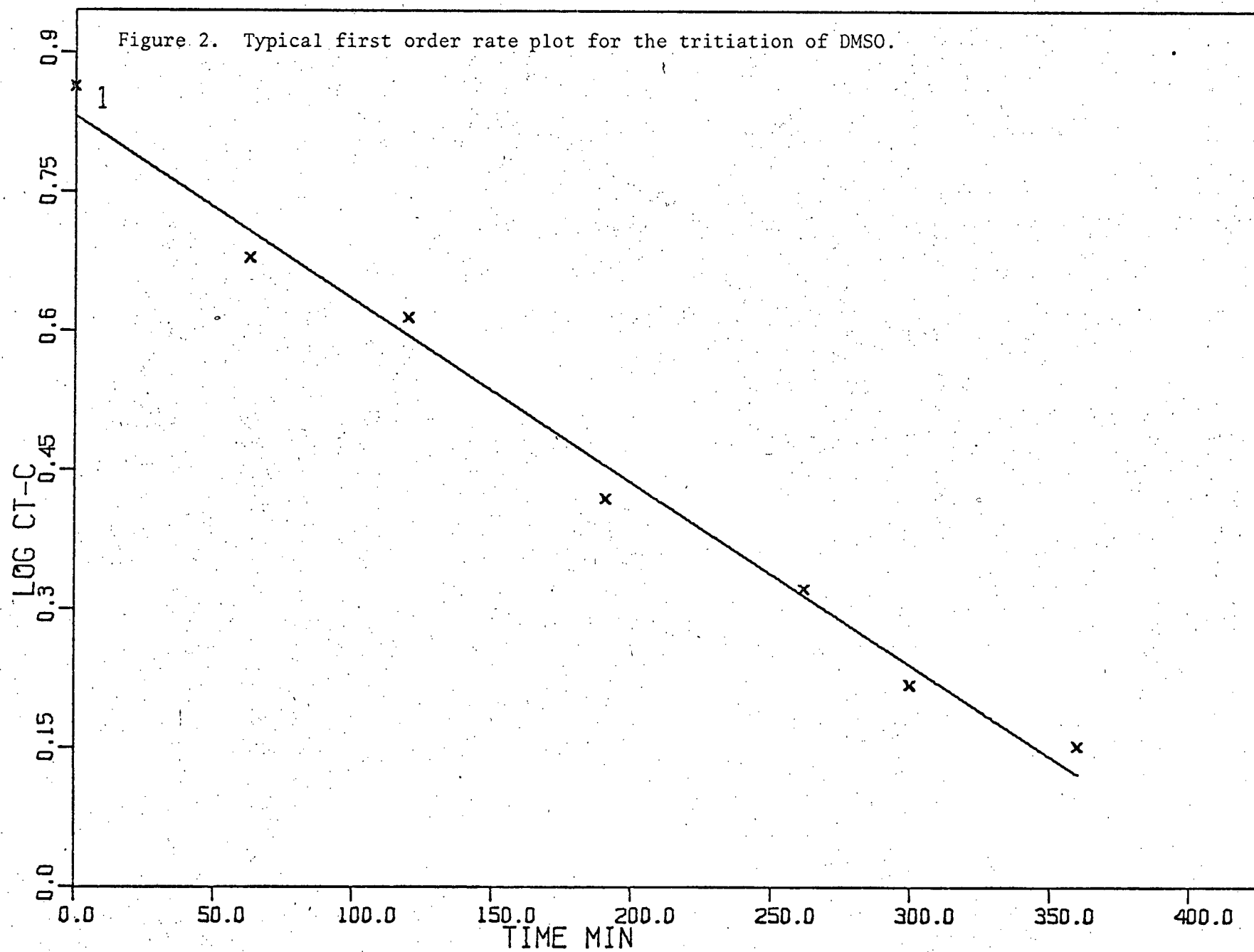
$$k = k_{\text{trit}} = \frac{2.303}{[\text{OR}^-]_t} \log \frac{[(\text{MeOT})_o - (\text{MeOT})_\infty]}{[(\text{MeOT})_o - (\text{MeOT})_t]} \quad (30)$$

$$k = k_{\text{detrit}} = \frac{2.303}{[\text{OR}^-]_t} \log \frac{[(\text{MeOT})_\infty - (\text{MeOT})_o]}{[(\text{MeOT})_\infty - (\text{MeOT})_t]} \quad (31)$$

A typical plot for the tritiation of DMSO - in 55% DMSO-water - is shown in figure 2. In the case where the base concentration differed from the standard value 0.01 M a correction was made using the equation:

$$H_- = H_- (0.01) + \log \frac{[\text{OR}^-]}{0.01} \quad (32)$$

The correction was never more than 0.1 unit. This correction is warranted by the fact that the  $H_-$  function for various concentrations of protic solvent and its conjugate base follow this equation for dilute basic solutions.



## IX. Reactions of nitrophenylmethanes

### a. Nuclear magnetic resonance (n.m.r.):

A solution of the nitrophenylmethane in HMPT was prepared in a drybox under nitrogen atmosphere. An n.m.r. spectrum of this solution was then recorded on a 100 M.Hz. Varian H.A.-100 spectrometer. A small amount of solid sodium methoxide was added to the solution and another spectrum was recorded immediately. The solution was then filtered through glass wool into another n.m.r. tube and a subsequent spectrum was recorded. Aside from the fact that the filtered solution gave "cleaner" spectra than the unfiltered one, there was no difference between them. This same solution was then used for the determination of the spectral characteristics of the anionic species.

Chemical shifts are reported in p.p.m. from an internal tetramethylsilane reference. A Cary spectrophotometer Model 16 was used for the measurements of the visible absorption spectra (up to a wavelength of 800 m $\mu$ ), and a Cary recording spectrophotometer Model 14 was used in the near infrared region (beyond 800 m $\mu$ ).

### b. Electron spin resonance (e.s.r.)

Tetra-n-propylammonium perchlorate (TPAP) was used as supporting electrolyte, and was prepared from tetra-propylammonium hydroxide and perchloric acid. The product was recrystallized from a (1:9) DMSO-water mixture. The electrolysis cell used in this work was designed by D.E. Kennedy<sup>101</sup> and spectra were recorded on a Varian E. 3 spectrometer. The nitrophenylmethane and TPAP were weighed in dry NO-SOL-VIT bottles, which were then fitted with rubber stoppers

(sleeve type). Aliquots of the appropriate mole percent DMSO-methanol solution were injected into these bottles. After complete dissolution of the solid nitrogen was bubbled through the solution for 10 minutes. The solution was then transferred to the electrolysis cell and degassed by connecting the cell to the vacuum system. The concentration of the supporting electrolyte was  $\sim 0.1$  M and that of the nitro-phenyl-methane  $\sim 0.01$  M. The potential applied to the cell for electrolysis was measured with respect to the mercury pool electrode, and was  $\sim 2$  volts with a current of  $\sim 50 \mu$  amp.

#### X. Computer treatment of data

A least square program with a plotting routine was used for treatment of much of the data. I would like to thank Messrs. A.M. Smolensky and D.E. Kennedy for help in writing the program.

All the figures in this thesis are reproductions of plotting output. The program and a sample of input and output is listed in Appendix C for reference.

#### XI. Preparation of compounds used in this work

##### A. Amines

##### a. 2,4-dinitrodiphenylamine series:-

2,4,4'-Trinitrodiphenylamine: was prepared by nitration of 2,4-dinitrodiphenylamine with nitric acid-acetic acid mixture according to the method of M.P. Juillard.<sup>57</sup> The product was recrystallized from toluene, acetic acid and finally from alcohol. melted at  $187-188^\circ$ . Lit. m.p.  $188^\circ$ .<sup>57</sup>

2,4,3''-Trinitrodiphenylamine: has been prepared<sup>12</sup> and purified previously in this laboratory. M.p. 192-194°. Recrystallized from pyridine.

2,4-Dinitro-4'-trifluoromethyldiphenylamine: has been synthesized and purified by Dr. A. Buckley in this laboratory by condensation of the chloro-dinitrobenzene with p-trifluoromethylaniline. M.p. 125-126.5°. Recrystallized from acetic acid and ethanol.

		C	H	F	N
Analysis	calcd.	47.71	2.46	17.42	12.84
	found	47.57	2.62	17.16	12.01

2,4-Dinitro-3'-trifluoromethyldiphenylamine: has been synthesized and purified by Dr. A. Buckley in this laboratory. M.p. 123-125°. Recrystallized from acetic acid and ethanol.

		C	H	F	N
Analysis	calcd.	47.71	2.46	17.42	12.84
	found	47.79	2.98	17.27	13.05

2,4-Dinitro-3'-chlorodiphenylamine: has been prepared and purified by Dr. A. Buckley in this laboratory. M.p. 180-182°. Recrystallized from ethanol. Lit. m.p. 182-183°. <sup>58</sup>

2,4-Dinitrodiphenylamine: obtained from Eastman Organic Chemicals and recrystallized from ethanol. M.p. 155-156°. Lit. m.p. 155°. <sup>59</sup>

2,4-Dinitro-3'-methyldiphenylamine: obtained from Aldrich Chemicals and recrystallized from ethanol. M.p. 161-162°. Lit. m.p. 160°. <sup>60</sup>

2,4-Dinitro-4'-aminodiphenylamine: obtained from Columbia Organics passed down an alumina column with a benzene/chloroform (1:1) mixture, then through another alumina column with chloroform as eluent.



M.p. 183-184°. Lit. m.p. 189°. <sup>61</sup>

		C	H	N
Analysis	calcd.	52.55	3.65	20.44
	found	52.76	3.75	20.20

(cf. spectral data as they differ from published <sup>12</sup> values).

b. 4-Nitrodiphenylamine series:-

4,4'-Dinitrodiphenylamine: has been prepared and purified previously <sup>12</sup> in this laboratory and was recrystallized from dioxane-water pair. M.p. 213-216°.

3,4'-Dinitrodiphenylamine: has been prepared <sup>4</sup> and purified previously in this laboratory and was recrystallized from benzene-petroleum ether pair. M.p. 215-216°.

4-Nitro-3'-trifluoromethyldiphenylamine: was prepared by condensation of 2-chloro-5-nitrobenzene sulfonic acid with m-trifluoromethylaniline followed by desulfonation according to the method of F. Ullmann and R. Dahmen. <sup>62</sup> (Another sample was previously prepared by Dr. A. Buckley in this laboratory). The product was from acetic acid and ethanol. M.p. 137.5-139°.

		C	H	N	F
Analysis	calcd.	55.31	3.19	9.93	20.21
	found	55.42	3.32	10.00	19.92

4-Nitro-3'-chlorodiphenylamine: prepared by the above mentioned method and purified by Dr. A. Buckley in this laboratory. Recrystallized from ethanol. M.p. 129-130°. Lit. m.p. 129°. <sup>63</sup>

4-Nitrodiphenylamine: obtained from Aldrich Chemicals and was recrystallized from acetic acid. M.p. 131-133°. Lit. m.p. 133°. <sup>63</sup>

4-Nitro-3'-methyldiphenylamine: synthesized and purified by Dr. A. Buckley in this laboratory. M.p. 127-128°. Recrystallized from ethanol.

Analysis		C	H	N
		calcd. 68.40	5.30	12.28
	found	68.24	5.29	12.12

4-Nitro-4'-aminodiphenylamine: prepared and purified by Dr. A. Buckley in this laboratory. M.p. 206-207°. Lit. m.p. 207-208°. <sup>62</sup>

c. Aniline series:-

2,4,6-Trinitroaniline: was obtained from Eastman Chemicals and recrystallized from ethanol, acetic acid. M.p. 191-192°. Lit. m.p. 192-195°. <sup>63</sup>

2,4-Dinitroaniline: was obtained from Eastman Chemicals and recrystallized from ethanol. M.p. 180-182°. Lit. m.p. 180°. <sup>63</sup>

4-Chloro-2-nitroaniline: was obtained from Brothers Chemicals Co. and recrystallized from ethanol. M.p. 115.5-116.5°. Lit. m.p. 116°. <sup>63</sup>

B. Phenols

All the phenols used were commercially available and were recrystallized from absolute ethanol under a nitrogen atmosphere and sublimed before a final recrystallization under nitrogen.

C. Hydrocarbons

2,4,2',4'-Tetranitrodiphenylmethane: was prepared in this laboratory according to the method of Parkes and Morley <sup>64</sup> and recrystal-

lized from acetic acid. M.p. 173-174°. Lit. m.p. 173°. <sup>63</sup>

4,4',4''-Trinitrodiphenylmethane (-tris-p-nitrophenyl)methane): was prepared by direct nitration of triphenylmethane with concentrated sulfuric and nitric acid mixture according to the method of Shoesmith, Sosson, Hetherington. <sup>65</sup> After several recrystallizations from chloroform-ether, the product was recrystallized from toluene and melted at 214-215°. Lit. m.p. 214.5°. <sup>65</sup>

4,4'-Dinitrodiphenylmethane (-bis-p-nitrophenyl-methane): was obtained from Eastman Chemicals and recrystallized from benzene. The compound melted at 183-183.5°. Lit. m.p. 183°. <sup>66</sup>

3,4'-Dinitrodiphenylmethane: was prepared from p-nitrobenzyl alcohol and nitrobenzene according to the method of Gattermann and Rudt <sup>67</sup>. The product was recrystallized from ethanol and melted at 104.5-105.5°. Lit. m.p. 103°. <sup>67</sup>

9-Phenylfluorene: was prepared by dehydration of triphenylcarbinol in phosphoric acid according to the method of Kliegl. <sup>68</sup> The product was recrystallized from ethanol and melted at Lit. m.p. 145°. <sup>62</sup> The tritiated compound was prepared by exchange according to the method of J.R. Jones. <sup>53</sup> 9-Phenylfluorene (1 gm) was dissolved in 5 ml of a (1:1) Dioxan-DMSO mixture. Tritiated water (0.1 ml of activity 10 mc/ml) was added and a few crystals of tetramethylammonium hydroxide pentahydrate. After three days the solution was neutralized with acid, and the solvent evaporated. The solid was added to 100 mls of water, to dissolve the salt, and the solution filtered. This dissolution - filtration step was repeated thrice before recrystallization of the 9-phenylfluorene-<sup>t</sup> from ethanol.

2,3-Benzofluorene: was obtained from K & K Laboratories and was recrystallized from petroleum ether. M.p. 207-208°. Lit. m.p. 208°. <sup>63</sup> The tritiated compound was prepared by Dr. J.R. Jones in this laboratory.

Fluorene: was obtained from K & K Laboratories and recrystallized from benzene/petroleum ether (30-60°), then sublimed, then recrystallized. The product melted at 116.5-117.5°. Lit. m.p. 116-117°. <sup>63</sup> The tritiated compound was prepared by direct exchange.

9-Ethylfluorene: was prepared by direct alkylation of fluorene in hexamethylphosphoramide in the presence of sodium hydride, according to the method of T. Cuvigny and H. Normant. <sup>70</sup> The product was vacuum distilled twice. B.p. <sub>10</sub> 102-104°. Lit. b.p. <sub>18</sub> 160° <sup>70</sup> and then purified by gas chromatography on a 20% silicone SF96 column temp. 240°. The tritiated compound was prepared by direct exchange.

9-Phenylxanthene: 9-phenylxanthenol was prepared from phenylmagnesium bromide and xanthenone in dry benzene. The xanthenol was then reduced by a formic acid/sodium formate mixture. The product was recrystallized from benzene-ethanol, then sublimed and recrystallized. M.p. 144.5-145°. Lit. m.p. 145°. <sup>71</sup> The tritiated compound was prepared by Dr. J.R. Jones by direct exchange.

Triphenylmethane-t: triphenylchloromethane was prepared from triphenylcarbinol and acetyl chloride in benzene then treated with sodium amalgam in ether to give triphenylmethanesodium. The sodium salt was then neutralized with HTO to give the tritiated hydrocarbon. After filtering off the NaOH thus precipitated, the solvent was evaporated. The product was then redissolved in ether and refiltered to take off

any remaining NaOH. This evaporation-filtration step was repeated thrice, before recrystallization of the triphenylmethane-t from ethanol.

## RESULTS AND DISCUSSION

### PART I: Indicator Measurements

#### I. Diphenylamine indicators $H_-^N$

From the derivation of the  $H_-$  function (pp. 4-6), it is evident that the anchoring of the scale in the water region is the most important step in the establishment of this scale.

Stewart and O'Donnell<sup>13</sup> chose 2,4,6-trinitroaniline ( $pK_a = 12.20$ ) as their anchor\* for the  $H_-^N$  scale in DMSO-water-0.001 M TMAOH. The pH of an 0.01 M aqueous sodium hydroxide solution is 11.939.<sup>72</sup> The pH of a 0.011 M aqueous TMAOH solution as measured on a Beckman pH meter model G (standardized at pH 12.45 and 10.00) is 11.95. The above mentioned  $H_-^N$  function<sup>13</sup> does not extrapolate to the expected value of 11.95 but to 11.65.

It is now known that 2,4,6-trinitroaniline forms a Meisenheimer complex in methanolic DMSO containing sodium methoxide.<sup>73</sup> In this work no such complex was detected by n.m.r. in aqueous DMSO, nevertheless the u.v. spectrum of the ionized molecule shows some disturbing

\* A careful re-examination of the ionization of 2,4,6-trinitroaniline in aqueous buffers and in sodium hydroxide solutions gave a  $pK_a$  value of 12.30. A subsequent determination of  $H_-$  values gave the following results.

mole % DMSO	0	0.5	1.	5.	10.
log I	-.25	-.16	-.08	.30	.50
$H_-$	12.05	12.14	12.22	12.60	12.80

features. Besides the peak at 414  $m\mu$ - assigned to the anion a smaller band appears at 470  $m\mu$ . Schaal<sup>74</sup> also noticed a band at 470  $m\mu$  in concentrated ethylene diamine solutions, and treated it as indicative of a second ionization for which he estimated a  $pK_a$  value of 17.55. This band (470  $m\mu$ ) disappears after 12 hours in a 24 percent DMSO-water-0.3 M TMAOH solution, while the ion peak did not decrease in intensity and shifted to slightly higher wavelength 426  $m\mu$ . The 470  $m\mu$  band was not observed in sodium hydroxide solutions.

These features led us to seek a more suitable anchor for the scale and our choice was 2,4,4'-trinitrodiphenylamine. Its  $pK_a$  was determined in aqueous glycine buffers and in sodium hydroxide solutions and was found to be 12.30 and 12.26 respectively. The value 12.30 was then used to determine  $H_-$  values for aqueous DMSO solutions up to 10 mole percent of DMSO. This same value was also used with the relative  $pK_a$  values of a series of substituted 2,4-dinitrodiphenylamines and 4-nitrodiphenylamines to calculate their thermodynamic  $pK_a$  values.

Table V contains a list of these indicators and their  $pK_a$  values determined in this work. These  $pK_a$  values were then used to calculate the  $H_-$  values for DMSO-water solutions up to 50 mole percent DMSO (this was done by using equation 10). These  $H_-$  values are averaged and the results are summarized in Table VI. These  $H_-$  values are in excellent agreement with the values of Dolman<sup>4</sup> which are based on 2,4-dinitrodiphenylamine,  $pK_a$  13.84. Figure 3 is a plot  $\log I$  ( $\log A^-/AH$ ) versus  $H_-$  for the indicators in Table V and is a reproduction of a computer output for the least squares fit for the lines.

0.011 M TMAOH.

DMSO-water-0.011 M TMAOH.

for the system:

(A/AH) versus H

plots of  $\log I$

Figure 3.

LOG R/RH

0.0 0.4 0.8 1.2

0.11 0.21 0.31 0.41 0.51 0.61 0.71 0.81 0.91 1.01 1.11 1.21

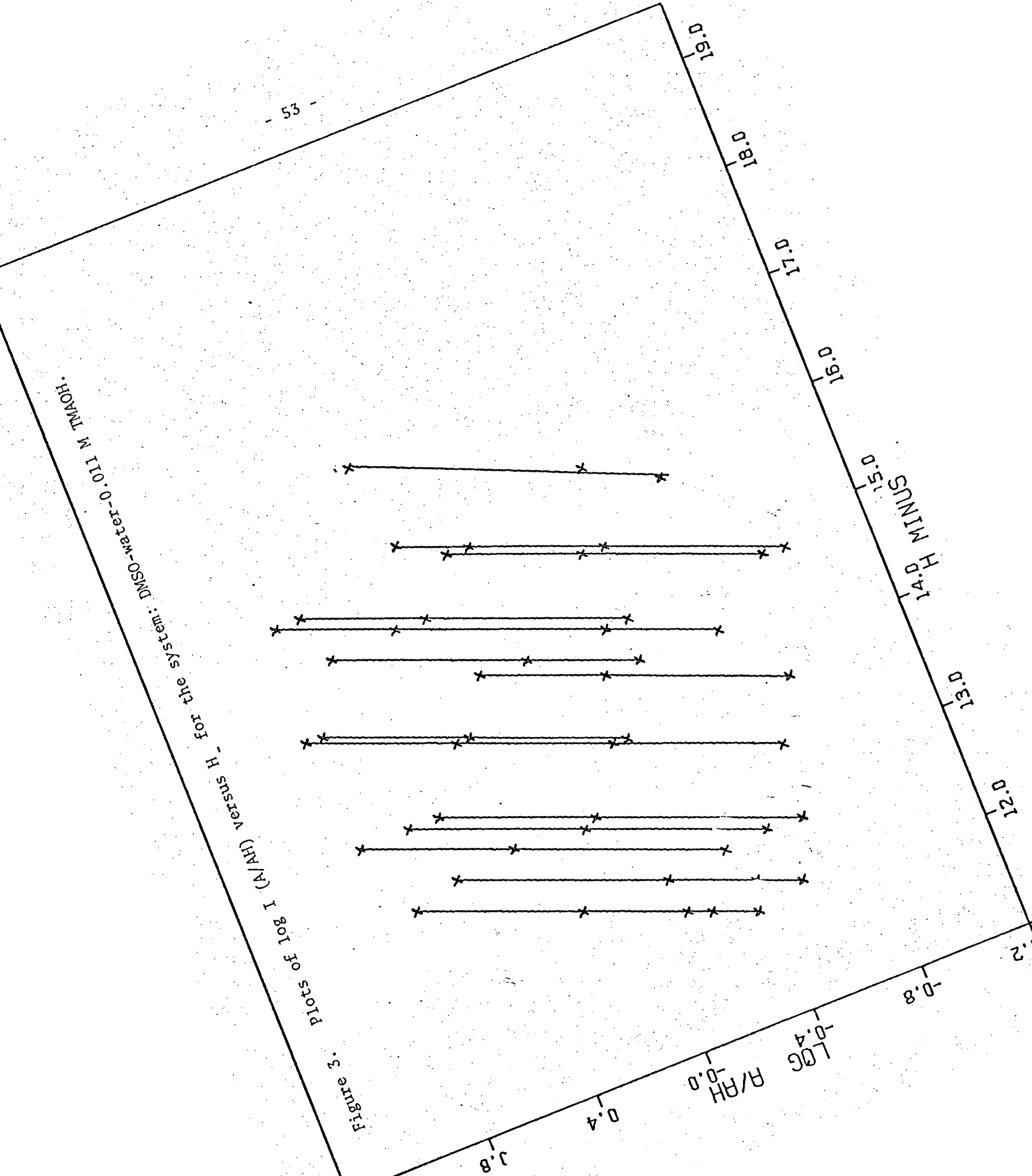




TABLE V

$pK_a$  values of various diphenylamines as determined in the aqueous DMSO system.

	$pK_a$	$pK_a$ reported	$\theta$	r	N	T
2,4,4'-Trinitrodiphenylamine	12.30	12.25*	1.002	.999	5	396.6
2,4,3'-Trinitrodiphenylamine	12.59	12.65*	1.002	.999	4	341.3
2,4-Dinitro-4'-trifluoromethyl- diphenylamine	12.87		0.999	.999	3	205.8
2,4-Dinitro-3'-trifluoromethyl- diphenylamine	13.06		1.004	.999	3	409.6
2,4-Dinitro-3'-chlorodiphenyl- amine	13.17		1.004	.999	3	463.8
2,4-Dinitrodiphenylamine	13.85	13.83*	1.001	.999	4	394.1
2,4-Dinitro-3'-methyldiphenyl- amine	13.90		0.999	.999	3	168.9
2,4-Dinitro-4'-aminodiphenyl- amine	14.48	14.64*	1.005	.999	3	452.3
4,4'-Dinitrodiphenylamine	---	14.08*	---	--	-	---
3,4'-Dinitrodiphenylamine	14.62	14.66†	1.005	.999	3	274.9
4-Nitro-3'-trifluoromethyldi- phenylamine	14.90	14.96†	1.001	.999	4	383.6
4-Nitro-3'-chlorodiphenylamine	15.00		1.004	.999	3	504.2
4-Nitrodiphenylamine	15.67	15.67†	0.997	.999	4	413.8
4-Nitro-3'-methyldiphenylamine	15.60		1.005	.999	3	422.5
4-Nitro-4'-aminodiphenylamine	16.40		0.926	.997	3	138.1

$\theta$  slope of plot of  $\log I$  vs.  $H_+$

r coefficient of correlation

N number of points

T student's test

\* Stewart and J.P. O'Donnell, ref. 13.

† Dolman and Stewart, ref. 4.

TABLE VI

$H_-^N$  values for the system DMSO-water-0.011 M  
tetramethyl ammonium hydroxide

mole % DMSO	$H_-^N$	$H_-^N$ reported*
0.4	11.95	
1.0	12.08	
2.0	12.20	
5.0	12.54	
10.0	13.04	
11.3	13.19	13.34
16.0	13.73	13.96
20.3	14.29	14.49
24.1	14.72	14.88
29.7	15.34	15.42
33.6	15.75	15.88
36.0	16.02	16.12
43.0	16.74	16.77
49.1	17.35	17.38

\* Dolman and Stewart, ref. 4.

The same set of indicators were also used to determine  $H_-$  functions for the systems DMSO-MeOH-0.01 M sodium methoxide and DMSO-EtOH-0.01 M NaOEt. In alcoholic DMSO convergence of the scales at  $H_- = pH = 11.98$  need not occur since all the  $pK_a$  values refer to water as the standard state. The anchor for the methanolic DMSO scale is the same as that for aqueous DMSO, i.e. 2,4,4'-trinitrodiphenylamine, and the anchor for ethanolic DMSO is 2,4-dinitrodiphenylamine.

The  $pK_a$  values for the individual diphenylamines and the  $H_-$  values for different solutions were arrived at in exactly the same way as for the aqueous DMSO system.

Tables VII and IX list the different  $pK_a$  values for these indicators as arrived at in the two systems, methanolic and ethanolic DMSO. The acidity functions for these two systems are given in Table VIII and X.

It is to be noted that an  $H_-^N$  function for methanolic DMSO containing 0.025 molar sodium methoxide has already been determined by Stewart, O'Donnell, Cram, and Rickborn.<sup>33</sup> If we assume that the difference in  $H_-$  values of DMSO-MeOH solutions containing 0.01 M or 0.025 M sodium methoxide is constant with changing composition, then we can reduce the  $H_-^N(0.025)$  to an  $H_-^N(0.01)$  for comparison by using equation (32).

$$H_- = H_-(0.01) + \log \frac{[OR^-]}{0.01} \quad (32)$$

Figure 4 is a reproduction of the least square fit for plots of  $\log I$  against  $H_-$  for the indicators in Table VII. Figure 6 is the analogous plot for the indicators in Table IX. Figures 5 and 7 are plots of  $H_-$  versus solvent composition for the methanolic and ethanolic DMSO systems.

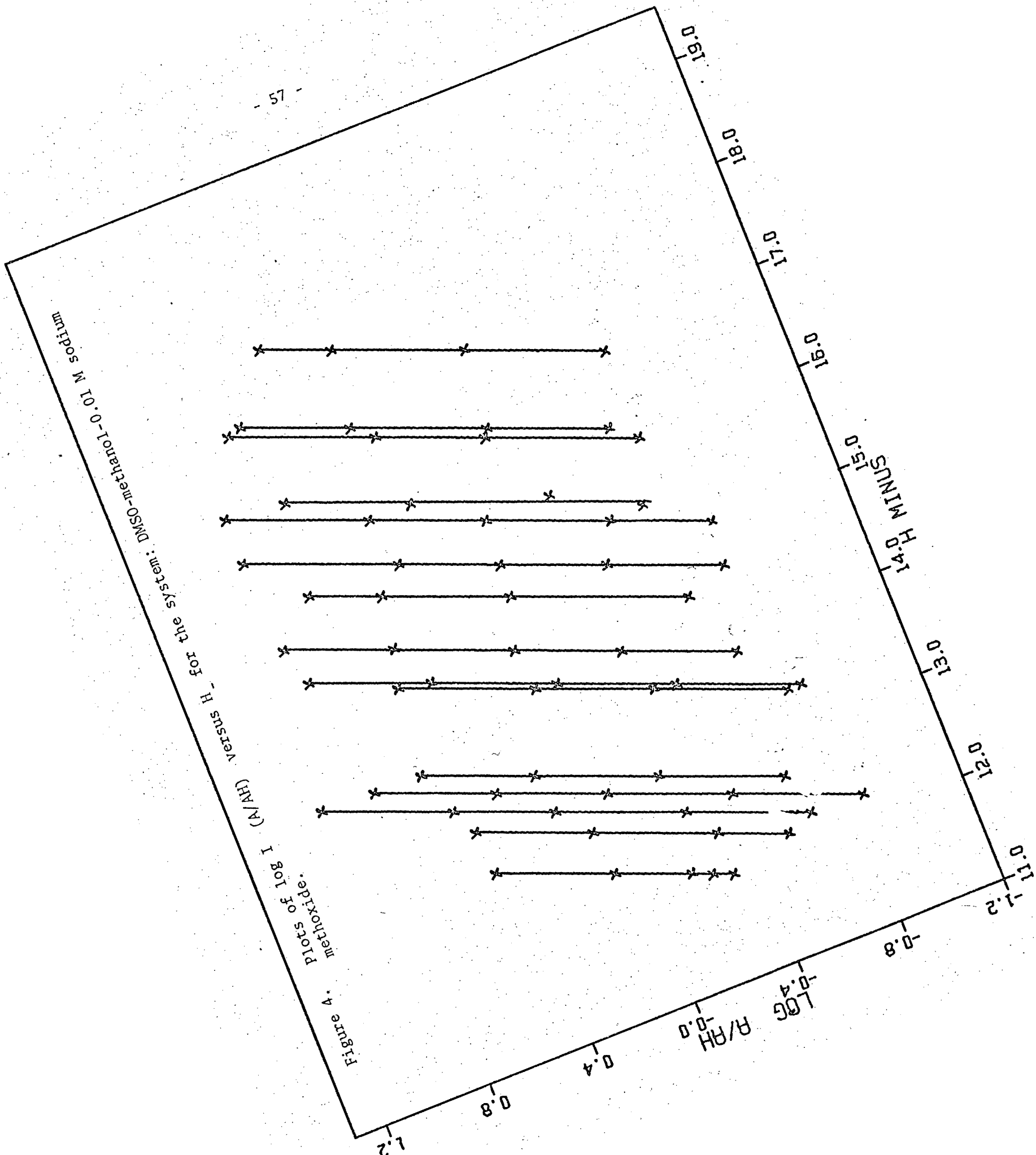


TABLE VII

$pK_a$  values of various diphenylamines as determined in the methanolic DMSO system.

	$pK_a$	$pK_a$ reported	$\theta$	r	N	T
2,4,4'-Trinitrodiphenylamine	12.25	12.35*	1.001	.999	5	261.9
2,4,3'-Trinitrodiphenylamine	12.65	12.65*	0.995	.999	4	372.4
2,4-Dinitro-4'-trifluoromethyl- diphenylamine	12.85		1.000	.999	5	289.6
2,4-Dinitro-3'-trifluoromethyl- diphenylamine	13.03		1.000	.999	5	289.6
2,4-Dinitro-3'-chlorodiphenyl- amine	13.20		1.000	.999	4	310.5
2,4-Dinitrodiphenylamine	14.05	13.84*	1.000	.999	4	333.3
2,4-Dinitro-3'-methyldiphenyl- amine	14.10		0.998	.999	5	557.4
2,4-Dinitro-4'-aminophenylamine	14.95	14.64*	1.001	.999	4	713.0
4,4'-Dinitrodiphenylamine	14.42	14.08*	0.994	.999	5	125.4
3,4'-Dinitrodiphenylamine	15.26		1.001	.999	5	517.4
4-Nitro-3'-trifluoromethyl- diphenylamine	15.69		1.001	.999	5	544.1
3-Nitro-3'-chlorodiphenylamine	15.85		1.022	.997	4	171.6
4-Nitrodiphenylamine	16.59	15.90*	1.004	.999	4	493.1
4-Nitro-3'-methyldiphenylamine	16.50		1.004	.999	4	557.4
4-Nitro-4'-aminodiphenylamine	17.35		1.001	.999	4	299.5

$\theta$  slope of plot of  $\log I$  vs.  $H_+$

r coefficient of correlation

N number of points

T student's test

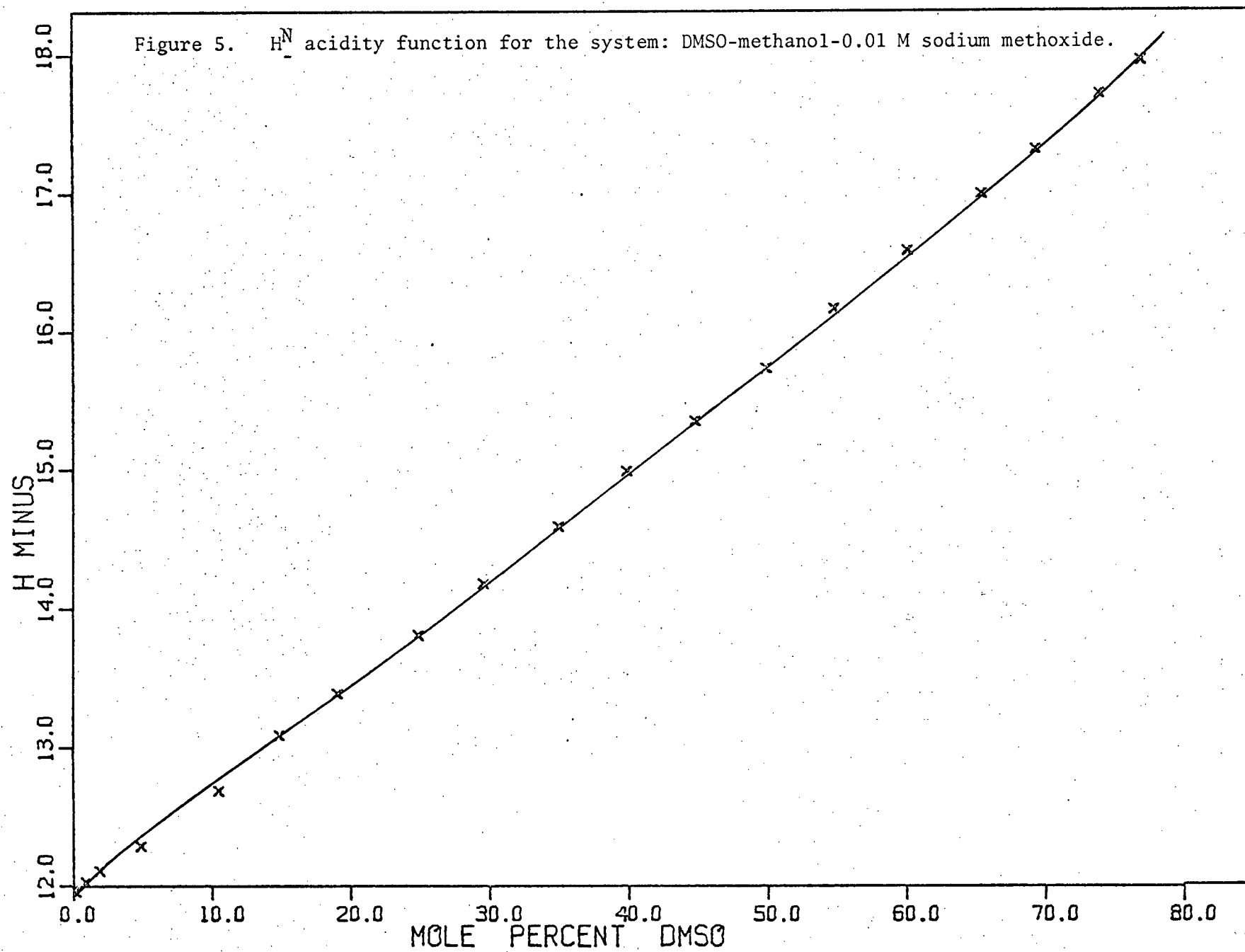
\* Stewart, O'Donnell, Cram and Rickborn, ref. 33.

TABLE VIII

$H_-^N$  values for the system DMSO-methanol-0.01 M  
sodium methoxide

Mole % DMSO	$H_-^N$	$H_-^N$ reported*
0.3	11.95	11.83
1.0	12.02	11.92
2.0	12.10	12.01
5.0	12.28	12.23
10.6	12.68	12.57
15.0	13.08	
19.2	13.38	13.27
25.0	13.80	
29.7	14.17	13.90
35.1	14.58	
40.0	14.98	14.44
44.9	15.34	
50.0	15.72	15.03
54.9	16.15	
60.2	16.57	15.76
65.5	16.98	
70.0	17.35	16.30
74.0	17.70	
77.0	17.94	

\* Stewart and O'Donnell, Cram and Rickborn, ref. 33.  
0.04 was substrated from each  $H_-$  value to account  
for difference in base concentration



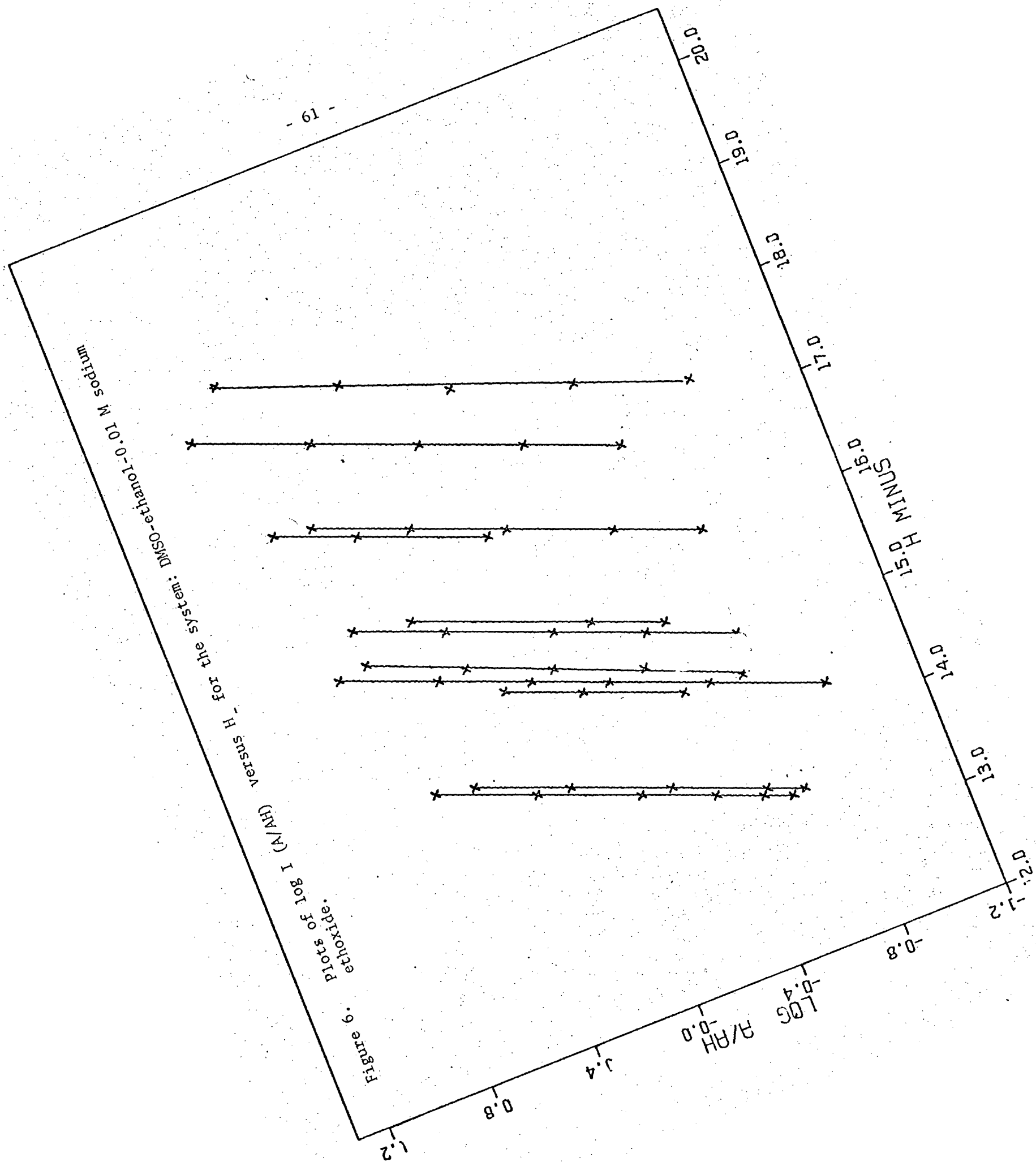




TABLE IX

$pK_a$  values of various amines as determined in the ethanolic  
DMSO system.

Amine	$pK_a$	$\theta$	r	N	T
2,4-Dinitrodiphenylamine	14.05	1.002	.999	6	508.0
2,4-Dinitro-3'-methyldiphenyl- amine	14.12	1.003	.999	5	450.5
2,4-Dinitro-4'-aminodiphenyl- amine	15.05	0.992	.999	3	186.2
4,4'-Dinitrodiphenylamine	--				
3,4'-Dinitrodiphenylamine	15.15	1.002	.999	6	836.1
4-Nitro-3'-trifluoromethyldi- phenylamine	15.63	1.003	.999	5	622.2
4-Nitro-3'-chlorodiphenylamine	15.73	1.005	.999	3	222.8
4-Nitrodiphenylamine	16.63	1.003	.999	5	599.6
4-Nitro-3'-methyldiphenylamine	16.55	1.009	.999	3	330.1
4-Nitro-4'-aminodiphenylamine	17.45	1.003	.999	5	617.5
2,4-Dinitroaniline	15.27	.960	.999	5	52.7
4-Chloro-2-nitroaniline	18.05	1.054	.999	5	39.0

$\theta$  slope of plot of  $\log I$  vs.  $H_+$

r coefficient of correlation

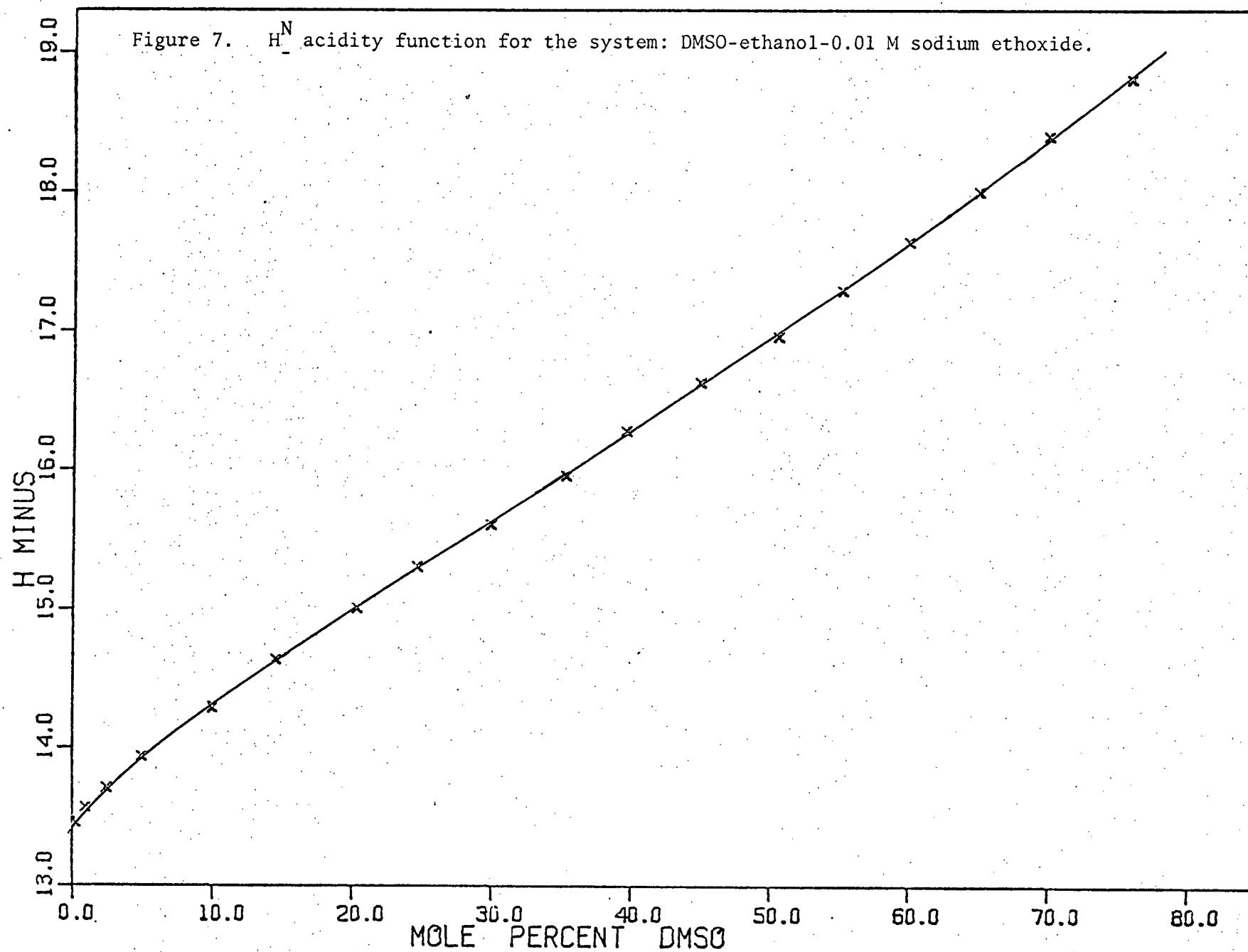
N number of points

T student's test

TABLE X

$H_{-}^N$  values for the system DMSO-ethanol-0.01 M  
sodium ethoxide

Mole % DMSO	$H_{-}^N$
0.3	13.46
1.0	13.57
2.5	13.71
5.0	13.94
10.0	14.29
14.6	14.64
20.4	15.01
24.7	15.31
30.0	15.60
35.4	15.96
39.7	16.28
45.0	16.63
50.6	16.96
55.2	17.29
60.0	17.64
65.0	18.00
70.0	18.40
75.9	18.81



### A. Validity of the $H^N$ scale in alcoholic DMSO

The validity of the stepwise procedure is based entirely on the reliability of Hammett's postulate. The postulate states that the activity coefficient term in equation 9 can be equated to zero.

$$pK_{HA} - pK_{HB} = \log \frac{[HA]}{[A^-]} - \log \frac{[HB]}{[B^-]} + \log \frac{f_{HA} f_{B^-}}{f_{HB} f_{A^-}} \quad (9)$$

The activity coefficient ratio of the indicator and indicator anion for two overlapping acid indicators being equal to unity in any given solution.

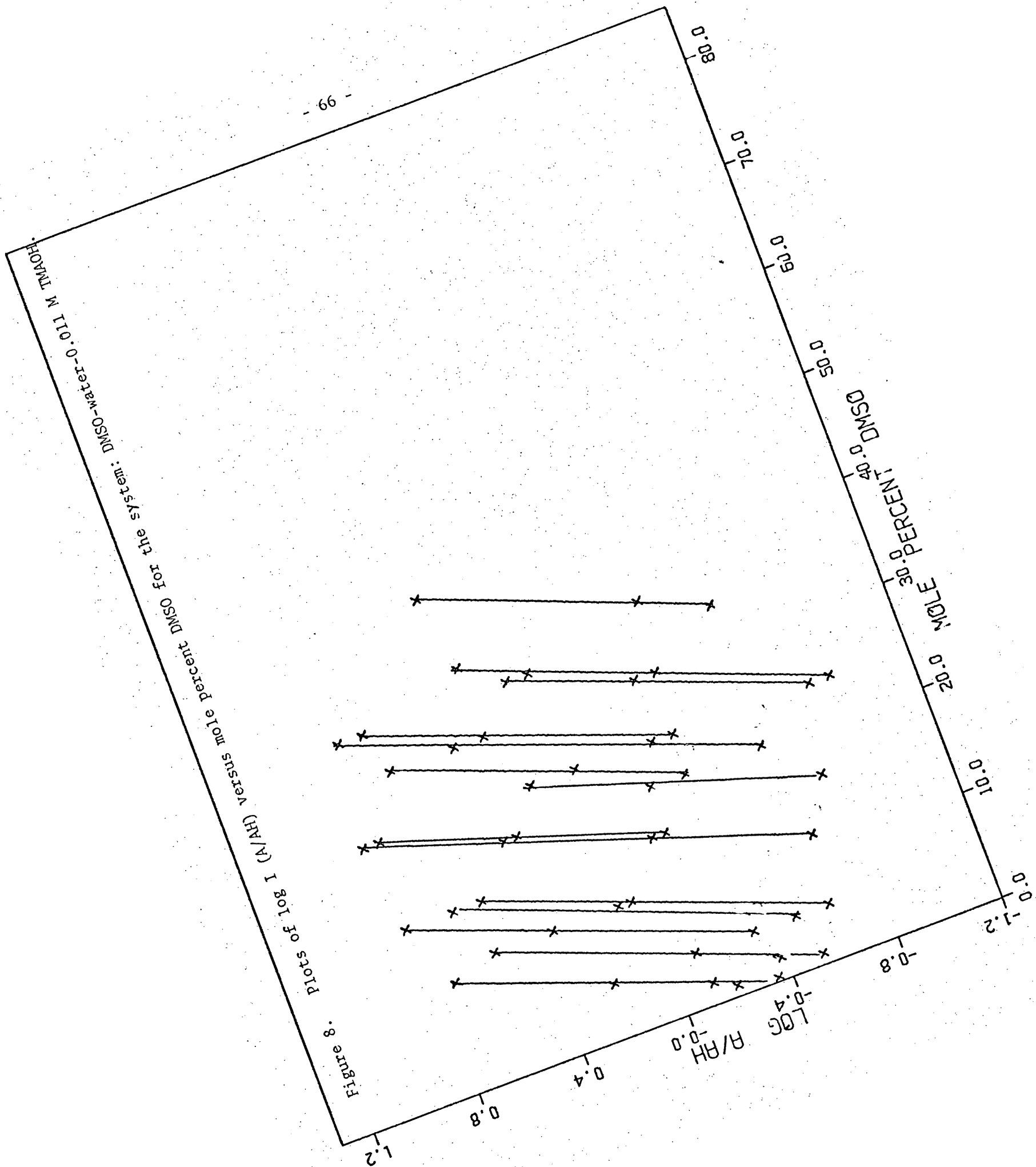
$$\frac{f_{HA}}{f_{A^-}} \cdot \frac{f_{B^-}}{f_{HB}} = 1$$

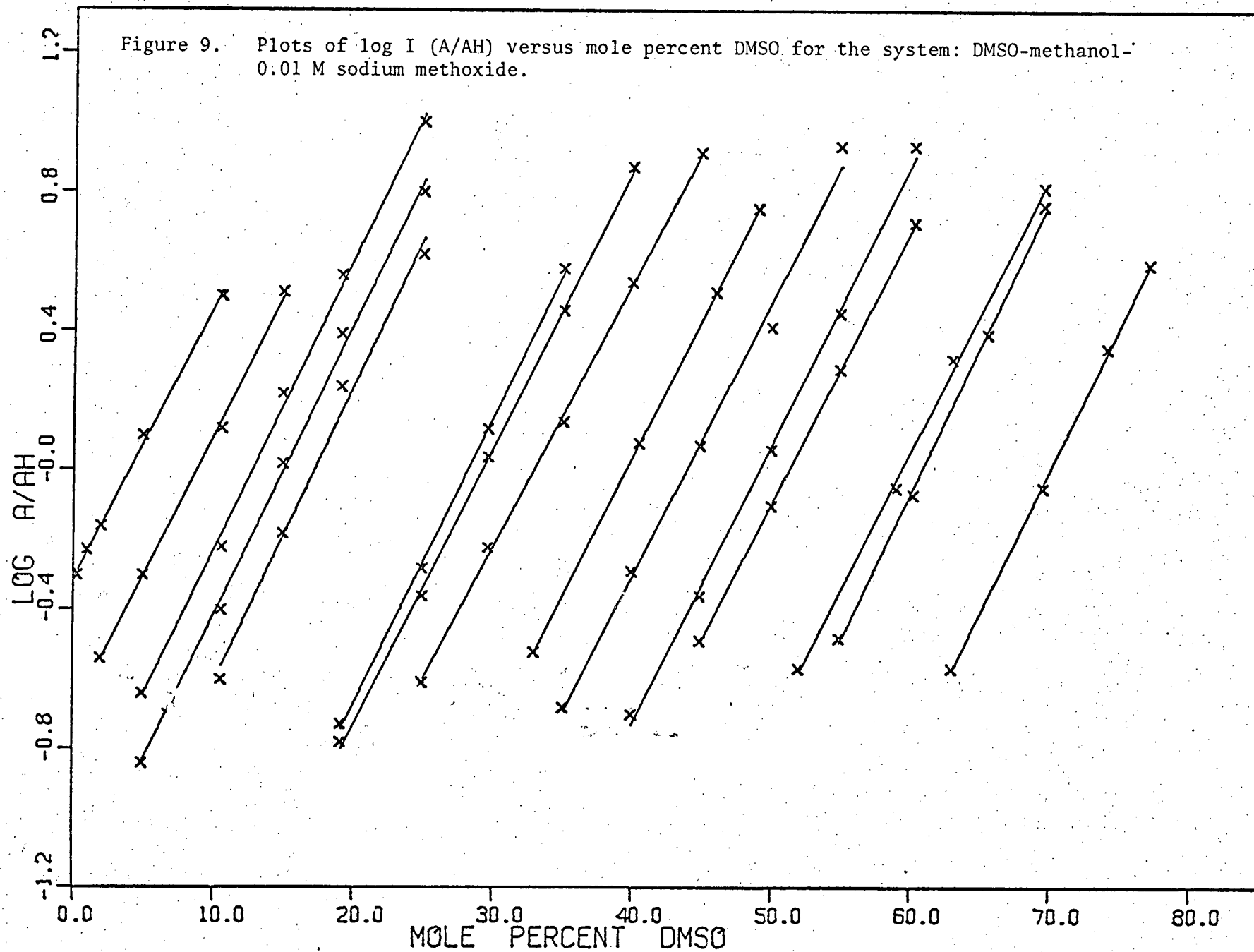
Applying this condition equation (9) reduces to (10).

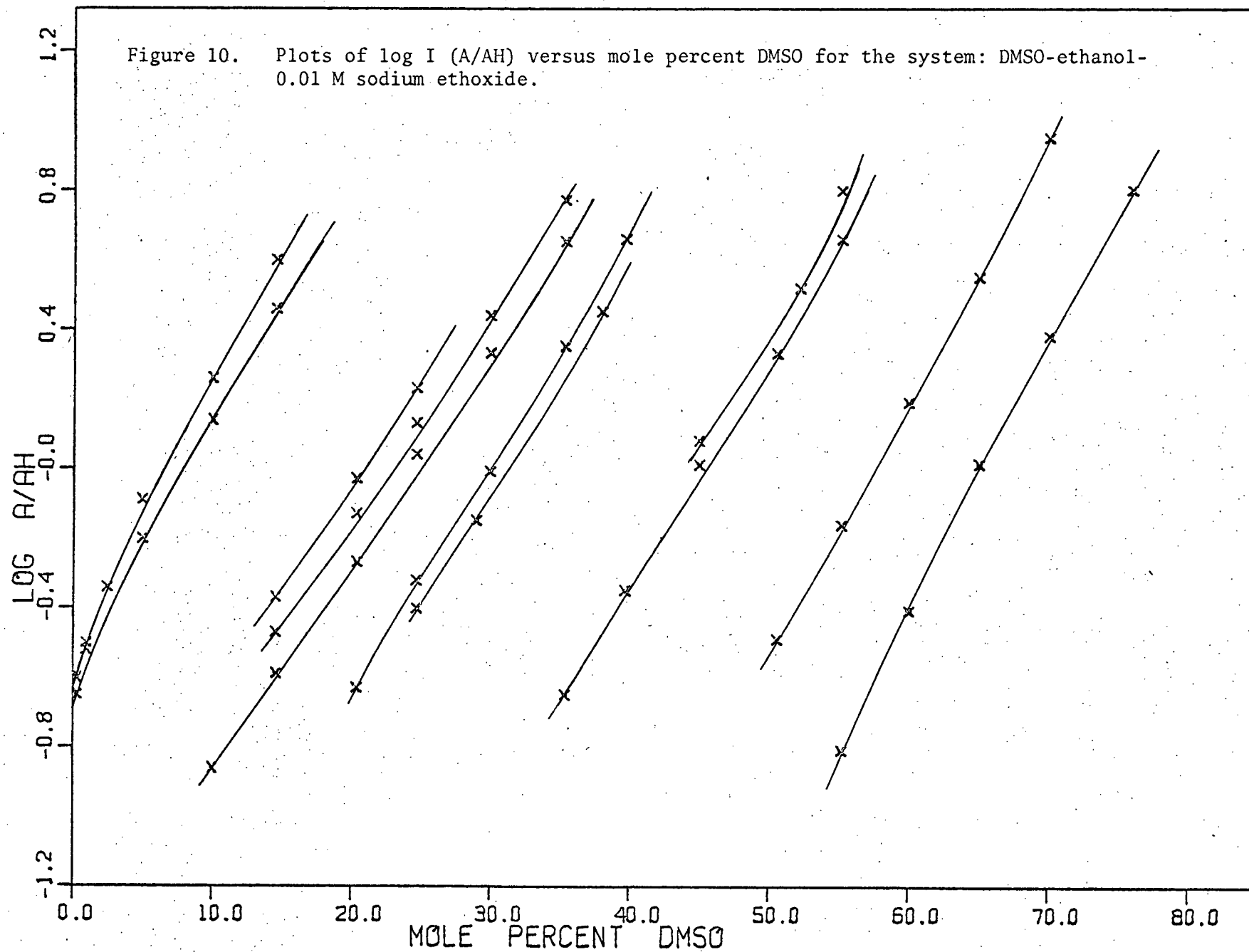
$$pK_{HA} - pK_{HB} = \log \frac{[HA]}{[A^-]} - \log \frac{[HB]}{[B^-]} \quad (10)$$

One obvious experimental test of the validity of equation (10) is that the term  $\log \frac{[HA]}{[A^-]} - \log \frac{[HB]}{[B^-]}$  remains constant as the medium is changed.<sup>75</sup> This constancy can be best examined by the parallelism in the plots of  $\log \frac{[HA]}{[A^-]}$  ( $\log I$ ) versus solvent composition for the different indicators studied.

In this work, figures 8, 9, and 10 are illustrations of this test, and it is evident that the plots of  $\log I$  vs mole percent DMSO







remain parallel for all the indicators. The reproducibility of any one  $pK_a$  determination using different solutions prepared over a period of several months was better than 0.05  $pK_a$  unit, which exceeds the accuracy of the  $H_-$  values (cf. experimental). There is a good agreement in the  $H_-$  values calculated using different indicators. The slopes of the lines of  $\log I$  versus  $H_-$  given in the  $pK_a$  tables are calculated by a least square method and are exceedingly close to unity. Correlation coefficients are also given and are close to unity. Student's test  $T$  evaluates the significance of the correlation, as a high correlation coefficient may easily arise by chance if the number of points plotted is small. These results would thus indicate that an  $H_-$  function can be defined in these systems.

It has been a prevalent opinion that the apparent relative strength ( $\log I_{HA} - \log I_{HB} = pK_{HA} - pK_{HB}$ ) of a series of Hammett indicators must remain uniform through drastic changes in solvent.<sup>46</sup>

This requirement for the validity of an  $H$  function will now be examined and its applicability considered in strongly acidic media, since there is a larger amount of data published on  $pK_{BH^+}$  than on  $pK_a$ .

The basis of Hammett's postulate is that if the indicators A and B are of similar structure one can expect  $\frac{f_A}{f_{AH^+}} \cdot \frac{f_{BH^+}}{f_B} = 1$ . Thirty years of work on acidity functions resulted in more stringent limitations being placed on structural variations. First considered was the molecular size, then the aromatic or aliphatic character then also the functional group - amino, amide, etc. Amines themselves have been differentiated into primary, secondary and tertiary. The existence of an  $H_0$  function in sulfuric acid systems has been asserted,<sup>75,78</sup>



and primary anilines were found to be reliable Hammett bases.<sup>78</sup> Even in such an "ideal" system, with reliable indicators many discrepancies arise.

The earlier colorimetric work is considerably less reliable than more recent work in which spectrophotometry has been used. Bascombe and Bell<sup>76</sup> redetermined  $pK_{BH^+}$  values for a number of Hammett indicators and found for example that, 4-methyl-2,6-dinitroaniline is 0.48 pK unit away from the "best value" given by Paul and Long<sup>75</sup> in their review article. Table XI lists  $pK_{BH^+}$  values for primary anilines, published between 1957 and 1964, all determined spectrophotometrically, and all in sulfuric acid media.\*

Although all the authors start with the same value for their anchor, 4-chloro-2-nitroaniline, or 2-chloro-6-nitroaniline,  $pK_{BH^+}$  values for the other indicators vary widely. Hogfeldt and Bigeleisen<sup>77</sup> measured their  $pK_{BH^+}$  values in  $H_2O-H_2SO_4$  and in  $D_2O-D_2SO_4$ . The average  $pK_{BH^+}$  difference ( $\Delta pK$ ) between the deuterio acid in heavy water solution, and the protio acid in water solution is 0.56 pK unit but some indicators show a much smaller  $\Delta pK$  value e.g. 2,6-dinitro-4-methylaniline  $\Delta pK = 0.40$ . From table XI one can see that there is a small difference between  $pK_{BH^+}$  values in  $H_2SO_4-H_2O$  and in  $D_2O-D_2SO_4$ , while there is a marked difference in  $pK_{BH^+}$  between aqueous sulfuric and  $H_2SO_4$ -sulfolane. This is probably due to the fact that there is

\* Paul and Long best values are only given as a reference, since Jorgensen and Harter<sup>78</sup> re-evaluated the  $pK_{BH^+}$  values of 2-bromo-4,6-dinitroaniline and 2,4,6-trinitroaniline and found them different from the best value by 0.23 and 0.38 pK unit respectively.

TABLE XI

$pK_{BH^+}$  of weak bases, in sulfuric acid media, from the literature

Anilines	$pK_{BH^+}$ water			$D_2O$	Sulfolane	
	a	b	c	d	e	f
2-nitro-	-0.29	-0.29		+0.30		
2-chloro-6-nitro-			-2.43			-2.42
4-chloro-2-nitro-	-1.03	-1.02		-0.46		
2,4-dichloro-6-nitro-	-3.32			-2.73	-3.37	-3.14
2,6-dinitro-4-methyl-	-4.44	-3.96		-4.04		
2,4-dinitro-	-4.53			-4.03	-4.36	-3.74
2,6-dinitro-	-5.41 <sup>g</sup>		-5.54			-4.50
2-bromo-4,6-dinitro-	-6.71	-6.64	-6.68		-6.55	-6.06
2,4,6-trinitro-	-9.41 -9.03 <sup>g</sup>		-10.10		-8.82	-8.21

<sup>a</sup> "best value" from Paul and Long, ref. 75.

<sup>b</sup> Bascombe and Bell, ref. 76.

<sup>c</sup> Jorgensen and Harter, ref. 78.

<sup>d</sup> Hogfeldt and Bigeleisen, ref. 77 these values are  $pK$  values of the deuterio acid in heavy water. The average difference  $\Delta pK$  between  $pK_{H_2SO_4}$  and  $pK_{D_2SO_4}$  is 0.56.

<sup>e</sup> Arnett and Douty, ref. 79a.

<sup>f</sup> Alder, Chalkley and Whiting, ref. 80.

<sup>g</sup> Value determined by Jorgensen and Harter, ref. 78 based on the  $H_o$  values of Paul and Long.

only a slight difference between water and heavy water while there is an enormous difference between water and sulfolane as solvents. The variation in  $pK_{BH^+}$  value does not go on increasing with decreasing basicity of the indicators, and therefore is a true difference and not due to a cumulative error in  $pK_{BH^+}$  determination. For example:

Indicator	$pK_{BH^+}$	difference in $pK_{BH^+}$ values between authors
2,6-dinitroaniline	$\sim 5$	1.04
2-bromo-4,6-dinitroaniline	$\sim 6$	0.62
2,4,6-trinitroaniline	$\sim 8-10$	1.90

Although most authors adopt a complaisant attitude towards the principle of  $pK$  values of Hammett bases, the data in Table XI do not warrant such a view. A not particularly drastic change in solvent system from aqueous to sulfolanic can give rise to widely different  $pK_{BH^+}$  values. Unfortunately few authors have published along with their results spectroscopic data of their indicators.

Only two groups of workers<sup>19,69</sup> have measured acidities of anilines by a non-photometric method. Ritchie and Uschold<sup>19</sup> measured potentiometrically the  $pK_a$  of four aniline type indicators in DMSO and found that the relative acidities differ only slightly from those measured spectrophotometrically in aqueous DMSO by Dolman and Stewart<sup>4</sup>. Birchall and Jolly<sup>69</sup> measured the acidities of a series of substituted anilines relative to 2,5-dichloroaniline, by n.m.r. in liquid ammonia at 31°. For the five anilines which have also been determined by Dolman and Stewart<sup>4</sup> none shows similar relative

acidities, in contrast with the above mentioned observation by Ritchie and Uschold. Therefore the relative acidities of anilines can vary with change in solvent, contrary to accepted premises.<sup>4,13</sup>

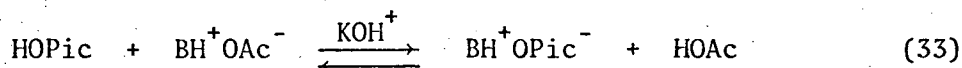
One must therefore study systematically Hammett type indicators to find a rationale for the fact that sometimes the acidity or the basicity of these indicators varies with solvent change and then sometimes does not.

The  $pK_a$  of an acid whose ionization occurs in the non-aqueous region is related to the standard state in water through a series of indicators with which it overlaps and with which it bears structural similarity. Ideally one would want to see a study of the relative strength of acids ( $HX$ ,  $HX_2$ ,  $HX_3...$ ) with respect to a fixed acid ( $HY$ ) in different solvent systems. Grunwald and Price<sup>81</sup> have noted that the relative strength of picric acid relative to acetic acid increases by almost two orders of magnitude in the solvent series  $HOH$ ,  $CH_3OH$ ,  $C_2H_5OH$ , while that of trichloroacetic acid remains nearly constant. Furthermore, the relative strength of picric acid with respect to phenol increases by the same amount while picric acid strength with respect to 2,4-dinitrophenol is constant. Therefore the increase in relative strength is not due to the chemical nature of the reference acid or phenol since, schematically we have:

change in relative $pK_a$ values	increase		constancy	
compound	picric acid	picric acid	trichloroacetic	picric acid
reference	acetic acid	phenol	acetic acid	2,4-dinitro- phenol

Grunwald and Price<sup>81</sup> postulated that this is due to dispersion effects which occur between the delocalized virtual electronic oscillators of the solute and the surrounding medium. Their argument is that if we compare a coloured indicator with a colourless reference compound (picric acid/acetic acid and picric acid/phenol) we can expect an increase in relative strength in the series HOH, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH; while if we compare a colourless acid with a colourless reference (trichloroacetic acid/acetic acid) or a coloured acid with a coloured reference (picric acid/2,4-dinitrophenol) we can expect constancy in relative strength.

These authors,<sup>81</sup> by studying the system



estimated the magnitude of these dispersion forces. The equilibrium constant  $K_{\text{BH}^+} = \frac{[\text{HOAc}][\text{BH}^+\text{OPic}^-]}{[\text{HOPic}][\text{BH}^+\text{OAc}^-]}$  increases by almost an order of magnitude in glacial acetic acid by varying BH<sup>+</sup> from NH<sub>4</sub><sup>+</sup> to (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>, while the corresponding equilibrium constant for trichloroacetic acid is insensitive to the change in BH<sup>+</sup>. Calculation using a model in which BH<sup>+</sup> is hydrogen bonded to the anionic oxygen atom in the ion pair gives a dispersion energy of -1.6 kcal/mole. They also suggested that the difference in relative base strength of aliphatic amines obtained by measurements in water or with colour indicators in solvents of low dielectric constant could be accounted for by the existence of strong dispersion effects.

The importance of dispersion effects was also noted by other workers. Ritchie and Uschold<sup>19</sup> in pointing out the failure of the  $H_C$  scale suggested that the ionization behaviour of hydrocarbon acids which have highly coloured conjugate bases is not the same as that of acids whose conjugate bases are not delocalized. J. Juillard<sup>82</sup> studied the dissociation of a few carboxylic acids in methanol and water and found a definite, though imprecise, correlation between the molecular polarizability of the acids and change in  $pK$  with different solvent.

A.J. Parker et. al.<sup>9b,83</sup> in their extensive studies on solvation of ions in protic and aprotic solvents have also pointed out the necessity of taking into account solvent structure and mutual polarizability interactions (dispersion forces) if we want to explain the significant changes in the chemistry of anions on transfer from water to methanol and dipolar aprotic solvents. If we rearrange the table of  $pK_a$  of acids from reference 83 to take into account colour, we find that although each acid has a different  $pK_a$  in every solvent, the relative strength of two acids  $\Delta pK$  of similar colour remains constant through change in solvent. This is not true, however, for any two acids in two different colour divisions.

Acid	$pK(H_2O)$		$pK(MeOH)$		$pK(DMF)$		$pK_{DMSO}$	
		$\Delta pK$		$\Delta pK$		$\Delta pK$		$\Delta pK$
dichloroacetic	1.29	1.57	6.4	1.30	7.2	1.8		
chloroacetic	2.86		7.7		9.0			
benzoic	4.20	1.34	9.1	1.4	10.2	1.2	11.0	
acetic	4.76	0.56	9.6	0.5	11.1	0.9	11.4	0.4
2,4-dinitrophenol	4.10		7.9		6.0		5.2	
4-nitrophenol	7.15	3.05	11.2	3.3	10.9	4.9	9.9	4.7

They also noted that for all the acids listed (17 of them) acidities in water and methanol show some correlation, as well as in DMF and DMSO, but there is no correlation between the acidities in a protic and an aprotic solvent. And so there is enough evidence of the nonuniformity of the relative strength for a series of related acids or bases, through changes in solvent, except if their similarity extends to their spectral characteristics.

By extending Grunwald and Price's argument to its logical conclusion, we can put forward the postulate that the relative strengths of indicators will remain unaltered through changes in solvent environment only if their spectral characteristics in both ionized and unionized forms are similar. Indicators which will comply with this limitation will be referred to as "similar colour indicators."

Table XII lists the  $pK_a$  measured in this work for the substituted 2,4-dinitro, and 4-dinitrodiphenylamines referred to hereafter as 2,4-dinitro series and 4-nitro series. Their spectral characteristics are listed in Tables XIII and XIV. One can see that the visible spectra of the 2,4-dinitro compounds are all quite similar with the exception of their 4'-nitro- and 4'-amino-derivatives. The substituted 4-nitro compounds also show a similarity in their absorbances, with again the exception of their 4'-nitro- and 4'-amino-derivatives.

The main difference is between the ionized form of these two classes of indicators, the 4-nitro compounds absorb at a longer wavelength and their molar absorptivities are twice as much as those of their 2,4-dinitro analogs. From Table XI one can also see that although

TABLE XII

Summary of the  $pK_a$  values of diphenylamines determined in this work

	H <sub>2</sub> O	MeOH	EtOH
2,4,4'-Trinitrodiphenylamine	12.30	12.25	
2,4,3'-Trinitrodiphenylamine	12.59	12.65	
2,4-Dinitro-4'-trifluoromethyldiphenylamine	12.87	12.85	
2,4-Dinitro-3'-trifluoromethyldiphenylamine	13.06	13.03	
2,4-Dinitro-3'-chlorodiphenylamine	13.17	13.20	
2,4-Dinitrodiphenylamine	13.85	14.05	14.05
2,4-Dinitro-3'-methyldiphenylamine	13.90	14.10	14.12
2,4-Dinitro-4'-aminodiphenylamine	14.48	14.95	15.05
4,4'-Dinitrodiphenylamine	14.08(?)	14.42	--
3,4'-Dinitrodiphenylamine	14.62	15.26	15.15
4-Nitro-3'-trifluoromethyldiphenylamine	14.90	15.69	15.63
4-Nitro-3'-chlorodiphenylamine	15.00	15.85	15.73
4-Nitrodiphenylamine	15.67	16.59	16.63
4-Nitro-3'-methyldiphenylamine	15.60	16.50	16.55
4-Nitro-4'-aminodiphenylamine	16.40	17.35	17.45



TABLE XIII

Absorption maxima and molar absorptivities of the indicators in  
absolute ethanol

	Observed Values $\lambda_{\max}$ (m $\mu$ )	$\epsilon$	Reported Values $\lambda_{\max}$ (m $\mu$ )	$\epsilon$	Ref.
2,4,4'-Trinitrodiphenylamine	390	18300	385	21900 <sup>b</sup>	13
2,4,3'-Trinitrodiphenylamine	354	20000	360	17850 <sup>c</sup>	13
2,4-Dinitro-4'-trifluoromethyl- diphenylamine	354	17900			
2,4-Dinitro-3'-trifluoromethyl- diphenylamine	354	17500			
2,4-Dinitro-3'-chlorodiphenyl- amine	356	17900			
2,4-Dinitrodiphenylamine	361	16900	352	17700 <sup>a</sup>	4b
2,4-Dinitro-3'-methyldiphenyl- amine	365	19200			
2,4-Dinitro-4'-aminodiphenyl- amine	378	14400	375	18300 <sup>c</sup>	13
4,4'-Dinitrodiphenylamine	418	33000	403	34100 <sup>a</sup>	4b
3,4'-Dinitrodiphenylamine	390	22200	375	23200 <sup>a</sup>	4b
4-Nitro-3'-trifluoromethyl- diphenylamine	394	21800	381	19200 <sup>a</sup>	4b
4-Nitro-3'-chlorodiphenyl- amine	396	25500	385	22700 <sup>a</sup>	4b
4-Nitrodiphenylamine	402	22000	400	19550 <sup>b</sup>	4b
4-Nitro-3'-methyldiphenyl- amine	410	24000	394	22300 <sup>a</sup>	4b
4-Nitro-4'-aminodiphenyl- amine	420	19100			
4-Chloro-2-nitroaniline	424	5300	417	3450 <sup>e</sup>	13
2,4-Dinitroaniline	346 384	14400 6600	336	14900 <sup>e</sup>	13

<sup>a</sup> in 95.6% ethanol    <sup>b</sup> in pyridine or aqueous pyridine    <sup>c</sup> in sulfolane or  
aqueous sulfolane    <sup>e</sup> in methanol

TABLE XIV

Absorption maxima and molar absorptivities of indicator anions in

DMSO-ethanol					
	Observed $\lambda_{\max}$ (m $\mu$ )	Values $\epsilon$	Reported $\lambda_{\max}$ (m $\mu$ )	Values $\epsilon$	Ref.
2,4,4'-Trinitrodiphenylamine	530	29900	520	27400 <sup>b</sup>	13
2,4,3'-Trinitrodiphenylamine	432	23600	450	18700 <sup>c</sup>	13
2,4-Dinitro-4'-trifluoromethyl-diphenylamine	435 474	20400 19500			
2,4-Dinitro-3'-trifluoromethyl-diphenylamine	435 474	20000 18900			
2,4-Dinitro-3'-chlorodiphenylamine	432 475	20400 18100			
2,4-Dinitrodiphenylamine	432 485	19700 16500	434	19000 <sup>a</sup>	4
2,4-Dinitro-3'-methyldiphenylamine	434 480	23000 19700			
2,4-Dinitro-4'-aminodiphenylamine	496	17400	495	18300 <sup>c</sup>	13
4,4'-Dinitrodiphenylamine	590	51000	580	37000 <sup>b</sup>	13
3,4'-Dinitrodiphenylamine	324 504	15000 36100			
4-Nitro-3'-trifluoromethyl-diphenylamine	506	36500			
4-Nitro-3'-chlorodiphenylamine	504	41800			
4-Nitrodiphenylamine	505	34800	508	34600 <sup>b</sup>	13
4-Nitro-3'-methyldiphenylamine	510	36200			
4-Nitro-4'-aminodiphenylamine	518	29800			
4-Chloro-2-nitroaniline	496 524	8300 8200	495 520	8440 <sup>a</sup> 8440	4
2,4-Dinitroaniline	388 392 502	17300 15400 12200	388 535	21100 <sup>b</sup> 15300	13

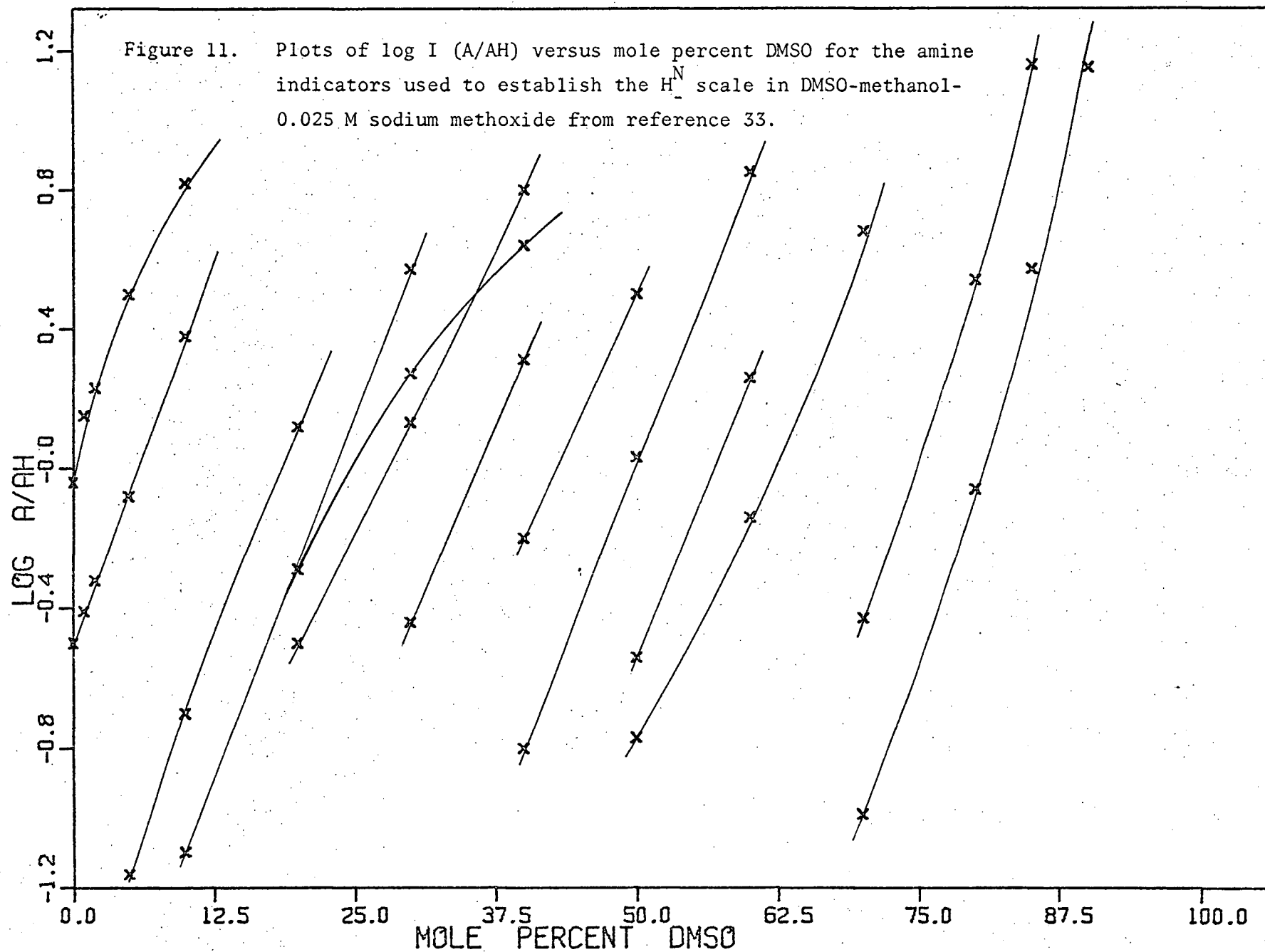
<sup>a</sup> in DMSO-water    <sup>b</sup> in pyridine    <sup>c</sup> in sulfolane

the  $pK_a$  of the 2,4-dinitro compounds remain the same in the three systems, the 4-nitro compounds are some 0.8 units higher in DMSO-MeOH and DMSO-EtOH than in DMSO-H<sub>2</sub>O.

The importance of the anchor in the establishment of an  $H_-$  function has been previously emphasized (pp.51-52). 2,4,4'-trinitrodiphenylamine has been used as an anchor for the DMSO-water and DMSO-methanol systems, while 2,4-dinitrodiphenylamine was used for the DMSO-ethanol system. Therefore if our assumption is valid we should find the relative strength of all the substituted 2,4-dinitrodiphenylamines constant. Also we should find that the relative strength of the substituted 4-nitrodiphenylamines constant. Only the relative strength of the 4-nitro series with respect to the 2,4-dinitro series should vary. Also if a linear free energy relationship is constructed between the  $pK_a$  values versus Hammett substituent constants the  $\rho$  value for the 4-nitro series should remain of the same order of magnitude through change in solvent system. Indeed this is the case as can be seen from Figure 12 and Table XV. As circumstantial evidence for the validity of the  $H_-$  scales defined, and the "similar colour indicator" assumption, the ionization of 2,4-dinitroaniline and 4-chloro-2-nitro-

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\* An  $H_-^N$  function in DMSO-MeOH-0.025 M NaOMe has been determined by Stewart, O'Donnell, Cram and Rickborn,<sup>33</sup> and these authors found that the  $pK_a$  values of all their indicators agreed with the determined values in aqueous DMSO. But aside from the fact that their anchor 2,4,6-trinitroaniline, has been shown subsequently to form Meisenheimer complex in DMSO-MeOH-NaOMe, a plot of log I versus mole percent DMSO shows several cases of nonparallelism between the indicators, Figure 11. These facts cast some doubt as to the validity of the  $H_-^N$  function defined by Stewart et al.,<sup>33</sup> and their listed  $pK_a$  values.



aniline was studied in the system DMSO-EtOH-0.01 M NaOEt. The  $pK_a$  assigned are:

	$pK_a$	$pK_a$ reported in DMSO-H <sub>2</sub> O, ref. 4.
3,4'-dinitrodiphenylamine	15.10	14.66
2,4-dinitroaniline	15.27	15.00
4-chloro-2-nitroaniline	18.05	17.08

The  $pK_a$  of 3,4'-dinitrodiphenylamine is also included as it has a  $pK_a$  similar to the one of 2,4-dinitroaniline in DMSO-EtOH, but its  $pK_a$  in DMSO-water is 0.5 unit lower than in ethanolic DMSO.

One can see that the spectral characteristics of 2,4-dinitroaniline are somewhat similar to those of the 2,4-dinitrodiphenylamine series, while spectral characteristics of 4-chloro-2-nitroaniline are quite different. According to the similar colour assumption the  $pK_a$  of the former should be comparable in both media (0.27  $pK_a$  units apart is within the experimental accuracy) while the latter should be quite different (1.00  $pK_a$  units away).

#### B. Correlation of Structure with Acidity

Preliminary results<sup>13</sup> on the acidity of substituted diphenylamines indicated the dominance of the nitro group, whose effect overwhelmed that of all other substituents. Enough data have now been gathered to make it possible for us to compare the linear free energy relationships of the A) substituted diphenylamines (D. Dolman<sup>4</sup> results), B) 4-nitro substituted DPA, C) 2,4-dinitro substituted DPA,

D) 2,4,6-trinitro substituted DPA (A. Buckley, unpublished results).

Figure 12 shows a plot of  $pK_a$  versus  $\sigma^\circ$  and it is obvious that there is a good correlation.

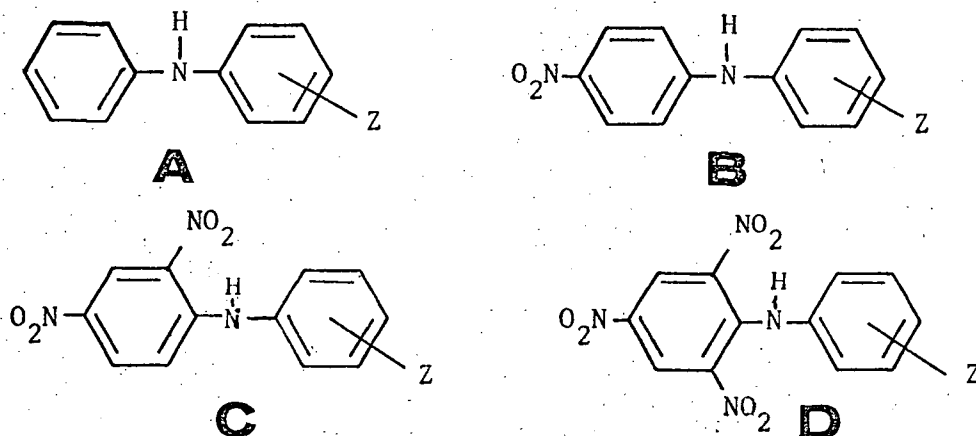


Table XV lists the  $\rho$  values, correlation coefficients and Students test's T computed for the plot in Figure 12.\*

The substituent constant  $\sigma^\circ$  usually correlates reactivities for reaction in which there is no conjugation between the substituents and the reaction center. They were derived by interposing a methylene group between the benzene ring and the reaction center, so that the resonance effect would be essentially constant for such a reaction series.  $\sigma^-$  is used for reaction in which there is direct conjugation, and  $\sigma$  for systems that possess the limited amount of conjugation present in benzoic acids.

For the "normal" substituents m-methyl, m-chloro, m-trifluoro, p-trifluoro and m-nitro the  $\sigma^\circ$  values are very similar to the  $\sigma$  value so one cannot really draw any conclusions from the correlation with  $\sigma^\circ$  except that there is no direct resonance interaction between these groups and the amide ion.

\*

In line "A" the 4'-nitro substituent has been omitted from the calculation since it requires an exalted  $\sigma$  value.

Figure 12. Hammett correlation of the acidity of substituted diphenylamines.

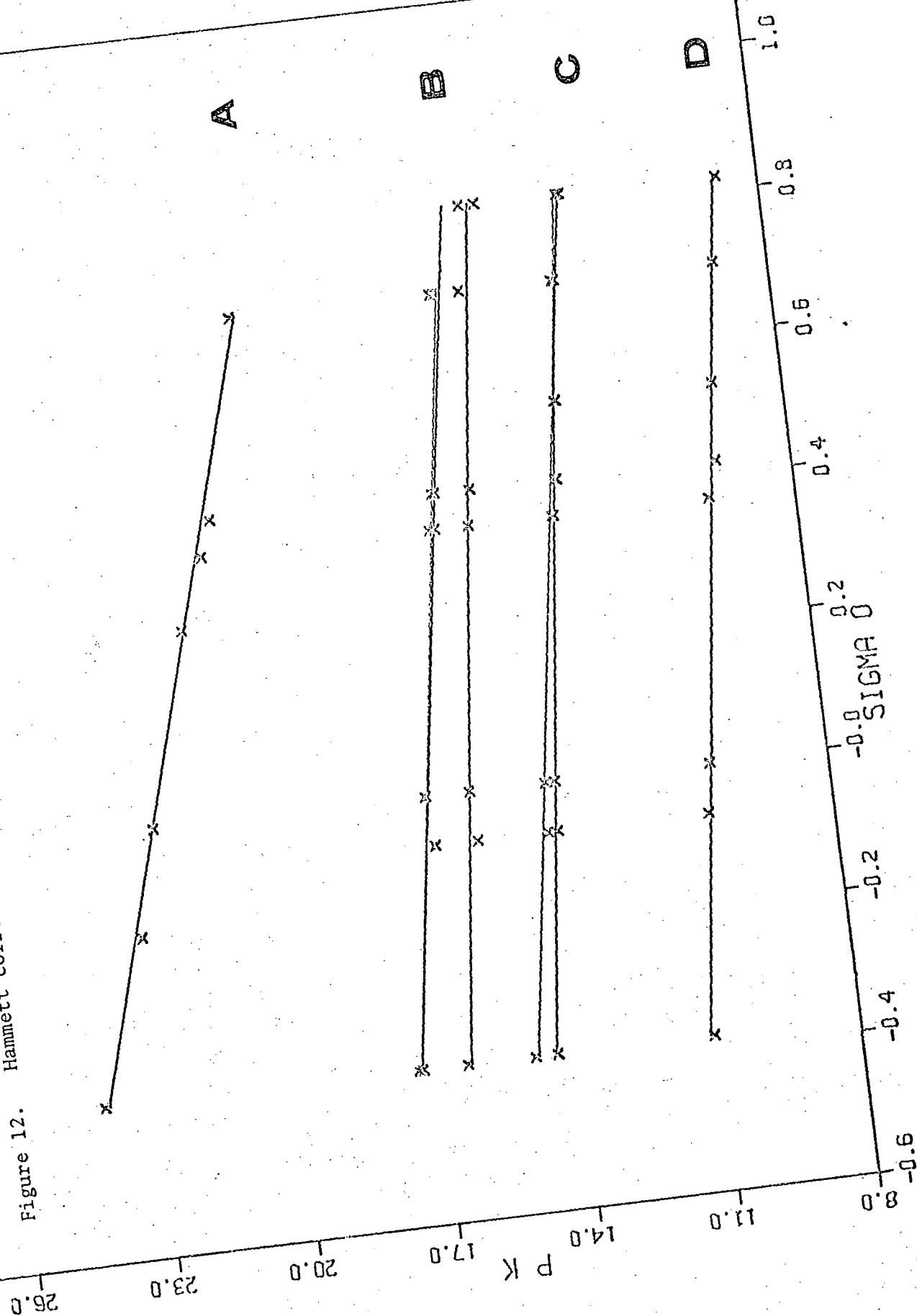
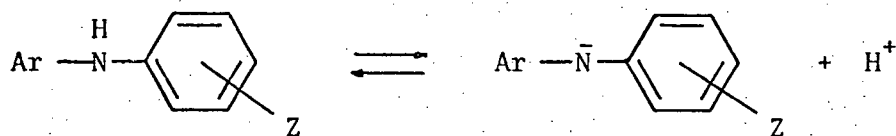


TABLE XV

Linear free energy correlation of diphenylamines acidities

computed by a least squares method



Ar	System	$\rho$	$\Delta\rho$	N	r	T
2,4,6-trinitrophenyl	aqueous buffers	-1.88	0.06	8	.997	32.1
2,4-dinitrophenyl	DMSO-H <sub>2</sub> O	-1.79	0.03	8	.999	60.0
	DMSO-MeOH	-2.17	0.08	8	.996	27.4
4-nitrophenyl	DMSO-H <sub>2</sub> O	-1.75	0.12	7	.987	13.6
	DMSO-MeOH	-2.17	0.20	7	.979	10.8
	DMSO-EtOH	-2.12	0.12	7	.993	17.3
phenyl	DMSO-H <sub>2</sub> O	-4.34	0.14	7	.997	31.0

N number of indicators used.

r coefficient of correlation.

T Student's test.



However the  $pK_a$  values for the p-amino substituent do not correlate with  $\sigma$  but with  $\sigma^\circ$ . This is because there is very little resonance between the amino substituent and the amide ion, and correlation with  $\sigma^\circ$  (no resonance) is expected. For the p-nitro resonance interaction of the following type is of prime importance.

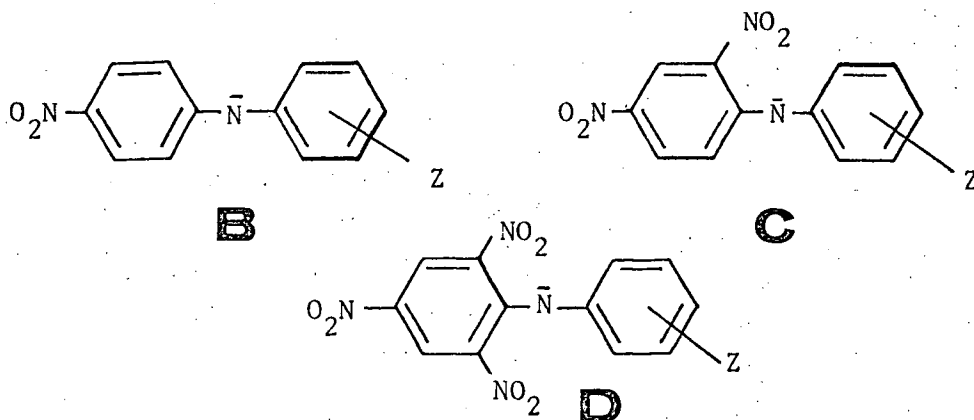


The substituent constant value for the 4-nitro group<sup>4</sup> is 0.78 in the ionization of benzoic acids ( $\sigma$ ); 0.82 in ionization of phenylacetic acids ( $\sigma^\circ$ ); 1.27 in the ionization of phenols and anilinium ions ( $\sigma^-$ ). Recently<sup>84</sup> a value of 1.70 was ascribed for  $\alpha$ -naphthol dissociation and 1.81 for  $\alpha$ -naphthoxide methylation. D. Dolman<sup>4</sup> assigned a  $\sigma^-$  value of 1.65 for the 4-nitro substituent in the ionization of diphenylamine, and D. Kroeger<sup>18</sup> assigned a  $\sigma^-$  of 1.73 to account for the effect of the p-nitro group in the  $\alpha$ -ring on the Lewis acidity of  $\alpha$ -cyanostilbenes. It is surprising that this same compound correlates well with the  $\sigma^\circ$  value in line b when it is looked upon as unsubstituted 4-nitrodiphenylamine instead of a diphenylamine substituted with a p-nitro group. Since the acidities of diphenylamines correlates with  $\sigma^\circ$ , we could conclude that there is very little conjugation between the substituent and the central atom. This brings us to the dichotomy in the magnitude of  $\rho$  between diphenylamines and nitro-diphenylamines.

The magnitude of the  $\rho$ -value is a measure of the susceptibility of diphenylamine ionization on the polar effect of the substituent Z.

Nitro-substituted diphenylamines have a  $\rho$ -value around 2, with a minimal increase from the 2,4,6-trinitro series to the 2,4-dinitro series and the 4-nitro series; while diphenylamine itself shows a higher response to substituent changes and has a  $\rho$ -value of 4.34. These  $\rho$ -values should be compared with  $\rho$ 's of 1.00 for benzoic acids, 2.23 for phenols and 2.89 for anilinium ions in aqueous systems at 25°, and 5.3 for anilines in liquid ammonia.<sup>69</sup> Thus the  $\rho$ -value for the ionization of diphenylamine is similar to the one for anilines and is twice as large as the  $\rho$ -value for the ionization of phenols; the latter being similar to the  $\rho$  for the ionization of nitrodiphenylamines. This dichotomy probably results from the greater enjoyment of charge delocalization by the diphenylamines and aniline anions than by the anions of nitro-substituted diphenylamines and phenols.

Thus the dominating feature of the p-nitro substituent can be put in its proper perspective. For nitro-diphenylamines a low degree of conjugation between the amino centre and the substituent is noted, since the negative charge on the amide ion is already delocalized into the nitrated ring, which is obvious from the need for an exalted  $\sigma^-$  value for the p-nitro substituent in the diphenylamine correlation. For B, C, D, the orientation of the ring with the Z-substituent is such that much of its contribution is sacrificed so



that the p-nitro group can heighten its conjugation. While for A maximum overlap occurs between the nitrogen orbitals and the ring with the substituent Z, thus the greater  $\rho$  value. Remembering, that acidities of substituted diphenylamine correlate with  $\sigma^\circ$ , there should be only a minimal and constant amount of resonance energy available for the ring and its substituents, so that in the case of the nitro diphenylamines the "pie" has to be divided between both rings while for the un-nitrated diphenylamines all of it goes to the ring with the substituent Z.

Dolman and Stewart<sup>4</sup> have explained deviations from additivity of the effect of nitro groups in compounds with nitro groups in both rings to the inability of both rings to attain simultaneously maximum overlap with the nitrogen atom, which is a similar type of argument.

## II. Phenol indicators $H_-^0$

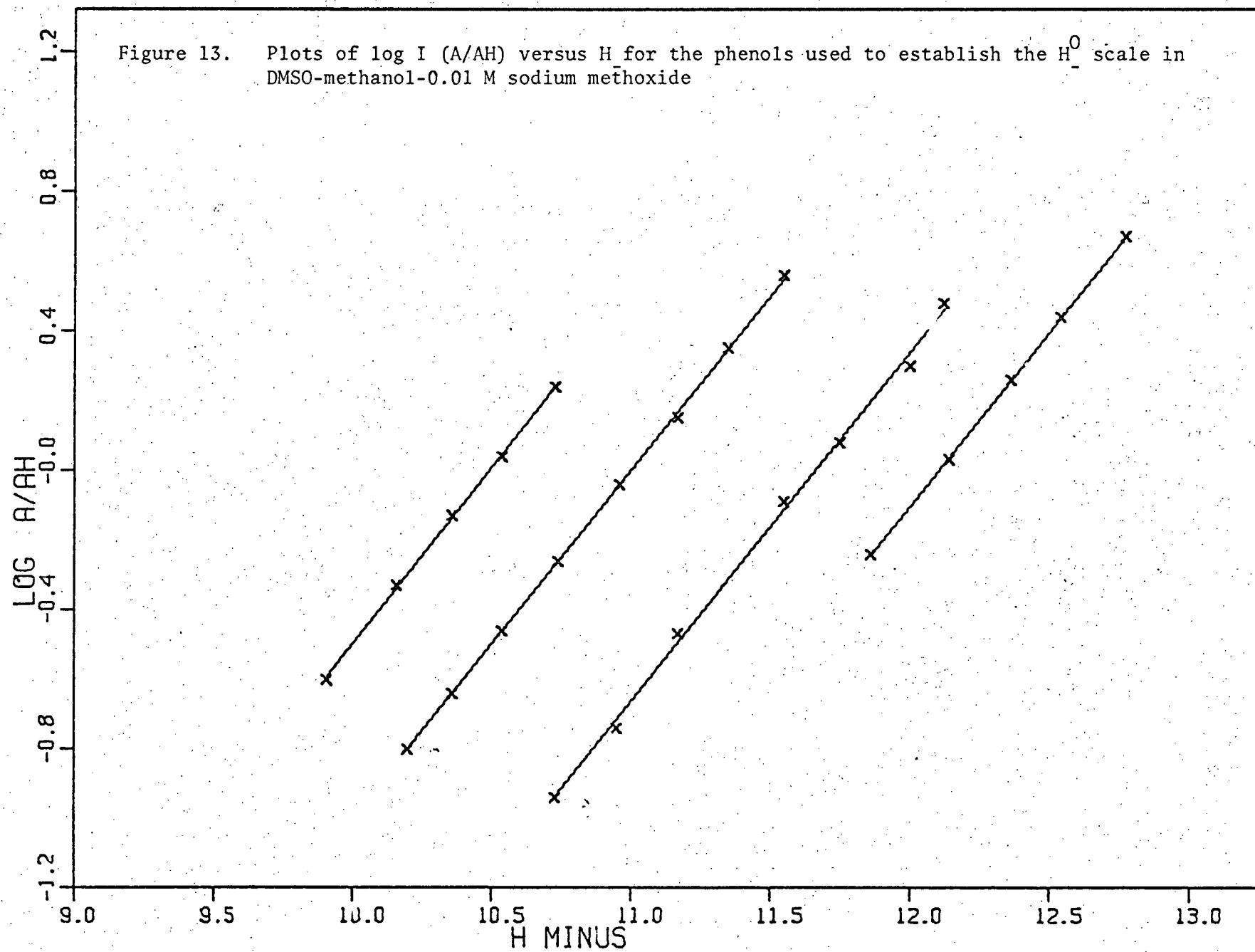
Many of the phenol indicators used in establishing the  $H_-^0$  scales in DMSO-methanol-0.01 M sodium methoxide and DMSO-ethanol-0.01 M sodium ethoxide are the same as those used by Rochester<sup>31</sup> to construct his scale in methanolic sodium methoxide.

The methanolic dimethylsulfoxide scale was anchored with 2-isopropyl phenol ( $pK_a=10.5$ ) and then checked with phenol itself ( $pK_a=9.98$ ) which is half ionized in a 0.01 M sodium methoxide solution. The ethanolic dimethylsulfoxide scale was anchored with 2,6-diisopropyl phenol ( $pK_a=11.0$ ).

Figures 13 and 14 show computer output plots of the measured values of  $\log I$  versus  $H_-$  for the phenol indicators in methanolic and ethanolic DMSO solutions. The plots are parallel and the slopes are very close to unity, as can be seen in Table XVII. The  $pK_a$  values assigned to these phenols are also listed in Table XVII.

The thermodynamic acidities of the anchors were determined in aqueous buffers and therefore the  $pK_a$  values obtained are relative to water as the standard state. The  $pK_a$  values determined by Rochester<sup>31</sup> were deduced by the method of Ridd and O'Ferrall<sup>32</sup> and are relative to methanol as the standard state. Cohen and Jones<sup>29</sup> values were determined spectrophotometrically in aqueous solutions and agree with the values determined in this work except for 2,4-di-t-butyl- and 2-t-butyl-phenol.

The  $H_-^0$  acidity functions for methanolic and ethanolic DMSO are given in Table XVI, and are plotted in Figure 15. A summary of



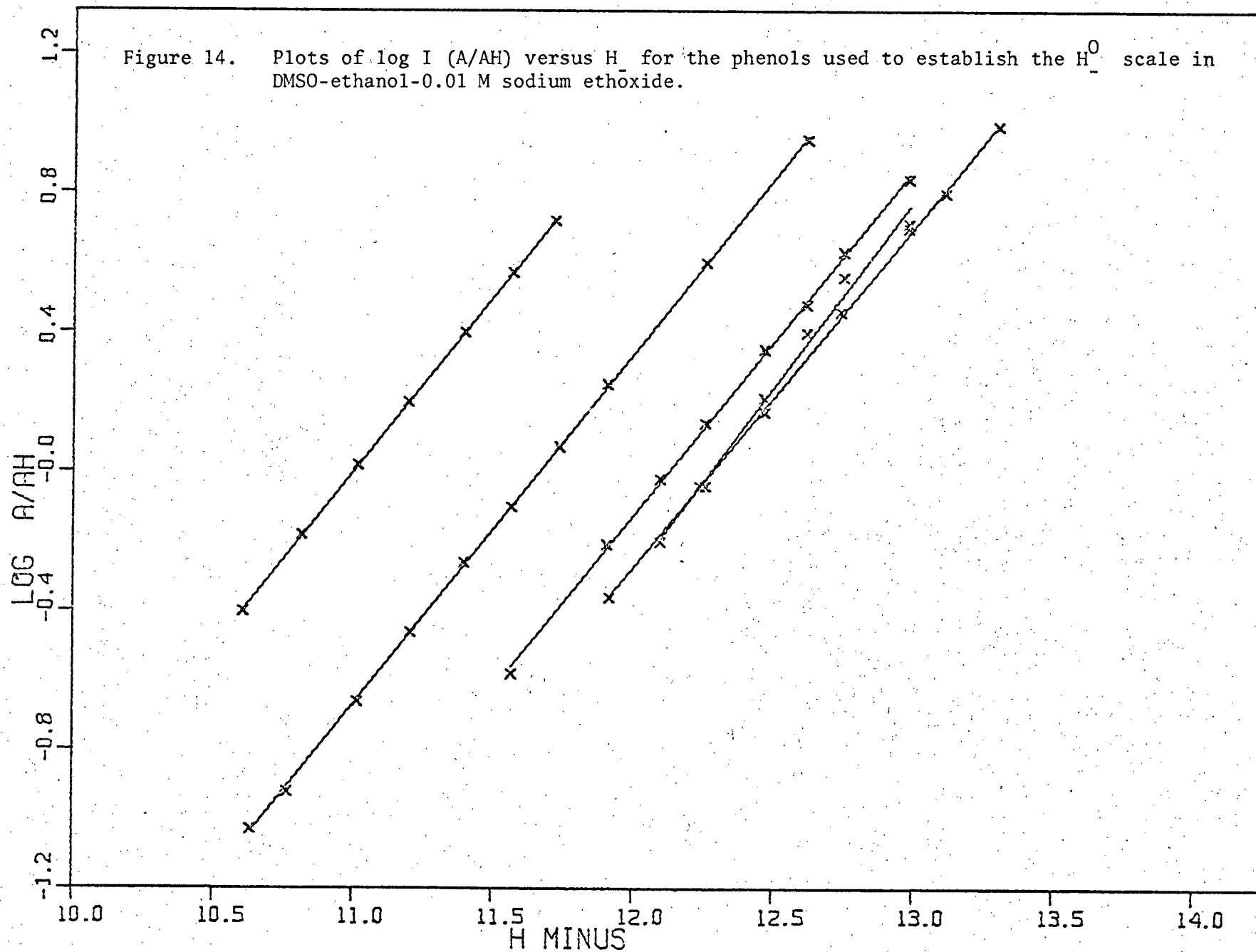


TABLE XVI

$H_{-}^O$  values for the systems DMSO-methanol 0.01 M  
sodium methoxide and DMSO-ethanol 0.01 sodium  
ethoxide

Mole % DMSO	$H_{-}^O$ (DMSO-MeOH)	$H_{-}^O$ (DMSO-EtOH)
0.0	9.92	10.62
1.0		10.77
5.0	10.17	11.02
10.0	10.35	11.21
15.0	10.53	11.41
20.0	10.73	11.56
25.0	10.94	11.74
30.0	11.17	11.91
35.0	11.36	12.10
40.0	11.55	12.26
45.0	11.75	12.46
50.0	11.98	12.62
55.0	12.20	12.75
60.0	12.42	12.98
65.0	12.63	13.11
70.0	12.84	13.31

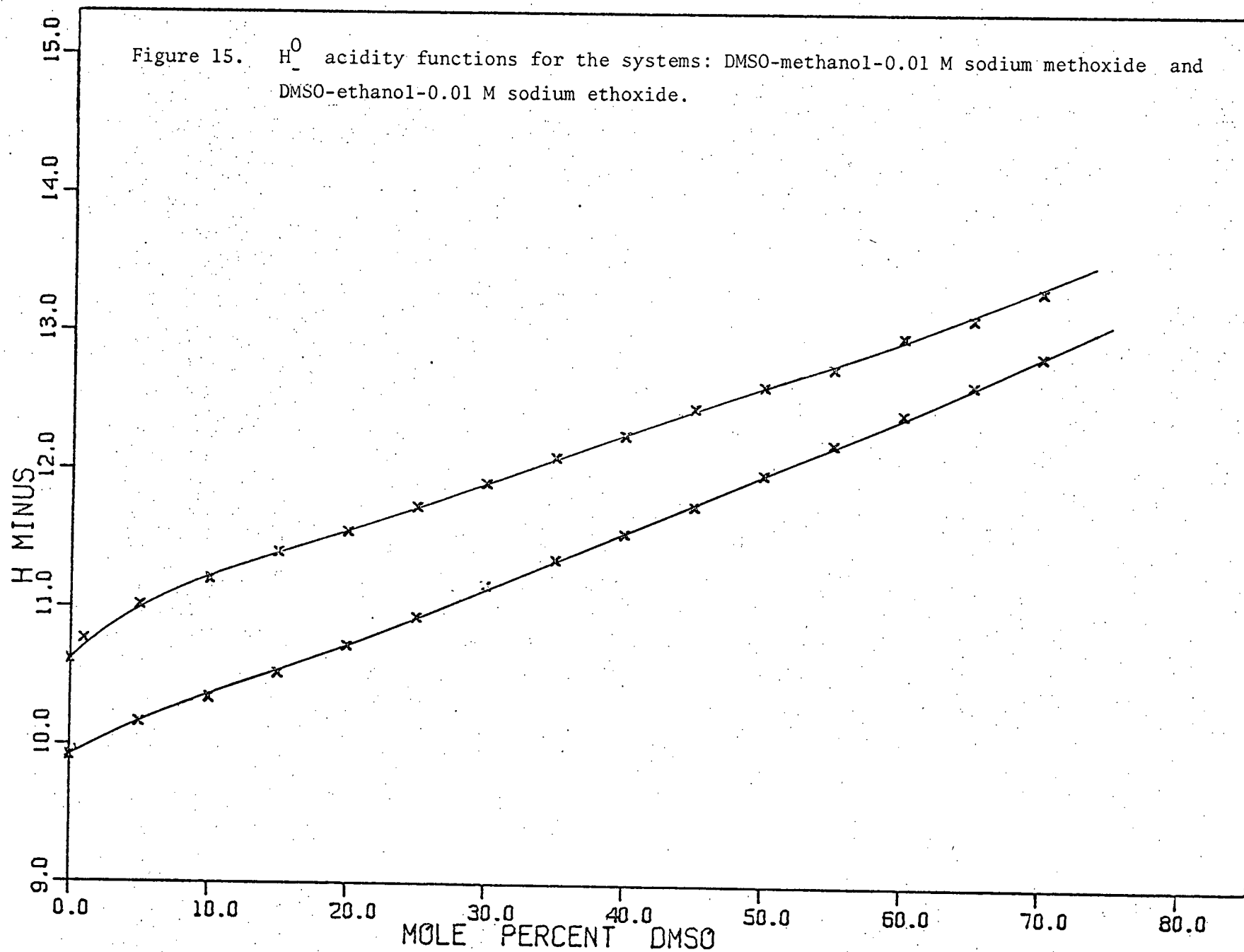




TABLE XVII

$pK_a$  values of phenols determined in aqueous solutions and in  
methanolic and ethanolic DMSO

Phenols	$pK_a$ in water	$pK_a$ in ( $\theta$ ) DMSO-MeOH	$pK_a$ in ( $\theta$ ) DMSO-EtOH	$pK_a$ reported
unsubstituted	9.98			9.97†14.10†
2-isopropyl	10.51	10.49(1.016)		
2,6-di-isopropyl	11.00	10.98(1.000)	11.00( .999)	
2- <u>t</u> -butyl	11.70	11.67(1.004)	11.67(1.008)	11.33*16.25†
2,4-di- <u>t</u> -butyl		12.10( .999)	12.12(1.002)	11.56*16.53†
2,6-di- <u>t</u> -butyl			?	11.70*17.08†
2,6-di- <u>t</u> -butyl-4-methyl			12.28( .982)	12.23*17.50†
2,4,6-tri- <u>t</u> -butyl			12.28(1.081)	12.19*17.40†

\* Cohen and Jones, ref. 29

† Rochester, ref. 31

$\theta$  Slope of plot of  $\log I$  vs.  $H_2$ .

TABLE XVIII

Absorption maxima and molar absorptivities of phenolate anions

Phenols	in DMSO solutions		in 85% DMSO-EtOH		in MeOH-MaOMe <sup>*</sup>	
	$\lambda_{\text{max}}$	$\epsilon \times 10^{-4}$	$\lambda_{\text{max}}$	$\epsilon \times 10^{-4}$	$\lambda_{\text{max}}$	$\epsilon_m \times 10^{-4}$
unsubstituted	312	.28	290		290	
2-isopropyl			290	.42	290	
2,6-di-isopropyl			300	.46		
2- <u>t</u> -butyl	318	.39	300		291	.36
2,4-di- <u>t</u> -butyl	320	.37	306		296	.34
2,6-di- <u>t</u> -butyl	318	.50	306		298	.52
2,6-di- <u>t</u> -butyl-4-methyl	325	.53	317		307	.49
2,4,6-tri- <u>t</u> -butyl	325	.50	312		302	.44

\* Rochester, ref. 31.

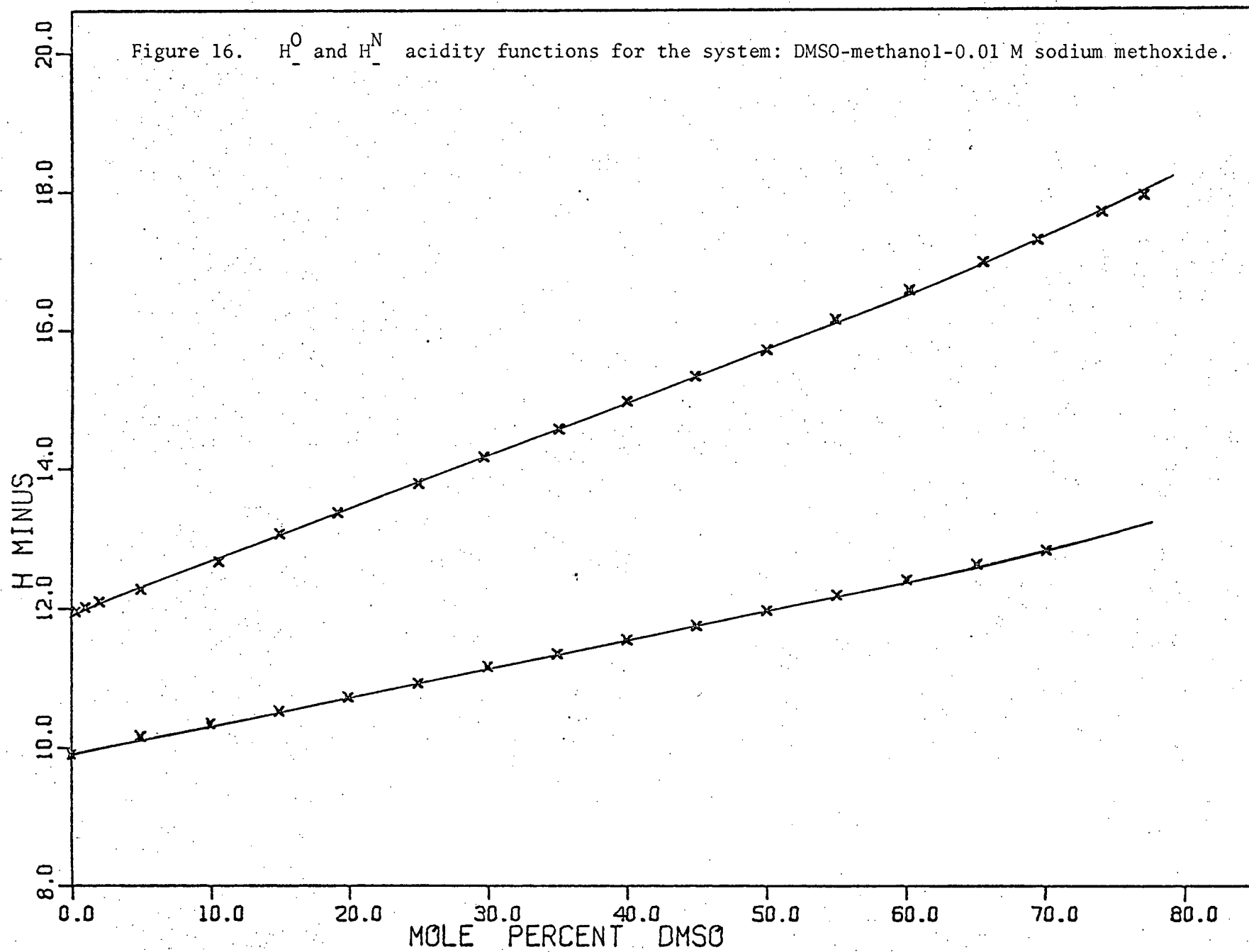
the absorption maxima and molar absorptivities for the phenol molecules and their conjugate base is given in Table XVIII. 2,6-di-t-butylphenol was not used in determining the  $H_-^0$  scale since the plot of log I versus solvent composition\* was not parallel to similar plots for 2-t-butyl- and 2,4-di-t-butyl-phenols. In point of fact it is more ionized in a 20 mole percent DMSO-ethanol solution than 2,4-di-t-butylphenol and less ionized in a 55 mole percent solution. The other two hindered phenols 2,4-di-t-butyl-6-methylphenol and 2,4,6-tri-t-butylphenol had slopes of 0.98 and 1.08 respectively for plots of log I versus  $H_-$ . These two indicators determined only two  $H_-^0$  values in 65 and 70 mole percent DMSO-ethanol. Since the other  $H_-^0$  values determined by these indicators did not differ from those determined by partially hindered phenols, they (65 and 70 percent values) were also included.

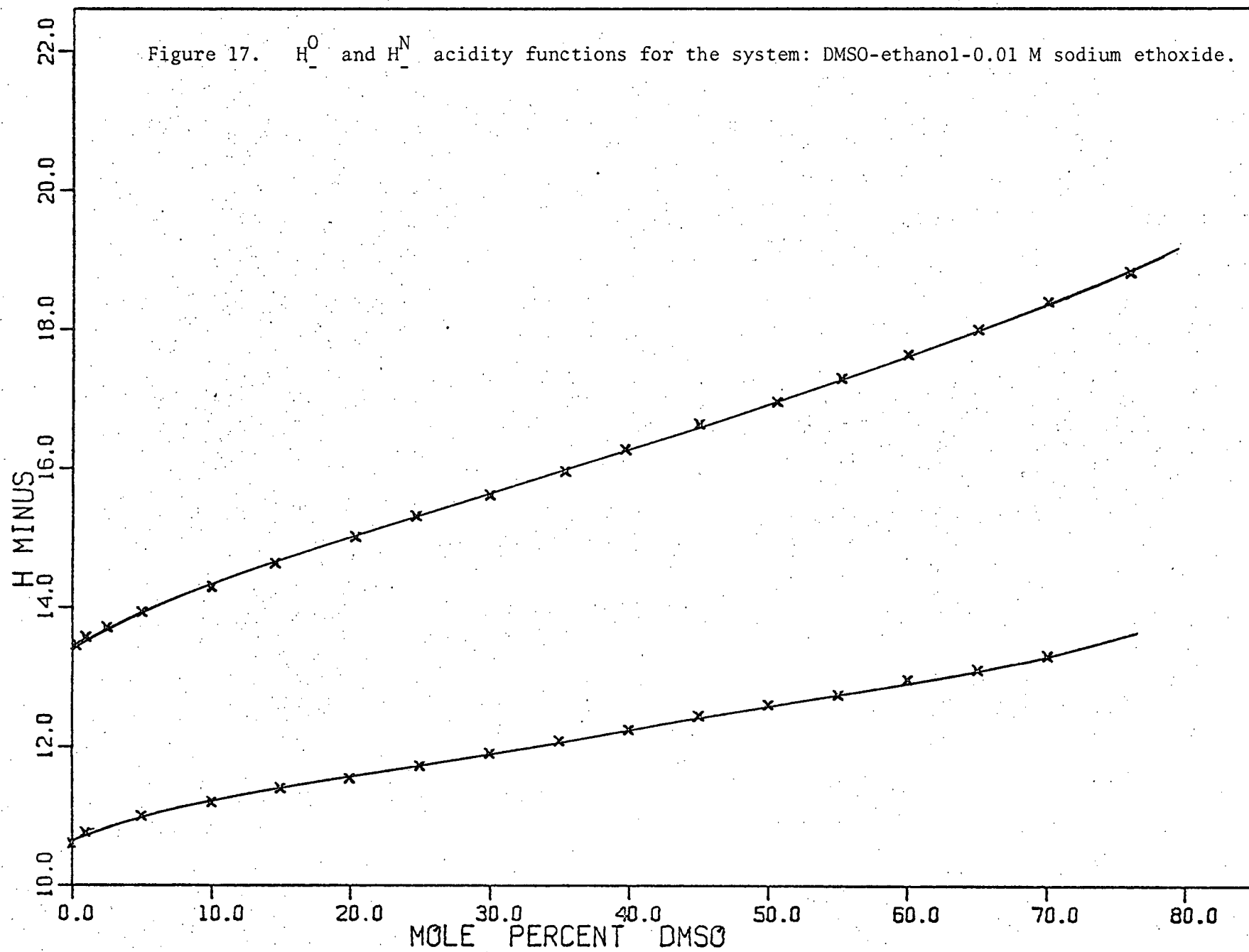
Figures 16 and 17 show clearly that the  $H_-^0$  scales, based on the ionization of phenols, differs markedly from those based on the ionization of nitrogen and carbon acids, a given solution being always more basic towards the latter than the former. This result is not unexpected since the negative charge of the anion is mainly centered on the phenolate oxygen. We can therefore expect the phenolate anion to react to solvents changes much like a small ion which is stabilized by hydrogen bonds i.e. it will be desolvated as the concentration of DMSO in the medium is increased, causing an increase in its activity. This will shift the equilibrium shown in

---

\* 2,6-di-t-butylphenol in DMSO-ethanol

mole						
%DMSO	10	20	30	40	45	55
$H_-$	11.21	11.57	11.91	12.26	12.47	12.75
log I	-0.63	-0.22	+0.07	+0.28	+0.39	+0.53





equation (34) to the right, thus partially counterbalancing the increase in activity of the alkoxide ion.



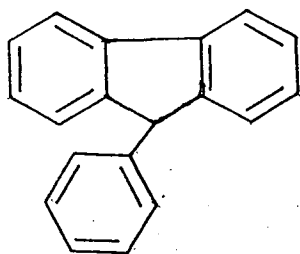
Conversely the amide ion and carbanions enjoy a large degree of charge delocalization and their solvation requirements are much less stringent, thus shifting the above equilibrium to the right. Presumably alcohols with no formal charge delocalization possible in their anions would generate a shallower  $\text{H}_-$  scale in which any increased basicity would be due merely to a concentration effect on the equilibrium shown in equation (34).

One can also note from figure 17 that the  $\text{H}_-^{\text{C}}$  scale, with all its defects, parallels the  $\text{H}_-^{\text{N}}$  scale in ethanolic DMSO. This fact gives some validity to the use of the  $\text{H}_-^{\text{N}}$  scale in the estimation of the acidities of weak carbon acids, and for the correlation with rates of reactions where the rate determining step is an ionization process from a carbon atom.

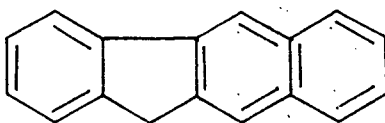
## PART II: Base catalyzed detritiation of hydrocarbons

Rate constants for the base catalyzed detritiation of 9-phenylfluorene, 2,3-benzofluorene, fluorene, 9-ethylfluorene, 9-phenylxanthene, and triphenylmethane have been measured in various ethanolic DMSO mixtures. These rates are listed in Tables XXIX, XXX.

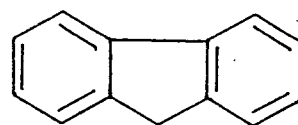
The logarithm of these rates,  $\log k$ , were correlated with the  $H_{-}^N$  value of the medium and the linear relationships obtained are shown in figure 18.



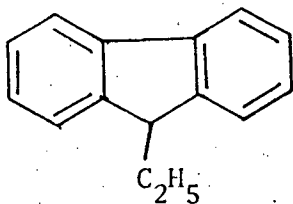
9-phenylfluorene



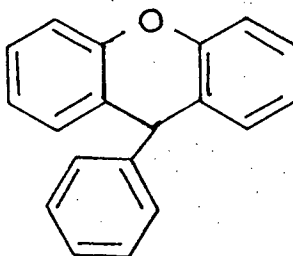
2,3-benzofluorene



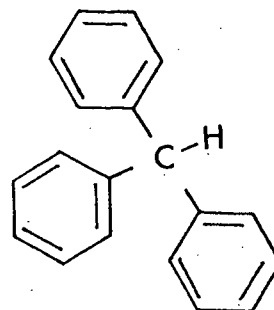
Fluorene



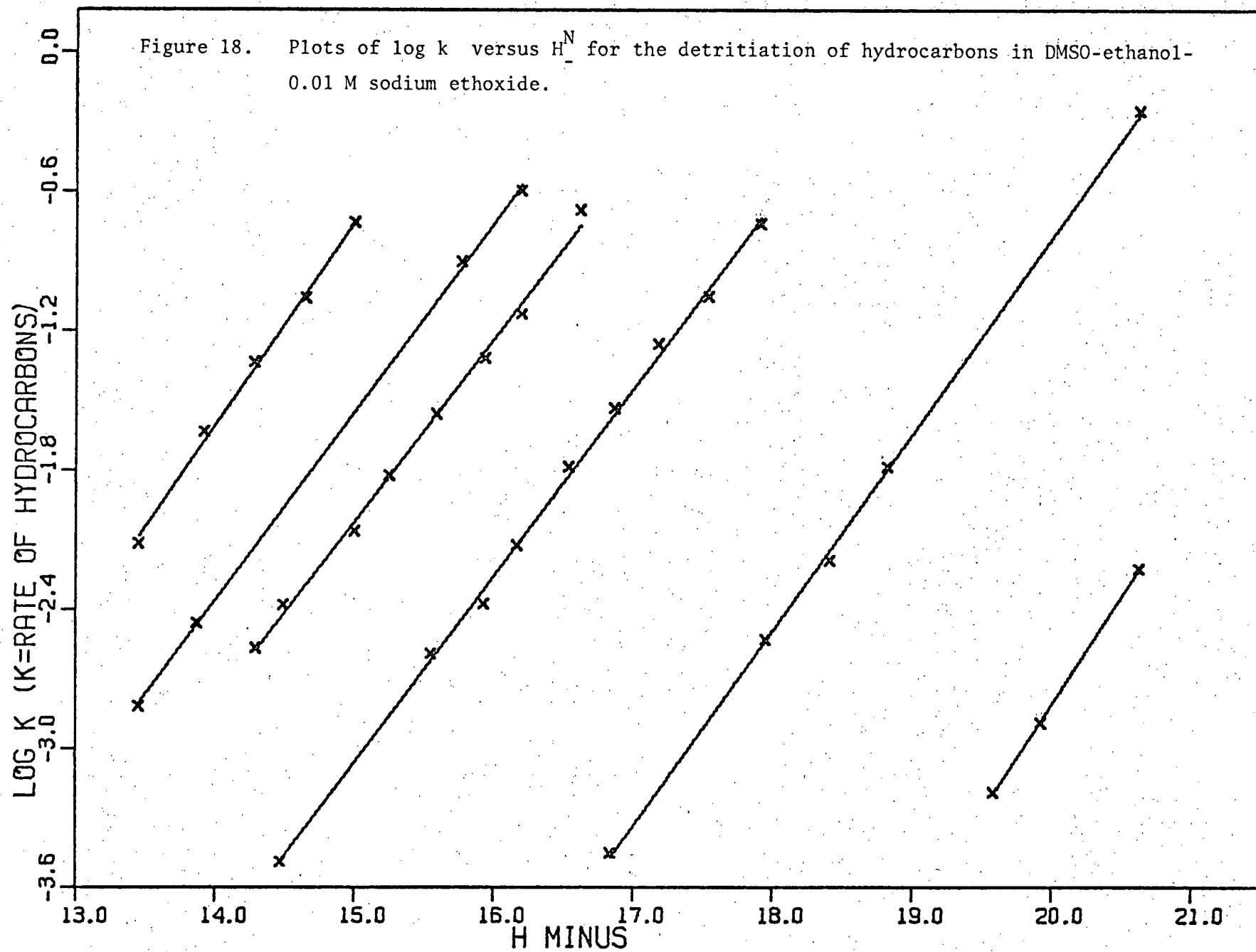
9-ethylfluorene



9-phenylxanthene



Triphenylmethane





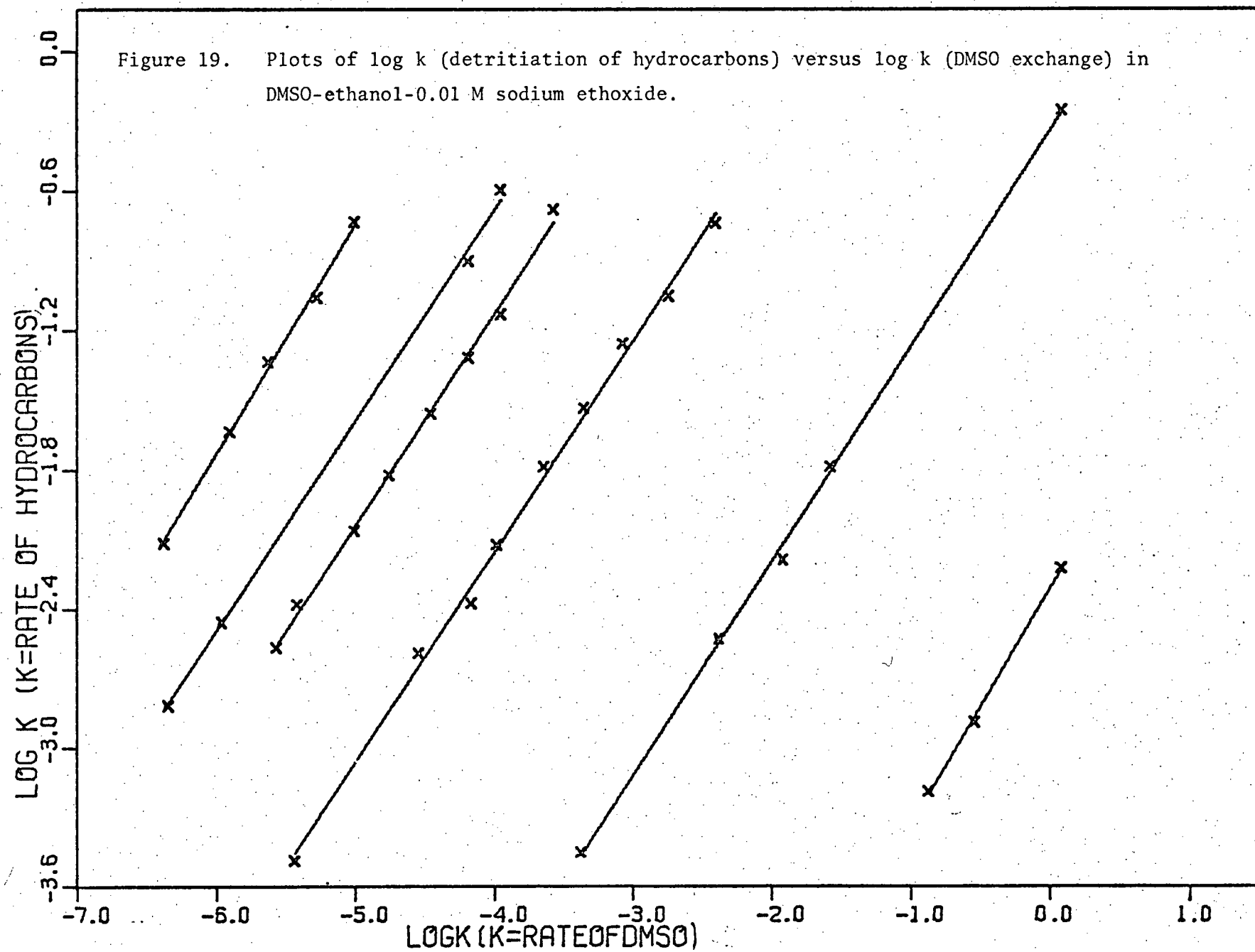


Table XIX lists the slopes of each of these lines and the corresponding coefficients of correlation and student's test T. The slopes are similar in magnitude for all the hydrocarbons and have an average value of 0.87. In the first approximation, the less-than-unit slope can be attributed to the fact that the  $H_-$  scale used was derived with amine indicators and not with hydrocarbons; therefore, the  $H_-$  scale reflects the response of nitrogen acids rather than carbon acids to the change in medium.

Indeed, it is surprising that such a good correlation is obtained, suggesting that the  $H_-^N$  and  $H_-^C$  scales are quite similar. One way to compensate for the use of  $H_-^N$  instead of  $H_-^C$  scale would be to plot  $\log k$  for the various hydrocarbons against  $\log k$  for a reference carbon acid to be chosen arbitrarily. It was thought that DMSO would be the most appropriate reference acid, since the solvent mixtures contain DMSO. And indeed, if we plot  $\log k_{\text{hydrocarbon}}$  vs  $\log k_{\text{DMSO}}$  the slopes of the correlations are much closer to unity (average of 0.95). Figure 19 shows a plot of such a correlation.

The rates of detritiation of fluorene in DMSO-water-0.01 M TMAOH have been measured, and Figure 20 shows a plot for the correlation between  $\log k$  and the  $H_-^N$  value of the medium.

The rates of the base-catalyzed tritiation of DMSO and detritiation of DMSO-t in the three media (aqueous, methanolic and ethanolic DMSO) were correlated with their respective  $H_-^N$  values. Figures 21, 22, and 23 show plots of such a correlation. Figure (2)

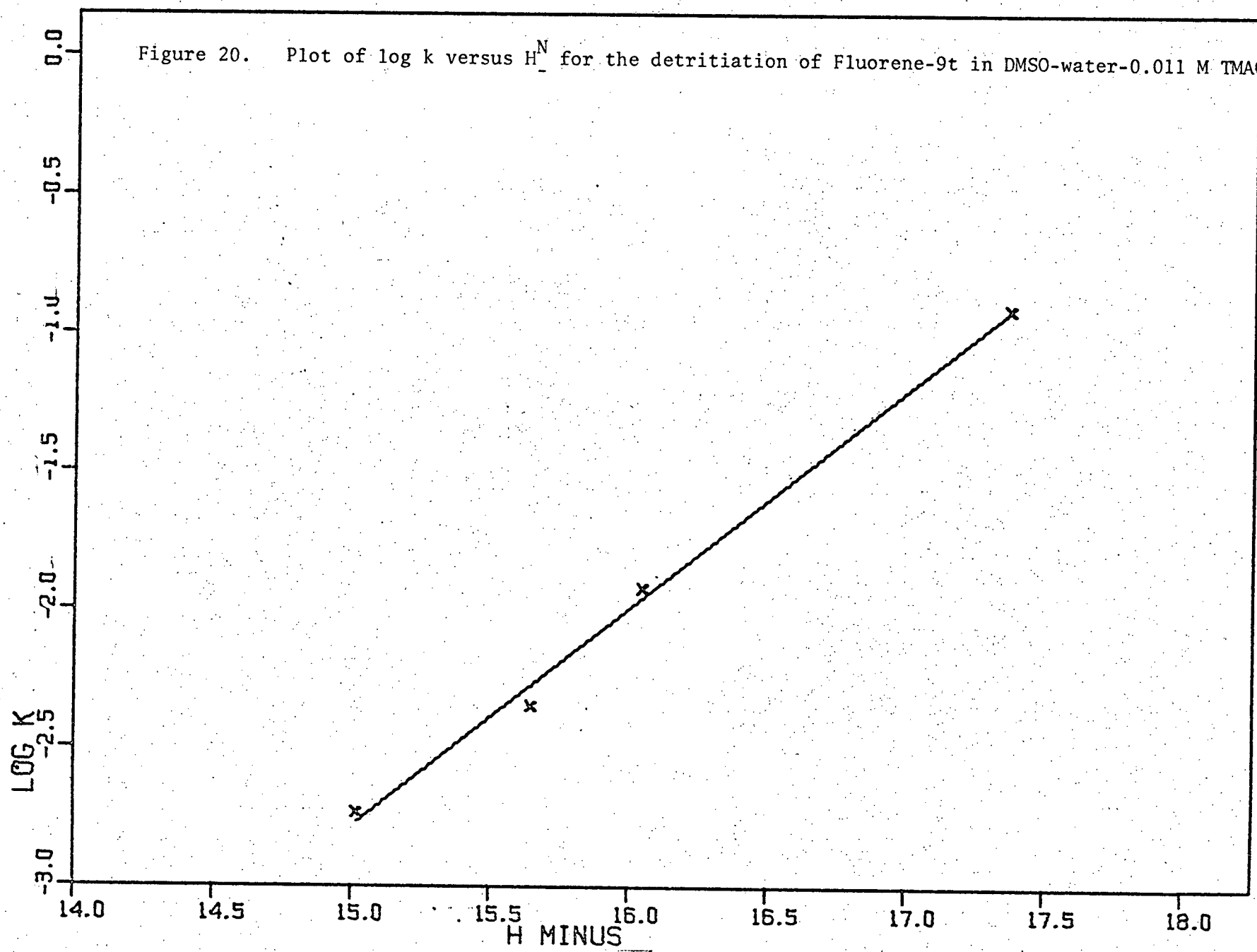


TABLE XIX

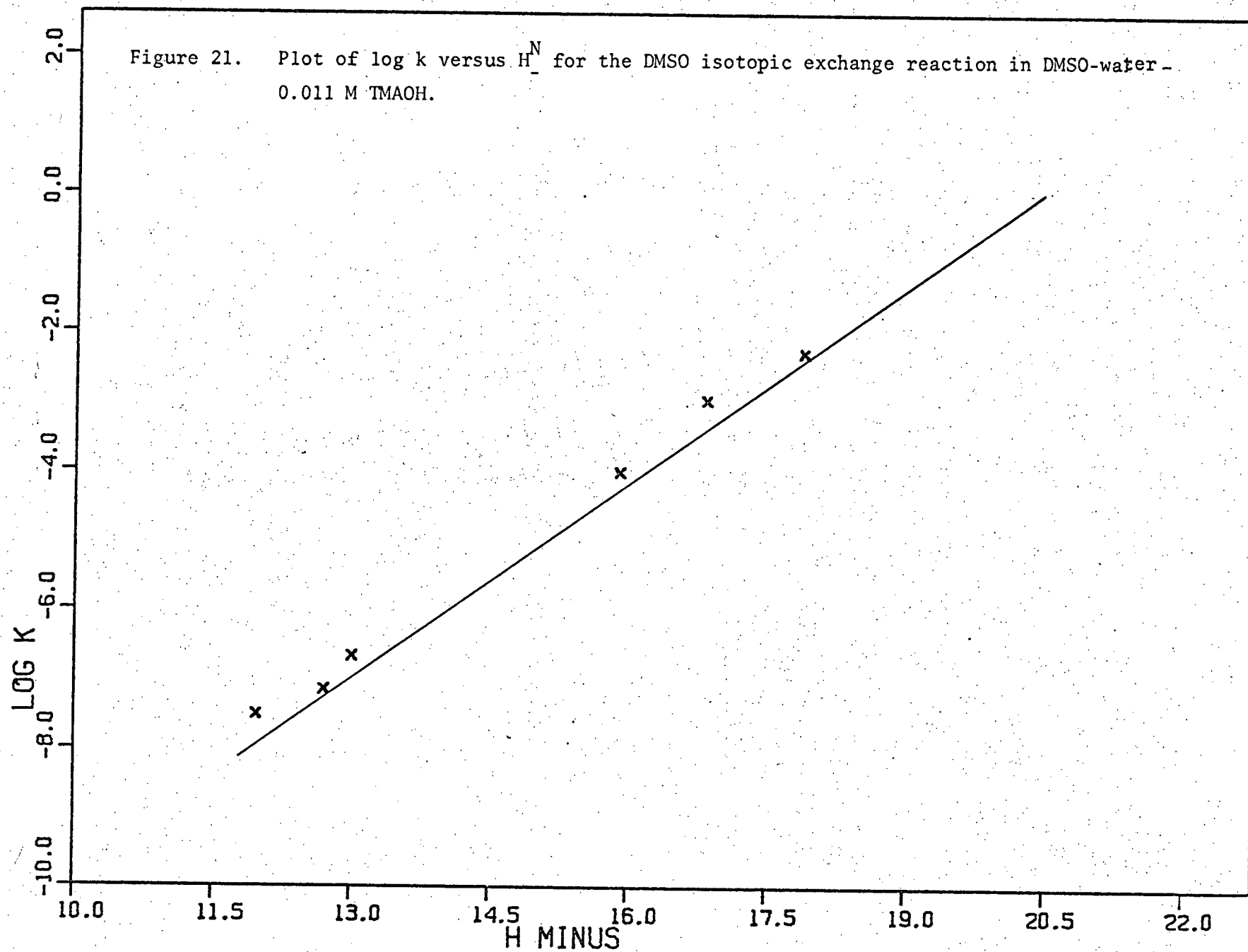
Correlation of  $\log k$  with  $H_{-}^N$  for the base catalyzed detritiation  
of hydrocarbons

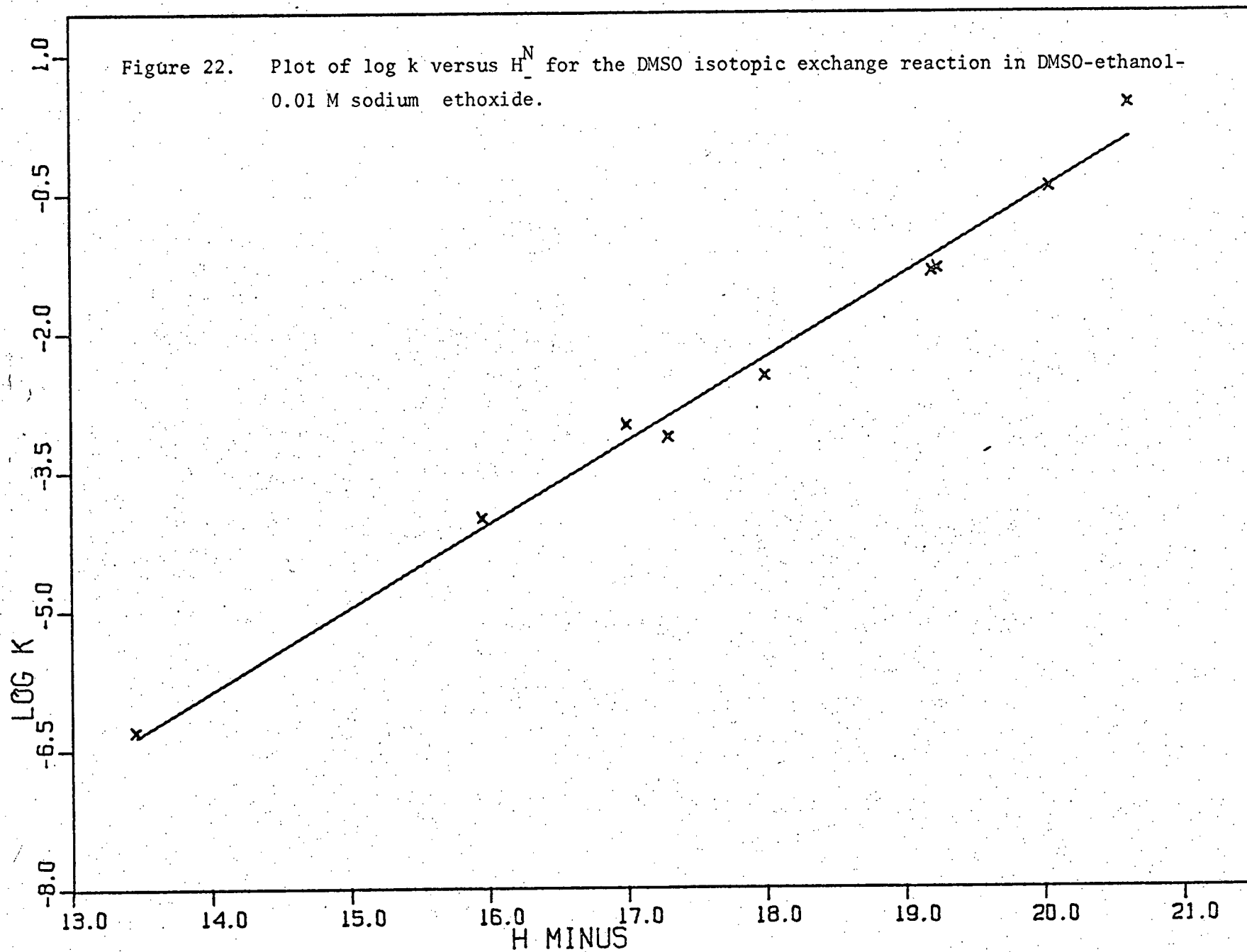
Compound	$\theta(\text{slope})$	r	N	T
a) $\log k$ vs. $H_{-}$				
9-phenylfluorene DMSO-EtOH	.873	.998	5	30.7
2,3-benzofluorene "	.809	.999	4	80.5
fluorene "	.782	.997	8	38.4
9-ethylfluorene "	.804	.999	9	62.3
9-phenylxanthene "	.848	.999	5	82.1
triphenylmethane "	.937	.999	3	53.4
DMSO "	.901	.995	9	26.6
fluorene DMSO-water	.790	.998	4	21.1
b) $\log k$ vs. $\log k$ (DMSO)				
9-phenylfluorene DMSO-EtOH	.983	.999	5	35.3
2,3-benzofluorene "	.904	.999	4	39.1
fluorene "	.914	.999	8	47.0
9-ethylfluorene "	.908	.998	9	46.4
9-phenylxanthene "	.928	.999	5	56.6
triphenylmethane "	1.029	.999	5	23.6

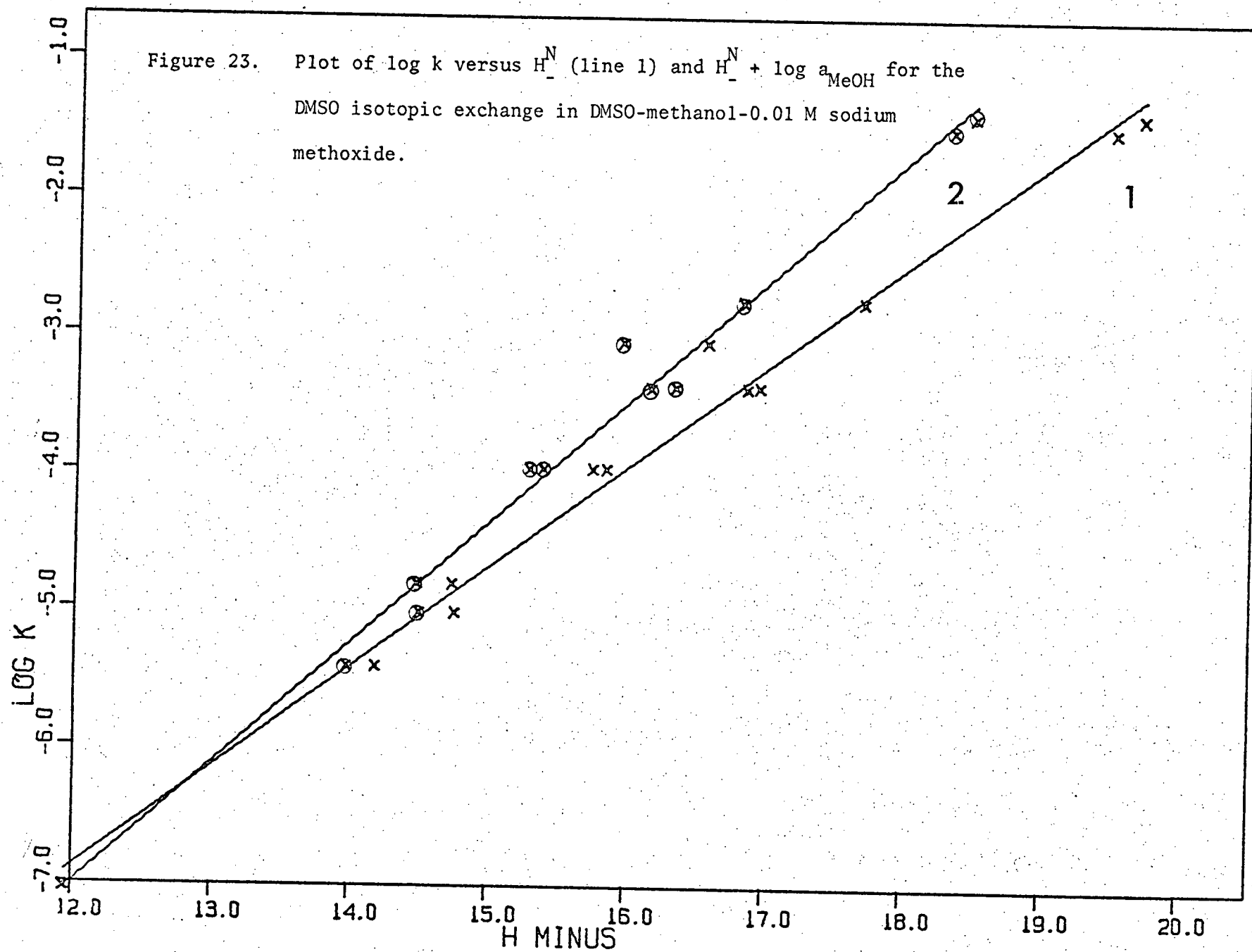
r is the coefficient of correlation

N is the number of points

T is the student's test







shows a typical run for the tritiation of DMSO. One can notice that the points are much more scattered than for hydrocarbon detrutiation. Although the reproducibility of the run is within  $\pm 10\%$ , the reproducibility of any one point is quite unreliable. This is mainly due to the method of aliquot preparation.

As explained in the experimental section, 3.5 mls of methanol was distilled from a DMSO and methanol mixture of total volume 8 mls. These 3.5 mls were then dried. A 3 mls aliquot was withdrawn and added to 7 mls of the scintillator solution. It has been found<sup>85</sup> that methanol acts as a diluter - a solvent which in the presence of decreasing toluene concentration produces a gradual drop in pulse height - while water is a strong quencher. The counting efficiency in the DMSO exchange runs were half as much as the counting efficiency in the hydrocarbon runs, and a small variation in the dryness of the methanol or in its purity will affect the reproducibility of any single determination. Nevertheless the rates of tritiation of DMSO in aqueous DMSO determined in this work compare favorably with the values published by Stewart and Jones<sup>37</sup>. The line drawn in figure (21) is the least square line from Stewart and Jones results<sup>37</sup> and the points are those determined in this work.

#### I. Evaluation of the kinetics

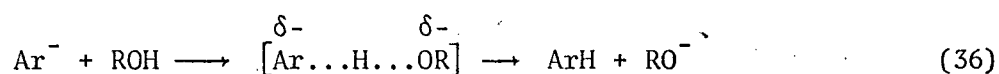
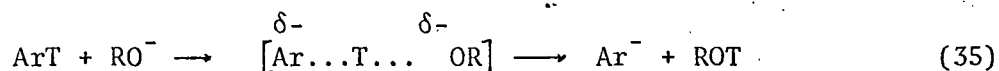
We are measuring in these kinetics the rate of loss of activity of a tritiated hydrocarbon. The radioactive isotope



concentration is very small at the beginning of the run (in trace quantity) and almost all of the activity is lost to the solvent sink. In a typical run where the activity at time zero is ~ 500,000 counts/min the activity at time infinity is less than 1000 counts/min.

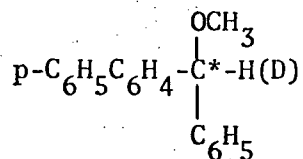
Internal return was shown to be of small importance even for the least acidic of these hydrocarbons<sup>86</sup>. By internal return is meant the reaction in which the hydrocarbon is ionized and the leaving group is then recaptured by the newly formed carbanion. For all these reasons it seems reasonable to associate the rate of detritiation of these hydrocarbons with their rate of ionization<sup>44,87</sup>.

The slow step of the isotopic exchange is undoubtedly the dissociation of the carbon acid i.e. the removal of the triton by the base. The simplest mechanism one can write is a simple one step abstraction with a hydrogen bonded transition state as

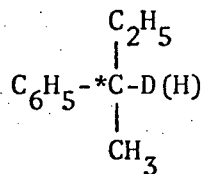


The reverse reaction of equation (35) is written in equation (36) to describe the isotopic exchange. This mechanism though, does not account for the possibility of isotopic exchange with retention of configuration, if the carbon attached to the exchangeable hydrogen is asymmetric this base catalyzed isotopic exchange with high retention of configuration has been noticed by Cram et al.<sup>86</sup> on optically active

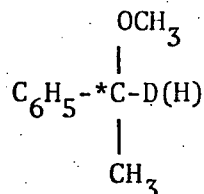
4-biphenylmethoxyphenylmethane



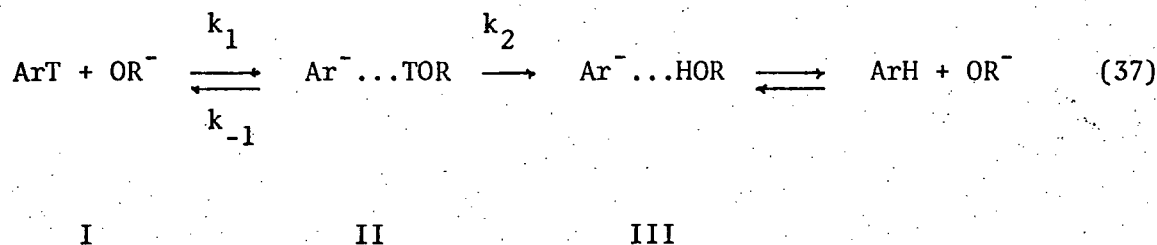
and 2-phenylbutane-2-d



and 1-phenylmethoxyethane-1-d



Another mechanism for proton transfer can be visualized. It involves an equilibrium step, giving rise to a hydrogen-bonded carbanion, followed by an isotopic exchange step, and finally a collapse of the complex to give the non-radioactive hydrocarbon. Considering only the forward reaction,



we will try to deduce the nuclear configuration of the transition state and in particular where the proton (triton) lies.

Applying a steady-state treatment

$$\frac{d[\text{Ar}^-\dots\text{TOR}]}{dt} = k_1[\text{ArT}][\text{OR}^-] - k_{-1}[\text{Ar}^-\dots\text{TOR}] - k_2[\text{Ar}^-\dots\text{TOR}] = 0 \quad (38)$$

$$[\text{Ar}^-\dots\text{TOR}] = \frac{k_1}{k_{-1} + k_2} [\text{ArT}][\text{OR}^-] \quad (39)$$

$$\frac{d[\text{Ar}^-\dots\text{HOR}]}{dt} = k_2[\text{Ar}^-\dots\text{TOR}] = \frac{k_2 k_1}{k_{-1} + k_2} [\text{ArT}][\text{OR}^-] \quad (40)$$

$$\text{and therefore } k_{\text{obs}} = \frac{k_2 k_1}{k_{-1} + k_2} \quad (41)$$

Cram et al<sup>2</sup> have proposed a dual mechanism (cf introduction) differentiated according to the relative magnitude of  $k_{-1}$  and  $k_2$ . If  $k_2 \gg k_{-1}$  i.e. if II goes to III faster than it returns to I then equation (41) reduces to (42)

$$k_{\text{obs}} = k_1 \quad (42)$$

The proton transfer takes place immediately after the hydrogen bonded complex is formed and before they can separate due to the thermal motion, i.e. its equivalent to having no preequilibrium as in equations (35) and (36).

If  $k_{-1} \gg k_2$  i.e. some kind of preequilibrium is rapidly established followed by a rate determining step. In this case equation (41) reduces to:

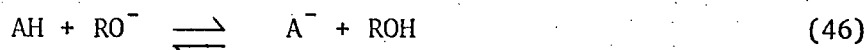
$$k_{\text{obs}} = \frac{k_1}{k_{-1}} k_2 = K k_2 \quad (43)$$

Obviously the transition states corresponding to these two mechanisms are quite different from one another, and it would seem quite unexpected to obtain a good Bronsted correlation for all these hydrocarbons, if the transition states are not similar. Also the slope  $\theta$  of these correlations ( $\log k$  vs  $H_-$ ) are of the same order of magnitude and therefore it would seem somewhat unlikely that a change in mechanism occurs. Cram also proposed a single mechanism for the isotopic exchange of hydrocarbons where the rate determining step is  $I \rightarrow II$  and with a transition state of increasing asymmetry. In this case the rate equation can be expressed

$$\frac{-d[\text{ArT}]}{dt} = k_a [\text{ArT}] [\text{RO}^-] \frac{f_{\text{ArT}} f_{\text{RO}^-}}{f^\ddagger} \quad (44)$$

which gives  $k_{\text{obs}} = k_a [\text{RO}^-] \frac{f_{\text{ArT}} f_{\text{RO}^-}}{f^\ddagger} \quad (45)$

One can derive the  $H_-$  function for an equilibrium (46) by considering the



equilibrium constant

$$K_{\text{HA}} = \frac{a_{\text{ROH}} a_{\text{A}^-}}{a_{\text{AH}} a_{\text{RO}^-}} \quad (47)$$

$$= \frac{[A^-]}{[AH]} \cdot \left[ \frac{f_{A^-}}{f_{AH} f_{RO^-}} \right] \cdot a_{ROH} \cdot \frac{1}{[RO^-]} \quad (48)$$

$$\text{and therefore } h_- = \frac{f_{A^-}}{f_{AH} f_{RO^-}} \cdot \frac{1}{[RO^-]} \cdot a_{ROH} \quad (49)$$

Combining equation (49) and (45) we get

$$k_{obs} = k_a \cdot (h_-)^{-1} a_{ROH} \cdot \left[ \frac{f_{ArT}}{f^\ddagger} \cdot \frac{f_{A^-}}{f_{AH}} \right] \quad (50)$$

taking the logarithms

$$\log k_{obs} = \log k_a + H_- + \log a_{ROH} + \log \left[ \frac{f_{ArT}}{f^\ddagger} \cdot \frac{f_{A^-}}{f_{AH}} \right] \quad (51)$$

The activity coefficient term has traditionally been assumed to be constant - if not equated to zero - because of the similarity between the indicator acids (AH) used to generate the  $H_-$  scale and the kinetic substrate (ArT) and also the similarity between the transition state ( $\ddagger$ ) and the indicator anion ( $A^-$ ). Therefore equation (51) reduces to:

$$\log k_{obs} = \text{constant} + H_- + \log a_{ROH} \quad (52)$$

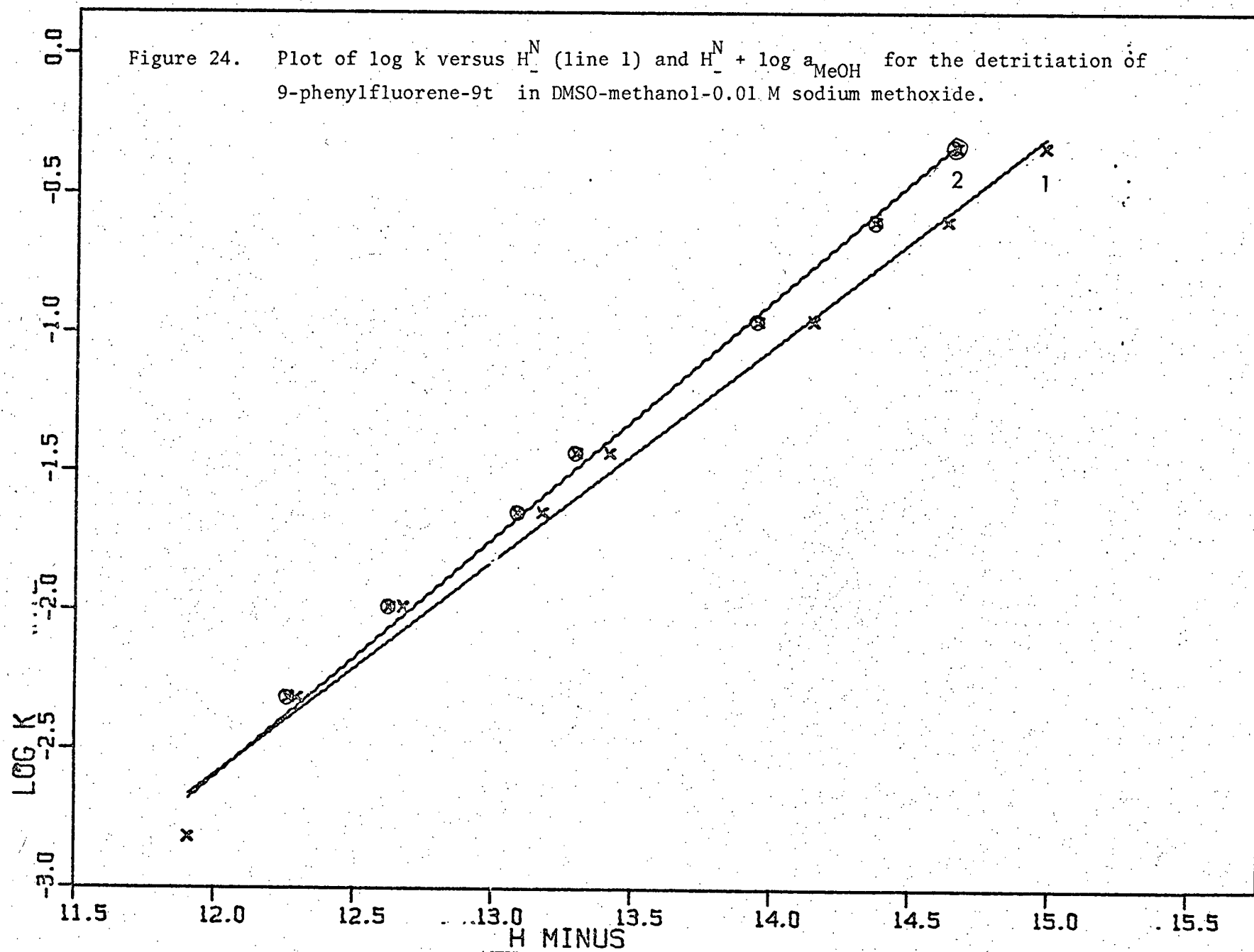
Equation (52) resembles the one derived by Anbar et al<sup>38</sup> for base catalyzed reactions where the slow step is a proton abstraction from the reactants (cf. introduction p.21), which is similar to the mechanism proposed for the detritiation of hydrocarbons and shown in equation (37).

There are no published data for the activity of ethanol in DMSO-ethanol mixtures, but activity coefficients have been determined for water in DMSO-water<sup>6</sup> and sulfolane-water<sup>7</sup> mixtures and also for methanol in DMSO-methanol<sup>8</sup> mixtures. The rates of detritiation of 9-phenylfluorene (9-t) were therefore determined in methanolic DMSO containing 0.01 M sodium methoxide. The line 1 in Figure 24 represents the correlation between  $\log k$  and  $H_-$  while line 2 represents the correlation between  $\log k$  and  $H_- + \log a_{\text{MeOH}}$ . The lines 1 and 2 in Figure 23 are the corresponding correlations for the isotopic exchange of DMSO in methanolic DMSO.

TABLE XX

Correlation of  $\log k$  with  $H_-$  and  $H_- + \log a_{\text{MeOH}}$  for the base catalyzed isotopic exchange in methanolic DMSO.

Compound	System	$\theta$	$r$	N	T
a) $\log k$ vs. $H_-$					
9-phenylfluorene	DMSO-MeOH	.770	.996	8	27.2
DMSO	"	.730	.993	12	27.1
b) $\log k$ vs. $H_- + \log a_{\text{MeOH}}$					
9-phenylfluorene	DMSO-MeOH	.859	.997	8	30.5
DMSO	"	.878	.994	12	28.1



The net result of plotting  $\log k$  for 9-phenylfluorene and DMSO versus  $H_- + \log a_{\text{MeOH}}$  is thus to steepen the curve as can be seen from Table XX. The value of  $\log a_{\text{MeOH}}$  is practically equal to zero up to 10 mole percent DMSO and decreases slowly to -0.21 for 30 mole percent DMSO then more rapidly as the DMSO content increases to 100 percent. Therefore since the slopes of  $\log k_{\text{hydrocarbon}}$  vs.  $\log k_{\text{DMSO}}$  plots are very close to unity (Table XIX) and that  $\log k$  vs  $H_- + \log a_{\text{MeOH}}$  have slopes which are 0.1 less than the former correlations, the  $H_-^C$  scale for DMSO systems should rise only slightly more rapidly with the DMSO content than the corresponding  $H_-^N$  scale.

A justification for the observed linear correlation between the logarithm of the rate constants and  $H_-$  has thus been obtained.

## II. Activation parameters

Activation parameters for these detritiation reactions have been measured horizontally and vertically in Figure 18. By horizontally is meant that an arbitrary rate constant at 25° was chosen for all the hydrocarbons (obviously the medium was quite different) and the enthalpy of activation was measured. Vertically means that the activation parameters were measured in one and the same medium (65% DMSO-EtOH) and the temperature range varied although the temperature limits are only 60° apart (from -5° to +55°). Table XXXII appendix B lists the rate-temperature data for these detritiation reactions and Table XXI lists the activation parameters deduced from these kinetics.



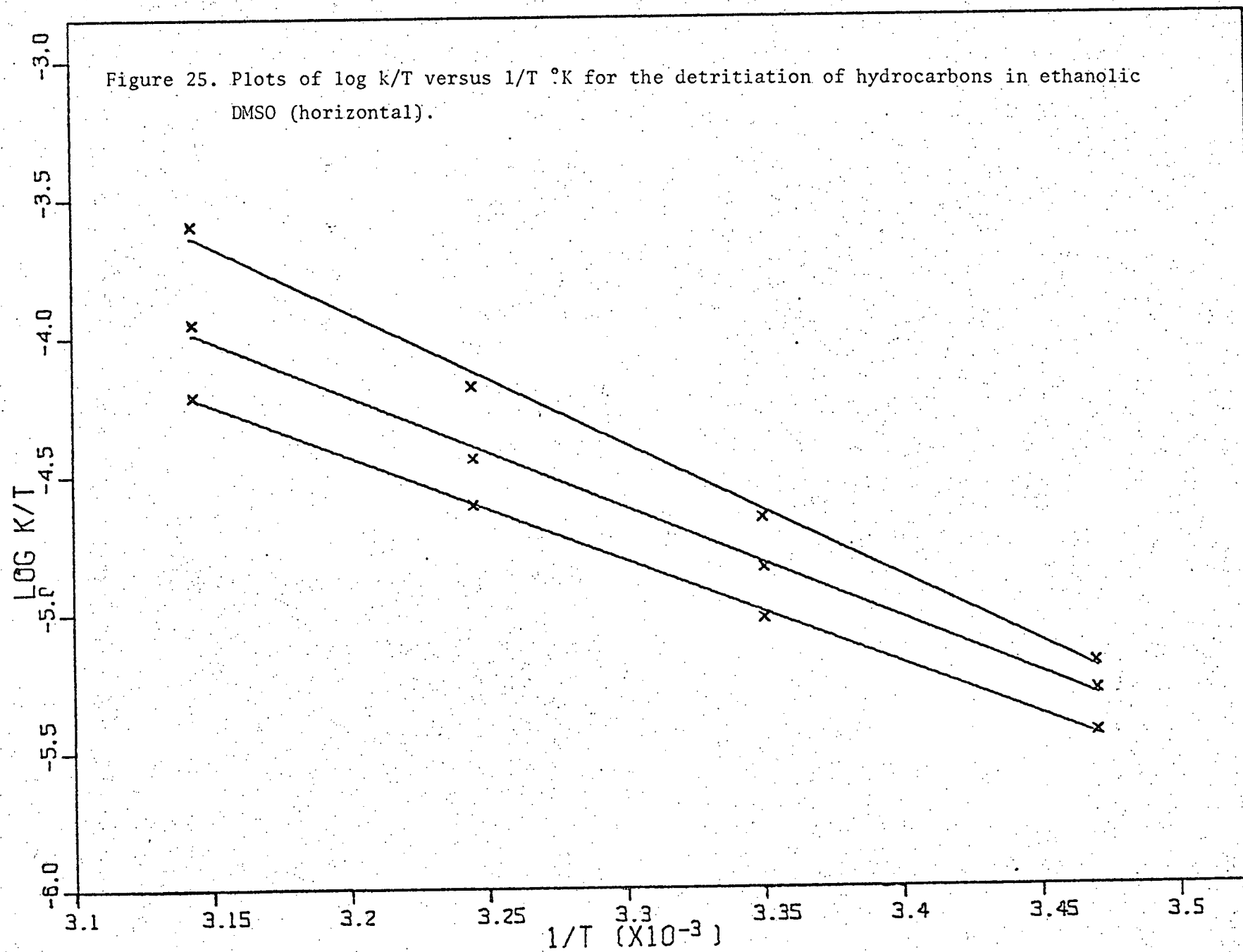
TABLE XXI

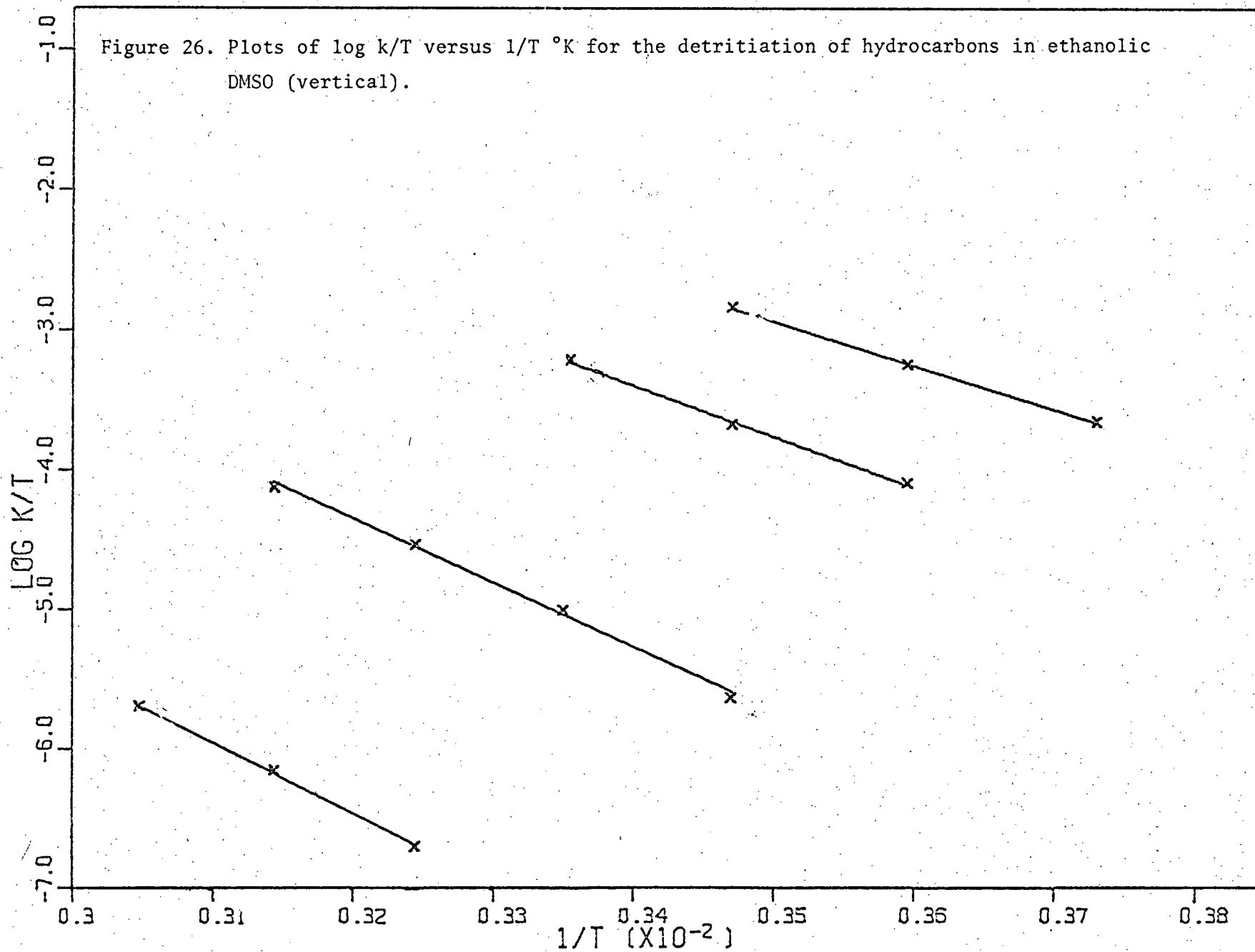
Activation parameters for the base-catalyzed  
detritiation of hydrocarbons.

	%DMSO	$\Delta H^\ddagger$ kcal.mole <sup>-1</sup>	$\Delta S^\ddagger$ e.u.
a) vertical			
Triphenylmethane	62.5	23.3 $\pm$ 0.6	-2.3 $\pm$ 2.0
9-phenylxanthene	62.5	21.1 $\pm$ 0.9	0.5 $\pm$ 3.0
9-ethylfluorene	62.5	16.7 $\pm$ 0.7	5.9 $\pm$ 2.6
Fluorene	62.5	14.4 $\pm$ 0.3	10.2 $\pm$ 1.2
b) horizontal			
9-phenylxanthene	70	22.1 $\pm$ 1.0	5.6 $\pm$ 3.2
9-ethylfluorene	35	18.6 $\pm$ 0.8	-7.1 $\pm$ 2.6
Fluorene	10	17.2 $\pm$ 0.3	-12.4 $\pm$ 1.1

4,4',4''-Trinitrotriphenylmethane has an activation energy of 11.3  $\pm$  0.2 kcal. mole<sup>-1</sup> for its ionization by sodium ethoxide in an ethanol-toluene mixture<sup>89</sup>.

One can see that as the hydrocarbon becomes less acidic the enthalpy of activation rises. This general trend in the enthalpy of activation has also been observed by two other groups of workers - Cram et al.<sup>2</sup> and Streitwieser et al.<sup>22</sup> - and would tend to indicate that the amount of bond-breaking in the transition state increases with increasing basicity of the hydrocarbon. The enthalpy of





activation should increase as  $\Delta pK$  increases, since the extent of the bond breaking in the transition state will increase as the  $RO^-$  moiety binds the proton more closely. Thus the greater the activation energy the more the transition state resembles the product II.

The significance of the rather small variation in activation entropy is uncertain owing to the limited number of hydrocarbons and the high experimental error. One can notice a trend toward more positive values as the hydrocarbon becomes less acidic and conclude that the charge must be more delocalized in the transition state derived from the weaker acids. Although Cram has found a change in  $\Delta S^\ddagger$  of 22 e.u. for the detritiation of hydrocarbons in 75% DMSO-MeOH-KOMe at 75°, Streitwieser found a very small change in  $\Delta S^\ddagger$  (6 e.u.) for the same reaction in methanol at 45°. Also the rate increase on going to higher DMSO concentration (higher  $H_-$  values) is accounted for mainly by the decrease in enthalpy of activation;  $\Delta H^\ddagger$  for fluorene in 10% DMSO is 17.2 and in 62.5% DMSO is 14.4.

This dependence has also been observed by Cram et al. in the catalyzed racemization of (+)-2-methyl-3-phenylpropionitrile in DMSO-methanol solutions. Parker and coworkers<sup>88</sup> also noted that protic-(dipolar aprotic)solvent effects on rate are usually reflected in the enthalpy rather than in the entropy of activation, and are quite strongly temperature dependent. This is to be expected since these effects are mainly attributed to hydrogen bonding interactions - solvation.

### III. Kinetic Thermodynamic correlation for hydrocarbon ionization

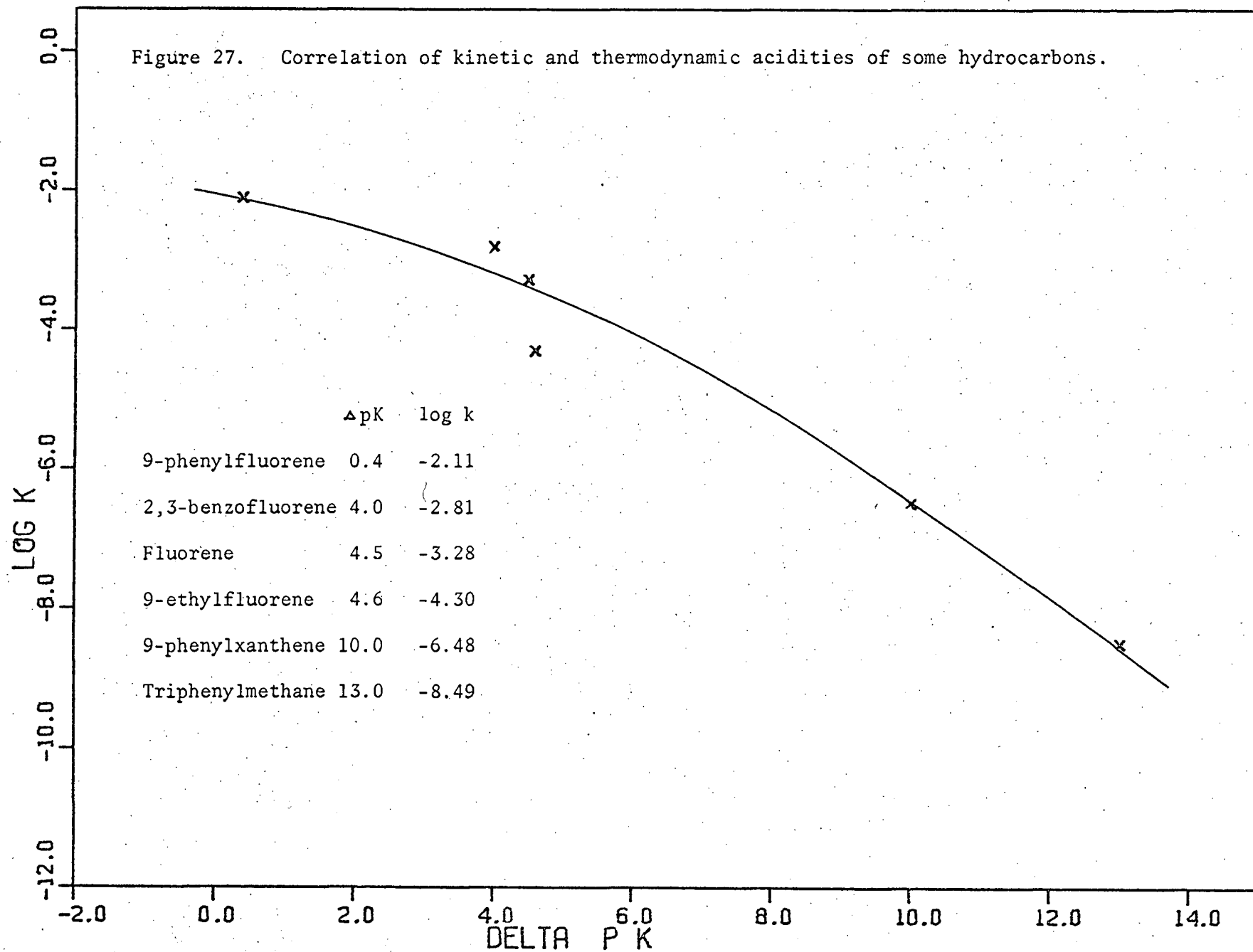
(log k vs  $\Delta pK$ )

In the case of hydrocarbons the electronic and spatial configuration of the acids and their conjugate bases are not identical, and therefore the Bronsted plot will show a broad transition from  $\alpha = 0$  to  $\alpha = 1$ , which occurs over a wide  $\Delta pK$  range.

By extrapolation of the lines in Figure 18 to an  $H_-$  of 13.45 ( $H_-^N$  for a 0.01 M ethanolic sodium ethoxide solution) we can compute a kinetic acidity for these hydrocarbons, and taking a value of 16.0 for the  $pK_a$  of ethanol,  $\Delta pK$  values can be calculated. The correlation of kinetic and thermodynamic acidities is shown in Figure 27. The average slope  $\alpha$  of the line is 0.5 but a curve will fit better the results with an initial slope of 0.3 and a final slope of 0.6.

The thermodynamic acidity of fluorene and 9-ethylfluorene are similar<sup>22</sup> while their kinetic acidity differs by  $\sim 2$   $pK_a$  units. Streitwieser correlated the rates of detritiation of 9-alkyl substituted fluorenes with the  $pK_a$  of the corresponding acetic acids and found that the relative rates are in the order  $F > 9\text{-MeF} > 9\text{-EtF}$ . But equilibrium measurements showed that the order of decreasing acidity is  $9\text{-Me} > F = 9\text{-Et} > 9\text{-isopropyl} > 9\text{-t-butyl}$ , which indicates a kinetic effect in this series. In Figure 29 at  $\Delta pK = 0$ , the slope of the log k -  $\Delta pK$  curve is not 0.5 but 0.3. This is to be expected though since the acceptor ROH and the donor  $R_3CH$  are of different acid-type, O- and C- type respectively<sup>5</sup>.

Figure 27. Correlation of kinetic and thermodynamic acidities of some hydrocarbons.



#### IV. Change of Isotope effect with the $pK_a$ of hydrocarbons

No measurements of isotope effects were made by us, in the ethanolic DMSO system, but both Cram et al.<sup>2</sup> and Streitwieser and coworkers<sup>21</sup> found a general trend in the variation of the magnitude of the isotope effect with the  $pK_a$  values. Cram et al. in 75% DMSO-MeOH (by volume) - 0.0026 M potassium methoxide found an isotope effect  $k_H/k_D$  of 6.75 at 25° for 2-(N,N-dimethylcarboxamido)-9-methyl fluorene ( $pK \sim 20$ ) and 2.5 at 126° for 4-biphenylmethoxy phenylmethane ( $pK_a \sim 30$ ). Streitwieser and coworkers<sup>21</sup> found a primary isotope effect  $k_D/k_T$  in sodium methoxide of 2.5 (25°) for 9 phenylfluorene ( $pK_a$  16.5) while  $k_D/k_T$  for triphenylmethane is 1.3 (99°). The progressive decrease in the isotope effect is quite marked, and one should note that for triphenylmethane,  $pK_a$  29.2, ( $\Delta pK \sim 13$ ) the isotope effect is about half that for 9-phenylfluorene for when  $pK_a$  16.5 ( $pK \sim 0$ ).

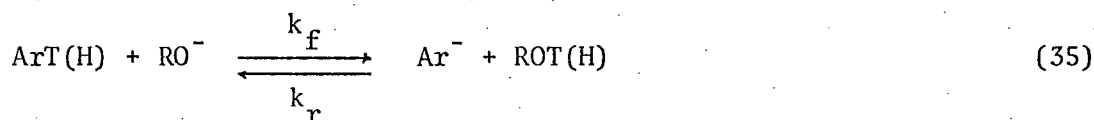
This lowering in kinetic isotope effect with increasing  $\Delta pK$  will tend to indicate an increase in asymmetry in the transition state. This is in line with recent suggestions,<sup>51,53</sup> that the isotope effect will be greater when the transition state is symmetrical and the symmetrical stretching mode  $\nu$  will not involve any motion of the proton. This would probably happen when both anion A and B are  $(\overset{\leftarrow}{A} \dots H \dots \overset{\rightarrow}{B})$  ( $\nu$ , no motion of H) of similar strength i.e.  $\Delta pK \approx 0$ . When on the other hand one anion is stronger than the other, the proton will be closer to the weaker base and the stretching will become unsymmetrical and will lead to a smaller  $\overset{\leftarrow}{A} \dots \overset{\rightarrow}{H} \dots \overset{\leftarrow}{B}$  (imaginary

frequency  $\nu_3$ ) isotope effect. This is exactly what we notice when  $\Delta pK > 0$  and the proton is closer to the  $RO^-$  moiety than to the carbanion.

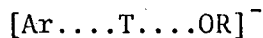
This mechanism thus does not require the isotope effect to vanish for high  $\Delta pK$  values and is one more reason to prefer this mechanism to Cram's dual mechanism. Of course if at  $\Delta pK \sim 0$  there is a maximum in the isotope effect correlation with  $\Delta pK$  one should be able to find an isotope effect of less than 7 for reactions where the carbon acid is a weaker base than ROH.

Thus all the kinetic data are accommodated by mechanism (37).

There is no real way to discriminate - at the present time - between mechanisms (35) and (37).



In both cases the rate equation is the same, and the configuration of the transition state of highest energy appears to be



with T in a symmetrical position if  $\Delta pK \sim 0$  and with  $k_H/k_D \sim 7$  and closer to RO if  $\Delta pK > 0$  and with  $k_H/k_D < 7$  and closer to Ar if  $\Delta pK < 0$  and with  $k_H/k_D < 7$ . But of course the mechanism shown in equation (35) cannot account for isotopic exchange reaction with retention of configuration<sup>86</sup>.



Ideally one would like to have an  $H_-^C$  scale for carbon acids and use these same indicators for isotopic exchange measurements, thus eliminating the uncertainty in the value of the activity coefficient terms in equation (51)

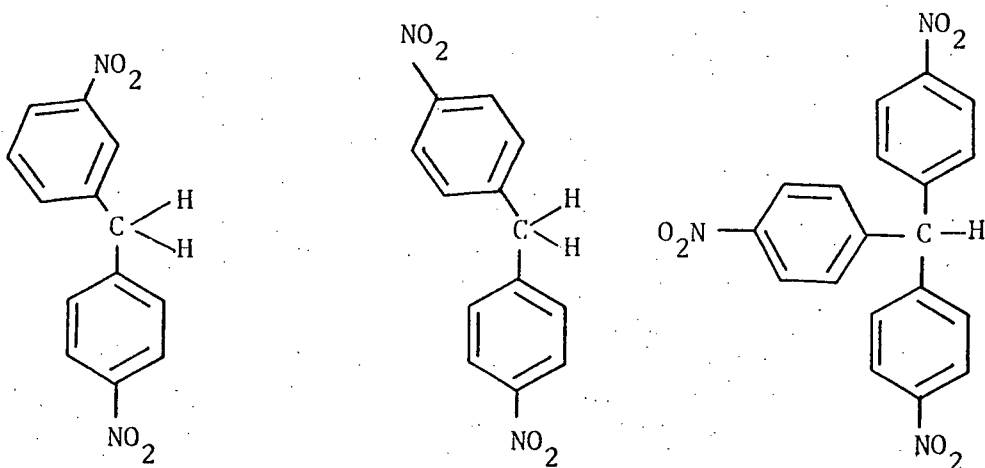
$$\frac{f_{ArT}}{f^{\dagger}} \cdot \frac{f_{A^{-}}}{f_{AH}}$$

Also if one had values for the activity of ethanol in DMSO mixtures that would eliminate the other unknown parameter in equation (51), namely  $\log a_{ROH}$ .

PART III: Interactions of Nitrophenylmethanes with base.

An attempt to measure the degree of ionization of 3,4'-dinitrodiphenylmethane in ethanolic sodium ethoxide showed that the u.v. absorption maximum of the "anion" had shifted to 430 m $\mu$  from the 575 m $\mu$  value observed in DMSO containing sodium ethoxide. E.s.r. spectroscopy indicated the presence of a large concentration of radicals ( $\sim 10^{-4}$  M in  $\sim 10^{-2}$  M indicator solution) in these basic medium. A similar behaviour was observed for two other carbon acids indicators, namely tris- and bis- (p-nitrophenyl)methane.

Bowden and Stewart<sup>17</sup> and Ritchie and Uschold<sup>19</sup> also noted that the spectrum of the conjugate base of tris-(p-nitrophenyl)methane showed a pronounced solvent effect ( $\lambda_{\max}$  of 582 m $\mu$  in ethanol, and  $\lambda_{\max}$  of 810 m $\mu$  in DMSO).

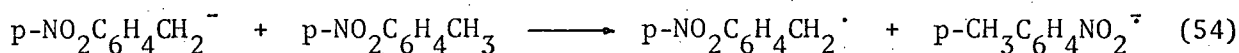
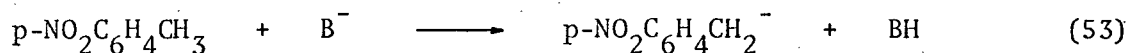


Since the formation of highly coloured solutions in the presence of base has often been considered indicative of proton abstraction (e.g. see reference 17) this large shift in absorption maxima suggests that another process is taking place.

A variety of interactions can occur between aromatic nitro-compounds and the unshared electron pair of the base, with in most cases, a concomitant formation of highly coloured solutions. Buncl, Norris and Russell<sup>90</sup> in their review listed the different species resulting from such reactions and the analytical techniques used to define them. For example, a partial transfer of electronic charge from the base to the aromatic nucleus can give rise to  $\pi$ -complexes (charge-transfer complexes). A radical-anion can be produced if an electron is completely transferred from the base to the nitro compound. The electron pair of the base can also participate in the formation of a covalent bond with an aromatic carbon atom to give a  $\sigma$ -complex or "Meisenheimer" type complex. Because the nitro group has a strong acid strengthening effect, the base could abstract a proton to form a carbanion. The possible existence of ion pairs as well as free ions in the cases of proton abstraction and radical-anion formation further complicates the picture. Ion pairs themselves can be differentiated into solvent separated and contact ion pairs.

Russell and Janzen<sup>91</sup> have studied extensively the reactions of o- and p- nitrotoluenes in strongly basic systems. They postulated that a spontaneous disproportionation reaction takes place to form the radical-anion derived from the parent nitrotoluene. These authors<sup>91</sup> suggested a mechanism for this disproportionation reaction in t-butanol containing potassium t-butoxide, in which the rate limiting step is the

ionization of the benzylic proton.



Two molecules of the radical  $\text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\cdot$  then couple to give p-p'-dinitrobibenzyl ( $\text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-p}$ ) which can be isolated from the reaction mixture .

In 80 percent DMSO-t-butanol-potassium t-butoxide, the disproportionation reaction is very rapid. Russell and Janzen<sup>91</sup> postulated a different mechanism in this case: The rate determining step is now the one shown in equation 54 and the ionization step shown in equation 53 becomes a fast pre-equilibrium. This is probably due to the higher basicity of the DMSO solutions.

Russell and Janzen suggested that this disproportionation reaction is quite general and would occur whenever hydrogen atoms are  $\alpha$  to an easily reducible group which also promotes the acidity of these hydrogens.

#### I. N.m.r. investigation

The disparity in the  $\text{pK}_a$  values of the carbon acids reported in Tables III and IV , the high degree of solvent dependence of the anions' spectral characteristics and the presence of appreciable amounts of radical-anions in basic solutions of nitrophenylmethanes led to the utilization of high resolution n.m.r. as an independent method for the

characterization of the ionic species formed in basic solutions. N.m.r. has been used previously to define the mode of ionization of amines in alkaline media<sup>73</sup>. Crampton and Gold<sup>92</sup> have shown that 2,4-dinitroaniline and 2,4-dinitrodiphenylamine in DMSO as a solvent and in the presence of methanolic sodium methoxide ionize to give an amide ion via proton abstraction.

In 1966 Birchall and Jolly<sup>69</sup> established a scale of acidities for anilines in liquid ammonia\* in presence of sodium amide by an n.m.r. method. The same authors<sup>69,93</sup> have attempted to study some hydrocarbons using the same technique but have not yet published the results of their investigation.

A basic system in which, hopefully, only proton abstraction occurs was sought for the nitrophenylmethanes. Since hexamethylphosphoramide (HMPT) containing sodium methoxide is easier to handle than liquid ammonia, it was used for this purpose. Preliminary results show that an HMPT-0.01 M TMAOH solution is some  $10^4$  times more basic\*\* than a DMSO-0.01 M TMAOH solution.

Tris-(p-nitrophenyl)methane    TNPM

The n.m.r. spectrum of TNPM in HMPT (0.042 M solution) consists of a sharp resonance at  $\delta = -6.60$  (relative area 1) which is assigned to

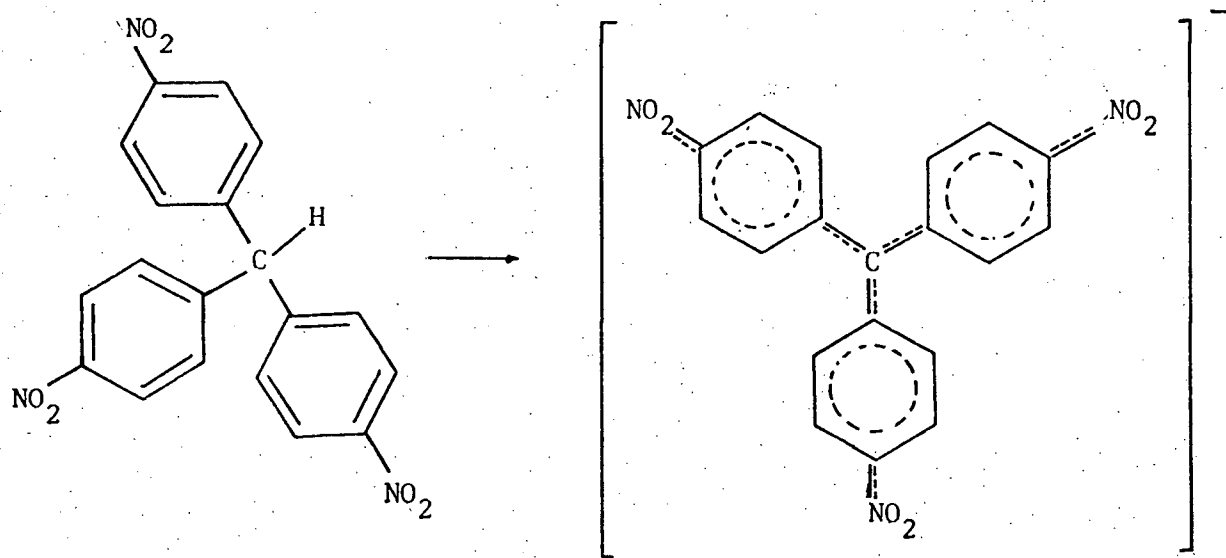
\_\_\_\_\_\*

Badoz-Lambling et al.<sup>94</sup> have developed a hydrogen electrode suitable for acidity measurements in liquid ammonia at  $-60^\circ$ . Lagowski et al.<sup>95</sup> have also used liquid ammonia as a strongly basic system and determined spectrophotometrically the acidity of o- and p- nitroacetanilide and di-p-tolyl- and di-p-anisyl- methane.

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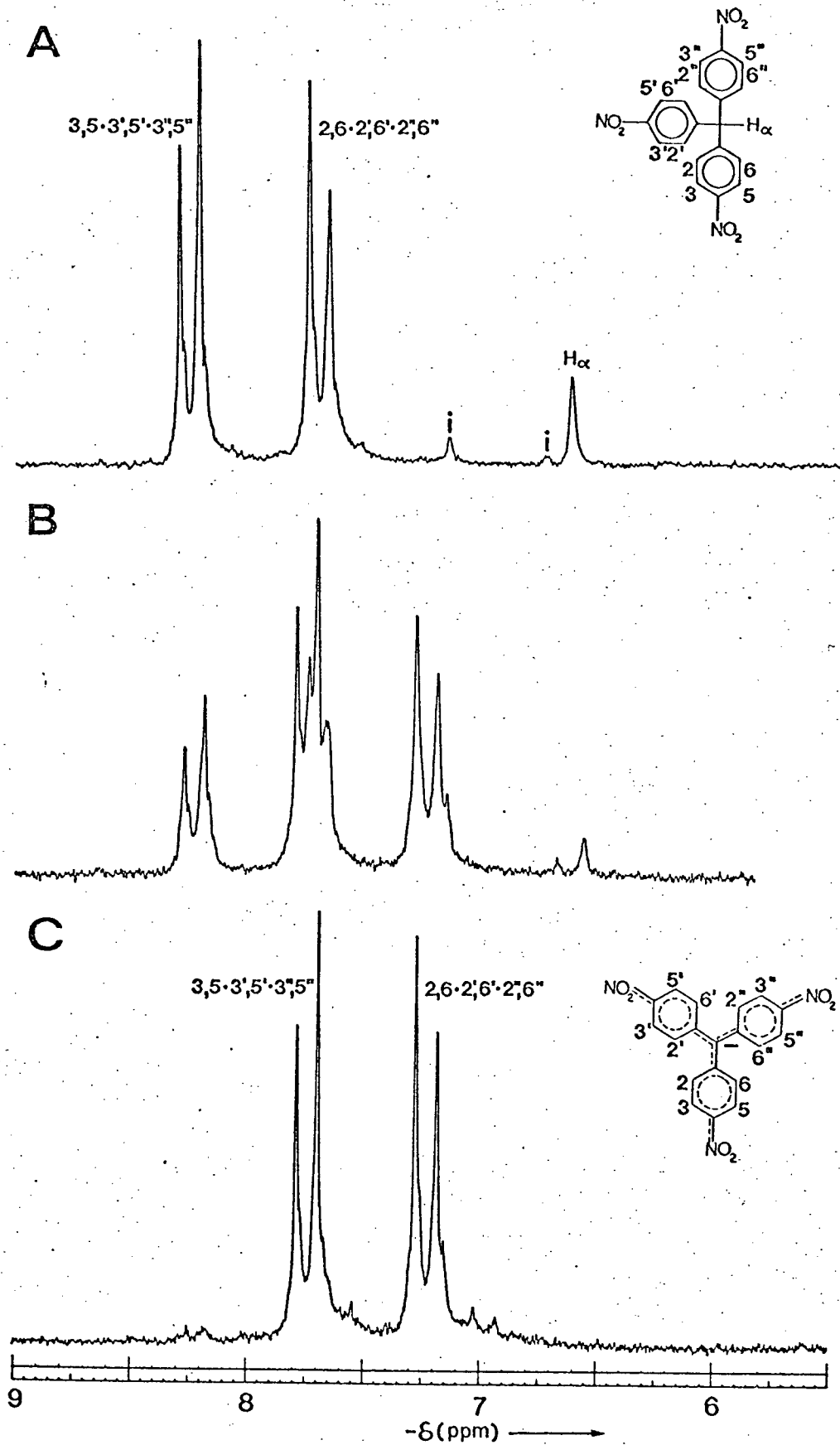
In a 91.2 mole % HMPT-water solution containing 0.01 M TMAOH, Aniline ( $pK_a = 27.3$ ) is one-tenth ionized and 3-trifluoromethylaniline ( $pK_a = 25.4$ ) is completely ionized. These results would thus indicate an  $H_a$  value of  $\sim 26.4$ . The  $H_a$  value for the corresponding DMSO solution is 21.2.

the methine hydrogen and an AA'XX' multiplet centered around  $\delta = -8.02$  (relative area 12) due to the aromatic hydrogens (figure 28a ). The addition of less than one equivalent of anhydrous sodium methoxide to this solution gives an intense green colouration. The intensity of the spectrum of the nitrophenylmethane decreases with the simultaneous appearance of another multiplet at higher field (figure 28b ). Both multiplets are quite sharp indicating a relatively slow rate of exchange between the two species. When more than one equivalent of base was added the original spectrum completely vanished leaving only the new multiplet centered around  $\delta = -7.56$  (figure 28c ). This spectrum is in agreement with that expected for the exclusive formation of an anion by proton removal from the methine carbon.



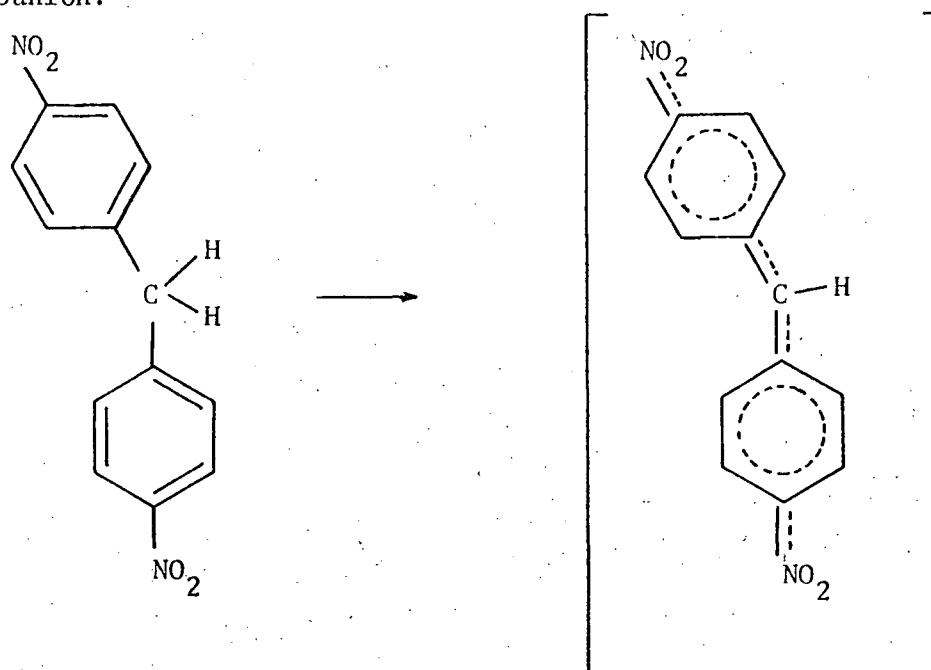
The visible spectrum of the ion was determined directly in a 0.0024 M solution and exhibited an absorbance at a  $\lambda_{\text{max}}$  of 770 m $\mu$  ( $\epsilon = 43,400$ ).

Figure 28. N.m.r. spectra of tris-(p-nitrophenyl)methane and anion in HMPT.



Bis-(p-nitrophenyl)methane BNPM

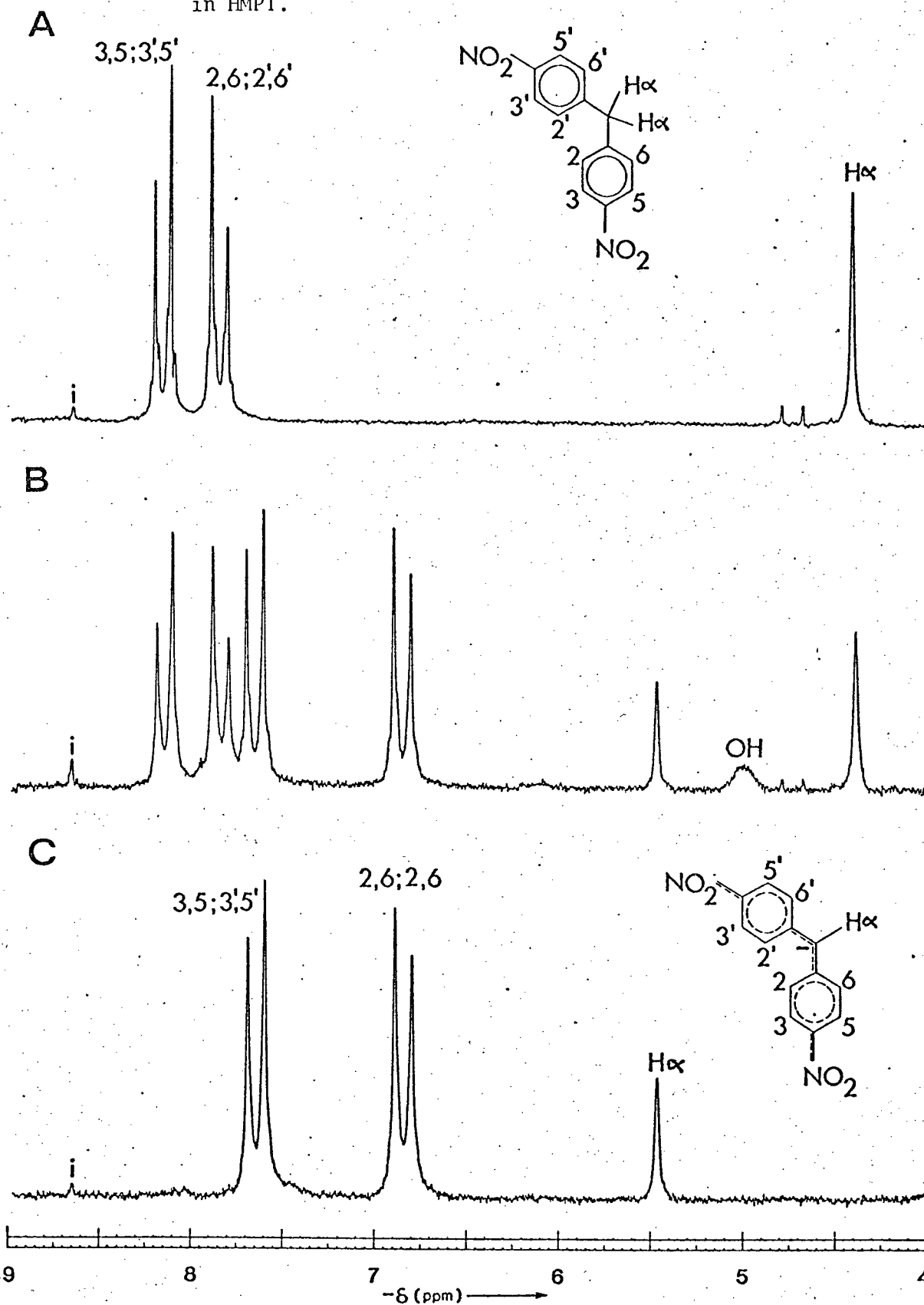
The n.m.r. spectrum of BNPM in HMPT (0.058 M solution) consists of a single resonance at  $\delta = -4.45$  (relative area 1) due to the methylene hydrogens and a AA'XX' multiplet centered at  $\delta = -8.04$  (relative area 4) assigned to the aromatic hydrogens (figure 29 a). Addition of anhydrous sodium methoxide to this solution gives a dark green colouration and causes a decrease in the intensity of the spectrum of BNPM along with the appearance of a new spectrum at higher field (figure 29 b). Both resonances are quite sharp and complete conversion to the spectrum at higher field is possible with the addition of more base. The new spectrum consists of a sharp resonance at  $\delta = -5.44$  (relative area 1) and a AA'XX' multiplet centered around  $\delta = -7.27$  (relative area 8) (figure 29 c). This new spectrum is indicative of the formation of the BNPM carbanion.



The visible spectrum of the carbanion was determined directly in a 0.024 M solution and exhibited an absorbance at a  $\lambda_{\text{max}}$  of 787m $\mu$  ( $\epsilon = 58,300$ ).



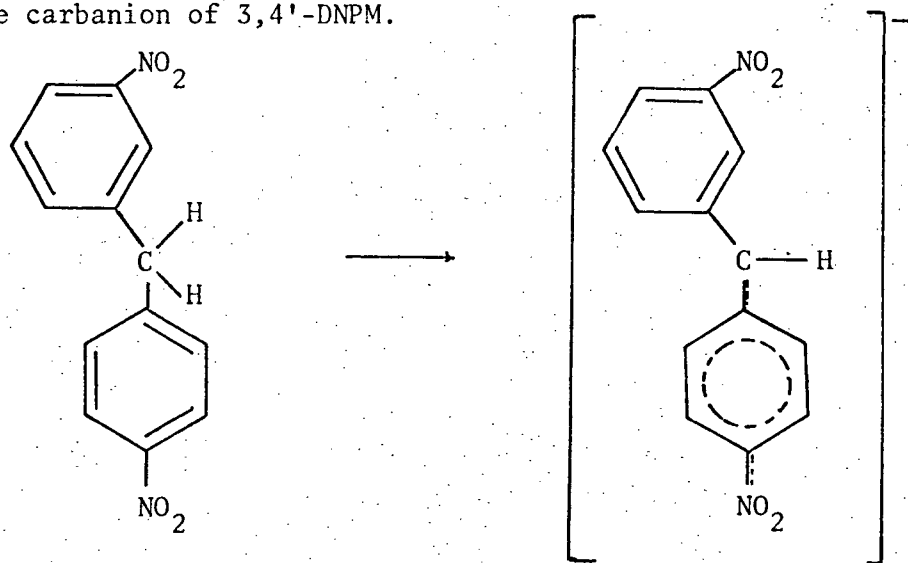
Figure 29. N.m.r. spectra of bis-(p-nitrophenyl)methane and anion in HMPT.



### 3,4'-dinitrodiphenylmethane 3,4'-DNPM

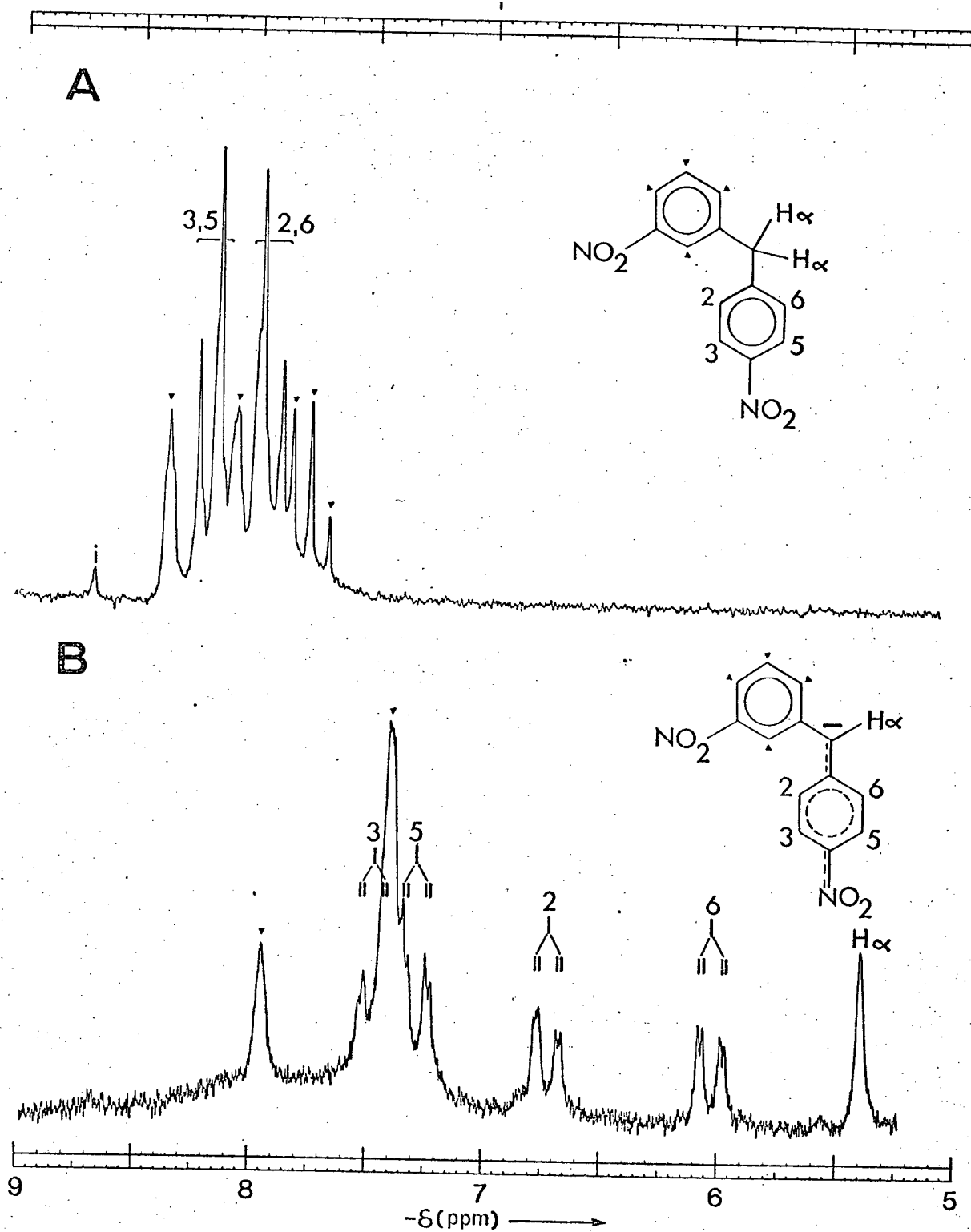
The n.m.r. spectrum of a 0.065 M solution of 3-4'-DNPM in HMPT is shown in figure 30 a and consists of a sharp resonance at  $\delta = -4.43$  (relative area 1) due to the two methylene protons as well as a series of lines at low field (relative area 4) assigned to the aromatic protons. The resonances due to the protons from the 4'-nitro ring are distinct from the resonances from the 3-nitro ring because of their symmetrical arrangement. They consist of a multiplet at  $\delta = -8.05$  with  $J_{AA'} = 2.2$ ,  $J_{XX'} = 2.2$ ,  $J_{AX'} = J_{A'X} = 0.5$ ,  $J_{AX} = J_{A'X'} = 8.2$  and  $\nu_{\delta_{AX}} = 46.1$  cps. where  $\nu_{\delta_{AX}}$  represents the chemical shift between nuclei A and X. Careful addition of an equivalent of sodium methoxide to this solution results in the disappearance of the substrate spectrum with the appearance of a new spectrum at higher fields. But unlike the two previous nitrophenylmethanes studied, addition of less than one equivalent of base causes a broadening (specially at high substrate concentration  $\sim 0.5$  M) in both spectrum at high and low fields.

The second spectrum can be rationalized in terms of the formation of the carbanion of 3,4'-DNPM.



The resonances at  $\delta = -7.95$  and  $-7.38$  are assigned to the 2 and

Figure 30. N.m.r. spectra of 3,4'-dinitrodiphenylmethane and anion in HMPT.



4,5,6 hydrogens respectively. The hydrogens of the symmetrical ring give rise to four doublets of major splittings  $\approx 8$  c.p.s. and smaller splittings  $\approx 2$  c.p.s. centered at  $\delta = -6.02$ ,  $-6.70$ ,  $-7.26$  and  $-7.44$  ppm.

If this is indeed the case, then the doublet at  $\delta = -7.44$  must be partially hidden by the resonances of the second ring. It is possible to achieve partial decoupling of the multiplet at  $\delta = -6.7$  by irradiation of the resonance at  $\delta = -7.44$ . Similarly, the doublet at  $\delta = -6.02$  is decoupled by irradiation of the doublet centered at  $\delta = -7.26$  and vice versa. These decoupling experiments thus confirm the validity of the peak assignment.

The visible spectrum of the carbanion was determined directly in a 0.0073 M solution and exhibited an absorbance at a  $\lambda_{\text{max}}$  of 593 m $\mu$  ( $\epsilon = 28,000$ ).

No detectable amount of ionization by proton abstraction was found by n.m.r. for 3,4'-DNPM, when DMSO is used as a solvent instead of HMPT. Bis- and tris- (p-nitrophenyl)methane ionize in DMSO<sup>96</sup> only to the extent of  $\approx 35$  and  $\approx 75$  percent respectively\*.

Addition of 10 - 20 percent methanol to a solution containing a mixture of the anion and neutral BNPM in HMPT causes substantial broadening of the substrate spectrum, but does not affect the anion spectrum. This probably results from rapid exchange between the substrate and the radical-anions produced in the system. At high methanol concentrations both spectra broaden and eventually disappear.

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\* The apparent molar absorptivity of tris-(p-nitrophenyl)methane in DMSO containing sodium methoxide is  $\approx 70$  percent of the value obtained in HMPT containing sodium methoxide.

Both these observations would indicate that if the solvent system is not basic enough to ionize the nitrophenylmethane by proton abstraction, side reactions become very important. This is obvious from the fact that the relative amount of carbanion formation increases with increasing acidity of nitrophenylmethanes in the DMSO-sodium methoxide system.

## II. E.s.r. investigation

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Russell and Janzen<sup>91</sup> noted that 2,4-dinitrotoluene radical-anions are produced only when the solvent mixture is deficient in base, while o- and p- nitrotoluenes radical-anions are produced at all base concentrations. This observation can also be explained since 2,4-dinitrotoluene is probably completely ionized in the DMSO-t-butanol mixture while o- and p- nitrotoluenes are not.

To examine the nature of the absorbing species at lower wavelength, the radical-anions of the nitrophenylmethanes were generated electrochemically in DMSO-methanol mixtures. It was found that the  $^{14}\text{N}$  hyperfine splitting constant ( $a_{\text{N}}$ ) was strongly solvent dependent. Nitrobenzenes<sup>97</sup> and nitric oxides<sup>99</sup> radical-anions also exhibit strong solvent dependent N splittings. Adams et al<sup>98</sup> and Pannell<sup>99</sup> reported several cases of  $a_{\text{N}}$  dependence on solvent composition.

A quantitative treatment has been given by Gendall et al.<sup>100</sup> who assumed that the changes in splittings arise from redistribution of the  $\pi$ -electron spin density near the functional group. Gendall et al.<sup>100</sup> also assumed that the interaction between the solvent and the radical is significant only at the site of the functional group. Furthermore, in a binary solvent mixture, if the exchange between the two solvent-radical

complexes is rapid enough, a model can be derived which can account for the hyperbolic dependence of the hyperfine splittings\* with the solvent composition ratio.

Kennedy<sup>101</sup> has shown that a simple extension of this model will give a linear dependence of the splitting on the mole fraction of the solvent. Table XXII lists the N splittings  $a_N$  with the mole percent DMSO in methanolic DMSO mixtures and these values are plotted in figures 31 and 32. It is obvious that a good straight line can be drawn through these points, thus confirming the correctness of the model proposed by Gendall<sup>100</sup> and altered by Kennedy<sup>101</sup> i.e. the solvent complexes are long lived with respect to their exchange time and the major effect on the spin density comes from the interaction of the solvent with the functional group. The e.s.r. spectra of tris-(p-nitrophenyl)methane radical-anions were rather broad and although a definitive change in  $a_N$  values was noted in going from pure methanol to pure DMSO, the inaccuracy in the measurements did not warrant their plotting.

Chambers and Adams<sup>102</sup> reported that the absorption maximum of the radical-anion of nitrobenzene shifts to lower wavelength with increasing water concentration in dimethylformamide (DMF). A blue shift of 42 m $\mu$  was observed for an addition of 20 weight percent water to DMF. Chambers and Adams<sup>102</sup> correlated this solvent shift of the absorption maximum with the change in  $a_N$ .

Although in this work, no direct determination of the u.v. spectrum of electrochemically generated radical-anions was attempted, a change in the colour of these radicals was observed visually.

\*

twice the difference of the average splitting from the arithmetic mean

TABLE XXII

Splitting constants  $a_N$  for BNPM and 3,4'-DNPM in methanolic DMSO mixtures.

mole % DMSO	BNPM		3,4'-DNPM		TNPM
	$a_N$		$a_N$		$a_N$
0	13.3	colourless			
1	13.3	colourless	13.15	colourless	13.6±1.6 colourless
24	12.7	faint yellow	12.5	faint yellow	12.5±0.6
53	11.8	blue	11.6	light blue	
73	11.24	green- blue	11.0	blue	
97	10.15	green	10.1	blue	9.6±1.6 green
100	10.0	green			

Figure 31. Plot of the average splitting constants versus mole percent DMSO for the radical-anion of 3,4'-dinitrodiphenylmethane in methanolic DMSO.

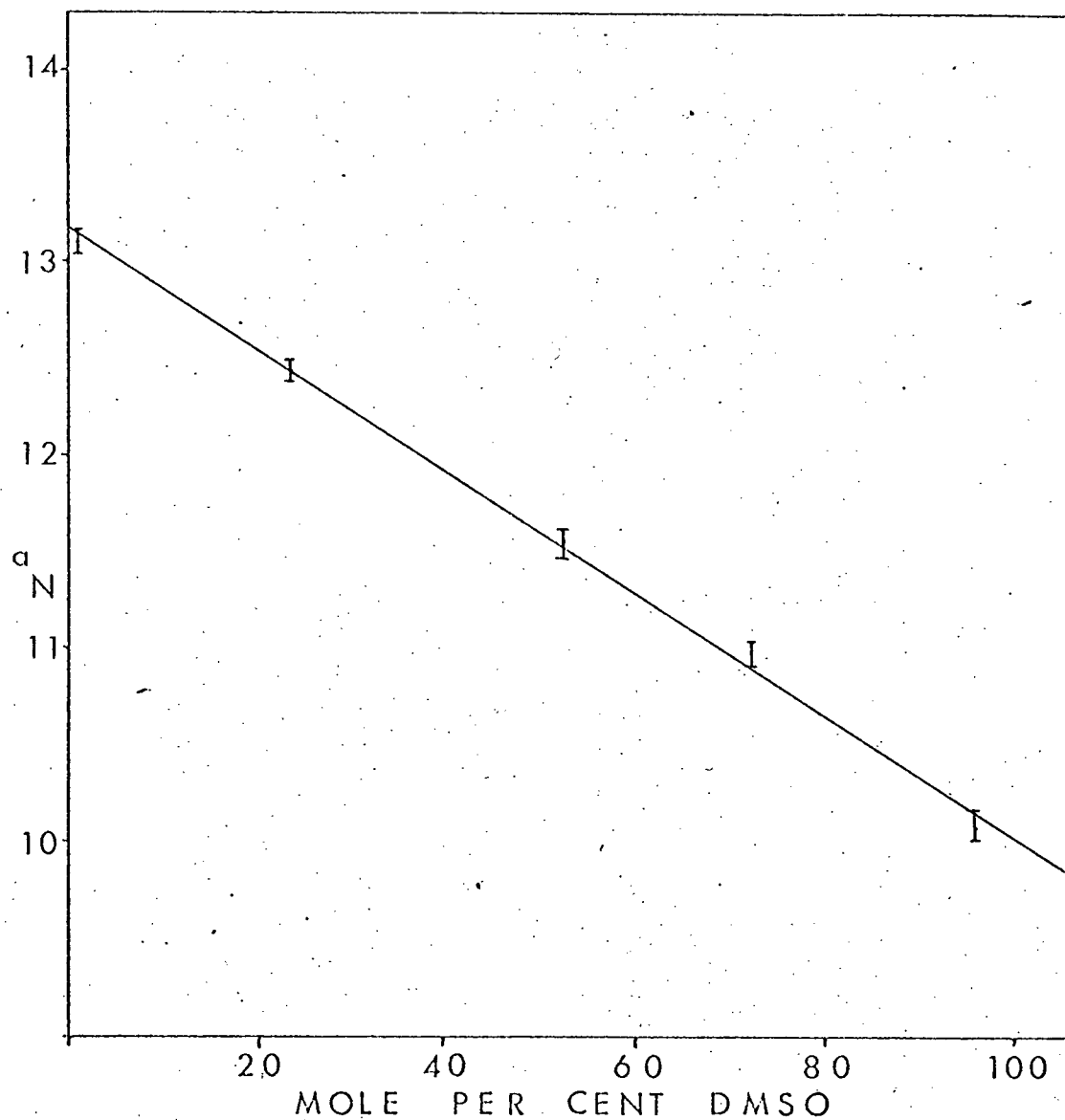




Figure 32. Plot of the average splitting constants versus mole percent DMSO for the radical-anion of bis-(p-nitrophenyl)methane in methanolic DMSO.

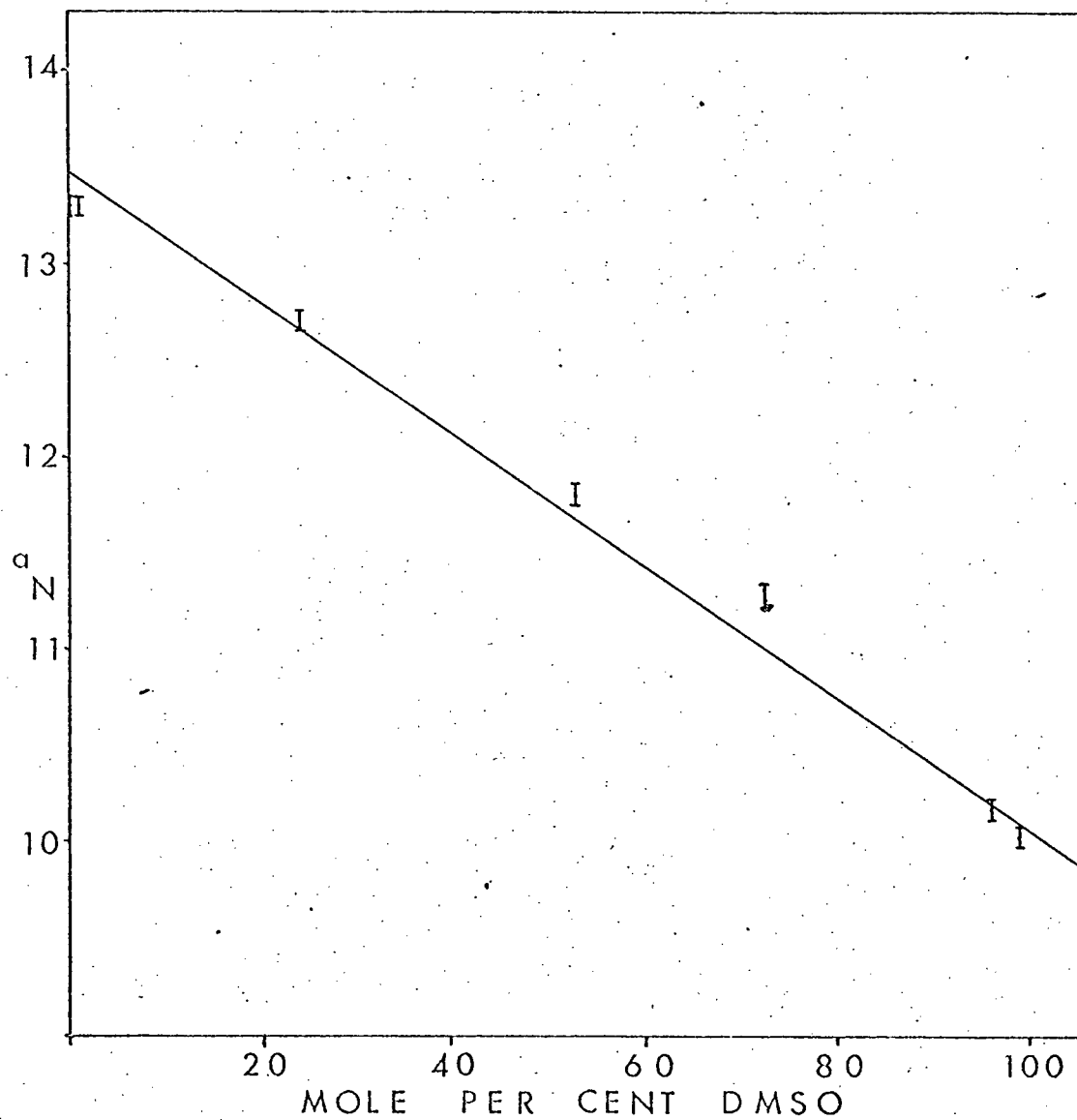


Table XXII lists the colour of the different DMSO-methanol solutions after the radical-anions were generated. One can estimate at  $\approx 200 \text{ m}\mu$  the shift in absorption maxima between methanol and DMSO.

If we assume that there exists a quantitative correlation between the absorption maxima of the radical-anions and their splitting constants<sup>\*</sup>, then we can account for the large solvent shifts observed in basic ethanolic DMSO solutions.

The carbanions of the nitrophenylmethanes have been identified by n.m.r. and their u.v. spectra directly recorded<sup>\*\*</sup> in the same solutions. Therefore the u.v. spectral characteristics of these carbanions are unequivocally defined and any absorption which occur at lower wavelength probably arises from other ionic species.

Table XXIII lists the spectral data determined in this work, as well as those determined by Bowden and Stewart<sup>17</sup> and Kroeger<sup>18</sup>.

The accumulated evidence thus suggests that in the methanolic sodium methoxide system, the u.v. absorption observed<sup>18</sup> arise from the nitrophenylmethane radical-anions. In ethanolic DMSO the situation is more complex, since both carbanions and radicals are present in the same solution. At high DMSO concentrations TNPM is probably almost completely in the carbanionic form ( $\lambda_{\text{max}} = 800 \text{ m}\mu$ ) while the absorption at a  $\lambda_{\text{max}}$  of  $580 \text{ m}\mu$  in ethanol indicates a preponderance of radicals. As a rule of thumb, the absorptions around  $750\text{-}800 \text{ m}\mu$  for TNPM and BNPM and around  $600 \text{ m}\mu$  for 3-4'-DNPM can be attributed to the carbanions, while those

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\*

i.e. a correlation similar to the one observed by Chambers and Adams.

\*\*

u.v. cells of path-length  $0.1$  and  $0.01 \text{ mm}$  have been used, but it was necessary to dilute the solutions by a factor of  $\approx 15$  to be able to determine the molar absorptivity on a Cary Model 16 spectrophotometer.

TABLE XXIII

Spectral data of nitrophenylmethanes in strongly basic solutions.

Compound/solvent	HMPT/NaOMe <sup>a</sup>		DMSO/EtOH <sup>b</sup>		MeOH/NaOMe <sup>c</sup>	
	$\lambda_{\max}$ m $\mu$	$\epsilon$	$\lambda_{\max}$ m $\mu$	$\epsilon$	$\lambda_{\max}$ m $\mu$	$\epsilon$
TNPM	775	43,400	707	19,300	530	25,600
			809	30,300 <sup>d</sup>		
			810	63,000 <sup>e</sup>		
BNPM	787	58,300	704	40,600	534	28,000
			707	41,900 <sup>g</sup>		
3,4'-DNPM	593	28,000	550	31,700	430 <sup>f</sup>	
			570	28,800 <sup>g</sup>		

<sup>a</sup> values determined in this work in HMPT containing sodium methoxide

<sup>b</sup> values determined by Bowden and Stewart<sup>17</sup> in ethanolic DMSO containing 0.01 M sodium ethoxide

<sup>c</sup> values determined by Kroeger<sup>18</sup> in methanolic sodium methoxide 0.01 M[OR]<sup>-</sup>

<sup>d</sup> value determined in this work in DMSO containing sodium methoxide

$\epsilon_{\text{DMSO}} \sim 70\%$  of the  $\epsilon_{\text{HMPT}}$  cf. footnote page 137.

<sup>e</sup> value determined by Ritchie and Uschold<sup>19</sup> in DMSO

<sup>f</sup> value determined in this work in methanolic sodium methoxide, the molar absorptivities could not be measured as the medium is not basic enough to completely ionize this compound.

<sup>g</sup> value redetermined in this work in 90% DMSO-ethanol-0.01 M sodium ethoxide.

at lower wavelength arise either from the exclusive presence of radicals or a mixture of radicals and carbanions.

Preliminary investigation of the interactions between nitrophenylmethanes and basic DMSO solutions showed that a variety of synergic reactions occur. These should be investigated more carefully as this type of reaction appear to be quite general<sup>91</sup>. The nitrophenylmethanes cover a wide range of acidities and are thus ideally suited for such an investigation.

### CONCLUSION

It is obvious from the results in this thesis that only carbon acids which ionize by proton abstraction should be used to determine acidity functions. In this area of study evidence should be obtained using more than one analytical technique since the traditional method, u.v. spectrophotometry, is inadequate<sup>90</sup> for the identification of ionization processes.

The whole field of acidity determination, both thermodynamic and kinetic, is still in its infancy as a result of our limited knowledge of solvent effects. Probably a step in the right direction would be to conceive a reference electrode whose response is independent of the medium. Recently Brenet<sup>103</sup> considered the theoretical aspects of such a reference electrode in non-aqueous systems.

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APPENDIX A: Ionization Ratio Data

TABLE XXIV

Experimental values of log I for diphenylamine indicators in the system

DMSO-water-tetramethylammonium hydroxide (0.011 M)

Indicator	2,4,4'-(NO <sub>2</sub> ) <sub>3</sub> DPA	2,4,3'-(NO <sub>2</sub> ) <sub>3</sub> DPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -4'-CF <sub>3</sub> DPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -3'-CF <sub>3</sub> DPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -3'-ClDPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> DPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -3'-MeDPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -4'-NH <sub>2</sub> DPA	Assigned H <sub>+</sub>
Mole% DMSO / pK <sub>a</sub>	12.30	12.59	12.87	13.06	13.17	13.85	13.90	14.48	
0.4	-.35								11.95
1.0	-.20	-.53							12.08
2.0	-.12	-.38							12.20
5.0	+.21	-.10	-.32	-.48	-.61				12.54
10.0	+.74								13.04
11.3		+.57	+.35	+.10	+.05	-.64			13.19
16.0			+.84	+.66	+.55	-.10	-.15	-.75	13.73
20.3						+.40	+.35	-.16	14.29
24.1						+.88	+.82	+.24	14.72

TABLE XXIV - Continued

Indicator	3,4'-(NO <sub>2</sub> ) <sub>2</sub> DPA	4-NO <sub>2</sub> -3-ICF <sub>3</sub> DPA	4-NO <sub>2</sub> -3-ICIDPA	4-NO <sub>2</sub> DPA	4-NO <sub>2</sub> -3-MeDPA	4-NO <sub>2</sub> -4-NH <sub>2</sub> DPA	Assigned H.
Mole% DMSO /pK <sub>a</sub>	14.62	14.90	15.00	15.67	15.60	16.40	
20.3	-.29	-.58					14.29
24.1	+.07	-.22	-.30	-.90	-.82		14.72
29.7	+.69	+.45	+.34	-.32	-.24		15.34
33.6		+.83	+.74	+.11	+.19	-.61	15.75
36.2				+.34		-.35	16.01
43.2						+.39	16.74

TABLE XXV.

Experimental values of  $\log I$  for diphenylamine indicators in the system

DMSO-methanol-sodium methoxide (0.01 M)

[illegible]

TABLE XXV - Continued

[illegible]



TABLE XXVI

Experimental values of log I for amine indicators in the system

DMSO-ethanol-sodium ethoxide (0.01 M)

Indicator	2,4-(NO <sub>2</sub> ) <sub>2</sub> DPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -3-MeDPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> -4-NH <sub>2</sub> DPA	2,4-(NO <sub>2</sub> ) <sub>2</sub> An	Assigned H <sub>+</sub>
Mole% DMSO /pK <sub>a</sub>	14.05	14.12	15.05	15.27	
0.3	-.60	-.65			13.46
1.0	-.50	-.52			13.57
2.5	-.34				13.71
5.0	-.09	-.20			13.94
10.0	+.26	+.14			14.29
14.6	+.60	+.46	-.37	-.59	14.64
20.4			-.03	-.27	15.01
24.7			+.23	+.04	15.31
30.0				+.33	15.60
35.4				+.66	15.96

TABLE XXVI - Continued

[illegible]

TABLE XXVII

Experimental values of log I for the substituted phenol indicators in the  
system DMSO-methanol-sodium methoxide (0.01 M)

Substituent	2-isopropyl	2,6-di-isopropyl	2-t-butyl	2,4-di-t-butyl	Assigned H <sub>+</sub>
Mole % DMSO /pK <sub>a</sub>	10.49	10.98	11.67	12.10	
0.0	-.60				9.92
5.0	-.33	-.80			10.17
10.6	-.13	-.64			10.35
15.0	+.04	-.46			10.53
19.2	+.24	-.26	-.94		10.73
25.0		-.04	-.74		10.94
29.7		+.15	-.47		11.16
35.1		+.35			10.35
40.0		+.56	-.09		11.55
44.9			+.08		11.75
46.0				-.24	--
50.0			+.30		12.97
53.0				+.03	12.13
59.0				+.26	12.36
63.0				+.44	12.54
69.7				+.69	12.79

TABLE XXVIII

Experimental values of log I for the substituted phenol indicators in  
DMSO-ethanol-sodium ethoxide (0.01 M)

Substituent	2,6-di-isopropyl	2-t-butyl	2,4-di-t-butyl	2,6-di-t-butyl-4'-methyl	2,4,6-tri-t-butyl	Assigned H <sub>+</sub>
mole% DMSO /pK <sub>a</sub>	11.00	11.67	12.12	12.28	12.28	
0.0	-.40	-1.03				10.62
1.1	-.18	-.92				10.78
5.0	+.02	-.66				11.02
10.0	+.20	-.46				11.21
14.8	+.40	-.26				11.40
20.4	+.57	-.10	-.58			11.56
24.7	+.72	+.07				11.73
30.0		+.25	-.21	-.36		11.91
35.4			-.02		-.20	12.10
39.7		+.60	+.14	-.04	-.04	12.25
45.0			+.35	+.17	+.21	12.47
50.6		+.95	+.48		+.40	12.63
55.2			+.63	+.46	+.56	12.77
60.0			+.84	+.70	+.71	12.98
65.0				+.80		13.11
70.0				+.99		13.31

Appendix B: Rate correlation data

TABLE XXIX

Rate of detritiation ( $1. \text{mole}^{-1} \text{sec}^{-1}$ ),  $k_{\text{OR}^-}$  at  $25^\circ$  for various hydrocarbons  
in basic DMSO-Ethanol solutions

Compound	mole% DMSO	$[\text{OEt}]^-$ M	$\text{H}^{\text{N}}_-$	$k_{\text{OR}^-}$
9-Phenylfluorene	0.0	.01	13.46	$7.684 \times 10^{-3}$
	5.0	.0098	13.93	$2.327 \times 10^{-2}$
	10.0	.01	14.29	$4.600 \times 10^{-2}$
	14.6	.0105	14.66	$8.726 \times 10^{-2}$
	20.4	.01	15.01	$1.844 \times 10^{-1}$
2,3-Benzofluorene	0.0	.01	13.46	$1.535 \times 10^{-3}$
	5.0	.0087	13.88	$3.516 \times 10^{-3}$
	33.5	.0103	15.78	$1.250 \times 10^{-1}$
	39.2	.0086	16.21	$2.523 \times 10^{-1}$
Fluorene	10.0	.0102	14.30	$2.723 \times 10^{-3}$
	12.5	.0112	14.50	$4.186 \times 10^{-3}$
	20.2	.01	15.01	$8.746 \times 10^{-3}$
	24.4	.0095	15.26	$1.520 \times 10^{-2}$
	30.3	.01	15.60	$2.766 \times 10^{-2}$
	35.0	.0103	15.95	$4.808 \times 10^{-2}$
	39.2	.0086	16.21	$7.443 \times 10^{-2}$
	44.6	.01	16.63	$2.083 \times 10^{-1}$
9-Ethylfluorene	12.5	.0107	14.48	$3.241 \times 10^{-4}$
	29.9	.0091	15.56	$2.575 \times 10^{-3}$
	35.0	.0095	15.94	$4.218 \times 10^{-3}$
	39.2	.009	16.18	$7.563 \times 10^{-3}$
	44.5	.0091	16.55	$1.631 \times 10^{-2}$
	49.1	.01	16.88	$2.934 \times 10^{-2}$
	54.6	.0085	17.19	$5.540 \times 10^{-2}$
	59.6	.009	17.55	$8.884 \times 10^{-2}$
	64.9	.0092	17.92	$1.811 \times 10^{-1}$

TABLE XXIX - Continued

Compound	mole% DMSO	[OEt] <sup>-</sup> M	H <sup>N</sup> -	k <sub>OR</sub> <sup>-</sup>
9-Phenylxanthene	49.1	.0094	16.85	3.514 x 10 <sup>-4</sup>
	64.9	.01	17.96	2.956 x 10 <sup>-3</sup>
	70.3	.014	18.42	6.528 x 10 <sup>-3</sup>
	75.0	.015	18.83	1.645 x 10 <sup>-2</sup>
	94.0	.01	20.63	5.530 x 10 <sup>-1</sup>
Triphenylmethane	83.5	.01	19.59	6.448 x 10 <sup>-4</sup>
	87.0	.01	19.93	1.287 x 10 <sup>-3</sup>
	20.6	.01	20.63	5.990 x 10 <sup>-3</sup>

TABLE XXX

Rates of detritiation ( $1.\text{mole}^{-1} \text{ sec}^{-1}$ ),  $k_{\text{OR}}^-$  at  $25^\circ$  for various hydrocarbons in basic DMSO solutions

	mole % DMSO	$[\text{OMe}]^-$ M	$\text{H}^{\text{N}}_-$	k
a)				
9-phenylfluorene	0.0	.0093	11.91	$1.525 \times 10^{-3}$
in DMSO-methanol solutions	5.3	.0095	12.30	$4.849 \times 10^{-3}$
	9.7	.0104	12.68	$1.035 \times 10^{-2}$
	15.7	.0108	13.18	$2.25 \times 10^{-2}$
	19.4	.0105	13.42	$3.673 \times 10^{-2}$
	28.8	.0108	14.15	$1.1 \times 10^{-1}$
	35.7	.0105	14.63	$2.513 \times 10^{-1}$
	40.1	.0099	14.98	$4.664 \times 10^{-1}$
b)				
	mole % DMSO	$[\text{TMAOH}]$ M	$\text{H}^{\text{N}}_-$	k
fluorene	27.1	.011	15.02	$1.832 \times 10^{-3}$
in DMSO-water solutions	33.0	.011	15.65	$4.473 \times 10^{-3}$
	36.4	.011	16.05	$1.200 \times 10^{-2}$
	49.2	.011	17.37	$1.225 \times 10^{-1}$

TABLE XXXI

Ionization rate constants (1.mole<sup>-1</sup> sec<sup>-1</sup>), k (DMSO), at 25° for DMSO  
in Basic DMSO solutions.

mole % DMSO	[OR] <sup>-</sup> M	H <sub>-</sub> <sup>N</sup>	detrification k	tritiation k
a) In water-DMSO solutions with TMAOH as base				
0.0	.01	11.98	3.046 x 10 <sup>-8</sup>	
0.0	.05	12.71	7.235 x 10 <sup>-8</sup>	
0.0	.10	13.01	2.175 x 10 <sup>-7</sup>	
33.5	.01	15.9 <sup>†</sup>		9.63 x 10 <sup>-5</sup>
43.3	.01	16.84 <sup>†</sup>		1.06 x 10 <sup>-3</sup>
55.3	.01	17.88 <sup>†</sup>		5.23 x 10 <sup>-3</sup>
b) In Ethanol-DMSO solutions with NaOEt as base				
0.0	.01	13.46	5.077 x 10 <sup>-7</sup>	
34.6	.01	15.96 <sup>†</sup>		9.92 x 10 <sup>-5</sup>
50.6	.011	17.00 <sup>†</sup>		1.00 x 10 <sup>-3</sup>
50.6	.022	17.30 <sup>†</sup>		7.43 x 10 <sup>-4</sup>
65.5	.01	18.00 <sup>†</sup>		3.43 x 10 <sup>-3</sup>
80.0	.098	19.21		4.57 x 10 <sup>-2</sup>
80.4	.01	19.24		4.79 x 10 <sup>-2</sup>
90.1	.01	20.05		3.61 x 10 <sup>-1</sup>
95.4	.098	20.62		2.88

.../continued



TABLE XXXI continued

mole% DMSO	[OR] <sup>-</sup> M	H <sub>-</sub> <sup>N</sup>	detritiation k	tritiation k
c) In Methanol-DMSO solutions with NaOMe as base				
0.0	.01	11.95	$9.14 \times 10^{-8}$	
30.0	.01	14.19	$3.89 \times 10^{-6}$	
36.0	.0095	14.74		$1.54 \times 10^{-5}$
36.0	.01	14.76	$9.55 \times 10^{-6}$	
50.1	.01	15.75		$1.05 \times 10^{-4}$
50.1	.013	15.85		$1.07 \times 10^{-4}$
60.1	.01	16.57		$8.91 \times 10^{-4}$
63.0	.0097	16.86		$4.09 \times 10^{-4}$
60.1	.024	16.95		$4.26 \times 10^{-4}$
74.0	.01	17.70		$1.74 \times 10^{-3}$
93.4	.01	19.50		$3.15 \times 10^{-2}$
94.6	.01	19.70		$3.99 \times 10^{-2}$

<sup>†</sup> The H<sub>-</sub> value of these solutions were determined spectrophotometrically, with amine indicators.

TABLE XXXII

Rate-temperature data for the base catalyzed detritiation of hydrocarbons  
in DMSO-EtOH-0.01 M NaOEt

Hydrocarbon	Temp°	1/T°(K)	k <sub>OR</sub> -( mole <sup>-1</sup> sec <sup>-1</sup> )	log k/T
<u>a</u>	55	0.003047	6.630 x 10 <sup>-4</sup>	-5.6946
triphenylmethane	45	0.003143	2.207 x 10 <sup>-4</sup>	-6.1589
	35	0.003245	6.140 x 10 <sup>-4</sup>	-6.7009
	45	0.003143	2.399 x 10 <sup>-2</sup>	-4.1227
9-phenylxanthene	35	0.003245	9.02 x 10 <sup>-3</sup>	-4.5337
	25	0.003350	2.955 x 10 <sup>-3</sup>	-5.0040
	15	0.003470	6.692 x 10 <sup>-4</sup>	-5.6332
	25	0.003354	1.811 x 10 <sup>-1</sup>	-3.2165
9-ethylfluorene	15	0.003470	6.092 x 10 <sup>-2</sup>	-3.6747
	5	0.003595	2.218 x 10 <sup>-2</sup>	-4.0984
fluorene	15	0.003470	4.207 x 10 <sup>-1</sup>	-2.8358
	5	0.00359	1.577 x 10 <sup>-1</sup>	-3.2464
	-5	0.00373	5.970 x 10 <sup>-2</sup>	-3.6524
<u>b</u>				
	15	0.003470	1.845 x 10 <sup>-3</sup>	-5.1937
9-phenylxanthene	25	0.003350	6.526 x 10 <sup>-3</sup>	-4.6603
70% DMSO	35	0.003245	2.019 x 10 <sup>-2</sup>	-4.1836
	45	0.003143	7.995 x 10 <sup>-2</sup>	-3.5998
	15	0.003470	1.444 x 10 <sup>-3</sup>	-5.2990
9-ethylfluorene	25	0.003350	4.218 x 10 <sup>-3</sup>	-4.8499
35% DMSO	35	0.003245	1.097 x 10 <sup>-2</sup>	-4.4486
	45	0.003143	3.49 x 10 <sup>-2</sup>	-3.9597
	15	0.003470	1.02 x 10 <sup>-3</sup>	-5.4510
fluorene	25	0.003350	2.776 x 10 <sup>-3</sup>	-5.0315
10% DMSO	35	0.003245	7.433 x 10 <sup>-3</sup>	-4.6176
	45	0.003143	1.9 x 10 <sup>-2</sup>	-4.2239

C  
C ALAIN /D.K./ A.M.S.  
C THIS PROGRAM DOES A LEAST SQUARES FIT FOR THE EXPRESSION  $Y=A+BX$   
C R IS A SIGNIFICANCE TEST FOR A STRAIGHT LINE  
C T IS A SIGNIFICANCE TEST FOR A STRAIGHT LINE  
C

```

0001      CALL PLOTS
0002      DIMENSION LABELX(15),LABELY(15)
0003      DIMENSION XX(2),YY(2)
0004      DIMENSION X(30),Y(30)
0005      DIMENSION TITLEG(20)
0006      DIMENSION TITLE (20)
0007      31  READ(5,3,END=99) TITLEG
0008      3    FORMAT(20A4)
0009      WRITE(6,4) TITLEG
0010      4    FORMAT(1H1,30X,20A4)
0011      READ(5,1) M
0012      READ(5,11) XU,XL,YU,YL
0013      11   FORMAT(4F10.5)
0014      XMIN=XL
0015      YMIN=YL
0016      DX=(XU-XL)/8.
0017      DY=(YU-YL)/6.
0018      READ(5,6)LX,LABELX
0019      READ(5,6)LY,LABELY
0020      6    FORMAT(13,15A4)
0021      CALL AXIS(0.0,0.0,LABELX,-LX,8.,0.0,XMIN,DX)
0022      CALL AXIS(0.0,0.0,LABELY,LY,6.,90.0,YMIN,DY)
0023      CALL PLOT(0.0,0.0,3)
0024      CALL PLOT(0.0,6.3,2)
0025      CALL PLOT(8.5,6.3,1)
0026      CALL PLOT(8.5,0.0,1)
0027      CALL PLOT(8.0,0.0,1)
0028      DO20 K=1,M
0029      READ(5,3)TITLE
0030      WRITE(6,4)TITLE
0031      READ(5,1) N
0032      1    FORMAT(12)
0033      READ(5,2,END=99)(X(I),Y(I),I=1,N)
0034      WRITE(6,2) (X(I),Y(I),I=1,N)
0035      2    FORMAT(2F12.6)
0036      CALL LEAST(X,Y,N,AA,BB)
0037      XXMAX=AMAX(X,N)
0038      XXMIN=AMIN(X,N)
0039      Y(N+1)= AA+BB*XXMIN
0040      Y(N+2)= AA+BB*XXMAX
0041      X(N+1)=XXMIN
0042      X(N+2)= XXMAX
0043      DO 10 I=1,N
0044      X(I)=(X(I)-XMIN)/DX
0045      Y(I)=(Y(I)-YMIN)/DY
0046      CALL SYMPL (X(I),Y(I),0.07,4,0.0,-1)
0047      10   CONTINUE
0048      XX(1)=(X(N+1)-XMIN)/DX
0049      XX(2)=(X(N+2)-XMIN)/DX

```

C050		YY(1)=(Y(N+1)-YMIN)/DY
C051		YY(2)=(Y(N+2)-YMIN)/DY
C052		CALL LINE (XX,YY,2,+1)
C053		P=X(1)+.15
C054		Q=Y(1)-.15
C055		AM=K
C056		CALL NUMBER(P,Q,0.14,AM,0.0,-1)
C057	20	CONTINUE
C058		CALL SYMBOL (0.5,9.4,0.14,TITLEG,0.0,80)
C059		CALL PLOT (11.0,0.0,-3)
C060		GO TO 31
C061	99	CALL PLOTND
C062		STOP
C063		END

0001		FUNCTION AMAX(X,N)
0002		DIMENSION X(30)
0003		B=X(1)
0004		DO 10 I=2,N
0005		IF(X(I).GT.B) B=X(I)
0006	10	CONTINUE
0007		AMAX=B
0008		RETURN
0009		END

0001		FUNCTION AMIN(X,N)
0002		DIMENSION X(30)
0003		B=X(1)
0004		DO 10 I=2,N
0005		IF(X(I).LT.B) B=X(I)
0006	10	CONTINUE
0007		AMIN=B
0008		RETURN
0009		END

```

SUBROUTINE LEAST(X,Y,N,AA,BB)
  DIMENSION X(30),Y(30),A(30),B(30),C(30),D(30),E(30),F(30)
C
C   LEAST SQUARE FIT OF STRAIGHT LINE  $Y = A + BX$ 
C
C   INITIALIZE
C
C     SX=0.
C     SY=0.0
C     SXX=0.
C     SXY=0.
C     SYY=0.
C
C   CALCULATION OF SLOPE AND INTERCEPT
C
C     DO 100 I=1,N
C       SX=SX+X(I)
C       SXX=SXX + X(I)*X(I)
C       SY=SY + Y(I)
C       SXY=SXY + X(I)*Y(I)
C       SYY=SYY+Y(I)*Y(I)
100    CONTINUE
C     XN=N
C     BB=(XN*SXY-SX*SY)/(XN*SXX-SX*SX)
C     AA=(SY-BB*SX)/XN
C     SDSQR=0.0
C     DO 101 I=1,N
C       F(I)=Y(I)-BB*X(I)-AA
101    CONTINUE
C     SDSQR=SDSQR+F(I)*F(I)
C     WRITE (6,2) SDSQR
C     WRITE (6,3) AA,BB
C     SIGMAS=(SDSQR/(XN-2.0))/(XN*SXX-SX*SX)
C     SIGMAA=SQRT(SIGMAS*SXX)
C     SIGMAB=SQRT(SIGMAS*XN)
C     WRITE(6,6)SIGMAA,SIGMAB
C
C   CALCULATION OF COEFFICIENT OF CORRELATION R
C
C     XB=SX/XN
C     YB=SY/XN
C     SC=0.0
C     DO 102 I=1,N
C       A(I)=X(I)-XB
C       B(I)=Y(I)-YB
C       C(I)=A(I)*B(I)
102    CONTINUE
C     SC=SC+C(I)
C     SE=SC/(XN-1.0)
C     SAXX=0.0
C     DO 103 I=1,N
C       D(I)=A(I)*A(I)
103    CONTINUE
C     SAXXP=SAXX+D(I)
C     SAXXP=SAXXP/(XN-1.0)

```

```
SBXX=0.0
DO 104 I=1,N
E(I)=B(I)*B(I)
SBXX=SBXX+E(I)
```

```
104 CONTINUE
SBXXP=SBXX/(XN-1.0)
R=SF/SQRT(SAXXP*SBXXP)
WRITE (6,4) R
```

C  
C CALCULATION OF STUDENTS TEST T

```
C
U=R*R
T=ABS(R*SQRT(XN-2.0)/SQRT(1.0-U))
WRITE (6,5) T
```

C  
C CALCULATION OF AVERAGE DEVIATION DELTA

```
C
SD=0.0
DO 105 I=1,N
SD=SD+ABS(F(I))
105 CONTINUE
DELTA=SD/XN
```

```
WRITE (6,19) DELTA
```

```
2 FORMAT (37H SUM OF THE SQUARES OF THE DEVIATION=,E20.9/)
```

```
3 FORMAT(12H INTERCEPT =,9X,E15.7,5X,8H SLOPE =,9X,E15.7)
```

```
4 FORMAT(29H COEFFICIENT OF CORRELATION =,E20.9/)
```

```
5 FORMAT (17H STUDENT TEST T =,E20.9/)
```

```
6 FORMAT(21H ERROR IN INTERCEPT =,E15.7,5X,17H ERROR IN SLOPE =,
1 E15.7)
```

```
19 FORMAT (7H DELTA=,E20.9)
```

```
WRITE(6,110)
```

```
110 FORMAT (62H0**** THIS SECTION ONLY RELEVANT FOR ACTIVATION STUDIE
1S ****//)
```

```
SACT=(AA-10.3187)*4.574
```

```
HACT=-BB*0.004574
```

```
WRITE(6,7)HACT,SACT
```

```
7 FORMAT( 31H0THE ENTHALPY OF ACTIVATION IS ,G10.3,32HKILOCALORIES P
1ER MOLE PER DEGREE/30H THE ENTROPY OF ACTIVATION IS ,G10.3,13HENTRO
2PY UNITS)
```

```
DHACT = SIGMAB*0.004574
```

```
DSACT = SIGMAA*4.574
```

```
WRITE(6,76)DHACT,DSACT
```

```
76 FORMAT(1X,35H ERROR IN ENTHALPY OF ACTIVATION IS,F10.5,21HKILOCALO
1RIES PER MOLE/34H ERROR IN ENTROPY OF ACTIVATION IS,F10.5,13HENTRO
2PY UNITS)
```

```
RETURN
```

```
END
```

Leaf 172 omitted in page numbering.

\$SIGNON ALAN T=.5M P=20 PRIO=V

\$RON LSG.\*BPL0T 9=-PLOT

RATE OF IONIZATION OF DMSO-T VS H.MINUS IN METHANOLIC DMSO

2

20.0 12.0 -1.00 -7.00

7H MINUS

22LOG K JK=RATE OF DMSO\*

METHANOL

12

11.95 -7.0391

14.19 -5.410

14.74 -4.813

14.76 -5.020

15.75 -3.979

15.85 -3.971

16.57 -3.050

16.86 -3.388

16.95 -3.371

17.70 -2.759

19.50 -1.502

19.70 -1.400

RATE OF IONIZATION OF DMSO-T VS H.MINUSQ LOG A

12

11.95 -7.0391

13.98 -5.410

14.48 -4.813

14.50 -5.020

15.29 -3.979

15.39 -3.971

15.96 -3.050

16.16 -3.388

16.34 -3.371

16.82 -2.759

18.33 -1.502

18.48 -1.400

\$ENDFILE

\$RON \*PLOTQ PAR=-PLOT

BLANK

\$SIGNOFF



---

RATE OF IONIZATION OF DMSO-T VS H. MINUS IN METHANOLIC DMSO

---

---

METHANOL

---

11.950000	-7.039100
14.190000	-5.410000
14.740000	-4.813000
14.759999	-5.020000
15.750000	-3.978999

---

15.849999	-3.971000
16.569992	-3.049999
16.859985	-3.388000
16.949997	-3.370999
17.699997	-2.759000
19.500000	-1.502000
19.699997	-1.400000

---

SUM OF THE SQUARES OF THE DEVIATION= 0.385278523E 00

INTERCEPT =	-0.1563901E 02	SLOPE =	0.7298280E 00
ERROR IN INTERCEPT =	0.4400714E 00	ERROR IN SLOPE =	0.2692217E-01
COEFFICIENT OF CORRELATION =	0.993264198E 00		

---

STUDENT TEST T = 0.271073608E 02

DELTA= 0.138269961E 00

---

\*\*\*\* THIS SECTION ONLY RELEVANT FOR ACTIVATION STUDIES \*\*\*\*

---

THE ENTHALPY OF ACTIVATION IS -0.334E-02KILOCALORIES PER MOLE PER DEGREE  
THE ENTROPY OF ACTIVATION IS -119. ENTROPY UNITS  
ERROR IN ENTHALPY OF ACTIVATION IS 0.00012KILOCALORIES PER MOLE  
ERROR IN ENTROPY OF ACTIVATION IS 2.01289ENTROPY UNITS

---

RATE OF IONIZATION OF DMSO-T VS H.MINUSQ LOG A

11.950000	-7.039100
13.980000	-5.410000
14.480000	-4.813000
14.500000	-5.020000
15.290000	-3.978999
15.389999	-3.971000
15.959999	-3.049999
16.159988	-3.388000
16.339996	-3.370999
16.819992	-2.759000
18.329987	-1.502000
18.479996	-1.400000

SUM OF THE SQUARES OF THE DEVIATION= 0.358504772E 00

INTERCEPT =	-0.1754129E 02	SLOPE =	0.8780563E 00
ERROR IN INTERCEPT =	0.4914843E 00	ERROR IN SLOPE =	0.3122991E-01
COEFFICIENT OF CORRELATION =	0.993734181E 00		

STUDENT TEST T = 0.281155701E 02

DELTA= 0.118043244E 00

\*\*\* THIS SECTION ONLY RELEVANT FOR ACTIVATION STUDIES \*\*\*

THE ENTHALPY OF ACTIVATION IS -0.402E-02KILOCALORIES PER MOLE PER DEGREE  
THE ENTROPY OF ACTIVATION IS -127. ENTROPY UNITS  
ERROR IN ENTHALPY OF ACTIVATION IS 0.00014KILOCALORIES PER MOLE  
ERROR IN ENTROPY OF ACTIVATION IS 2.24805ENTROPY UNITS  
PLOTING WILL TAKE APPROX. 2 MIN 56 SEC  
SUCCESSFULL PLOT.

STOP 0  
EXECUTION TERMINATED

\$RUN \*PLOTQ PAR=-PLOT  
EXECUTION BEGINS  
WHAT TYPE OF PAPER DO YOU WANT? REPLY "BLANK" OR "LINED"  
PLOT FILE IS OK AND IS IN SYSTEM  
EXECUTION TERMINATED

\$SIGNOFF