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MECHANISMS OF BASE-CATALYZED REACTIONS:

PART III

THE ACIDITIES OF SOME HYDROXYLIC COMPOUNDS IN t-BUTYL ALCOHOL

BY

CHARLES FREDERICK SEGER III - 1943

A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

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MASTER OF SCIENCE IN CHEMISTRY

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1967

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DEDICATED

TO

CHARLES F. SEGER, JR.

"THE FATHER WHO IS ALWAYS BEHIND HIS SON."

ABSTRACT

The K_{HA} of water and five alcohols were determined in t-butyl alcohol employing sodium and potassium t-butoxides. The order of acidity is methanol>water>ethanol> 2-propanol≈cyclohexanol>menthol. It was also shown that potassium t-butoxide was twice as strong a base as sodium t-butoxide. A spectrophotometric method was employed with p-nitroaniline as the indicator. Calculations were made employing the methods of Stearns and Wheland and of Hine and Hine.

ACKNOWLEDGEMENTS

The author is indebted to Dr. D. S. Wulfman for his guidance and encouragement without whose aid and backing, portions of the present research would not have been realized.

Appreciation is extended to Dr. S. B. Hanna and Dr. G. L. Bertrand for their valuable suggestions during the investigation.

Acknowledgement is made to the Chemistry Department for research support and financial aid during the period of September 1965 through May 1967.

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

Historically, the pK_a data of weak acids ($pK_a > 14$) listed in the literature have been incomplete, and are based on many false assumptions. These include such assumptions as "pK_a's are not a function of solvent or temperature", that "ion pairs have no effect on acidity" and that "there are no aggregates formed in solvents of low polarity". On examining various pK_a values for a specific indicator, it appears that the values are dependent upon the solvent and the base employed.

In this work a visible spectroscopic method was used to determine the K_{HA}'s of water, methanol, ethanol, 2-propanol, cyclohexanol and menthol in t-butyl alcohol with sodium and potassium t-butoxides. The method is accurate, but has the shortcoming of using concentrations much lower than those employed in the kinetic studies.

Previous workers have determined ionization constants by colorimetry, infrared spectrometry, UV-Visible spectrometry, nuclear magnetic resonance, conductimetry and polarimetry using a variety of solvent systems and bases.

CHAPTER I

LITERARY REVIEW

A systematic determination of ionization constants of weak acids was initiated by Conant and Wheland (1) in 1932. They established a scale for a number of weak acids by studying competitive equilibria of the type

$$RH + R'M \rightleftarrows RM + R'H$$

by colorimetry. The position of equilibrium was determined by comparison of the spectra of their individual salts and the spectra exhibited by the reaction mixture at equilibrium.

McEwen (2) expanded the list of pK_a's of weak acids by examining alcohols, amines, and hydrocarbons using colorimetry and polarimetry. The polarimetric method used depended on the differences in optical activity of mixtures of an optically active alcohol, its salts and a weak acid, in which the values of the optical activity of the optically active alcohol and its salts were known. McEwen has established a base for most of the work done on pK_a determinations (Table III and IV).

In 1947 Stearns and Wheland (3) developed an advanced spectrophotometric method for determining the pK_a values of 4,4',4"-trinitrophenylmethane, 2,4-dinitrodiphenylamine, 2,4-dinitroaniline and 4-nitrodiphenylamine in ethanol and of 4-nitrobenzyl cyanide in water. A large shift in the position of the absorption maxima of the undissociated indicator and the ion of the indicator in the visible region allows the determination of the concentration of the negative ion by standard spectrometric methods, provided Beer's law is obeyed and the extinction coefficient of the colored ion is known. It is also important that the Debye-Huckel limiting law holds in the solvent system being studied. The pK_a values can be determined by varying the ratio of base to indicator concentrations. The values obtained for some of the indicators in ethanol are given in Table I.

Hine and Hine (4) determined the relative acidities of water, methanol and 48 weak acids, including alcohols, glycols and amides in isopropyl alcohol with sodium isopropoxide using an expansion of Stearns and Wheland spectrophotometric method. They measured the change in optical density when a weak acid was added to an indicator with base present. This method gives a pK_a for each acid relative to the indicator employed.

Stewart and O'Donnell (5) determined the pK_a's of 14 substituted diphenylamines and 8 substituted anilines in four solvent systems: water, pyridine-water, sulfolane-water, and dimethylsulfoxide-water, each containing tetraalkylammonium hydroxide. The data in Table I show their results in two of these solvent systems. The values for indicators in sulfolane-water and pyridine-water show only a slight difference in the pK_a values. Stewart and O'Donnell (6) also ran a comparative study of substituted phenols and anilines, examining the inductive, electromeric and steric effects by adding nitro and/or chloro groups around the rings (Table II). They found that the difference in pK_a values, ΔpK_a, between substituted phenols and anilines is almost a constant quantity and lies between 10.80 and 12.17 pK_a units.

TABLE I

pK$_a$'s of Indicators in Various Solvents Systems

	Ethylene diamine water	Ethanol amine water	Hydra-zine water	Hydrz-zine water	Sulpholane water	Sulfolane water	Pyridine water	Ethanol
Reference	10	10	10	9	12	5	5	3
4-Nitrobenzyl cyanide	13.45	13.45	13.45	13.43	13.43	---	---	13.4
6 Bromo 2,4-dinitroaniline	---	---	---	---	13.71	13.60	13.66	---
3-Nitrocarbozole	15.10	15.10	15.01	14.16	---	14.03	14.16	---
4,4-Dinitrodiphenyl amine	14.97	14.97	14.90	14.48	---	14.00	14.09	---
2,4-Dinitrodiphenyl amine	14.65	14.65	---	---	---	13.38	13.38	17.71
2,4-Dinitroaniline	15.80	---	---	---	15.43	15.02	---	18.46
4-Nitrodiphenyl amine	>19	16.95	---	15.43	15.76	15.90	---	20.6
4,4'Dinitrodiphenyl methane	---	---	---	15.90	15.82	---	---	---
4,4,4" Trinitrotriphenyl methane	---	---	---	---	---	---	---	17.44
2-Nitroaniline	>19	718.75	---	---	---	17.88	---	---
4-Nitroaniline	>19	---	---	---	18.47	18.37	---	---
2-Nitrodiphenyl amine	>19	18.85	---	---	---	17.57	---	---

TABLE II

Comparison of the Acidities of Anilines and Phenols

Substituent	pK_a Aniline	 Phenol	ΔpK_a
2-Nitro-	17.88	7.08	10.80
4-Nitro-	18.37	7.15	11.22
2,4-Dinitro-	15.00	4.07	10.93
2-Nitro-4-chloro-	17.22	6.36	10.86
2,6-Dichloro-4-nitro	15.55	3.48	12.17
2,4,6-Trinitro-	12.00	0.3	11.9

Stewart, O'Donnell, Cram and Rickborn (7) published data which permit calculation of relative acidities, but not pK_a values, of some indicators in methanolic DMSO. They describe the Hammett acidity function H_- as the ability of a solvent to remove a proton from a very weak acid, essentially neutral except to strong bases. H_- is defined by the equation:

$$H_- = - \log \frac{a_{H+} \; f_{A'}}{f_{HA}} = pK_a + \log \frac{(A^-)}{(HA)}$$

In very dilute aqueous solutions H_- becomes identical with pH. The ratio of log A^-/HA is determined spectrophotometrically and when it is plotted against the H_- values the pK_a's can be computed.

Ridd and More-O'Ferrall (8) determined the acidity function H_- in methanol containing sodium methoxide. Ionization constants of six substituted anilines and amines were determined. If the indicator had one nitro group, its pK_a was determined in methanol with sodium methoxide; if there were two nitro groups isopropyl alcohol with sodium isopropoxide was used; and if another system was needed t-butyl alcohol with sodium t-butoxide was used. When another alcohol other than methanol was used, the values were converted to comply with the acidity function in methanol. The corresponding extinction coefficients at the absorption maxima were used to calculate the ionization ratio ($R=C_{A^-}/C_{HA}$) for the indicator in methanol. The pK_a values of these six indicators are shown in Table I.

The first attempt to construct an acidity function in a binary solvent system was made by Deno (9) in 1952. He varied the concentration of hydrazine from 5 to 60% (by weight) hydrazine in water. The acidity function varied from 11 in 5% hydrazine up to 15.93 in 60% hydrazine. The pK_a values for indicators determined in hydrazine-water system are shown in Table I.

In 1955 Schaal and co-workers (10) determined the acidity functions for ethylenediamine-water, ethanolamine-water, hydrazine-water and t-amyl alcohol containing sodium amyloxide. The pK_a's of some indicators in these solvent systems are shown in Table I. They found a limiting H_- value of 15.53 for anhydrous ethanolamine, 18.2 for ethylenediamine and 19.4 for t-amyl alcohol. The agreement of H_- values obtained with 4-nitrobenzyl cyanide for ethylenediamine-water, ethanolamine-water and hydrazine-water is excellent. On the other hand, the pK_a's of 3-nitrocarbazole and 4,4'-dinitrodiphenylamine vary slightly in hydrazine-water. The values for 3 indicators in hydrazine-water reported by Schaal and co-workers are slightly higher than those communicated in the work of Deno.

Paul and Long (11) commented that this large discrepancy casts considerable doubt on the assumption that these H_- scales are independent of the indicator employed and makes it imperative that this be tested by studies with other indicators.

Langford and Burwell (12) determined the pK_a's of 10 hydrocarbons, substituted anilines and substituted amines in sulfolane-water solvent using phenyltrimethylammonium hydroxide as the base. Employing a spectrophotometric method, they obtained an acidity function value near 20 for a solution of 5 mole % water, 95 mole % sulfolane and 0.013 molar phenyltrimethyl ammonium hydroxide. They pointed out that sulfolane containing 5% water is a million times more basic than pure water when both contained 0.01 molar hydroxide ion. This increased activity is due to the increased activity coefficient of the hydroxide ion.

Streitwieser, Brauman, Hammons and Pudjaatmake (13) worked on a precise method for determining equilibrium acidity measurements for the range 18-34 pK_a units. They used lithium and cesium salts of cyclohexylamine in cyclohexylamine solvent system to measure the concentration of the two anions at equilibrium with the aid of visible spectra of the solution. The pK_a's of 11 hydrocarbons were determined; some of these are shown in Table III.

Steiner and Gilbert (14) obtained comparable pK_a values for hydrocarbons in DMSO, DMSO-methanol and DMSO-water mixtures (Table III). They related the pK_a's of triphenylmethane and diphenylmethane, plus several other indicators by Stearns and Wheland's method to place DMSO in an overall acidity scale. Steiner and Gilbert's data diverged seriously from the data obtained by Streitwieser and coworkers. The pK_a's in DMSO are on the order of 2 to 5 units lower

TABLE III

pK_a's of Hydrocarbons

References	(12)	(14)	(13)	(13)
	McEwen	DMSO Systems	CsCHA in CHA	LiCHA in CHA
9-Phenylfluorene	21	18.38	(18.49)[b]	(18.49)[b]
3,4-Benzofluorene	--	--	19.45	19.38
Indene	--	18.2	19.93	29.97
1,2-Benzofluorene	--	--	20.05	20.24
Benzanthrene	--	--	21.17	20.67
4,5-Methyl nephenanthrene	--	(20.0)[c]	22.63	22.60
Fluorene	25	20.5	22.74	22.83
2,3-Benzofluorene	--	<19.5	23.17	23.16
9-Phinylanthrene	--	24.2	28.5	--
Triphenylmethane	33	27.2	31.48	--
Diphenylmethane	35	28.6	33.1	--
4-Nitroanaline	--	18.6	--	--
_t_-Butyl alcohol	19	--	--	--
DMSO	--	31.3	--	--
Methanol	16	--	--	--

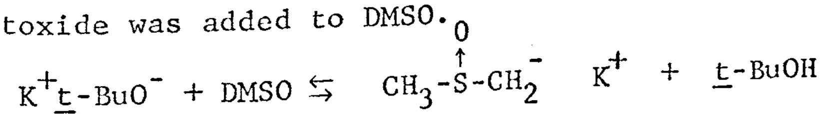
than in cyclohexylamine. The difference may be a solvent effect and/or an ion-pairing effect. In DMSO the equilibria involve largely dissociated ions and in cyclohexylamine ion pairs are formed.

Bethell and Cockerill (15) using visible spectrophotometry measured the pK_a's of seven substituted anilines in t-butyl alcohol containing different t-butoxides as bases. The cations employed were potassium, sodium and benzyltrimethylammonium. It was found that the potassium t-butoxide was twice as strong a base as sodium t-butoxide, but was no more than one-one thousandth as strong a base as benzyltrimethylammonium t-butoxide. When a small cation is used ionization is incomplete, but when a large cation is employed complete ionization seems to occur. They also found that when the temperature of a solution of base in t-butyl alcohol was increased the basicity of the solution decreased. When they added dimethylsulfoxide, tetrahydrothiophen-S, S-dioxide or pyridine-N-oxide to a base in t-butyl alcohol, the basicity of the solution increased substantially. A shift of the λ_{max} in the direction observed for benzyltrimethylammonium t-butoxide, was also noted when one of these solutions was added to an indicator containing potassium t-botoxide.

The first pK_a studies with DMSO were initiated by Corey and Chaykovski (16) in 1962, when they prepared the conjugate base of DMSO, methylsulfinyl carbanion known as the "dimsyl ion". It was prepared by reacting powdered sodium hydride with excess dry DMSO. Dimsyl sodium is highly basic as is shown by its rapid reaction with triphenylmethane to produce a deep red solution of triphenylmethyl carbanion. Deuteration of a known amount of dimsyl ion and triphenylmethane with excess D_2O in DMSO gave an equilibrium constant of 21±4 (25°) measured by the ratio of triphenylmethane: triphenylmethane-d_1.

Price and Whiting (17) working with dimsyl sodium in DMSO found that under anaerobic conditions, titration of weak acids can be carried out quickly, with the end point being located to a single drop of dimsyl sodium using triphenylmethane as the indicator (Table IV). Steiner and Gilbert (18) carried out a similar study using dimsyl potassium. They found end points were being reached when about one half the predicted amount of dimsyl potassium had been added, if the weak acid was an alcohol or an amine. Their values appear in Table IV.

There is some doubt as to the validity of the work of Steiner and Gilbert, and of Ledwith and McFarlane (19), because the dimsyl potassium produced from potassium and DMSO under reduced pressure was probably contaminated with methane-sulfenate ($CH_3SO^-M^+$) as has been shown by O'Conner and Lyness (20). Ledwith and McFarlane made the assumption that the gases given off from the reaction mixture of potassium and DMSO were dimethyl sulfide and hydrogen, when actually they were dimethyl sulfide and methane. Ledwith and McFarlane did find that the dimsyl ion was formed when potassium *t*-butoxide was added to DMSO.



$$K^+\underline{t}\text{-}BuO^- + DMSO \leftrightarrows CH_3\text{-}\overset{O}{\overset{\uparrow}{S}}\text{-}CH_2^- \quad K^+ + \underline{t}\text{-}BuOH$$

Kinetic methods have also been employed to determine the relative acidities of weak acids. Deuterium exchange experiments have been followed primarily by infrared spectrometry, but occasionally with visible and nuclear magnetic resonance spectrometry.

TABLE IV

Comparison Weak-Acids with Dimsyl Bases

Acid	Lit. pK_a	Moles of dimsyl ion per mole of acid to give visible conc. of Ph_3C^-	
		Na^{+b}	K^+
Reference	1,2, & 4	17	18
Benzoic acid	4.2		1.01
Acetic acid	4.8	1.03	
2,4,6-Trichlorophenol	6.2		1.01
Phenol	9.9	1.02	0.99
Formanilide			(1.00)[c]
Glycerol		1.56	1.00
1-Methoxy-2-propanol			0.54
Dipropylene glycol methyl ether			0.54
Tripropylene glycol methyl ether			0.53
Water	15.7	1.00	0.64
Ethanol	18		0.31
n-Butyl alcohol		0.98	0.45
t-Butyl alcohol	19	1.06	0.33
Cyclopentadiene	17	0.99	0.97
Indene	21	0.98	0.98
Diphenylamine	23	0.99	1.00
Aniline	27	0.01	0.01
Triphenylmethane	33		

Shatenshtein (21) concluded that the strengths of weak acids could be determined from the rate of hydrogen exchange, the point of equilibrium in protolytic reactions and its rate of attainment.

Dessy, Okuzumi and Chen (22) used infrared spectrometry to measure the rate of exchange of benzylic hydrogens of acetylenic and aromatic hydrocarbons with deuterium oxide in DMF-trimethylamine solvent system. The rate of exchange was followed by the appearence of the peak due to the formation of DOH.

Richie and Uschold (23) reported that 4,5-methylenephenylanthrene has a pK_a of 20.0 and that 9-methylfluorene has a pK_a of 19.7 in DMSO. The rate of proton transfer was followed spectrophotometrically. They noted that the rates of proton transfer between fluorene and its lithium salt in DMSO is approximately 10^6 M^{-1} sec^{-1}. The work of Eigen (24) shows that D_2O has a rate of proton transfer of $8.4x10^{10}$ $M^{-1}sec^{-1}$ at 298^oK, H_2O (ice) a rate of $8.6x10^{12}M^{-1}sec^{-1}$ at 263^oK, and H_2O a rate of $1.4x10^{11}$ $M^{-1}sec^{-1}$ at 298^oK. This shows there is a great difference in the ability of a dipolar aprotic solvent and protic solvent to transfer a proton.

Eigen determined pK_a's of organic compounds (Table V) in water by a perturbation method noting the changes in electrical properties of the system. Pearson and Dillon (25) in 1952 employed conductimetry in measuring the rates of bromination to determine the rate of ionization of 48 weak acids comprising ketones, aldehydes, esters, acids, amides, mitriles, sulfones and nitro compounds (Table V).

TABLE V

pK_a'a Determined in Water

Reference	(25) Pearson & Dillion pK_a	(24) Eigen pK_a
Acetone	20	20
Acetoacetic ester	methyl 10	$[CH_3CO\overline{CH}COOR]$
	ethyl 10.7	10.68
Acetylacetone	9	9.0
Diethyl Malonate	13.3	--
Diethyl Ethylmalonate	15	--
Water	--	15.75
Ice	--	21.4
Deuterium oxide	--	16.5

Charman, Tiers and Kreevoy (26) employed NMR to measure the rate of base-catalyzed hydrogen exchange between phenylacetylene and water. These rates were followed by the broadening of the acetylenic hydrogen NMR peaks caused by the exchange.

Another method for determining the acidities of hydrocarbons is to follow the rate of exchange of a tritiated compound with a hydrocarbon. By using liquid scintillation counting techniques, the amounts of each tritiated compound can be determined. Hofmann, Muller and Schriesheim (27) used tritiated dimethylsulfoxide with potassium _t_-butoxide to determine pK_a's of 40. They have worked primarily with toluene and polyalkylbenzenes. The instrumentation involves a radio-assaying gas chromatograph to determine the amount of exchange.

CHAPTER II

THEORY

In 1936 Stearns and Wheland (3) showed that the K_{eq} and K_{true} for an indicator could be determined by the following method. They showed that if the absorption of a solution of indicator is measured at a wave length at which the conjugate base of the indicator absorbs, but the undissociated indicator does not, and if the concentration of indicator used is negligible compared to the concentration of base, then

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon_{In^-}} + \frac{1}{(OR-)} \cdot \frac{1}{(\epsilon_{In^-}K_{eq})} \qquad (1)$$

At the wave length employed, ϵ_{In^-} or $K_{true} \cdot C_{HIn}$ is the molecular extinction coefficient of the conjugate base of the indicator, ϵ' is called the apparent extinction coefficient and is equal to the optical density divided by the formal concentration of indicator, (OR^-) is the original concentration of base added to the solution; therefore, for the equilibrium

$$HIn + OR^- \rightleftarrows In^- + ROH$$
$$K_{eq} = \frac{(In^-)}{(HIn)\ (OR^-)} \qquad (2)$$

The equilibrium constant of a weak acid K_{HA} can be determined for the equilibrium,

$$HA + \underline{t}\text{-}BuO^- \rightleftarrows A^- + \underline{t}\text{-}BuOH$$
$$K_{HA} = \frac{(A^-)}{(HA)\ (\underline{t}\text{-}BuO^-)} \qquad (3)$$

To determine the K_{HA} for a weak acid, the concentrations of A^-, HA and t-BuO⁻ are obtained by the following procedure. From Beers law, the concentration of indicator anion is

$$(In^-) = \frac{A}{K_{true}(l)} \qquad (4)$$

where In^- is the concentration of indicator anion, A is the absorption measured, l is the cell width (which is 1 cm in all cases and K_{true} is the graphically-determined extinction coefficient for the system employed. The concentration of indicator is

$$(HIn) = C_{HIn} - (In^-) \qquad (5)$$

where C_{HIn} is the concentration of indicator added to the solution. Then the concentration of $t\text{-}BuO^-$ or B^- is determined by

$$B^- = \frac{(In^-)}{(HIn)\ K_{eq}} \qquad (6)$$

where the K_{eq} is determined for the blank employed in a run.

The total concentration of bases present is

$$C_B = (B^-) + (In^-) + (A^-), \qquad (7)$$

then

$$(A^-) = C_B - (B^-) - (In^-) \qquad (8)$$

The concentration of HA is

$$(HA) = C_{HA} - (A^-) \qquad (9)$$

where C_{HA} is the original concentration of acid added to the solution.

After attaining the values for A^-, HA, and B^- the value of K_{HA} is determined,

$$K_{HA} = \frac{(A^-)}{(HA)\ (B^-)}$$

CHAPTER III

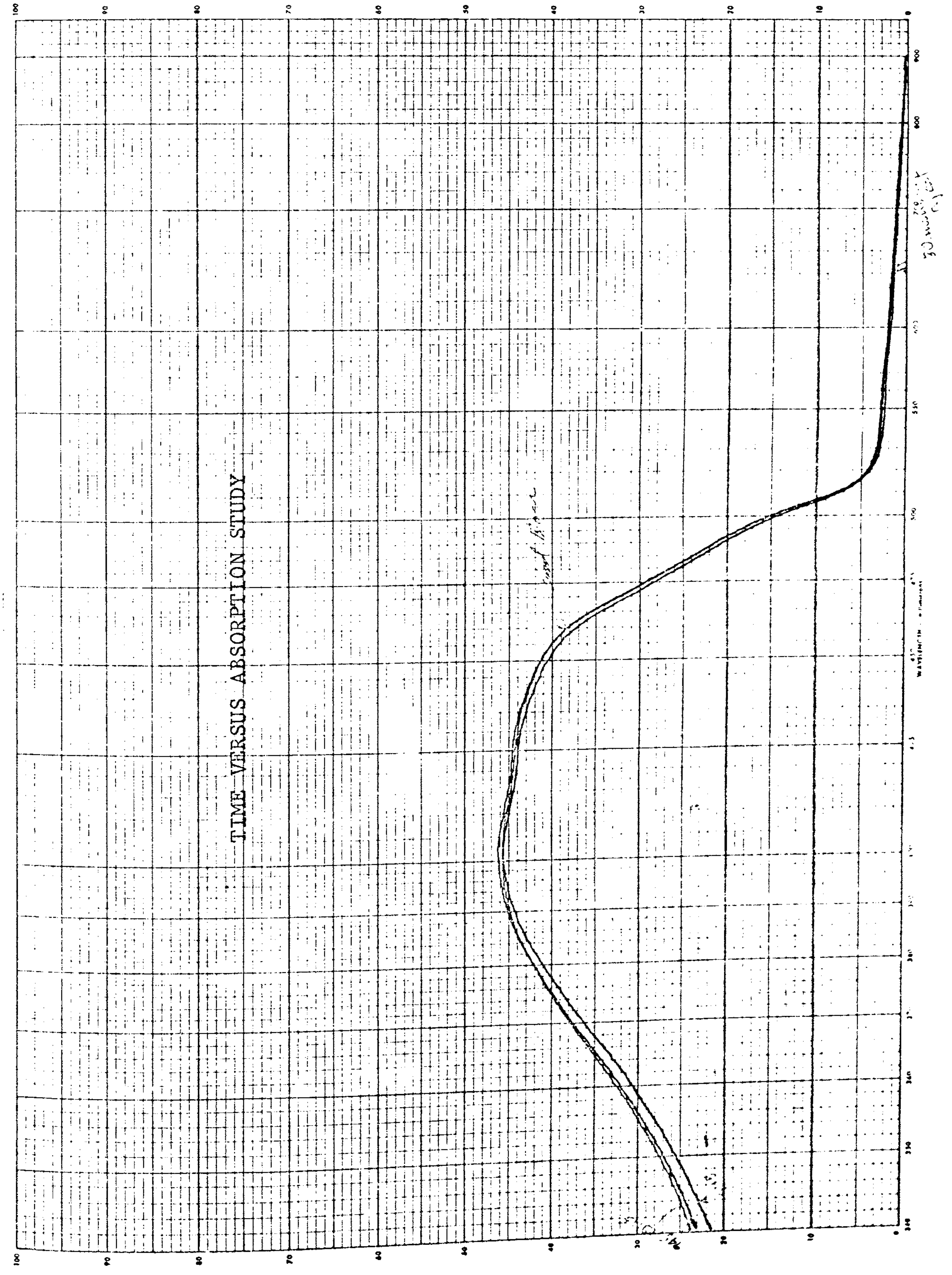
EXPERIMENTAL

The equilibrium constant K_{HA} has been determined for water, methanol, ethanol, iso-propanol, cyclohexanol and menthol in t-butyl alcohol with variation of the t-butoxide base.

A. Analytical Method

Solutions of the alcohols and indicator were prepared by weight on an electric analytical balance followed by volumetric dilutions with calibrated pipettes. All dilutions were carried out in a dry box with a nitrogen atmosphere at 30°C. The concentrations of the bases employed were determined by titration, with standardized hydrochloric acid employing phenolphthalein as the indicator. Immediately after the solutions of base and indicator or base, indicator and alcohol were mixed, the optical density was measured in a Beckman DU Spectrophotometer. Absorption measurements were at 450mμ (The maximum for the anion of the indicator is at 432mμ in t-butyl alcohol). The measurement of absorption of the indicator anion at 450mμ would require the subtraction of the amount of absorbance by the indicator. A time versus absorption study shown in Spectrum No. 1 was run with 2.8×10^{-5}M p-nitroaniline in t-butyl alcohol with 2.2×10^{-2}M potassium t-butoxide. This measurement was run on a Beckman DK-2A Recording Spectrophotometer to determine if there were any spectral changes with time. It was found that there was less than a one percent change in absorption per hour. All solutions were mixed at such concentration as to give optical density readings in the range of 0.3 to 0.6 absorption units.

SPECTRUM I


TIME VERSUS ABSORPTION STUDY
100
90
80
70
60
50
40
30
20
10
0
WAVELENGTH

B. Preparation of compounds

t-Butanol was Fisher Certified Reagent grade. It was dried by adding 1 mole of sodium to 4.5 liters of alcohol and refluxed for 48 hours. It was then distilled at 81°C at 740mmHg. Only the middle portion of distillate was employed.

Potassium t-butoxide solutions were prepared by dissolving reagent potassium t-butoxide in purified t-butanol. It was also prepared by reacting potassium metal with purified t-butanol.

Sodium t-butoxide was prepared by reacting metallic sodium with purified t-butyl alcohol

p-Nitroaniline was purified by triple recrystallization from 95% ethanol and 5% water. It was then dried and had a melting point of 147-8°C.

Ethanol - Anhydrous ethanol was prepared from 99.5% ethanol by reaction with sodium metal following refluxing with diethylphthalate. The ethanol was then distilled at 87°C with only the middle portion employed for these studies.

Methanol - Anhydrous methanol was prepared by reacting Fisher ACS anydrous methanol with magnesium metal. Cooling was employed to control the rate of reaction. The methanol was then distilled at 64°C using only the middle portion of distillate.

2-Propanol - Anhydrous 2-propanol was prepared by distillation from sodium hydride at 82°C. Only the middle portion of distillate was employed.

Cyclohexanol - Anhydrous cyclohexanol (Matheson Coleman & Bell) was prepared by distillation from sodium hydride at 160°C. Only the middle portion of distillate was employed.

<u>Water</u> - Distilled water was always freshly redistilled to remove all carbon dioxide.

<u>Menthol</u> - ℓ-Menthol (Aldrich Chemical) was distilled at 64°C at 18mmHg. Only the middle portion of distillate was employed.

C. Determination of K_{HIn} for p-nitroaniline

To determine the K_{eq} for the weak acids it was first necessary to determine the K_{true} and the K_{HIn} for the indicator in sodium and potassium *t*-butoxides. K_{true} and K_{HIn} were determined by noting the change in absorption versus varying concentration of base, while holding the concentration of indicator constant. In Tables VI and VII the data for the runs in sodium and potassium *t*-butoxide These values are plotted in Figure 1. The graphic values obtained were

	K_{HIn}	K_{true}
Potassium *t*-butoxide	51.64	2.40×10^4
Sodium *t*-butoxide	23.14	2.42×10^4

D. Determination of K_{HA} for weak acids

Once the K_{HIn} and K_{true} for a particular base have been determined a solution of base and indicator was chosen that gave an absorption in the range of 0.3 to 0.6 absorption units. After choosing the correct set of concentrations, weak acids were introduced and the change in absorption was noted. The data for the runs in potassium and sodium *t*-butoxides are shown in Tables VIII and IX respectively. The results are shown in Tables X and XI.

E. Sample calculations

A sample calculation is shown for methanol in potassium *t*-butoxide.

Concentration of p-nitroaniline	$2.8 \times 10^{-5}M$
Concentration of methanol	$7 \times 10^{-2}M$
Concentration of potassium _t_-butoxide	$2.66 \times 10^{-2}M$
Absorption of blank	
Absorption of methanol	1.25

$K_{true} = 2.40 \times 10^4$

$K_{HIn} = 30.3$

$$[In^-] = \frac{.125}{2.40 \times 10^4} = .52 \times 10^{-5}M$$

$$[HIn] = 2.8 \times 10^{-5}M - .52 \times 10^{-5}M = 2.28 \times 10^{-5}M$$

$$[B^-] = \frac{.52 \times 10^{-5}}{2.28 \times 10^{-5}(30.3)} = 7.54 \times 10^{-3}$$

$$[A^-] = 2.66 \times 10^{-2} - .754 \times 10^{-2} - .52 \times 10^{-5} = 1.906 \times 10^{-2}$$

$$[HA] = 7 \times 10^{-2} = 1.91 \times 10^{-2} = 5.09 \times 10^{-2}$$

$$K_{MeOH} = \frac{1.91 \times 10^{-2}}{(5.09 \times 10^{-2})\ (7.54 \times 10^{-3})} = 49.7$$

TABLE VI

Data for K_{HIn} Determination with Potassium *t*-Butoxide

Concentration of p-nitroaniline 2.8×10^{-5}M

Concentration of potassium *t*-butoxide	Absorption
4.16×10^{-2}	.520
2.60×10^{-2}	.380
2.08×10^{-2}	.345
1.56×10^{-2}	.320
1.04×10^{-2}	.240
5.2×10^{-3}	.086

TABLE VII

Data for K_{HIn} Determination with Sodium *t*-Butoxide

Concentration of p-nitroaniline 2.8×10^{-5} M

Concentration of sodium *t*-butoxide	Absorption
1.63×10^{-1}	.540
9.75×10^{-2}	.470
6.50×10^{-2}	.410
3.25×10^{-2}	.328
1.63×10^{-2}	.212
3.25×10^{-3}	.065

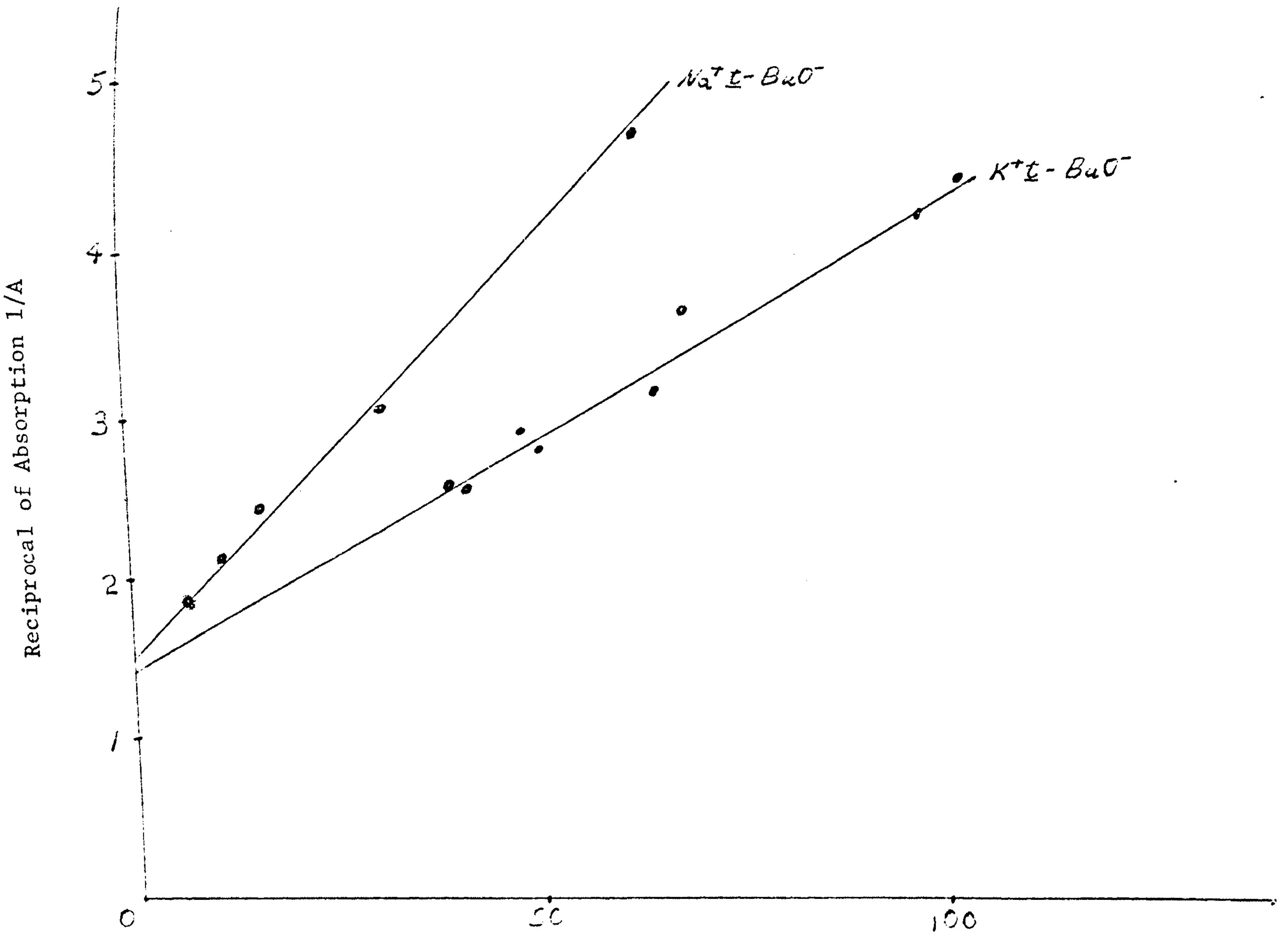


Figure 1 Reciprocal of Base 1/B

TABLE VIII

Data for K_{HA} Determinations with Potassium *t*-Butoxide

	Run I	Run II
Concentration of indicator	2.8×10^{-5} M	2.8×10^{-5}M
Concentration of base	2.15×10^{-2}	2.66×10^{-2}M
Concentration of HA	1×10^{-1} M except Menthol 4.3×10^{-2}	7×10^{-2} M except Menthol 1×10^{-1}M
K_{HIn}	45.0	33.0
K_{true}	2.40×10^{4}	2.4×10^{4}

Absorption Data

	Run I	Run II
Blank	.330	.300
Methanol	.108	.125
Water	.128	.140
Ethanol	.218	.212
2-propanol	--	.263
Cyclohexanol	--	.265
Menthol	.312	.282

TABLE IX

Data for K_{HA} Determination with Sodium *t*-Butoxide

	Run III	Run IV
Concentration of indicator	$2.8 \times 10^{-5}M$	$2.8 \times 10^{-5}M$
Concentration of base	$1.13 \times 10^{-1}M$	$6.82 \times 10^{-2}M$
Concentration of HA	$1 \times 10^{-1}M$	$1 \times 10^{-1}M$ except isopropanol, cyclohexanol and menthol $-2 \times 10^{-1}M$
K_{HIn}	23.6	23.7
K_{true}	2.42×10^{4}	2.42×10^{4}

Absorption Data

	Run III	Run IV
Blank	.495	.420
Menthol	.348	.220
Water	NA	NA
Ethanol	.427	.314
2-propanol	.475	.350
Cyclohexanol	.478	.352
Menthol	.490	.410

TABLE X

K_{HA} Determined with Potassium t-Butoxide

	Run I	Run II
Methanol	48.9	49.7
Water	37.3	40.2
Ethanol	10.3	12.8
2-propanol	--	3.74
Cyclohexanol	--	3.70
Menthol	2.95	1.26

TABLE XI

K_{HA} in t-Butyl Alcohol with Sodium t-Butoxide

	Run III	Run IV
Methanol	47.0	45.2
Water	--	--
Ethanol	10.1	13.7
2-propanol	5.50	3.00
Cyclohexanol	3.3	2.92
Menthol	128	139

ERRATUM

P. 29

The standard free energy change for the exchange of potassium and sodium ions between anions of the alcohols is approximately zero.

$RO^-K^+ + \underline{t}\text{-}BuO^-Na^+ \rightleftarrows RO^-Na^+ + \underline{t}BuO^-K^+ \; \Delta G \ddagger 0$

However, the standard free energy change for the exchange of sodium and potassium ions between the anions of the alcohol and the indicator is not equal to zero.

$RO^-K^+ + Na^+In^- \rightleftarrows RO^-Na + K^+In^-: \; \Delta G \ddagger 0$

CHAPTER IV

DISCUSSION

A. Discussion of results

The results obtained in the determination of K_{HA} in t-butyl alcoholwere methanol>water>ethanol> 2-propanol≈cyclohexanol>menthol, which is in agreement with the order of those values obtained by Hine and Hine (4) in 2-propanol (Table XII). The values obtained for the weak acids are given in Table X and XI. Water was not measurable in sodium t-butoxide, because the solution became cloudy due to the formation of solid sodium hydroxide.

The values of methanol and water show methanol to be a much stronger acid than water. Methanol is approximately four times stronger than ethanol while ethanol is about four times stronger than 2-propanol.

The values of K_{HA} for 2-propanol and cyclohexanol are approximately the same. This would be predicted, since the two compounds are structurally the same. Menthol has the same basic structure, but is a weaker acid than 2-propanol and cyclohexanol, apparently because the iso-propyl group alpha to the hydroxyl group blocks the abstraction of the hydroxyl proton.

The values of K_{HA} obtained in potassium t-butoxide and sodium t-butoxide are found to be the same. These values would be expected to be the same, since the only difference in the measurements is the amount of base employed to obtain a measurable color change of the indicator. The K_{HA} of the weak acid is therefore shown to be independent of the cationic change in the bases. It was found when

TABLE XII

K_{HA} Determined by Hine & Hine in 2-propanol

	K_{HA}
Methanol	4.0
Water	1.20
Ethanol	0.95
2-Propanol	0.5

determining the K_{eq} for the indicator, that potassium t-butoxide is twice as strong a base as sodium t-butoxide. This effect was also shown by Cockerill and Bethell (15) on various indicators by changing the t-butoxide cation in t-butyl alcohol. The difference in basic strength gives a slight insight to the amount of ion-pairing, but one needs to be cautious in describing the amount of ion pairing in this type system.

B. Discussion of method

p-Nitroaniline was selected as the indicator, because it had been employed throughout the literature and was in the desired range of the weak acids to be determined.

There are four factors which must be considered when choosing a solvent for K_{eq} determinations. They are: 1) the basicity of the solvent or the limiting acidity function; 2) dispersion interaction of highly colored anion with the solvent; 3) the amount of hydrogen bonding in the solvent; and 4) the electrostatic effects of the solvent.

t-Butyl alcohol was employed as the solvent, because it was desirable to know the relative acidities of the alcohols in t-butyl alcohol for Michael reaction studies.

The spectrophotometric method employed is simple and easily repeatable. Once the proper concentrations are determined, a set of solutions may be prepared and run in a short period of time. The precision of measurements may be imporved by employing greater accuracy in the measurements of concentrations in each of the samples. It is important to remember that these solutions are very hygroscopic and must be employed quickly when taking measurements.

In reading the absorbances it is important to read them as carefully as possible to three significant figures, because any deviation will change the K_{HA} significantly. Another important precaution is to measure the absorption of the base to see if it absorbs at the wave length being empolyed. If the base blank does absorb the value must be subtracted from all the absorption values obtained for that run.

An attempt was made to determine the K_{HA} for four malonate esters in t-butyl alcohol with potassium t-butoxide employing p-nitroaniline as the indicator. It was found that a reaction was occurring between the malonate esters and the indicator in the presence of potassium t-butoxide. This reaction was discovered by employing an amount of ester equal to the amount of indicator and noting any change in absorption. This change could not have been due to the K_{HA} of the ester, since concentrations one thousand times greater would be needed to see any change in absorption due to the K_{HA} of the ester.

Attempts were also made to determine equilibrium constants in DMSO, but two diffulties arose. First the hygroscopic nature of DMSO is so great that a sophisticated system is needed to handle samples. It was found that stoppered silica cells will keep the system stable, but a shortage of silica cells and the time interval in preparation of samples made measurements extremely difficult. The second difficulty involves the preparation of dimsyl bases without the color. When preparing dimsyl sodium from sodium hydride and DMSO it was found that a colorless solution could be attained only if the temperature was kept below 50°C. Over a period of three hours the color of solution became a faint yellow and then slowly turned green. Attempts to make dimsyl lithium as a colorless solution failed. It was found that the solution turned pink at 30° and 70°C. When attempts were made to prepare dimsyl potassium from potassium amide, the potassium amide exploded. It should be noted that potassium is readily attacked by oxygen to give highly dangerous oxides of potassium, which can explode upon contact with the amide.

Futher studies should be made in ethanol to determine the values of methanol and water. It may be possible to find a relationship between solvent systems, if enough systems and compounds are measured. This may be accomplished by relating the K_{HA} values obtained for weak acids in these systems.

CHAPTER V

CONCLUSIONS AND RESULTS

The K_{HA} have been determined for water and five alcohols in _t_-butyl alcohol employing sodium and potassium _t_-butoxide. The K_{HA} values are methanol 47.8, water 38.7, ethanol 11.7, isopropanol 3.3, cyclohexanol 3.3 and menthol 1.24. It was also shown that in _t_-butyl alcohol p-nitroanaline has a K_{HIn} value of 51.6 employing potassium _t_-butoxide and 23.1 employing sodium _t_-butoxide. The K_{HIn} values show that potassium _t_-butoxide is twice as strong a base as sodium _t_-butoxide.

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