KINETIC AND EQUILIBRIA STUDIES

IN HIGHLY BASIC SYSTEMS

by

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"EQUILIBRIUM AND KINETIC STUDIES IN STRONGLY BASIC SYSTEMS"

ABSTRACT

Using α-cyanostilbenes as Lewis acids, Lewis acidity scales have been established in the systems DMSO-ethanol and DMSO-methanol containing the appropriate 0.01M sodium alkoxide and in the system sodium methoxide-methanol. This scale, designated H_{R^-}, describes the ability of the solvent to add an alkoxide ion to an alkene. The H_R- values range from 11.73 in methanol to 21.74 in 98.27 mole % DMSO in ethanol.

The most acidic indicator used to establish the scale was α-cyano-2, 4-dinitrostilbene with a pK of 12.73 in DMSO-methanol. The least acidic was α-cyano-3-trifluoromethylstilbene with a pK of 21.98 in DMSO-ethanol.

The effects of substituents in the two aromatic rings of α-cyanostilbenes on the Lewis acidity of these compounds has been measured. Using σ values, an average ρ of 2.2 was obtained for the β-phenyl ring in the various solvent systems studied. Using σ^- values, the ρ for α-cyanostilbenes with substituents in the α-ring is 4.77 in DMSO-ethanol and 4.24 in DMSO-methanol. In the α-phenyl ring the 4-nitro group exhibits a greatly exalted sigma value (1.75).

In order to compare the H_R- and H_- scales in one system, the H_- scale has been established in sodium methoxide-methanol using various carbon acids as indicators. The two scales are nearly parallel.

The rates of the base catalyzed isomerization of α-cyano-cis-stilbenes were found to correlate with the H_R-function. Plots of the logarithms of the apparent first order rate constants (k_1) for the isomerization against the H_R- values gave excellent straight lines with slopes ranging from 0.425 to 0.665. The slopes of these lines depend on the substituent present in the α-phenyl ring and on the solvent system. The slopes were shown to be a measure of how closely the transition state for the isomerization reaction resembles the carbanion formed by the equilibrium addition of alkoxide ion to an alkene.

The effect of substituents on the rate of isomerization of α-cyano-cis-stilbenes has been determined. Using σ values the ρ for substituents in the α-phenyl ring is 3.07 in DMSO-ethanol and 2.82 in DMSO-methanol.

The activation parameters for the base catalyzed isomerization reaction have been determined in DMSO-methanol. The enthalpies of activation range from 14.3 to 16.7 kcal. mole $^{-1}$ and the entropies of activation range from -9.3 to -13.7 e.u. depending on the substituent.

The base catalyzed isomerization of α-cyano-cis-stilbenes is first order in base and first order in reactant. The mechanism of this reaction is discussed in terms of the kinetic-acidity function correlation, the substituent effects, and the activation parameters.

The reactions of 1,1-bis-(4-nitrophenyl) ethene and 4,4'-dinitrobenzophenone with hydroxide or alkoxide ions in DMSO are described.

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ABSTRACT

DIETRICH J. KROEGER. KINETIC AND EQUILIBRIA STUDIES IN HIGHLY BASIC SYSTEMS. Supervisor: Professor R. Stewart

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INTRODUCTION

A. Acids, Bases and Acidity Functions

Acids and bases have intrigued chemists for centuries. From as early as 1663, when Boyle reported that acids gave a red color to the blue vegetable coloring matter litmus (1), the study of acids and bases has led to a fuller understanding of the fundamentals of chemistry.

The development of a definition for acids and bases has paralleled the increased understanding of their nature. Lavoisier, in the 1770's, noticed that when elements like carbon, nitrogen and sulfur were burned in oxygen, the products yielded acids in water. This led him to postulate that oxygen was an element common to all acids (1). With the discovery by Davy that hydrogen, rather than oxygen was the element common to acids, Liebig defined acids as those ". . . compounds containing hydrogen in which the hydrogen can be replaced by metals"(1). The development of the theory of electrolytic dissociation by Ostwald and Arrhenius in the 1880's (1) eventually led to the Bronsted concept of acids and bases (2). According to this definition, an acid is a proton donor and a base is a proton acceptor.

Up until this time, definitions of acids and bases were restricted to those systems which involved the transfer of a proton. The realization that some of the characteristic properties of acids and bases were possessed by substances not containing protons led Lewis to propose a broader, more inclusive definition of acids and bases. According to this concept, an acid is a substance which can accept an electron pair and a base is one able to donate an electron pair (3).

Although the Lewis definition is quite inclusive and may include the Bronsted acids as a special case, Gillespie feels that it is reasonable to regard proton acids as a separate class with particular properties (4). In the Bronsted sense, acid-base reactions involve only the transfer of a proton, no matter what the acid may be. Since these proton transfer reactions are usually very fast, they lend themselves readily to equilibrium measurements. In one solvent system the strength of an acid is dependent only on the degree of dissociation and independent of the base with which it is reacting. No such simple relationship exists in acid-base reactions when Lewis type acids are involved. In this latter case, an acid-base reaction involves the complete molecule and its strength as an acid depends on the base with which it is reacting.

In order to measure the strength of acids, measurements on the equilibrium involving at least two acids are necessary (5a).

$$AH + B \rightleftharpoons A + BH \qquad (1)$$

(The charges have been omitted in this equation in order to make it more general. In all cases the charge on A will be one less than that on AH.) The thermodynamic equilibrium constant for this reaction is then given by the expression *

$$K = \frac{(A)(BH)}{(AH)(B)} \qquad (2)$$

Since equilibrium constants often vary by many powers of ten, it is customary to use the definition

$$pK = -\log K \qquad (3)$$

Although the above pertains specifically to Bronsted acids, analogous equations can be derived for Lewis acids.

In the case where water is the solvent and also the base in equation (1), then the equilibrium constant in equation (2) becomes

* The symbols (), [ ] and f will be used to denote the activity, concentration and activity coefficient on the molar scale respectively.

$$K = \frac{(A)_{aq}(H_3O^+)_{aq}}{(AH)_{aq}} = \frac{[A]_{aq}[H_3O^+]f_A f_{H_3O^+}}{[AH]_{aq} f_{AH}} \qquad (4)$$

where the subscript aq refers to the species solvated by water. Since in dilute aqueous solution, the activity of water is effectively unity when water is taken as the standard state (6), the term (H_2O) in equation (4) has been included in K. When AH is an uncharged molecule, then the equilibrium constant in equation (4) is denoted as K_{AH} and is known as the acid dissociation constant (7a).

Since equation (4) involves the activities of ions, which cannot easily be measured, the usual practice is to measure the dissociation constant

$$K_c = \frac{[A][H_3O^+]}{[AH]} \qquad (5)$$

which is the equilibrium constant using concentrations rather than activities. The concentration measurements are then made as a function of ionic strength and extrapolated to infinite dilution (8). That this procedure will give the value for the thermodynamic equilibrium constant is evident from the expression

$$(X) = [X]f_X \qquad (6)$$

where X refers to any species. The activity coefficient

term f_X is a measure of how far the behavior of X deviates from ideality and will be equal to unity in the standard state. On applying equation (3) to equation (4), the latter becomes

$$pK = -\log \frac{(A)}{(AH)} - \log (H_3O^+) \qquad (7)$$

In dilute aqueous solutions, $-\log (H_3O^+)$ is closely approximated by the pH, although pH is now defined on an operational basis (7b). Equation (7) allows one to measure the ionization constants of acids and bases in dilute aqueous solutions of low ionic strength. Since the ionic strength must remain low, the pK values of acids and bases measurable in aqueous solutions are restricted to the pH range from 1 to 12.

Many weak acids and bases have pK values outside the range of 1 to 12 and the measurement of these has been a difficult problem. One of the most popular methods of overcoming this difficulty was developed by Hammett and Deyrup (9). For acids which ionize according to the equation

$$BH \rightleftharpoons B + H \qquad (8)$$

where the water of solvation and ionic charges have been omitted, the pK is given by the expression

$$pK = -\log \frac{(B)(H)}{(BH)} = -\log \frac{[B]}{[BH]} - \log \frac{(H)f_B}{f_{BH}} \qquad (9)$$

For any two acids, BH and CH, which ionize to a measurable extent in the same solvent, the ΔpK is given by

$$\Delta pK = pK_{BH} - pK_{CH} = -\log \frac{[B][CH]}{[BH][C]} - \log \frac{f_{Bf_{CH}}}{f_{BH}f_C} \qquad (10)$$

Since the ratios $[B]/[BH]$ and $[C]/[CH]$ can be obtained experimentally, one can then obtain, by this stepwise process, ΔpK values for a variety of acids which ionize according to equation (8), provided the last term in equation (10) is close to zero. If one acid ionizes in the pH range, then all the other pK values are based on water as the standard state and are thus true thermodynamic pK values. In addition to the pK values, a measure of the acidity or basicity of the medium is also obtained. This is given by the acidity function defined as

$$H = \log \frac{[B]}{[BH]} + pK_{BH} = -\log \frac{(H)f_B}{f_{BH}} \qquad (11)$$

The postulate that H is dependent only on the solution and independent of the particular indicator used to measure it is based on the fundamental assumption that the ratio of the activity coefficients, f_B/f_{BH}, is the same for

different acids in a given solution.

The Hammett acidity function was first developed for systems which ionize according to equation (12)

$$BH^+ \rightleftharpoons B + H^+ \qquad (12)$$

in a highly acidic medium such as sulfuric acid (9). Since the conjugate base in these cases is an uncharged molecule, the appropriate acidity function was designated as H_o where the subscript refers to the charge on the conjugate base (9). Since the initial work of Hammett and his co-workers (9, 10), a considerable amount of work has been done using various concentrated acids. The early work on acidity functions was reviewed in 1957 by Paul and Long (11). A bibliography of acidity function values reported since then has recently been published by Deno (12).

Although the early H_o functions were based largely on amine indicators (9 - 11), it was hoped that one function would hold for a variety of similar indicators which ionized by protonation. That this ideal does not hold for acids which differ substantially in structure has since been conclusively shown. Whether or not the ionization behavior of an acid follows the H_o function can be determined by a plot of log $[B]/[BH^+]$ versus H_o. If the ionization behavior of the acid follows H_o, this plot should give a straight line of unit slope. It has

been shown that for several classes of compounds, such as ethers (13), pyrroles (14), azulenes (15), amides (16 - 18), tertiary amines (19) and indoles (20), the above criterion was not followed. This must mean that the Hammett postulate only holds for a narrow range of acids which differ only slightly in structure. As a result, separate and self-consistent H_o functions have been established for the protonation of primary (21, 22) and tertiary (19) amines, amides (23 - 25) and indoles (20).

Although the above compounds all react, in acid medium, according to simple protonation equilibria, carbinols do not. Instead, they react with sulfuric acid according to the equation

$$ROH + H_2SO_4 \rightleftharpoons R^+ + H_2O + HSO_4^- \quad (13)$$

For equilibria of this type, Gold and Hawes (26) derived an acidity function called J_o. For mathematical convenience, they factored equation (13) into three auxiliary steps

$$H_2SO_4 \rightleftharpoons HSO_4^- + H^+ \quad (14)$$

$$ROH + H^+ \rightleftharpoons ROH_2^+ \quad (15)$$

$$ROH_2^+ \rightleftharpoons R^+ + H_2O \quad (16)$$

with equilibrium constants K_1, K_2, and K_3 respectively. The overall equilibrium constant K_I, was then

$$K_I = K_1K_2K_3 = \frac{(R^+)(HSO_4^-)(H_2O)}{(ROH)(H_2SO_4)} \qquad (17)$$

By using the definition that

$$h_o = \frac{(H^+)\ f_B}{f_{BH^+}} \qquad (18)$$

equation (17), upon rearrangement, gave

$$K_{ROH} = \frac{(R^+)(H_2O)}{(ROH)} \cdot \frac{f_{ROH}}{h_o f_{ROH_2^+}} \qquad (19)$$

Upon taking logarithms and rearranging, equation (19) then became

$$H_o + \log(H_2O) = -pK_{ROH} + \log\frac{[ROH]}{[R^+]} + \log\frac{f_{ROH_2^+}}{f_{R^+}} \qquad (20)$$

From the definition that

$$J_o = -pK_{ROH} + \log\frac{[ROH]}{[R^+]} \qquad (21)$$

it followed that H_o and J_o were related by the equation

$$J_o = H_o + \log(H_2O) + \log\frac{f_{R^+}}{f_{ROH_2^+}} \qquad (22)$$

By assuming that $f_{R^+}/f_{ROH_2^+}$ was unity in all solvents considered, Gold and Hawes (26) were able to calculate J_o values for sulfuric acid solutions using the known H_o values and the measured activity of water in sulfuric acid solutions. In testing this relationship they found that a plot of log $[R^+] / [ROH]$ against J_o for 4,4',4"-trinitrotriphenylmethanol in 80 to 90% sulfuric acid yielded a straight line of slope 1.16.

Although the above assumption was at first accepted by Deno, Jaruzelski and Schriesheim (27), they later established a self-consistent acidity function in sulfuric acid for the equilibrium (28)

$$R^+ + H_2O \rightleftharpoons ROH + H^+ \qquad (23)$$

The acidity function, H_R, was defined as

$$H_R = pK_{R^+} - \log \frac{[R^+]}{[ROH]} \qquad (24)$$

$$= -\log(H^+) + \log(H_2O) + \log \frac{f_{R^+}}{f_{ROH}}$$

where the difference between H_R and J_o was shown to be

$$H_R - J_o = \log \frac{f_{R^+}}{f_{ROH_2^+}} \qquad (25)$$

By using 18 arylmethanols, they showed that the value of $(H_R - J_o)$ decreased gradually to a value of -5 at 82% sulfuric acid, above which it was stationary. This evidence indicated that the activity coefficient ratio, $f_{R^+}/f_{ROH_2^+}$, is not equal to unity below 82% sulfuric acid. The fact that Gold and Hawes tested their postulate in 80 to 90% sulfuric acid and obtained a straight line of near unit slope when plotting $\log [R^+] / [ROH]$ against the calculated J_o values (26), is in accordance with this later evidence.

By evaluating the H_R function in perchloric and nitric acids, Deno et al (29) were able to show that the pK_{R^+} values are largely the same for a given alcohol, even though measured in different aqueous solutions. This showed that for arylmethanols, the values of the activity coefficient ratio, f_{R^+}/f_{ROH}, are largely independent of the arylmethyl group.

Closely connected with the H_R acidity function is the arylolefin-arylmethyl cation equilibrium. This was investigated by Deno, Grover and Saines (30) for several diarylolefins for which the equilibrium protonation can be written as

$$ol + H^+ \rightleftharpoons R^+ \qquad (26)$$

where ol represents the olefin and R^+ the corresponding

methyl cation. From the equilibrium constant for equation (26), the expression

$$pK'_{R^+} = -\log(H^+) + \log\frac{[R^+]}{[ol]} + \log\frac{f_{R^+}}{f_{ol}} \qquad (27)$$

can be obtained. Combining equation (27) with equation (24), with the assumption that f_{R^+}/f_{ROH} and f_{R^+}/f_{ol} are equal, resulted in the definition for H_R' as given in equation (28).

$$H_R' = H_R - \log(H_2O) = pK'_{R^+} + \log\frac{[ol]}{[R^+]} \qquad (28)$$

The data for the six diarylolefins studied satisfactorily fit equation (28) rather than equation (24) or the H_o function (30). This evidence indicated that a separate acidity function H_R' governs the protonation of olefins.

As can be seen from the above, the protonation of neutral species has been thoroughly studied. In contrast to this, comparatively little work has been done on studying the protonation of negatively charged species. According to the proposal of Hammett (9, 10), the acidity function describing the medium in which the protonation of a negatively charged species takes place, as described by the equilibrium

$$HA \rightleftharpoons A^- + H^+ \qquad (29)$$

would be the H_- function. This is then defined by

$$H_- = pK_{HA} + \log \frac{[A^-]}{[AH]} \qquad (30)$$

$$= - \log h_-$$

where

$$h_- = \frac{(H^+)\, f_{A^-}}{f_{AH}} \qquad (31)$$

In order to study equilibria of the type represented by equation (29) outside the dilute aqueous region, very strong acids in strongly acid medium (31, 32), or conversely, weak acids and strongly basic systems (33) must be employed. In acidic medium, Phillips established a H_- scale for aqueous hydrochloric acid solutions using phosphate type indicators (31) and Boyd established a H_- scale for sulfuric and perchloric acids using cyanocarbon acids as indicators (32). In highly basic regions, H_- scales have been established for a variety of systems employing a number of different types of indicators (33). It is this latter area which will be summarized here.

Strongly basic systems can be established in any one of three ways. One way is to increase the concentration of the salt of the conjugate base of a

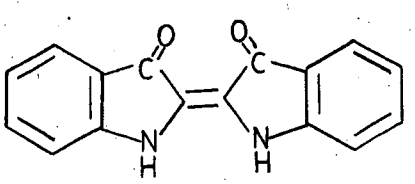
protic solvent in that solvent. H_- scales for this type of system have been developed for potassium hydroxide-water (34), sodium hydroxide-water (34, 35), lithium hydroxide-water (36), benzyltrimethylammonium hydroxide-water (36), lithium (37), potassium (37, 38) and sodium (37, 39 - 41) methoxide-methanol solutions.

In dilute solutions, for example 0.01 to 1M sodium hydroxide in water, the equation

$$H_- = pK_w + \log [OH^-] \qquad (32)$$

holds fairly well (35). But at higher concentrations of hydroxide ion, the "effective pH" increases more rapidly than the value of log $[OH^-]$ would indicate (35, 36), thus giving rise to a H_- scale.

Schwarzenbach and Sulzberger (34) were the first to attempt to set up a H_- scale. They used concentrated solutions of aqueous sodium and potassium hydroxides employing indigo derivatives (I) and substituted



I

glutacondialdehyde dianils (II) as indicators.

R-N=CH-CH=CH-CH=CH-NH-R

II

In certain cases, some glutacondialdehyde dianils showed anomalous ionization behavior which was attributed to hydroxide ion addition in contrast to proton removal. Recently, Edward and Wang (35) have reinvestigated the H_- scale in aqueous sodium hydroxide solutions using thioacetamide as an indicator. They confirmed the H_- scale of the earlier workers and suggested that the anomalous behavior of the glutacondialdehyde dianils was due to a difference in hydration rather than a different ionization process.

Several workers have recently attempted to apply the rationalization of Bascombe and Bell (42), who showed that the high acidities in concentrated acid solutions are mainly due to extensive desolvation of the proton, to concentrated aqueous alkaline solutions (35, 43). For the equilibrium

$$HA + OH^- \rightleftharpoons A^- + (p + 1)H_2O \qquad (33)$$

where HA, OH^- and A^- represent the hydrated species and p represents the difference in hydration number between (HA + OH^-) and A^-, Edward and Wang (35) derived the expression

$$\frac{[A^-]}{[HA]} = K_{HA} [OH^-] \frac{(H_2O)^{r-p-1}}{K_w} \qquad (34)$$

using the approximation that

$$r \log (H_2O) \approx \log \frac{f_{HA} f_{OH^-}}{f_{A^-}} \qquad (35)$$

A plot ($\log [A^-]/[HA] - \log [OH^-]$) versus $\log (H_2O)$ for thioacetamide in aqueous sodium hydroxide solutions gave an approximately straight line with the slope (r-p-1) being equal to 3.2. Using this value, they calculated the H_- values using the equation

$$H_- = pK_w + \log [OH^-] + (r-p-1) \log(H_2O) \qquad (36)$$

and found that the calculated H_- values agreed reasonably well with the experimental ones. More recently, Yagil and Anbar (43) carried out a similar treatment for aqueous sodium and potassium hydroxide solutions. With the term (r-p-1) in equation (36) replaced by -(n + 1) and using the H_- values of Schwarzenbach and Sulzberger (34), Yagil and Anbar found that the calculated H_- values agreed with the experimental ones only when n was equal to 3. In this treatment, n was regarded as the number of water molecules solvating the hydroxide ion (43). These two treatments indicate that the increased basicity of concentrated alkaline solutions is primarily due to a lessening of the degree of solvation of the hydroxide ion due to its greater concentration resulting in an ion with a higher activity.

A similar treatment has recently been attempted by Rochester (41) for sodium methoxide solutions. Using the equation

$$H_- = pK_{MeOH} + \log [NaOMe] - (n + 1)\log(MeOH) \quad (37)$$

where [NaOMe] was the stoichiometric concentration of sodium methoxide and assuming that $\log(f_{OMe^-}f_{AH}/f_{A^-})$ was approximately zero, he calculated values of n using various phenols as indicators. The average values of n were fairly large, ranging from 3.0 for pentamethylphenol to 5.6 for 2,6-di-t-butylphenols. Not much significance was attached to these figures because of the lack of knowledge about the values of activity coefficients in methanolic solutions.

A second way in which strongly basic systems can be established is by using a two component system in which one component is of itself comparatively basic and the other component usually being water. As the concentration of water is decreased, the basicity increases. Using this type of system, H_- scales have been developed for hydrazine-water (44, 45), ethylenediamine-water (46) and 2-aminoethanol-water (47) systems.

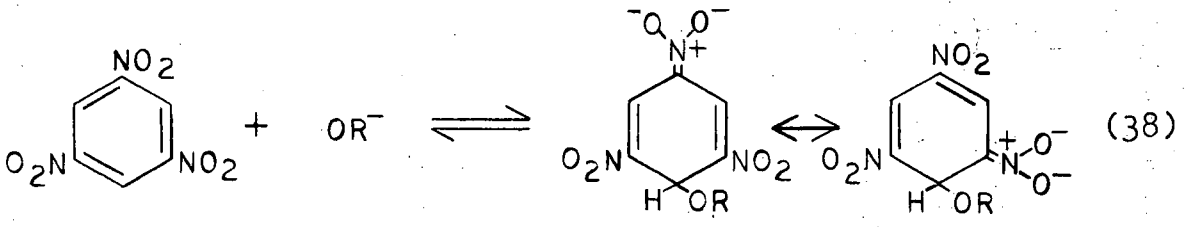
The third method of obtaining highly basic systems is to use protic-aprotic polar component systems. Since such systems are not inherently basic, it is

necessary to add a certain amount of base, such as a salt of the conjugate base of the protic component, to the system. The basicity of these systems can be increased either by increasing the base concentration; or, more commonly, by keeping the concentration of the base constant and increasing the proportion of the aprotic component. H_- scales for such systems have been established for sulfolane-water (36, 48), pyridine-water (36), dimethylsulfoxide-water (36, 49), dimethylsulfoxide-methanol (50) and dimethylsulfoxide-ethanol (51) systems.

Of all the systems studied, the most highly basic system established so far has been in dimethylsulfoxide (DMSO) containing 0.011M tetramethylammonium hydroxide (36, 49). With this system, a maximum H_- value of 26 was obtained in 99 mole % DMSO-water (49). The H_- values for the various other systems are listed in the recent review by Bowden (33).

A variety of indicators have been used in these studies in highly basic systems. The indicators used by Schwarzenbach and Sulzberger (34) and Edward and Wang (35) have already been mentioned. Other workers in this field have relied heavily on substituted arylamines as indicators (36 - 39, 44 - 50). Recently, highly hindered phenols have also been used (40, 41, 52). In addition to these, substituted fluorenes and polyarylmethanes have been employed in setting up H_- scales (48, 51).

Although Schaal and co-workers (53, 54) have measured the apparent pK values of some polynitrobenzenes (III), the mode of ionization of these compounds cannot be a simple proton loss as given by equation (29). Instead, an ionization process such as



III IV (38)

was visualized (53). That such a Meisenheimer type complex (IV) (55) can be formed by polynitrobenzenes in basic solutions has recently been shown with the aid of NMR spectroscopy (56, 57).

Since equilibria of the type described in equation (38) do not follow a H_- function, a function designated J_- has been suggested (26, 58) for such processes. Rochester (58) considered the addition of base to an indicator in terms of the two reversible equilibria

$$AH \rightleftharpoons H^+ + A^- \qquad (K_1) \qquad (39)$$

$$A^- + H_2O \rightleftharpoons AHOH^- \qquad (K_2) \qquad (40)$$

From these, by letting $K = K_1K_2$, the expression

$$\log\frac{[AHOH^-]}{[AH]} = -pK + H_- + \log(H_2O) + \log\frac{f_{A^-}}{f_{AHOH^-}} \qquad (41)$$

was obtained. With J_- defined as

$$J_- = pK + \log\frac{[AHOH^-]}{[AH]} \qquad (42)$$

the relationship between H_- and J_- was given by the equation

$$J_- = H_- + \log(H_2O) + \log\frac{f_{A^-}}{f_{AHOH^-}} \qquad (43)$$

The relationship between J_- and H_- is then analogous to that between J_o and H_o (26).

Up to the present, only one J_- scale has been established. Using 2,4-dinitroanisole, 2,4-dinitroaniline, picric acid and 2,4,6-trinitroanisole, Rochester attempted to establish a J_- scale for sodium methoxide in methanol (59). However, the two or three possible equilibria involved in each case would tend to cast some doubt on the validity of a scale using such indicators.

B. The Correlation of Kinetics with Acidity Functions

The correlation of the kinetics of acid catalyzed reactions with acidity functions has been well documented (60). In contrast to the work in acid regions, few correlations of base catalyzed reactions with the appropriate acidity function have been made.

The relationship between kinetics and acidity functions in aqueous alkaline solutions for various types of mechanisms has been discussed by Anbar et al (61). They showed that the logarithm of the rate constant either correlates with H_- or with H_- + log C_{H_2O}, where C_{H_2O} is the concentration of water not bound by solvation.

The case where a rapid pre-equilibrium is set up followed by a slow unimolecular reaction was represented by the equations

$$SH + OH^- \rightleftharpoons S^- + H^+ \qquad (44)$$

$$S^- \xrightarrow{\text{slow}} \text{products} \qquad (45)$$

With the assumption that $f_{SH}/f^{\ddagger} = f_{AH}/f_{A^-}$, where AH and A^- refer to the indicators used to establish the H_- scale and $f^{\ddagger}$ is the activity coefficient for the transition state in the reaction, it was shown that the relation between k, the rate constant, and H_- is given by the expression (61)

$$\log k = H_- + \text{constant} \qquad (46)$$

An example of this type was first reported by Ridd et al (62, 63). They studied the decomposition of chloroform in sodium methoxide-methanol solutions. The slow step in this reaction had previously been shown to be the decomposition of the conjugate base, CCl_3^-, to form the carbene. Using the H_- scale which they had previously established (39), O'Ferrall and Ridd (63) reported that a plot of log k versus H_- gave a reasonably straight line with a slope of about 0.8. Another example of this type is the correlation between the rate of the base catalyzed racemization of (+)-2-methyl-3-phenylpropionitrile and the basicity of the medium, as measured by a H_- scale for the DMSO-methanol system containing 0.025 molar sodium methoxide as base (50). The excellent correlation between log k and H_-, as evidenced by a straight line for a basicity change of seven powers of ten with a slope of 0.87, was used to argue in favor of a rapid equilibrium formation of an "asymmetrically solvated carbanion" followed by a slow rate determining racemizing step.

When the substrate SH is in rapid pre-equilibrium with its conjugate base S^-, as given in equation (44), which is followed by a bimolecular rate determining reaction of S^- with another reactant Y to form the products

$$S^- + Y \xrightarrow{\text{slow}} \text{products} \qquad (47)$$

then the relation between the rate constant and H_- is still given by equation (46) if the assumption that $f_Y f_{SH}/f^{\ddagger} = f_{AH}/f_{A^-}$ is true (61). An example of this was reported to be the reaction of ammonia with chloramine in concentrated alkaline hydroxide solutions (61). The kinetics of this reaction was found to correlate with H_- giving a slope of 0.90 (64).

In the case where the rate determining step is the nucleophilic attack of the hydroxide ion, either in the proton removal or the substitution step, it was shown that the kinetics should correlate with $H_- + \log C_{H_2O}$ (61). In the base catalyzed elimination reaction of dl-serine phosphate (V),

$$H_2PO_3\text{-}O\text{-}CH_2CH(NH_2)CO_2H$$

V

which was shown by deuterium isotope effect to react by a slow rate determining proton removal step followed by a rapid decomposition to products (65), the plot of log k versus $H_- + \log C_{H_2O}$ gave a straight line with a slope of 0.98 (61, 65). For the alkaline hydrolysis of ethyl iodide, which goes by the S_N2 mechanism, it was shown that a plot of log k versus $H_- + \log C_{H_2O}$ gave a straight line with a slope of 1.03 (61). Similarly in the hydrolysis of chloramine, which is thought to involve a

slow nucleophilic attack of hydroxide ion on chloramine (66), the plot of log k versus H_- + $\log C_{H_2O}$ gave a straight line of slope 1.00 (61). These examples support the proposals by Anbar et al (61).

Several less valid correlations of H_- with rate data have also been reported. These include the degradation of 4-dinitrobenzene (67), 2-dinitrobenzene (68), and 2- and 4-chloronitrobenzenes (69) in methanolic alkoxide solutions and the hydrolysis of carbon disulfide in concentrated alkaline hydroxide solutions (70). These studies have the common feature that it is unlikely that the mechanisms involve a fast equilibrium ionization by the loss of a proton to form an anion followed by a rate-determining decomposition of the anion. Instead, these reactions likely proceed either by a fast equilibrium addition of a base molecule followed by a rate-determining decomposition of the base adduct, or by a slow rate-determining addition of base to the unsaturated system. Because these rates were correlated with acidity scales derived by using indicators ionizing by a proton loss, there is doubt as to the meaning of such correlations.

Such reactions as above should be correlated with a J_- type acidity function. One such kinetic correlation with a J_- scale has been attempted. Using equation (43) with the assumption that $\log(f_{A^-}/f_{AHOH^-})$

was zero and employing the H_- values of Schwarzenbach and Sulzberger (34) coupled with the activity of water in aqueous sodium hydroxide, Rochester correlated log k for the disappearance of 2,4-dinitroanisole with J_- (71). It was found that a plot of log k versus $H_- + \log(H_2O)$, or J_-, gave a straight line with a slope of 1.11.

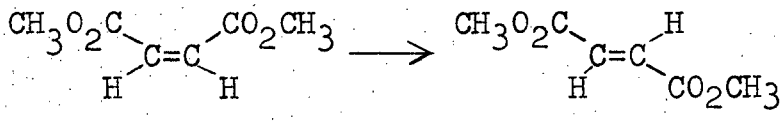
C. Base Catalyzed cis-trans Isomerizations

In order for nucleophilic reagents to react with carbon-carbon double bonds, the unsaturated system must be activated by strongly electron withdrawing groups. Such activated carbon-carbon double bonds can react with a variety of nucleophilic reagents to give a variety of products. A common characteristic of all these reactions is that the first step is the attack of the nucleophilic reagent on the positively polarized carbon resulting in an unstable carbanion (72, 73). The fate of the carbanion is dependent on the nature of the attached groups, the nature of the solvent and other molecules present in the solution which may participate in the reaction in subsequent stages (72). The various types of nucleophilic attacks and the resulting products have recently been reviewed by Patai and Rappoport in a book edited by Patai (73).

Of the reactions which activated carbon-carbon double bonds can undergo with nucleophilic reagents, the

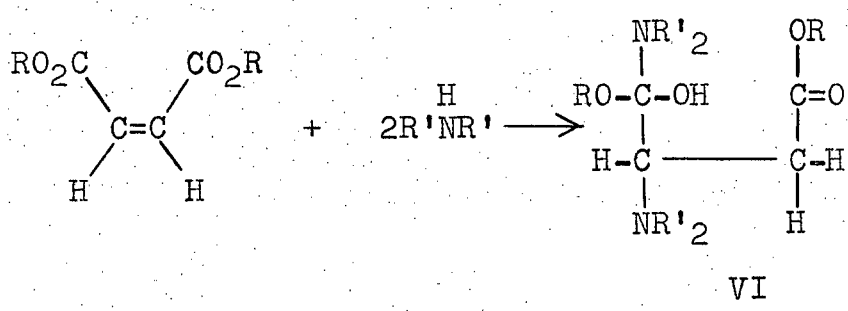
simplest is the cis-trans isomerization. In this simple case, the nucleophile adds to the double bond forming the carbanion which is then free to rotate or invert, followed by the elimination of the nucleophile.

One of the earliest studies of base catalyzed cis-trans isomerizations was that of the transformation of methyl maleate to methyl fumarate.



(48)

Clemo and Graham (74) found that this transformation was catalyzed by primary and secondary amines but not by tertiary amines. In a later study, Nozaki (75) found that the reaction was first order in the unsaturated ester and second order in amine. It was also found that the rates correlated with the base strength (pK_{BH^+}) of the amine. The rate determining step was then postulated to be

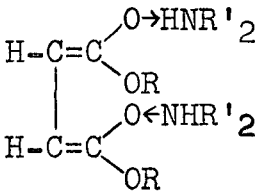


(49)

VI

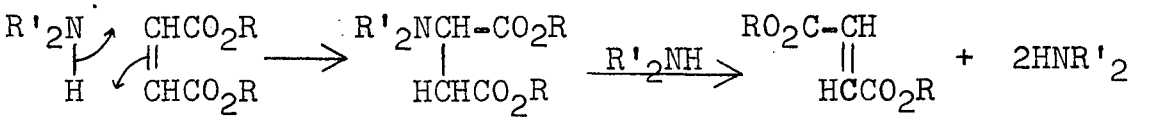
where (VI), is the corrected structure for the "activated

complex" given by Davis and Evans (76). Instead of structure VI, Davis and Evans preferred structure VII,



VII

where the transition complex involves two actual or incipient "dative" bonds (76). On the other hand, Rappoport, Degani and Patai (77) postulated that a four-center $\alpha\beta$-addition was possible with primary and secondary amines, as shown in equation (50), to form the amine adduct VIII

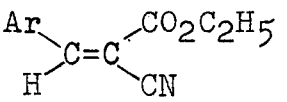


VIII

(50)

Due to the presence of free amine molecules, a base-catalyzed removal of amine was thought to be possible to give fumarate. This explained the overall third-order kinetics and also the correlation between the reactivity of the amines and their respective proton basicity.

With more highly activated carbon-carbon double bonds, such as in IX, the amine catalyzed cis-

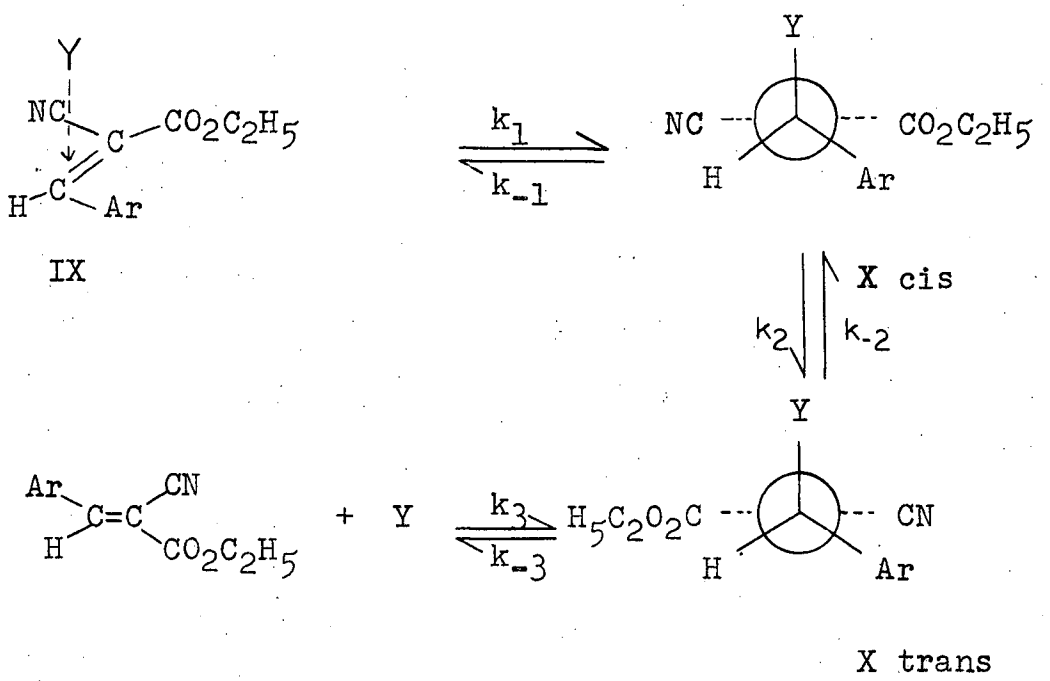


IX

trans isomerization reverts from third to second-order kinetics, and tertiary as well as primary and secondary amines catalyze the reaction (77). Not only amines but also other nucleophiles were found to enhance the rate of isomerization. Hydroxide ion and the carbanions of active methylene compounds such as ethyl cyanoacetate and malononitrile were strong catalysts whereas water and ethanol were much weaker (78).

The postulated mechanism for isomerizations, using a variety of nucleophiles Y as catalysts, is shown in the following scheme (77, 78):

Scheme I



In the case where the attacking nucleophile Y was an amine, a zwitterionic intermediate was thought to be formed. In this case, using the steady state approximation, it was rationalized that the experimental first order rate constant will be given by

$$k_{exp} = \frac{k_1 k_2}{k_{-1}} \qquad (51)$$

where $k_{-1} > k_2$ (77). If the same mechanism were to be followed when nucleophiles such as hydroxide, ethoxide or methoxide ions were acting as catalysts, then it may be expected that the rate of isomerization might be

correlated with an appropriate acidity function.

In the case of the amine catalyzed isomerization of IX, Rappoport, Degani and Patai (77) found that the energies of activation were in the range from 2.7 to 5.0 kcal. mole^{-1} and the entropies of activation ranged from -43 to -66 e.u., depending on the particular amine used as catalyst. The low energies of activation were rationalized by applying the equation

$$E_{exp} = E_1 + E_2 - E_{-1} \qquad (52)$$

where the subscripts refer to the individual steps in reaction Scheme I. By taking values from the literature for E_1 as being in the order of 13 kcal. mole^{-1}, by assuming that E_{-1} was less than 30 kcal. mole^{-1}, which is the normal value for base catalyzed elimination reactions, and by assuming that E_2 was higher than 2 to 6 kcal. mole^{-1}, which is the value for sterically hindered rotations, an energy of activation was calculated which agreed reasonably well with the experimental values.

In a manner analogous to the above, the entropy of activation was given by

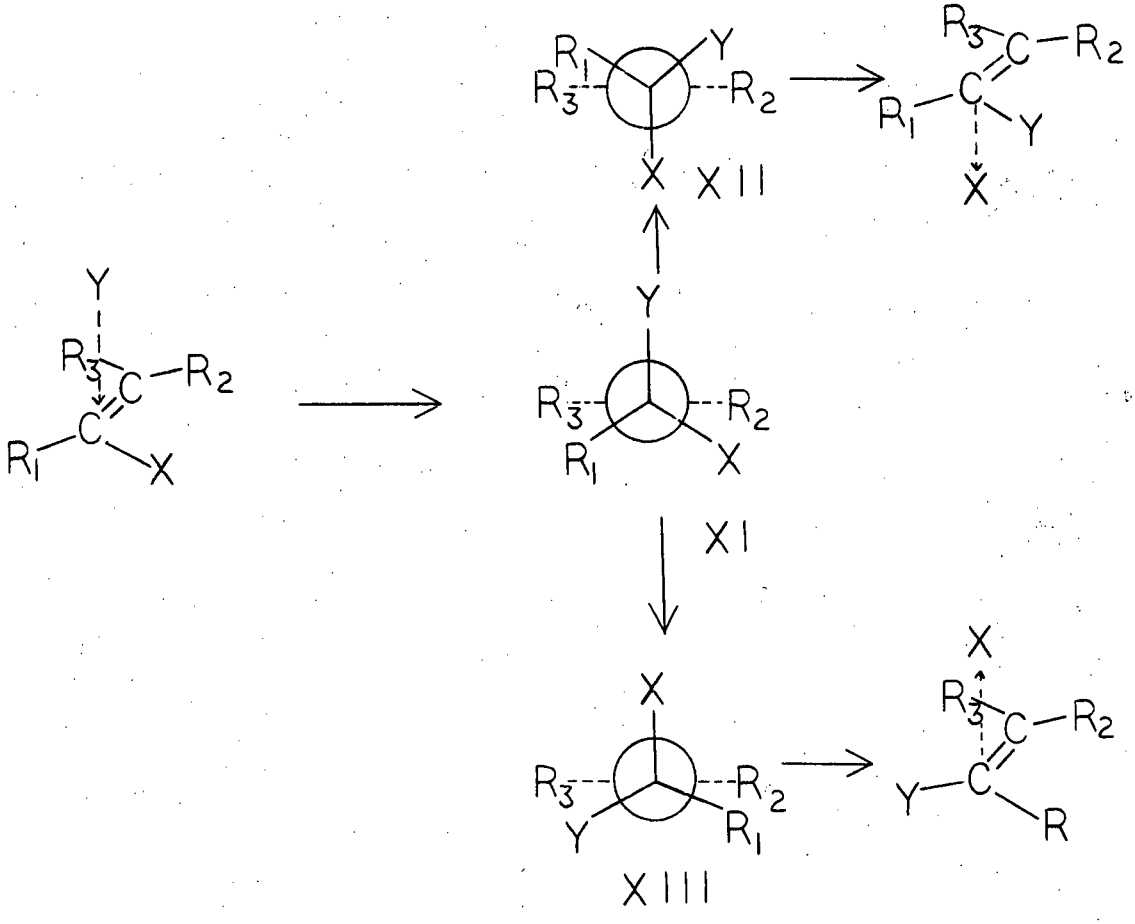
$$\Delta S^{\neq}_{exp} = \Delta S^{\neq}_1 + \Delta S^{\neq}_2 - \Delta S^{\neq}_{-1} \qquad (53)$$

The large negative entropy of activation was thought to

be due to the relatively small value for $\triangle S_2^{\neq}$ compared with the large positive value for $\triangle S_{-1}^{\neq}$, due to two neutral molecules being formed from a zwitterion, and a large negative value for $\triangle S_1^{\neq}$, as a result of a zwitterion being formed from two neutral species (77).

The assumption that $k_{-1} > k_2$, or that the elimination is faster than the rotation, is in agreement with the finding that in certain cases, vinylic substitutions occur with retention of configuration (79, 80). Jones et al (80) found that the reaction of ethyl-β-chloro-cis- and trans-crotonates with nucleophiles such as thioethoxide in ethanol, gave mainly products with retention of configuration although some isomerization took place. Similarly, Miller and Yonan (79) found that the early stages of the reaction of p-nitro-α-bromostyrene with iodide proceeded largely with retention of configuration. The results of such reactions have been explained on the basis of rotational energy barriers (80). If the incoming nucleophile attacks perpendicular to the plane of the double bond and the eliminated group leaves similarly, then the group X can be eliminated from either the carbanionic intermediate XII or XIII. The conformer XII results from a 60° rotation in the primary intermediate XI whereas the conformer XIII results from a 120° rotation.

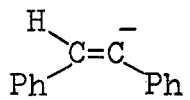
Scheme II



If the elimination is faster than the rotation, then the vinylic substitution should go via XII, due to a lesser amount of rotation resulting in less eclipsed forms, with an overall retention of configuration (73).

In cases where a carbon-carbon double bond system has one $-CHR_2$ group attached to it, base catalyzed cis-trans isomerizations can take place via an allylic carbanion (81, 82). But this process depends upon the acidity of the proton rather than the ease of nucleophilic attack on the alkene bond.

In one case, the mechanism of a base catalyzed isomerization was postulated to go through a vinyl carbanion (81). Cram and Hunter studied the t-butoxide catalyzed isomerization of cis-stilbene, which was shown, by deuterium exchange studies, to go through a vinyl carbanion of structure XIV. This reaction is much slower



XIV

than previously studied isomerizations as shown by the fact that when cis-stilbene (0.67M) was heated with potassium t-butoxide (0.255M) in t-butanol at 146° for 36.7 hours only 1% trans-stilbene was produced. This is much slower than the reactions studied by Patai and co-workers (73, 77, 78).

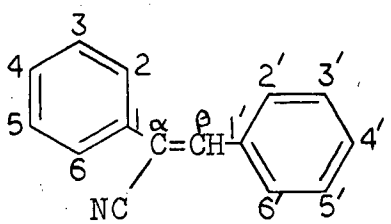
OBJECT OF THE PRESENT RESEARCH

This work was undertaken to develop a set of indicators of appropriate Lewis acidity in order to study the Lewis basicity of some highly basic systems. Several workers (53, 58, 59, 83) have attempted to study the Lewis acidity of polynitrated benzenes and substituted benzenes as well as the Lewis basicity of such bases as hydroxide (53, 58) and methoxide (59, 83) ions. Polynitrated benzenes are not the ideal choice for such a study because of:

the possibility of more than one place of attack,

the possibility of substitution giving nitrite ion (67, 68, 84) and the possibility of more than one type of ionization, especially when polynitrated anilines are used (58, 59).

As a result, indicators were desired which did not have these disadvantages and yet involved a system in which the Lewis acidity could be changed substantially by altering the substituents in a phenyl ring. The system of indicators which was finally chosen were substituted α-cyanostilbenes with the numbering system as indicated in XV.



XV

In order to change the Lewis acidity of these indicators various types of electron withdrawing and donating groups could be placed in the phenyl rings. Thus a study of the relationship between the substituents and the ionization constants was possible.

Since H_- scales had already been established in DMSO-alcohol (50, 51) and concentrated sodium methoxide-methanol (37, 39 - 41) solutions, these systems were thought to be the most promising in which to establish a Lewis basicity scale. The Lewis basicity of aqueous systems was also desirable; but, since the type of compounds used as indicators are subject to rapid hydrolysis in basic aqueous solutions (73, 85, 86) this was unattainable.

One of the ideas underlying the establishment of acidity scales is their bearing on the mechanism of acid or base catalyzed reactions. One possible reaction which might be dependent on the Lewis basicity of the medium is the base catalyzed cis-trans isomerization of substituted α-cyano-cis-stilbenes. A study of this reaction was undertaken in an attempt to correlate the kinetics with the Lewis basicity of the system. In conjunction with this, the effects of substituents and the effect of a change in the temperature on the rates were also studied in order to gain further insight into the mechanism of this reaction.

METHODS OF APPROACH

The indicators used to develop the Lewis acidity scale all absorbed energy in the ultraviolet or visible region of the spectrum. In addition, the wavelength of maximum absorption of an ion differed considerably from that for the corresponding molecule so that UV spectroscopy could be used to measure the concentration of the species. Since the molecule's absorption was small or zero at the wavelength of maximum absorption of the ion this latter absorption was used in all cases to measure the extent of ionization of the indicators.

Since the wavelength of maximum absorption and the extinction coefficient of the electronic spectra of the trans-α-cyanostilbenes differed substantially from that of the cis-α-cyanostilbenes, the wavelength of the maximum absorption of the trans-isomer afforded a convenient means of following the kinetics of the base catalyzed cis-trans isomerization. This method of analysis was used in all the kinetic studies.

EXPERIMENTAL

A. Purification of Solvents and Preparation of Solutions

1. Purification of dimethylsulfoxide (DMSO) (49)

Baker analyzed grade DMSO was stirred over night over calcium hydride and then distilled from it under nitrogen at reduced pressure using a 34 cm Vigreux column. Only the center fractions were used in subsequent work. The purified DMSO was stored in glass-stoppered flasks in a dry box.

2. Preparation of dry ethanol

Dry ethanol was prepared according to Vogel (87a). To one litre of absolute alcohol in a 2 l flask equipped with a reflux condenser and drying tube was added 7 g of clean sodium. When this had reacted, 27.5 g of ethyl phthalate was introduced and the mixture refluxed for two hours. The purified ethanol was then distilled under nitrogen using a 21 cm Vigreux column and the center fraction collected in flasks each fitted with a short sidearm and an appropriate rubber stopple. The ethanol was stored under nitrogen until used.

3. Preparation of dry methanol

Dry methanol was prepared according to the

method of Vogel (87b). To 5 g of magnesium and 0.5 g of iodine in a 2 l round bottom flask equipped with a water condenser and drying tube was added 50 to 75 ml of methanol. This was warmed slightly and after the reaction had started, it was controlled by cooling. To this was added 900 ml of methanol and refluxed for 45 minutes. This was then distilled under nitrogen using a 21 cm Vigreux column, and the center fraction collected and stored as in the case of ethanol.

4. Preparation of a solution of sodium ethoxide in ethanol

To 45 ml of dry ethanol was added approximately 0.6 g of sodium. Prior to the addition, the sodium was cleaned and allowed to react with clean ethanol for a short time. After the reaction was complete, aliquots of the stock solution were titrated with standard acid. The stock solution was kept under nitrogen and stored in the refrigerator. In this way no decomposition occurred over long periods of time.

5. Preparation of a solution of sodium methoxide in methanol

This was prepared in the same way as described for the sodium ethoxide solution. In this case, the methoxide solution was not stored in a refrigerator.

6. Preparation of DMSO-alcohol stock solutions

The DMSO-alcohol stock solutions were made up according to weight for approximately every 5 mole per cent DMSO from 0 to 100 per cent DMSO. Dry bottles, which had been flushed with dry nitrogen and equipped with well fitting rubber stopples, were weighed. Into each of these was syringed the required volume of purified DMSO under an atmosphere of nitrogen in a dry box. The stoppered bottles containing the DMSO were weighed again to give the weight of DMSO. To this was then added the appropriate amount of alcohol. This was done via syringe through the rubber stopples, thus minimizing the contact with air and moisture.

The bottles containing the stock solutions were weighed for the final time giving the weight of added alcohol. These stock solutions were kept under nitrogen and stored in a desiccator over silica gel. The DMSO-ethanol and the DMSO-methanol solutions were made up in the above manner.

7. Preparation of stock solutions of indicators or reactants

An accurately weighed quantity of the indicator, or reactant, was placed in a 10 ml volumetric flask. In a dry box, under nitrogen, an appropriate amount of DMSO,

or other solvent, was added to the sample which was then transferred to a small brown bottle which was fitted with a rubber stopple. This afforded an easy means of withdrawing 30 µl of stock solution via syringe without exposing it to the air or moisture.

B. Equilibria Measurements

All equilibria measurements were made using a Bausch and Lomb spectrophotometer, Model No. 502 with the cells thermostated at 25° ± 0.1° by means of water passing through a metal block from a constant temperature bath.

The general procedure in making the measurements was as follows. The quartz UV cell was fitted with a Neoprene stopper which was easily punctured by syringe needles. Two needles, one connected to a nitrogen cylinder and the other serving as an outlet, were both inserted through the stopper a short distance into the cell. The cell was then flushed with dry nitrogen for a short time; after which 2.47 ml of the desired DMSO-alcohol solution was added through the stopper via a needle and 5 ml syringe equipped with a channey adaptor. Dry nitrogen was then bubbled through the DMSO-alcohol solution for about 10 minutes. To this was added, in the same way, 30 µl of the indicator stock solution using a 50 µl Hamilton syringe with a fixed needle and channey adaptor. The solution was then allowed to equilibrate for a short time

in the cell block of the spectrophotometer.

The cells containing the indicator and the reference cell were handled identically except that the reference cell did not contain the 30 μl of DMSO indicator stock solution. The spectrum of the molecule was recorded and the zero absorption line adjusted in the region of maximum absorption of the ion. Using a 50 μl syringe with a fixed needle, the appropriate amount of alkoxide solution (35 μl of sodium methoxide solution or 36μl of sodium ethoxide solution) was added by inserting the needle a short distance through the stopper. The spectrum was then recorded at least at two different times to ensure that the ion was stable. If the ion were not stable, the absorbance was measured as a function of time and extrapolated back to zero time. This, then, gave the absorbance of the ion at the wavelength of its maximum absorption.

The spectral data for the various compounds are given in Tables I - III. The wavelengths of maximum absorption and the molar extinction coefficients are listed for many of the molecular and ionic forms of the indicators and reactants.

C. Treatment of the Spectral Data in the Equilibrium Measurements

The absorption data for indicators which ionize

according to the equation

$$A + HOR \rightleftharpoons AOR^- + H^+ \qquad (54)$$

can be treated in the usual manner. If α is the fraction ionized, and if the solutions are dilute enough so that Beer's Law is followed (88), then

$$\frac{[AOR^-]}{[A]} = \frac{\alpha}{1-\alpha} = \frac{\epsilon - \epsilon_A}{\epsilon_{AOR^-} - \epsilon} \qquad (55)$$

where: ϵ is the molar extinction coefficient at the wavelength of the measurement in a solution in which the indicator is partially ionized;

ϵ_A is the molar extinction coefficient of the unionized molecule; and

ϵ_{AOR^-} is the molar extinction coefficient of the ion.

Since in many cases the absorbance of the molecule was negligible at the wavelength at which the measurements were taken, ϵ_A could be neglected. This resulted in the simpler expression

$$\frac{\alpha}{1-\alpha} = \frac{\epsilon}{\epsilon_{AOR^-} - \epsilon} \qquad (56)$$

Since the same concentrations of indicators were used for each measurement, the molar extinction coefficient ϵ was replaced by the absorbance A.

The ionization data for the various indicators have been recorded in Tables IV - VII. These data have been recorded in the form of log I values for the various solvent compositions where $I = [AOR^-]/[A]$. In the case of the carbon acids, the data for $I = [A^-]/[AH]$ have been recorded in the Tables VIII and IX.

D. Kinetic Measurements

In measuring the kinetics of the base catalyzed cis-trans isomerization of α-cyano-cis-stilbenes, the procedure in making up the solutions in the quartz UV cells was the same as that already described in the case for equilibria measurements. The only difference was in the length of time allowed for the solutions to come to thermal equilibrium. In the kinetic measurements, before the addition of the alkoxide solution, the solution in the UV cells was allowed to come to thermal equilibrium for approximately 30 minutes.

Many of the kinetic measurements were made using a Beckman DU Spectrophotometer Model 2400 with thermospacers. After thermal equilibrium had been attained the absorbance of the cis-isomer at the wavelength of the maximum absorption of the trans-isomer was measured. After the addition of the alkoxide solution to the reference cell, the reference energy was balanced. Then the same amount of

alkoxide solution was added to the sample cell and the absorbance recorded as a function of time.

In studying the effect of a change in temperature on the rate of isomerization, a Bausch and Lomb Model No. 502 spectrophotometer was used because of better thermal contact between the constant temperature block and the cells. The procedure was similar to that used with the Beckman DU Spectrophotometer. The temperature of the cell block was measured by means of a copper-iron constantan thermocouple placed in a brass probe in the constant temperature block, with the reference thermocouple in an ice bath, using a Honeywell Model No 2732 Potentiometer. The thermocouple had previously been calibrated against a mercury thermometer using a constant temperature water bath. The averaging of several emf readings as measured by the potentiometer during the course of the reaction and the subsequent interpolation from the appropriate calibration curve gave the average temperature at which the reaction took place.

E. Treatment of the Kinetic Data

For a bimolecular reaction of the type

$$X + C \longrightarrow Y + C \qquad (57)$$

where C is a true catalyst and is regenerated, the rate expression is given by

$$\frac{dY}{dt} = k_2(X)(C) \tag{58}$$

where k_2 is the second order rate constant. If the concentration of the catalyst is in large excess, equation (58) simplifies to an apparent first order reaction with the rate expression

$$\frac{d\alpha}{dt} = k_1 \{1 - \alpha\} \tag{59}$$

where α is the relative proportion of Y present and k_1 is the apparent first order rate constant. The integration of this yields

$$\ln \frac{1}{1 - \alpha} = k_1 t \tag{60}$$

If X and Y are the only species absorbing at a particular wavelength, then it can easily be shown that

$$\alpha = \frac{\epsilon_t - \epsilon_X}{\epsilon_Y - \epsilon_X} \tag{61}$$

and

$$1 - \alpha = \frac{\epsilon_Y - \epsilon_t}{\epsilon_Y - \epsilon_X} \tag{62}$$

where: ϵ_X is the molar extinction coefficient of the reactant X;

ϵ_Y is the molar extinction coefficient of the product Y; and

ϵ_t is the molar extinction coefficient of the solution at a time t, all taken at one particular wavelength.

If the solutions are sufficiently dilute so that Beer's Law holds, then the molar extinction coefficients can be replaced by absorbances. Since the absorbance of the reactant will be given by that at time zero, it follows that ϵ_X can be replaced by A_o, and since the absorbance of the product will be given by that at the completion of the reaction, then ϵ_Y can be replaced by A_∞, then the rate expression is given by the equation

$$\ln \frac{A_\infty - A_o}{A_\infty - A_t} = k_1 t \qquad (63)$$

In this case, a plot of $\log(A_\infty - A_o)/(A_\infty - A_t)$ versus time will give a straight line with the apparent first order rate constant k_1 being equal to 2.3026 times the slope. All the kinetic data were treated in the above manner. When the second order rate constants were desired, as in the temperature study, k_1 was divided by the concentration of the base.

F. Preparation of Indicators and Reactants

1. 1,1-Bis-(4-nitrophenyl)ethene

1,1-Diphenylethane was prepared from benzene and stryene according to the method of Szmant and Yoncoskie (89). This was then nitrated with fuming nitric acid below 10° to give 1,1-bis-(4-nitrophenyl)ethane (90), which in turn was brominated with N-bromosuccinimide in carbon tetrachloride using benzoyl peroxide as catalyst. The crude bromide was then dehydrohalogenated according to Szmant and Deffner (90) by refluxing in pyridine to give 1,1-bis-(4-nitrophenyl)ethene. This was then recrystallized from methanol and from ethyl acetate to give yellow-orange platelets melting at 174 - 5° (lit. value: 175 - 176.5° (90)).

2. α-Cyano-2,4-dinitrostilbene

To a solution of 0.7 g of 2,4-dinitrobenzyl cyanide, prepared according to Fairbourne and Fawson (91), and 0.4 g of benzaldehyde in 20 ml of ethanol was added 4 drops of piperidine and the mixture was refluxed for 16 hours. The solution was cooled, some of the ethanol was evaporated and the dark colored solid filtered to yield 0.6 g of crude material for a 60% yield. This was recrystallized from acetic acid to a constant melting point of 160 - 161°.

Analysis:	carbon	hydrogen	nitrogen
calculated	61.02	3.07	14.23
found	60.93	3.24	14.17

3. α-Cyano-4,4'-dinitrostilbene

α-Cyano-4,4'-dinitrostilbene was prepared by condensing 4-nitrobenzyl cyanide with 4-nitrobenzaldehyde in ethanol using piperidine as the catalyst according to the method of Merckx (92). The product was recrystallized from acetic acid to a constant melting point of 214 - 215°. (lit. value: 211 - 212° (92)).

4. α-Cyano-3'-chloro-4-nitrostilbene

To a solution of 1.6 g 4-nitrobenzyl cyanide and 1.4 g 3-chlorobenzaldehyde in 50 ml of ethanol at 50° was added 10 drops of 1N sodium ethoxide-ethanol solution. After 15 to 20 minutes, the solution was cooled and the resulting crystals were filtered and washed with ethanol to give 1.8 g of material for a yield of 63%. This was recrystallized from ethanol and from acetic acid to a constant melting point of 168 - 168.5°. (lit. value: 161.5° (93)).

5. α-Cyano-4-nitrostilbene

To a solution of 2 g 4-nitrobenzyl cyanide and 1.25 ml of benzaldehyde in ethanol was added a small amount of a 1N sodium ethoxide solution and heated at 50° for about 10 minutes. Upon cooling, the solid product was filtered collecting 1.0 g of product for a yield

of 31%. This was recrystallized from ethanol to a constant melting point of 176 - 176.5°. (lit. value: 175.6° (94)).

6. α-Cyano-4'-methyl-4-nitrostilbene

The condensation of 4-nitrobenzyl cyanide and 4-methylbenzaldehyde in ethanolic sodium ethoxide, according to the method of Schonne, Braye and Bruylants (94), gave the corresponding α-cyanostilbene in 84% yield. This was recrystallized once from ethanol and twice from petroleum ether (fraction boiling at 64 - 110°) to give slightly yellow crystals melting at 146 - 147°. (lit. value: 146 - 147° (95)).

7. α-Cyano-4'-methoxy-4-nitrostilbene

The condensation of 4-nitrobenzyl cyanide and p-anisaldehyde in ethanolic sodium ethoxide, according to the method of Schonne, Braye and Bruylants (94), gave the corresponding substituted α-cyanostilbene in 85% yield. This was recrystallized from acetic acid to a constant melting point of 162 - 163°. (lit. value: 165° (95)).

8. α-Cyano-4'-dimethylamino-4-nitrostilbene

This was prepared by condensing 4-nitrobenzyl cyanide with 4-dimethylaminobenzaldehyde in ethanol using

piperidine as the catalyst according to the method of Merckx (92). The product was recrystallized to a constant melting point of 244.5 - 245.5°. (lit. value: 244 - 246° (92)).

9. α,4-Dicyano-4'-nitrostilbene

4-Cyanobenzyl cyanide was prepared in low yield from 4-cyanobenzyl bromide and potassium cyanide in ethanol and water according to the method of Gabriel and Otto (96). The 4-cyanobenzyl cyanide was recrystallized from water to give slightly pink crystals melting at 99 - 100°. (lit. value: 100° (97)).

The purified 4-cyanobenzyl cyanide was condensed with 4-nitrobenzaldehyde in ethanol using piperidine as catalyst, according to the method of Merckx (92), to give a 56% yield of α,4-dicyano-4'-nitrostilbene. This was recrystallized from acetic acid to give fine yellow needles melting at 212 - 212.5°.

Analysis:	carbon	hydrogen	nitrogen
calculated	69.81	3.30	15.27
found	69.58	3.98	15.14

10. α,4-Dicyano-3'-chlorostilbene

4-Cyanobenzyl cyanide, prepared as described above, was condensed with 3-chlorobenzaldehyde in ethanolic sodium ethoxide at 40° according to the method of Schonne,

Braye and Bruylants (94). The product, collected in 63% yield, was recrystallized from ethanol and acetic acid to a constant melting point of 195 - 195.5°.

Analysis:	carbon	hydrogen	nitrogen
calculated	72.60	3.43	10.58
found	72.76	3.55	10.62

11. α,4-Dicyanostilbene

The condensation of 4-cyanobenzyl cyanide, prepared as described above, and benzaldehyde in ethanolic sodium ethoxide at 50°, according to the method of Schonne, Braye and Bruylants (94), gave the α,4-dicyanostilbene in 89% yield. This was recrystallized from ethanol to give colorless crystals melting at 144.5 - 145.5°. (lit. value: 145° (98)).

12. α,3-Dicyanostilbene

The condensation of 3-cyanobenzyl cyanide, which was prepared in the manner described by Ipatieff et al (99), with benzaldehyde in ethanolic sodium ethoxide yielded the α,3-dicyanostilbene in 95% yield. The product was recrystallized from ethanol to give colorless crystals melting at 148 - 149°.

Analysis:	carbon	hydrogen	nitrogen
calculated	83.46	4.38	12.17
found	83.72	4.22	12.04

13. α-Cyano-2-nitrostilbene

The condensation of 2-nitrobenzyl cyanide, which was prepared in the manner described by Pschorr and Hoppe (100), with benzaldhyde in ethanol with piperidine as the catalyst gave the α-cyano-2-nitrostilbene in 54% yield. The product was recrystallized from ethanol to a constant melting point of 114 - 114.5°. (lit. value : 115° (101)).

14. α,3-Dicyano-4-chlorostilbene

3-Cyano-4-chlorotoluene was prepared from 3-amino-4-chlorotoluene by the Sandmeyer reaction according to the method described by Vogel (87c). The 3-cyano-4-chlorobenzyl bromide was prepared by brominating 6.4 g of 3-cyano-4-chlorotoluene with 9 g of N-bromo-succinimide in 125 ml carbon tetrachloride using benzoyl peroxide as the catalyst by refluxing for 3.5 hours. After removing the carbon tetrachloride, the crude product was dissolved in 100 ml of ethanol and reacted with 2.6 g of potassium cyanide in 20 ml of water. After refluxing for 45 minutes, the ethanol was evaporated and the resulting oil was extracted with ether. After evaporating the ether, the oil solidified and was recrystallized from water; 0.3 g of material was obtained. This was condensed with 0.1 g of benzaldehyde in 5 ml of ethanol and a few

drops of a 1N ethanolic sodium ethoxide solution at 40°. This gave a 78% yield of α,3-dicyano-4-chlorostilbene which was recrystallized from ethanol to a constant melting point of 156 - 157°.

Analysis:	carbon	hydrogen	nitrogen
calculated	72.60	3.43	10.58
found	73.83	4.06	10.30

15. α-Cyano-2-chloro-4-nitrostilbene

This indicator was prepared according to the method of Meerwein, Buchner and van Emster (102). To the filtered solution of the diazonium salt of 2-chloro-4-nitroaniline, prepared according to the method described by Vogel (87d), was added 3.5 g of sodium acetate, 2.1 g of cinnamonitrile in 19 ml of acetone and 0.68 g of cupric chloride in 2 ml of water. The aqueous solution in the distillation flask was decanted and the residue taken up in acetone and passed through an alumina column using benzene as the elutent. The resulting dark colored product, left after evaporating the benzene, was recrystallized from acetic acid, using charcoal to decolorize it, to give a small amount of yellow crystals melting at 174 - 175°.

Analysis:	carbon	hydrogen	nitrogen
calculated	63.28	3.19	9.84
found	63.61	3.65	10.01

16. α-Cyano-3-trifluoromethylstilbene

3-Trifluoromethylbenzyl cyanide was prepared in 78% yield from 3-trifluoromethylbenzyl chloride and potassium cyanide in an ethanol-water solution according to the method of Rosenkrantz et al (103). The 3-trifluoromethylbenzyl cyanide was condensed with benzaldehyde in ethanolic sodium ethoxide solution at 55° according to the method described by Schonne, Braye and Bruylants (94) to give a 70% yield of the corresponding α-cyanostilbene. The product was recrystallized once from ethanol and twice from methanol to give colorless crystals melting at 80 - 81°.

Analysis:	carbon	hydrogen	nitrogen
calculated	70.33	3.69	5.13
found	70.54	3.68	5.02

17. α-Cyano-3-nitrostilbene

3-Nitrobenzyl cyanide was prepared in 60% yield from the reaction of 3-nitrobenzyl chloride with sodium cyanide in an ethanol-water solution according to the method described by Bent et al (104). The product distilled at 144 - 145° at 0.7mm (lit. value: 160 - 165° at 3mm (104)) and melted at 55 - 56°. The 3-nitrobenzyl cyanide was condensed with benzaldehyde in an ethanolic sodium ethoxide solution according to the method described by Schonne, Braye and Bruylants (94) to give the α-cyano-

3-nitrostilbene. The product was recrystallized from ethanol to a constant melting point of 165 - 166° (lit. value: 165° (94)).

18. α-Cyano-3-chlorostilbene

This was prepared by condensing 3-chlorobenzyl cyanide with benzaldehyde in an ethanolic sodium ethoxide solution according to the method described by Schonne, Braye and Bruylants (94). The product was recrystallized from ethanol to a constant melting point of 95 - 96° (lit. value: 94 - 95° (105)).

19. α-Cyano-4-chlorostilbene

The condensation of 4-chlorobenzyl cyanide with benzaldehyde in an ethanolic sodium ethoxide solution, according to the method described by Schonne, Braye and Bruylants (94), gave the α-cyano-4-chlorostilbene in 80% yield. The product was recrystallized from ethanol to a constant melting point of 112 - 113°. (lit. value: 110 - 112° (105)).

20. α-Cyano-cis-stilbene

α-Phenyl-trans-cinnamic acid was prepared by condensing phenylacetic acid with benzaldehyde in triethylamine and acetic anhydride according to the method

of Buckles and Bremer (106). After one recrystallization from ethanol and water, a 54% yield of product was obtained melting at 169.5 - 170.5°. (lit. value: 172 - 173° (106)).

α-Cyano-cis-stilbene was prepared according to the method of Codington and Mosettig (107). A solution of 10 g of α-phenyl-trans-cinnamic acid in 15 ml thionyl chloride was heated to solution and then refluxed for 40 minutes, followed by the evaporation of the thionyl chloride. The resulting oil was dissolved in 100 ml of dry benzene and ammonia was passed through the solution. After filtering the ammonium chloride, the benzene was evaporated and the resulting oil solidified and was recrystallized from acetone giving 5 g of material melting at 112 - 122°. A mixture of 5 g of the crude amide, 10 g of phosphorus pentoxide and 25 ml of xylene was refluxed for one hour with stirring. The hot xylene solution was decanted and the residue was further extracted with 10 ml of hot xylene. The xylene was then distilled and the residue distilled under reduced pressure; 1.6 g of yellow material boiling at 114 - 115° at 0.15mm was collected (lit. value: 90 - 100° at 0.05mm (107)). This was redistilled and then further purified by vapor phase chromotography using a 10 foot silicon column with the column temperature at 220°.

21. α-Cyano-cis-4-chlorostilbene

4-Chlorophenylacetic acid was prepared by hydrolyzing 4-chlorobenzyl cyanide in sulfuric acid in the manner described by Vogel (87e). The product was recrystallized from high boiling petroleum ether.

α-(4-Chlorophenyl)-trans-cinnamic acid was prepared, as described by Codington and Mosettig (107), by condensing the sodium salt of 4-chlorophenylacetic acid with purified benzaldehyde in redistilled acetic anhydride. The product was recrystallized from ethanol to give a 51% yield of product melting at 173 - 178° (lit. value: 180 - 181° (107)). The amide was prepared by reacting the acid chloride, prepared from the reaction of α-(4-chlorophenyl)-trans-cinnamic acid with thionyl chloride, with ammonia in benzene (107). The dehydration of the amide with phosphorus pentoxide in xylene, as described by Codington and Mosettig (107), resulted in the α-cyano-cis-4-chlorostilbene. This was recrystallized from methanol and low boiling petroleum ether to a constant melting point of 55.5 - 57.5°. (lit. value: 56 - 57.5° (107)).

22. α-Cyano-cis-3-chlorostilbene

The sodium salt of 3-chlorophenylacetic acid, prepared by reacting 10 g of 3-chlorophenylacetic acid with 1.35 g of sodium in methanol and then evaporating the

methanol, was condensed with 6.2g of purified benzaldehyde in 39 ml of distilled acetic anhydride by heating at 100° for 17 hours (107). This solution was poured into 100 ml of water and heated to boiling with vigorous stirring. After cooling, the solid was filtered and recrystallized from ethanol to give 9.2 g of product for a 61% yield.

To the α-(3-chlorophenyl)-trans-cinnamic acid, from above, was added 15 ml of thionyl chloride; the mixture was heated to effect solution and then was refluxed for 40 minutes. The excess thionyl chloride was distilled and the resulting oil dissolved in benzene which was then saturated with ammonia. The benzene was evaporated and the resulting oil recrystallized from petroleum ether-ethanol to give the desired amide. A mixture of 3.7 g of this amide, 6.5 g of phosphorus pentoxide and 25 ml of xylene was refluxed with stirring for one hour. The xylene was decanted and the residue was extracted with a further 10 ml of hot xylene. The xylene was then distilled giving the crude α-cyano-cis-3-chlorostilbene as an oil. This was purified by micro distillation followed by passage through a short carbon-celite column and, finally, by vapor phase chromotography using a 10 foot silicon column with the column temperature at 220°. In the infrared spectrum, a peak at 2200 cm^{-1} indicated the presence of the cyano group.

Analysis:	carbon	hydrogen
calculated	75.16	4.20
found	74.85	4.20

23. α-Cyano-cis-4-methoxystilbene

α-(4-Methoxyphenyl)-trans-cinnamic acid was prepared by condensing 25 g of 4-methoxyphenylacetic acid with 16 g of purified benzaldehyde in 15 g of triethylamine and 71 ml of distilled acetic anhydride by refluxing for 48 hours according to the method of Cadogan, Duell and Inward (108). The product was recrystallized once from an ethanol-water mixture.

The crude cinnamic acid (27.7 g) from above was dissolved in 70 ml of thionyl chloride by heating and then refluxed for a further 35 minutes. The excess thionyl chloride was distilled and the resulting oil dissolved in benzene which was then saturated with ammonia. The ammonium chloride was filtered and the benzene filtrate was evaporated leaving an oil which crystallized on standing. This was recrystallized from carbon tetrachloride to give 5.7 g of the amide. A mixture of this amide, 10 g of phosphorus pentoxide and 35 ml of xylene was refluxed with stirring for 1.25 hours. The hot xylene solution was decanted and the residue was further extracted with 20 ml of hot xylene. The xylene was distilled under reduced pressure leaving the crude α-cyano-cis-4-methoxystilbene

as an oil. This was further purified by a micro distillation followed by passage through a short carbon-celite column and finally by vapor phase chromotography using a 7 foot silicon gum rubber column with the column temperature at 220°. In the infrared spectrum, a peak at 2200 cm^{-1} indicated the presence of the cyano group.

Analysis:	carbon	hydrogen
calculated	81.68	5.57
found	81.24	5.54

24. α-Cyano-cis-3-nitrostilbene

3-Nitrophenylacetic acid (13.3 g), prepared by hydrolyzing 3-nitrobenzyl cyanide in sulfuric acid (87e), was condensed with 7.8 g of purified benzaldehyde in 9.7 g of triethylamine and 45 ml of distilled acetic anhydride by refluxing for 48 hours according to the method of Cadogan, Duell and Inward (108). The product was recrystallized from ethanol giving 5.8 g of fairly crude α-(3-nitrophenyl)-trans-cinnamic acid.

The 5.8 g of acid from above was dissolved in 10 ml of thionyl chloride by heating and the solution refluxed for a further 40 minutes. The excess thionyl chloride was distilled and the resultant solid dissolved in 75 ml of benzene which was then saturated with ammonia. The resulting solid was filtered and the benzene filtrate evaporated to dryness giving very little product. The

solid material was then heated with ethanol, filtered and the ethanol filtrate evaporated giving a solid which was recrystallized from benzene to give 4.0 g of the amide melting at 151 - 155°. A mixture of 4.0 g of this amide, 7.0 g of phosphorus pentoxide and 30 ml of xylene was refluxed with stirring for 1.25 hours. The hot xylene solution was decanted and the residue was further extracted with 15 ml of hot xylene. The xylene solution was distilled under reduced pressure leaving 2.9 g of α-cyano-cis-3-nitrostilbene as a solid. This was recrystallized from ethanol to a constant melting point of 121 - 122°. The infrared spectrum had a sharp band at 2200 cm^{-1} indicating the presence of the cyano group.

Analysis:	carbon	hydrogen	nitrogen
calculated	71.99	4.03	11.20
found	71.95	4.39	10.88

25. α-Cyano-cis-4-nitrostilbene

α-(4-nitrophenyl)-trans-cinnamic acid was prepared by condensing the sodium salt of 4-nitrophenylacetic acid with purified benzaldehyde in distilled acetic anhydride according to the method of Schmid (109). The crude product was recrystallized once from acetic acid giving yellow crystals melting at 221 - 223°. (lit. value: 227 - 228° (109)).

α-(4-Nitrophenyl)-trans-cinnamic acid (14.9 g)

was dissolved in 50 ml of thionyl chloride by heating and then refluxed for a further 45 minutes. The excess thionyl chloride was distilled under reduced pressure leaving a solid which was dissolved in 190 ml of benzene which was then saturated with ammonia. The resulting solid was recrystallized from ethanol and 6.6 g of yellow crystals melting at approximately 210° was collected. A mixture of 6.6 g of this amide, 11.5 g of phosphorus pentoxide and 70 ml of xylene was refluxed with stirring for 1.25 hours. The hot xylene solution was filtered and the resultant filtrate distilled under reduced pressure leaving the α-cyano-cis-4-nitrostilbene as a yellow solid. This was recrystallized from ethanol to a constant melting point of 135 - 136°. In the infrared spectrum, a peak at 2200 cm^{-1} indicated the presence of the cyano group.

Analysis:	carbon	hydrogen	nitrogen
calculated	71.99	4.03	11.20
found	72.10	5.04	10.93

26. α-Cyano- α'-methoxy-cis- and trans-stilbenes

α-Cyanodesoxybenzoin was prepared by reacting benzyl cyanide with ethyl benzoate in benzene and potassium according to the method described by Wislicenus, Butterfass and Koken (110). This was recrystallized from carbon tetrachloride to give the purified α-cyanodesoxy-

benzoin.

The two isomers of α-cyano-α'-methoxystilbene were prepared by the reaction of α-cyanodesoxybenzoin with alkaline dimethyl sulfate according to the method of Matti and Reynaud (111). The two geometrical isomers were separated by fractional recrystallization as described by Matti and Reynaud (111). The lower melting isomer melted at 84 - 85° and the other at 105 - 106°. (lit. values: 84.5 and 106° (111)).

27. 4,4'-Dinitrotriphenylmethane

4,4'-Dinitrodiphenylmethyl bromide was prepared by brominating 10 g of 4,4'-dinitrodiphenylmethane with 2 ml of bromine in 160 ml of carbon tetrachloride using 0.6 g of benzoyl peroxide as catalyst according to the method of Wragg, Stevens and Ostle (112). After evaporating the solvent and recrystallizing the product from carbon tetrachloride, 7.7 g of material was obtained for a yield of 59%. To 7.7 g of 4,4'-dinitrodiphenylmethyl bromide dissolved in 100 ml dry thiophene free benzene was added 6.1 g of aluminum chloride and the mixture was then refluxed with stirring for two hours during which a thick black tar separated. The benzene solution was decanted and evaporated to dryness. The small amount of 4,4'-dinitrotriphenylmethane (1.8 g) was recrystallized repeatedly from toluene to a constant melting point of

175 - 176°.

Analysis:	carbon	hydrogen	nitrogen
calculated	68.26	4.22	8.38
found	68.52	4.51	8.31

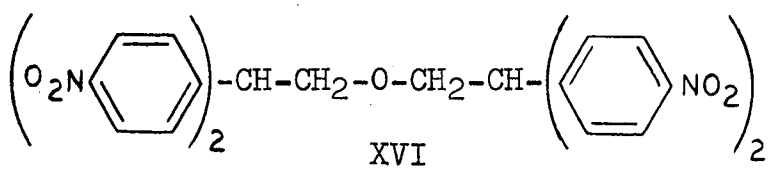
G. Reactions of 1,1-Bis-(4-nitrophenyl)ethene

1. With hydroxide ion in DMSO

Purified 1,1-bis-(4-nitrophenyl)ethene (1 g) was dissolved in 300 ml of purified DMSO in a short-necked flask fitted with a rubber stopple. After passing nitrogen through the solution for one hour, 6.5 ml of a 10% tetramethylammonium hydroxide-water solution was added via a syringe, thus not exposing the system to the air. After about one minute, the reaction was quenched by the addition of 6 ml of acetic acid. The resulting solution was poured onto 1.5 l of ice water whereupon a fine suspension formed. Sodium chloride was added to aid in breaking up the suspension and the yellow solid which separated was filtered and washed well with water. The resulting solid was recrystallized from benzene-acetone to yield 0.43 g of product with a melting point of 188 - 189°.

Analysis:	hydrogen	carbon	nitrogen	mol. weight
calculated	3.98	60.21	10.03	555
found	4.07	60.23	10.04	544

The calculated values are for di-1,1-bis-(4-nitrophenyl)-ethyl ether (XVI), and the molecular weight was determined



XVI

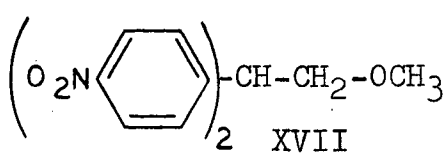
by the Rast method.

2. With sodium methoxide in DMSO

To 0.5 g of 1,1-bis-(4-nitrophenyl)ethene in a short-necked flask fitted with a rubber stopple was added 200 ml of purified DMSO. Nitrogen was bubbled through the solution for one hour and then 6 ml of approximately 1N sodium methoxide solution was added via a syringe and needle. After 10 minutes, the reaction was quenched by the addition of 6 ml of glacial acetic acid. The solution was poured onto ice and the breaking up of the emulsion was aided by the addition of sodium chloride. The solid was filtered, washed well with water and recrystallized from ethanol and a petroleum ether-ethanol mixture to a constant melting point of 118 - 119°.

Analysis:	carbon	hydrogen	nitrogen
calculated	59.60	4.67	9.27
found	59.77	4.62	8.58

The calculated values in the analysis are for 1,1-bis-(4-nitrophenyl)-2-methoxyethane (XVII).



XVII

The NMR spectrum of this compound dissolved in hot tetrachloroethylene was obtained. This shows a singlet at 6.56τ, a doublet at 6.06τ and 5.95τ with a coupling constant of 6 cps, and an obscure triplet centered at 5.48τ with an approximate coupling constant of 6 cps. The areas of the singlet:doublet:triplet are in the ratio of 3:2:1. The aromatic portion of the spectrum has two doublets, one at 2.48τ and 2.63τ and the other at 1.71τ and 1.84τ, each with a coupling constant of 9 cps.

TABLE I

Absorption Maxima and Molar Extinction Coefficients for α-Cyanostilbenes in DMSO-Ethanol

Substituent	Observed Values		Reported Values		
	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	ref.
α-Cyano-trans-stilbenes					
4,4'-dinitro	336	32,500	336	30,000[a]	95
3'-chloro-4-nitro	332	28,000			
4-nitro	336	27,600	334	26,500[a]	95
4'-methyl-4-nitro	350	28,600	348	18,200[a]	95
4'-methoxy-4-nitro	372	29,800	370	26,500[a]	95
4-cyano-4'-nitro	336	30,100			
4'-dimethylamino-4-nitro	456	38,400	445	41,700[b]	92
4-cyano-3'-chloro	321	29,500			
4-cyano	326	30,000			
3-cyano-4-chloro	318	26,000			
3-cyano	315	23,000			
3-trifluoromethyl	316	22,400			
3-nitro	311	25,200[c]			
3-chloro	315	23,400[c]			
4-chloro	318	25,800[d]	316	27,500	107
hydrogen	318	21,800[c]	312	25,700	107
4-methoxy	333	24,800[c]			
α-Cyano-cis-stilbenes[d]					
4-nitro	309	12,200			
3-nitro	277	17,200			
3-chloro	290	13,100			
4-chloro	296	14,700	295	15,800	107
hydrogen	291	13,100	295	16,600	107
4-methoxy	313	10,700			

a In 0.002M methanolic HCl
b In alcohol
c From isomerization of the cis-isomer
d In methanol

TABLE II

Absorption Maxima and Molar Extinction Coefficients for the Anions AOR^-

Substituent	In DMSO-Ethanol		In DMSO-Methanol	
	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε
α-Cyanostilbenes				
2,4-dinitro			480	27,100
4,4'-dinitro	553	42,100	553	41,100
3'-chloro-4-nitro	547	43,700	547	42,600
4-nitro	547	42,600	548	42,700
4'-methyl-4-nitro	547	42,800	548	42,400
4'-methoxy-4-nitro	547	42,500	549	42,300
4-cyano-4'-nitro	393	44,000	395	44,200
4'-dimethylamino-4-nitro	552	43,300	552	43,400
4-cyano-3'-chloro	402	47,200		
4-cyano	402	47,400	402	47,700
2-nitro	603	7,630		
3-cyano-4-chloro	374	33,600		
3-cyano	363	28,500		
3-trifluoromethyl	353	23,700		
2-chloro-4-nitro	550	40,500		
Others				
1,1-bis-(4-nitrophenyl) ethene	710	25,700		

TABLE III

Absorption Maxima and Molar Extinction Coefficients for Indicator Anions of Carbon Acids in Sodium Methoxide-Methanol Solutions

Indicator	Observed Values		Reported Values		
	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	ref.
methyl fluorene-9-carboxylate	387	4,220	389	4,690[a]	51
4,4',4"-trinitro-triphenylmethane	530	25,600	650 707	20,000[b] 19,300[c]	44 51
4,4'-dinitro-diphenylmethane	534	28,000	570 704	45,700[b] 40,600[c]	44 51
4-nitrobenzyl cyanide	530	30,700	528	28,700	39
2-nitrobenzyl cyanide	546	10,200			
4,4'-dinitro-triphenylmethane	506	20,900			

a In ethanol
b In aqueous hydrazine solutions
c In DMSO-ethanol solutions

TABLE IV

Values of log $[AOR^-]/[A]$ for the α-Cyanostilbenes Used as Indicators to Establish the H_R- Scale in DMSO-Ethanol

Mole % DMSO in Ethanol	4,4'-dinitro	3'-chloro-4-nitro	4-nitro	4'-methyl-4-nitro	4'-methoxy-4-nitro	4-cyano-4'-nitro	4'-dimethylamino-4-nitro
0.98	-.417						
1.99	-.366						
3.51	-.209	-.983					
5.63	-.042	-.810					
10.82	+.364	-.412					
15.54	+.724	-.080	-.827				
20.09		+.243	-.500	-.844			
25.09		+.589	-.169	-.516	-.959		
30.09		+.959	+.182	-.180	-.611		
35.07			+.528	+.185	-.276	-.869	
40.16			+.878	+.517	+.115	-.532	
45.22				+.886	+.473	-.196	-.860
50.27					+.865	+.173	-.504
55.03						+.543	-.153
59.62						+.907	+.207
64.59							+.611
69.26							+.938

TABLE IV (Continued)

Mole % DMSO in Ethanol	4-cyano-3'-chloro	4-cyano	2-nitro	3-cyano-4-chloro	3-cyano	3-trifluoro-methyl
50.27	-.662					
55.03	-.305					
59.62	+.045	-.883				
64.59	+.459	-.523				
69.26	+.894	-.152	-1.035			
74.15		+.281	-.599	-.815		
79.11		+.841	-.108	-.340		
84.12			+.422	+.188	-.936	
89.17				+.743	-.297	-.854
93.29					+.274	-.218

TABLE V

Values of log $[AOR^-]/[A]$ for the α-Cyanostilbenes Used as Indicators to Establish the H_R- Scale in DMSO-Methanol

Mole % DMSO in Methanol	2,4-dinitro	4,4'-dinitro	3'-chloro-4-nitro	4-nitro	4'-methyl-4-nitro	4'-methoxy-4-nitro	4-cyano-4'-nitro
0.68	-.898						
2.32	-.695						
5.39	-.362						
8.75	-.005						
15.30	+.618	-1.011					
20.60		-.560					
25.54		-.138	-.767				
30.47		+.308	-.358				
35.14		+.715	+.040	-.706	-1.042		
39.88			+.444	-.274	-.631		
44.05			+.809	+.088	-.279	-.706	
49.95				+.594	+.231	-.181	-.981
54.79				+.991	+.644	+.244	-.565
59.61					+1.029	+.676	-.144
64.32							+.275
69.63							+.724

TABLE V (Continued)

Mole % DMSO in Methanol	4'-dimethyl-amino-4-nitro	4-cyano-3'-chloro	4-cyano	2-nitro	3-cyano-4-chloro	3-cyano	3-trifluoro-methyl
59.61	-.736	-.882					
64.32	-.312	-.464					
69.63	+.188	+.011	-.932				
74.26	+.626	+.458	-.495				
78.52	+1.081	+.954	-.056	-.990			
83.52			+.526	-.429	-.609		
88.24				+.178	-.007	-1.120	
93.98				+1.022	+.747	- .195	-.687
97.61						+ .724	+.332

TABLE VI

Values of log $[AOR^-]/[A]$ for the α-Cyanostilbenes Used as Indicators to Establish the H_R- Scale in Sodium Methoxide-Methanol Solutions

Sodium Methoxide conc. (mole l^{-1})	2,4-dinitro	4,4'-dinitro	3'-chloro-4-nitro	4-nitro	4'-methyl-4-nitro	4'-methoxy-4-nitro	4'-dimethyl-amino-4-nitro
0.010	-.842						
0.056	-.087						
0.115	+.253						
0.229	+.616	-.813					
0.464		-.370	-.978				
0.697		-.075	-.686				
0.952		+.219	-.408				
1.19		+.482	-.153	-.808			
1.48		+.836	+.164	-.504	-.858		
1.78			+.476	-.214	-.568	-.979	
2.07			+.809	+.091	-.289	-.686	
2.36				+.402	+.016	-.385	
2.65				+.722	+.332	-.094	
2.93					+.652	+.220	-.917
3.24						+.582	-.680
3.51						+1.000	-.425
3.82							-.160
4.08							+.116
4.73							+.613

TABLE VII

Values of log $[AOR^-]/[A]$ for Lewis Acids
Not Used to Establish the H_R- Scale in DMSO-Ethanol

Mole % DMSO in Ethanol	α-cyano-2-chloro-4-nitrostilbene	1,1-bis-(4-nitrophenyl)ethene
15.54	-1.025	
20.09	-.607	
25.09	-.250	
30.09	+.135	
35.07	+.500	
40.16	+.913	
59.62		-.798
64.59		-.404
69.26		+.020
74.15		+.498
79.11		+1.037

TABLE VIII

Values of log $[A^-]/[AH]$ for Various Carbon Acids Used as Indicators to Establish the H_- Scale in Sodium Methoxide-Methanol Solutions

Sodium Methoxide conc. (moles l^{-1})	methyl fluorene-9-carboxylate	4-nitrobenzyl cyanide	4,4',4"-trinitro-triphenylmethane	2-nitrobenzyl cyanide	4,4'-dinitro-diphenylmethane
0.01	-.582				
0.024	-.174				
0.056	+.184				
0.115	+.538	-.782	-1.034		
0.229	+.988	-.415	-.684	-1.049	
0.460			-.214		
0.464		+.141		-.591	
0.697		+.421	+.094	-.271	
0.952		+.748		+.052	
0.977			+.343		
1.19			+.706	+.308	
1.78				+.902	-1.070
2.07					-.744
2.10					-.702
2.36					-.423
2.40					-.363
2.65					-.122
2.66					-.036
2.93					+.199
2.97					+.284
3.24					+.567
3.51					+.814

TABLE IX

Values of log $[A^-]/[AH]$ for Various Carbon Acids Studied in DMSO-Ethanol

Mole % DMSO in Ethanol	2-nitrobenzyl cyanide	4,4',4''-trinitro-triphenylmethane	4,4'-dinitro-triphenylmethane	4,4'-dinitro-diphenylmethane	1,1-bis-(4-nitro-phenyl)ethane
0.97	-.354	-.569			
1.81		-.508			
3.41		-.406			
5.88	+.052	-.218			
10.72	+.405	+.094			
15.77	+.780	+.376	-.752		
21.11		+.654	-.427		
25.45		+.871	-.180		
30.63			+.116	-.663	
35.56			+.363	-.248	
40.20			+.612	+.146	
45.27				+.594	
49.94				+1.009	-.485
54.86					-.146
59.98					+.304
64.98					+.760

RESULTS

A. The H_R- Function

The ionization behavior of indicators which ionize in highly basic systems by the addition of base to the unsaturated system, rather than by an abstraction of a proton by the base, will not follow a H_- function. Such indicators will generate a separate acidity scale, termed H_R- in this thesis. If A is an unsaturated Lewis acid, then the addition equilibria between A and a Lewis base such as the methoxide or ethoxide ion (OR^-) can be formulated as in equation (54). For analysis sake, equation (54) can be factored into the two equilibria:

$$A + OR^- \rightleftharpoons AOR^- \tag{64}$$

$$HOR \rightleftharpoons H^+ + OR^- \tag{65}$$

where

$$K' = \frac{(AOR^-)}{(A)(OR^-)} \tag{66}$$

and

$$K_{ROH} = \frac{(H^+)(OR^-)}{(HOR)} \tag{67}$$

Then if $K = K'K_{ROH}$, then

$$K = \frac{(AOR^-)(H^+)}{(A)(HOR)} = \frac{[AOR^-]\, f_{AOR^-}(H^+)}{[A]\ f_A\ (HOR)} \tag{68}$$

From this H_R- can be defined as

$$H_R- = -\log \frac{(H^+)f_{AOR^-}}{(HOR)\, f_A} = pK + \log \frac{[AOR^-]}{[A]} \quad (69)$$

where

$$h_R- = \frac{(H^+)\, f_{AOR^-}}{(HOR)f_A} \quad (70)$$

B. Equilibria Studies in DMSO-Alcohol Solutions

In DMSO-alcohol solutions containing 0.01M sodium alkoxide, the ratio of the ionized to unionized indicator concentrations ($I = [AOR^-]/[A]$) was measured as described in the previous section. After plotting log I, for each indicator, as a function of the solvent composition in mole % DMSO, a smooth curve was drawn through the points for which log I was between 1 and -1. This corresponded to using only that part of the ionization curve for which the indicator was between 10 and 90% ionized. The plots of log I for the various indicators used versus the solvent composition in mole % DMSO are given for DMSO-ethanol in Figure 1, and for DMSO-methanol in Figure 2. The numbers on the plots refer to those of the indicators listed in Table X. Using Hammett's method (10), pK values were then obtained by a graphical technique. For any two indicators, i and j,

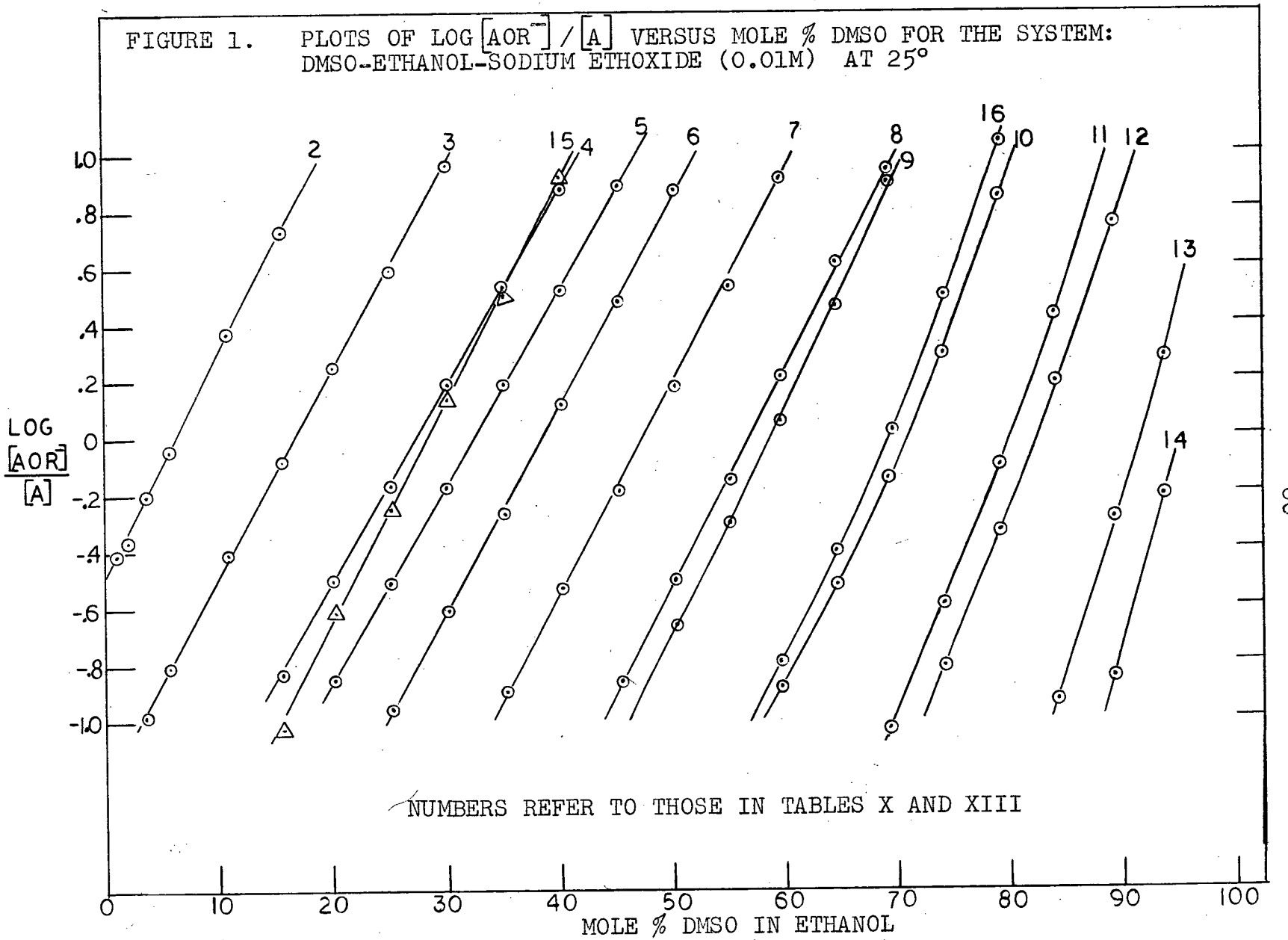
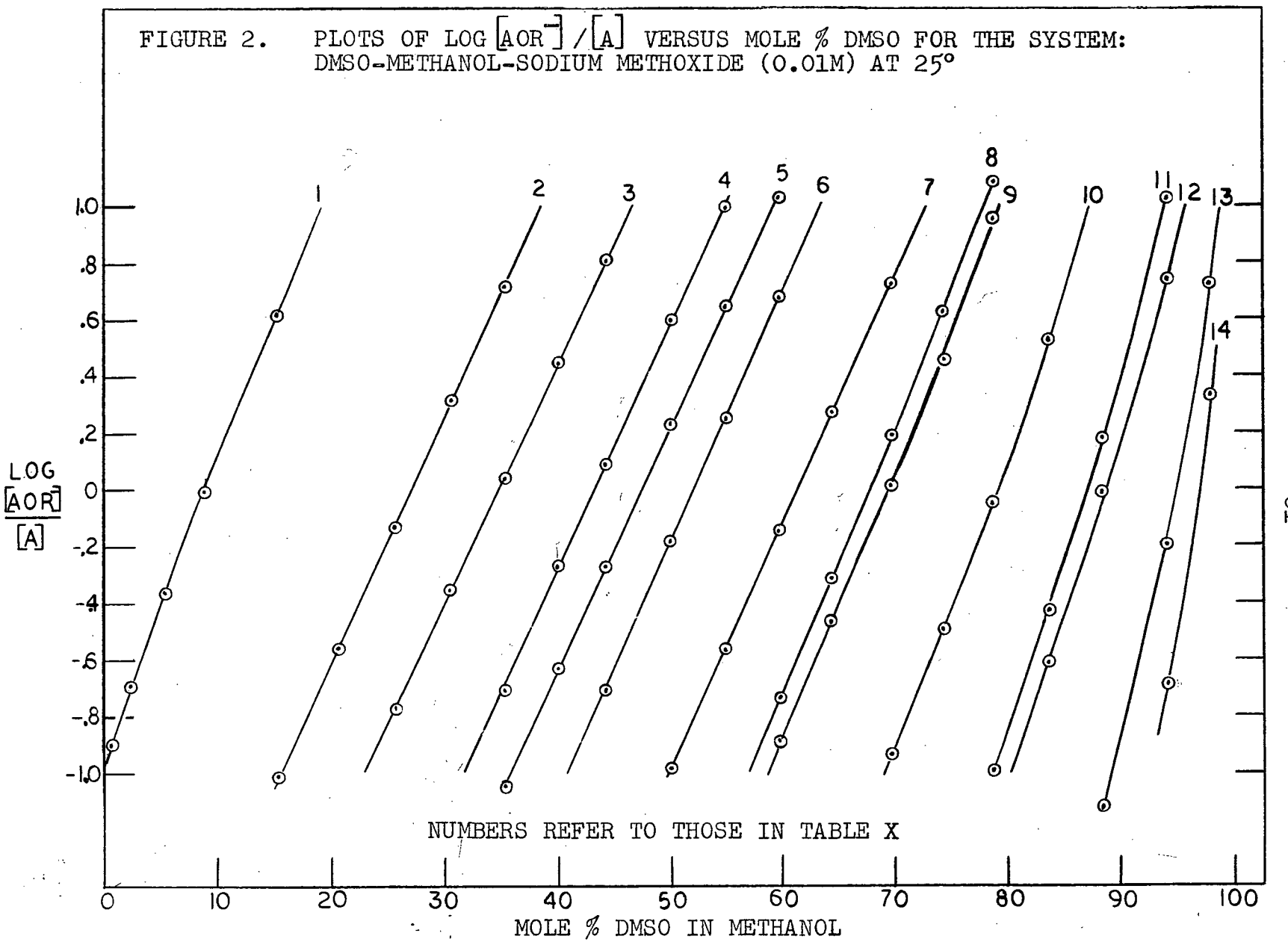


FIGURE 1. PLOTS OF LOG [AOR⁻] / [A] VERSUS MOLE % DMSO FOR THE SYSTEM: DMSO-ETHANOL-SODIUM ETHOXIDE (0.01M) AT 25°
LOG [AOR⁻] / [A]
1.0
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-1.0
2
3
15
4
5
6
7
8
16
9
10
11
12
13
14
NUMBERS REFER TO THOSE IN TABLES X AND XIII
0
10
20
30
40
50
60
70
80
90
100
MOLE % DMSO IN ETHANOL

FIGURE 2. PLOTS OF LOG $\frac{[AOR^-]}{[A]}$ VERSUS MOLE % DMSO FOR THE SYSTEM: DMSO-METHANOL-SODIUM METHOXIDE (0.01M) AT 25°



which ionize to an appreciable extent in a given solvent, the ΔpK value is given by the expression

$$\Delta pK = \log I_i - \log I_j \qquad (71)$$

where I_i and I_j refer to the ionization ratios of the two indicators in a solvent of one particular composition.

By interpolating log I values for indicators i and j from Figures 1 and 2 at regular intervals of solvent composition, a number of ΔpK values were obtained by using equation (71). These were then averaged to obtain the ΔpK value between indicators i and j.

Since α-cyanostilbenes are readily hydrolyzed in basic aqueous solutions, the pK of no indicator could be determined in aqueous buffer solutions. Due to this difficulty, an arbitrary pK value of 14.42 was given to the indicator α-cyano-4,4'-dinitrostilbene which was then used as a standard to which all other pK values were referred. The value of 14.42 was arrived at by assuming a H_R- value of 14.00 for a 0.01M sodium ethoxide solution in ethanol, which is the same as the H_- value reported by Bowden and Stewart (51) when carbon acids were used as indicators. It was reasoned that the H_R- and H_- values should be nearly identical in dilute basic solutions. Then by inserting the experimental value of -0.42 for log I for α-cyano-4,4'-dinitrostilbene in the above solution into equation (69), the pK value of

14.42 was obtained.

The pK values of a number of substituted α-cyanostilbenes were measured relative to the arbitrary standard. The values obtained in DMSO-ethanol and DMSO-methanol are listed in Table X.

By substituting the pK values from Table X and the experimental log I values into equation (69), H_R- values were calculated for the various DMSO-ethanol and DMSO-methanol solutions. Due to the overlapping of the ionization curves of indicators, several H_R- values were often obtained for a solvent of a particular composition. The averaged H_R- values for the DMSO-ethanol solvent system containing 0.01M sodium ethoxide are listed in Table XI and those for the DMSO-methanol solvent system containing 0.01M sodium methoxide are listed in Table XII. The graphical representations of how the H_R- values vary with the solvent compositions are given in Figures 3 and 4 for DMSO-ethanol and DMSO-methanol respectively.

The pK values of two indicators, which were not used to establish the H_R- scale, were measured in the DMSO-ethanol system. The pK values were estimated to be equal to the values of H_R- for the solutions in which the indicators were half ionized. Because a plot of log I versus H_R- for the indicator α-cyano-2-chloro-4-nitrostilbene did not give a line of unit slope, this indicator was not used to establish the H_R- scale.

TABLE X

pK Values of α-Cyanostilbenes Used As Indicators to Establish the H_R- Scales in the DMSO-Ethanol, DMSO-Methanol and Sodium Methoxide-Methanol Systems

Indicator Number	Substituent	pK in DMSO-Ethanol	pK in DMSO-Methanol	pK in Sodium Methoxide-Methanol
1	2,4-dinitro		12.73	12.96
2	4,4'dinitro	14.42	14.42	14.42
3	3'-chloro-4-nitro	15.20	15.08	15.06
4	4-nitro	15.95	15.81	15.73
5	4'-methyl-4-nitro	16.31	16.17	16.10
6	4'-methoxy-4-nitro	16.74	16.59	16.52
7	4-cyano-4'-nitro	17.38	17.38	
8	4'-dimethylamino-4-nitro	18.07	17.97	17.76
9	4-cyano-3'-chloro	18.23	18.13	
10	4-cyano	19.20	19.08	
11	2-nitro	20.11	20.02	
12	3-cyano-4-chloro	20.34	20.23	
13	3-cyano	21.44	21.20	
14	3-trifluoromethyl	21.98	21.54	

TABLE XI

H_R- Values for the DMSO-Ethanol System at 25°

Containing 0.01M Sodium Ethoxide

Mole % DMSO	H_R-	Ave. Dev. from the Mean	Indicators[a]
0.98	14.00	-	2
1.99	14.05	-	2
3.51	14.21	0.01	2, 3
5.63	14.38	0.01	2, 3
10.82	14.78	0.01	2, 3
15.54	15.13	0.01	2 - 4
20.09	15.45	0.01	3 - 5
25.09	15.79	0.01	3 - 6
30.09	16.14	0.01	3 - 6
35.07	16.48	0.02	4 - 7
40.16	16.84	0.02	4 - 7
45.22	17.20	0.01	5 - 8
50.27	17.57	0.03	6 - 9
55.03	17.92	0.01	7 - 9
59.62	18.29	0.02	7 - 10
64.59	18.68	0.01	8 - 10
69.26	19.06	0.05	8 - 11
74.15	19.50	0.03	10 - 12
79.11	20.01	0.03	10 - 12
84.12	20.52	0.02	11 - 13
89.17	21.12	0.04	12 - 14
93.27	21.74	0.03	13, 14

a Numbers refer to those in TABLE X

TABLE XII

H_R- Values for the DMSO-Methanol System at 25°

Containing 0.01M Sodium Methoxide

Mole % DMSO	H_R-	Ave. Dev. from the Mean	Indicators[a]
0.00	11.73	-	by extrapolation
0.68	11.83	-	1
2.32	12.03	-	1
5.39	12.37	-	1
8.75	12.72	-	1
15.30	13.38	0.03	1, 2
20.60	13.87	0.01	1, 2
25.54	14.29	0.02	2, 3
30.47	14.72	0.01	2 - 4
35.14	15.12	0.01	2 - 5
39.88	15.53	0.01	3 - 5
44.05	15.89	0.01	3 - 6
49.95	16.40	0.01	4 - 7
54.79	16.82	0.02	4 - 7
59.61	17.25	0.02	6 - 9
64.32	17.63	0.05	7 - 9
69.63	18.14	0.03	7 - 9
74.26	18.59	0.01	8 - 10
78.52	19.05	0.03	8 - 11
83.52	19.61	0.02	10 - 12
88.24	20.17	0.09	11 - 13
93.98	21.14	0.17	12 - 14
97.61	21.65	0.27	12 - 14

a Numbers refer to those in TABLE X

FIGURE 3. H_R- VALUES FOR DMSO-ETHANOL SOLUTIONS CONTAINING 0.01M SODIUM ETHOXIDE

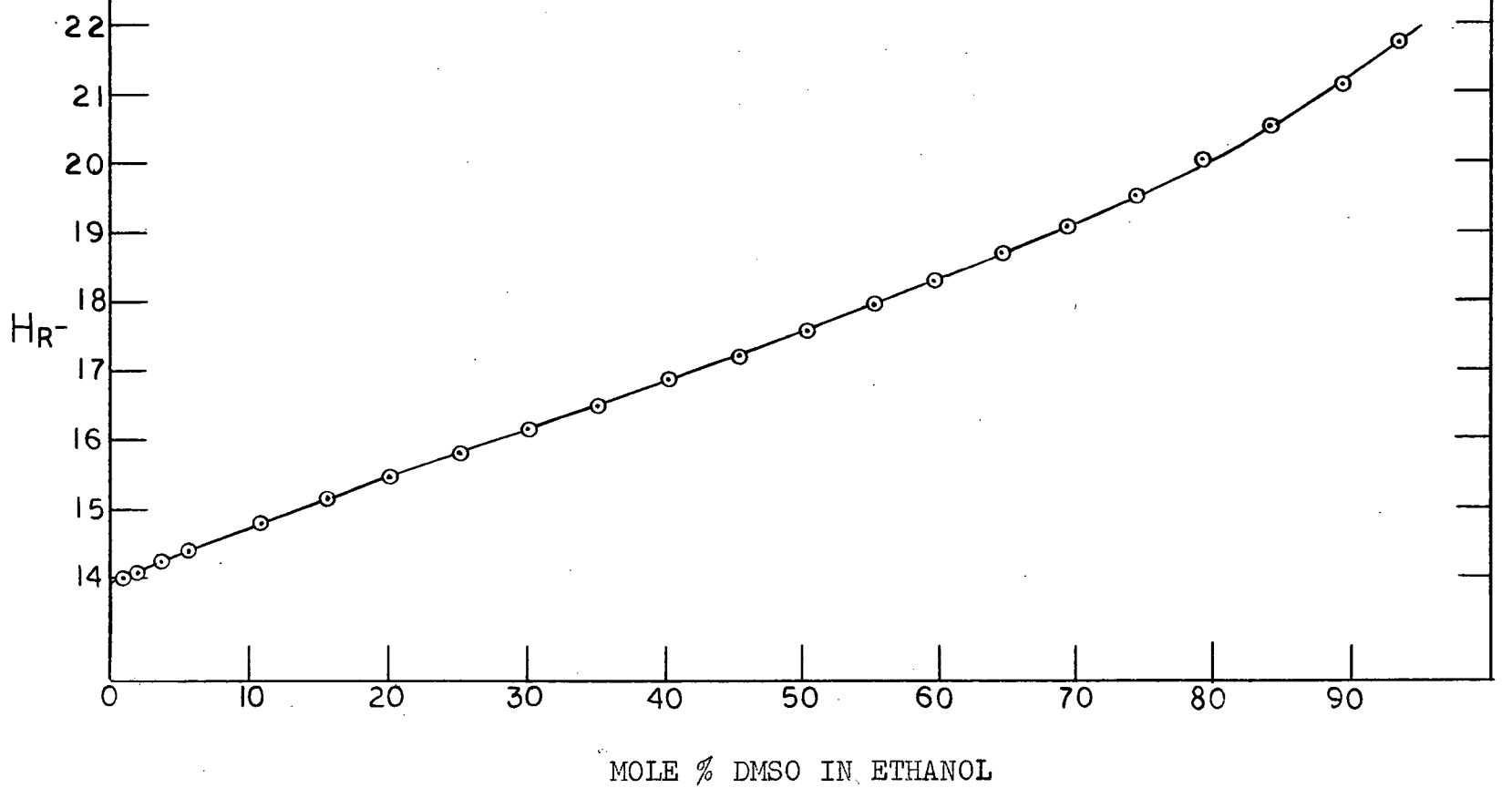
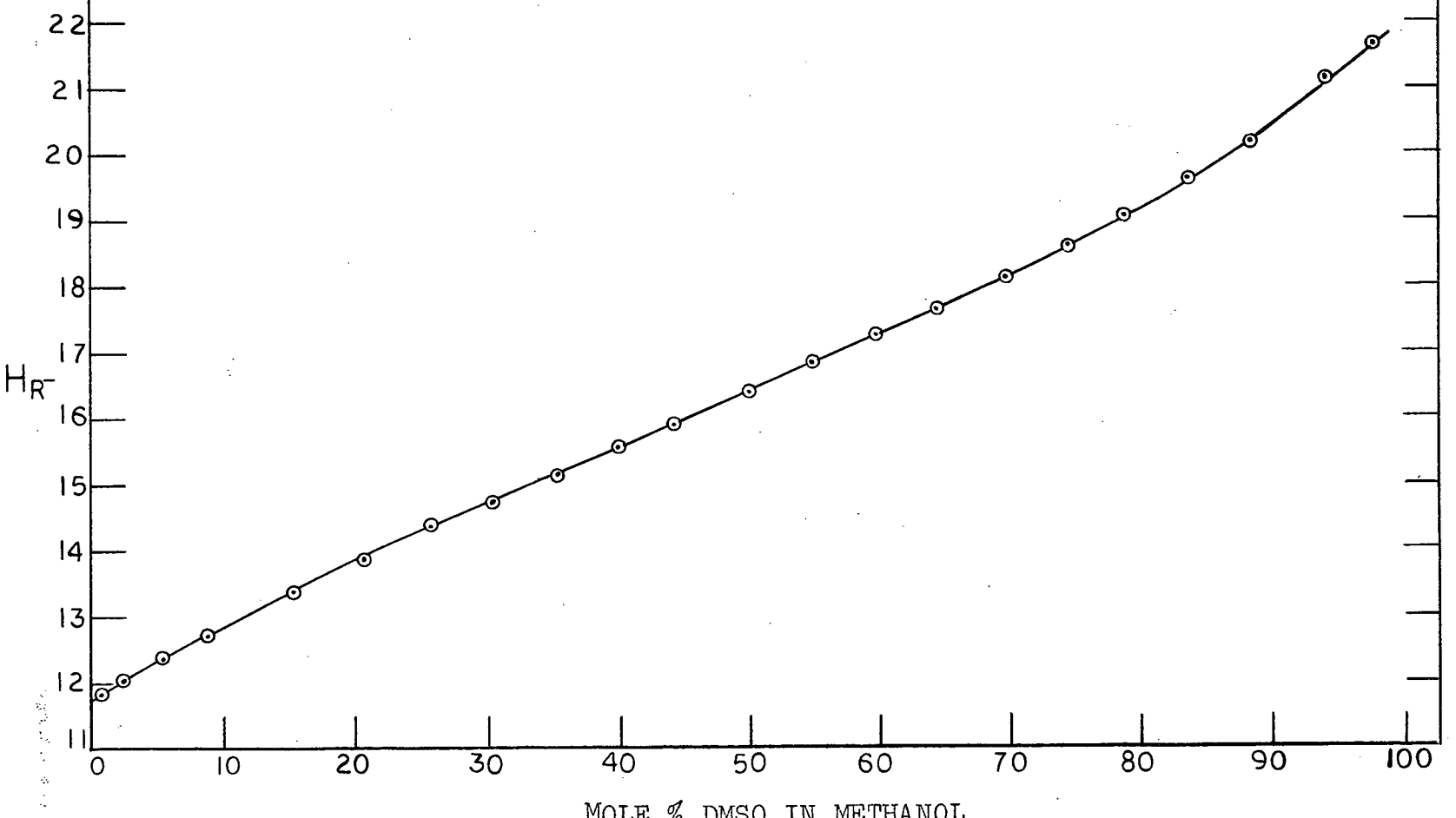


FIGURE 4. H_R- VALUES FOR DMSO-METHANOL SOLUTIONS CONTAINING 0.01M SODIUM METHOXIDE



In the case of 1,1-bis-(4-nitrophenyl)ethene, a plot of log I versus H_R- gave a fairly good straight line of near unit slope. This indicator was not used to establish the H_R- scale because it was desirable to keep the indicators used to set up the scale as structurally similar as possible. The pK values for these two indicators are listed in Table XIII.

TABLE XIII

pK Values of Indicators in DMSO-Ethanol

Not Used to Establish the H_R- Function

Indicator Number	Indicator	Mole % DMSO-EtOH in which half-ionized	pK in DMSO-Ethanol
15	α-cyano-2-chloro-4-nitrostilbene	28.40	16.06
16	1,1-bis-(4-nitrophenyl)-ethene	69.05	19.08

C. Equilibria Studies in Concentrated Sodium Methoxide Solutions

Using the pK value of 14.42 for α-cyano-4,4'-dinitrostilbene as the standard, pK values for a number of substituted α-cyanostilbenes were determined, as described previously, in concentrated sodium methoxide solutions. The plots of log I as a function of the methoxide ion concentration for the various indicators are given in Figure 5. The pK values for the indicators used to establish the H_R- scale have been included in Table X.

Using equation (69), H_R- values were calculated from the pK values listed in Table X and the experimental log I values. The averaged H_R- values for the various concentrations of sodium methoxide in methanol are listed in Table XIV.

In order to compare the H_R- scale with a H_- scale in the same solvent system, the latter was developed using carbon acids as indicators. The method of determining the pK_{HA} values was the same as described above. The plots of log I as a function of the methoxide ion concentrations are given in Figure 6.

By using a pK_{HA} value of 12.88 for methyl fluorene-9-carboxylate, as reported previously by Bowden and Stewart (51), the pK_{HA} values of the other indicators were determined by the graphical method and

FIGURE 5. PLOTS OF LOG $[AOR^-]/[A]$ VERSUS THE CONCENTRATION OF SODIUM METHOXIDE IN METHANOL

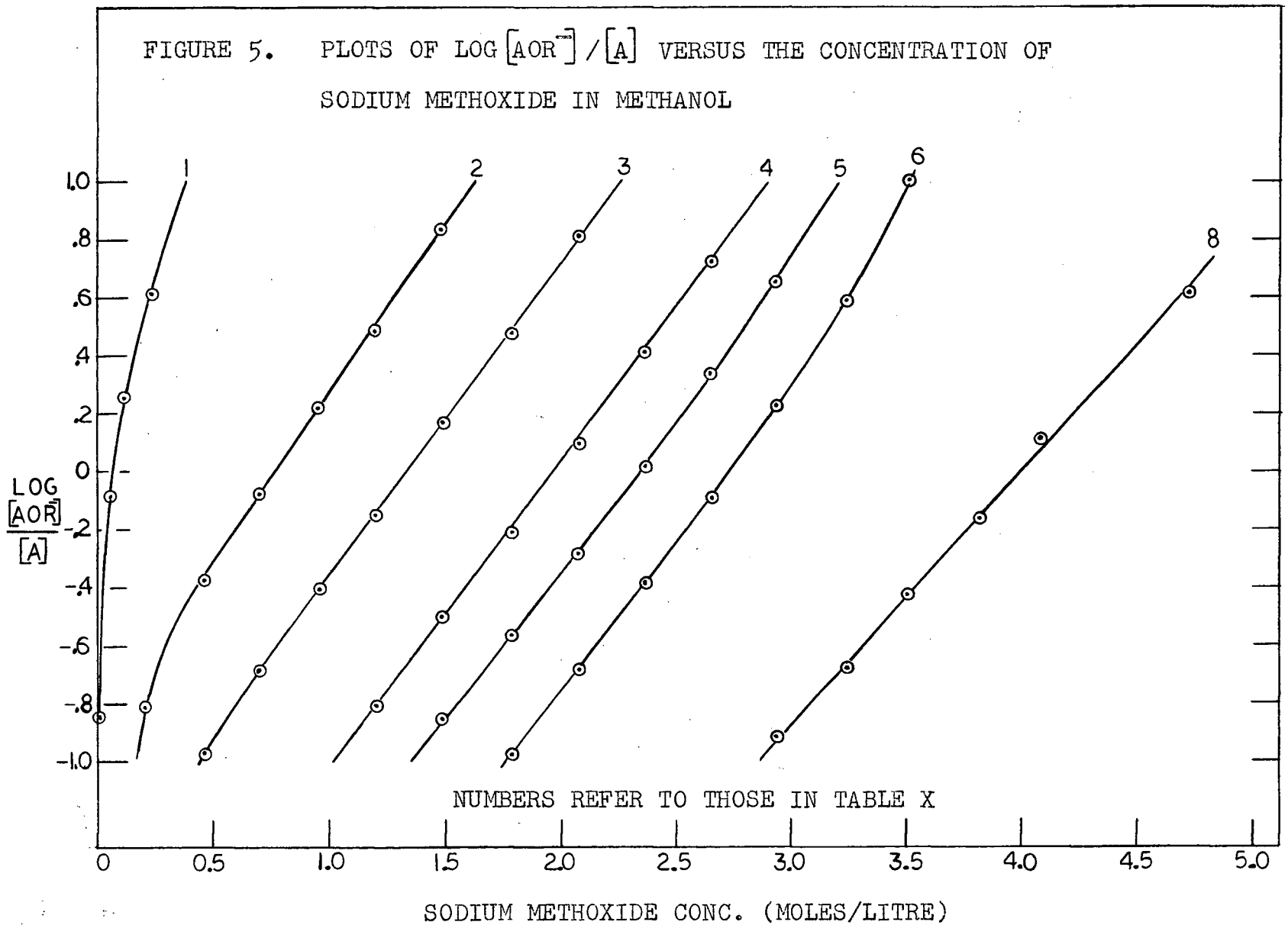


TABLE XIV

H_R- Values for the

Sodium Methoxide-Methanol System at 25°

Sodium Methoxide Conc. (moles l^{-1})	H_R-	Ave. Dev. from the Mean	Indicators[a]
0.01	12.12	-	1
0.0562	12.87	-	1
0.115	13.23	0.02	1, 2
0.229	13.59	0.01	1, 2
0.464	14.06	0.02	2, 3
0.697	14.36	0.01	2, 3
0.952	14.64	0.01	2, 3
1.19	14.91	0.01	2 - 4
1.48	15.23	0.02	2 - 5
1.78	15.53	0.01	3 - 6
2.07	15.83	0.03	3 - 6
2.36	16.13	0.01	3 - 6
2.65	16.44	0.01	4 - 6
2.93	16.75	0.01	5, 6
3.24	17.12	0.05	5, 6, 8
3.51	17.43	0.10	6, 8
3.82	17.60	-	8
4.08	17.88	-	8
4.73	18.37	-	8

a Numbers refer to those in TABLE X, page 84

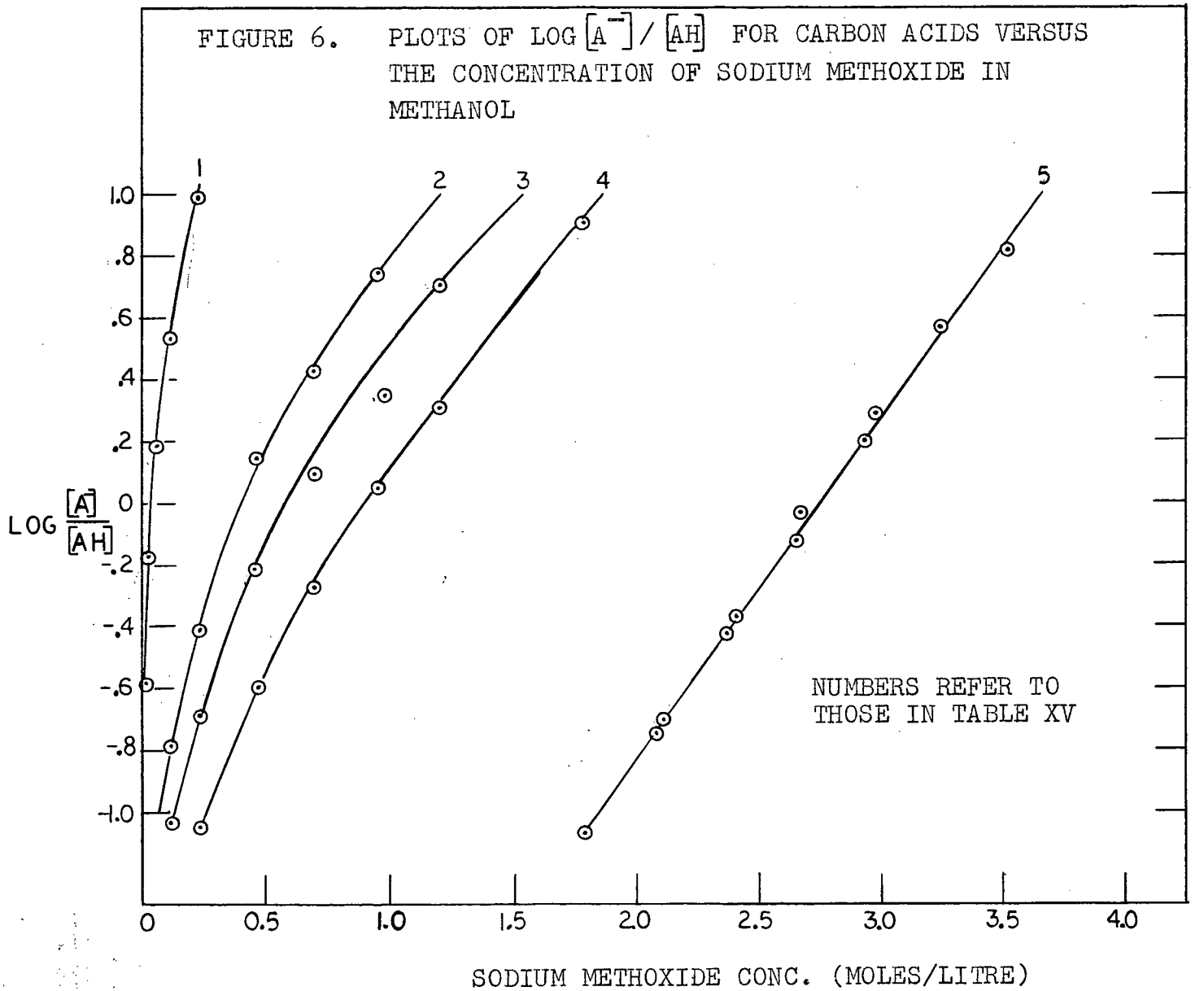


FIGURE 6. PLOTS OF LOG $[A^-]/[AH]$ FOR CARBON ACIDS VERSUS THE CONCENTRATION OF SODIUM METHOXIDE IN METHANOL

are given in Table XV. This table also includes previously reported pK_{HA} values where found in the literature.

TABLE XV

pK_{HA} Values of Indicators
Used to Establish the H_- Scale
in the Sodium Methoxide-Methanol System

Indicator Number	Indicator	pK_{HA}	Lit. value pK_{HA}
1	methyl fluorene-9-carboxylate	12.88[a]	12.88 (51)
2	4-nitrobenzyl cyanide	14.24	13.45 (45, 48)
3	4,4',4"-trinitro-triphenylmethane	14.56	14.32 (51)
4	2-nitrobenzyl cyanide	14.94	
5	4,4'-dinitro-diphenylmethane	16.89	15.85 (51)

a Starting value taken from reference (51)

Using the pK_{HA} values listed in Table XV and the experimental log I values, H_- values were calculated, using equation (30), for the various concentrations of sodium methoxide in methanol. The average H_- values

are given in Table XVI. For easier comparison, the graphical representations of the H_R- and H_- scales are both plotted in Figure 7 as a function of the concentration of sodium methoxide in methanol.

D. Ionization Behavior of Carbon Acids in DMSO-Ethanol Solutions

Because of some large discrepancies in the determined pK_{HA} values listed in Table XV with those found in the literature, a check on the pK_{HA} and H_- values in DMSO-ethanol solutions containing 0.01M sodium ethoxide was attempted. The indicators used for this study are listed in Table XVII. While the ionization data for the indicators, reported as log I values for the various DMSO-ethanol solvent compositions, are listed in Table IX, the graphical representation is shown in Figure 8. Because of the non-paralled slopes of the ionization curves for the various indicators, neither the pK_{HA} values for the indicators nor the H_- values of the medium could be calculated with any degree of certainty.

TABLE XVI

H_- Values for the

Sodium Methoxide-Methanol System at 25°

Sodium Methoxide Conc. (moles l^{-1})	H_-	Ave. Dev. from the Mean	Indicators[a]
0.01	12.26	-	1
0.024	12.71	-	1
0.0562	13.06	-	1
0.115	13.44	0.02	1, 2
0.229	13.86	0.04	1 - 4
0.460	14.35	-	3
0.464	14.36	0.02	2, 4
0.697	14.66	0.01	2 - 4
0.952	14.99	0.0	2, 4
0.977	14.90	-	3
1.19	15.26	0.01	3, 4
1.78	15.83	0.01	4, 5
2.07	16.15	-	5
2.10	16.19	-	5
2.36	16.47	-	5
2.40	16.53	-	5
2.65	16.77	-	5
2.66	16.85	-	5
2.93	17.09	-	5
2.97	17.17	-	5
3.24	17.46	-	5
3.51	17.70	-	5
4.01	18.18	-	5

a Numbers refer to those in TABLE XV

FIGURE 7. H_R- AND H_- VALUES FOR CONCENTRATED SODIUM METHOXIDE SOLUTIONS

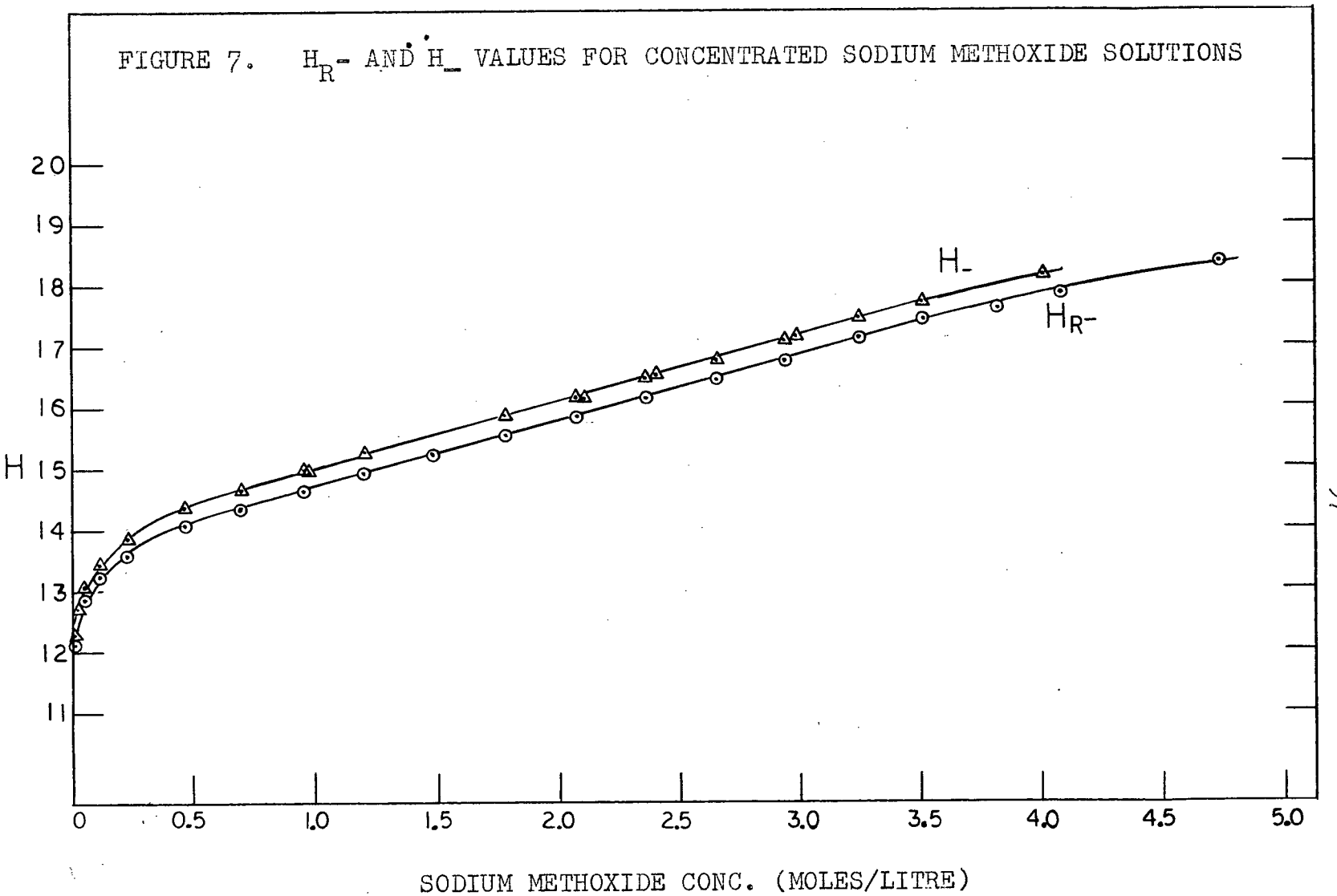


FIGURE 8. PLOTS OF LOG $[A^-]/[AH]$ VERSUS MOLE % DMSO IN ETHANOL FOR VARIOUS CARBON ACIDS

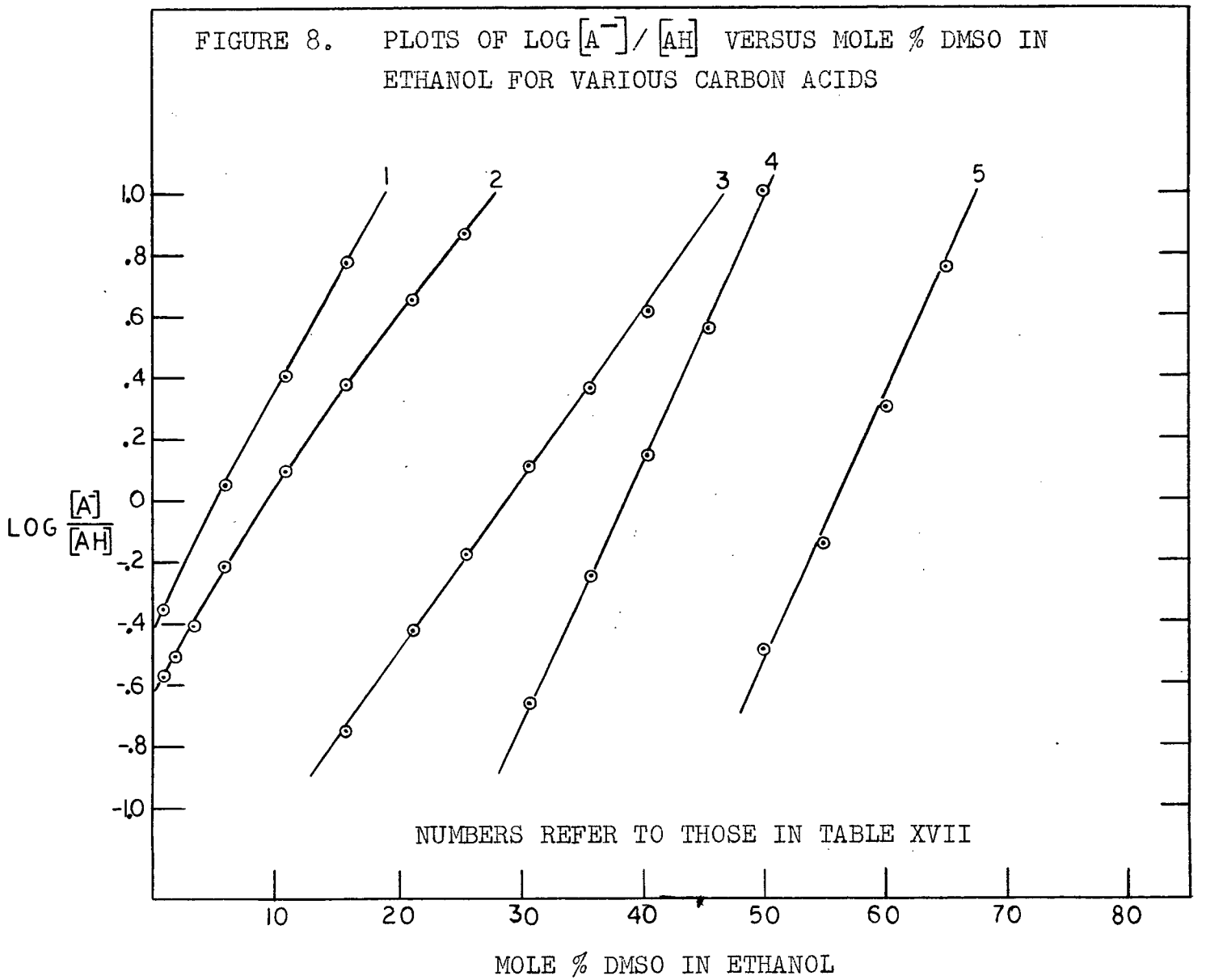


TABLE XVII

Indicators Used in an Attempt
To Establish a H_- Scale in DMSO-Ethanol

Indicator Number	Indicator
1	2-nitrobenzyl cyanide
2	4,4',4"-trinitrotriphenylmethane
3	4,4'-dinitrotriphenylmethane
4	4,4'-dinitrodiphenylmethane
5	1,1-bis-(4-nitrophenyl)ethane

E. Estimate of Error

In any determination of pK and H values by the Hammett overlap method (10), it is very difficult to estimate the absolute error. Errors in pK values for two overlapping indicators are usually in the order of ± 0.02 to ± 0.05. But since these errors may accumulate on going from the most acidic to the least acidic indicators, it is difficult to estimate the error in pK for the less acidic indicators. For these it is estimated that the error in pK is in the order of ± 0.2 to ± 0.3. Thus, although the pK values are listed to two figures, the second significant figure is meaningless unless the

pK values of two overlapping indicators are compared. The accumulation of errors in pK and H values can be minimized by using a large number of indicators so that a large number of points of overlap may be obtained. This reduces the dependence of the value of H on any one indicator. As can be seen from Tables XI, XII, and XIV, H_R- values for one solution have been calculated from as many as four indicators. The situation was not as fortunate in the calculation of the H_- values. Thus the error in the H_- values is likely greater than that in the H_R- values.

F. Kinetics of the Base Catalyzed Cis-trans Isomerization of Substituted α-Cyano-cis-stilbenes in DMSO-Alcohol Solutions

The kinetics of the base catalyzed isomerization of a number of substituted α-cyano-cis-stilbenes was studied in the DMSO-ethanol and DMSO-methanol solvent systems. Since in all cases the α-cyano-trans-stilbenes absorb at a higher wavelength and have a larger molar extinction coefficient than the cis-isomers, following the change in absorbance at the wavelength of maximum absorption of the trans-isomer was a convenient way of following the kinetics. Because approximately 1000 fold excess base was used, first order plots of log $(A_\infty - A_o)/(A_\infty - A_t)$

versus the time gave good straight lines with the apparent first order rate constant being equal to 2.3026 times the slope. A representative plot is shown in Figure 9. This clearly shows that the reaction is first order in the α-cyano-cis-stilbene.

In order to establish the order of the reaction with respect to the base, the isomerization of α-cyano-cis-4-nitrostilbene was studied in methanol using various amounts of base. Table XVIII gives the apparent first order rate constants as a function of the base concentration. The second order rate constant k_2 was calculated by dividing the apparent first order rate constant by the concentration of the base. The constancy of these second order rate constants indicates that the reaction is first order in base.

The extent to which the cis to trans isomerization goes to completion was checked by means of the UV spectra. In the case of α-cyano-4-nitrostilbene, the trans-isomer has a molar extinction coefficient of 2.74×10^4 at 335 mμ. Using a solution in which the concentration of the cis-isomer was 2.97×10^{-5} moles l^{-1}, the absorbance at 335 mμ at the end of the reaction was 0.805 resulting in an extinction coefficient of 2.71×10^4. In another kinetic run, the concentration of the cis-isomer was 2.91×10^{-5} moles l^{-1}. The absorbance at 335 mμ at the end of the reaction was 0.792 resulting in an extinction

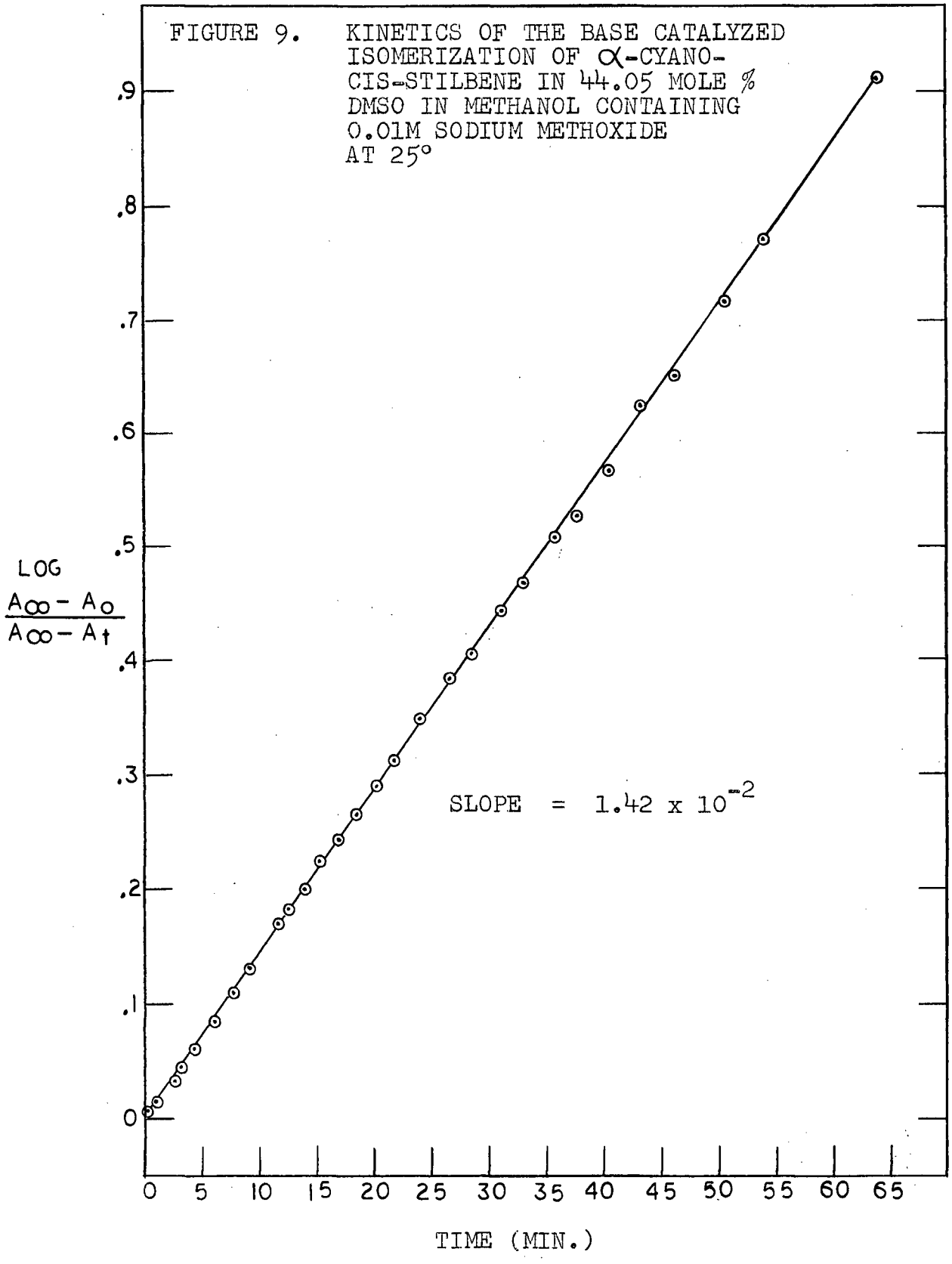


FIGURE 9. KINETICS OF THE BASE CATALYZED ISOMERIZATION OF α-CYANO-CIS-STILBENE IN 44.05 MOLE % DMSO IN METHANOL CONTAINING 0.01M SODIUM METHOXIDE AT 25°
LOG (A∞ - A0)/(A∞ - At)
SLOPE = 1.42 x 10^-2
TIME (MIN.)
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
0 5 10 15 20 25 30 35 40 45 50 55 60 65

TABLE XVIII

Kinetics of the Base Catalyzed Isomerization of α-cyano-cis-4-nitrostilbene in Methanol at 25°

Sodium Methoxide Conc. (moles l^{-1})	k_1 min^{-1}	k_2 l $moles^{-1}$ min^{-1}
0.00548	0.138	25.2
0.0107	0.263	24.5
0.0212	0.504	23.8
0.0412	0.962	23.3

coefficient of 2.72×10^4. In these cases, a comparison of the two extinction coefficients at the end of the reactions (2.71×10^4 and 2.72×10^4) with the extinction coefficient for α-cyano-trans-4-nitrostilbene (2.74×10^4) indicates that these isomerization reactions went essentially to completion.

When the changes in UV spectra of the reactions were followed as a function of time, very good isobestic points were observed. This shows that no substantial side reactions occur in these isomerization reactions.

Since the kinetic study was undertaken to determine the relationship between the rates and the H_R- function, the rates of the base catalyzed isomerization

of various substituted α-cyano-cis-stilbenes were studied at 25° in the DMSO-ethanol and DMSO-methanol solvent systems containing the appropriate 0.01M sodium alkoxide as base. Table XIX contains the logarithms of the apparent first order rate constants, log k_1, for the isomerization in the DMSO-ethanol solvent system. The analogous rate data for the isomerization in the DMSO-methanol solvent system are contained in Table XX. The graphical representations of the data in Tables XIX and XX in the form of plots of log k_1 versus H_R- are given in Figures 10 and 11 for the DMSO-ethanol and DMSO-methanol solvent systems respectively. The slopes of the plots of log k_1 versus H_R- were determined by a least square analysis. These slopes, as well as the correlation coefficient r and the standard deviation of the slope Sρ are contained in Table XXI for the two solvent systems.

In an attempt to gain further insight into the isomerization mechanism, a study of the effect of a change in temperature on the rate was carried out. Using α-cyano-cis-stilbene and α-cyano-cis-3-chlorostilbene, the rates of isomerization in 41.12 mole % DMSO in methanol containing 0.01M sodium methoxide were studied at five temperatures between 10 and 45°. Using α-cyano-cis-stilbene and α-cyano-cis-4-methoxystilbene, the rate of isomerization in 64.21 mole % DMSO in methanol containing 0.01M sodium methoxide

TABLE XIX

Values of log k_1 for the Base Catalyzed Isomerization of Substituted α-Cyano-cis-stilbenes in DMSO-Ethanol Containing 0.01M Sodium Ethoxide at 25°

Mole % DMSO-EtOH	H_R-	Substituent 4-NO_2	3-NO_2	3-Cl	4-Cl	H	4-OCH_3
0.98	14.00	0.029	-0.914				
1.99	14.05		-0.852				
3.51	14.21	0.141	-0.810	-1.878			
5.63	14.38	0.212	-0.724	-1.783	-2.115		
10.82	14.78	0.395	-0.501	-1.560	-1.924		
15.54	15.13		-0.330	-1.377	-1.730		
20.09	15.45		-0.198	-1.169	-1.538		
25.09	15.79			-0.986	-1.339	-2.182	
30.09	16.14			-0.718	-1.126	-1.963	
35.07	16.48			-0.486	-0.875	-1.739	
40.16	16.84			-0.307	-0.686	-1.507	
45.22	17.20				-0.442	-1.286	-2.063
50.27	17.57				-0.236	-1.030	-1.800
55.03	17.92					-0.771	-1.612
59.62	18.29					-0.608	-1.398
64.59	18.68					-0.307	-1.100
69.26	19.06						-0.853
74.15	19.50						-0.551
79.11	20.01						-0.226
84.12	20.52						+0.114
89.17	21.12						+0.558

TABLE XX

Values of log k_1 for the Base Catalyzed Isomerization of Substituted α-Cyano-cis-stilbenes In DMSO-Methanol Containing 0.01M Sodium Methoxide at 25°

Mole % DMSO-MeOH	H_R-	Substituent 4-NO_2	3-NO_2	3-Cl	4-Cl	H	4-OCH_3
0.68	11.83	-0.551	-1.495				
2.32	12.03	-0.492	-1.422				
5.39	12.37	-0.343	-1.266				
8.75	12.72	-0.202	-1.147	-1.981			
15.30	13.38	+0.076	-0.835	-1.726			
20.60	13.87	+0.318	-0.591	-1.430	-1.818		
25.54	14.29		-0.380	-1.197	-1.591		
30.47	14.72		-0.093	-0.957	-1.347		
35.14	15.12			-0.724	-1.158	-1.913	
39.88	15.53			-0.490	-0.898	-1.662	
44.05	15.89			-0.279	-0.682	-1.486	
49.95	16.40				-0.394	-1.136	-1.993
54.79	16.82				-0.117	-0.918	-1.742
59.61	17.25					-0.673	-1.490
64.32	17.63					-0.402	-1.227
69.63	18.14					-0.121	-0.906
74.26	18.59						-0.630
78.52	19.05						-0.374
83.52	19.61						+0.035
88.24	20.17						+0.427

FIGURE 10. PLOTS OF LOG k_1 VERSUS H_R- FOR THE ISOMERIZATION OF SUBSTITUTED α-CYANO-CIS-STILBENES IN DMSO-ETHANOL CONTAINING 0.01M SODIUM ETHOXIDE AT 25°

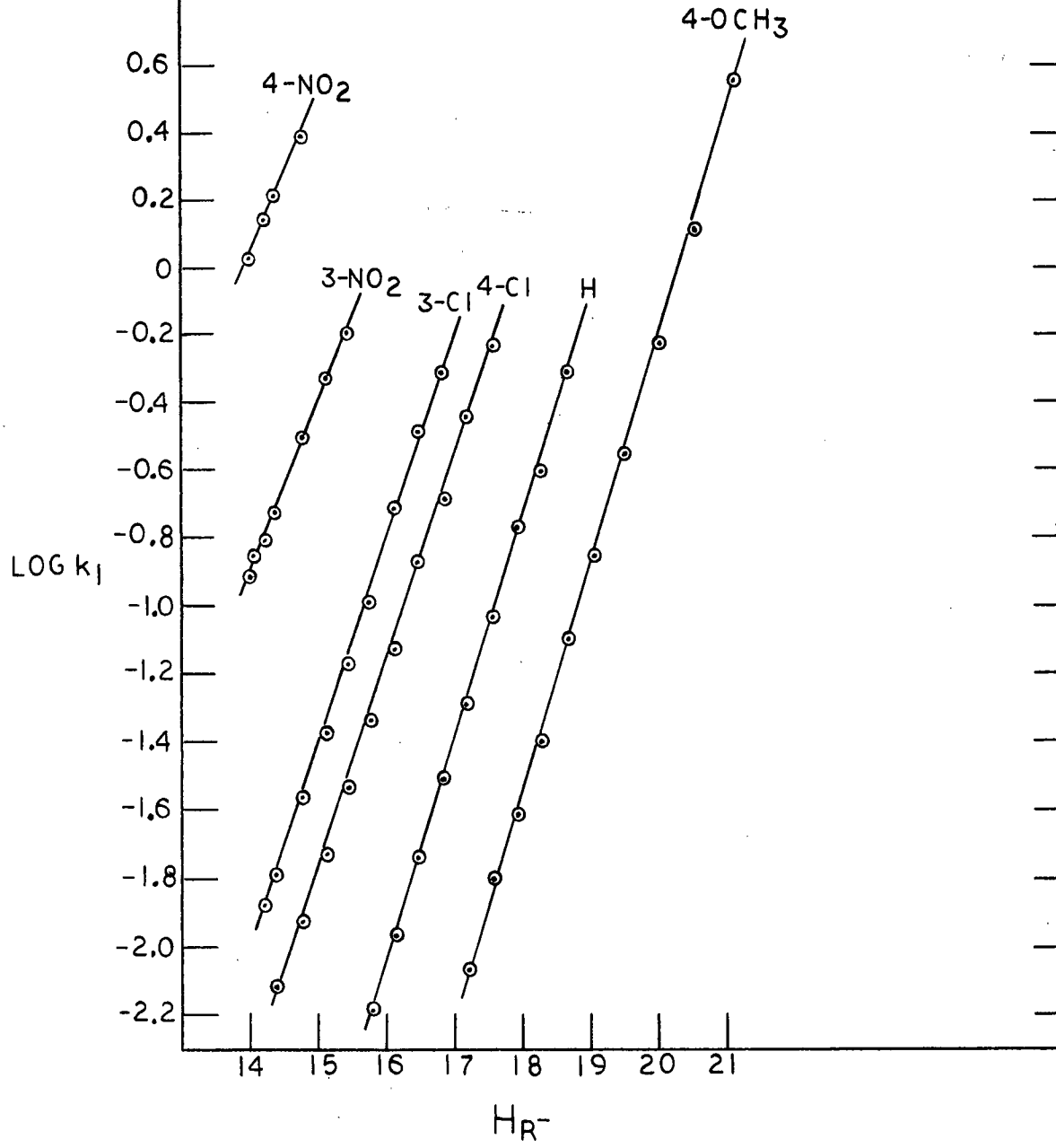


FIGURE 11. PLOTS OF LOG k_1 VERSUS H_R- FOR THE ISOMERIZATION OF SUBSTITUTED α-CYANO-CIS-STILBENES IN DMSO-METHANOL CONTAINING 0.01M SODIUM METHOXIDE AT 25°

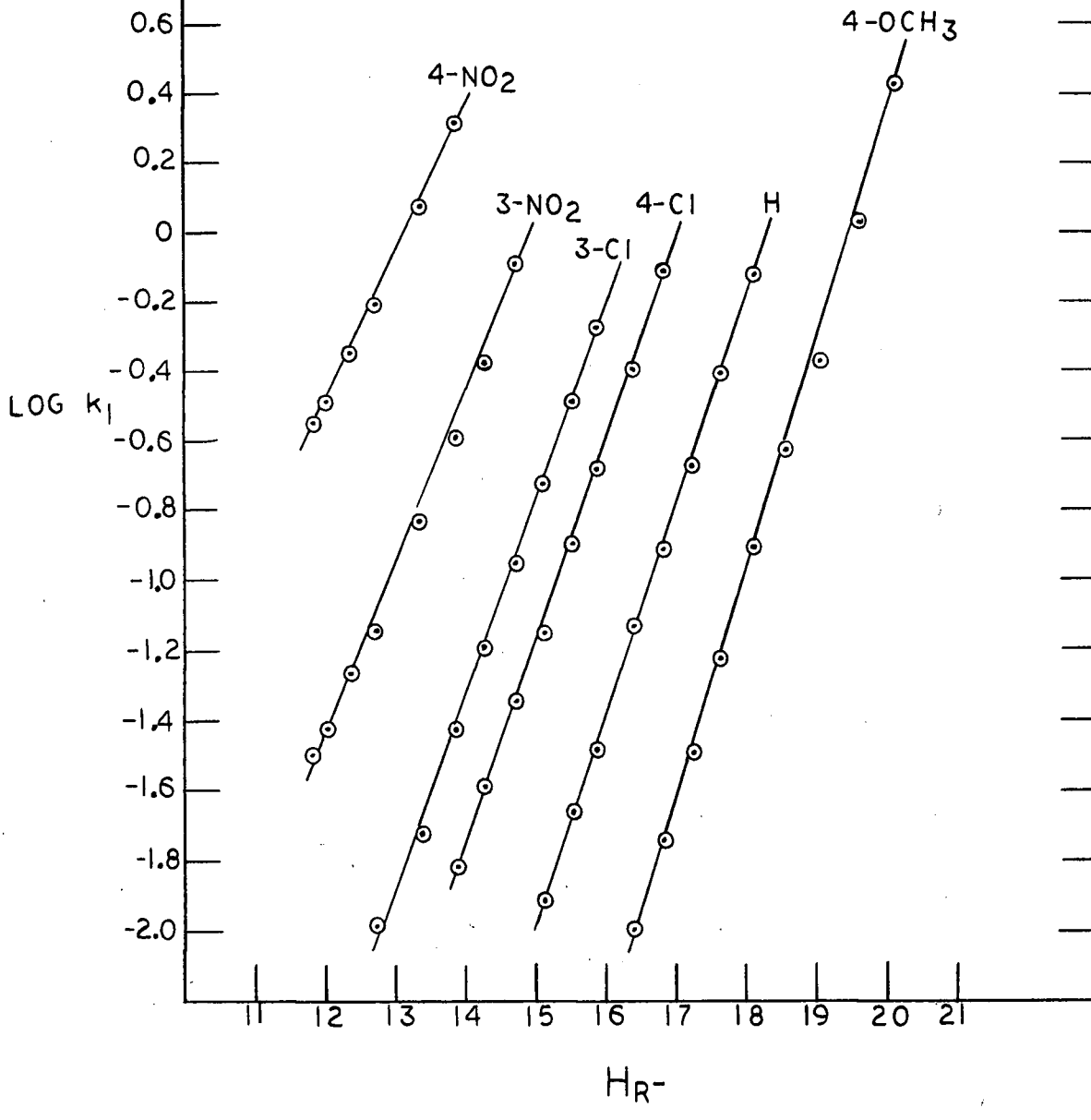


TABLE XXI

Correlation of log k_1 with H_R-
for the Base Catalyzed Isomerization of
Substituted α-Cyano-cis-stilbenes at 25°

Substituent	Slope = $\frac{d(\log k_1)}{d(H_R-)}$	Standard Dev. of the Slope	Correlation Coefficient r
	DMSO-Ethanol		
4-nitro	0.464	0.058	0.9954
3-nitro	0.494	0.013	0.9984
3-chloro	0.607	0.011	0.9989
4-chloro	0.602	0.008	0.9992
hydrogen	0.646	0.008	0.9994
4-methoxy	0.665	0.006	0.9999
	DMSO-Methanol		
4-nitro	0.426	0.009	0.9989
3-nitro	0.475	0.014	0.9972
3-chloro	0.549	0.012	0.9986
4-chloro	0.574	0.008	0.9994
hydrogen	0.595	0.007	0.9994
4-methoxy	0.638	0.007	0.9994

were studied at five temperatures between 10 and 45°. By employing the density measurements of Lindberg (113) at various temperatures, the concentration of the methoxide ion was corrected for the expansion or contraction of the solution. Using these temperature corrected concentrations of methoxide ion, second order rate constants were calculated. The appropriate rate data are contained in Table XXII and the plots of log k_2 versus 1/T°K are shown in Figure 12. A least square analysis of the plots of log k_2 versus 1/T°K gave the slopes. With these, the energies of activation E_a were calculated using the relation (114)

$$E_a = 4.576 \times \text{slope} \qquad (72)$$

The enthalpies of activation $\Delta H^{\ddagger}$ were then determined using the equation (114)

$$\Delta H^{\ddagger} = E_a - RT \qquad (73)$$

where R is the gas constant and T is the absolute temperature. Then by using the transition state theory equation (114)

$$k = \frac{KT}{h} e^{\left(-\frac{\Delta H^{\ddagger}}{RT}\right)} e^{\frac{\Delta S^{\ddagger}}{R}} \qquad (74)$$

TABLE XXII

Rate-temperature Data for the Base-Catalyzed Isomerization of Substituted α-Cyano-cis-Stilbenes in DMSO-Methanol

Substituent	Mole % DMSO	Temp.°K	k_2(l moles^{-1} sec^{-1})	log k_2
3-chloro	41.12	284.26	0.158	-0.800
		291.59	0.308	-0.511
		298.10	0.540	-0.268
		308.34	1.226	+0.088
		317.39	2.522	+0.402
hydrogen	41.12	284.34	0.00924	-2.034
		291.56	0.0201	-1.696
		298.21	0.0358	-1.447
		308.37	0.0894	-1.048
		317.42	0.204	-0.691
hydrogen	64.21	284.26	0.164	-0.784
		291.58	0.323	-0.491
		298.10	0.571	-0.244
		308.34	1.310	+0.117
		317.41	2.770	+0.442
4-methoxy	64.21	284.34	0.0208	-1.682
		291.60	0.0454	-1.353
		298.19	0.0861	-1.065
		308.36	0.220	-0.657
		317.41	0.511	-0.291

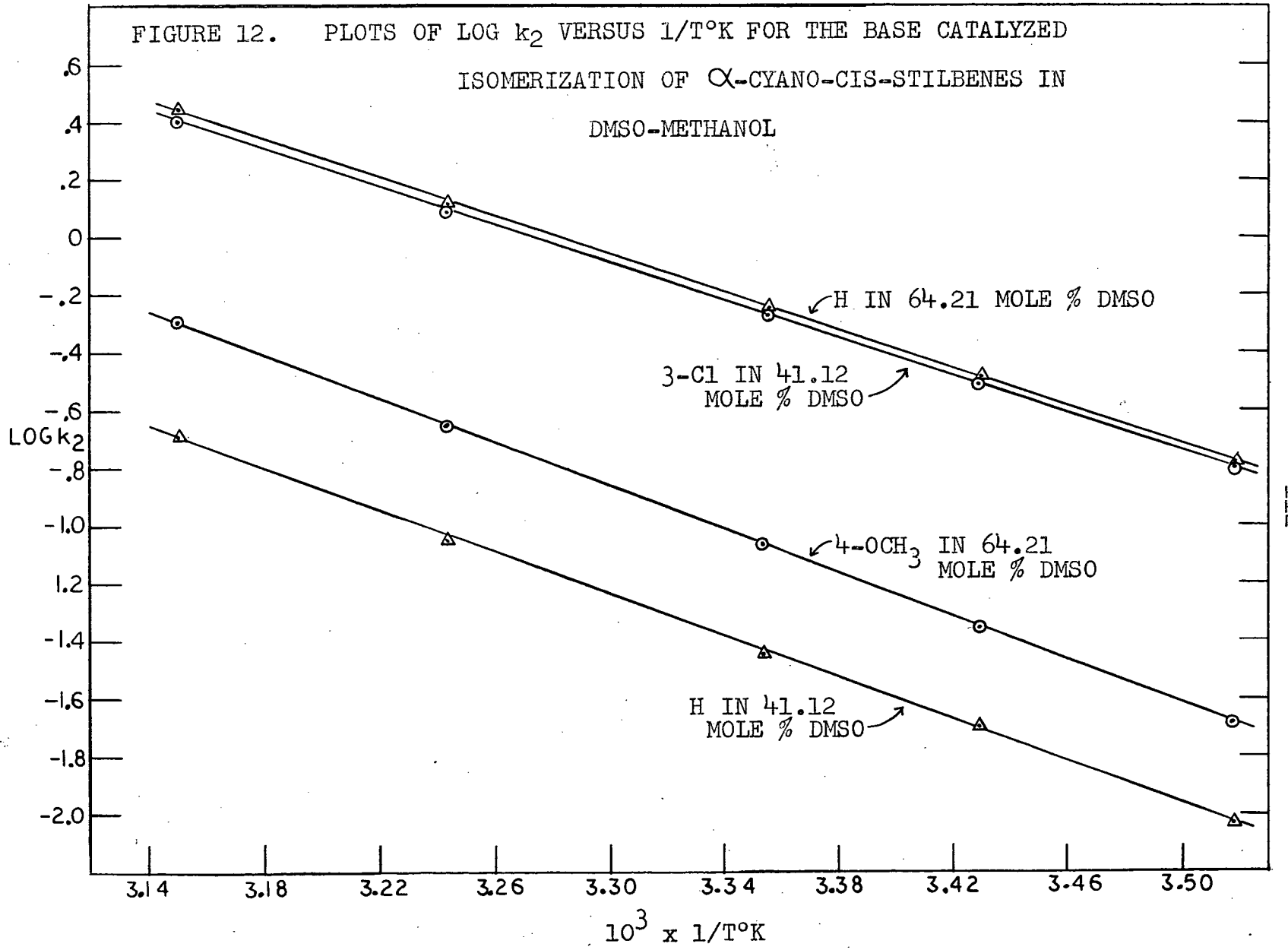


FIGURE 12. PLOTS OF LOG k_2 VERSUS 1/T°K FOR THE BASE CATALYZED ISOMERIZATION OF α-CYANO-CIS-STILBENES IN DMSO-METHANOL
H IN 64.21 MOLE % DMSO
3-Cl IN 41.12 MOLE % DMSO
4-OCH_3 IN 64.21 MOLE % DMSO
H IN 41.12 MOLE % DMSO
LOG k_2
.6
.4
.2
0
-.2
-.4
-.6
-.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
3.14
3.18
3.22
3.26
3.30
3.34
3.38
3.42
3.46
3.50
10^3 x 1/T°K

where: K is the Boltzmann constant,

h is Planck's constant, and

T is the absolute temperature,

the entropies of activation $\Delta S^{\ddagger}$ were calculated, for T equal to 298°K. The activation parameters are summarized in Table XXIII.

TABLE XXIII

Activation Parameters for the Base Catalyzed Isomerization of Substituted α-Cyano-cis-stilbenes in DMSO-Methanol

Substituent	Mole % DMSO	E_a (kcal. moles^{-1})	$\Delta H^{\ddagger}$ (kcal. moles^{-1})	$\Delta S^{\ddagger}$ (e.u.)
3-chloro	41.12	14.93 ± 0.05	14.34	-13.7
hydrogen	41.12	16.59 ± 0.25	16.00	-13.5
hydrogen	64.21	15.21 ± 0.04	14.61	-12.6
4-methoxy	64.21	17.32 ± 0.09	16.72	- 9.3

G. The Reaction of α-Cyano-α'-methoxy-cis- and trans-stilbenes in DMSO-Methanol Solutions

In order to establish that the base catalyzed isomerization of the α-cyano-cis-stilbenes did not take place by proton removal, the two isomers of α-cyano-α'-methoxy-stilbene were prepared. A preliminary study was carried out on the isomerization of the lower melting isomer, taken to be the cis-stilbene. In 74.26 mole % DMSO in methanol, the lower melting isomer had a maximum absorption at 290 mμ. When sodium methoxide was added to the solution, the wavelength of maximum absorption changed gradually to 287 mμ and the absorbance increased somewhat. On the other hand, in 74.26 mole % DMSO in methanol, the higher melting isomer had a maximum absorption at 286 mμ. When sodium methoxide was added to this, the wavelength of maximum absorption shifted to 287 mμ and the absorbance dropped somewhat.

H. The Reaction of 1,1-bis-(4-nitrophenyl)ethene in Highly Basic Systems

The electronic spectra of 1,1-bis-(4-nitrophenyl)-ethene in DMSO-methanol has an absorption maximum at 306 mμ. When enough sodium methoxide solution was added to make a 0.01M solution, the absorbance at 306 mμ decreased and a peak with a maximum absorption at 710 mμ

was formed. On making the solution acidic by the addition of acetic acid, the absorption at 710 mμ disappeared with the peak in the region of 282 to 306 mμ reappearing, the exact location of the latter depended on the mole % DMSO used. As the concentration of DMSO was increased from 60 to 90 mole %, the wavelength of maximum absorption of the species formed when the reaction was quenched with acetic acid decreased from 299 mμ to 282 mμ with a fairly good isobestic point at 294 mμ.

I. The Reaction of 4,4'-Dinitrobenzophenone in Highly Basic Systems

When tetramethylammonium hydroxide was added to a solution of 4,4'-dinitrobenzophenone in DMSO, an absorption peak with a maximum at 434 mμ developed very quickly. When acetic acid was added, this peak disappeared virtually instantaneously.

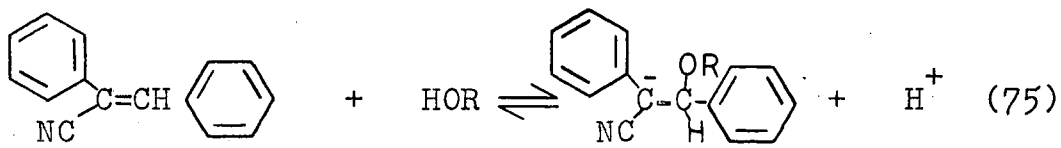
It was also found that the anion of 4-nitrophenol had a maximum absorption at 434 mμ in DMSO with a molar extinction coefficient of 3.38×10^{4}. Since the concentration of 4,4'-dinitrobenzophenone was 2.88×10^{-5} moles l^{-1}, if one mole of p-nitrophenolate ion was produced per mole of 4,4'-dinitrobenzophenone, then the expected absorbance at 434 mμ would be 0.973. Since the observed absorbance at 434 mμ was 0.900, the ratio of the observed to the calculated absorbances was 0.900/0.973 = 0.925.

It was also noted that at lower concentrations of DMSO in water, the rate of increase in the absorbance at 434 mμ occurred at a measurable rate.

DISCUSSION

A. The Validity of the H_R- Function

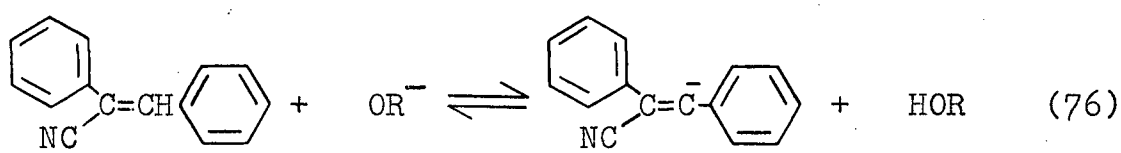
The H_R- function has been developed to describe the basicity of a solution in which the base adds to an unsaturated system to form the negatively charged species. The α-cyanostilbene system of indicators was chosen as an appropriate system to study such an equilibrium addition of base. This equilibrium is described in the equation



(75)

That the equilibrium studied was that described in equation (75) is fairly certain. There are several other possible methods of ionization which will now be discussed.

Instead of ionizing by an equilibrium addition of the Lewis base a proton might be abstracted by the base. Then the equilibrium



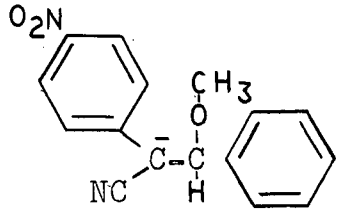
(76)

XVIII

would give rise to a H_- function. That such an ionization

is possible in the case of stilbenes was shown by Hunter and Cram (81) by deuterium exchange studies. By using potassium t-butoxide in t-butanol they showed the half life for the deuterium exchange at 116° to be approximately 100 hours. This shows that the deuterium exchange is very slow and that the equilibrium, as expressed in equation (76), must be far to the left. In addition, Zinn et al (115) were able to show that while ethyl cinnamate, ethyl β-phenylcinnamate, chalcone and trans-cinnamonitrile underwent deuterium exchange at the α-position in deuterioethanol with catalytic amounts of sodium ethoxide, ethyl α-phenylcinnamate did not undergo any deuterium exchange at all. These two pieces of evidence strongly suggest that the ionization does not involve the removal of the proton from the β-carbon to a significant extent.

Spectral evidence is also in support of the ionization by equation (75) rather than by equation (76). It would be expected that the electronic spectra of the anions XIX and XX would be very similar. In fact the



XIX

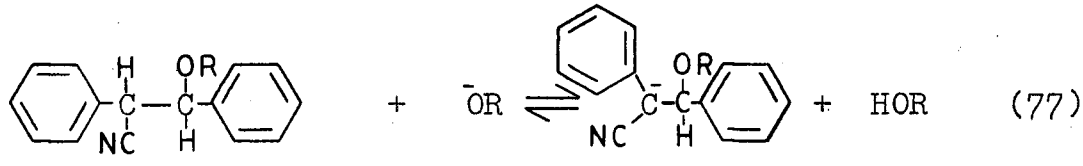
XX

electronic spectra of XIX has a maximum at 548 mμ in DMSO-

methanol and XX has a maximum at 540 mμ in 95 mole % sulfolane in water (116) with the general shape of the spectra being similar as well. Such a close similarity would not be expected for the electronic spectra of structures XVIII and XX.

The effect of substituents on the equilibrium (vide infra) also strongly supports alkoxide addition rather than proton removal.

Another equilibrium which is possible in basic solutions is the proton removal from the alcohol addition product.



(77)

This equilibrium is always possible for all the indicators used to establish the H_R- scale; but, whether it is important or not depends on the relative pK values for equilibria (75) and (77). If 4-nitrobenzyl cyanide can be taken as a model compound for the reaction shown in equation (77), then we can obtain some idea as to the relative pK values for the two processes. The pK_{HA} value most often quoted for 4-nitrobenzyl cyanide is 13.45 (45, 48). This value can be taken as a rough estimate even if the ionization behavior of 4-nitrobenzyl

cyanide is in doubt (116). The estimated pK value for the addition of ethoxide ion to α-cyano-4-nitrostilbene is 15.95 in DMSO-ethanol. At a H_R- value of 14.95, the ratio of the ionized to unionized forms of α-cyano-4-nitrostilbene would be 0.10. This is approximately the lower limit of possible measurements. If the H_R- and H_- values are approximately equivalent in this region, 4-nitrobenzyl cyanide would be 97% ionized. This indicates that only a small amount of the alcohol adduct was present at any time and that the equilibrium measured was really that in equation (75).

Spectral evidence also supports the above argument. The alcohol adduct does not absorb to an appreciable extent in the region where the α-cyano-stilbene absorbs. Thus if equation (77) made an appreciable contribution to the overall equilibrium, no isobestic point would be observable. The fact that a reasonable isobestic point was obtained again indicates that the reaction shown in equation (77) does not make an appreciable contribution to the overall equilibrium.

The use of the Hammett postulate (9, 10) to establish an acidity scale H_R- using a series of structurally similar indicators seems to be justified. The Hammett postulate (9, 10) stipulates that the value of $(\log I_i - \log I_j)$ be constant for two overlapping

indicators when measured in the same solution. This implies that the activity coefficient ratio in equation (10) is close to unity. The close parallelism between lines for overlapping indicators when log I was plotted against solvent composition can be seen from Figures 1, 2 and 5. This conforms to the basic Hammett postulate. This is also shown, in a different way, in the small relative error in the values of H_R- calculated for one solution from the ionization data for several indicators (see Tables XI, XII and XIV).

The Hammett postulate also implies that the pK values should be independent of the solvent system. In cases where a Lewis base is involved, this must be restricted to the same base in different solvent systems (4). That this holds fairly well for DMSO-methanol and sodium methoxide-methanol solutions can be seen from Table X. On closer inspection of the pK values in DMSO-methanol and sodium methoxide-methanol, it can be seen that apart from indicators 1 and 8, the other indicators differ, at the most, by 0.08 pK units in the two solvent systems. This is a good indication that the pK values for the equilibrium addition of methoxide ion to α-cyanostilbenes is independent of the solvent in which measured.

The difference in the measured pK values for

α-cyano-4'-dimethylamino-4-nitrostilbene in DMSO-methanol and sodium methoxide-methanol is 0.20 units. This indicator was the last one used in the sodium methoxide-methanol system. Because of this there was doubt as to whether the indicator was completely ionized in the most basic solution used. As a result, the difference in the pK values for this indicator in the two solvent systems is likely an experimental error.

The difference in the pK values for α-cyano-2,4-dinitrostilbene of 0.23 units in the two solvent systems is more serious. Since the pK of α-cyano-4,4'-dinitrostilbene was taken as an arbitrary starting point in all solutions, the difference in ΔpK between the two indicators due to solvent change is a direct reflection on the reliability of the experimental measurements. It should first of all be noted that the ΔpK value between the two indicators was found to be 1.69 in DMSO-methanol. This is nearing the limit for effective overlap. As the amount of overlapping in the ionization curves of two indicators decreases, the error in the ΔpK values increases because, in the first place, of a smaller number of experimental points over which the ΔpK values can be averaged. The increased error also arises from the fact that the most accurate spectral measurements are possible when the indicator is between 10 and 90%

ionized. As these limits are reached, errors in individual spectral measurements increase and are reflected in the error of the ΔpK measurements. Associated with these two causes is the rapid rise in H_R- at low concentrations of sodium methoxide in methanol. It was felt that these causes of error were enough to explain the difference of 0.23 units in the pK values for indicator number 1 in the two solvent systems.

B. Interpretation of the Lewis Basicity of the Solutions

The addition of DMSO to ethanol or methanol containing 0.01M sodium alkoxide was found to have a profound effect on the ability of the alkoxide ion to act as a Lewis base. The H_R- values were found to increase from 14.00 in 0.98 mole % DMSO in ethanol to 21.74 in 93.27 mole % DMSO in ethanol and from 11.73 in methanol to 21.65 in 97.61 mole % DMSO in methanol. In the first case, the Lewis basicity of the ethoxide ion increases by approximately 7 powers of 10 and in the second case, the Lewis basicity of the methoxide ion increases by about 10 powers of 10. This shows that DMSO has a substantial effect on the Lewis basicity of the alkoxide ions.

From equation (69), with the aid of equation (65), the expression

$$H_{R^-} + \log K_{HOR} = \log (OR^-) + \log \frac{f_A}{f_{AOR^-}} \qquad (77)$$

can be obtained. From this, it can be seen that the value of H_{R^-} is dependent on two terms: the logarithm of the activity of the alkoxide ion and the logarithm of the activity coefficient ratio. Because little is known about activity coefficient behavior in alcohol solutions, to a first approximation, it can be assumed that the last term in equation (77) makes only a small contribution to the H_{R^-} value. If this is so, then the increase in the H_{R^-} value must be due to an increase in the activity of the alkoxide ion.

The activity of the alkoxide ion could be increased by desolvation. If the alkoxide ion is somewhat like the hydroxide ion (35, 43) then it is likely that the alkoxide ion has around it a sheath of solvating protic solvent molecules. The number of methanol molecules solvating the methoxide ion have been estimated to range from 3 to 5.6 for various hindered phenols (41). Thus, as the proportion of DMSO is increased, the amount of alcohol available to solvate the alkoxide ion will be decreased. This may account for the rise in the H_{R^-} value as the amount of alcohol present becomes small.

It has also recently been proposed that the increase in activity of the methoxide ion as DMSO is added could be the result of a breakdown of the methanol

solvent structure (117). The structure of methanol has been considered to be psuedo polymeric (118). That the addition of DMSO to methanol has a disruptive effect on the solvent structure of methanol can be seen from the NMR spectrum (119). On adding DMSO to methanol, the proton resonance is shifted to a higher field. This was regarded as meaning that the hydrogen bond between two methanol molecules is stronger than that between a methanol and a DMSO molecule. The disruptive effect of DMSO on the structure of methanol is also evident from viscosity measurements. The viscosity of DMSO-methanol mixtures was reported to show negative deviations, although small, from what would be expected from additive considerations (113). A greater fluidity than expected on the addition of DMSO is in agreement with a breakdown of the structure of methanol.

C. The Validity of the H_- Scales

There appears to be some doubt as to the validity of the H_- scale in sodium methoxide-methanol solutions. Some evidence points towards it being a valid self-consistent scale whereas other evidence is not as favorable.

On looking closely at the ionization behavior of the indicators used, it can be noted from Figure 5 that the plots of log I versus the concentration of

sodium methoxide are quite closely parallel. This, then, points towards the Hammett postulate applying in this case. The small relative error in the H_- value calculated for one solution from the ionization data for several overlapping indicators (see Table XIV) is also in agreement with the above Hammett postulate.

On the other hand, the discrepancies between the determined pK_{HA} values and those found in the literature are, to say the least, disturbing. A large discrepancy exists between the determined pK_{HA} value for 4-nitrobenzyl cyanide (14.24) and that reported in the literature (13.45) (45, 48). But this may be misleading since it was found that 4-nitrobenzyl cyanide was half ionized in 0.38M sodium methoxide containing 0.67 mole % DMSO whereas O'Ferrall and Ridd (39) reported it to be half ionized at approximately 0.5M sodium methoxide. Since the small amount of DMSO would tend to increase the H_- value by approximately 0.1 unit, the two results are fairly close considering that the difference in H_- values between 0.38M and 0.50M sodium methoxide is 0.2 units.

An even larger discrepancy exists in the case of 4,4'-dinitrodiphenylmethane. In sodium methoxide-methanol solutions, the ΔpK_{HA} value between methyl fluorene-9-carboxylate and 4,4'-dinitrodiphenylmethane was found to be 4.01 pK_{HA} units whereas Bowden and Stewart

(51) reported a value of 2.97 in the DMSO-ethanol solvent system. This amounts to a difference of over a unit in the ΔpK_{HA} values on going from methanol to DMSO-ethanol. These differences may be due to a solvent effect. In the majority of cases, the differences in the ΔpK values on going from one solvent to another, for example on going from water to methanol to ethanol, are not large but differences as great as 1 pK unit are not uncommon (120a). For example, the ΔpK_{BH^+} value between 4-nitro- and 4-fluoroanilines in methanol was reported to be 4.199 and in ethanol to be 4.759 (121). This results in a difference of 0.56 pK units in the ΔpK_{BH^+} values determined in methanol and ethanol.

In order to further check the differences in the ΔpK_{HA} values as measured in methanol and ethanol, the previous work in DMSO-ethanol was repeated. The ionization behavior of the various indicators is illustrated in Figure 8. This figure clearly illustrates that the plots of log I versus solvent composition for 4,4',4"-trinitrotriphenylmethane and 4,4'-dinitrodiphenylmethane are neither parallel nor do they overlap to any extent. Both parallelism and good overlapping are of paramount importance in the establishment of a H_- scale. In order to achieve the overlap, 4,4'-dinitrotriphenylmethane was prepared. Although a plot of log I versus solvent

composition for 4,4'-dinitrotriphenylmethane overlapped with that for 4,4',4"-trinitrotriphenylmethane and 4,4'-dinitrodiphenylmethane, the ionization behavior of 4,4'-dinitrodiphenylmethane was not parallel to that of the other two, which were parallel between themselves. Furthermore, the maximum absorption of the electronic spectra of the anions of both 4,4',4"-trinitrotriphenylmethane and 4,4'-dinitrotriphenylmethane underwent such drastic shifts in wavelength as the DMSO content was increased -- shifts of around 100 mμ to higher wavelengths were observed -- that attempts to correct for these shifts were impossible. With such large shifts, there was no assurance that the extinction coefficients did not change as well as the wavelength of maximum absorption with a change in solvent. This clearly indicates that indicators like 4,4',4"-trinitrotriphenylmethane and 4,4'-dinitrotriphenylmethane cannot be used to establish a H_- scale in DMSO-ethanol solutions. This of course also points to the necessity of redetermining the H_- scale for carbon acids in DMSO-ethanol solutions.

The difficulties encountered in the equilibria measurements using carbon acids in DMSO-ethanol were not encountered in sodium methoxide-methanol solutions. Thus it is reasonable to expect that the H_- scale for carbon acids in the sodium methoxide-methanol system is a self-consistent one with some validity.

D. The Comparison of the H_{R^-} Scales with other Scales

Before comparing the H_{R^-} scales with other scales, it is necessary to explain the choice of H_{R^-} as a symbol for the acidity function describing the equilibrium addition of base to an unsaturated system. Rochester has already used the symbol J_- for such an acidity function (58) in which the relationship between J_- and H_- was given by equation (43). This relationship is the same as that between J_o and H_o, which was given by equation (22). In both cases, the activity coefficient term was assumed to be unity. In the acid region, Deno, Jaruzelski and Schriesheim (28) were able to show that the activity coefficient ratio was not unity and thus established the acidity function H_R given by equation (24). Since h_- was given by equation (31) and h_{R^-} by equation (70), then

$$\frac{h_{R^-}}{h_-} = \frac{f_{AOR^-}\, f_{AH}}{(HOR)\, f_A f_{A^-}} \qquad (78)$$

and

$$H_{R^-} - H_- = \log(HOR) - \log \frac{f_{AOR^-}\, f_{AH}}{f_A f_{A^-}} \qquad (79)$$

By using equations (43) and (79), the relationship between

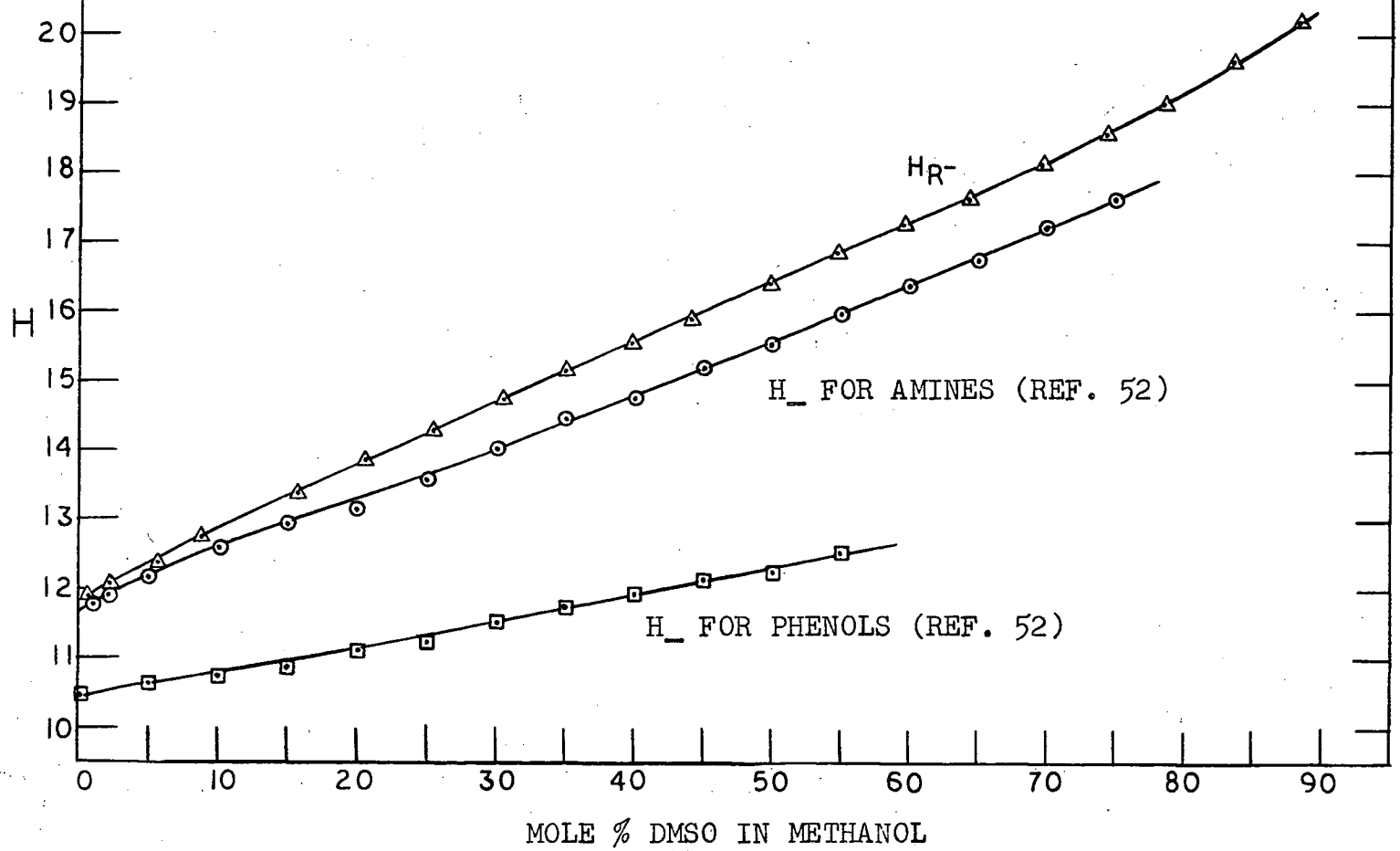
H_{R^-} and J_- is given by the expression

$$H_{R^-} - J_- = \log \frac{f_{A^-}}{f_{AOR^-}} \qquad (80)$$

From this it can be seen that the relationship between H_{R^-} and J_- is identical to that between H_R and J_o. Therefore the symbol H_{R^-} was chosen in keeping with the symbolism developed by Deno et al (29) and now in general use.

If, in the first approximation, the activity coefficient term in equation (79) can be neglected, then for acids having approximately the same solvation requirements, the H_- scale should rise faster than the H_{R^-} one as the activity of the alcohol decreases. That this is not so for the acidity scales established so far in highly basic solutions containing DMSO can be seen from Figure 13. In referring to equation (79), it is reasonable to assume that the activity coefficient ratio for neutral species, f_{AH}/f_A, would be close to unity. Then, for the H_{R^-} scale to rise faster than the H_- scale as the DMSO content in the system is increased suggests that the activity coefficient term f_{AOR^-} for the base adduct for carbon-carbon unsaturated systems must decrease more rapidly than the activity coefficient term f_{A^-} for anions from nitrogen or oxygen acids. This may be due to carbanions having

FIGURE 13. A PLOT OF H VALUES VERSUS MOLE % DMSO IN METHANOL CONTAINING 0.01M SODIUM METHOXIDE FOR VARIOUS INDICATORS



greater solvation requirements than nitrogen or oxygen anions.

In the DMSO-ethanol solvent system, the H_R- and H_ scales for carbon acids (51) cannot be compared since it was pointed out previously that the validity of the H_ scale for carbon acids was in doubt.

The H_R- and H_ scales were both determined in the sodium methoxide-methanol solvent system. For greater ease of comparison, these two scales have been plotted on one graph in Figure 7. At low concentrations of sodium methoxide, the H_ scale rises more quickly than the H_R- scale; but from 0.8 to 4.0M sodium methoxide, the two scales are almost parallel. The comparison of the H_R- and H_ scales, by using the activity values for methanol in sodium methoxide solutions reported recently by Freeguard, Moodie and Smith (122), is given in Table XXIV. Because the two scales have slightly different starting points, the differences (H_R- - H_) were adjusted so that it is zero at the lowest methoxide ion concentration used. By inserting the experimental values for H_R-, H_ and log(CH_3OH) into equation (79), it is possible to calculate values of log f_{AOR^-}/f_{A^-} and f_{AOR^-}/f_{A^-}. These values are given in the last two columns of Table XXIV. From this, it can be seen that the assumption that f_{AOR^-}/f_{A^-} is close to unity is obeyed to a reasonable extent for these two scales. This is in contrast to the

relationship between the H_R and J_o scales in sulfuric acid solutions where the difference between the two scales (H_R - J_o) was found to decrease to a value of -5 at 82% sulfuric acid (28).

In comparing the H_R and J_o functions, the activity coefficient f_{R^+} refers to a carbonium ion whereas the activity coefficient $f_{ROH_2^+}$ refers to a species with the positive charge residing on the oxygen. The two species R^+ and ROH_2^+ then likely have different solvation requirements resulting in the ratio of the activity coefficients being different from unity. However, in comparing the H_{R^-} and J_- functions, the negative charge in the carbanions AOR^- and A^- resides on a carbon atom in each case. In this case, the two negatively charged species are quite similar and therefore the ratio of the activity coefficients would likely be close to unity.

According to the above evidence, it is likely that Rochester's J_- values in sodium hydroxide solutions (71) are reasonably close to the H_{R^-} values, if these could be determined in the aqueous system. One doubtful point remaining is that the H_- values used by Rochester (71) were based on nitrogen indicators and this scale may not be entirely applicable to carbon acids.

TABLE XXIV

The Comparison of the H_R- and H_- Scales in Concentrated Sodium Methoxide Solutions

Sodium Methoxide Conc. (moles l^{-1})	$(CH_3OH)^a$	log (CH_3OH)	H_R- - H_- [b]	log (CH_3OH) - log $(H_R$- - $H_-)$	f_{AOR}-/f_{A}-
0.01	0.999	0.000	0	0	1
0.0562	0.997	-0.001	-0.05	+0.049	1.12
0.115	0.991	-0.004	-0.07	+0.066	1.16
0.229	0.981	-0.008	-0.13	+0.122	1.32
0.464	0.960	-0.018	-0.16	+0.142	1.39
0.697	0.939	-0.027	-0.16	+0.133	1.36
0.952	0.913	-0.040	-0.21	+0.170	1.48
1.19	0.886	-0.053	-0.21	+0.157	1.44
1.78	0.804	-0.095	-0.16	+0.065	1.16
2.07	0.767	-0.115	-0.18	+0.065	1.16
2.36	0.722	-0.142	-0.20	+0.058	1.14
2.65	0.680	-0.168	-0.19	+0.022	1.05
2.93	0.639	-0.194	-0.20	+0.006	1.01
3.24	0.598	-0.223	-0.20	-0.023	0.95
3.51	0.563	-0.250	-0.13	-0.12	0.76

a Taken from Reference (122)

b Taken from Tables XIV and XVI and corrected for the difference at 0.01M Sodium Methoxide

E. A Comparison of pK Values

A comparison of the pK values for the various indicators in Table X, shows that the pK values determined in the DMSO-ethanol system are, with one exception, all larger than those determined in the DMSO-methanol system. This may reflect a solvent effect on the pK values. It has already been mentioned that differences as great as 1 pK unit in the ΔpK values between two indicators on going from one solvent to another are not uncommon (120a).

A solvent effect on the pK values, however, does not give the complete picture. When studying the equilibrium addition of alkoxide ions to unsaturated systems, the complete base molecule is involved in the carbanion. It is therefore not necessary, and hardly expected, that the pK values for one indicator using two different bases should be identical.

The pK values for the equilibrium addition of ethoxide ion to two unsaturated compounds were measured but were not used in the calculation of the H_R- scale. The indicator α-cyano-2-chloro-4-nitrostilbene was not used to calculate the H_R- scale because the plot of log I versus the solvent composition is not parallel to that of the other indicators. This may be due to impure material since insufficient material was obtained for complete purification. In any case, it is interesting

that the pK value, determined from the H_R- value of the solution in which the indicator was half ionized, is higher than that for α-cyano-4-nitrostilbene. This may reflect a steric effect of the ortho-chloro group. In this regard it can be noted that α-cyano-2-nitrostilbene was found to have an abnormally high pK value of 20.11 when compared to a pK value of 15.95 for α-cyano-4-nitrostilbene in DMSO-ethanol solutions. These results cannot be explained on the basis of electronic effects since these would be expected to be nearly the same for the nitro group in the two positions. Here again, a steric effect of the ortho group may explain the results. The substituents in the ortho position may be causing the phenyl ring to twist to some degree. This would cause the amount of resonance interaction between the nitro group and the α-carbanion center to be reduced. Since the nitro group strongly stabilizes an α-carbanion by resonance interaction, any reduction in this resonance interaction will increase the pK value of the indicator.

Other cases where an ortho-nitro group exhibits a weaker acid strengthening effect than the para-nitro group are known. For example, the pK_{HA} for 2-nitrodiphenylamine (17.91) is greater by 2.24 units than that for 4-nitrodiphenylamine (15.67) (49). Similarily, the pK_{HA} for 2-nitrophenol (7.22) is 0.07 units greater than that for 4-nitrophenol (7.15) (8). The greater pK_{HA} values

for the ortho-nitro acids in these two cases can be attributed to a hydrogen bonding effect. However, this argument cannot be used to explain the higher pK value for α-cyano-2-nitrostilbene as compared to that for α-cyano-4-nitrostilbene. In the equilibrium addition of ethoxide ion to an alkene, no hydrogen bonding effect is possible.

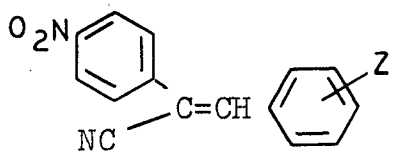
Although the ionization curve for 1,1-bis-(4-nitrophenyl)ethene is parallel to that for the other indicators, the structure of this indicator is quite different from that of the other indicators used to establish the H_R- scales. None the less, this ethene appeared to be a good indicator and its reactions in basic systems will be discussed later.

F. Correlation of Structure with Lewis Acidity

An inspection of Table X shows that the Lewis acidities of substituted α-cyano-stilbenes are very sensitive to the type of group present in the phenyl rings. One of the most widely used methods of quantitatively estimating this sensitivity is the Hammett $\sigma\rho$ correlation (120b). This correlation was carried out for a number of substituents in two or three solvent systems. These are shown in Figures 14, 15 and 16. All the slopes were determined by the method of least square analysis (123)

and these are recorded in the figures along with the correlation coefficients r (123).

When substituents were placed in the β-ring of α-cyano-4-nitrostilbene (XXI), the pK values



XXI

were found to correlate with the respective σ values. A plot of the pK values, when Z was 4'-nitro, 3'-chloro, hydrogen, 4'-methyl, 4'-methoxy and 4'-dimethylamino, against the respective σ values (120c) gave reasonably straight lines with ρ and the correlation coefficient r being equal to 2.27 and 0.996 in DMSO-ethanol, 2.21 and 0.992 in DMSO-methanol and 2.09 and 0.993 in sodium methoxide-methanol respectively.

The fact that the pK values for XXI correlate with the respective σ values shows that there is little resonance interaction between the substituent in the β-ring and the anion formed in the equilibrium addition of alkoxide ion. σ Values are determined by measuring the ionization constants of substituted benzoic acids and in the anion of benzoic acid, represented by structure XXII, there is no way of drawing a resonance

FIGURE 14. HAMMETT CORRELATIONS OF THE LEWIS ACIDITY OF α-CYANOSTILBENES IN DMSO-ETHANOL

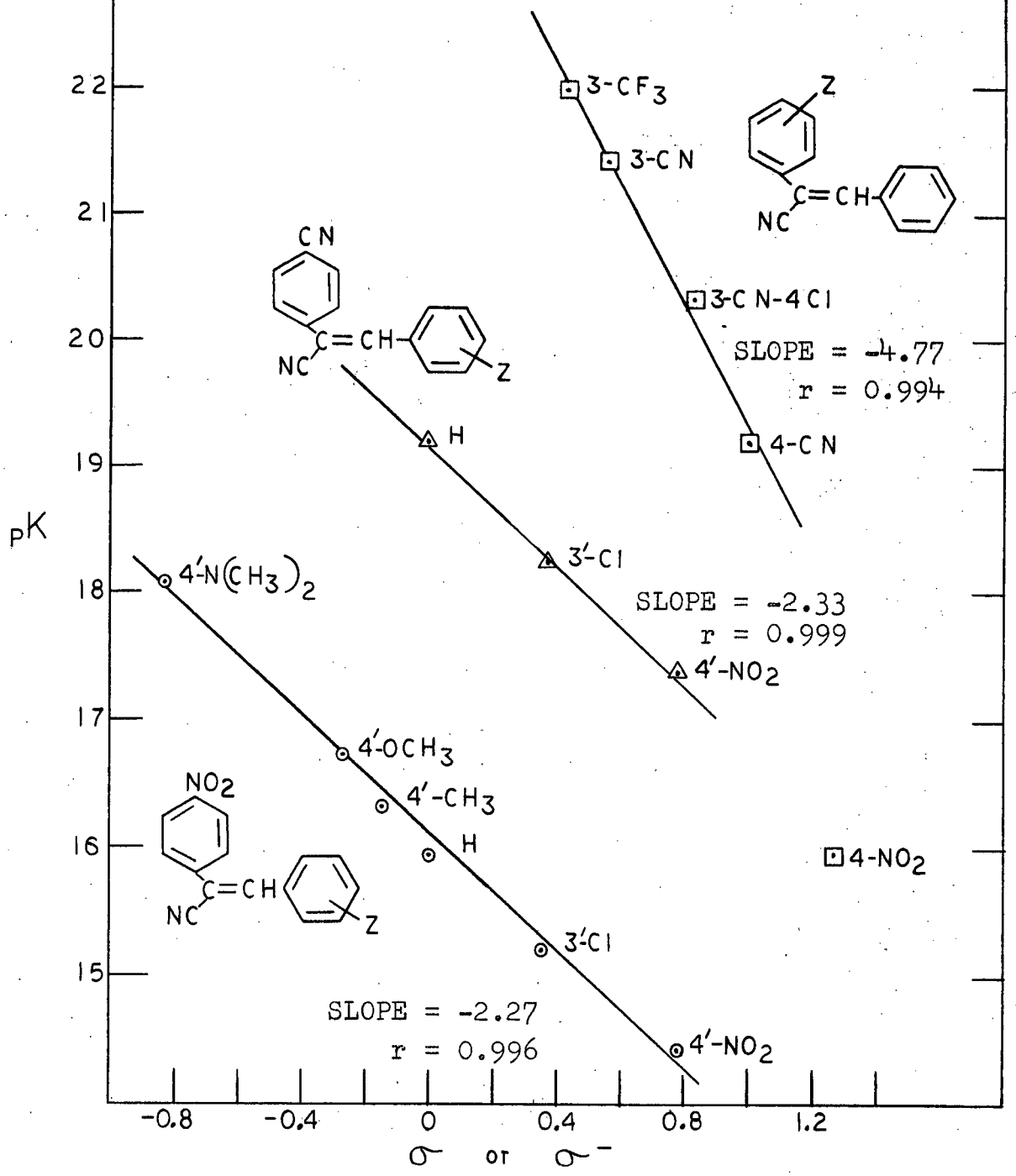


FIGURE 15. HAMMETT CORRELATIONS OF THE LEWIS ACIDITY OF α-CYANOSTILBENES IN DMSO-METHANOL

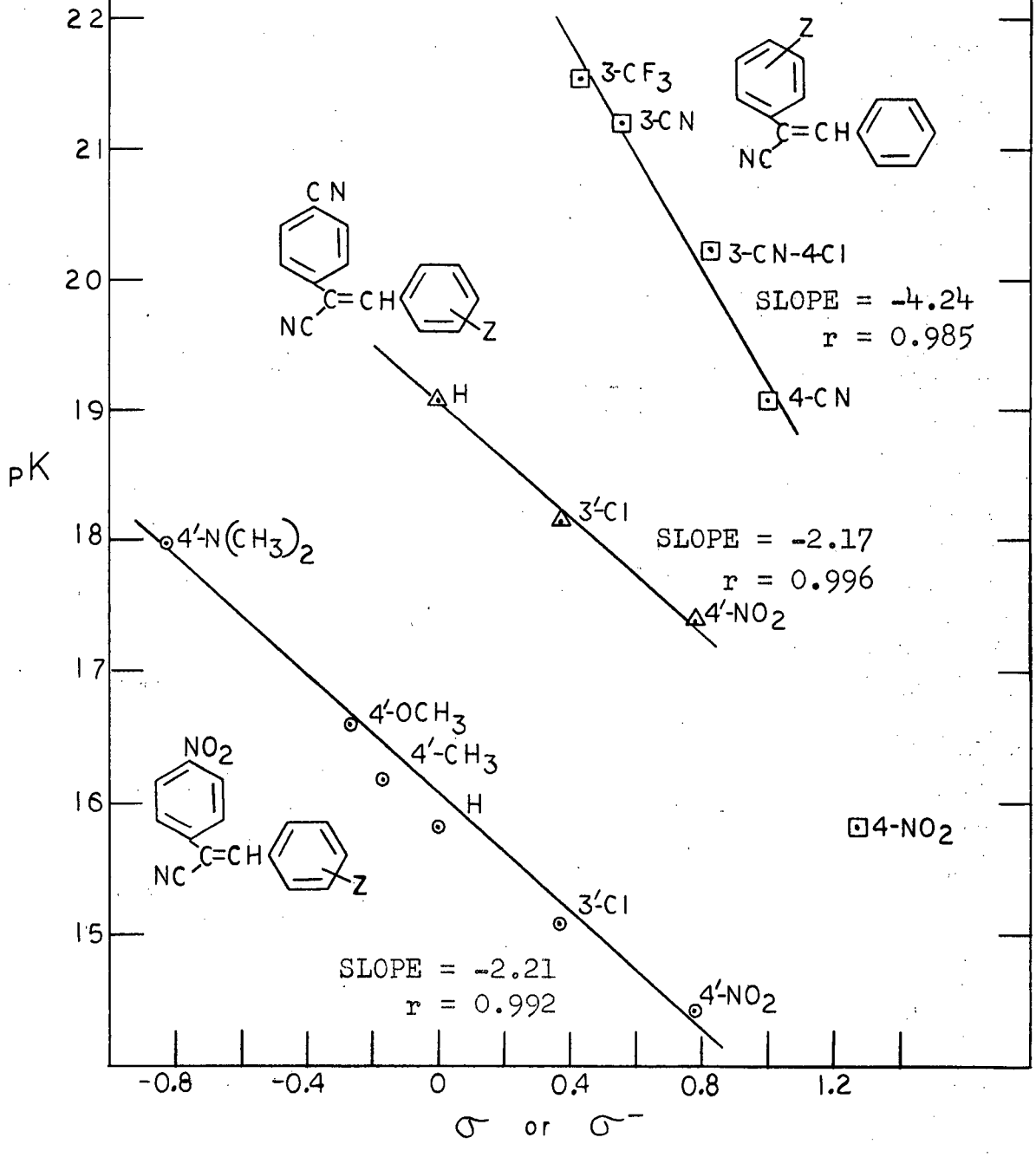
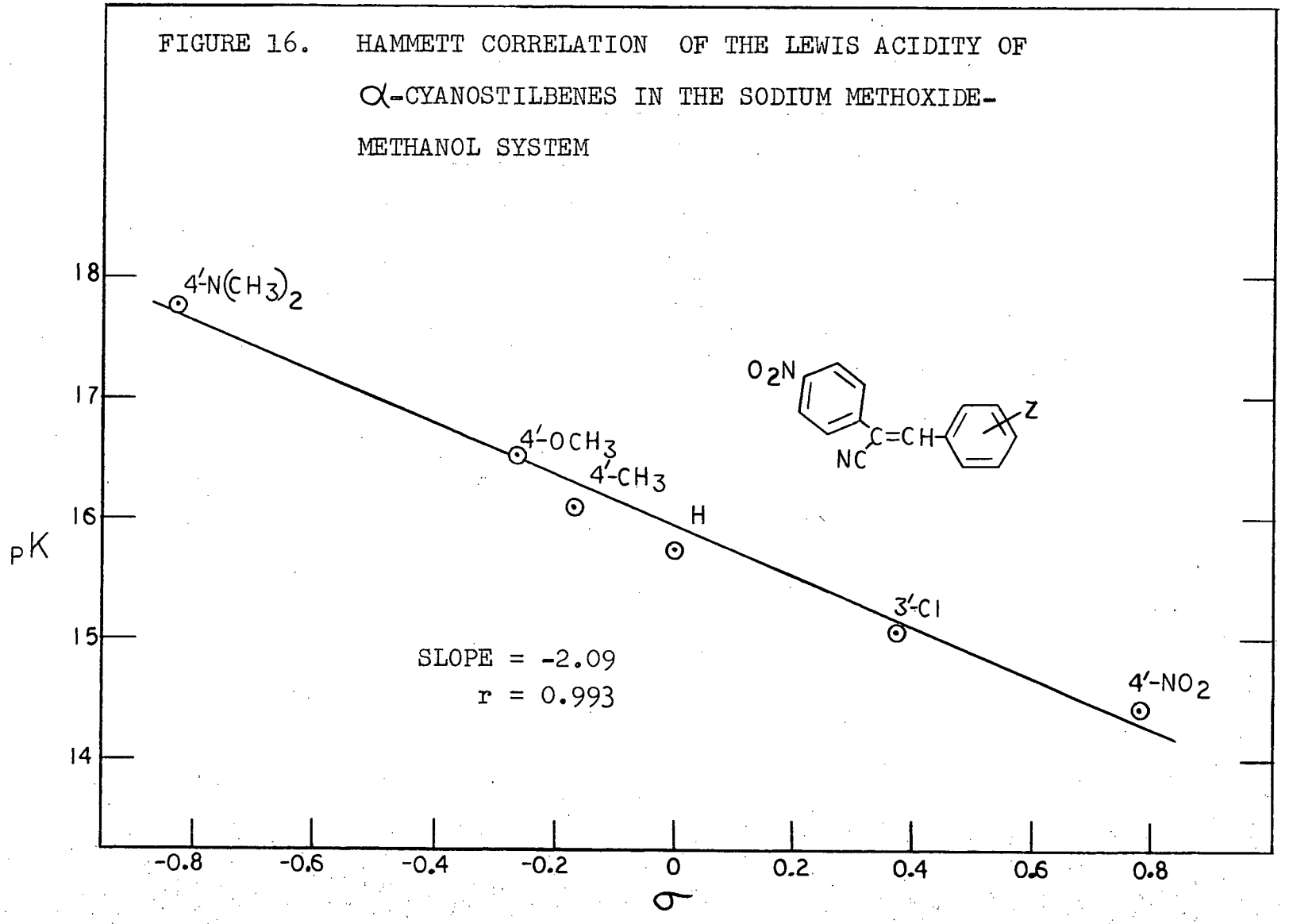
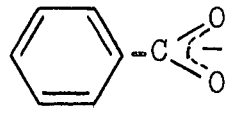


FIGURE 16. HAMMETT CORRELATION OF THE LEWIS ACIDITY OF α-CYANOSTILBENES IN THE SODIUM METHOXIDE-METHANOL SYSTEM



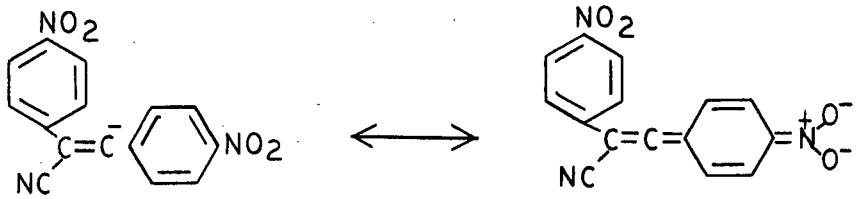
structure with the negative charge residing in the ring.



XXII

Therefore, σ^- values essentially measure the inductive effect of substituents (5b). That the appropriate value for the 4'-nitro group in XXI is 0.78 (120c), rather than the σ^- value of 1.27 (5b), clearly indicates that only as much resonance interaction is occurring between the substituent in the β-ring and the anion formed from the alkoxide addition to XXI as there is in the case of the anions of substituted benzoic acids.

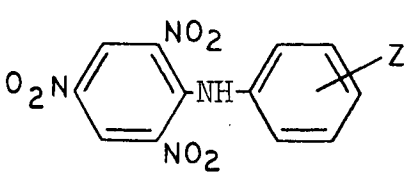
The above evidence also sheds further light on the mode of ionization of the α-cyanostilbenes. If the ionization took place by a proton removal, as indicated in equation (76). then the nitro group in the 4' position would undergo a strong resonance interaction with the resultant anion as shown below.



XXIII

In other words, structure XXIII would be expected to make a large contribution to the overall resonance hybrid. If this were the case, the appropriate sigma value for the 4'-nitro group should be the σ^- value of 1.27. The σ^- value refers to the interaction between a substituent and an anion where resonance interaction is possible as in the case of the ionization of phenols. That the appropriate sigma value for the 4'-nitro group is 0.78 rather than 1.27 strongly suggests that the ionization described by equation (76) is unimportant.

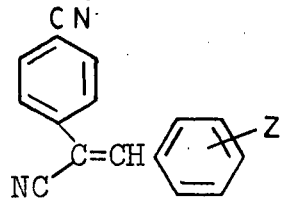
The magnitude of ρ for the ionization of XXI gives a quantitative estimate of the sensitivity of the Lewis acidity on the electronic effects of groups in the β-ring. A ρ value of about 2.1 for this equilibrium, the exact value of which is dependent on the particular solvent system used, can be compared with ρ values of 1.00, 2.11 and 2.77 for the ionization of benzoic acids, phenols and anilinium ions respectively in water at 25° (120d), a value of 4.07 for the ionization of diphenylamines in DMSO-water (49), and a value of 1.88 for the ionization of 2,4,6-trinitrodiphenylamines (XXIV)



XXIV

in aqueous solutions (52). This comparison shows that the Lewis acidities of α-cyano-4-nitrostilbenes are about as dependent on the electronic nature of substituents in the β-ring as are the acidities of phenol and anilinium ions.

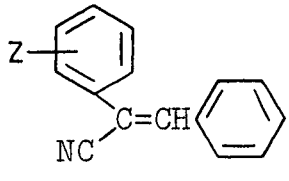
A plot of the pK values for α,4-dicyanostilbenes (XXV), where Z was 4'-nitro, 3'-chloro and hydrogen, against the respective σ values yielded ρ and r values



XXV

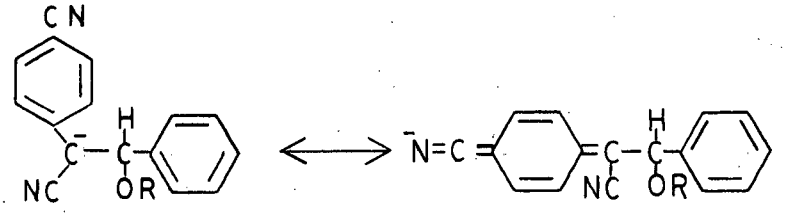
of 2.33 and 0.999 in DMSO-ethanol and 2.17 and 0.996 in DMSO-methanol respectively. Since only three points were used in each case, the reliability of these ρ values is not great. But they do show that the ρ value for the ionization of XXV is very similar to that for the ionization of XXI.

In the ionization of α-cyanostilbenes (XXVI)



XXVI

with substituents in the α-ring, a plot of the pK values versus the respective σ^- values (5b) for the substituents 4-cyano, 3-cyano-4-chloro, 3-cyano and 3-trifluoromethyl gave ρ and r values of 4.77 and 0.994 respectively in DMSO-ethanol and 4.24 and 0.985 respectively in DMSO-methanol. Because only four points were used to determine the ρ values, the error in ρ may be high. Nevertheless, it appears that this ρ value is slightly higher than the value of 4.07 for the ionization of diphenylamines (49). The high positive ρ value and the fact that the appropriate sigma value for the 4-cyano group is the σ^- value of 1.00 indicates that structures such as XXVIII make a considerable contribution to the structure of the base adduct XXVII.



XXVII XXVIII

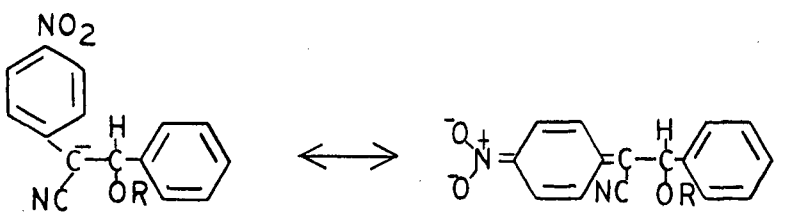
Considering the ρ values of 2.11 for the ionization of phenols (120d) and 4.07 for the ionization of diphenylamines (49), one might have anticipated a much higher ρ value for the equilibrium addition of alkoxide ions to α-cyanostilbenes. A ρ value as high as ten has been estimated for the ionization of toluenes (49).

However, the ability of the α-cyano group to effectively stabilize the negative charge would tend to have a "swamping" effect. This recalls the reduced ρ value observed for the ionization of 2,4,6-trinitrodiphenylamines (XXIV), 1.88, compared to that for the ionization of diphenylamines, 4.07.

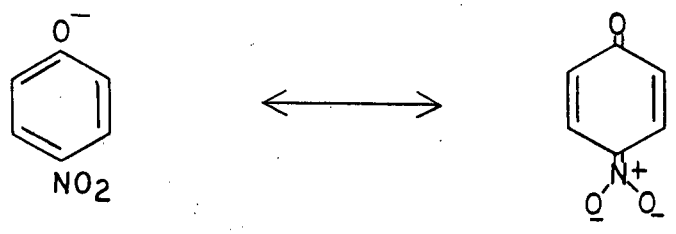
From Figure 14, it can be seen that the ρ value for the equilibrium addition of ethoxide ion to XXI or XXV averages out to 2.30, whereas the ρ value for the addition to α-cyanostilbenes with the substituents in the α-ring is 4.77. This means that the ρ value for the β-ring, where the substituted phenyl ring is removed by one carbon atom from the site of the carbanion, is 0.48 of the ρ value for the α-ring where the substituted phenyl ring is adjacent to the carbanion. This compares closely with the ratio of the ρ values for the ionization of substituted benzoic and phenylacetic acids. The ρ value for the ionization of benzoic acids is 1.00 and that for the ionization of phenylacetic acids is 0.49 (5b). In phenylacetic acid, the phenyl ring is one carbon atom farther away from the carboxyl group than in benzoic acid.

It is also evident from Figures 14 and 15 that the 4-nitro group is exceptionally good in stabilizing the negative charge of the anion formed from the equilibrium addition of alkoxide ion to α-cyano-4-nitrostilbene.

In these plots of pK versus σ^- , effective sigma values of 1.70 in DMSO-ethanol and 1.81 in DMSO-methanol had to be attributed to the 4-nitro group in order to bring it onto the straight line joining the other four points. While this analysis used only a small number of substituents, it is clear that an exalted σ^- value is required for the para-nitro group. There are other cases where an exalted σ^- value has been reported for a para-nitro group. In the ionization of diphenylamines, Dolman found an effective σ^- value of 1.65 for the 4-nitro group (49). Fisher, Riddols and Vaughan (124) have reported values of 1.70 and 1.81 for the 4-nitro group in the ionization of substituted 1-naphthols and in the methylation of 1-naphthoxide ions respectively. A comparison of these exalted σ^- values with those of 1.27 for the ionization of phenols and 0.78 for the ionization of benzoic acids implies that structures such as XXX must make a greater contribution to the carbanion XXIX than structures such as XXXII do to the anion XXXI formed from the ionization of 4-nitrophenol.



XXIX XXX



XXXI XXXII

G. The Correlation of Rates with the H_R- Function

One of the underlying purposes of establishing an acidity function is to aid in the elucidation of the mechanisms of acid or base catalyzed reactions (60). However, the prospect that different acidity scales exist for each narrow class of structurally similar compounds in the highly acid regions (125) has cast a wave of uncertainty on the interpretations of kinetic correlations with acidity functions. Because of this, great care must be exercised in interpreting such correlations in cases where the reactants used in the kinetic study are structurally quite different from the indicators used to establish the acidity scale.

In the case where the reactants used in the kinetic study and the indicators used to set up the acidity scale are structurally very similar the interpretation of the kinetics-acidity function correlation should be on firmer ground. Such a case

exists here. The substituted α-cyano-trans-stilbenes used to establish the H_R- scale are nearly identical to the substituted α-cyano-cis-stilbenes used in the kinetic study of the base catalyzed isomerization. The only differences are the substituents in the phenyl rings and the geometrical arrangement. Solvation differences in the same solution should be reduced to a minimum.

The existence of a good linear relation between the logarithm of the apparent first order rate constant, log k_1, and the acidity scale H_R- is evident from Figures 10 and 11. The closeness to linearity of this correlation is also reflected in Table XXI. The correlation coefficient r gives a measure of how good a straight line is produced by the experimental points. The closer r is to one, the better the straight line (126). From Table XXI, it can be seen that all the values of r are greater than 0.995. This shows that very good straight lines are obtained when values of log k_1 were plotted against the respective H_R- values in both DMSO-ethanol and DMSO-methanol. Although the lines are straight, the slopes are far from unity.

In the acid region there are cases when a log k-acidity function correlation results in slopes of less than unity for reactions involving a slow proton transfer step. Kresge and Chiang (127) found that for the loss of tritium ion from 1,3,5-trimethoxy-$[-2-H^3]$-

benzene in aqueous perchloric acid, a plot of log $k_{exchange}$ versus H_o gave a straight line of slope 1.07. But the protonation of 1,3,5-trimethoxybenzene should follow the H_R' function and in the region in which the kinetics were measured, the expression

$$2H_o = H_R' \qquad (81)$$

holds approximately (127). The slope of the plot of log $k_{exchange}$ versus H_R' would then be 0.53. It was also shown that the hydrogen exchange in 1,3,5-trimethoxybenzene followed the Bronsted catalysis relation with α being equal to 0.518 with a standard deviation of 0.007 (128).

Noyce and co-workers have studied the acid catalyzed isomerization of cis-benzalacetophenone (129), cis-cinnamic acid (130 - 132) and cis-stilbenes (133). They found that the kinetics of the isomerization of the cis-cinnamic acids paralleled the acidity function H_o with nearly unit slope (130, 131) and that a plot of log k versus H_o for the isomerization of cis-stilbene gave a slope of 1.25 (133). In both cases, a slow proton addition was proposed as the first step on the basis of a substantial solvent isotope effect (132, 133) and a large negative ρ value (131, 133). If one considers that the H_R' function should be applicable rather than the H_o function and that equation (81) holds, then the

slopes of the log k-H_R' correlation would be approximately the same as that found by Kresge and Chiang (127).

The results of Kresge and Chiang (127, 128) and those of Noyce and co-workers (130 - 133) suggest that when the proton is transferred in the rate determining stage, a plot of log k versus the appropriate acidity function gives a slope of less than unity. The same may apply to base catalyzed reactions.

When an alkoxide ion acts as a nucleophile and adds to an unsaturated system in the rate determining step, the appropriate correlation of the kinetics is with the H_R- function. The mechanism for the base catalyzed isomerization of α-cyano-cis-stilbenes can be represented by the equation

$$C + OR^- \rightleftharpoons COR^- \rightleftharpoons T + OR^- \qquad (82)$$

where C, T, and OR^- represent the cis and trans isomers and the base respectively. The rate of the reaction can then be given by the expression

$$\frac{v}{[C]} = k_1 = k_2 [OR^-] \frac{f_C f_{OR^-}}{f^{\ddagger}} \qquad (83)$$

where v is the rate of the reaction, $-d[C]/dt$, k_1 is the apparent first order rate constant, k_2 is the second

order rate constant and $f^{\ddagger}$ is the activity coefficient for the transition state. If the transition state for the cis-trans isomerization has a structure intermediate between that of the structures of C + OR^- and COR^-, then the activity coefficient of the transition state can be written in terms of the activity coefficients of the two limiting forms (134).

$$f^{\ddagger} = (f_C f_{OR^-})^{1-\alpha} (f_{COR^-})^{\alpha} \qquad (84)$$

Here α is a measure of the degree to which the transition state resembles the intermediate COR^-, and as such should have a value between 0 and 1. By using equation (84), equation (83) becomes

$$k_1 = k_2 [OR^-] \left(\frac{f_C f_{OR^-}}{f_{COR^-}} \right)^{\alpha} \qquad (85)$$

The activity coefficient term in equation (85) can be expressed in terms of an acidity function. For the equilibrium

$$TOR^- \rightleftharpoons T + OR^- \qquad (86)$$

an acidity function b_- can be defined as

$$b_{-} = \frac{f_T(OR^-)}{f_{TOR^-}} = K \frac{[TOR^-]}{[T]} \qquad (87)$$

where K is the equilibrium constant for equation (86). From equation (87) one can obtain the expression

$$\frac{f_T f_{OR^-}}{f_{TOR^-}} = \frac{b_{-}}{[OR^-]} \qquad (88)$$

Since T and C differ only in geometric arrangement, the corresponding activity coefficient terms f_T and f_C must be almost identical; and, since the activity coefficient terms f_{TOR^-} and f_{COR^-} refer to virtually identical intermediates, the activity coefficient term in equation (85) can be replaced by a measurable quantity. Equation (85) then becomes

$$\frac{k_1}{[OR^-]} = k_2\left(\frac{b_{-}}{[OR^-]}\right)^{\alpha} \qquad (89)$$

By using equations (70) and (87), the expression

$$b_{-} = \frac{K_{HOR}}{h_{R^-}} \qquad (90)$$

can be obtained where K_{HOR} is the ionization constant for the solvent. Using this expression, equation (89) then becomes

$$\frac{k_1}{[OR^-]} = k_2\left(\frac{K_{HOR}}{[OR^-]h_{R^-}}\right)^{\alpha} \qquad (91)$$

Upon taking logarithms and simplifying, the equation

$$\log k_1 = \alpha H_{R^-} + \text{constant} \qquad (92)$$

is obtained since k_2 and K_{HOR} are constants and in the solutions in which the equilibria and kinetics were studied, the concentration of the alkoxide ion was kept constant. This analysis shows that the slope of a plot of log k versus the appropriate acidity function gives an indication of how closely the transition state resembles the intermediate anion in cases where the base concentration is kept constant.

On inspection of Table XXI, it can be seen that the kinetics of the base catalyzed isomerization of α-cyano-cis-stilbenes correlate very well with the acidity function H_{R^-} with slopes of between 0.426 and 0.665. This implies that the transition state for the isomerization has a structure approximately half way between that for the starting material (C + OR^-)

and the intermediate anion (COR^-).

It is also evident from Table XXI that as the substituents become more electron withdrawing, the slope decreases in value. This suggests that the fractional displacement of the transition state along the reaction coordinate is lessened as electron withdrawing substituents are placed in the ring.

In addition to this, the slopes of the kinetic-H_R- correlation were found to be greater for each reactant when ethoxide ion was the base than when methoxide ion was the catalyst. If these slopes can be taken as an indication of the extent of the bond formation in the transition state between the reactant and the alkoxide, as proposed above, then the extent of the bond formation in the transition state when ethoxide is the base must be greater than in the case when methoxide ion is the base. Due to an additional methylene group, the ethoxide ion is larger sterically than the methoxide ion. The greater size of the ethoxide ion may necessitate a greater decoupling of the π-electrons in the carbon-carbon double bond before the isomerization can take place.

The kinetics of certain aromatic nucleophilic displacements in concentrated sodium methoxide solutions were found to correlate with the appropriate H_R- function. Schaal and Peure (67) studied the alkaline degradation of 4-dinitrobenzene in sodium methoxide-methanol solutions

and the slope of the log k versus H_M plot was near unity. The H_M scale had previously been determined by Schaal and Lambert (37) and is based on methanol as the standard state using mainly substituted anilines and diphenylamines as indicators. Using the kinetic data of Schaal and Peure (67), a plot of log k versus H_R- gives a good straight line of slope 0.80. More recently, Schaal and Latour studied the alkaline decomposition of 2-dinitrobenzene in sodium methoxide-methanol solutions. Here again a plot of log k versus H_M gave a straight line of near unit slope (68) while a plot of log k versus H_R- gives a slope of 0.81. On looking at the indicators used to establish the H_M and H_R- scales, one would expect that aromatic nucleophilic substitutions should correlate better with the H_R- than with the H_M scale. The slightly less than unit slopes for the log k-H_R- correlations may be due to experimental errors. This is in favor of a mechanism with a pre-equilibrium followed by the slow rate determining step.

H. Substituent Effects on the Reactivity

In order to determine the effect of substituents on the rates of isomerization, it is necessary to compare the rates at one H_R- value or in a solvent of fixed composition. From Figures 10 and 11, it can be seen that this comparison was only possible with extrapolation

in some cases. By using the slopes calculated by the method of least square analysis and recorded in Table XXI, it is possible to calculate log k_1 values for the various substituted α-cyano-cis-stilbenes at a H_R- value of 16.00 in DMSO-ethanol and DMSO-methanol solutions. The results of these calculations are recorded in Table XXV.

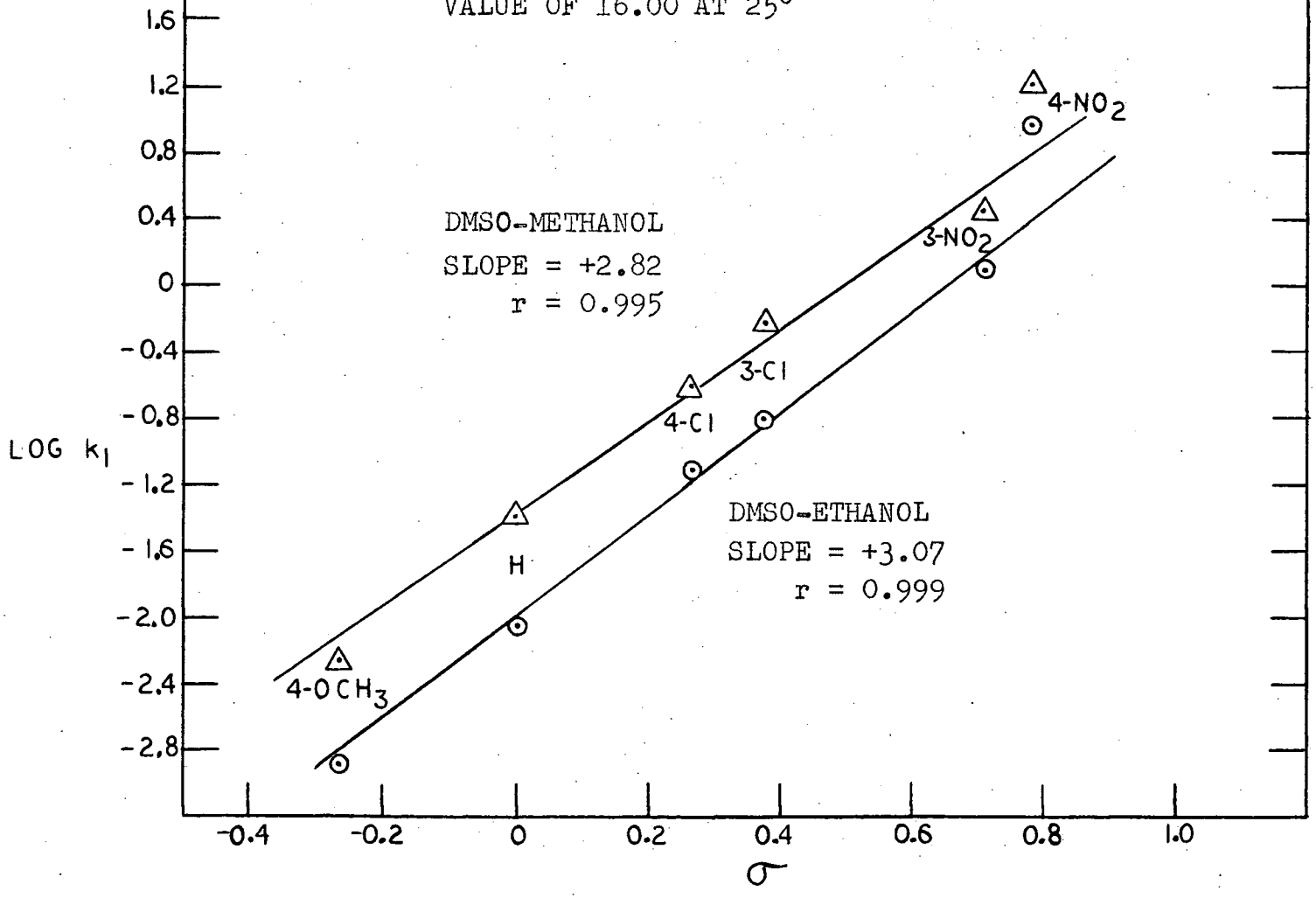
Using the log k_1 values recorded in Table XXV, a plot of the log k_1 values for the base catalyzed isomerization of substituted α-cyano-cis-stilbenes versus the respective σ values gave reasonably straight lines. These plots are recorded in Figure 17. The ρ values,

TABLE XXV

Calculated log k_1 Values for the Isomerization of Substituted α-Cyano-cis-stilbenes in DMSO-Ethanol and DMSO-Methanol at a H_R- Value of 16.00

Substituent	log k_1 in DMSO-Ethanol	log k_1 in DMSO-Methanol
4-nitro	+0.963	+1.208
3-nitro	+0.087	+0.450
3-chloro	-0.817	-0.242
4-chloro	-1.187	-0.616
hydrogen	-2.049	-1.394
4-methoxy	-2.882	-2.271

FIGURE 17. HAMMETT CORRELATIONS OF THE RATES OF ISOMERIZATIONS OF SUBSTITUTED α-CYANO-CIS-STILBENES IN DMSO-ETHANOL AND DMSO-METHANOL AT A H_R-VALUE OF 16.00 AT 25°



as determined by the method of least square analysis, are 3.07 and 2.82 in DMSO-ethanol and DMSO-methanol respectively. This shows that considerable negative charge is developed in the transition state. These ρ values can be compared with a value of 2.54 for the saponification of ethyl benzoates in 85% ethanol at 25° (120d) and a value of 3.3 for the nucleophilic substitution by ethoxide ion of 4-substituted-2-nitrophenyl fluorides in ethanol at 49.6° (135). Although the ρ value for the isomerization is not as high as that for the aromatic nucleophilic substitution, it is higher than that for the saponification of ethyl benzoates.

The ρ value for the isomerization of α-cyano-cis-stilbenes can also be compared with the ρ value for the equilibrium addition of alkoxide ions to α-cyanostilbenes. In DMSO-ethanol, the ratio of the ρ value for the isomerization to that for the equilibrium addition of ethoxide ion is 0.64, and in DMSO-methanol, the corresponding ratio is 0.66. The values of these ratios indicate that the ionization constants are much more sensitive to substituent effects than are the rates of isomerization. It is also interesting to note that the values of these ratios are in approximate agreement with the slopes of the kinetic-acidity function correlation.

Figure 17 shows that the point for the 4-nitro

substituent falls off the line joining the other five points regardless of whether the σ or σ^- value is used. The average effective σ^- value for the 4-nitro substituent was calculated to be 0.95. This suggests that the resonance interaction of the 4-nitro group is reduced but not completely eliminated.

Trans-stilbene has a coplanar structure whereas cis-stilbene cannot assume such a structure because the ortho-hydrogens would overlap. As a result, one of the phenyl rings is forced to rotate out of the plane of the rest of the molecule (136). It is very likely that the same situation exists in the case of α-cyano-cis-stilbenes. It is thus possible that the resonance interaction of the 4-nitro substituent with the reaction site is reduced because of the twisting of one of the phenyl rings out of the plane of the rest of the molecule. This would explain the effective σ^- value of 0.95 for the 4-nitro group in the isomerization of α-cyano-cis-stilbenes.

I. Activation Parameters

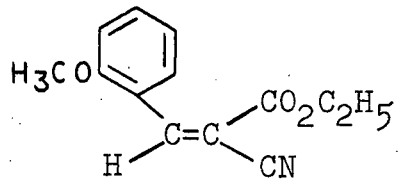
In any kinetic study, it is desirable to have an estimate of the activation parameters. By comparing the experimental values with the values found in the literature, some mechanisms may be favored while others may be discounted.

The activation parameters in Table XXIII show that the rate increase for the isomerization of α-cyano-cis-stilbene on going from 41.12 to 64.21 mole % DMSO in methanol is due largely to a decrease in the enthalpy of activation $\Delta H^{\ddagger}$, aided slightly by an increase in the entropy of activation $\Delta S^{\ddagger}$. The dependence of the rate increase, on going to higher DMSO concentrations, on the decrease in $\Delta H^{\ddagger}$ is in agreement with the results of Cram et al (137) for the base catalyzed racemization of (+)-2-methyl-3-phenylpropionitrile in DMSO-methanol solutions and the results of Kingsbury (117) for the reaction of $C_6H_5CH_2S^-K^+$ with 4-fluoronitrobenzene in DMSO-methanol solutions. Both Cram et al (137) and Kingsbury (117), however, reported decreases in $\Delta S^{\ddagger}$ as the concentration of DMSO was increased. Roberts (138), on the other hand, reported that in the hydrolysis of various esters in aqueous DMSO solutions, the $\Delta S^{\ddagger}$ tended to increase as the proportion of DMSO increased. These results suggest that no general trend in $\Delta S^{\ddagger}$ can be expected as the DMSO content is increased.

In general, the entropy and enthalpy of activations listed in Table XXIII are approximately in line with those for a bimolecular reaction between a charged ion and a neutral molecule. For example, in the nucleophilic substitution of methyl bromide by ethoxide

ion at 55°, the entropy of activation is -13.9 e.u. and the energy of activation is 20.0 kcal. mole^{-1}. In the analogous reaction of ethyl bromide, the entropy of activation is -11.6 e.u. and the energy of activation is 21.0 kcal. mole^{-1} (139). These values are fairly close to the entropy of activation of -13.5 e.u. and the energy of activation of 16.6 kcal. mole^{-1} for the methoxide ion catalyzed isomerization of α-cyano-cis-stilbene in 41.12 mole % DMSO in methanol at 25°.

On the other hand, the activation parameters listed in Table XXIII are quite different from those reported by Rappoport, Degani and Patai (77) for the amine catalyzed isomerization of ethyl α-cyano-β-2-methoxyphenylacrylate (XXXIII). These workers reported energies



XXXIII

of activation (Ea) in the range of 5.06 to 2.71 kcal. mole^{-1}, with the exact value depending on the particular amine used as catalyst. Accompanying these low values for Ea were very negative values for $\Delta S^{\ddagger}$, ranging from -43 to -66 e.u. These low values for Ea and high negative values for $\Delta S^{\ddagger}$ were explained in terms of a zwitterionic

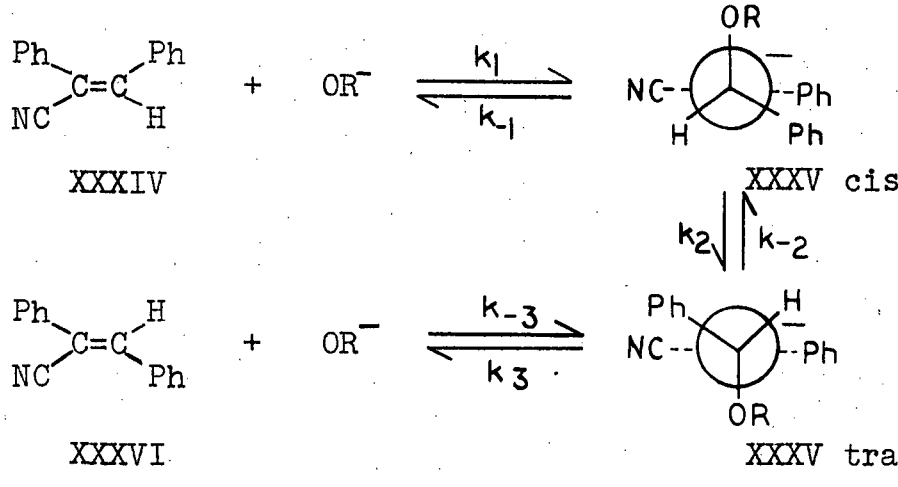
intermediate or transition state. This shows that the replacement of the negative methoxide ion as a base by a neutral amine has an extremely large effect on the activation parameters even though the two mechanisms may be similar in other respects.

J. A Further Discussion of the Isomerization Mechanism

It has already been pointed out that the base catalyzed isomerization of α-cyano-cis-stilbenes is first order in base and first order in reactant. In addition, it has also been shown that the base catalyzed isomerizations go to completion, and that no substantial side reactions occur.

A mechanism, similar to that proposed by Rappoport, Degani and Patai (77) can then be proposed for the base catalyzed isomerization of α-cyano-cis-stilbenes.

Scheme III



In this mechanism, the first step is the reversible attack of the nucleophile on the unsaturated system forming the cis-carbanion (XXXV cis). Since the hindrance to the rotation around the α-β carbon bond in XXXV, or to the rapid inversion of the carbanions, should not be great, a rapid equilibrium should be established between XXXV cis and XXXV trans. The last step in the reaction then involves the elimination of the nucleophile from XXXV trans to form the α-cyano-trans-stilbene (XXXVI).

A steady state treatment of the above scheme then gives the expression

$$\frac{d[T]}{dt} = \frac{k_1k_2k_3[C][B] - k_{-1}k_{-2}k_{-3}[T][B]}{k_{-1}k_3 + k_{-1}k_{-2} + k_2k_3} \qquad (93)$$

where T, C and B refer to the trans-isomer, the cis-isomer and the base respectively. Since no reaction was observed with the trans-isomer under the conditions used to study the isomerization of the α-cyano-cis-stilbenes, this must mean that the equilibrium lies far towards the trans-isomer. This means that $k_1k_2k_3$ must be greater than $k_{-1}k_{-2}k_{-3}$. It has previously been suggested that the rate of attack of a nucleophile on a cis-isomer is approximately the same as that on a trans-isomer (77). This means that k_1 and k_{-3} are essentially equal and that

$k_2k_3 > k_{-1}k_{-2}$. The experimental rate constant k_{exp} in equation (93) then reduces to

$$k_{exp} = \frac{k_1}{1 + k_{-1}/k_2 + k_{-1}k_{-2}/k_2k_3} \qquad (94)$$

Since k_2k_3 is considerably greater than $k_{-1}k_{-2}$, then $k_{-1}k_{-2}/k_2k_3$ can be ignored with respect to unity and equation (94) is reduced to the expression

$$k_{exp} = \frac{k_1}{1 + k_{-1}/k_2} \qquad (95)$$

If this analysis were correct, then according to Rappoport, Degani and Patai (77), there are three possible situations:

(a.) When the elimination step is faster than the rotation, then $k_{-1} > k_2$ and the equation

$$k_{exp} = \frac{k_1k_2}{k_{-1}} \qquad (96)$$

results.

(b.) When the rates of elimination and rotation are approximately the same, then $k_{-1} \approx k_2$ and equation (95) applies.

(c.) When the rate of rotation is faster than the

elimination, then $k_2 > k_{-1}$ resulting in the equation

$$k_{exp} = k_1 \qquad (97)$$

In the present case, equation (96) can be eliminated because the first possibility implies the existence of a pre-equilibrium. In a mechanism with a pre-equilibrium, the activity coefficient of the transition state, $f^{\ddagger}$, would either resemble that of the cis-carbanion (XXXV cis) or some intermediate form between that of XXXV cis and XXXV trans. In such a case, since the activity coefficients for XXXV cis and XXXV trans should be nearly identical, the correlation of the kinetics with the H_R- function should give a straight line of unit slope. Since unit slopes were not obtained the first possibility can be rendered unlikely.

The available data cannot distinguish between the other two possible situations. In both cases, the experimental rate constant would not be far different from k_1.

The values for the energy of activation for the isomerization (Table XXIII) are in the range of 14.9 to 17.3 kcal. $mole^{-1}$. These compare very closely with the values of 11.7, 13.1 and 16.2 kcal. $mole^{-1}$ for the base catalyzed hydrolysis of 4-methoxybenzylidenemalononitrile,

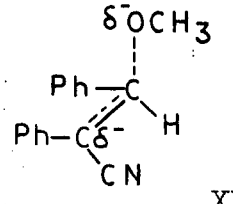
ethyl α-cyano-β-4-methoxyphenylacrylate and α-cyano-β-4-methoxyphenylacrylamide respectively (86). In these cases the rate determining step was considered to be the attack of the hydroxide ion on the carbon-carbon double bond. In the base catalyzed hydrolysis of chalcone, values of 20.0 kcal. $mole^{-1}$ and -10.6 e.u. were reported for the energy of activation and the entropy of activation respectively (140). Here again the attack by the hydroxide ion on the carbon-carbon double bond was considered to occur in the rate determining step. From this comparison it can be seen that the activation parameters for the base catalyzed isomerization of α-cyano-cis-stilbenes correspond quite closely to those found in cases involving a slow rate determining addition of a nucleophile to a carbon-carbon double bond. This supports the contention that the experimental rate constant is governed largely by the rate constant for the first step (k_1).

The activation parameters in Table XXIII can also be compared with those for the cyanoethylation of alcohols. Feit and Zilkha (141) reported an energy of activation of 18.7 kcal. $mole^{-1}$ and an entropy of activation of -7.2 e.u. for the cyanoethylation of methanol. The rate determining step was considered to be the attack of the methoxide ion on acrylonitrile. The higher energy of activation for the cyanoethylation reaction than for the isomerization may be due to a less

activated double bond in acrylonitrile than in α-cyano-cis-stilbene. Similarily, the less negative entropy of activation for the cyanoethylation reaction may well be due to a less hindered unsaturated system in acrylonitrile than in the case of α-cyano-cis-stilbenes. This again supports the view that $k_{exp} \approx k_1$.

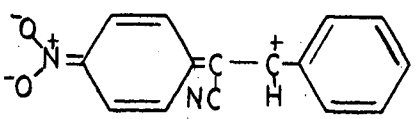
From the previous discussion, it is seen that the effects of substituents on the rate of isomerization of α-cyano-cis-stilbenes are twofold. Figure 17 shows that the ρ value is fairly large and positive for the isomerization, indicating that a considerable amount of negative charge is developed on the α-carbon atom in the transition state. From Table XXI it can be seen that the substituents also have an effect on the slopes of the log k_1-H_R- correlation. This slope, termed α in equation (92), was shown to be a measure of how closely the transition state resembled the intermediate carbanion. In the structure of the carbanion intermediate from the addition of methoxide ion to α-cyano-cis-stilbene, one unit of negative charge can be represented as residing on the α-carbon atom even though it is realized that the greater portion of the charge must be delocalized into the phenyl ring and the α-cyano group. The transition state in the methoxide ion catalyzed isomerization of α-cyano-cis-stilbene can then be represented by

structure XXXVII



XXXVII

The portion of the negative charge residing on the α-carbon in XXXVII, i.e. in the α-portion of the molecule, would be about half that of the total negative charge in the transition state. As the substituents in the α-phenyl ring become more electron withdrawing, the proportion of the negative charge residing in the α-portion of the molecule in the transition state becomes less. The evidence for this is the observed decrease in the slope of the log k-H_R- correlation as the substituents in the α-phenyl ring become more electron withdrawing. With strongly electron withdrawing groups in the α-phenyl ring, the double bond character of the α-β carbon bond may be lessened due to some contribution of resonance structures such as XXXVIII to the total structure. In such a case, a smaller amount of bond formation between the methoxide ion and the β-carbon atom may be necessary before rotation about the α-β carbon bond is possible. This would explain the decrease in the slope α as the substituents become more electron withdrawing.



XXXVIII

In addition to the mechanism proposed in Scheme III, another possibility exists. Hunter and Cram (81) found that cis-stilbene underwent base catalyzed isomerization as well as deuterium exchange through a vinyl carbanion. This suggests that the isomerization of α-cyano-cis-stilbenes may take place by a proton removal reaction giving a transition state of structure similar to XVIII. If this were the mechanism, then α-cyano-α'-methoxy-cis-stilbene should not isomerize under basic conditions. Since it was shown that α-cyano-α'-methoxy-cis-stilbene did isomerize in DMSO-methanol containing 0.01M sodium methoxide, this must mean that the isomerization mechanism does not take place through a vinyl carbanion of structure XVIII. This is supported by the finding by Zinn et al (115) that ethyl α-phenyl-cinnamate did not undergo deuterium exchange when treated with catalytic amounts of sodium ethoxide in deuterioethanol.

K. The Reaction of 1,1-Bis-(4-nitrophenyl)ethene in Highly Basic Systems

When 1,1-bis-(4-nitrophenyl)ethene (XXXIX) was reacted with tetramethylammonium hydroxide in DMSO, the isolated product had a molecular weight of 544, as determined by the Rast method, and the analysis corresponded to that calculated for the compound with structure XVI. This compound can be accounted for by the following reaction route:

$$(4\text{-}NO_2Ph)_2C{=}CH_2 \quad (\text{XXXIX}) \quad + \quad OH^- \rightleftharpoons (4\text{-}NO_2Ph)_2\bar{C}\text{-}CH_2OH \rightleftharpoons (4NO_2Ph)_2CH\text{-}CH_2O^-$$

$$(4\text{-}NO_2Ph)_2CH\text{-}CH_2O^- \quad + \quad (4\text{-}NO_2Ph)_2C{=}CH_2 \rightleftharpoons$$

$$(4\text{-}NO_2Ph)_2\text{-}CH\text{-}CH_2OCH_2\text{-}\bar{C}\text{-}(Ph\text{-}4\text{-}NO_2)_2$$

$$\downarrow \text{ acetic acid}$$

$$(4\text{-}NO_2Ph)_2\text{-}CH\text{-}CH_2OCH\text{-}CH\text{-}(Ph\text{-}4\text{-}NO_2)_2 \quad (\text{XVI})$$

The isolation of the diether (XVI) illustrates the complications which can arise when attempting to use hydroxide ion as a Lewis base. Once the hydroxide ion has been added to an unsaturated system. the proton

can shift from the oxygen to the carbon atom. This leaves an alkoxide ion as base which can undergo further reactions as a Lewis base.

When XXXIX was reacted with methoxide ion in DMSO, the product isolated had a NMR spectrum and analysis in agreement with the structure of 1,1-bis-(4-nitrophenyl)-2-methoxyethane (XVII). In the NMR spectrum, the singlet at 6.56 τ is in the region associated with that of a methoxy group (142). The integrated peak heights of the triplet, doublet and singlet were in the ratio of 1:2:3. This is also in agreement with structure XVII. The triplet can be assigned to the single proton at the α-position, the doublet to the two protons at the β-position and the singlet to the three protons in the methoxy group.

Further insight into the reaction of XXXIX with alkoxide ions in DMSO was obtained from the electronic spectra. When sodium ethoxide was added to a solution of the ethene (XXXIX) in about 90 mole % DMSO in ethanol, an absorption peak centered at 710 mμ was evident. This was likely due to the anion formed by the addition of ethoxide ion to the ethene since the anion of 4,4'-dinitrodiphenylmethane has a maximum absorption at 704 mμ (51). It would be expected that the two ions would have very similar absorption spectra. The addition of acetic acid caused the absorption at 710 mμ to disappear. This

supports the contention that this peak was due to the anion. However, the addition of acetic acid did not regenerate the ethene; instead, a mixture of the ethene and the alcohol addition product was formed. The proportion of each of these present depended on the extent of ionization prior to the addition of acetic acid. As the solutions became more basic due to an increased concentration of DMSO, the addition of ethoxide ion to the ethene became more complete as evidenced by the increase in the absorption at 710 mμ with the position of the absorption maximum of the acidified solution being shifted from 306 mμ to 282 mμ. It is noteworthy that the electronic spectrum of XVII has a maximum absorption at 283 mμ in DMSO solution. Since the replacement of a methoxy group by an ethoxy group should have little effect on the electronic spectra, the product from the reaction of XXXIX with sodium ethoxide in DMSO followed by the addition of acetic acid is likely 1,1-bis-(4-nitrophenyl)2-ethoxy-ethane (XL).

$$(4\text{-}NO_2C_6H_5)_2CH\text{-}CH_2\text{-}OCH_2CH_3$$

XL

The reaction of XXXIX with sodium ethoxide in DMSO-ethanol solutions can be illustrated by the scheme:

$(4\text{-}NO_2C_6H_5)_2C{=}CH_2 \quad + \quad {}^{-}OEt \rightleftharpoons (4\text{-}NO_2C_6H_5)_2\bar{C}\text{-}CH_2\text{-}OCH_2CH_3$

XXXIX

k_2 | | k_{-2} (acetic acid or ethanol)

$(4\text{-}NO_2C_6H_5)_2\text{-}CH\text{-}CH_2\text{-}OCH_2CH_3$

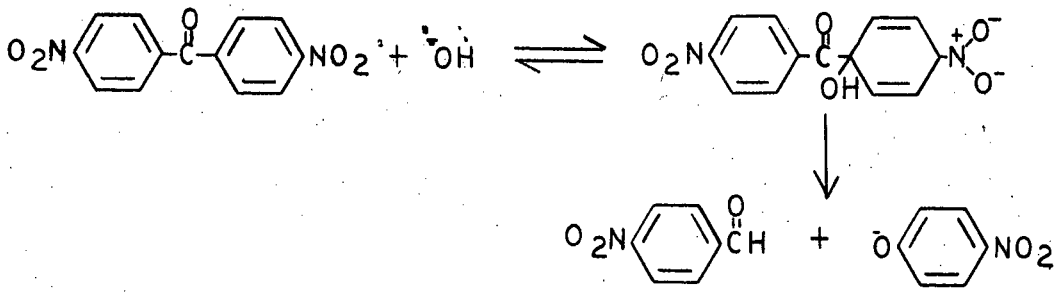
XL

An idea as to the relative importance of the two equilibria in this scheme can be obtained from an estimate of the pK values for XXXIX and XL. XXXIX was, according to spectral measurements, half ionized in 69 mole % DMSO in ethanol while 1,1-bis-(4-nitrophenyl)ethane, as a model for XL, was half ionized in 56 mole % DMSO in ethanol. This suggests that the second equilibrium (k_2/k_{-2}) may make some contribution to the overall equilibria, especially at lower DMSO concentrations when XXXIX would be only partially ionized.

L. The Reaction of 4,4'-Dinitrobenzophenone with Hydroxide ion in DMSO

The study of the reaction of 4,4'-dinitrobenzophenone with hydroxide ion in DMSO-water solutions was preliminary in nature. The spectral evidence outlined previously suggests that 4-nitrophenol is one of the products in this reaction. The production of

4-nitrophenol in such a reaction could arise by the following route:



SUGGESTIONS FOR FURTHER WORK

In this thesis it has been shown that ethoxide and methoxide ions catalyze the isomerization of α-cyano-cis-stilbenes. Other nucleophiles such as thioalkoxides and fluoride ions may also catalyze this isomerization. The reactivity of small anions, such as the fluoride ion, is greater in polar aprotic solvents than in protic ones (143). The catalytic strength of such nucleophiles as well as how their catalytic behavior changes on increasing the proportion of a polar aprotic solvent, such as DMSO, in a protic solvent may be a fruitful area of study.

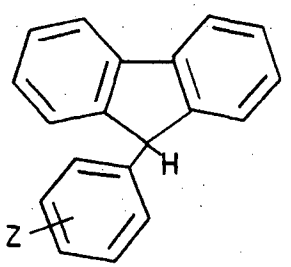
It may also be possible to measure the Lewis basicity of some additional anions using α-cyanostilbenes as indicators.

Compounds such as α-cyanostilbenes are known to hydrolyze readily in aqueous base (73, 85, 86). The rates of the base catalyzed hydrolysis of α-cyano-cis- and trans-stilbenes may furnish some idea of the Lewis basicity of the hydroxide ion and how this varies with an increase in the DMSO content in aqueous solutions.

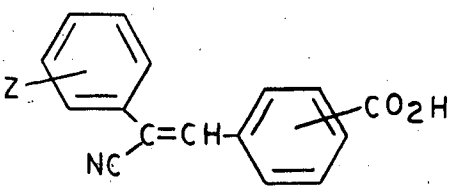
A preliminary study was reported on the reaction of 4,4'-dinitrobenzophenone with hydroxide ion in aqueous DMSO solutions. An analysis of the UV spectrum indicated

that 4-nitrophenol was one of the products. This is peculiar in that cleavage of ketones usually results in a mole of acid and a mole of hydrocarbon being formed (144 - 146). A complete product analysis and kinetic study of this reaction should help in elucidating the mechanism.

In this thesis results were presented which suggest that the H_- scale in DMSO-ethanol solutions for carbon acids, as determined by Bowden and Stewart (51), may need to be redetermined using indicators for which the electronic spectra are not solvent dependent. The substituted 9-phenylfluorenes (XLI) with the substituents in the phenyl ring may be a promising system.



XLI



XLII

A $H_=$ scale has recently been reported for carboxylic substituted anilines and diphenylamines (147). Similarily, a $H_R=$ scale may be of interest using indicators such as carboxylic substituted α-cyano-stilbenes (XLII).

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