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I am submitting herewith a thesis written by Gary Boyd Mullinax entitled "The Substituent Effects of Methyl, Cyclopropyl, and Phenyl at the Cationic Center." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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THE SUBSTITUENT EFFECTS OF METHYL, CYCLOPROPYL, AND PHENYL AT THE CATIONIC CENTER

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Gary Boyd Mullinax

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ABSTRACT

The relative heats of protonation of a group of ketones with methyl, cyclopropyl, and phenyl substituents were measured in a variety of acid systems. The decreasing order of relative stabilities determined by the enthalpies was usually found to be c-Pr>Me>Ph. It was found that the relative order of stabilities due to the substituent is dependent upon the rest of the molecule. The results suggest that there is a cooperative effect between the substituents.

There exists a major discrepancy between conclusions based on enthalpies and predictions based on ^{13}C chemical shifts as to the relative order of ion stabilities. The phenyl group always produces the least stable ion whereas ^{13}C chemical shifts indicate that phenyl is the best at delocalizing the positive charge.

Acidity function data were used to calculate equilibrium constants for protonation in high acid concentrations where protonation is essentially complete. The free-energies calculated from the equilibrium constants are combined with enthalpies of protonation measured in the same acid to yield the relative entropies of protonation. The entropy values indicate that the solvent is more ordered in the more exothermic reactions.

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CHAPTER I

INTRODUCTION

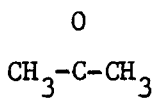
A. Background

In the last few years there has been a growing interest in the effects of substituents on the charge delocalization and thermodynamic stability of carbocations. The methods of analysis that have been used are molecular orbital (MO) calculations,[1] carbon-13 nuclear magnetic resonance (^{13}C nmr),[2-5] rates of solvolysis,[6,7] solution calorimetry,[8,9] and acidity function studies.[10] One problem of particular interest is the controversy between G. A. Olah and H. C. Brown concerning the relative order of carbocation stabilities where the substituents involved are methyl (Me), cyclopropyl (c-Pr), and phenyl (Ph). This is important because it involves the manner in which different major classes of substituents interact with carbocations.

Olah and co-workers have concluded that Ph>c-Pr>Me in their abilities to delocalize charge based on ^{13}C nmr chemical shifts. This trend was first observed in a set of tertiary carbocations, $R(CH_3)_2C^+$ (where R = Me, c-Pr, and Ph).[11] They did extensive experimentation to see if the trend is consistent with other series of carbocations containing these substituents. All of the other possible combinations of these substituents in tertiary carbocations as well as the secondary species were studied. The ions were formed by protonation of the alcohol precursors in SO_2ClF-SbF_5 or SO_2ClF-FSO_3H-SbF_5 acid systems at low temperatures (-60 to -90°C).[2] In each set of compounds the same

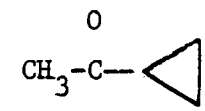
order of delocalization abilities was determined by the ^{13}C chemical shifts of the central sp^2 hybridized carbons. A comparison of these chemical shifts is contained in Table I.

Olah has also measured the ^{13}C chemical shifts of the ketones with methyl, cyclopropyl, and phenyl groups directly attached to the carbonyl carbon (I-VI) and their protonated species. The ions were formed by protonation in a FSO_3H-SbF_5(1:1)-SO_2Cl solution at -70°C.



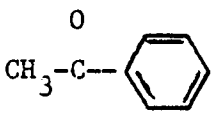
acetone

I



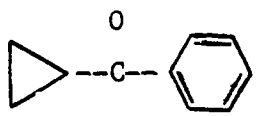
cyclopropyl methyl ketone

II



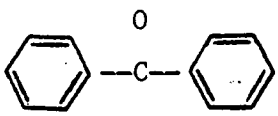
acetophenone

III



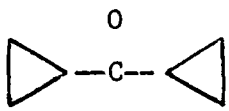
cyclopropyl phenyl ketone

IV



benzophenone

V

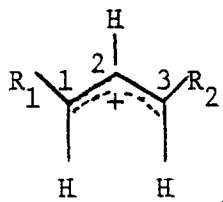


dicyclopropyl ketone

VI

The carbonyl carbon of conjugated ketones is more shielded where conjugation exists.[12] The differences in carbonyl ^{13}C chemical shift should be enhanced in the protonated form since the strongly electron-withdrawing oxygen atom has a formal positive charge. Once again it was determined that Ph>c-Pr>Me in their charge delocalization abilities. Their chemical shifts are shown in Table II.

A third series of carbocations with the substituents of interest were prepared by protonation of allylic alcohols to form the alkenyl cations (VII).[4] It was determined by the ^{13}C chemical shifts of C-1



VII

TABLE I

COMPARISON OF ^{13}C CHEMICAL SHIFTS[a] IN 2° AND 3° CARBOCATIONS

2° IONS	C+ Chemical Shift	3° IONS	C+ Chemical Shift
$CH^+-(CH_3)_2$	-125.0	$C^+-(CH_3)_3$	-135.4
$CH^+-(c\text{-}Pr)_2$	-59.9	$C^+-CH_3)_3$	-135.4
$CH^+-(c\text{-}Pr)_2$	-59.9	$C^+-(c\text{-}Pr)_3$	-77.8
$CH^+-(Ph)_2$	-6.9	$C^+-(Ph)_3$	-18.1
$CH_3CH^+-CH_3$	-125.0	$(CH_3)_2C^+-CH_3$	-135.4
$CH_3CH^+-c\text{-}Pr$	-59.1	$(CH_3)_2C^+-c\text{-}Pr$	-86.8
CH_3CH^+-Ph	-40	$(CH_3)_2C^+-Ph$	-60.6
$c\text{-}PrCH^+-CH_3$	-59.1	$(c\text{-}Pr)_2C^+-CH_3$	-81.6
$c\text{-}PrCH^+-c\text{-}Pr$	-59	$(c\text{-}Pr)_2C^+-c\text{-}Pr$	-77.8
$c\text{-}PrCH^+-Ph$	-32.6	$(c\text{-}Pr)_2C^+-Ph$	-67.3
$PhCH^+-CH_3$	-40	$(Ph)_2C^+-CH_3$	-35.5
$PhCH^+-c\text{-}Pr$	-32.6	$(Ph)_2C^+-c\text{-}Pr$	-41.3
$PhCH^+-Ph$	-6.9	$(Ph)_2C^+-Ph$	-18.1

a) relative to TMS

TABLE II

^{13}C CHEMICAL SHIFTS IN PROTONATED (FSO_3H) METHYL, CYCLOPROPYL, AND PHENYL KETONES

Compound	Carbonyl	CH_3	cyclopropyl CH	cyclopropyl CH_2	phenyl Ci	phenyl Co	phenyl Cm	phenyl Cp
$CH_3COH^+CH_3$	250.3	32.6						
CH_3COH^+(c-Pr)	243.4	(22.2,29.0,30.5,31.1,31.8,34.2)[a]						
	240.5							
$CH_3COH^+C_6H_5$	220.4	27.8			131.4	133.4	133.4	147.9
(c-Pr)$COH^+C_6H_5$	223.2		26.4	33.3	132.2	133.1	133.1	144.4
$C_6H_5COH^+C_6H_5$	210.0				132.3	141.0	133.3	146.3
					131.4	137.5		144.2
(c-Pr)COH^+(c-Pr)	238.2		20.6	27.8				
			29.9	27.2				

[a]Assignments uncertain

and C-3 that c-Pr $\gtrsim$Ph>>Me in charge delocalization abilities. This result is different from that observed in the previous systems. The reason given for this discrepancy was attributed to the conformational effect of the cyclopropyl group on a carbocationic center. It was also noted that a comparison of tertiary species to secondary species must be made with extreme caution since steric hindrance is a much greater factor in the tertiary case.

H. C. Brown and co-workers have shown by solvolysis of the esters, RMe_2COPNB, in 80% aqueous acetone that the relative ability of the substituents to stabilize the transition states is c-Pr>Ph>Me.[6] Brown's conclusion is based on the Hammond postulate which suggests that the stabilities of the transition states indicate the stabilities of the carbocation intermediates because they are so closely related in energy.[13] In systems where the ground state energies are insignificant the solvolytic rates indicate the relative stabilities. A recent paper by Arnett[14] supports the use of solvolysis data to infer carbocation stability.

Brown used paranitrobenzoate(OPNB) as the leaving group and acetone as the solvent because polar solvents accelerate reactions where charges are formed. As the R group was changed the relative rates were methyl (1.00), phenyl (10^3), and cyclopropyl ($10^{5.5}$). The intermediate carbocations formed are the same tertiary species produced by Olah in his experimentation, but there is no correlation between the ^{13}C chemical shifts and the rates of solvolysis. Brown has also pointed out that there is a discrepancy in the chemical shifts of the para carbons of the phenyl groups in the tertiary species where a

methyl and a phenyl group are constant as the third substituent is changed. Those chemical shifts suggest that c-Pr>Ph>Me in their charge delocalization abilities even though the chemical shifts of the central carbons indicate otherwise. In the series where two phenyl groups are constant and the third substituent is changed, the order of chemical shifts of the para carbons show that Ph>c-Pr>Me which is in good agreement with the chemical shifts of the central carbon. Brown has also obtained the solvolytic rates of some of the other tertiary species which also indicate that c-Pr>Ph in their abilities to stabilize the positive charge. Other substituents where steric strain exist were used to show that the relief of strain in the cyclopropyl group is not a significant factor upon the rate of solvolysis.[7]

A different study that was done a few years prior to the work of Olah and Brown gives a third method which can be used to analyze substituent effects. E. M. Arnett and co-workers used solution calorimetry to determine the relative basicity of weak bases. They measured the enthalpy of formation of a great number of carbocations in FSO_3H acid systems.[8] Among the compounds protonated were four of the ketones with methyl, cyclopropyl, and phenyl substituents (I, III, V, and VI). It is noticed that the enthalpy terms are less exothermic when phenyl groups are present instead of methyl or cyclopropyl groups. This implies that the carbocations formed are less stable with phenyl substituents which contradicts both of the studies listed previously.

These three independent studies clearly show a discrepancy in the effect which methyl, cyclopropyl, and phenyl groups have on

carbocations. The calorimetric data provides a very reliable method to obtain relative stabilities of the carbocations. It is a direct measurement of the energies involved in the ionization process. The family of ketones where the substituents of interest are directly attached to the carbonyl carbon atom (I-VI) provide a system where the protonated species can be examined by both ^{13}C nmr and calorimetric analysis. A thorough study of this system is reported in this thesis.

B. Carbocations

The first direct observation of stable carbocations was the preparation of crystalline salt derivatives of triphenylmethane.[15] Direct evidence for carbocations in solution was provided by Hantzch when he showed that the absorption spectra of triphenylmethanol in sulfuric acid was identical to those of the conducting solutions of triphenylmethylchloride in nonaqueous solvents.[16] Following these basic developments, a great number of studies have been done concerning the properties and structures of carbocations. This is an area of great importance since many organic reactions in solution have carbocation intermediates.

As the studies of carbocations advanced, sulfuric acid became less useful as a protonation solvent. As weaker bases were studied, the ions became less stable. In order to be able to protonate weaker bases, a new class of highly acidic media was developed. These strong acid systems are referred to as "super acids." The work in this area has vastly broadened the range of organic cations that can be studied directly.[17] The term "super acid" is now considered to be any strong acid that is equal to or greater than 100% sulfuric acid.[18]

"Super acids" have low nucleophilicity and a large liquid range. The low freezing points allow studies of many ions that may react or rearrange at room temperature. Gillespie and Birchall developed the use of fluorosulfonic acid (FSO_3H)[19] while the group at Royal Dutch Shell pioneered the use of liquid HF.[20] The introduction of "super acids" along with the advancement of nuclear magnetic resonance makes the identification of carbocations a routine process.

A number of factors govern the energies of carbocations and one area of interest is the role of substituents. The stabilization of carbocations is determined in part by the ability of the substituents to delocalize the positive charge. This stability has been traditionally explained by inductive and resonance effects. The methyl, cyclopropyl, and phenyl groups are of particular interest in the roles they take in stabilizing positive charge. A brief analysis of each substituent is listed below.

1. Methyl

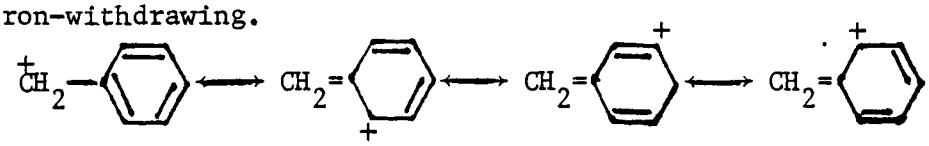
Alkyl groups are electron releasing by the inductive effect, so the more substituted the carbocation, the more stable it is.

$$\underset{\text{increasing stability}\rightarrow}{CH_3^+ < MeCH_2^+ < Me_2CH^+ < Me_3C^+} \qquad (1)$$

2. Phenyl

Aromatic groups have a conjugated π system and can further delocalize the π electrons to the empty p orbital when coplanarity exist to allow maximum overlap of the p orbitals. This dispersion of the charge or resonance stabilization allows the positive charge to be located on the ortho and para carbon atoms. This can best be

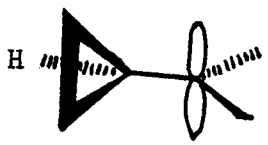
represented by the benzyl cation. The inductive effect of phenyl is electron-withdrawing.



(2)

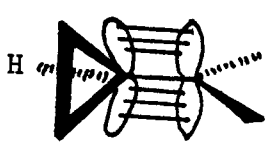
3. Cyclopropyl

The ability of cyclopropyl to stabilize an adjacent carbocation has been examined[21] and equilibria studies have shown that it is often better at stabilizing positive charge than a phenyl group.[22] The geometry necessary for carbocation stabilization to be the bisected form (VIII).[23-25]



VIII

In this position the cyclopropyl ring has the best interaction with the empty p orbital at the cationic site. This ability to stabilize the positive charge is more than an inductive effect alone. Inductive effects of cyclopropyl groups have been shown to be slightly electron-withdrawing compared to other alkyl groups.[26,27] The orbitals in the plane of the ring are very high in p character which overlap each other to form what are known as "banana bonds" (IX). This formation allows a π-π interaction with the adjacent sp^2 carbon.[22,28,29]



IX

From the known internal stabilizing effects alone it would be predicted that the order of stabilities due to inductive effects

would be Me>c-Pr$\overset{>}{\sim}$Ph. When resonance effects are isolated it would be predicted that Ph$\overset{\sim}{\sim}$c-Pr>>Me.

C. NMR

Cryoscopic and conductivity experiments first indicated the existence of carbocations but the development of nuclear magnetic resonance has provided a method by which the structures can be examined routinely and in detail. The introduction of Fourier-transform spectrometers about 1970 has allowed nmr to be used for nuclei having low abundance such as carbon-13. Almost any nucleus with a magnetic moment can now be detected in a fairly routine manner.

Several theoretical treatments have been used to determine the factors that are involved in ^{13}C chemical shifts.[30,31] There are three basic terms that contribute to the total shielding σ (3) where σ_d is the diamagnetic contribution, σ' the neighboring group contribution, and σ_p the paramagnetic contribution.

$$\sigma = \sigma_d + \sigma' + \sigma_p \qquad (3)$$

The diamagnetic term is due to the currents involving electrons on the nucleus as if it were a free atom. The influence of charge on σ_d for ^{13}C chemical shifts is determined by direct calculation of the charge on the carbon atom under consideration. D. M. Grant has shown that the effect of charge on σ_d is due to two factors.[32] First, an increase in electron density increases the diamagnetic current density resulting in an upfield shift. Secondly, an increase in electron density increases the effective radius of the orbitals which by shielding the nuclear charge results in a downfield shift. These two effects cancel such that σ_d cannot make a principle contribution to the chemical shift.

The σ' term represents electron circulations on all other atoms and specific anisotropic groups such as phenyl and carbonyl. The effect that these groups have is very small and does not contribute more than a few parts per million to the chemical shift. This term is considered to be negligible in ^{13}C chemical shift analysis.

The main contribution to the ^{13}C chemical shift comes from the σ_p term. The factors that affect this term are the average excitation energy of the electrons ΔE, the hybridization, and the charge polarization. The ΔE term has traditionally been assumed to be negligible in determining the chemical shift but is now considered to be of some importance in certain cases.[33] Hybridization significantly affects the chemical shift. Carbons of sp^3 hybridization show up at a high field whereas sp^2 carbons yield low field shifts. Charge polarization effects are considered to dominate the paramagnetic term. The effects of substituents on ^{13}C chemical shifts are additive and it is seen that direct substitution with an electron-withdrawing character creates the largest variation. Remote substituents also affect the chemical shift but are more complex in nature.

When a series of compounds with similar hybridization are studied in the same solvent system, the chemical shifts should reflect the π electron densities.

The first correlation of ^{13}C chemical shifts to calculated charge densities was made by Spiesecke and Schneider in 1961.[34] About 1970 this correlation was examined further by Olah and Mateescu.[35] Their results are illustrated in Figure 1. In the tetraphenylcyclobutadiene and triphenylcyclopropenium ions, it was necessary to use

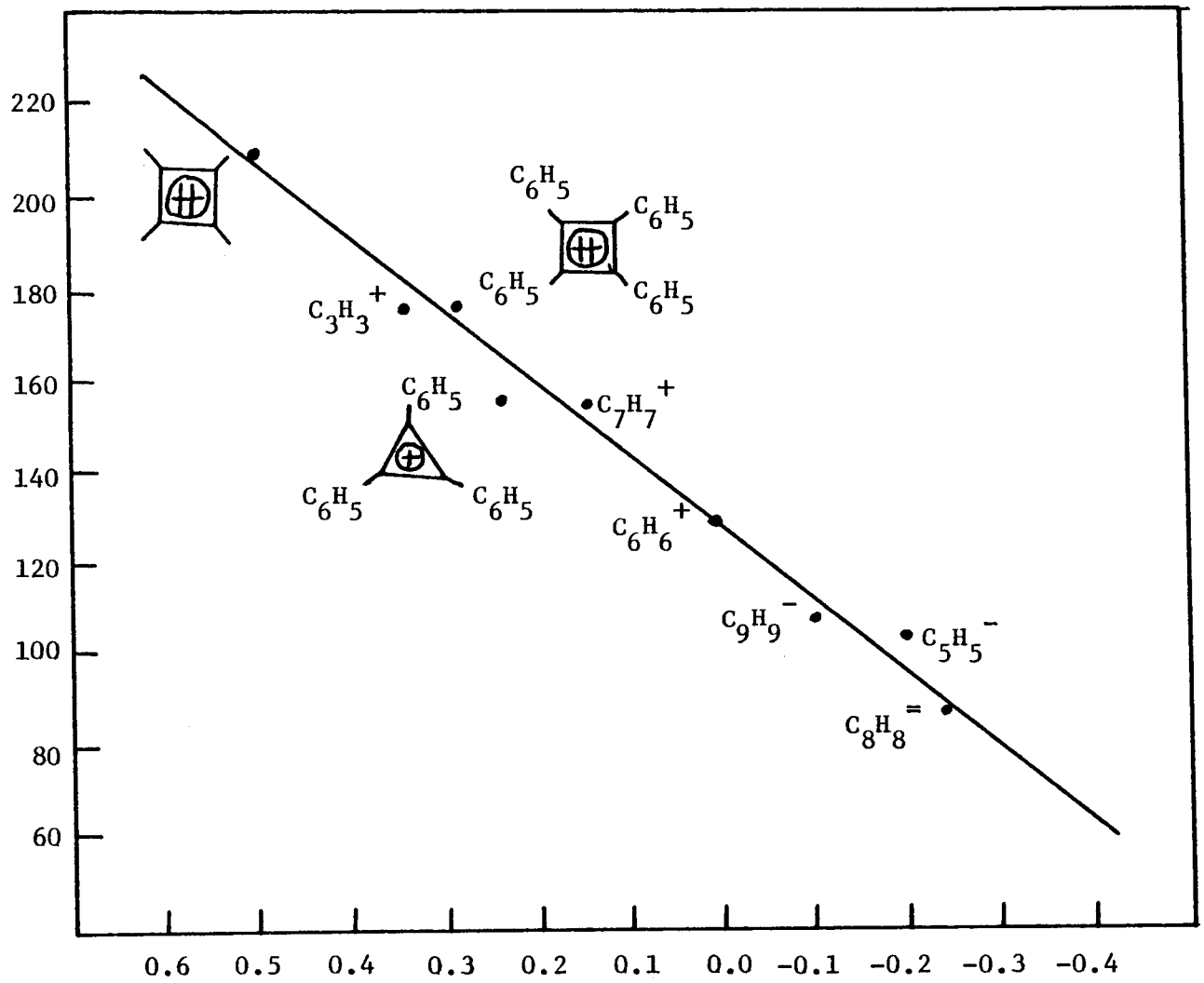


Figure 1. Dependence of carbon-13 chemical shifts on charge density.

a model that gives π charge only and not total charge so that a good correlation line would be formed. It was also assumed that the methyl groups in the tetramethylcyclobutadiene ion do not bear any of the positive charge. If these effects had also been considered the correlation would be changed slightly.[36] This suggests that calculated charge density versus ^{13}C chemical shift plots will give slightly different correlations depending on the parameters that are considered. There is considerable evidence that a high positive charge produces a downfield shift. It is of specific interest here to see how the methyl, cyclopropyl, and phenyl substituents contribute to the ^{13}C chemical shifts and how well these shifts correlate with ion stabilities.

A large number of studies have been made of ^{13}C chemical shifts of carbocations with methyl substituents. It has been shown that methyl groups do alter the chemical shifts of the cationic carbon. When the t-butyl cation (330ppm) is compared to the isopropyl cation (320ppm) it can be deduced that there is more positive charge in the tertiary species so a methyl group deshields the cationic carbon. The large number of carbocations examined by Olah and co-workers show that a methyl group always deshields the central atom. One contradiction does exist in that a second methyl substituent on a cationic site creates an upfield shift in some cases.[37]

There is considerable experimental evidence that substituents do alter chemical shifts and that they reflect the electron densities for carbon atoms with similar hybridization. ^{13}C nmr gives information about charge distribution that is not obtainable by any other technique.

D. Calorimetry

The development of new carbocations in "super acid" media led E. M. Arnett and co-workers to investigate the thermodynamics of their formation. The ability to measure the enthalpy of these reactions forming the carbocations has given a great deal of information concerning the stabilizing factors in carbocations.[38-40] The strong acid most frequently used was fluorosulfonic acid. The procedure used was protonation of the parent compounds in a solution calorimeter. The enthalpies were obtained from the measured heats of reaction. Since structures of the ions are clearly seen in the nmr with no side products formed, the heat observed is simply the sum of the heat of formation and solvation of the carbocation, the heat of formation of the anion and its solvation, and the heat of solution of the ion precursor. Measurement of the heats of reaction for a series of ions from similar starting materials cancel out the contribution made by the anion because it is constant. Correction for intramolecular forces in the ion precursor is made by measuring the heats of solution of the precursor in an inert solvent such as carbon tetrachloride. When this value is subtracted from the heat of reaction yields the heat of protonation (4). Therefore the reported

$$\Delta H_c^+ = \Delta H_{Rxn} - \Delta H_s, CCl_4 \qquad (4)$$

values represent relative heats of protonation quite accurately for a series of compounds.

E. Acidity Functions

The ability to measure acid strength has been a problem of great importance.[41] The aqueous pH scale has been the standard

measurement of acidity but in concentrated aqueous acid solutions or non-aqueous solutions the pH concept fails. The acidity of such media is expressed using acidity functions first introduced by Hammett and Deyrup.[42,43]

The dissociation constant, (K_{BH}^+), for a weak base B, reacting with a strong protic acid is defined by equation (6) where a = activity and f = molar activity coefficient. The ionization ratio $[BH^+]/[B]$ is usually measured spectroscopically. The activity coefficient term is

$$B + H^+ \underset{\longrightarrow}{\overset{K_{BH}^+}{\rightleftharpoons}} BH^+ \qquad (5)$$

$$pK_{BH}^+ = \log(a_B a_{H^+}/a_{BH}^+) = \log[BH^+]/[B] - \log[H^+] - \log(f_B f_{H^+}/f_{BH}^+) \qquad (6)$$

assumed to be the same for all weak bases leading to an acidity function H_o which is a unique function of the acid concentration. This assumption is known as Hammett's activity coefficient postulate. The H_o scale has the standard state of infinite dilution in water where the activity coefficients become unity such that equation (6) becomes equation (7). The H_o scale is an extension of the pH scale into strong acid media where the pH method breaks down.

$$H_o = pK_{BH}^+ - \log[BH^+]/[B] = -\log[H^+] - \log(f_B f_{H^+}/f_{BH}^+) = pH \qquad (7)$$

A series of primary anilines are anchored to the pH scale where some members of the series are at the end of the pH scale and the beginning of the H_o scale. This is done by the indicator overlap method. The pK_{BH}^+ for an indicator base that follows the pH scale is determined and then the pK_{BH}^+ value is used to determine the H_o value of a slightly stronger acid concentration using equation (7). This H_o

value is then used to determine the pK_{BH}^+ value of the next weaker base which again is used to determine the H_o of slightly stronger acidic media. This procedure can be repeated as long as two carbocations whose indicator ratios are capable of being measured can be formed in the same acid solution. The strength of any unknown weak base can be determined as long as it is a suitable indicator such that the concentration of the protonated species can be measured.

The H_o function is the most used measure of acidity of strong acid systems and was defined by the use of primary anilines as weak base indicators. Figure 2 gives the H_o values for some common strong acid systems. The H_o value of pure fluorosulfonic acid is about -15 which was extrapolated from the data of the H_2SO_4-FSO_3H system.[44]

It has been found that the protonation of different types of bases is described by different acidity functions.[45] The acidity function relies on the assumption that the activity coefficient term is the same for all weak bases. Different classes of bases have different activity coefficients and so generate different acidity functions. H_o has proven to be a valuable tool in the study of mechanisms and kinetics of reactions in strong acids.[41,46] Since there are many possible acidity functions, the cancellation assumption can only be applied to a single class of compounds and cannot be used between different classes. Figure 3 illustrates many of the acidity functions that have been studied in aqueous sulfuric acid.

In order to improve the acidity functions Bunnett and Olsen developed a technique using a linear free energy relationship.[47] They related the Hammett equation (7) to the ionization ratio for any weak

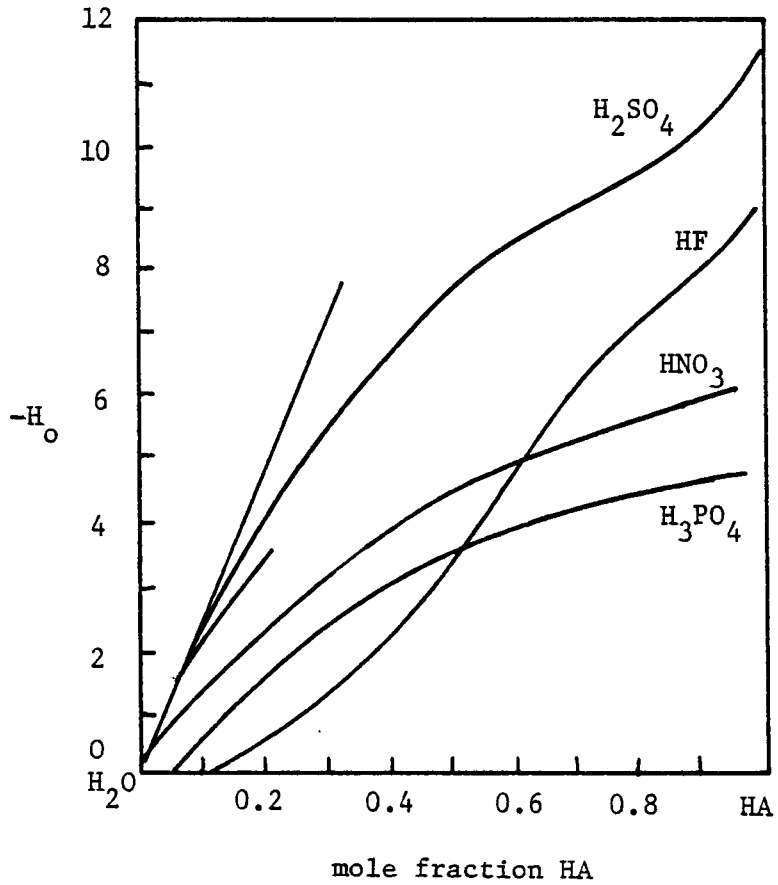


Figure 2. Hammett acidity function (H_o) values for some acid-water systems.

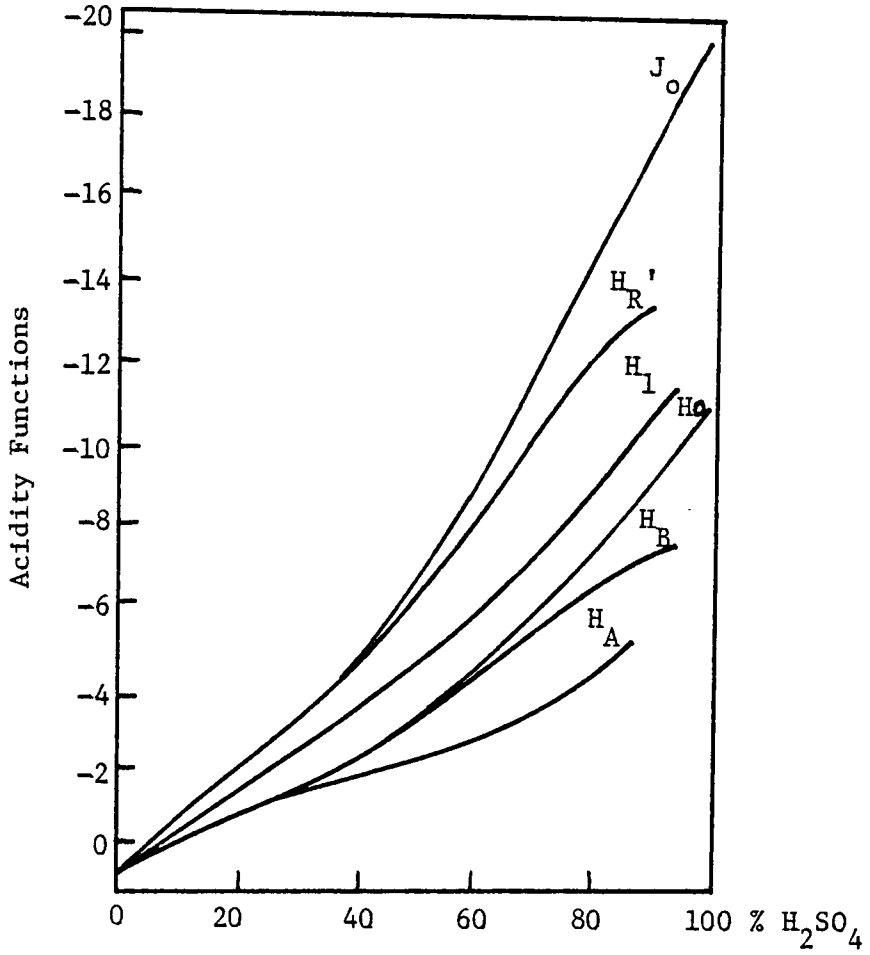


Figure 3. Comparison of acidity functions for aqueous sulfuric acid. Scales are: J_o (triarylcarbinols), H_R' (diarylalkenes), H_1 (indoles) = ca. H_o^m (tertiary amines), H_B (benzophenones), H_A (amides).

base by equation (8). ϕ is the slope of the log $[BH^+]/[B] + H_o$ versus $H_o + \log [H^+]$ linear plot. It is the measure of the response of the

$$\log \frac{[BH^+]}{[B]} + H_o = \phi (H_o + \log [H^+] + pK_{BH^+} \quad (8)$$

equilibrium to changing acid concentration. The intercept of this linear plot is the pK_{BH^+} for the base so the slope ϕ must remain constant for each base down to acid concentration at which $H_o + \log [H^+] = 0$. It was assumed that the activity coefficient is an average term for all primary aromatic amines. This linear equation has allowed different bases to be compared using a single acidity function and has been used successfully.[48,49] Data from concentrated solutions have been extrapolated down to the acidity range where acidity functions and pH have the same values.

The Hammett cancellation assumption has been eliminated by other groups who have only considered the linearity assumption.[50-52] The linearity assumption which says that the acidity functions are linearly relative to each other, has proven to be quite successful.[53] Recently K. Yates has extensively used this assumption to develop a new method for determining basicities in aqueous acid mixtures.[10] This technique generalizes the acidity function concept using a function of the acid, X. The differences between the activity coefficients $(f_B f_{H^+}/f_{BH^+})$ follow the same function (X) and differ from base to base only by a constant scaling factor (m^*) resulting in equation (9). When equation (9) is substituted into the Hammett equation (6) results in equation (10). Values of $[H^+]$ are known for some aqueous acids and log $[BH^+]/[B]$

$$\log (f_B \, f_{H^+}/f_{BH^+}) = m^* X \quad (9)$$

$$\log \frac{[BH^+]}{[B]} - \log [H^+] = m^* X + pK_{BH^+} \quad (10)$$

is known as a function of weight percent of the acids. The m^* and pK_{BH^+} terms must be determined for each base. X is unknown but is constant for all bases using the linearity assumption. All three of these unknown terms are determined using computer algorithms. For details concerning the computer techniques used the article published by Cox and Yates[10] should be consulted. X is characteristic of the acid system and the m^* values are based on a reference compound with a value of 1.000 which is a hypothetical primary aromatic amine that follows the H_o scale.

CHAPTER II

EXPERIMENTAL

A. General Procedure

All of the compounds used in this study were commercially available. Liquid compounds were dried over molecular sieves and distilled when necessary. Solid compounds were purified by recrystallization. The purity and structure of all precursors and solvents were verified by nuclear magnetic resonance.

B. Preparation of Compounds

1. Carbon Tetrachloride

Carbon Tetrachloride (Fisher, Certified ACS) was dried over molecular sieves (Davison 4Å). A clean nmr spectra indicated the solvent was free of contaminates.

2. Cyclopropyl Methyl Ketone

Cyclopropyl methyl ketone (Aldrich 99%) was fractionally distilled using a Nestor Faust spinning band column. The middle fraction bp 112-113°C was collected into small glass vials sealed with Teflon lined caps and stored over anhydrous calcium sulfate (Drierite) in a nitrogen flushed dessicator. Purity and structure was confirmed by nmr spectra.

3. Cyclopropyl Phenyl Ketone

Cyclopropyl phenyl ketone (Aldrich) was fractionally distilled using a Nestor Faust spinning band column under reduced pressure. The middle fraction bp 92°C/2.5 mm Hg was collected into small glass vials sealed with Teflon lined caps and stored over anhydrous calcium

sulfate (Drierite) in a nitrogen flushed desiccator. The clear liquid was tested for purity and structure by nmr.

4. Dicyclopropyl Ketone

Dicyclopropyl ketone (Aldrich 95%) was fractionally distilled using a Nestor Faust spinning band column. The middle fraction bp 160-161°C was collected into small glass vials sealed with Teflon lined caps and stored over anhydrous calcium sulfate (Drierite) in a nitrogen flushed desiccator. Purity and structure were confirmed by nmr spectra.

5. Acetone

Acetone (Fisher, Certified ACS) was dried over molecular sieves (Davison 4Å). Purity and structure were confirmed by nmr spectra.

6. Acetophenone

Acetophenone (Fisher, Certified ACS) was dried over molecular sieves (Davison 4Å). Purity and structure were confirmed by nmr spectra.

7. Benzophenone

The solid benzophenone (Eastman) was recrystallized by the method of Perrin.[54] The crude solid was recrystallized from absolute ethanol. The crystals were pulverized with mortar and pestle and dried for 24 hours under vacuum. The white powder was checked for purity and structure by nmr spectra and stored over P_2O_5 in a desiccator.

8. Fluorosulfonic Acid

Fluorosulfonic acid (FSO_3H) was obtained reasonably pure from Allied Chemicals (Baker and Adamson), but was distilled prior to use.

A 28 ounce vial of the acid was placed in a clean oven dried 2 liter flask. The system was then flushed for 30 minutes with dry nitrogen to remove the excess HF by the use of a fritted bubbler. The clean clear liquid bp 159-161°C (lit.[55] bp 162°C/760 mm Hg) was distilled using an air cooled condenser and stored in a stoppered glass flask in a dessicator containing anhydrous calcium sulfate (Drierite).

9. Sulfuric Acid

Sulfuric acid is commercially available in high purity (Ashland Chemical Co., Reagent ACS) and was used without further purification. In order to maintain consistency in concentrations, all of the sulfuric acid used in this study came from the same batch (S-961).

10. 1,2-Dichloroethane

1,2-dichloroethane (Fisher, Certified ACS) was dried over molecular sieves (Davison 4Å). Purity and structure was confirmed by nmr spectra.

11. Antimony Pentachloride

Antimony pentachloride ($SbCl_5$) is commercially available from Apache Chemicals in very high purity (99.999%). A 1.85 M stock solution was made up in a dry box by adding 1,2-dichloroethane to 25g of antimony pentachloride until 45 ml of solution was achieved. Ten ml of the stock solution was added to 175 ml of 1,2-dichloroethane in the calorimeter vessel to achieve the desired 0.10 M $SbCl_5$ solution.[56]

C. Calorimetry

1. Calorimeter Description

The solution calorimeter was designed by Arnett and co-workers.[57] Only slight modifications have been made and a detailed report of the

calorimeter's construction has been given by Metzner[40] so only a brief description of the apparatus will be given.

The calorimeter vessel is a 250 ml Dewar flask tightly fitted with a Teflon cap. This inert insulating cap is fitted with a thermistor (Victory Engineering Corp., Springfield, N.J.) and an electrical heater. There are two holes drilled into the top, one for the stirring rod, and another for injecting the samples. The stirring rod was fitted with a Teflon paddle and was driven by a variable speed stirrer. A Wheatstone bridge circuit driving a recorder (Sargent S-RG) was used for detecting and displaying heat changes in the calorimeter.

Two different calorimeters were used. One was used for the work with CCl_4 to determine the heats of solution where glass coated thermistors were used unshielded. For super acid media another calorimeter was set up in the hood and the thermistors were placed in Teflon tubes in order to protect the thermistors and their electrical leads from the acid. This tube is partly filled with toluene (Fisher, Reagent ACS) in order to maintain a good transfer of heat to the thermistors. These were the only differences in the two calorimeters used.

2. Calorimetric Procedure

In measuring heats of solution or heats of reaction, both sides of the calorimeter were filled with 185 ml of solvent such that a small air space existed between the solvent and the top of the Dewar flask. The temperature of the calorimeter was checked before and after each use to insure that measurements were made at a temperature

of 25±1°C. The stirred solvents were first allowed to reach equilibrium. The heats of stirring were then adjusted in order to achieve a straight base line that was slightly non-horzontal. This was done by varying the stirrer speed. Liquid samples were injected by a 500 ml Hamilton gas tight syringe equipped with a Teflon needle. The syringe was filled and the air bubbles removed. After the syringe had reached thermal equilibria in the Dewar flask the calorimeter was calibrated by introducing measured amounts of heat through the heater and measuring the resulting pen displacement on the recorder. The electrical heat (Q_E) in calories is produced by a current I (amps) through a resistance heater R (ohms) for a time t (sec) given by equation (11). After two of the heating curves were recorded, the

$$Q_E = \frac{I^2Rt}{4.184} \tag{11}$$

amount of sample in excess of 300 ml in the syringe was injected to remove any solvent permeated sample in the tip of the needle as well as to indicate whether the reaction is endothermic or exothermic. Three calibrated amounts of sample of about 100 µl each were injected by the use of machined stops. The weight of each sample injection is known. Solid samples were introduced using a plastic syringe cut off and fitted with a Teflon stopper.[57] Each solid sample (about 100 mg) was weighed individually. After three sample injections were recorded, an additional two heating curves were made. The heats of reaction can be determined by relating the calibration curves to the sample injection curves. The voltage I_{std} across a standard resistance R_{std} in series with the heater is measured during the heating cycle as shown

in equation (12). The ratio of heat added (Q_E) to the pen deflection

$$Q_E = \frac{t\ (E_{std})^2 R}{(R_{std})^2\ 4.184} = t\ k\ (E_{std})^2 \qquad (12)$$

(Δ^C) calibrates the system in terms of cal/mm which allows one to relate heat in calories (Q_R) associated with the injection sample by equation (13). The heat per mole can easily be calculated by equation (14) since the molecular weight of the sample is known.

$$Q_R = (Q_E/\Delta^C)(\Delta^R) \qquad (13)$$

$$\Delta H \text{ kcal/mole} = \frac{Q_R(\text{cal})\ \text{M.W.}}{\text{mg}} \qquad (14)$$

At least six determinations were made to yield the ΔH values and standard deviation errors (15) reported.

$$S = \sqrt{\sum_{i=1}^{N} (X_i - m)^2/N-1} \qquad (15)$$

Periodic checks on the accuracy of the calorimeter were made for accuracy and precision by comparison of ΔH_s of ethanol in water.[58]

D. NMR Spectra

The samples for carbon-13 nmr studies were made by adding ketones to rapidly stirred H_2SO_4 and $SbCl_5$ solutions. The initial solutions were made of approximately 10% ketone by weight and further dilutions were made when necessary. The samples were made in 20 ml glass vials sealed with Teflon lined caps in order to keep the solutions air free. The samples were refrigerated and used to obtain the spectra within a few hours. The spectra were graciously obtained by Orville Weyrich, Jr. using the following procedure.

The ^{13}C Fourier-transform nmr spectra were obtained on a Nicolet TT-14/Brücker WH-60 spectrometer at a frequency of 15.0880 MHz. The spectra were proton decoupled by a broad-band pink-noise generator with a band-center frequency about 4ppm downfield from tetramethylsilane (TMS). A four-pole Butterworth filter with a -3dB cutoff frequency of 4KHz was incorporated into the receiver, and a phase alternating pulse sequence (PAPS) was used to eliminate residual non-coherent system noise, spin-echo effects, and DC components of the free-induction decay (FID). Data acquisition utilized 8.192 K of computer memory. A 90° pulse was used, requiring a pulse width of about 30 μsec. A delay of 200 μsec was allowed between the end of the pulse and the start of data acquisition to eliminate pulse breakthrough. The sweep width of the spectra was typically 4273.50 Hz. A time delay of 5.0 sec was allowed between pulse-acquisitions, and typically 300 pulse-acquisitions were gathered for each spectrum. Prior to Fourier transformation, the FID was exponentially multiplied to improve the signal-to-noise ratio, at the expense of some line broadening. The line broadening was typically 1.0Hz.

Sample temperature and spinning rate were not monitored or controlled. The magnet temperature was regulated at about 40°C, while the sample was cooled somewhat by the air-jet of the sample spinner. Severe heating of the sample (about 60°C) was observed when H_2SO_4 was used as the solvent, due to absorption of the proton decoupler signal. The samples were contained in thin-walled tubes having an outside diameter of 3.5 mm. An inner tube was filled with TMS as a reference, and was held in place by two Teflon vortex plugs

which had holes of the approximate size drilled through their center. An internal standard of tetramethylammoniumfluoroborate ($TMABF_4$) was also used in some cases. The magnet field was stabilized by locking onto an external sample of D_2O.

In the case of the $SbCl_5$ samples, difficulty was experienced due to an extremely strong solvent peak which did not allow the sample peaks to be brought out of the background noise due to the limited dynamic range of the computer memory. Solubility problems were observed in those samples sufficiently concentrated to bring the sample resonances above that of the noise.

CHAPTER III

RESULTS AND DISCUSSION

A. Objective

The main objective of this research was to investigate the effects of a selected group of substituents on a carbocation in solution. The substituents under consideration are methyl, cyclopropyl, and phenyl. The parent compounds that were used are the six possible ketones (I-VI) where these substituents are directly attached to the central sp^2 carbon atom. The carbocations are formed by protonation of the ketones in acidic media and by adduct formation with a strong Lewis acid, $SbCl_5$. The factors which make this study of these carbocation stabilities attractive include:

1. These ions are formed rapidly and cleanly at room temperature which makes them ideal for nuclear magnetic resonance and calorimetric analysis.

2. The ions formed are relatively free of steric hindrance that often occurs with bulky substituents in tertiary carbocations.

3. The ions formed are free of rearrangements that often occur in secondary carbocations.

The tasks completed in this investigation were the purification of the ion precursors, verification of the structure of the ions using Fourier-transform ^{13}C nmr, determination of the heats of formation using solution calorimetry, and calculations of relative free-energies and entropies of protonation using available acidity function data in H_2SO_4 systems.

B. NMR Spectra

The proton decoupled ^{13}C nmr spectra of the carbocations in H_2SO_4 and $SbCl_5$ solutions were obtained by the Fourier-transform method. G. A. Olah and co-workers have provided the chemical shift assignments for the parent ketones (I-VI) which are listed in Table III.[3] The supporting nmr evidence for the carbocations has also been published by Olah.[3] In that work, the carbocations were formed by protonation of ketones in a FSO_3H-SbF_5(1:1) SO_2Cl solution at -70°C. The chemical shift assignments for these ions are listed in Table II. Olah and co-workers used the methods of D. M. Grant to interpret the spectra and make signal assignments.[59] Those methods used included "off resonance" decoupling experiments, relative signal intensities, and molecular symmetry. The chemical shifts (δ) are listed in parts per million (ppm) downfield from external TMS. The values reported by Olah in the CS_2 scale have been converted to the TMS scale using CS_2 = 194.6 ppm downfield from external TMS.[36]

1. Sulfuric Acid

The ^{13}C nmr spectra of these carbocations have been reproduced in concentrated H_2SO_4 (99.9%). The best results were obtained using a 10% by weight solution of the ketone in H_2SO_4. In this work external TMS was used as the standard; the data are contained in Table IV. The signal assignments were determined by analogy with the assignments made by Olah in the FSO_3H system. The comparisons of the nmr data for the carbocations formed in H_2SO_4 to the FSO_3H system are listed below.

a. Acetone. The ^{13}C nmr spectrum of the ion formed in H_2SO_4

TABLE III

^{13}C CHEMICAL SHIFTS IN METHYL, CYCLOPROPYL, AND PHENYL KETONES

Compound	Carbonyl	CH_3	Cyclopropyl		Phenyl			
			CH	CH_2	Ci	Co	Cm	Cp
CH_3COCH_3	206.9	29.9						
CH_3CO(c-Pr)	209.5	31.8	23.1	12.2				
$CH_3COC_6H_5$	197.8	26.7			138.4	130.2	130.2	133.4
(c-Pr)COC_6H_5	201.8		18.9	13.4	140.3	130.7	130.1	134.8
$C_6H_5COC_6H_5$	197.0				139.3	131.6	130.0	134.1
(c-Pr)CO(c-Pr)	211.9		23.0	12.5				

TABLE IV

^{13}C CHEMICAL SHIFTS IN PROTONATED (H_2SO_4) METHYL, CYCLOPROPYL, AND PHENYL KETONES

Compound	Carbonyl	CH_3	Cyclopropyl CH	Cyclopropyl CH_2	Phenyl Ci	Phenyl Co	Phenyl Cm	Phenyl Cp
$CH_3COH^+CH_3$	245.6	31.8						
CH_3COH^+(c-Pr)		(19.0,21.3,24.9,27.3,29.3,29.7)[a]						
	239.8							
$CH_3COH^+C_6H_5$	219.9	25.3			130.6	131.7	135.9	145.3
(c-Pr)$COH^+C_6H_5$	221.9		25.1	29.8	131.7	131.7	133.2	143.0
$C_6H_5COH^+C_6H_5$	209.3				130.7	137.4	131.6	143.1
(c-Pr)COH^+(c-Pr)	236.6		24.1	24.4				

[a]Assignments uncertain

is shown in Figure 4. The carbonyl carbon has shifted upfield by 4.7 ppm from that reported in the FSO_3H solution. The methyl carbons have shifted upfield by only 0.8 ppm. The acetone sample was diluted further with H_2SO_4 to insure that full protonation was occurring. Decreasing the acetone content will increase the acidity of the medium. If partial protonation was occurring, this would lead to an upfield shift of the peaks due to the increase in protonated acetone concentration. No such shift was observed. The acidity function data shows half protonation of acetone at 83.3% H_2SO_4 so full protonation would be expected at 99.9% H_2SO_4.

b. Cyclopropyl Methyl Ketone. The carbonyl carbon has shifted downfield by 1.3 ppm from the value reported in the FSO_3H solution. The other six peaks are not individually assignable but are consistent with the shifts reported in FSO_3H. There were two peaks that appeared on the spectrum at 46.9 ppm and 95.0 ppm. The temperature of the sample got very hot while in the probe and these peaks are probably due to ring opening of the cyclopropyl group or another decomposition reaction.

c. Acetophenone. The ^{13}C nmr spectrum of the ion formed in H_2SO_4 is shown in Figure 5. The carbonyl carbon has shifted upfield by 2.5 ppm from the value reported in the FSO_3H solution. In the phenyl substituent, all of the carbons shifted upfield, the ipso carbon by 0.8 ppm, the ortho carbons by 1.7 ppm, the meta carbons by 2.5 ppm, and the para carbon by 2.6 ppm. The acetophenone sample was diluted further with sulfuric acid to insure that full protonation was occurring. The acidity function data also suggests that acetophenone is fully protonated in concentrated sulfuric acid.

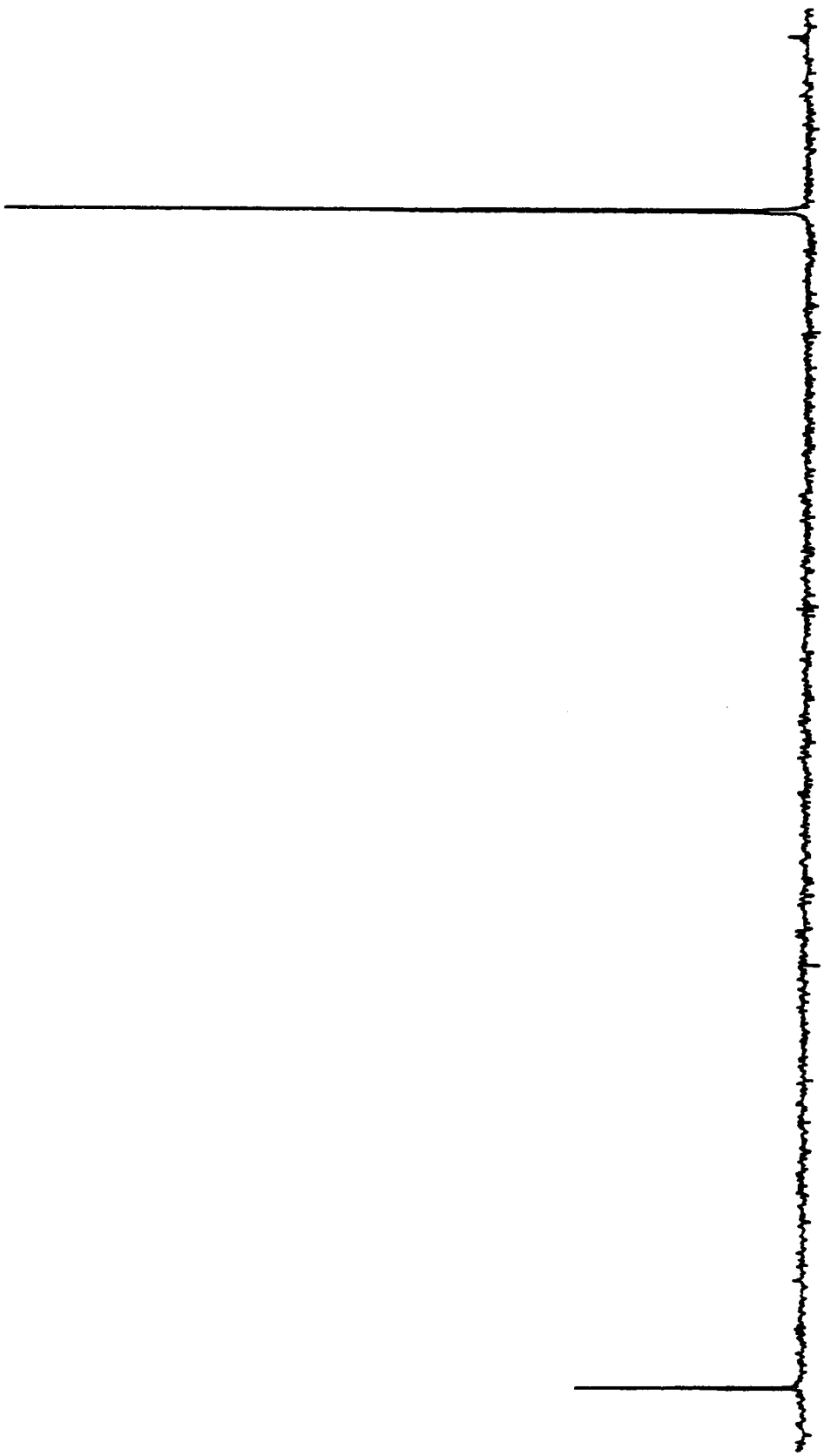


Figure 4. ^{13}C NMR Spectrum of Protonated Acetone in 99.9% H_2SO_4.

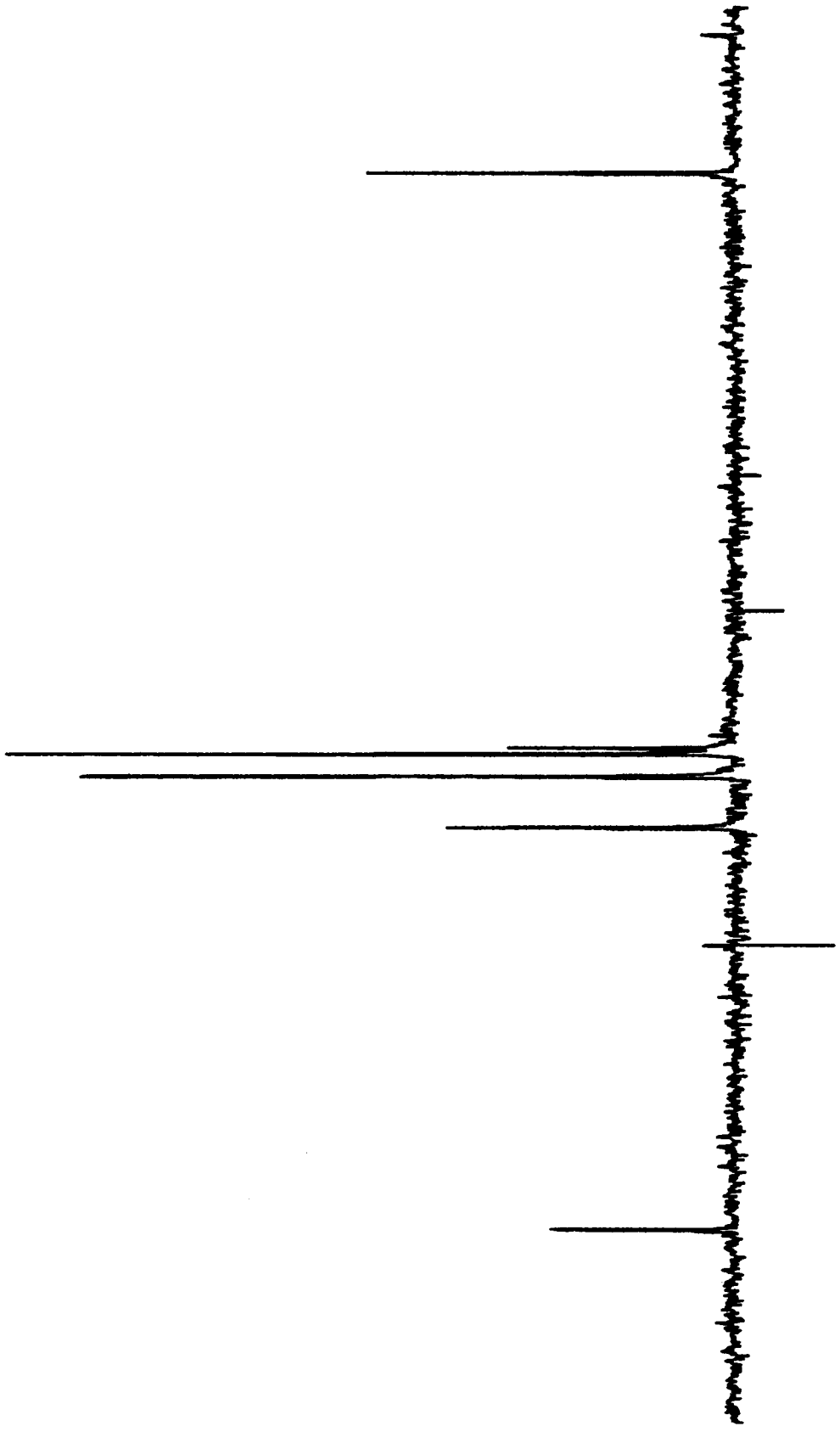


Figure 5. ^{13}C NMR Spectrum of Protonated Acetophenone in 99.9% H_2SO_4.

d. Benzophenone. The carbonyl carbon has shifted upfield by only 0.7 ppm from the value reported in the FSO_3H solution. The ipso carbons have shifted downfield by only 0.2 ppm, the ortho carbons have shifted downfield by 1.1 ppm, the meta carbons have shifted upfield by only 0.3 ppm, and the para carbons have shifted upfield by 2.7 ppm.

e. Cyclopropyl Phenyl Ketone. The carbonyl carbon has shifted upfield by 1.3 ppm from the value reported in the FSO_3H solution. In the cyclopropyl group, the CH carbon has shifted upfield by 1.3 ppm and the CH_2 carbons by 3.5 ppm. In the phenyl substituent, the ipso carbon has shifted upfield by only 0.5 ppm, the ortho carbons have shifted upfield by 1.4 ppm, the meta carbons have shifted downfield by only 0.1 ppm, and the para carbon has shifted upfield by 1.4 ppm.

f. Dicyclopropyl Ketone. The carbonyl carbon has shifted upfield by 1.6 ppm from the value reported in the FSO_3H solution. Since dicyclopropyl ketone is a comparatively strong base, an upfield shift here also indicates that upfield shifts in the ketones are due to solvent effect and not partial protonation. Olah has reported two peaks each for the CH and CH_2 carbons suggesting that there are two conformations but in our spectrum only two distinct peaks are seen suggesting only one conformation or an average of the two.

There are several observations which are noteworthy. Almost all the chemical shifts in H_2SO_4 are slightly upfield from the values reported in FSO_3H. In the ions where phenyl groups are present the ortho and para carbons are shifted much more than the meta and ipso carbons which do not bear any of the positive charge by resonance

effects. The largest change occurs in the chemical shift of the carbonyl carbon of acetone which is 4.7 ppm upfield from the ion recorded in FSO_3H.

2. Antimony Pentachloride

Two successful spectra have been obtained of the carbocations formed in a solution that is 1.4m $SbCl_5$ in 1,2-dichloroethane. The solvent peak in the ^{13}C nmr required that the solution be at least 1.4m in $SbCl_5$ in order to obtain measurable peaks for the ions. At less concentrated solutions the strong solvent peak would not allow the sample peaks to be distinguished from the background noise. The two successful spectra were the carbocations formed from acetone and dicyclopropyl ketone. At low concentrations lightly colored solutions were formed. At high concentrations the colors became very dark and a fine white precipitate formed. Benzophenone and cyclopropyl methyl ketone were slower to react in this manner than were cyclopropyl phenyl ketone and acetophenone which precipitated immediately. Lower temperatures had no effect on the reaction leading to precipitate formation. The solvent, 1,2-dichloroethane, freezes at -35°C. The comparisons of the nmr data for the ions that were formed successfully are listed below.

a. Acetone. The ^{13}C nmr spectrum of the ion formed in the $SbCl_5$ solution is shown in Figure 6. The carbonyl carbon has shifted upfield by 20.8 ppm from the value reported in the FSO_3H solution. The methyl carbons have shifted upfield by only 0.4 ppm. This is the most dilute solution that could be used to obtain a spectrum of the complex so it is not proven that complexation is complete at these

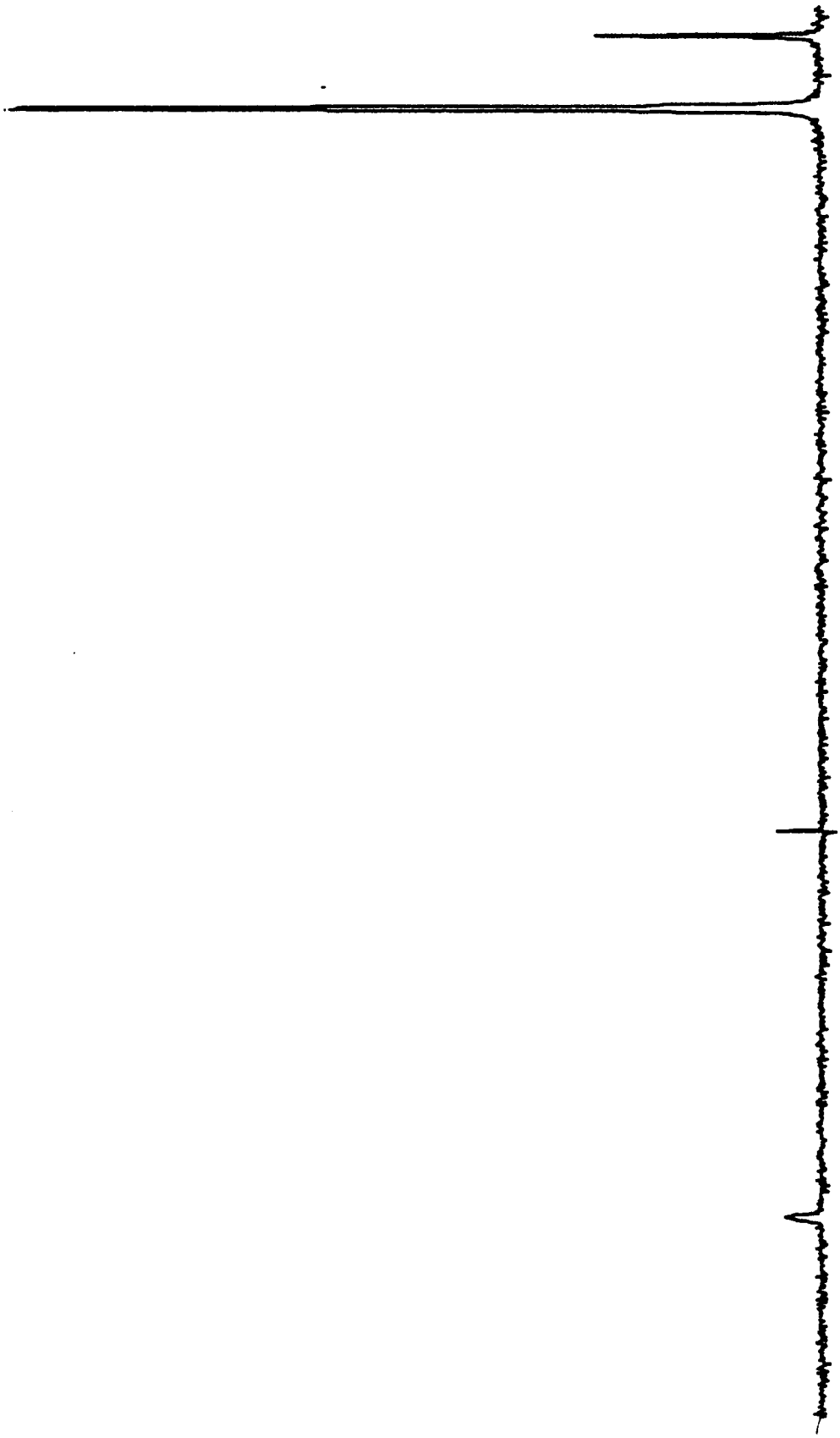


Figure 6. ^{13}C NMR Spectrum of Protonated Acetone in 1.4M $SbCl_5$.

very high concentrations. The work of Olofsson has shown that complex-action does occur in the dilute ($\sim 10^{-3}$m) solutions used in calorimetry.[56]

b. Dicyclopropyl Ketone. After the sample had been in the probe for 2.5 hours the yellow solution turned into a thick dark red substance but the spectrum obtained was in good agreement with the spectra obtained in FSO_3H and H_2SO_4 solutions. The carbonyl carbon has shifted upfield by only 1.7 ppm from the value reported in the FSO_3H solution. There are only two distinct peaks for the cyclopropyl carbons as observed in H_2SO_4 instead of the four peaks reported in FSO_3H. These values are in good agreement with the reported values.

c. Summary. It has been shown that ^{13}C chemical shifts are a good method for studying the structure of carbocations when all factors involved are properly considered.[36] Since we have a series of compounds of the same hybridization with similar substitution and size, the ^{13}C chemical shifts reflect the charge densities.[60] It has also been shown that a substantial positive charge produces a downfield shift. When the chemical shifts of the carbons are compared for the series of ketones it is concluded that ph>c-Pr>CH_3 in their charge delocalization abilities.

C. Heats of Protonation or Complexation

The relative heats of formation were measured using the solution calorimetric technique developed by Arnett and co-workers (see experimental section for details). ^{13}C nmr has been used to verify that the carbocations are cleanly formed so the enthalpy values for these

reactions can be obtained by the calorimetric technique. In order to calculate the enthalpy from the heat of reaction, the correction factor for the intramolecular forces in the ion precursor must be obtained. This is done by adopting solution in CCl_4 as the standard state. That is, rather than starting with pure ketones and reporting their heats of protonation, we start with the ketones in dilute solution in CCl_4 and report the heats of transfer from CCl_4 to the acid.

Four of the six ketones used in this study (I-VI) were studied previously in FSO_3H by Arnett.[61] Methyl cyclopropyl ketone and phenyl cyclopropyl ketone have not been studied previously. In order to work with strong acid systems, a solution calorimeter was set up in a hood. The calorimeter was checked for precision and accuracy by measuring the heat of solution of absolute ethanol in water. This system has been thoroughly studied and the reported value is -2.433±0.012 kcal/mole at 25°C.[58] The right Dewar produced a value of -2.52±0.23 kcal/mole and the left Dewar produced a value of -2.37±0.50 kcal/mole. Both of these values are accurate within the experimental error. This method was used periodically throughout the study to insure that the calorimeter was in proper working order.

1. Fluorosulfonic Acid

The heats of reaction of methyl cyclopropyl ketone and phenyl cyclopropyl ketone in pure FSO_3H and their heats of solution in CCl_4 were measured to complete the data for the six ketones. The heats of reaction, heats of solution, and heats of protonation of these two compounds are listed in Table V along with the values of the other ketones from Arnett's data.[61] An additional check was taken to be

TABLE V

THERMODYNAMIC QUANTITIES FOR PROTONATION OF METHYL, CYCLOPROPYL, AND PHENYL KETONES IN FSO_3H AT 25°C

Compound	ΔH_s, CCl_4 (Kcal/mole)	$-\Delta H_{Rxn}$ (Kcal/mole)	$-\Delta H_C^+$ (Kcal/mole)
CH_3COCH_3	0.79±0.02	18.3±0.1	19.1±0.1
$CH_3CO(c\text{-}Pr)$	0.66±0.03	21.8±0.3	22.5±0.3
$CH_3COC_6H_5$	0.79±0.01	18.1±0.2	18.9±0.2
$(c\text{-}Pr)COC_6H_5$	0.91±0.05	19.0±0.3	19.9±0.3
$C_6H_5COC_6H_5$	5.26±0.25	11.6±0.2	16.9±0.3
$(c\text{-}Pr)CO(c\text{-}Pr)$	0.06±0.02	20.7±0.2	20.8±0.2

certain that the procedure used in this study is equivalent to the work done by Arnett's group. The heat of reaction of acetophenone was found to be -18.4±0.2 kcal/mole which is in good agreement with the reported value of -18.1±0.2 kcal/mole.[61]

In order to consider the relative order of stabilities due to a substituent, the rest of the molecule must remain constant throughout the series with only one substituent changing. When a methyl group is held constant, it is determined that c-Pr>Me$\gtrsim$Ph in their ability to stabilize the cation relative to the starting ketone. When a phenyl group is held constant, it is determined again that c-Pr>Me>Ph. When this approach is used with a cyclopropyl group constant, a slightly different order is found. The relative stabilities are found to be Me>c-Pr>Ph. The change in order is the relative positions of the methyl and cyclopropyl groups. There are three observations made from this analysis. (1) The general trend is reversed from that which is expected by resonance and inductive effects. (2) The trend can change somewhat depending on the rest of the molecule. This suggests that there is a cooperative effect between the substituents. (3) The phenyl group always yields the least stable ion which directly contradicts the analysis based on ^{13}C chemical shifts. ^{13}C chemical shifts suggest that the phenyl group delocalizes charge better than methyl or cyclopropyl since the phenyl group produces the smallest downfield shift in the carbonyl carbon. It is assumed that the most delocalized ion is the most stable.

Since relative stabilities as predicted by ^{13}C chemical shifts do not give the same results as stabilities measured by the enthalpy

values, it is of interest to know if there is a correlation between the two measurements. It was found that there is generally a linear correlation between the heats of protonation and the ^{13}C chemical shifts of the carbonyl carbon. Figure 7 shows the plot of the ^{13}C chemical shifts versus the enthalpy values. A good linear correlation is observed with the exception of the ion formed from acetone. The heat of protonation is a measured difference in enthalpy between the precursor and the ion so a better comparison would be the difference in ^{13}C chemical shifts ($\Delta\delta$) between the precursor and the ion. The $\Delta\delta$ values of the carbonyl carbons are shown in Table VI. Figure 8 shows the plot of the $\Delta\delta$ values versus the ΔH values. A similar correlation is seen. As before acetone is the exception. The trend observed is the opposite of the expected in that the ion which produces the most heat upon protonation produces the largest downfield chemical shift. The greatest enthalpy produces the most stable ion whereas the ion with the greatest downfield shift suggests instability in that the charge is the least delocalized.

The change in chemical shifts of the methyl carbons were also analyzed in the above manner. The chemical shifts in cyclopropyl methyl ketone are not individually assignable so only acetone and acetophenone were compared. The methyl carbons in acetone produce the greater downfield shift. This order is in agreement with the analysis of the carbonyl carbons. When the same approach is taken with the para carbons of the phenyl substituted ketones, the order of decreasing chemical shifts is: acetophenone > benzophenone > cyclopropyl phenyl ketone. There is no correlation whatsoever between the

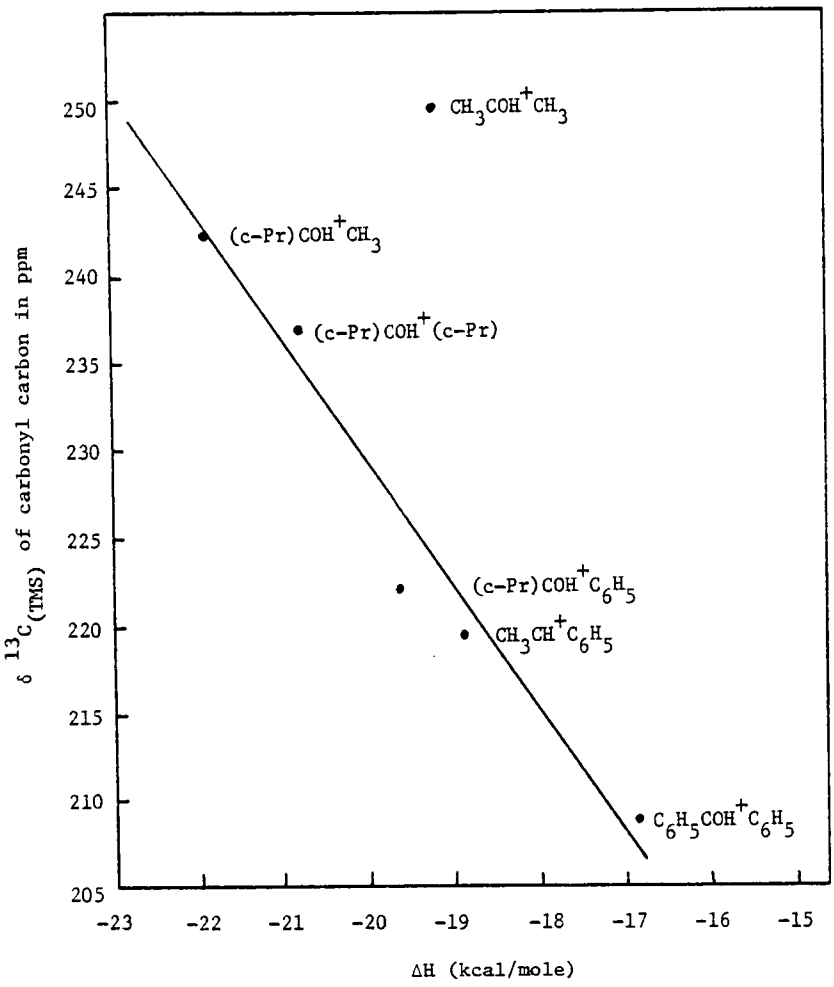


Figure 7. Correlation of ^{13}C chemical shift versus enthalpy in FSO_3H.

TABLE VI

^{13}C CHEMICAL SHIFTS OF CARBONYL CARBON IN THE PARENT AND PROTONATED KETONES

Compound	Parent Carbonyl	$\delta^{13}C(FSO_3H)$	$\Delta\delta^{13}C(FSO_3H)$	$\delta^{13}C(H_2SO_4)$	$\Delta\delta^{13}C(H_2SO_4)$
CH_3COCH_3	206.9	250.3	43.4	245.6	38.7
CH_3CO(c-Pr)	209.5	243.4	33.9	244.7	35.2
$CH_3COC_6H_5$	197.8	220.4	22.6	219.9	22.1
(c-Pr)COC_6H_5	201.8	223.2	21.4	221.9	20.1
$C_6H_5COC_6H_5$	197.0	210.0	13.0	209.3	12.3
(c-Pr)CO(c-Pr)	211.9	238.2	26.3	236.6	24.7

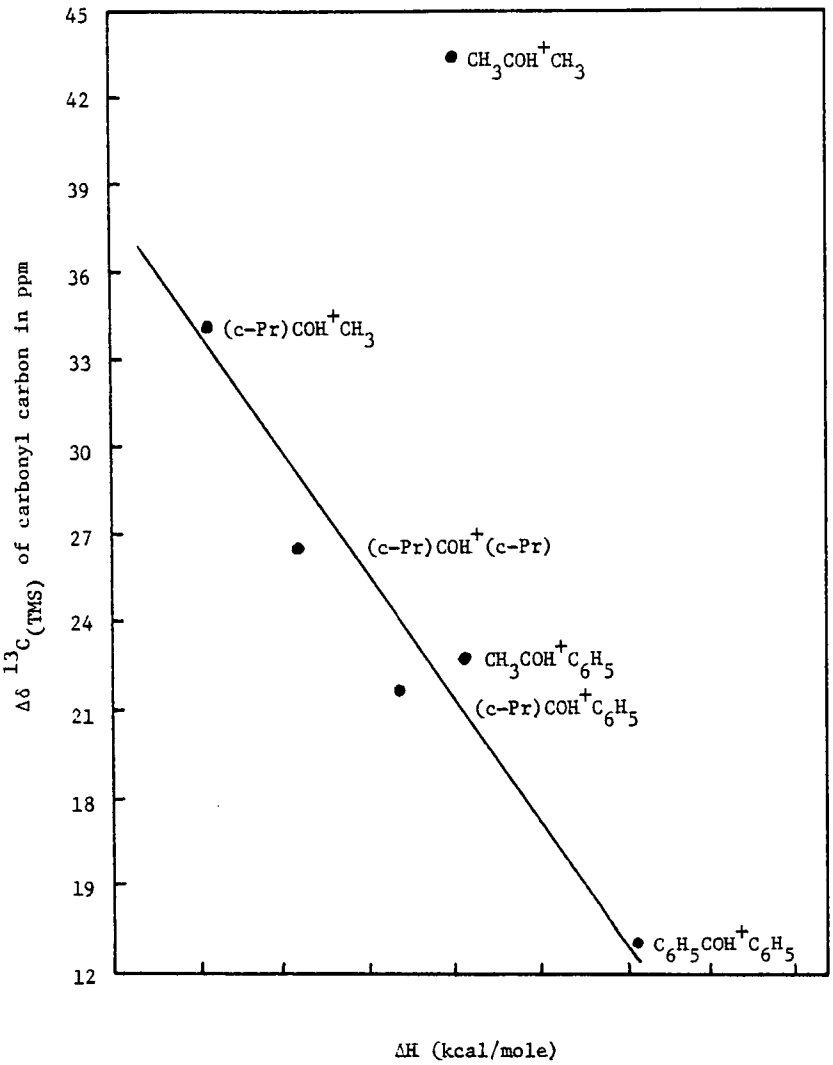


Figure 8. Correlation of change in ^{13}C chemical shift versus enthalpy in FSO_3H.

enthalpy values and para carbon chemical shifts. This was quite unexpected. Our knowledge of the electron delocalization and the factors affecting ^{13}C chemical shifts in this system is obviously incomplete.

2. Sulfuric Acid

Sulfuric acid provides an additional strong acid system where the ketones can be protonated. It has been shown by ^{13}C nmr that the carbocations formed in concentrated H_2SO_4 are the same as in FSO_3H with primarily small differences in chemical shifts.

Concentrated H_2SO_4 was obtained and two additional stock solutions were made by dilution with distilled water. These solutions must be strong enough to fully protonate the ketones being studied. The concentration of each solution was determined using the heats of protonation of water and the data of W. F. Giaque.[62] This was done by injecting distilled water into the acid solutions and comparing the heat measured with the literature values which are reported as a function of weight percent of the acid. The concentrated acid solution produced a heat of solution of -8.79 kcal/mole which correlates to a 99.9% H_2SO_4 solution by weight. The first dilution was made about 90% by volume which produced a heat of solution of -6.98 kcal/mole. This value correlates to a 93.0% H_2SO_4 solution by weight. The second dilution was made as 85% by volume which produced a heat of solution of -5.77 kcal/mole. This value correlates to an 87.4% H_2SO_4 solution by weight. Each of the six ketones (I-VI) was ionized in each of the three H_2SO_4 solutions. The heats of reaction and heats of protonation are listed in Table VII. The enthalpies of protonation reported are the actual observed values. The nmr data

TABLE VII

THERMODYNAMIC QUANTITIES FOR PROTONATION OF METHYL, CYCLOPROPYL, AND PHENYL KETONES IN H_2SO_4 AT 25°C

Compound	$-\Delta H_{Rxn}$ (99.9%) kcal/mole	$-\Delta H_C+$ (99.9%) kcal/mole	$-\Delta H_{Rxn}$ (93.0%) kcal/mole	$-\Delta H_C+$ (93.0%) kcal/mole	$-\Delta H_{Rxn}$ (87.4%) kcal/mole	$-\Delta H_C+$ (87.4%) kcal/mole
CH_3COCH_3	11.7±0.4	12.5±0.4	10.2±0.2	10.9±0.2	8.6±0.3	9.4±0.3
CH_3CO(c-Pr)	14.7±0.5	15.3±0.5	12.6±0.3	13.2±0.3	10.8±0.3	11.5±0.3
$CH_3COC_6H_5$	11.9±0.4	12.7±0.4	10.0±0.1	10.8±0.1	8.3±0.2	9.1±0.2
(c-Pr)COC_6H_5	11.7±0.5	12.7±0.5	9.8±0.3	10.7±0.3	8.2±0.6	9.2±0.6
$C_6H_5COC_6H_5$	4.2±1.5	9.5±1.5	2.4±1.0	7.7±1.0	2.0±0.6	3.2±0.6
(c-Pr)CO(c-Pr)	16.1±0.4	16.2±0.4	13.5±0.2	13.6±0.2	12.3±0.2	12.4±0.2

has indicated that complete protonation does occur at high sulfuric acid concentration. Complete protonation may not be occurring for the weaker bases at the lower acid concentrations. The acidity function data necessary to correct the observed enthalpies to the enthalpies for complete protonation is not available.

An analysis of the substituent effects on relative stabilities was done by the method used previously for the FSO_3H system. The analysis for each series of ketones is listed for each acid concentration in Table VIII. It is found again that there is a cooperative effect between the substituents. The relative order of substituents based on ΔH values change slightly depending on the rest of the molecule. The general trend for all the H_2SO_4 concentrations gives the relative order of stability c-Pr>Me$\tilde{>}$Ph when a methyl group is held constant. The trend when a phenyl group is held constant gives the relative order c-Pr$\tilde{>}$Me>Ph and for the series where a cyclopropyl is constant, c-Pr>Me>Ph. There is no significant change in the sub-substituent effect upon changing the concentration of the acid.

In order to confirm that the enthalpy terms correlate to the change in ^{13}C chemical shifts of the carbonyl carbon, the values for H_2SO_4 are plotted and shown in Figure 9. A near linear correlation is shown similar to the correlation found in the FSO_3H system. Once again acetone was found to be an exception to this linear correlation. The analysis of methyl and phenyl para carbons also give similar results to those found previously in the FSO_3H system.

3. Antimony Pentachloride

G. Olofsson has published the heats of complexation of several

TABLE VIII

SUBSTITUENT EFFECTS BASED ON RELATIVE STABILITIES DETERMINED BY ENTHALPIES IN H_2SO_4 SOLUTIONS

Ketone Series	H_2SO_4 (99.9%)	H_2SO_4 (93.0%)	H_2SO_4 (87.4%)
$CH_3-\overset{O}{\overset{\|}{C}}-R$	c-Pr>Me≳Ph	c-Pr>Me≳Ph	c-Pr>Me≳Ph
$Ph-\overset{O}{\overset{\|}{C}}-R$	c-Pr≳Me>Ph	Me≳c-Pr>Ph	c-Pr≳Me>Ph
c-Pr-$\overset{O}{\overset{\|}{C}}$-R	c-Pr>Me>Ph	c-Pr>Me>Ph	c-Pr>Me>Ph

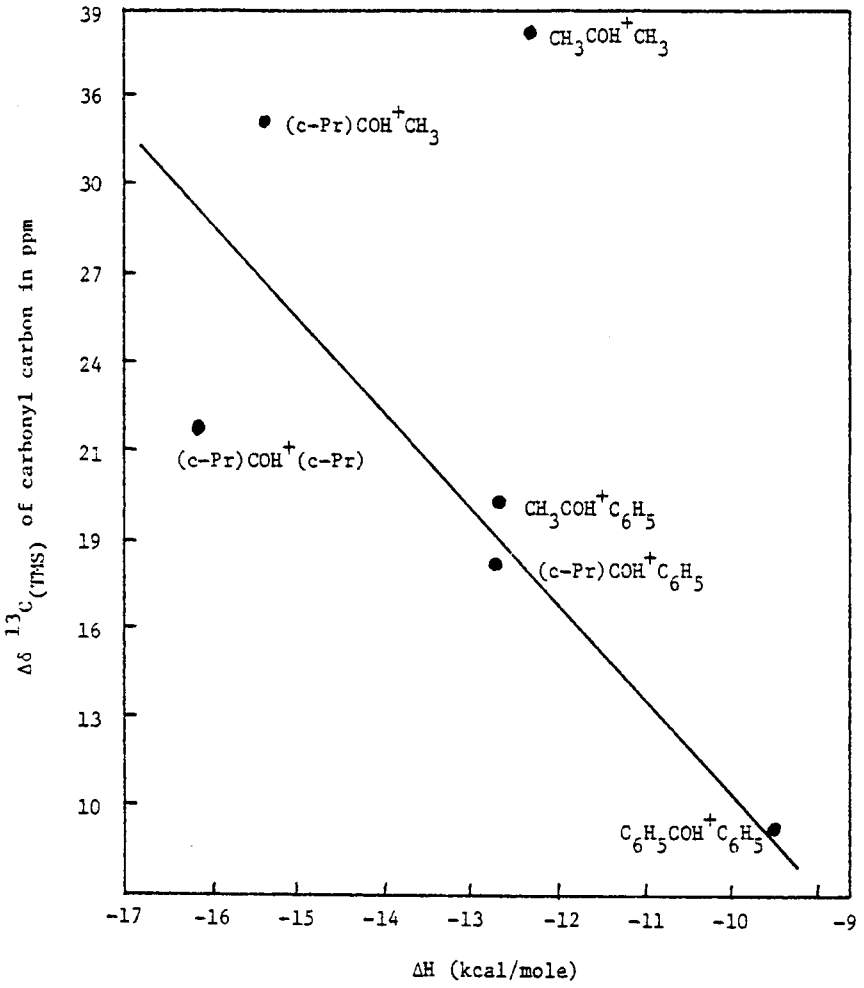


Figure 9. Correlation of change in ^{13}C chemical shift versus enthalpy in H_2SO_4 (99.9%).

series of carbonyl compounds in a strong Lewis acid, $SbCl_5$.[56,63,64] These studies were done in a solvent, 1,2-dichloroethane ($ClCH_2CH_2Cl$), that has only weak solute-solvent interactions. Olofsson has shown that the Lewis acid-base reactions produce carbocations similar to those formed in strong protic acids.[56] An $SbCl_5$ solution was used such that the electron acceptor was in large excess.

At the high concentrations necessary to obtain ^{13}C nmr spectra, a fine white precipitate formed in most of the reactions. At low concentrations used in calorimetry, no precipitate formation occurred. Apparently condensation reactions occur in the concentrated solutions necessary for nmr studies but do not occur in the dilute ($\sim 10^{-3}$M) solutions used in calorimetry. It was of specific interest to see if a Lewis acid system would produce similar substituent effects to the strong protic acid systems.

A different inert solvent, 1,2-dichloroethane, was used so the first necessary step was to find the ΔH_s term to correct for the intramolecular forces of the ion precursors. The heats of solution for each of the ketones (I-VI) were measured in 1,2-dichloroethane. The values of the ΔH_s, $ClCH_2CH_2Cl$ terms are listed in Table IX. The values are small as expected and each value is approximately 1 kcal/mole more exothermic than the corresponding values in CCl_4 except for dicyclopropyl ketone which is about the same. The only ketone that Olofsson studied which is also studied here is acetone. The heat of solution that Olofsson reported for acetone was -0.36 kcal/mole which corresponds very well to the value obtained here, -0.33±0.01 kcal/mole.

The ketone samples were injected into the calorimeter which was

TABLE IX

THERMODYNAMIC QUANTITIES FOR COMPLEXATION OF METHYL, CYCLOPROPYL, AND PHENYL KETONES IN $SbCl_5/ClCH_2CH_2Cl$ AT 25°C

Compound	ΔH_s, $ClCH_2Cl$ (kcal/mole)	$-\Delta H_{Rxn}$ (kcal/mole)	$-H_C+$ (kcal/mole)
CH_3COCH_3	-0.32±0.01	17.9±0.3	17.6±0.3
CH_3CO(c-Pr)	-0.29±0.01	19.8±0.5	19.5±0.5
$CH_3COC_6H_5$	-0.14±0.01	17.7±0.4	17.6±0.4
(c-Pr)COC_6H_5	0.20±0.02	18.0±1.5	18.2±1.5
$C_6H_5COC_6H_5$	4.76±0.42	10.9±2.7	15.6±2.7
(c-Pr)CO(c-Pr)	0.10±0.02	20.9±0.3	31.0±0.3

charged with 185 ml of the 0.10M $SbCl_5$ solution. The heats of reaction and the heats of complexation are reported in Table IX. The enthalpy terms obtained here are slightly less exothermic for each compound compared to the enthalpies in FSO_3H. The order of relative stabilities due to the substituents is analyzed by the same technique as was used previously for the protic acid systems. The relative stabilities are very comparable to the trends found in FSO_3H and H_2SO_4. The relative order of stability when a methyl group is held constant is c-Pr>Me$\tilde{>}$Ph. The trend when a phenyl or cyclopropyl group is held constant gives the relative order c-Pr>Me>Ph.

Olofsson used a calorimetric technique where 3-5 mmoles of $SbCl_5$ was added to 99.97 ml of 1,2-dichoroethane. After this solution had reached equilibrium a sealed glass ampoule of a known amount of the precursor was broken and the heats of reaction were recorded. In this study a 0.10M solution was always used so the ions would be formed in the same molar solution each time. The only compound to which we can compare our data to that published by Olofsson is acetone. The reported value for the heat of complexation from acetone was -17.03±0.04 kcal/mole which is in acceptable agreement with our value of -17.6±0.3 kcal/mole.

D. Conclusion

The relative stabilities of a series of carbocations have been shown based on the heats of protonation or complexation which were obtained by solution calorimetric techniques. The one characteristic that stands out is the fact that the phenyl substituted carbocations are less stable than the methyl substituted ions. The change in

^{13}C chemical shifts have indicated that the converse is true in that the carbonyl carbon of methyl substituted species has the highest charge density. It has traditionally been generalized that the more delocalized ion is the most stable.[65] With the increased use of ^{13}C nmr and its use to indicate charge densities, the data obtained suggests that one or both of these generalizations have serious limitations. The factors that have been considered in determining the stabilities of the charged species have all been internal factors which exist within the molecule. All of the systems that have been studied are in the solvent phase. Solvation is an external factor that must be considered. It is suggested here that carbocations are capable of polarizing the solvent when a high charge density is present. In the ions where resonance effects exist such as the case where a phenyl ring is present, the charge is delocalized over a large area within the molecule. In ions where the charge has a high density on a central atom or atoms such as the methyl substituted species, the ion is capable of polarizing the solvent in order to stabilize the ion. The solvation term takes affect only when called upon and becomes a predominating factor in ion stabilities. This explanation of an external solvent effect providing stability could explain the data presented in this thesis and the correlation with ^{13}C chemical shifts which only measure the internal effects.

The effect of the solvent could be eliminated in these systems if the reactions were carried out in the gas phase. This comparison would provide a good method to determine the solvent effect as long as the gas phase reactions protonate only the carbonyl oxygen atom.[66]

It would also be of significant value to compare the ΔH values to the free-energies (ΔG) and to obtain the entropies (ΔS). The entropies of the ions should give a clue to the solvation effect.

A second possibility is that the resonance interactions with phenyl are stabilizing, but this stabilization is overwhelmed by a second, large, destabilizing influence. The inductive electron-withdrawing by phenyl might be this destabilizing factor.

CHAPTER IV

RESULTS AND DISCUSSION

It has been shown that the predicted stabilities based on ^{13}C chemical shifts give opposite results from the carbocation stabilities measured by heats of protonation or complexation. This contradiction may be due to an "external" stabilization which depends on the nature of the solvent and the part it plays in stabilizing charged species. Accordingly an investigation of the solvation of a series of cations for which a conflict in ^{13}C nmr and thermodynamic data exist was undertaken. A combination of Gibbs free-energies (ΔG) and enthalpies (ΔH) for cation formation will yield the relative entropies (ΔS) of formation which should change from ion to ion as the specific solvation of the ions vary. The information that is now obtainable from the acidity functions in addition to the thorough studies available on aqueous sulfuric acid allows us to calculate the necessary values of ΔG, ΔH, and ΔS. The basis of the method is to use acidity functions to calculate equilibrium constants for protonation in high acid concentrations when protonation is essentially complete. The free-energies calculated from these equilibrium constants can be combined with enthalpies of protonation measured in the same acid to yield the relative entropies of protonation.

A. The Yates Method

A method to determine basicities of weak bases in aqueous acid mixtures was developed recently by K. Yates.[10] This method can be used to calculate relative equilibrium constants for protonation at

high acid concentrations. Yates used equation (16) where log I measurements and log $[H^+]$ values are known to obtain m^*, pK_{BH^+}, and X which are unknown constants. m^* and pK_{BH^+} are characteristics of

$$pK_{BH^+} = \log I - \log [H^+] - m^*X \tag{16}$$

each individual base where X is a characteristic of the acid and has only one value per acid system. These values were solved by iterative solutions using computer technology.[10]

The pK_{BH^+} value represents the dissociation of the protonated base BH^+ (17) at high dilution in water, the standard.[47] The dissociation of the conjugated base will be the reaction used in the following

$$BH^+ \underset{}{\overset{K_{BH^+}}{\rightleftharpoons}} B + H^+ \tag{17}$$

procedure.

The values for log $[H^+]$ in aqueous sulfuric acid were obtained from various publications which deal with the dissociation of the bisulfate ion in different acid concentrations.[10] Yates has published the log $[H^+]$ values as a function of weight percent aqueous sulfuric acid from 0.002 to 99.5% which are illustrated in Figure 10.

If the ionization constant I could be determined for the entire acid range one could obtain curves for each base to represent its acidity function. The log I term is used for simplicity to represent the ionization ratio $[BH^+]/[B]$. Log I is determined for most bases in acid concentrations such that approximately 50% ionization occurs. Log I is measured spectroscopically and the error in the measurements increase with increasing distance from 50% ionization.[67] This information was used by Yates to calculate m^*, pK_{BH^+}, and X values. Since the log I term is not available over the entire acid range, it was

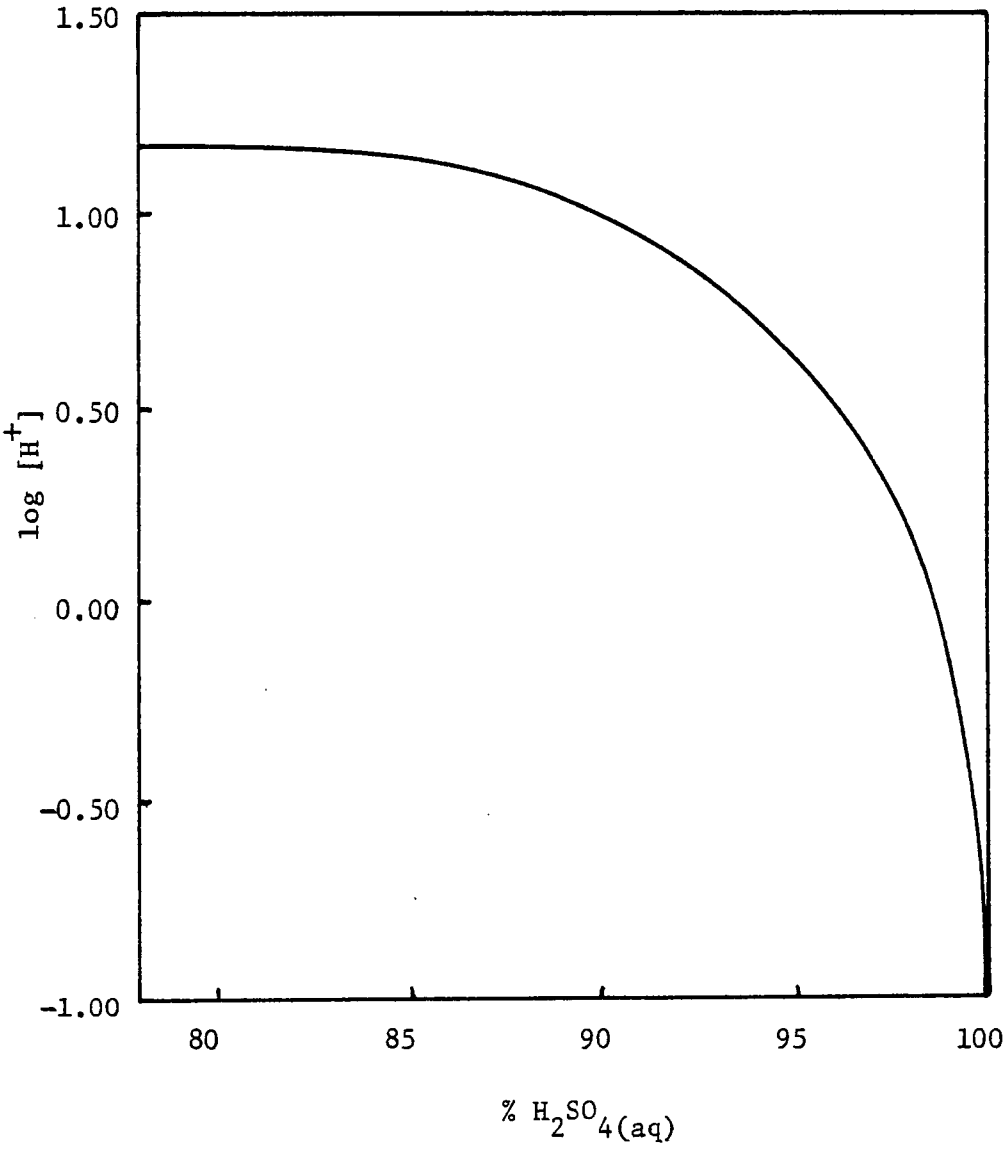


Figure 10. Values of log $[H^+]$ for high concentrations of aqueous sulfuric acid.

assumed that all possible curves for weak bases are related to acidity functions which are linear in one another.[52] This linearity assumption was based on experimental observations.[51,68] The difference between log $[H^+]$ and the acidity function of each base follows the same function X. The X value differs from base to base by a constant multiplier m^*. The overlap method of adjacent indicator bases is no longer necessary using the method derived by Yates because the X functions are always 0 in the standard state. The X values are shown in Figure 11 as a function of weight percent aqueous sulfuric acid.

Once the unknown constants in the Yates Equation (16) have been solved, it is possible to calculate the log I term at high acid concentration using those values. The log I values at high concentration make it possible to calculate the relative equilibrium constants for the protonated bases at high acid concentration. The method used to calculate relative log K values is permitted for a series of protonated bases in the same acid concentration.

The Yates Equation (16) becomes Equation (18) when $-\log K_{BH}^+$ is substituted for pK_{BH}^+. If some base A is arbitrarily set as the

$$\log K_{BH}^+ = -\log I + \log [H^+] + m^*X \qquad (18)$$

standard base, other bases can be compared to it by subtracting the log K_{BH}^+ Equation (18) for base A from the same equation for any other base B resulting in a relative log K_{BH}^+ term represented by Equation (19). This approach will enable the calculation of equilibrium constants for

$$\log K_{BH}^+/K_{AH}^+ = \log I_A/I_B + X(m_B^*-m_A^*) \qquad (19)$$

a series of bases relative to a standard base A in the same acid system.

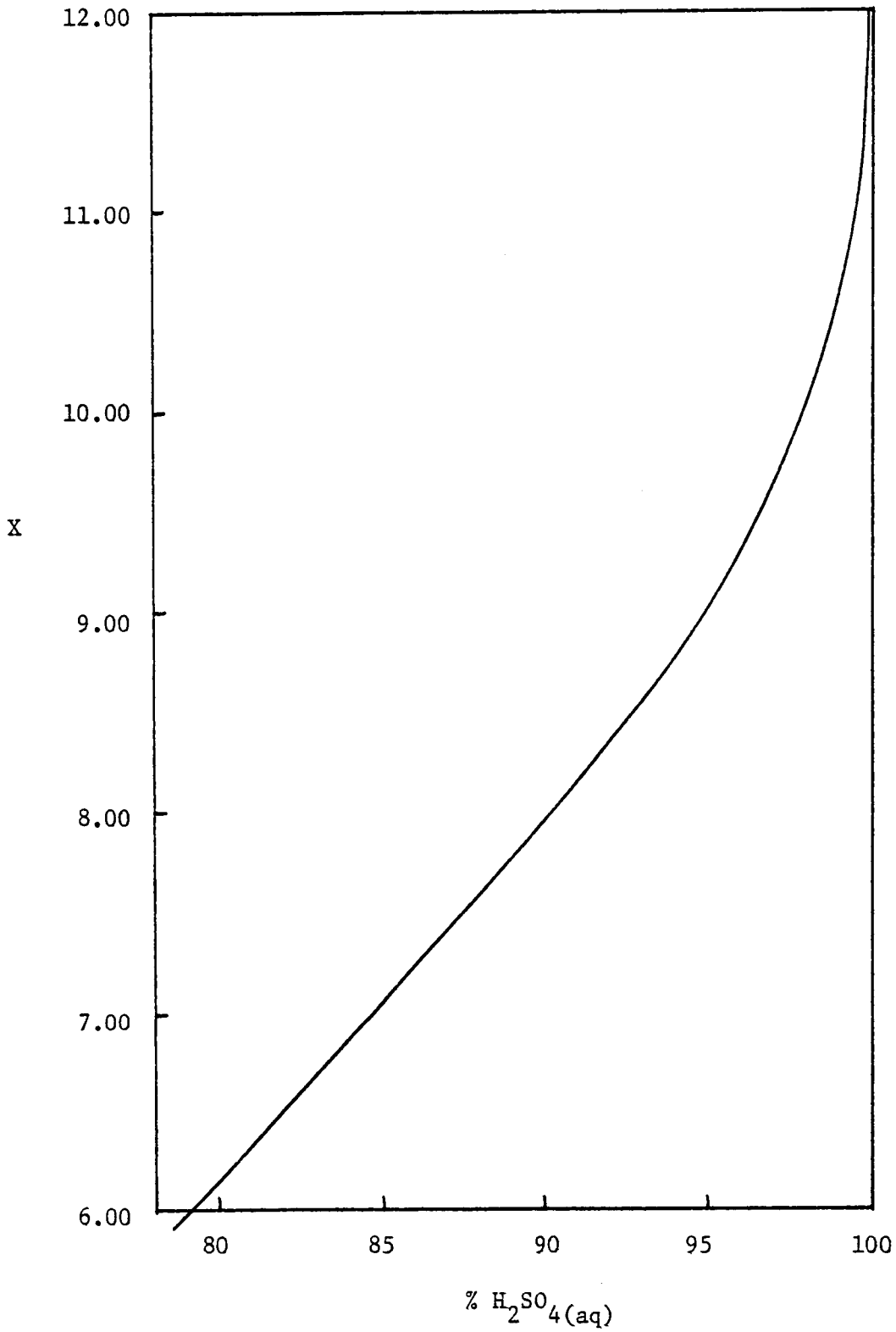


Figure 11. Values of X for high concentrations of aqueous sulfuric acid.

The nitroanilines listed in the Yates data[10] were used to test this method. Nitroanilines obey the Hammett assumption so that log $f_B f_{AH^+}/f_{BH^+} f_A = 0$ where A and B are any two Hammett bases. The 4-nitroaniline is arbitrarily made the standard base, A, because it has the most exothermic enthalpy of protonation. The enthalpies of protonation were measured by Arnett in 96.5% H_2SO_4.[69] The log I values for the nitroanilines are also calculated for 96.5% H_2SO_4 and are listed in Table X. Benzaldehyde can also be evaluated by this method and is reported in Table X. The X value is 9.45 and the log $[H^+]$ value is 0.47 at this concentration. All of the log K_{BH^+}/K_{AH^+} values for the series are relative to protonated 4-nitroaniline. The relative log K values have been calculated and are reported in Table X.

By using the Equation (20) that connects ΔG for a reaction to the equilibrium constant K yields the relative free-energies. The ΔG values are relative to the standard base, A, in 96.5% H_2SO_4 just

$$\Delta G = -RT \ln K \tag{20}$$

as the log K values are relative to the standard base represented by Equation (21). The $\delta\Delta G$ values for the nitroanilines have been calculated and are reported in Table X. The relative change in Gibbs

$$\delta\Delta G = -RT \ln \frac{K_{BH^+}}{K_{AH^+}} \tag{21}$$

free-energies for the dissociation of protonated bases gets more exothermic as the electron-withdrawing substituents on the benzene ring are increased.

The $\delta\Delta G$ values can be compared to relative change in enthalpies using the heats of protonation of the bases published by Arnett.[69]

TABLE X

THERMODYNAMIC QUANTITIES AND PARAMETERS FOR PROTONATED (96.5% H_2SO_4) BASES DETERMINED BY THE YATES METHOD

Compound[a]	$pK_{BH}+$	m^*	ΔH (cal/mole)	log I	log $K_{BH}+/K_{AH}+$	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole K)
4-NO_2-An	1.040	0.97	20,000	10.67	std	std	std	std
2-NO_2-An	-0.274	1.00	17,400	9.64	1.31	-1,700	-2,600	-2.7
4-Cl-2-NO_2-An	-1.01	1.00	16,200	8.91	2.04	-2,800	-3,800	-3.4
2,5-DiCl-4-NO_2-An	-1.72	0.97	14,900	7.63	2.76	-3,800	-5,100	-4.5
2,6-Di-Cl-4-NO_2-An	-3.36	1.05	12,200	7.03	4.40	-6,000	-7,800	-6.0
2,4-Di-NO_2-An	-4.57	1.11	9,900	6.43	5.56	-7,600	-10,100	-8.4
2,6-Di-NO_2-An	-5.23	0.99	8,800	4.59	6.27	-8,500	-11,200	-8.9
2-Br-4,6-Di-NO_2-An	-5.88	0.89	7,500	3.00	6.91	-9,400	-12,500	-10.3
Benzaldehyde	-3.70	0.48	9,400	5.01	1.03	-1,400	-10,600	-30.9

[a] An = Aniline

The ΔH values for the protonated bases are simply the reverse sign of the ΔH values recorded for the bases. The $\delta\Delta H$ values are calculated using 4-nitroaniline as the standard by which to compare the rest of the nitroanilines. The $\delta\Delta H$ values for the protonated bases in 96.5% H_2SO_4 are listed in Table X. The $\delta\Delta H$ values are more negative than the $\delta\Delta G$ values but the general trend for the series is very comparable, as would be expected. The relative change in enthalpies for the dissociation of the protonated bases become more exothermic as electron-withdrawing substituents are added to the ring. Clearly the reaction is enthalpy controlled.

The relative change in enthalpies and free-energies have been measured by independent methods which gives us the ability to calculate the relative change in entropies using the Equation (22) for Gibbs free-energy at constant temperature and pressure. The relative change

$$\delta\Delta G = \delta\Delta H - T\delta\Delta S \tag{22}$$

in entropies have been calculated for the series of nitroanilines and benzaldehyde and are reported in Table X. The relative change in entropies get more negative as electron-withdrawing substituents are added. The more exothermic the reaction the more highly structured are the solvated products compared to the solvated reactants. This implies that specific solvation makes an important contribution to the stability of the ions.

In order to compare bases in different acid systems it is necessary to relate the activity coefficients of the base in one solvent to its values in another. If Equation (19) for some base in a standard acid, H_1^+, Equation (23) results. Any acid system can

$$\log K_{BH_1^+}/K_{AH_1^+} - \log K_{BH_2^+}/K_{AH_2^+} = \log [(I_A/I_B)_1 (I_B/I_A)_2] + X_1(m_B^*-m_A^*) + X_2(m_A^*-m_B^*) \tag{23}$$

arbitrarily be set as the standard acid, H_1^+. This equation can be used to calculate the changes in free-energy and entropy difference caused by changing the acid systems. The relative free-energies ($\delta_{solv}\ \delta_{sub}\ \Delta G$) can be calculated using the relative log K's calculated by Equation (24). The relative entropies ($\delta_{solv}\ \delta_{sub}\ \Delta S$) can then be

$$\delta_{solv}\ \delta_{sub}\ \Delta G = -RT\ \ln[(I_A/I_B)_1(I_B/I_A)_2 + X_1(m_B^*-m_A^*) + X_2(m_A^*-m_B^*)] \qquad (24)$$

calculated using the relative enthalpies by Equation (25). The relative entropies should reflect the solvent effect on the base. Any base could be studied by this approach if the thermodynamic parameters were

$$\delta_{solv}\ \delta_{sub}\ \Delta S = \frac{\delta_{solv}\ \delta_{sub}\ \Delta H - \delta_{solv}\ \delta_{sub}\ \Delta G}{T} \qquad (25)$$

determined by the Yates treatment[10] and the enthalpies of the base were measured in various acid systems.

B. The "Crossover" Method

The Yates method that was developed to determine relative ionization constants appears to work very well but the necessary data for all weak bases are not available. The ketones (I-VI) that have been analyzed in this thesis have not been examined by Yates so an alternate method has been developed to obtain the relative log K values. G. Scoranno has recently studied five of the ketones and has determined the ionization ratio at half protonation in aqueous sulfuric acid.[68] The one compound that has been omitted by Scoranno is cyclopropyl phenyl ketone.

Scoranno used the Bunnett-Olsen approach in his studies. The

Bunnett-Olsen Equation (26) is a linear equation which reduces the number of different acidity functions which describe the protonation of different bases to one. The ϕ value is the slope of the log

$$\log I + H_o = \phi(H_o + \log[H^+]) + pK_{BH^+} \quad (26)$$

$[BH^+]/[B] + H_o$ versus $H_o + \log[H^+]$ linear plot. The intercept of the linear plot is the pK_{BH^+} value. Scoranno has determined the ϕ and pK_{BH^+} values for some ketones.[68]

The ϕ and pK_{BH^+} values allow us to calculate the log I values at high sulfuric acid concentration using Equation (26). The review by Paul and Long supplies the H_o values as a function of acid concentration at 25°C.[46] The H_o values for the upper sulfuric acid region has been revised by Jorgenson and Hartter.[69] The revised H_o values are plotted as a function of weight percent aqueous sulfuric acid in Figure 12. Once the log I values are obtained for high acid concentration it is possible to cross over to the Yates method. The log I values are used to calculate the m^* values for each base using Equation (16). The log I values and the m^* values can then be used to determine the relative log K values by Equation (19) as was previously described in the Yates method.

In order to test this approach, the nitroanilines that were used to test the Yates method are also used in the "crossover" method in order to compare the two approaches. The log I values were calculated for 96.5% aqueous sulfuric acid using the Bunnett-Olsen Equation (26) and are listed in Table XI. The Hammett assumption was based on the nitroanilines[42] so the ϕ values are equal to 0 which reduces the Bunnett-Olsen Equation (26) to Equation (27) for these compounds. The

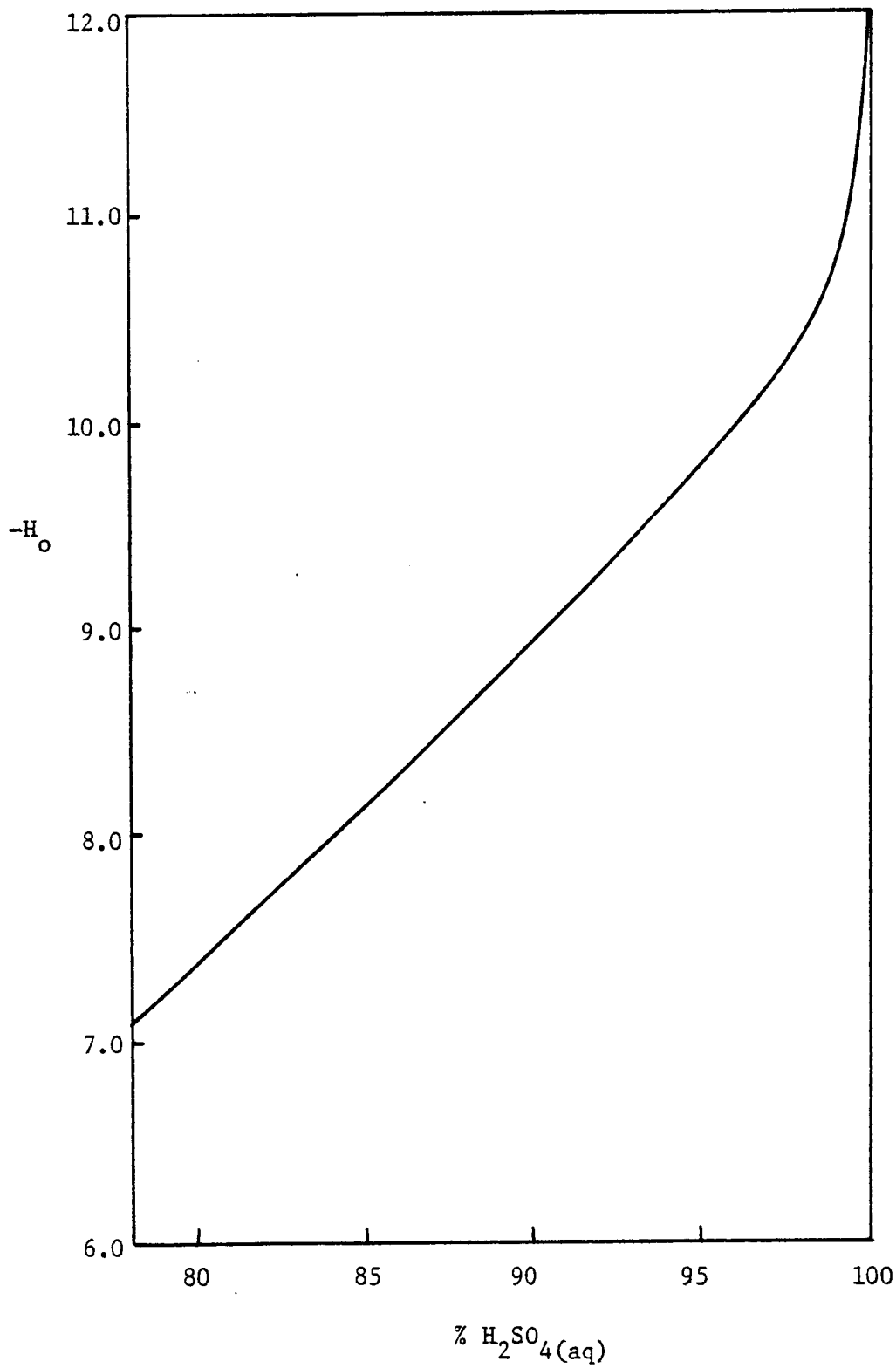


Figure 12. Plot of revised H_o values against % sulfuric acid for the upper sulfuric acid region.

TABLE XI

THERMODYNAMIC QUANTITIES AND PARAMETERS FOR PROTONATED (96.5% H_2SO_4) BASES DETERMINED BY THE "CROSSOVER" METHOD

Compound[a]	pK_{BH}^+	ΔH (cal/mole)	log I	log K_{BH}^+/K_{AH}^+	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole °K)
4-NO_2-An	1.040	20,000	11.16	std	std	std	std
2-NO_2-An	-0.274	17,400	9.85	1.31	-1,800	-2,600	-2.7
4-Cl-2-NO_2-An	-1.01	16,200	9.11	2.05	-2,800	-3,800	-3.4
2,5-Di-Cl-4-NO_2-An	-1.72	14,900	8.40	2.76	-3,800	-5,100	-4.5
2,6-Di-Cl-4-NO_2-An	-3.36	12,200	6.76	4.40	-6,000	-7,800	-6.1
2,4-Di-NO_2-An	-4.53	9,900	5.59	5.57	-7,600	-10,100	-8.4
2,6-Di-NO_2-An	-5.23	8,800	4.89	6.27	-8,700	-11,200	-8.9
2-Br-4,6-Di-NO_2-An	-5.88	7,500	4.24	6.92	-9,400	-12,500	-10.3
Aniline (ϕ=0;m^*=0.91)	4.60	25,500	14.72	-3.56	4,900	5,500	2.2
2,4-Di-Cl-An (ϕ=0;m^*=0.91)	2.00	21,000	12.12	-0.96	1,300	1,000	-1.1
Ethyl Acetate (ϕ=0.40;m^*=0.55)	-4.61	10,600	1.65	9.51	-13,000	-9,400	12.0

[a]An = Aniline

m^* values for each base was calculated using the Yates Equation (16).

$$\log I = pK_{BH}^+ - H_o \tag{27}$$

The m^* values produced by this method are all equal to 0.91 which compare to the m^* values produced by the Yates method with a range of 0.94 to 1.11 for the nitroaniline series. Since all the m^* values are the same the Yates Equation (16) reduces to Equation (28) for the nitroanilines. The log K_{BH}^+/K_{AH}^+ values have been calcu4ated and are

$$\log K_{BH}^+/K_{AH}^+ = \log I_A/I_B \tag{28}$$

reported in Table XI. The ϕ values for several other compounds are obtainable[48] and their thermodynamic quantities are also reported relative to 4-nitroaniline and are listed in Table XI. The log K_{BH}^+/K_{AH}^+ values were used to calculate the relative Gibbs free-energies ($\delta\Delta G$) and entropies ($\delta\Delta S$) by the same procedure used in the Yates method. The $\delta\Delta G$ and $\delta\Delta S$ values calculated by this procedure are reported for the nitroaniline series and other compounds in Table XI. The relative log K values were practically the same as those determined by Yates method so the $\delta\Delta G$ values are also the same. The $\delta\Delta H$ terms are also unchanged which makes the $\delta\Delta S$ values essentially the same as calculated previously. Once again the $\delta\Delta S$ values are more negative as electron-withdrawing substituents are added to the benzene ring. Therefore, the more exothermic the reaction the more structured are the products, compared to the reactants. As before, this is consistent with solvation changes playing an important role in determining relative ion stabilities.

Since the "crossover" method works the same for Hammett bases it should also be an acceptable technique by which to analyze the ketones. The ketones were protonated in three concentrations (99.9%, 93.0%, and

87.4% by weight of aqueous sulfuric acid. The necessary log $[H^+]$, X, and H_o values for each acid concentration were determined from the respective graphs in Figures 10, 11, and 12. The pK_{BH}^+ and ϕ values for the ketones were obtained from Scoranno.[68] In order to be able to calcualte the correct ΔH values it is necessary to correct the observed enthalpy values to the enthalpies for complete protonation in those cases where partial protonation occurs.

The log I values for the ketones in all three acid concentrations were calculated using the Bunnett-Olsen Equation (26) and are reported in Tables XII, XIII, and XIV. Some of the log I values indicate that ionization is not complete. For example, the log I values for cyclopropyl methyl ketone and acetone indicate that ionization is not complete in 99.9% H_2SO_4. The log I values for cyclopropyl methyl ketone indicates near complete ionization but the value for acetone suggests that there is less protonation than there is at half protonation in 83.3% H_2SO_4. This is an impossible result. The log I values were calculated using the ϕ values from Scoranno's data.[68] This result indicates that the ϕ values for acetone is erroneous. Due to this uncorrectable error, the free-energy and entropy values for acetone can not be determined.

The observed enthalpies where partial protonation occurs can be corrected to complete protonation by simultaneously solving Equation (29) and (30) for $[BH^+]$. The resulting Equation (31) is used to

$$I = \frac{[BH^+]}{[B]}$$

$$C = [BH^+] + [B]$$

$$\text{where } C = \frac{\text{moles of sample}}{\text{volume in calorimeter}}$$

$$[BH^+] = IC/(I + 1) \qquad (31)$$

TABLE XII

THERMODYNAMIC QUANTITIES AND PARAMETERS FOR PROTONATED METHYL, CYCLOPROPYL, AND PHENYL KETONES DETERMINED BY THE "CROSSOVER" METHOD IN 99.9% H_2SO_4

Protonated Ketones	pK_{BH^+}	ϕ	m^*	ΔH_f (cal/mole)	log I	log K_{BH^+}/K_{AH^+}	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole °K)
$c(Pr)COH^+(c\text{-}Pr)$	-2.42	0.58	0.15	16,200	2.09	std	std	std	std
$(c\text{-}Pr)COH^+CH_3$	-3.01	0.61	0.28	16,400	1.11	2.52	-3,400	200	12.1
$CH_3COH^+CH_3$	-2.85	0.75	0.39		-0.54				
$CH_3COH^+C_6H_5$	-4.28	0.40	0.29	12,700	2.55	1.20	-1,600	-3,500	-6.4
$C_6H_5COH^+C_6H_5$	-4.95	0.27	0.28	9,500	3.56	0.074	-100	-6,700	-22.1

TABLE XIII

THERMODYNAMIC QUANTITIES AND PARAMETERS FOR PROTONATED METHYL, CYCLOPROPYL, AND PHENYL KETONES DETERMINED BY THE "CROSSOVER" METHOD IN 93.0% H_2SO_4

Protonated Ketones	ΔH_f (cal/mole)	log I	log K_{BH^+}/K_{AH^+}	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole °K)
(c-Pr)COH^+(c-Pr)	13,600	2.03	std	std	std	std
(c-Pr)COH^+CH_3	14,000	1.18	1.96	-2,700	400	10.4
$CH_3COH^+CH_3$		-0.81				
$CH_3COH^+C_6H_5$	11,000	1.73	1.49	-2,000	-3,600	-5.4
$C_6H_5COH^+C_6H_5$	7,700	2.18	0.96	-1,300	-5,900	-15.4

TABLE XIV

THERMODYNAMIC QUANTITIES AND PARAMETERS FOR PROTONATED METHYL, CYCLOPROPYL, AND PHENYL KETONES DETERMINED BY THE "CROSSOVER" METHOD IN 87.4% H_2SO_4

Protonated Ketones	ΔH_f (cal/mole)	log I	log K_{BH^+}/K_{AH^+}	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole ° K)
$(c\text{-}Pr)COH^+(c\text{-}Pr)$	12,600	1.58	std	std	std	std
$(c\text{-}Pr)COH^+CH_3$	12,800	1.18	1.38	-1,900	200	7.0
$CH_3COH^+CH_3$		0.10				
$CH_3COH^+C_6H_5$	9,500	1.28	1.35	-1,800	-3,100	-4.4
$C_6H_5COH^+C_6H_5$	3,200	2.18	0.38	-500	-9,400	-29.9

calculate enthalpy values for complete ionization by Equation (32).[70]

$$\Delta H_f = \frac{\Delta H_{obs}}{[BH^+]\ V} \qquad (32)$$

The corrected ΔH_f values for the ketones in each acid concentration are reported in Tables XII, XIII, and XIV. The other thermodynamic quantities were then calculated and reported in the same tables.

The trend in $\delta\Delta S$ values is the same for all three acid concentrations so the results are discussed only once. The $\delta\Delta S$ values decrease as the reactions become less endothermic. This suggests that solvation of the ions become more ordered as the reaction becomes more exothermic.

C. FSO_3H Method

Both the Yates and "crossover" methods that have been developed to calculate thermodynamic quantities have worked well but there is not enough data available for most weak bases. A large number of weak bases have been studied by Arnett who obtained the enthalpies in FSO_3H.[61,69] If all of these bases could be examined by the same method, it would give a uniform way to compare many weak bases. Such a method has been developed using the Hammett assumption. The acidity function, H_o, for pure FSO_3H is -15.07 which was extrapolated from the H_2SO_4-FSO_3H system.[44] The log I values can be calculated by the Hammett Equation (27) using the acidity function for FSO_3H. The relative log K values can then be calculated by Equation (28) since the activity coefficient term is defined as unity by the Hammett assumption.

The nitroaniline series have been analyzed by this method in order to compare it to the two previous methods. The enthalpies for the nitroanilines in FSO_3H as reported by Arnett[69] are given in Table

XV. The free-energies and entropies were calculated as shown previously using the relative log K data and are also reported in Table XV. The general trend of the entropy values is the same as determined previously in that the entropy values decrease as the reactions become less endothermic. There are a couple of exceptions, however, which are not readily explainable. The largest deviation to the trend is 2,4-dinitroaniline which has the largest entropy value but produces the third least endothermic reaction.

In order to compare the great number of weak bases that have been studied in FSO_3H, the thermodynamic quantities were calculated by this method relative to triethylamine. This compound was arbitrarily chosen as the standard base because it has the most exothermic enthalpy of protonation. The thermodynamic quantities and parameters are reported in Table XVI. Two bases can be compared by this method but with severe limitations. Bases which do not follow the Hammett acidity function can not be compared since the activity coefficient term is not unity.

D. Conclusion

Three different methods have been devised to obtain the relative free-energies and entropies of the dissociation of protonated weak bases. The results are generally the same for all three methods in that more order is achieved as the reaction becomes more exothermic. These results suggest that stabilization is dominated by solvation. The more solvated species are more stable. The more disorder suggests there is more free solvent.

This result coupled with the analysis of the protonated methyl,

TABLE XV

THERMODYNAMIC QUANTITIES AND PARAMETERS FOR PROTONATED NITROANILINES DETERMINED BY THE FSO_3H METHOD

Nitroanilines	pK_{BH}^+	ΔH_f (cal/mole)	log I	log $\frac{KB}{KA}$	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole °C)
4-NO_2-An	1.040	31,100	16.11	std	std	std	std
2-NO_2-An	-0.274	26,800	14.80	1.31	-1,787	-4,300	-8.43
4-Cl-2-NO_2-An	-1.01	25,300	14.06	2.05	-2,796	-5,800	-10.08
2,5-Di-Cl-4-NO_2-An	-1.72	24,100	13.36	2.76	-3,765	-7,000	-10.86
2,6-Di-Cl-4-NO_2-An	-3.36	21,800	11.71	6.40	-6,002	-9,300	-11.07
2,4-Di-NO_2-An	-4.53	21,500	10.54	5.57	-7,597	-9,600	-6.72
2,6-Di-NO_2-An	-5.23	17,900	9.84	6.27	-8,552	-13,200	-15.60
2-Br-4,6-Di-NO_2-An	-5.88	17,400	9.19	6.92	-9,439	-13,700	-14.30

TABLE XVI

THERMODYNAMIC QUANTITIES FOR PROTONATED BASES DETERMINED BY THE FSO_3H METHOD

No.	Compound	log I	log K_{BH^+}/K_{AH^+}	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole °K)
		Tertiary Amines				
1	Triethylamine	25.8	std	std	std	std
2	Tri-n-butylamine	25.0	0.8	-1,100	-4,000	-9.7
3	N,N-Dimethylaniline	20.1	5.7	-7,800	-11,500	-12.4
		Secondary Amines				
4	Diethylamine	26.1	-0.3	410	-1,500	-6.4
5	Di-n-butylamine	26.3	-0.5	680	-2,800	-11.7
6	2,6-Lutidine	21.8	4.0	-5,500	-7,900	-8.1
7	Pyridine	20.3	5.5	-7,500	-10,600	-10.4
8	3-Bromopyridine	17.9	7.9	-11,000	-14,600	-12.1
		Primary Amines				
9	4-Fluoroaniline	19.7	6.1	-8,300	-12,000	-12.4
10	4-Methylaniline	20.2	5.6	-7,600	-12,300	-15.8
11	4-Chloroaniline	19.1	6.7	-9,100	-13,600	-15.1
12	2-Methylaniline	19.5	6.3	-8,600	-13,600	-16.8
13	4-Bromoaniline	18.9	6.9	-9,400	-14,000	-15.4
14	4-Iodoaniline	18.9	6.9	-9,400	-14,700	-17.8
15	3-Chloroaniline	18.6	7.2	-9,800	-15,000	-17.4
16	3-Nitroaniline	17.5	8.3	-11,000	-15,200	-14.1
17	Aniline	19.7	6.1	-8,300	-15,200	-23.2

TABLE XVI (CONTINUED)

No.	Compound	log I	log K_{BH}^+/K_{AH}^+	$\delta\Delta G$ (cal/mole)	$\delta\Delta H$ (cal/mole)	$\delta\Delta S$ (cal/mole °K)
18	2-Fluoroaniline	18.3	7.5	-10,000	-15,300	-17.8
19	2-Chloroaniline	17.7	8.1	-11,000	-16,700	-23.2
20	4-Nitroaniline	16.1	9.7	-13,000	-18,100	-17.1
21	2-Iodoaniline	17.6	8.2	-11,000	-16,800	-19.5
22	2,4-Dichloroaniline	17.1	8.7	-12,000	-18,900	-23.2
23	2-Nitroaniline	14.8	11.0	-15,000	-22,400	-24.8
24	2,4,6-Tribromoaniline	15.9	9.9	-14,000	-23,900	-33.2
25	4-Chloro-2-nitroaniline	14.1	11.7	-16,000	-23,900	-26.5
26	2,5-Dichloro-4-nitroaniline	13.4	12.4	-16,900	-25,100	-27.5
27	2,6-Dichloro-4-nitroaniline	11.7	14.1	-19,200	-27,400	-27.5
28	2,4-Dinitroaniline	10.5	15.3	-20,800	-27,700	-23.2
29	2,6-Dinitroaniline	9.8	16.0	-21,800	-31,300	-31.9
30	2-Bromo-4,6-dinitroaniline	9.2	16.6	-22,600	-31,800	-30.9
31	2,4,6-Trinitroaniline	5.0	20.8	-28,400	-36,000	-25.5
		Aliphatic Ketones				
32	Hexachloroacetone	0.4	25.4	-34,600	-51,100	-55.4
33	Cyclobutanone	7.4	18.4	-25,100	-34,800	-32.6
34	Cyclododecanone	8.3	17.5	-23,900	-33,200	-31.2
35	Cyclodecanone	8.8	17.0	-23,200	-32,300	-30.5
36	2-Norboranone	8.9	16.9	-23,000	-32,100	-30.2
37	Cyclopentanone	9.2	16.6	-22,600	-31,600	-30.2
38	Adamantanone	9.2	16.6	-22,600	-31,600	-30.2
39	Cyclohexanone	9.5	16.3	-22,200	-31,000	-29.5
40	Cycloheptanone	9.5	16.3	-22,200	-31,000	-29.5
41	2-Pentanone	9.9	15.9	-21,700	-30,400	-29.2

TABLE XVI (CONTINUED)

No.	Compound	log I	log $K_{BH}+/K_{AH}+$	δΔG (cal/mole)	δΔH (cal/mole)	δΔS (cal/mole °K)
42	Acetone	10.0	15.8	-21,500	-30,100	-28.9
43	Crotonaldehyde	10.3	15.5	-21,100	-29,700	-28.9
44	Dicyclopropyl ketone	11.0	14.8	-20,200	-28,400	-27.5
		Aldehydes				
45	4-Nitrobenzaldehyde	7.0	18.8	-25,600	-35,500	-33.2
46	3-Nitrobenzaldehyde	7.3	18.5	-25,200	-34,900	-32.6
47	Benzaldehyde	8.4	17.4	-23,700	-33,100	-31.5
48	4-Isopropylbenzaldehyde	8.6	17.2	-23,500	-32,700	-30.9
49	4-Methylbenzaldehyde	8.9	16.9	-23,000	-32,100	-30.5
50	2,4,6-Trimethylbenzaldehyde	9.6	16.2	-22,000	-30,900	-29.9
		Aromatic Ketones				
51	3-Chloroacetophenone	8.5	17.3	-23,600	-32,800	-30.9
52	4-Chloroacetophenone	8.9	16.9	-23,000	-32,100	-30.5
53	2,4,6-Trimethylacetophenone	9.0	16.8	-22,900	-32,000	-30.5
54	3-Nitroacetophenone	9.4	16.4	-22,400	-31,300	-29.9
55	4-Nitroacetophenone	9.8	16.0	-21,800	-30,500	-29.2
56	Acetophenone	9.9	15.9	-21,700	-30,300	-28.9
57	3-Methylacetophenone	10.0	15.8	-21,500	-30,200	-29.2
58	3-Methoxyacetophenone	10.9	14.9	-20,300	-28,600	-27.9
59	1-Acetylnapthalene	9.4	16.4	-22,400	-31,200	-29.5
60	2-Acetylnapthalene	9.5	16.3	-22,200	-31,100	-29.9
61	3-Acetylbiphenyl	19.9	5.9	-8,100	-12,600	-15.1
62	2-Acetylfluorene	20.9	4.9	-6,700	-10,800	-13.8

TABLE XVI (CONTINUED)

No.	Compound	log I	log $K_{BH}+/K_{AH}+$	δΔG (cal/mole)	δΔH (cal/mole)	δΔS (cal/mole °K)
63	Fluorenone	7.3	18.5	-25,200	-35,000	-32.9
64	2,3:6,7-Dibenzocycloheptadienone	8.6	17.2	-23,500	-32,700	-30.9
65	2,3:6,7-Dibenzocycloheptatrienone	9.9	15.9	-21,700	-30,400	-29.2
66	Anthrone	10.1	15.7	-21,400	-30,000	-28.9
67	Coumarin	10.3	15.5	-21,100	-29,600	-28.5
68	Xanthone	10.9	14.9	-20,300	-28,600	-27.9
69	Diphenylcyclopropenone	12.7	13.1	-17,900	-25,300	-24.8
70	2,6-Dimethyl-4-pyrone	16.9	8.9	-12,100	-17,800	-19.1
71	4,4-Dichlorobenzophenone	7.7	18.1	-24,700	-34,300	-32.2
72	4-Chlorobenzophenone	8.1	17.7	-24,100	-33,600	-31.9
73	4-Bromobenzophenone	7.8	18.0	-24,500	-34,100	-32.2
74	Benzophenone	8.8	17.0	-23,200	-32,300	-30.5
75	4-Methylbenzophenone	9.3	16.5	-22,500	-31,400	-29.9
76	4,4-Dimethylbenzophenone	9.5	16.3	-22,200	-31,100	-29.9
77	4-Methoxybenzophenone	10.7	15.1	-20,600	-29,000	-28.2
78	4,4'-Dimethoxybenzophenone	16.2	9.6	-13,000	-19,100	-20.5
	Other Bases					
79	4-Dichloromethyl-4-methyl-cyclo-hexadienone	11.3	14.5	-19,800	-27,900	-27.2
80	Mesityl Oxide	12.7	13.1	-17,900	-25,300	-24.8
81	Ethyl benzoate	7.5	18.3	-25,000	-34,700	-32.6
82	Ethyl acetate	9.1	16.7	-22,800	-31,800	-30.2
83	Triphenylphosphine	17.8	8.0	-10,900	-20,500	-32.2
84	Triphenylphosphine oxide	13.0	12.8	-17,500	-26,200	-29.2
85	Nitrobenzene	2.7	23.1	-31,500	-42,600	-37.2

cyclopropyl, and phenyl ketones indicates that solvation plays an important role in ion stabilities. The overall stabilization of an ion is a combination of internal and external factors. These results clearly point out the fact that it is very important to identify the effects of the solvent and the substituents in the stabilization of carbocations.

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