

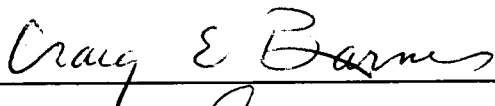
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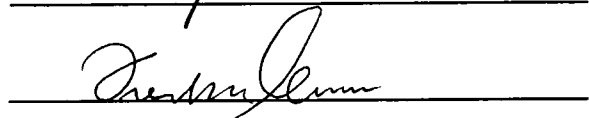
I am submitting herewith a thesis written by Priscilla Rose Higgins entitled "Gas Phase Ion-Molecule Chemistry: 1. Geometric Dependence in the Acidity of the Amines 2. Reversal of the Gas Phase Acidity of the Long Chain Alcohols (1-pentanol and beyond)." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Chemistry.



John E. Bartmess, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:



Associate Vice Chancellor and
Dean of The Graduate School

GAS PHASE ION-MOLECULE CHEMISTRY: 1. GEOMETRIC DEPENDENCE IN
THE ACIDITY OF THE AMINES 2. REVERSAL OF THE GAS PHASE
ACIDITY OF THE LONG CHAIN ALCOHOLS (1-PENTANOL AND BEYOND).

A Thesis

Presented for the

Master of Science

Degree

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Priscilla Rose Higgins

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ABSTRACT

The Ion Cyclotron Resonance mass spectrometer has been used to study gas phase ion-molecule reactions.

1,1,1,3,3,3-Hexamethyldisilazane was found to be more acidic than expected in the gas phase by 15 kcal/mol, relative to other functional groups, based on the solution phase data. Its conjugate base will not deprotonate simple ketones in the gas phase, although that is the common use of the lithiated salt in the condensed phase. Theoretical calculations have shown that there is a geometry change upon removal of the hydrogen at the nitrogen center. The Si-N-Si bond angle became linear. This strengthening of acidity in the gas phase and the geometry change must be due to one of the following: polar, polarizability, resonance or rehybridization effect. In order to determine which effect was the principal contributor to the strengthening in the gas phase acidity and the change in geometry, a geometrically constrained molecule was chosen, 1,1,3,3-tetramethyl-1,3-disila-2-aza-cyclopentane, and its acidity was measured. 1,1,3,3-Tetramethyl-1,3-disila-2-aza cyclopentane was found to be 10.5 kcal/mol more weakly acidic than the hexamethyldisilazane. By comparing the theoretical calculations of the silylamines and alkylamines, it is postulated the strengthening in acidity of hexamethyldisilazane must be due to rehybridization at the nitrogen center.

As for the acidities of the aliphatic alcohols, it has been shown in the kinetic method, which is a method that measures the acidities of the ions formed from fragmenting dimer ions, that there was a linear strengthening in acidity of the branched and primary alcohols (carbon lengths up to four). The long chain primary alcohols (carbon lengths greater than four), showed a monotonic strengthening in acidity, but not a linear one. In the equilibrium method, which is a method that measures the acidities of free ions, the long chain alcohols did not show a monotonic strengthening in acidity as was shown in the kinetic method. The acidities of the long chain alcohols by our method, equilibrium method, were as follow at 25°C: $C_3 < C_4 < C_9 < C_7 < C_8 < C_5 < C_6$. This non-monotonic trend in acidities among the long chain alcohols might be due to the alkoxides forming cyclic structures. The tail-end methyl group is capable of approaching the anionic site with increasing carbon length. However, our results also showed the long chain alcohols (1-pentanol and beyond) were less acidic relative to propionitrile. When using the ΔS values for linear and cyclizing alcohols to calculate ΔG for the long chain alcohols, the long chain alcohols should have been more acidic than the carbon acids. Therefore, something else is occurring in the long chain alcohols, in which there is a need for further studies.

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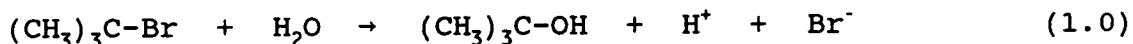
CHAPTER 1

ION CYCLOTRON RESONANCE MASS SPECTROMETRY

A. Introduction

1. Gas Phase Versus Condensed Phase Chemistry

It has been discovered that solvents can play an important role in determining the outcome of reactions.¹ Solvents can affect the reaction rate as well as the acidity and basicity of the reactants.¹ For example, the effect of the solvent on the reaction rate can be observed in the following reaction (1.0):



This $\text{S}_{\text{N}}1$ reaction will occur at a faster rate in a polar solvent (dielectric constant greater than fifteen)² than in a nonpolar solvent (dielectric constant between two and fourteen).^{2,3} It has been postulated³ that a polar solvent solvates the charges formed as the carbon-halide bond breaks in the transition state (1.1).



In the transition state of an $\text{S}_{\text{N}}1$ reaction, the reactants have an increasing localized charge on them. A polar solvent can stabilize both partial positively and negatively charge species. This allows the carbocation forming to react with a weak nucleophile. This solvation will decrease

the energy of activation and increase the reaction rate.

However, in a nonpolar solvent, the partial charges in equation (1.1) are not solvated as well. A nonpolar solvent is not capable of forming a hydrogen bond with the anion or stabilizing a carbocation as well. Because the partial charges formed in the transition state are not solvated, the energy of activation will not be lowered and the rate of reaction will be slower.

The lack of stabilization of the partial charges in the transition state also occurs in the gas phase. The gas phase has a dielectric constant of one, the ultimate nonpolar solvent. In the gas phase, there is no solvent to solvate the partial charges formed in the transition state. Therefore, the energy of activation will not be lowered and the rate of reaction will be even slower. This is why there are no gas phase studies of S_N1 reactions. However, stabilization of the charges needed to reach the transition state in an S_N2 reaction can be accomplished in the gas phase. The rate constants for S_N2 reactions are dependent on the strength of the nucleophile. In protic solvents, a more polarizable nucleophile will react faster than a less polarizable nucleophile. A less polarizable nucleophile has a localized negative charge on it, which will be more solvated in protic solvents than in comparison to a more polarizable nucleophile. The increased solvation of a less polarizable nucleophile will decrease its nucleophilicity

(ability to act as a nucleophile), because the nucleophile must shed some of its solvent molecules to be more reactive. For example, using a halide as a nucleophile for the following S_N2 reaction (1.2):⁴



where Y is the incoming nucleophile, ie. one of the halides.

The nucleophilicity of the halides proceeds in this order:

$I^- > Br^- > Cl^- > F^-$.⁴ Iodide is the best nucleophile of the halides, because it is more polarizable than the others.

Because it is more polarizable, iodide will not be as solvated as the others and thus more nucleophilic. Fluoride is the least nucleophilic, because of its concentrated negative charge. Fluoride will be more solvated than the other halides. However, in the gas phase, it has been shown the order of nucleophilicity of the halides is the opposite order of that in solution ($F^- > Cl^- > Br^- > I^-$).⁵ In the gas phase, there is no solvent to solvate the negative charge on the halides. A halide with a concentrated negative charge in the gas phase will be very reactive. In fact, a nucleophile having a concentrated negative charge such as fluoride, will form a stronger bond with an electrophile than a nucleophile having a diffuse negative charge. Therefore, a nucleophile having a concentrated negative charge will be more reactive in the gas phase than a nucleophile having a diffuse negative charge.

As mentioned above, the solvent can affect the acidity

and the basicity of the reactants. For example, the basicity of the alkylamines in solution is based on two factors: solvation and polar effects.⁶ The solvation effect is based on the ability of the alkylamines to form hydrogen bonds with a polar solvent. Ammonia, for instance, is strongly solvated in polar solvents. Even more strongly solvated in polar solvents is the ammonium ion. The solvation decreases with increasing number of methyl groups replacing hydrogens on the nitrogen. The more basic alkylamine or ammonium counterpart is the one that is more solvated by a polar solvent. However, the polar effect counteracts the solvation effect. Methyl groups are electron-donors relative to hydrogen and will aid in stabilizing the positive charge on a protonated nitrogen. So with increasing methyl groups, the basicity will increase. When both effects are combined, the order of basicity in solution is $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 \approx (\text{CH}_3)_3\text{N} > \text{NH}_3$.⁶ However in the gas phase, there is only one factor that will affect the basicity of the alkylamines. It is the polar effect. The successive replacement of hydrogens by methyl groups increases the basicity. The order of basicity in the gas phase is $\text{R}_3\text{N} > \text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3$.⁷ The ability for the charge to be stabilized by the polar effect has been seen in other systems, such as carboxylic acids and alcohols.⁸ This polar effect is in competition with solvation effects in the condensed phase. Consequently, gas phase ion chemistry can

give a better understanding of how solvents affect reactivity. Gas phase chemistry can be studied using an Ion Cyclotron Resonance (ICR) mass spectrometer and this will be discussed in the thesis.

2. The Evolution of Ion Cyclotron Resonance Mass Spectrometry

The first mass spectrometer that trapped ions and detected them as they spiralled towards the detector plates was the Omegatron of Somer, Thomas, and Hipple.⁹ The purpose of developing this instrument was to determine the mass of a proton by measuring the cyclotron resonance frequency of the proton in a fixed magnetic field.

In the late 1960's, there was an increased interest in ion-molecule reactions. A double-resonance Ion Cyclotron Resonance (ICR) mass spectrometer was developed by Baldeschwieler and co-workers.¹⁰ They had shown that it was possible to eject one ion and observe another in order to study ion-molecule reactions. It was useful for determining which compound was involved in a complex reaction.

However, up to this time, detection of ions of different mass to charge ratio required keeping the radio frequency field constant while sweeping the magnetic field. This took time to generate the spectrum. It was in the early 1970's when the Fourier transform method was adapted from other instruments, such as infrared and NMR

spectroscopy. Marshall and Comisarow were the people who developed the first FT/ICR.¹¹ This method excited and detected the whole spectrum at once by sweeping the radio frequency field while the magnetic field was held constant. This allowed the entire mass range to be detected in a minimum amount of time. Therefore, FT/ICR made it possible to study ion/molecule reactions more efficiently.

3. Theory of Ion Cyclotron Resonance Mass Spectrometry

Once ions are generated by electron ionization, they experience a force due to the magnetic field, as given by equation (1.3)¹²

$$F = m(V \times B) \quad (1.3)$$

F is the force of the magnetic field, m is the mass of the ion, V is the velocity of the ion, and B is the magnetic field. The magnetic field causes the ions to travel with circular motion normal to the field. This circular motion is the cyclotron motion. While moving in the cyclotron motion, the ions are traveling at a certain frequency, which is characteristic of their mass. This is the cyclotron frequency and is represented by the equation (1.4)¹³

$$\omega_c = (qB)/m \quad (1.4)$$

ω_c is the cyclotron frequency, q is the charge on the ion, B is the magnetic field, and m is the mass of the ion. By rearranging equation (1.4), one gets equation (1.5):

$$B/\omega_c = m/q \quad (1.5)$$

By applying the appropriate radio frequency signal to the cell's plates, the ions will absorb energy when their cyclotron frequency matches the applied frequency. The ions' radius of the ions path will increase and this indicates the ions are in resonance with the applied frequency. The ions can then be detected as described later under the section entitled "Ion Detection."

B. Experimental

1. Instrumentation

The instrument used throughout this research is a homebuilt Ion Cyclotron Resonance (ICR) mass spectrometer. A diagram of this instrument appears in Figure 1 (page 8). The instrument is controlled by a 486DX-50 PC using Tecmar Labmaster interface boards. The analyzer system consists of a five liter stainless steel manifold which contains an ion trap (McIver cell).¹⁵ This is the location where the ion-molecule reactions take place. This system typically has a pressure of 1×10^{-8} torr after an overnight bake-out at a temperature of 100°C. The pressure is attained by a Balzers TPU100 110 l/s turbomolecular pump, which is backed by a Alcatel 2008A 200 l/min rotary mechanical pump. The neutral pressure is measured by a Huntington Mechanical Labs/Bayard-Alpert ionization gauge that is used with a Granville-Phillips series 270 gauge controller. The stainless steel

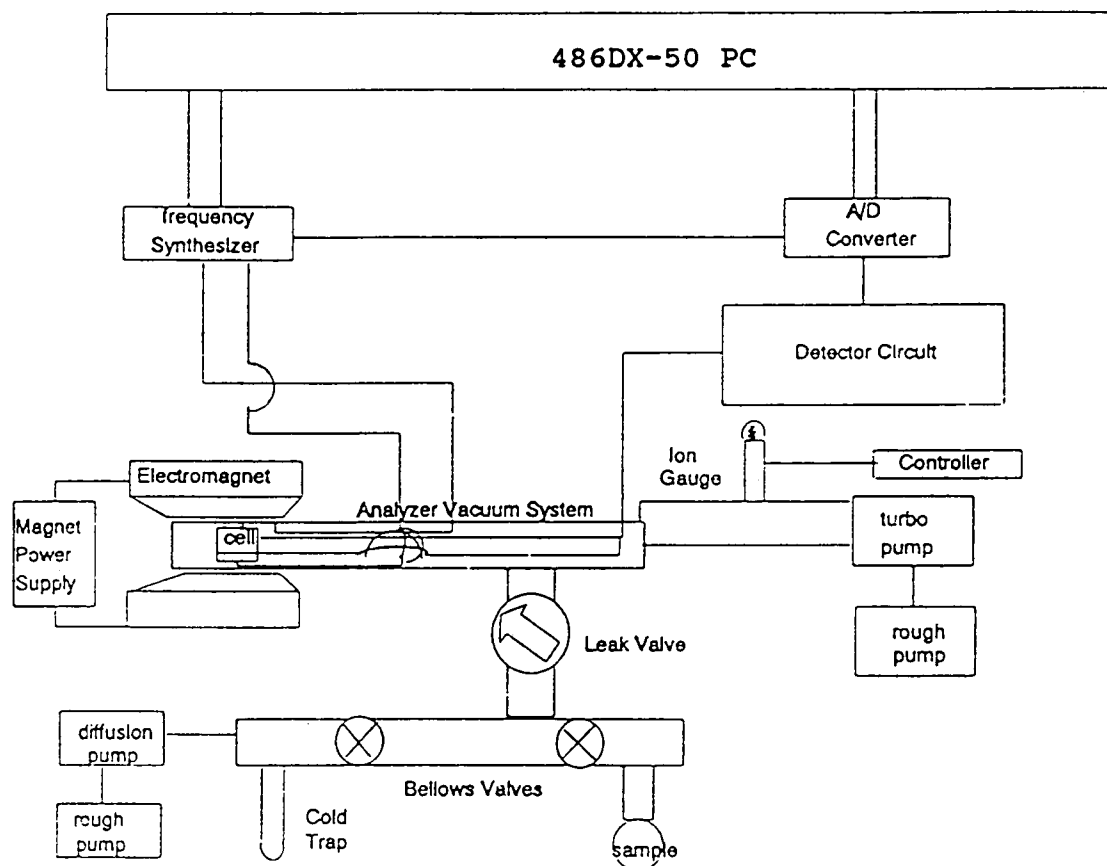


Figure 1. A block diagram of the UTK ICR mass spectrometer.¹⁴

manifold is located between the poles of a Varian 9" 1.4 tesla electromagnet, which is usually operated at 1.3 tesla for thermal reasons. The foreline system consists of a 2" CVC, VMF-21, air cooled diffusion pump, which holds the foreline at a pressure of ca. 1×10^{-6} torr. Samples are admitted into the analyzer system through the foreline system by the Varian 951-5106 variable sapphire leak valves. Volatile samples are degassed by several freeze-pump-thaw cycles before being admitted into the foreline system. The radio frequency signal generated by the Rockland Synthesizer is used to bring the ions into resonance in the cell. Ions are detected by using a capacitance bridge detector. Ion signals are digitized by the Tecmar A/D into the computer to generate the spectrum. Real time signals can be monitored on a Tektronix 5110 oscilloscope, and the digitized signal displayed on the 486DX-50 colored monitor screen. A hard copy of the spectrum can be printed on the Tektronix 4662 interactive digital xy-plotter.

2. Ion Detection

Once the neutral gas enters the analyzer manifold, it becomes ionized upon electron impact in the McIver cell, as shown in Figure 2 (page 10), by an electron beam. This electron beam is generated by a rhenium filament when heated by several amperes of DC current. The filament is mounted outside of the cell, but not in contact with it.

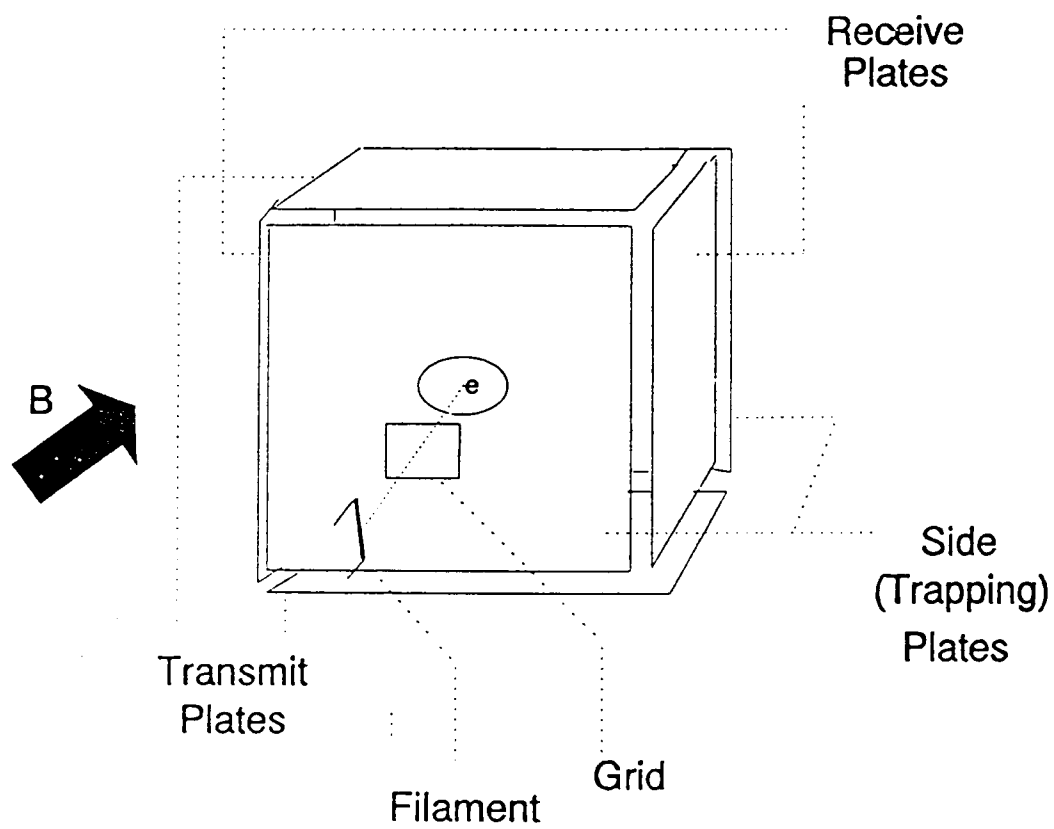


Figure 2. A McIver Cell.¹⁵

The electron beam is allowed into the cell by the grid, located behind the filament. The voltage on the grid is pulsed for several milliseconds at time zero of the experiment to allow electrons to enter the cell. When the voltage on the grid is more positive than the filament (ca. 5 volts more positive), the electron beam will enter the cell. When the voltage on the grid is more negative than the filament, the electron beam will not enter into the cell. Once formed, the ions are trapped in the cell by both the magnetic and electric fields. The magnetic field traps the ions perpendicular to its field and causes the ions to travel with a cyclotron motion. The ions are also trapped parallel to the magnetic field by the electrostatic field of the side plates. The side plates have a voltage applied to them (ca. 2-3 volts), which is the same sign as the charge on the ions being trapped. The ions can be trapped in the cell for several seconds this way. During this trapping, ion-molecule chemistry can occur. To detect the ions, a radio frequency field is applied to the upper and lower plates. When the ions' cyclotron frequency matches the applied frequency, resonance occurs.¹⁶ Resonance occurs when the ions absorb the energy, supplied by the applied frequency, and are accelerated. The ions' cyclotron radius increases until the ions come near the receive plates. The image current induced by the ions on the plates will unbalance the capacitance bridge of the detector. This

signal is amplified and sent through a filter to remove the background radio frequency. The signal can be observed on the oscilloscope and it is digitized to the PC. When the radio frequency field is turned off, the ions relax back to their thermal cyclotron radius, via collision with the neutral gas.

This instrument also has the capability of trapping and detecting negative ions. This is done by changing the sign of the potential on the sideplates. This will only trap the negative ions. The detection is the same as for positive ions.

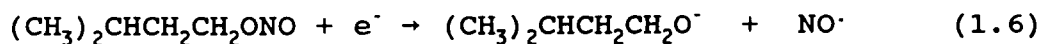
3. Anion Generation

Recently there has been an increasing interest in gas phase negative ion chemistry. However, not as many neutral molecules can form negative ions as efficiently as those forming positive ions, via electron ionization. One reason is that an electron must be retained once it is captured by a neutral molecule. Once an electron is captured by a neutral molecule, it proceeds through a vertical transition between two potential energy curves by the Franck-Condon principle.¹⁷ For the negative molecule formed to be stable, the potential energy surface of the negative molecule must be lower than the potential energy surface of its neutral molecule. Another factor is the electron energy distribution. In mass spectrometry, the probability for

production of negative ions is a function of the electron energy. The electron energy is the translational energy of the electrons going into the cell. The electron energy needed to generate negative ions typically has a narrow range over a few electron volts in both dissociative and non-dissociative electron attachment. In dissociative electron attachment, an electron is captured by the molecule, which goes into the excited state on the Franck-Condon region of the potential energy curve, as shown in Figure 3A (page 14). The molecule then dissociates into a radical and a negative ion. For this process, the electron energy range is typically between 0.0 and 15.0 electron volts.¹⁸ In non-dissociative electron attachment, the electron attaches to a neutral molecule, and the resulting anion exists in an excited state as shown in Figure 3C (page 14). The excited anion is stabilized by colliding with other molecules to rid itself of the excess energy. The maximum probability of parent-negative-ion formation is usually at 0.0 electron volts of electron energy.¹⁸ Being off by even a few tenths of an electron volt can result in reduced production of negative ions.

An example of a compound that was used in generating negative ions for this thesis work is isoamyl nitrite. It forms a negative ion upon dissociative electron attachment

(1.6)



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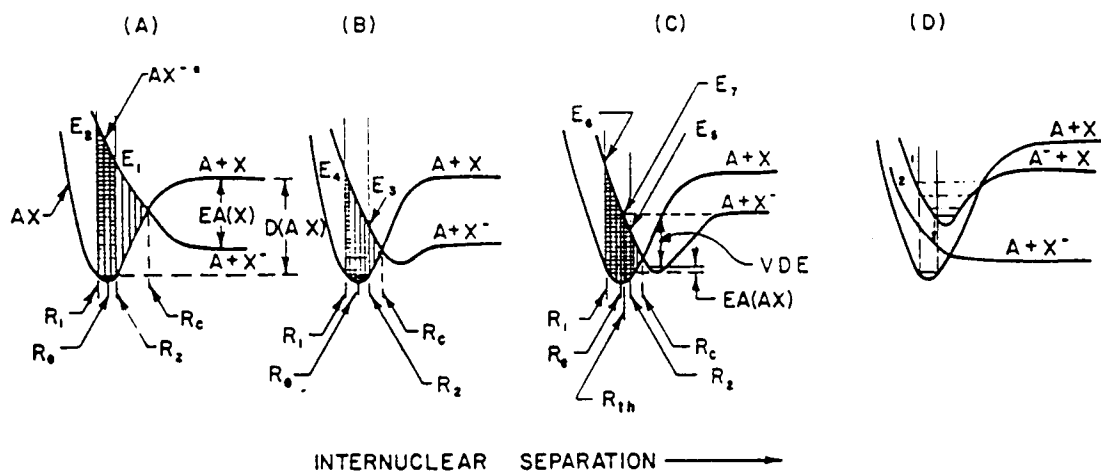


Figure 3. Potential energy diagrams of dissociative and non-dissociative electron attachment, where AX is the neutral molecule.¹⁸

The isoamyl alkoxide formed through this process would then abstract a proton from another compound. This would form anions of the compounds to be studied.

C. Modes of Operation and Equilibrium Studies

The ICR spectrometer in this laboratory can be operated in the unquenched or quenched mode. The unquenched mode allows the ions to remain in the cell until they are neutralized upon colliding with the neutral molecules and/or the cell wall.¹⁹ This mode is used to determine what ions are present. The other mode, quenched, is used to monitor the time dependence of ion-molecule reactions. This mode allows the ions to react with other ions for a set time after formation during the electron beam event. After detection, the ions are neutralized by changing one of the side plates' voltage to the opposite sign of the ions' charge. The ions will become neutralized by colliding with the cell wall.

Being able to trap ions for a specific time brings about the discussion of equilibrium studies. The quenched mode is used for doing equilibrium studies on reactions such as (1.7),



The equilibrium constant, K_{eq} , for reaction (1.7) can be calculated as shown in equation (1.8).

$$K_{eq} = [AH][B^-]/[BH][A^-] \quad (1.8)$$

B^- and A^- are the measured intensities taken from the spectrum. The pressures of AH and BH are known from measuring the neutral gas pressures, via the ionization gauge and capacitance manometer systems. The ionization gauge measures the ion current generated by electron ionization of the gas. The sensitivity of the ion gauge is not the same for all molecules. The sensitivity will be greater than 1.0 for molecules having larger ionization cross sections than N_2 . The opposite will occur for molecules with smaller cross section than N_2 . The neutral gas pressures as measured by the ionization gauge are then corrected to the true pressure by multiplying them by the Baratron factor. This Baratron factor is determined experimentally at the end of the day by using the MKS Baratron Capacitance manometer. The capacitance manometer measures the true pressure of the neutral molecules pressing against a thin metal diaphragm. The Baratron factor is then found by plotting the ion gauge reading versus the Baratron manometer reading at several different pressures. The relationship should be linear, with an intercept of zero. The slope is equal to the Baratron factor (B/I), which is multiplied by the ion gauge's pressure to give the true pressure. Not only can the Baratron factor be found experimentally, it can be calculated from an empirical method based on polarizability of the molecule.²⁰

Using the equilibrium constant, free energy can be used to express relative acidities for different compounds by equation (1.9)

$$\Delta G = -RT \ln K_{eq} \quad (1.9)$$

where ΔG is the relative free energy, R is the gas constant, and T is the temperature in Kelvin. According to the relative acidity value, the compound is either more or less acidic than the equilibrating acid having an absolute acidity value. The relative acidity value can then be subtracted or added to the equilibrating acid's absolute acidity value to get the absolute acidity of the compound studied.

CHAPTER 2

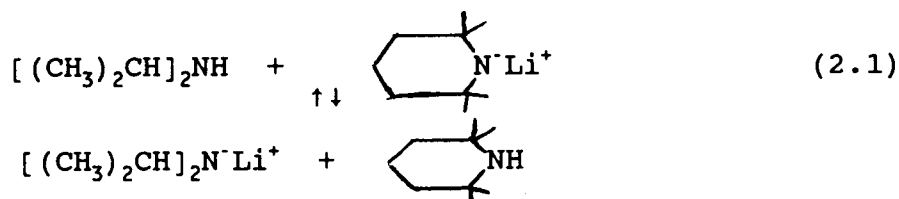
HEXAMETHYLDISILAZIDE ANION WILL NOT DEPROTONATE KETONES IN THE GAS PHASE

A. Introduction

Chemists have frequently used the strongest base possible for deprotonation of carbonyls, amides, amines, and nitriles, so as to ensure success.²¹ However, concentration, counterions, chelating species, and degree of aggregation have been shown to alter the reactivity of the bases in solution.^{22,23,24} Therefore, there is a need to know the intrinsic basicity of such species in order to understand their reactivity. Several researchers have undertaken the task of measuring the basicity of various anions, particularly those with lithium counterions. These workers used various solvents in determining the compounds' basicities.

Fraser and co-workers²⁵ performed carbon-13 NMR studies on lithiated amides in tetrahydrofuran. They were studying the lithium-hydrogen exchange rate. Their studies showed 2,2,6,6-tetramethylpiperidine was more weakly acidic by 1.6 pK_a units compared to diisopropylamine. When using diisopropylamine in comparison to other compounds, they showed the order of acidity over a range of 2 pK_a units as

follows: cis-2,6-dimethylpiperidine > diisopropylamine > 2,2,6,6-tetramethylpiperidine.²⁵ This trend agreed with previous studies.²⁶ Additionally, while looking at the acidity of bulky amines, they discovered the lithium-hydrogen exchange rate was dependent on the size of the alkyl groups. For example, the reaction between diisopropylamine with lithium 2,2,6,6-tetramethylpiperidide (2.1)



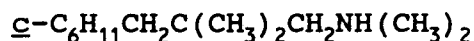
showed a lithium exchange barrier of $\Delta G^\ddagger = 16.8$ kcal/mol, which was lower by 2 kcal/mol than for the reaction between lithium diisopropylamide and cis 2,6-dimethylpiperidine.²⁵ This indicated that for steric reasons the bulkier the amine, the faster the lithium-hydrogen exchange rate.

Subsequently, Fraser²⁷ reported another study on lithiated amines, but focused the study primarily on the size of the alkyl groups. The less bulky amines were more acidic. It was found that sec-butyl propylamine (1) has $\text{pK}_a = 35.0$, (2-methylheptyl)isopropylamine (2) has $\text{pK}_a = 37.6$ and N,N-dimethyl(3-cyclohexyl-2,2-dimethylpropyl)amine(3) has $\text{pK}_a = 39.1$.



1

2



3

However when investigating alkyl(trimethylsilyl)amines, they noticed that the lithium-hydrogen exchange was slower in comparison to the dialkylamines. Moreover, these alkyl(trimethylsilyl)amines were more strongly acidic by 4-6 pK_a units than dialkylamines.²⁸ Upon comparing alkylamines to silylamines, diisopropylamine has $pK_a = 35.7$, isopropyl(trimethylsilyl)amine has $pK_a = 31.4$, and hexamethyldisilazane has $pK_a = 25.8$.²² Therefore, hexamethyldisilazane was more acidic than diisopropylamine by 9.9 pK_a units.

Arnett and Moe²⁴ performed calorimetric work on many lithiated amides with different functional groups in various solvents. They found that lithium hexamethyldisilazide was only 8 kcal/mol stronger as a base than lithium diisopropylamide. However, they noticed while performing their studies that lithiated amides were more likely to form high-order aggregates in comparison to cesium amides. This is due to the atomic radii of the cations. Since lithium ion has a smaller radius than cesium ion, there is less steric hindrance to the nitrogen's lone-pair chelation with another amide's lithium ion. This interaction has been known to affect the pK_a values.²⁴ Therefore, the basicities of lithiated amides cannot be accurately measured in this solution. This led to the work performed in the gas phase by our research group. Solvent effects and aggregations are not present in the gas phase, so that the intrinsic

acidities can be determined. Previously, gas phase experiments were performed upon various anionic bases that are commonly used for deprotonation of carbonyls, amides, amines, and nitriles.²⁹ Results of the study in comparison to the solution phase counterparts can be seen in Figures 4 (page 22) and 5 (page 23). There is a general correlation between condensed and gas phase reactivities. Some structural trends were seen based on steric bulk. The general trend is for parallel effects: a strong base in the gas phase is also a strong base in solution. However during this work, it was noticed that hexamethyldisilazane was more strongly acidic in the gas phase by 15 kcal/mol than in solution, relative to the other acidities investigated. This indicated that hexamethyldisilazide anion will not deprotonate ketones and nitriles in the gas phase, although that is the common use of the lithiated salt in solution. In order for such proton transfers to occur in the gas phase, they would have to proceed through a pathway endothermic by 13 kcal/mol.²⁹

Several effects could be the cause of this difference in the gas phase. One is the polar or inductive effect of the silicons next to the nitrogen center. In the present case (the calculated acidity of disilylamine), the trimethylsilyl group appears to strengthen the acidity by acting as an electron-accepting group (4), although it has always been thought of as an electron-donating group.³⁰

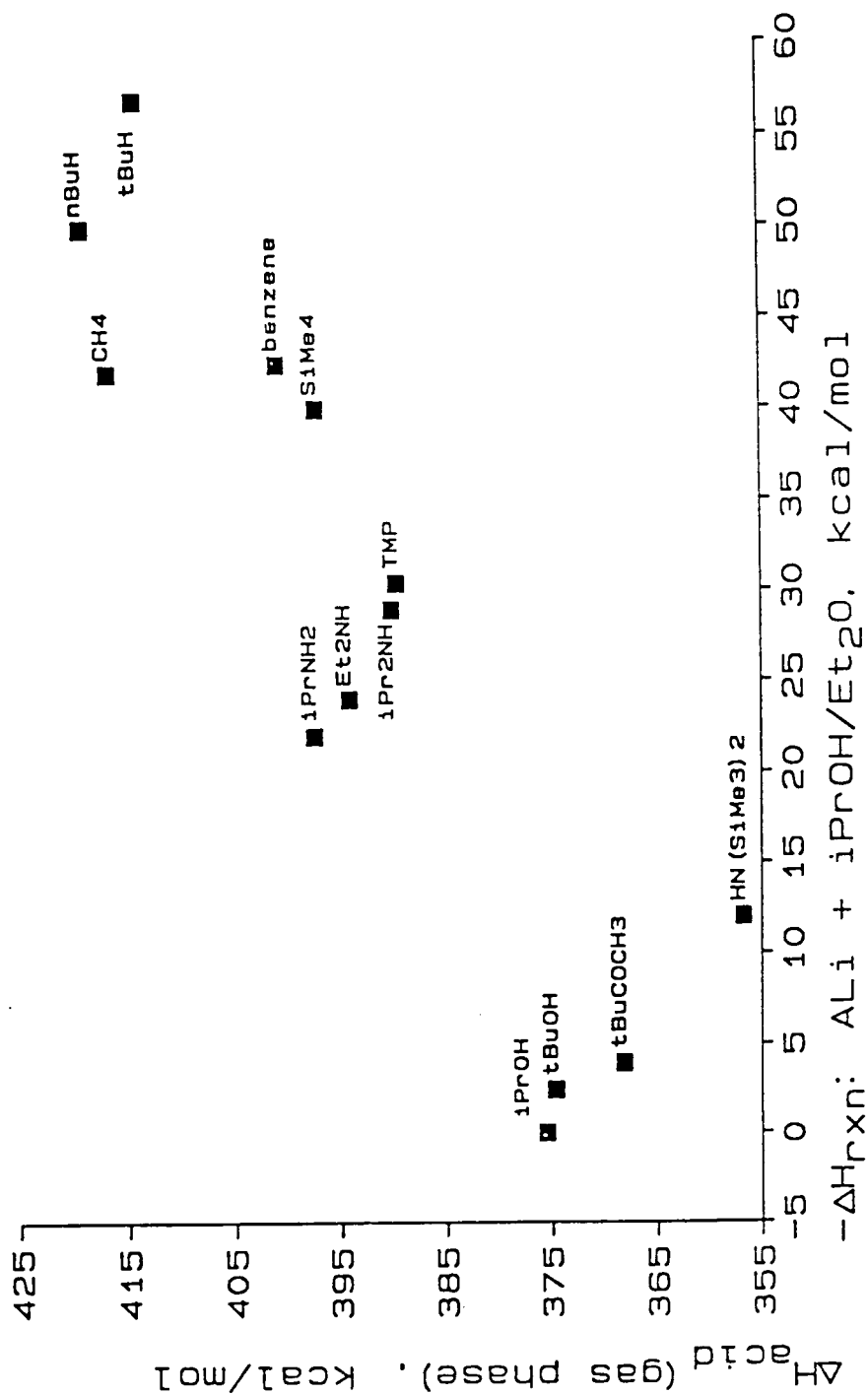


Figure 4. Gas phase anion proton affinity (ΔH_{acid}) versus enthalpy of solution phase proton transfer from 2-propanol to lithiated anions in 90% diethyl ether/hexane solvent, in kcal/mol.²⁹

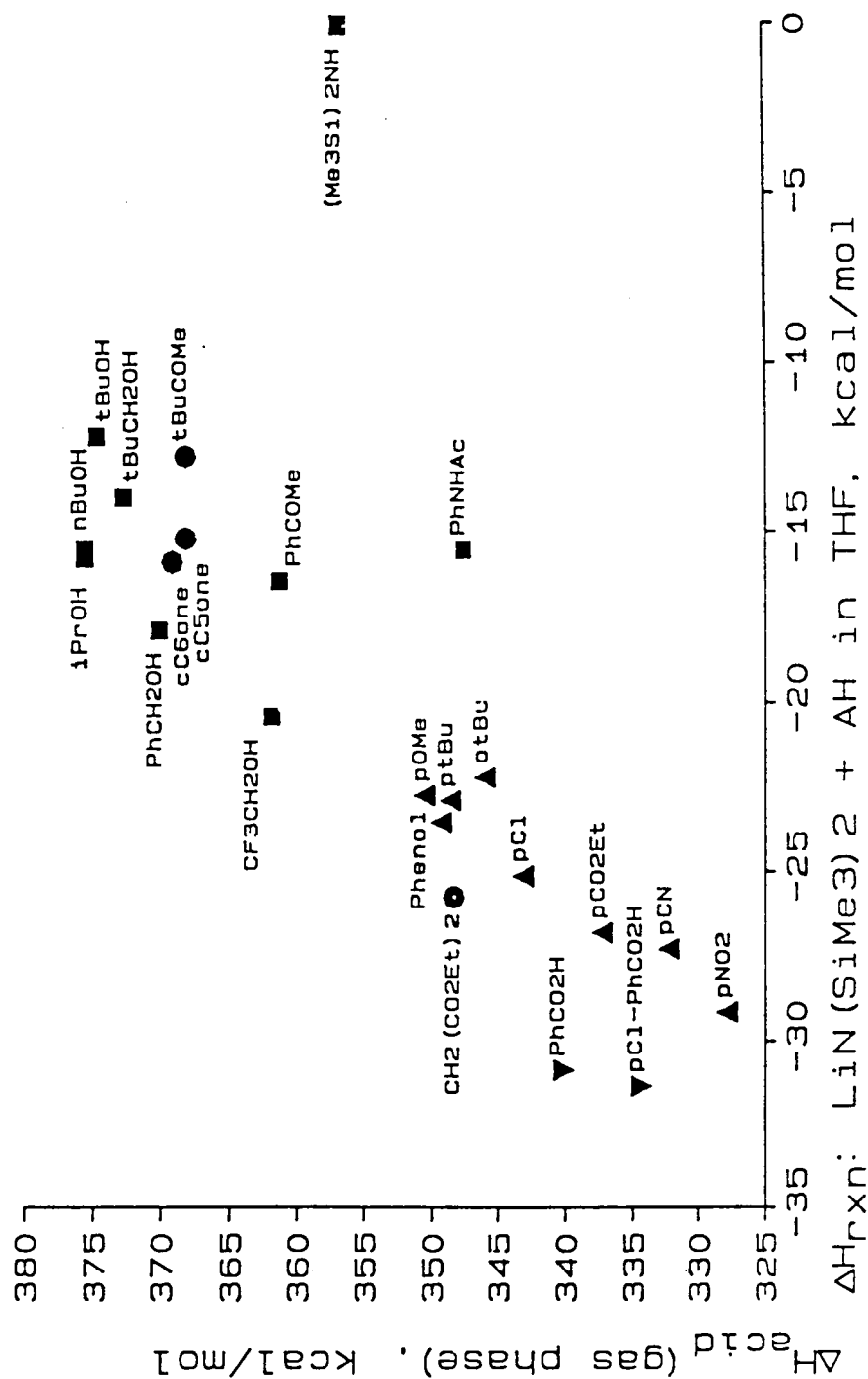
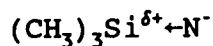


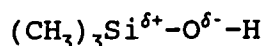
Figure 5. Gas phase anion proton affinity (ΔH_{acid}) versus enthalpy of solution phase proton transfer from various acids to lithium hexamethyldisilazide in THF solvent, kcal/mol: (Δ) phenols, (▽) benzoic acids, (●) ketones and esters, (■) "localized" OH, NH acids.²⁹



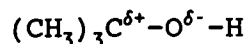
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This would increase the acidity of bis(trimethylsilyl)amine.

Polarizability is another effect that may stabilize the anion. It has been shown by a gas phase study, that a trimethylsilyl group will strengthen the acidity of the hydroxy group.³¹ A trimethylsilyl group stabilizes an oxygen anion in the gas phase just like a tertiary butyl group does (5 and 6), via a polarizability effect.³²



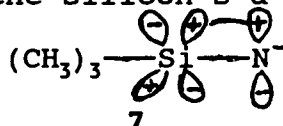
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6

Because a trimethylsilyl group has been shown in the gas phase to stabilize an oxygen anion, a trimethylsilyl group next to a negatively charged nitrogen could be stabilizing the anion by its polarizability.

Another possible reason for this major acidity strengthening in the gas phase could be p-d π resonance stabilization. Silicon's electron-accepting property can be attributed to its empty d-orbital.³³ Upon deprotonation of the nitrogen, the negative charge in the p-orbital can be distributed back into the silicon's d-orbital (7).



The nitrogen's p-orbital and silicon's d-orbital must be comparable in energy for this to occur. The nitrogen's p-orbital energy (about -2.7 eV in the anion and -8.55 eV in

the neutral) is near the silicon's d-orbital energy (about 0 eV) in the anionic species³⁴. This would allow for the two orbitals (p and d-orbitals) to mix. In the neutral species, the p-orbital energy level of the nitrogen is not close enough in energy to the d-orbital of the silicon; thus p-d π bonding does not occur in the neutral species.³⁵ Consequently in the anionic species, the p-d orbital overlap should cause the bond length between the nitrogen and the silicon to shorten. In fact, theoretical calculations performed on the disilylamine and the dimethylamine indicate that the bond length shortens upon deprotonation. This p-d π resonance could contribute to stabilizing the anion, which would strengthen its acidity.

A fourth reason for the change in acidity could be a rehybridization at the nitrogen center. Based on the geometries found in the calculations, the nitrogen is going from sp^2 to sp hybridization upon deprotonation. It has been shown that a hybridization change will increase the acidity in the carbon acids, Table 1 (page 26). When going from ethane to acetylene (hybridization from sp^3 to sp), there is a strengthening of the acidity. The more s character the orbital containing the negative charge has, the more stable it is in comparison to one having more p character. Therefore, an sp hybridized carbon is lower in energy than an sp^2 hybridized carbon. However, in the case of the nitrogen atom here, the negative charge, from

Table 1. Hybridization effects on carbon acidity

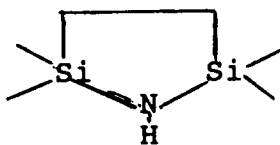
Anion	$\Delta H_{\text{acid}}^{\text{a}}$	$\text{pK}_{\text{a}}^{\text{b}}$	Hybridization
CH_3CH_2^-	420.1	50	sp^3
$\text{CH}_2=\text{CH}^-$	409.4	44	sp^2
$\text{HC}\equiv\text{C}^-$	378.0	25	sp

a. Ref 34, gas phase, in kcal/mol.

b. Ref 36, in cyclohexylamine.

deprotonation, occupies a p-orbital. As stated before, a p-orbital is more electropositive than a s-orbital, so this gives a less stable anion. However, the electrons gained from the loss of the hydrogen are occupying degenerate HOMOs. The electrons are, therefore, spread out in space, which will aid in stabilizing the anion. By allowing the electrons to spread out in space, the likelihood for p-d orbital overlap with both silicons is also increased. This rehybridization of nitrogen will result in a shorter bond length between itself and the other atoms. This can be seen in the hexamethyldisilazane. The nitrogen in hexamethyldisilazane is changing from sp^2 to sp hybridization upon deprotonation, and the Si-N bond length shortens by $0.13\text{\AA}$ according to the calculations. In fact, x-ray studies have shown that the Si-N-Si angle is wider than expected for the lithium hexamethyldisilazide (180.0°).³³ This hybridization change could explain the strengthening of the gas phase acidity.

In order to determine which reason explains the change in acidity in the gas phase, experimental and theoretical work were performed on a silylamine having a geometrically constrained nitrogen center. A compound that met this criterion was 1,1,3,3-tetramethyl-1,3-disila-2-azacyclopentane (8).



8

It does not have the capability of adopting a linear geometry on the Si-N-Si group upon deprotonation without severe increase in ring strain and thus, should be more weakly acidic than hexamethyldisilazane, the open chain equivalent. Theoretical calculations will be discussed along with the experimental results later in this chapter.

B. Experimental

1. Instrumentation

A Bruker AC250MHz nuclear magnetic resonance spectrometer was used to obtain proton spectra. Spectra were determined for compounds dissolved in deuterated chloroform. Tetramethylsilane was the internal standard. A Hewlett Packard 5890A gas chromatograph/mass spectrometer was used to determine which gas chromatograph peak was the desired compound by interpreting mass fragments of the chromatograph peaks. This information was used when purifying the compound by preparatory gas chromatography. Electron ionization studies were carried out using the Ion Cyclotron Resonance (ICR) mass spectrometer described in Chapter 1. Hartree-Fock ab initio calculations were

performed with the Gaussian 90 program, on an IBM 3090/400E mainframe by Professor John Bloor. The semi-empirical calculations were carried out with two different programs. MNDO (Modified Neglect of Diatomic Differential Overlap) calculations were carried out on an IBM model 70 PS/2 computer, utilizing a locally modified version of QCMP004. The AM1 method and the MNDO for radicals were carried out with QCPE 455 (MOPAC 5.0) on a Vax 8650. Complete geometry optimization were done on all structures. For the radical species, the calculations were done at the UHF level.

2. Methods

A pulsed Ion Cyclotron Resonance (ICR) mass spectrometer was used to generate and detect anions as described in Chapter 1. The quenched mode was used in all the experiments. The delay time was varied from 100 up to 1000 milliseconds, while scanning the masses 60 through 300 amu. The radio frequency amplitude, trapping voltage, and the filament current were set to give maximum signals. The electron energy was set between -2.00 to +0.10 volts depending on the day-to-day instrumental tuning at the above conditions. Isoamyl nitrite was used as a source to generate isoamyl alkoxide upon electron ionization, which then deprotonated the neutral 1,1,3,3-tetramethyl-1,3-disila-2-aza-cyclopentane. The ion gauge pressure of isoamyl nitrite was kept in the region of 1×10^{-7} torr. Neutral pressures of

the 1,1,3,3-tetramethyl-1,3-disila-2-aza-cyclopentane and the equilibrating acids were varied with a total ion gauge pressure ranging from 6×10^{-6} torr to 9×10^{-6} torr depending on the combination and the acidities.

3. Compounds

Isoamyl nitrite, 2,2,2-trifluoroethanol, N-methyl aniline were purchased from Aldrich Chemical Company. Benzyl alcohol was distilled prior to use from a non-commercial (no label) bottle. Acetaldoxime was sublimed prior to use from a sample synthesized by a previous group member. The purity of all compounds except the acetaldoxime was checked prior to use by gas chromatography.

1,1,3,3-Tetramethyl-1,3-disila-2-aza-cyclopentane

Synthesis of this compound was by the method of Baney and Haberland.³⁷ A 500-mL three-neck round bottom flask was equipped with an adapter for pressure release, magnetic stir bar, and a dry ice condenser. Ammonia gas from a cylinder was condensed by flowing through the dry ice condenser. Approximately 5.0 mL (0.23 mol) of ammonia gas was condensed in the flask. 5.00 grams (0.0232 mol) of 1,2 bis-(dimethylchlorosilyl)ethane and 20.0-mL (0.0464 mol) of diethyl ether were added to the flask containing the liquid ammonia. The reaction was allowed to reflux for 30 minutes, while stirring vigorously. The excess ammonia was allowed

to evaporate and the solid ammonium chloride was gravity filtered from the solution. An attempt to fractionally distill the solution was unsuccessful due to a misfitted adapter; only the diethyl ether was distilled. The crude mixture was retained in the flask. The product was not separated from the mixture with another distillation attempt. This could have been due to the vacuum pump not working properly. The gas chromatograph/mass spectrometer spectrum had shown two peaks. The first one was the unreacted 1,2-bis-(chlorodimethylsilyl)ethane and the second peak was the product. The product was purified prior to use in the ICR by preparatory gas chromatography (10% Carbowax 20M on Chromosorb W). ^1H NMR (CDCl_3) 0.0273-0.0582ppm (s, 9H, CH_3), 0.1210-0.2518ppm (s, 4H, CH_2), 0.6598-0.7320ppm (s, 1H, NH); GC/MS of the second peak m/z (relative intensities) 159 (M^+ , 35), 144 (100), 116 (70), 73 (50), 45 (25).

C. Results and Discussion

The acidity of the 1,1,3,3-tetramethyl-1,3-disila-2-aza-cyclopentane was determined by direct equilibration with compounds of known acidity. The cyclic disilazane was equilibrated with several acids for determining the equilibrium constant, K_{eq} . The ICR was operated at a temperature of 302 K during the reaction. The equation used

to calculate the acidity was (2.2)

$$\Delta G_{\text{acid}} = -RT \ln K_{\text{eq}} \quad (2.2)$$

It was assumed the entropy value was due solely to the loss of the proton, $\Delta S_{\text{acid}} = 26.0 \text{ cal/mol-K}^{38}$, since there is negligible loss of rotation and no change in symmetry number on simple deprotonation. The enthalpy was then calculated by using equation (2.3)

$$\Delta H_{\text{acid}} = \Delta G_{\text{acid}} + T \Delta S_{\text{acid}} \quad (2.3)$$

Table 2 (page 33) shows the acids and the results when they were reacted with 1,1,3,3-tetramethyl-1,3-disila-2-azacyclopentane. The cyclic disilazane is 10.5 kcal/mol less acidic than the acyclic disilazane (hexamethyldisilazane). The cyclic disilazane, therefore, has $\Delta H_{\text{acid}} = 367 \pm 2.1$ kcal/mol. There is some error in this result, which is about ± 2.0 kcal/mol in absolute acidity value, but only ± 0.2 kcal/mol in relative acidity value.³⁸ This absolute error is due to the anchoring technique. The anchoring technique involves using acids of known absolute acidities to equilibrate with the acid whose absolute acidity is unknown. These acids of known absolute acidities have an uncertainty of ± 2 kcal/mol. This uncertainty is reflective of the average measured acidities found using the equilibrium and kinetic methods.

Ab initio calculations were performed by Professor John Bloor³⁹ on both the dimethylamine and the disilylamine at the 6-31G//6-31+G (Tables 3 (page 34) and 4 (page 35)) and

Table 2. Experimental results using the bracketing technique in kcal/mol.

Acid	ΔG_{acid}	comparison
$\text{Et}_2\text{NOH}^{\text{a}}$	364.0	too weak
meta-methylaniline ^a	359.9	0.4 less acidic
1,1,3,3-tetramethyl-1,3-disila-2-aza-cyclopentane ^b	359.5	
acetoxime ^a	359.1	0.4 more acidic
2,2,2-trifluoroethanol ^a	354.1	too strong
Hexamethyldisilazane ^c	349.0	
Ethanethiol	348.9	0.1 more acidic

a. Ref. 35

b. Experimental

c. Ref. 30

Table 3. Geometries and energies of the dimethylamine performed at the 6-31+G//6-31+G level.^a

acids	C-N, Å	N-H, Å	C-N-C°	HNCC° ^b	C-H ^c	E _{HF} ^d
Me ₂ NH ^e	1.457	0.998	115.3	131.4	1.082 1.087	-134.182
Me ₂ N ⁻	1.449	----	115.0	----	1.104 1.108	-133.504
Me ₂ NLi	1.464	1.761	126.4	159.9	1.091 1.093	-141.032
Me ₂ N ⁻	1.459	----	113.8	----	1.078 1.088	-133.569

- a. 6-31+G//6-31+G calculations, Gaussian 90.
 b. Dihedral angle, in the Z matrix convention.
 c. First number is anti H to the HN, second is gauche.
 d. In units of Hartrees.
 e. $\Delta E\{\text{acid}\} = 425.5 \text{ kcal/mol}$.

Table 4. Geometries and energies for disilylamine performed at the 6-31+G//6-31+G level.^a

acids	Si-N, Å	N-H, Å	1	2 ^b	Si-H ^c	E _{HF} ^d
S _i -H ^e	1.771	1.001	129.8	180.0	1.489 1.494	-636.266
S _i ⁻	1.658	----	180.0	----	1.553 1.531	-635.658
S _i -Li	1.746	1.787	126.8	179.9	1.500 1.508	-643.142
S _i [·]	1.762	----	178.1	----	1.490 1.492	-635.625

- a. 6-31+G//6-31+G calculations, Gaussian 90.
b. Dihedral angle, in the Z matrix convention.
c. First number is anti H to the HN, second is gauche.
d. In units of Hartrees.
e. $\Delta E(\text{acid}) = 381.5 \text{ kcal/mol}$.
S_i (H₃Si)₂N-
1 Si-N-Si°
2 HN-SiSi°

Table 5. Geometries and energies of dimethylamine and the disilylamine performed at the 6-31+G^{*}//6-31+G^{*} level, X = Si or C; Y = H.^a

acids	X-N, Å	N-Y, Å	X-N-X°	YNXX° ^b	X-H° ^c	E _{HF} ^d
R _N -H ^e	1.453	0.996	115.3	134.7	1.086 1.087	-134.233
R _N ⁻	1.419	----	115.1	----	1.109 1.110	-133.569
S _i -H ^f	1.735	1.004	131.0	180.0	1.472 1.477	-636.392
S _i ⁻	1.624	----	180.0	----	1.509 1.509	-635.808

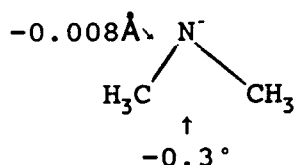
- a. 6-31+G^{*}//6-31+G^{*} calculations, Gaussian 90.
b. Dihedral angle, in the Z matrix convention.
c. First number is anti H to HN, second is gauche.
d. In units of Hartrees.
e. ΔE{acid} = 416.7 kcal/mol.
f. ΔE{acid} = 366.3 kcal/mol.
R_N Me₂N-
S_i (H₃Si)₂N-

$6-31+G^*/6-31+G^*$ (Table 5 (page 36)) levels. Both the geometries and the energies were calculated for: 1.) the neutral acid; 2.) the anionic conjugate base; 3.) the species in which the hydrogen was replaced by a lithium on the nitrogen; and 4.) the radical formed from removal of the hydrogen on the nitrogen. The first two, the neutral acid and the anionic conjugate base, are for evaluating the acidity reaction, the lithiated species is a model for the anion/counterion species present in solvents such as tetrahydrofuran, and the radical is part of the thermochemical cycle for evaluating gas phase acidities.

Experimentally the dimethylamine was found to be 6.4 kcal/mol less acidic than diisopropylamine.³⁴ However, the acidity of the parent disilylamine has not been determined. It was assumed that the acidity of $(H_3Si)_2NH$, disilylamine, would be a reasonable approximation for the acidity of hexamethyldisilazane, at least within several kcal/mol. It has been shown⁴⁰ that alkyl for hydrogen replacement in H_3SiOH has little effect on the gas phase acidity. This can be rationalized in that methyl versus hydrogen substitution on a sp^3 carbon results in a considerable increase in acidity for a variety of gas phase acids, due to polarizability effects. The corresponding replacement on silicon results in both the expected polarizability effect (anion stabilizing), plus an offsetting polar effect (carbon more electronegative than silicon) not present in the alkyl

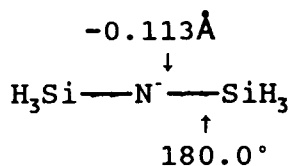
case. Therefore, methyl-for-hydrogen replacement in silanols and silylamines should have a much smaller negative ion stabilizing effect than in alcohols and alkylamines.

Upon deprotonation of the dimethylamine in Table 3 (page 34), the C-N bond length decreases very little by 0.008Å (0.039Å with polarization functions) and the C-N-C bond angle only decreases by 0.3° (0.2° with polarization functions) (9).



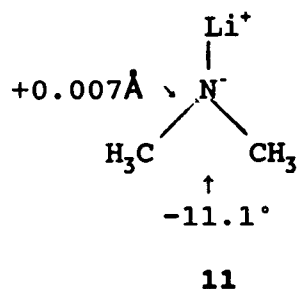
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However upon deprotonation of the disilylamine in Table 4 (page 35), the Si-N bond length shortens drastically by 0.113Å (0.111Å with polarization functions) and the Si-N-Si angle becomes linear to be 180.0°. The Si-N-Si bond angle increases by about 50.2° (49.0° with polarization functions) (10).

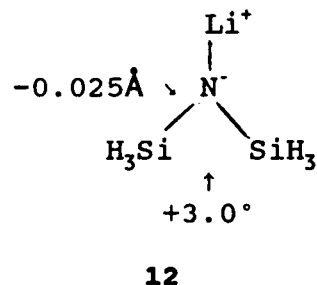


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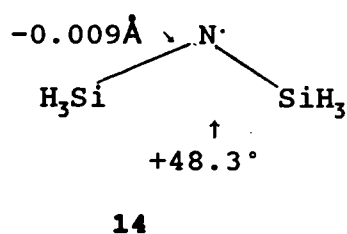
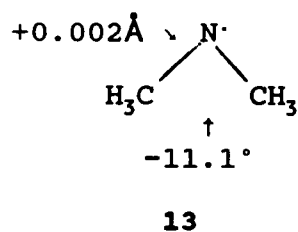
As for the lithiated dimethylamine (Table 3 (page 34)), the C-N bond length increases very little by 0.007Å and the C-N-C bond angle decreases by 11.1° in comparison to the neutral molecule (11).



For the lithiated disilylamide (Table 4 (page 35)), the Si-N bond length decreases very little in comparison to the anionic case by 0.025Å and the Si-N-Si bond angle increases only by 3.0° (12).

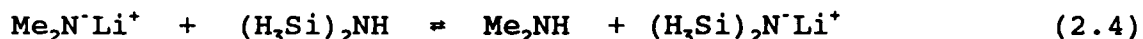


For the radical case, both the dimethylamine and the disilylamine's bond lengths do not change (the C-N bond length increases by 0.002Å and the Si-N bond length decreases by 0.009Å) as much as on hydrogen loss. However, there are differences in the bond angles. The C-N-C bond angle in the dimethylamine (13) decreases by 11.1°, while the Si-N-Si bond angle in the disilylamine (14) increases by as much as the anionic case by 48.3° to be near linear.



From the above calculations between the neutral and the anionic species, the dimethylamine essentially remains pyramidal even upon loss of the hydrogen. Also, the bond lengths do not change to as great an extent as in the disilylamine anion. The disilylamine Si-N bond length shortens and its Si-N-Si bond angle becomes essentially linear upon loss of the hydrogen. Furthermore, the above results were also seen in another theoretical calculation using Gaussian 88 with d-orbital parameters.⁴¹ The results were an increase of 0.0154Å for the difference between the neutral molecule of dimethylamine (C-N bond length) and the anionic form, and an increase of 0.1050Å for the difference between the neutral and the anion of the disilylamine (Si-N bond length).

Also from the calculations (6-31+G) in Tables 3 (page 34) and 4 (page 35), the reactions of disilylamine and dimethylamine can be compared in an isodesmic equilibrium (2.3).



Disilylamine is calculated (6-31+G) to be 44 kcal/mol stronger as an acid than the dimethylamine. The experimental value for hexamethyldisilazane was 39.3 kcal/mol more acidic. The isodesmic comparison for the lithiated species (2.4) and their conjugate acids indicates

that the disilylamine is 16.0 kcal/mol more acidic than the dimethylamine, while Arnett and Moe found hexamethyldisilazane to be 17 kcal/mol more acidic in 90% hexane/10% ether solvent.²⁴ In equation (2.5), the N-H homolytic bond strength in dimethylamine is calculated to be 17.8 kcal/mol weaker than disilylamine. There is an experimental value for $DH^\circ(\text{Me}_2\text{N-H})$ of 91.5 ± 2.0 kcal/mol⁴², but only a lower limit of >106.3 kcal/mol for the N-H in hexamethyldisilazane.⁴³ This gives the experimental bond strength difference of >14.8 kcal/mol, which is near the calculated value.

MNDO and AM1 semi-empirical calculations were performed including the calculations of the cyclic disilazane, Table 6 (page 42) and Table 7 (page 43). MNDO has in the past predicted some basicities incorrectly for neutral nitrogen bases. Furthermore, MNDO does not give good results for an anion in which the charge is concentrated on a single atom.⁴⁵ The AM1 calculations, however, have been shown in the past to be closer in numerical value to the experimental acidity value of dimethylamine. Therefore, the AM1 calculation was used to determine the approximate acidity of the cyclic disilazane.

According to the MNDO calculations, the changes in the Si-N-Si bond angle and the Si-N bond length are similar to those from the ab initio calculations for the disilylamine upon deprotonation. As for the hexamethyldisilazane, its

Table 6. MNDO energetics for R₂NY species

AH:	Me ₂ NH	1 ^h	TMP ^a	2 ^b	HMDS ^d	3 ^c
$\Delta H_f(\text{AH})$	-6.6	-20.4	-15.3	-40.1	-123.6	-121.5
exp: ⁴⁴	-4.4	-34.4			-122.8	
$\Delta H_f(\text{A}^-)$	8.5	-9.2	-6.6	-27.5	-112.0	95.2
exp: ⁴⁴	26.4	-9.9			-113.9	
$\Delta H_f(\text{A}^\cdot)$	25.0	6.5	9.7	11.6	-75.4	-66.2
$\Delta H_f\text{ALi}$	-4.9	-2.7	-17.7	-39.9	-125.7	-114.0
ΔH_{acid}	380.8	377.0	374.7	378.3	377.3	392.0
exp: ³⁴	396.5	390.2			356.8	367.3
BDE N-H	83.7	78.6	77.1	103.8	100.3	107.4
exp: ⁴²	91.5				(>106)	
EA _{ad} eV	0.72	0.66	0.71	1.69	1.58	1.26
$\Delta(\text{X-N})^e$	0.061	-0.056	-0.053	-0.130	-0.135	-0.068
$\Delta(\text{Z})^f$	0.3	0.0	-2.0	49.5 ^g	43.0 ^g	-1.5

a. 2,2,6,6-Tetramethylpiperidine

b. Disilylamine

c. 1,1,3,3-Tetramethyl-1,3-disila-2-aza-cyclopentane

d. Hexamethyldisilazane

e. Change in C-N or Si-N bond length on proton removal, Å.

f. Change in C-N-C or Si-N-Si bond angle on proton removal, degrees.

g. Anion Si-N-Si geometry linear to within 0.5°.

h. Diisopropylamine

Table 7. AM1 energetics for R_2NY^a

AH:	Me ₂ NH	iPr ₂ NH	1 ^g	HMDS ^h	2 ⁱ
$\Delta H_f(\text{AH})$	-5.6	-25.6	-27.4	-117.2	-110.1
exp: ^a	-4.4	-34.4		-122.8	
$\Delta H_f(\text{A}^-)$	22.4	1.8	-30.2	-118.4	-91.7
exp: ^a	36.4	-9.9		-113.9	
$\Delta H_f(\text{A}^\cdot)$	26.4	8.7	19.6	-69.2	-47.2
ΔH_{acid}	393.7	393.1	362.9	364.5	384.1
exp: ^b	396.5	390.2		356.8	367.3
BDE N-H	84.1	86.4	99.1	100.1	115.0
exp: ^c	91.5			(>106)	
EA _{ad} eV	0.17	0.30	2.16	2.13	1.93
$\Delta(\text{X-N})^d$	-0.047	-0.048	-0.114	-0.123	-0.084
$\Delta(\text{X-N-X})^e$	1.3	0.3	48.5 ^f	41.1 ^f	3.6

a. Ref. 44

b. Ref. 34

c. Ref. 42

d. Change in C-N or Si-N bond length on proton removal, Å.

e. Change in C-N-C or Si-N-Si bond angle on proton removal, degrees.

f. Anion Si-N-Si geometry linear to within 0.5°.

g. Disilylamine.

h. Hexamethyldisilazane.

i. 1,1,3,3-Tetramethyl-1,3-disila-2-aza cyclopentane.

bond angle and bond length changes are close to the disilylamine's. The Si-N bond length shortens by as much as disilazane ($0.130\text{\AA}$ vs $0.135\text{\AA}$) and the Si-N-Si bond angle increases similarly (49.5° vs 43.0°) to a near linear structure. The changes in the geometries about the nitrogen in the cyclic amines (2,2,6,6-tetramethylpiperidine {TMP} and 1,1,3,3-tetramethyl-1,3-disila-2-aza-cyclopentane), are also similar. The TMP C-N bond length shortens by $0.053\text{\AA}$ and the cyclic disilazane Si-N bond length shortens by $0.068\text{\AA}$. Likewise, TMP C-N-C bond angle decreases by 2.0° and the cyclic disilazane Si-N-Si bond angle decreases by 1.5° . This implies that p-d π bonding is a minor contributor to the cyclic disilazane acidity, since this constrained geometry would not allow for adequate p-d orbital overlap. The geometry change of the acyclic disilazane might be due to rehybridization at the nitrogen, a polarizability effect or a polar effect.

As for the AM1 method, there are differences between the calculated and the experimental results. For the cyclic disilazane, the AM1 method has the S-N-Si bond angle increasing by 3.6° , whereas the MNDO method has the bond angle decreasing by 1.5° upon loss of the hydrogen. However, note that the differences in the bond length and the bond angle for the hexamethyldisilazane are not much different than in the MNDO method.

Dimethylamine and TMP have similar calculated acidities

as shown in the MNDO calculations. However, the calculated acidities of the acyclic and cyclic disilazane are not similar to each other. This implies that the ability to become linear at the nitrogen center is critical to the strengthening in acidity of the acyclic disilazane. The strengthening in acidity of the acyclic disilazane cannot be due to a polarizability or a polar effect, since neither is expected to cause a geometry change. The strengthening in acidity can only be due to either a p-d π resonance or rehybridization effect in which the negative charge would be delocalized between the R_3Si^- group and the nitrogen.

When looking at the Mulliken charges reported by Gaussian 90, the negative charge remained on the nitrogen in the disilylamine. There was no change in the charge on the H_3Si^- groups. This supports the idea that p-d π bonding is not the reason for the shortening of the Si-N bond and the increase in acidity. It also implies that a polar effect is not the reason as well or the negative charge on the nitrogen would have been withdrawn by the $(CH_3)_3Si^-$ group.

The only other explanation of the increase in acidity of the hexamethyldisilazane is a rehybridization effect. Having the electrons occupying a degenerate HOMO level, where they are spread out, the negative charge can remain on the nitrogen just as the Mulliken charges reported by Gaussian 90. Also, shortening of the Si-N bond length and change in geometry are the results of a rehybridization

effect.

Applying this reasoning to the cyclic disilazane, its rigid geometry cannot adopt a linear structure upon deprotonation of the nitrogen without a great increase in ring strain. In fact, from the theoretical calculations, the Si-N-Si bond angle did not change as much as in the acyclic disilazane. The nitrogen remains essentially sp^2 hybridized. This would cause the cyclic disilazane to be less acidic than its acyclic counterpart. This was found experimentally to be true. From our experimental results, the cyclic disilazide anion would be able to deprotonate ketones in the gas phase. Therefore, the acidity differences between non-cyclic disilylamines and the dialkylamines must be due to the rehybridization change at the nitrogen center.

For the future, there should be calorimetric studies performed on the cyclic and acyclic disilazanes using different counterions to determine if there are any acidity differences in the solution phase. Furthermore, x-ray studies should be performed on both with different counterions to see if there are any changes in the Si-N bond length and the Si-N-Si bond angle.

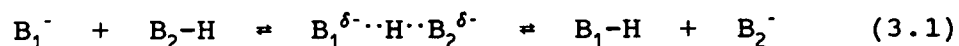
CHAPTER 3

GAS PHASE ACIDITIES OF LONG CHAIN ALCOHOLS

A. Introduction

Mass spectrometry has been useful for obtaining structural information about reactants in gas phase ion-molecule reactions. The information can be used to explain how, for example, intrinsic structure affects the acidities and the basicities of the reactants. For instance, it was shown by Gäumann and co-workers⁴⁶ that there was a constant strengthening in acidity of the aliphatic primary alcohols up to 1-heptanol with each increase of a methylene group. Harrison and Haas⁴⁷, upon re-examining the alcohols' acidities, found a monotonic strengthening, but not a linear one, in acidity of the primary alcohols past 1-pentanol.

These acidities were not measured by the usual equilibrium method, but rather by the kinetic method of Cooks and co-workers.⁴⁸ In the kinetic method, one of the two neutral species to be studied is ionized and then that ion plus the other neutral is allowed to form a dimer ion. The dimer ion will then undergo dissociation, when excess energy is present. How the dimer ion fragments reflects which species is more acidic as shown in the following equation (3.1):



where B_1^- and B_2^- are the species being studied. The acidities of the two species (B_1H and B_2H) are determined by equating the ratio of the ion signals' intensities with the ratio of the average relative rate constants as shown in equation (3.2):⁴⁸

$$\ln(I_{B_2}/I_{B_1}) = \ln(k_2/k_1) = -\Delta(\Delta G)/RT \quad (3.2)$$

I_{B_2} and I_{B_1} are the ion intensities of B_2H and B_1H , k_1 and k_2 are the average relative rate constants for the two species being studied, $\Delta(\Delta G)$ represents the difference in the free energies of acidity, R is the gas constant, and T is the "effective" temperature in Kelvin. The ratio of the average relative rate constants is dependent on the ratio of the vibrational frequencies of the two species being studied (ν_2/ν_1). The vibrational frequencies represent the hydrogen bonds to B_1 and B_2 in equation (3.1). However, the actual vibrational frequencies are not known. It is assumed the vibrational frequencies of the hydrogen bonds are equal ($\nu_1=\nu_2$).⁴⁸ Consequently, the vibrational frequencies cancel, and do not appear in equation (3.2). Furthermore, the average relative rate constants depend on the "effective" temperature, the internal temperature of the dimer population.⁴⁸ This temperature does not represent the thermodynamic temperature of the dimer population, but just a proportionality constant between the rates and the thermodynamic ratio. This means the "effective" temperature is the estimated temperature of the dissociating dimer ion.

Therefore, entropic and enthalpic effects cannot be exactly determined using this method.

Several researchers have determined the acidities of various branched and primary alcohols by using the kinetic method.^{46,47} It was shown by Gäumann and co-workers⁴⁶, while using a high energy CID (Collision-Induced Dissociation) method, that there was a strengthening in acidity of the alcohols with increasing carbon length. This was attributed to polarizability effects of the alkyl groups. Also, a methyl substitution at the alpha position of the anion would strengthen the alcohol's acidity. The greatest effect was for the primary alcohols (3.1 kcal/mol per methyl for alpha hydrogen substitution) and fell rapidly in magnitude for the secondary (1.8 kcal/mol) and the tertiary alcohols (1.1 kcal/mol).⁴⁶ The effect was less for methyl substitution at the beta position, but was nearly constant going from a primary to secondary to tertiary alcohols (1.8 kcal/mol, 1.7 kcal/mol, and 1.8 kcal/mol respectively).⁴⁶ The effect was even less for methyl substitution at the gamma position. As the length of the carbon chain increases, the incremental strengthening of acidity decreased slowly and reached a near constant $\Delta(\Delta G_{\text{acid}}) = 0.5$ kcal/mol beyond 1-heptanol.⁴⁶ A similar trend was also shown by the results of Harrison and Haas⁴⁷ using a low energy CID method.

A leveling off in $\Delta(\Delta G)$ value with increasing carbon length has been observed in the basicity of the primary

alkylamines. The primary alkylamines showed a constant increment in basicity of 0.2 kcal/mol ($\Delta(\Delta G_{\text{base}})$) beyond butylamine.⁴⁹ This was interpreted as a coiling effect (15).



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Both Gäumann and Harrison agreed that the long chain alcohols' (carbon length past five) acidities were the result of a coiling effect as well.^{46,47} However, when comparing Gäumann's high energy CID and Harrison's low energy CID results as shown in Figure 6 (page 51), the long chain alcohols are removed from the linear trend of the other alcohols.

Another investigator, Catalàn,⁵⁰ disagreed with the idea that a coiling effect was strengthening the acidities of the long chain alcohols. He did a literature comparison of the acidities of the long chain alcohols, as determined by the kinetic method, to their ionization potentials. He too noticed a strengthening in acidity from 1-pentanol to 1-nonanol. He, however, indicated that an important contribution to the strengthening in acidity was due to ionic intramolecular hydrogen bonding. He supported his argument by comparing the literature basicity measurements of the primary alkylamines to the acidities of the primary alcohols. He showed there was a linear correlation of the primary alkylamines' basicities with their ionization

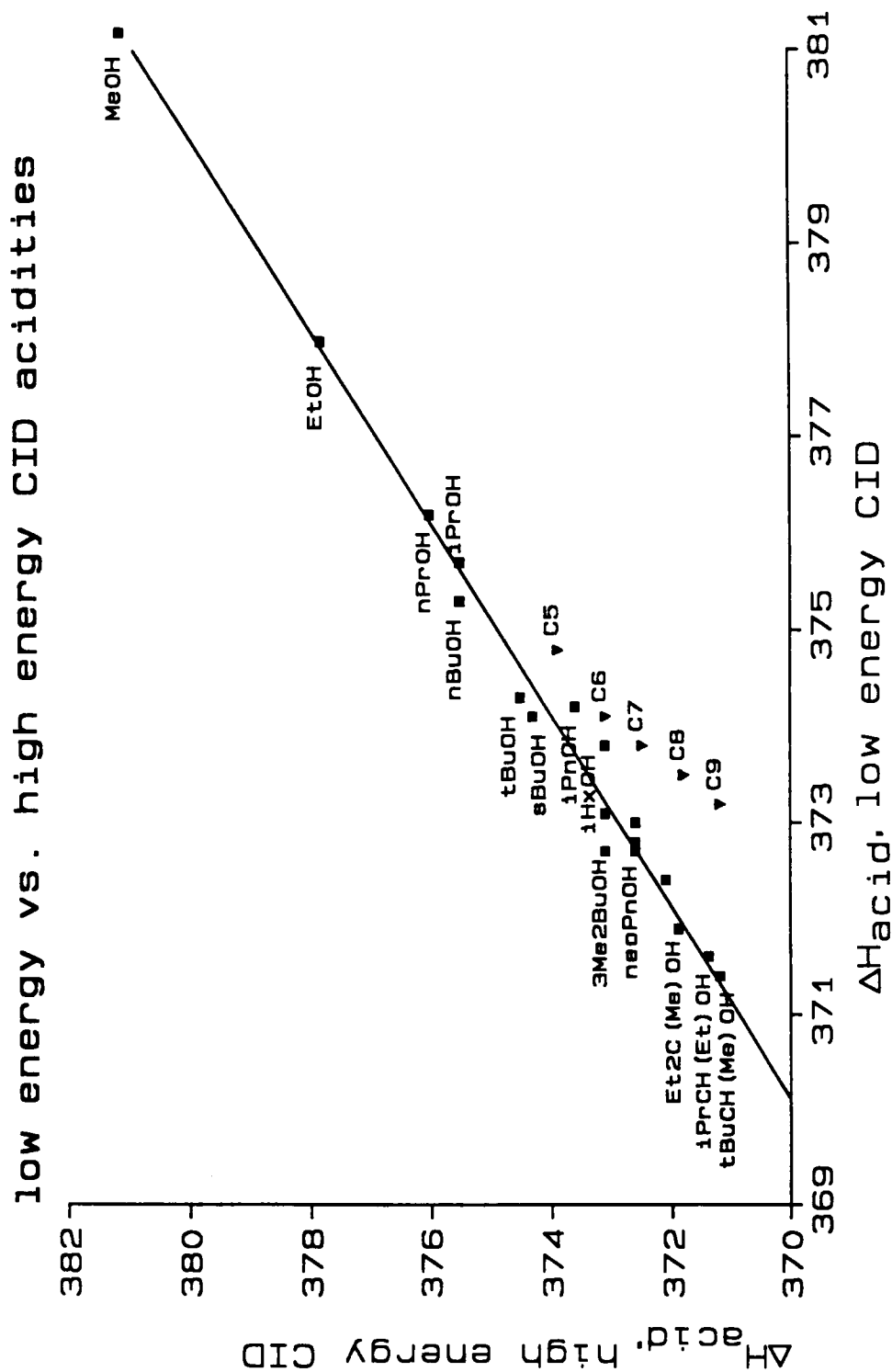
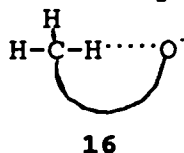


Figure 6. A plot showing various alcohols' acidities using a high energy and a low energy CID method.

potentials, which means the primary alkylamines are not coiling with increasing carbon length. The long chain alkoxides, however, did not show a linear relationship with their ionization potentials. Therefore, the strengthening in acidity of the long chain alcohols, he argued, was due to ionic intramolecular hydrogen bonding. An ionic intramolecular hydrogen bond, as he discussed, is the interaction of the end-methyl group's hydrogens complexing with the oxygen anion to form a cyclic structure (16).



This type of interaction ($\text{C}-\text{H} \cdots \text{O}^-$) has been shown by Meot-Ner and co-worker⁵¹ to stabilize a structure by ≈ 6 and 4 kcal/mol. This type of stability can strengthen the long chain alcohols' acidities. In contrast, an ammonium ion cannot accept a hydrogen from the end-methyl group, since there are no lone-pair electrons available on the nitrogen. This could explain why there was linear correlation between the primary alkylamines' basicities and their ionization potentials.

It is possible for longer carbon chain lengths in a homologous functional group series to form cyclic structures, via intramolecular hydrogen bonds. It has been shown with diols that cyclization of the structures would affect their acidities.⁵² The diols showed a strengthening in acidity by $\Delta G_{\text{acid}} = 8-13$ kcal/mol compared to the

corresponding $\text{Me}(\text{CH}_2)_n\text{OH}$ alcohols.⁵² The strengthening in acidity was attributed to the formation of intramolecular hydrogen bonds in the anions of the diols. Compounds that can form six- and seven-member rings, such as 1,3-propanediol and 1,4-butanediol, would have an intramolecular hydrogen bond strength of 12.7 kcal/mol in ΔG , whereas an intermolecular hydrogen bond is about 21 kcal/mol in ΔG for $\text{CH}_3\text{O}^-\cdots\text{H}-\text{OCH}_3$.⁵³ An intramolecular hydrogen bond strength would be less than an intermolecular bond, because some cyclic structures (less than a seven-member ring) would have strained geometries if the O-H-O bond angle was linear, which would weaken the acidity.

To resolve the acidity differences of the long chain alcohols in comparison to the other alcohols, we carried out equilibrium measurements of the gas phase acidities of many of the branched and primary alcohols using the ICR mass spectrometer. The results from using the equilibrium method should help explain the reason for the strengthening in acidity of the long chain alcohols. If the long chain alcohols are coiling, it should be revealed using this method. Under CID conditions, the high "effective" temperature might inhibit the coiling of the alkoxides. The high "effective" temperature places more internal energy into the dimer ion. So, upon dissociation, the anions would not favor the coiled species. The anions would prefer the linear structure. Therefore, the acidity measurements

attained from the kinetic method would only represent the linear alkoxides.

B. Experimental

1. Methods

The Ion Cyclotron Resonance (ICR) mass spectrometer was used to generate and detect anions as described in Chapter 1. The quenched mode was used when carrying out the acidity measurements. The grid length was set at 100 msec. The delay time was varied from 200 up to 1200 milliseconds, while scanning the masses 30 through 300 amu. The radio frequency amplitude, trapping voltage, and the filament current were set to give maximum signals. The electron energy was set between 0.00 and 0.23 volts at the above conditions. The instrument was run at 25°C, as measured outside of the analyzer manifold. Methoxide was generated by a methanol and isoamyl nitrite mixture.⁵⁴ The methoxide formed would then deprotonate one of the neutral molecules. The ion gauge pressure of methoxide was maintained about 7×10^{-7} torr. The combination of the two equilibrating acids pressures were 2×10^{-6} to 6×10^{-6} torr total pressure. The ion gauge was degassed for five minutes then allowed to cool for twenty minutes before admitting the compounds into the instrument, so as to remove any residue from the ion gauge.

2. Compounds

1-Hexanol, 1-heptanol, 1-octanol, 1-nonanol, acetonitrile, isobutyronitrile, propionitrile, dimethylsulfoxide, 2-methoxyethanol, neopentanol, 2-methyl-3-pentanol, 2-methyl-2-hexanol, 3,3-dimethylbutanol, and isoamyl nitrite were purchased from Aldrich. Tertiary-butyl alcohol and 1-butanol were purchased from Mallinckrodt. 1-Pentanol was purchased from Baker. 2-Propanol was purchased from Fisher Scientific. Another sample of 1-hexanol came from a noncommercial bottle. The commercial and the noncommercial 1-hexanol were distilled and further purified by preparatory gas chromatography, due to acetone impurities. 1-Pentanol, 2-methoxyethanol, and isobutyronitrile were distilled prior to use in the ICR.

C. Results and Discussion

The equilibrium method was used to determine the acidities of the long chain and the branched alcohols. The branched alcohols were measured to determine if their acidity measurements fell on the linear trend along with the short chain alcohols' acidity measurements previously done by others.^{46,47} The results from this investigation of the branched and the long chain alcohols were used to calculate the equilibrium constant, K_{eq} , which was then used to express the acidities of the alcohols as ΔG_{acid} , see Chapter

2.

Table 8 (page 57) and Figure 7 (ladder) (page 58) show the results when the carbon acids were equilibrated with the alcohols. The branched alcohols' results in Table 8, when equilibrated with acetonitrile, were similar to the results attained by Gäumann and co-workers using a high energy CID method.⁴⁶ Gäumann's measured acidities were as follow: 3,3-dimethyl butanol has $\Delta G_{\text{acid}} = 365.0$ kcal/mol, 2-methyl-2-hexanol has $\Delta G_{\text{acid}} = 364.3$ kcal/mol, and 2-methyl-3-pentanol has $\Delta G_{\text{acid}} = 364.2$ kcal/mol.⁴⁶

As shown in both Table 8 (page 57) and Figure 7 (page 58), there is not a monotonic trend among the long chain alcohols' acidities. The results attained at 25°C show 1-hexanol more acidic than 1-heptanol, the occurrence of the non-monotonic trend. However, the results attained by equilibrating the alcohols with dimethyl sulfoxide (DMSO) in Table 8 (page 57) cannot be trusted, since DMSO is known to be hygroscopic. Any trace of water will skew the gas phase acidity measurement. Furthermore, our acidity measurements for the alcohols at 72°C are not reported here due to instrumental problems with measuring the "hot" temperatures.

It was then thought this non-monotonic trend was possibly wrong due to pressure problems, so the long chain alcohols were equilibrated with each other. As shown in both Table 8 (page 57) and Figure 7 (page 58), the relative acidity measurements are the same as those attained when the

Table 8. The acidity of the long alkyl chain alcohols using the equilibrium method, $\Delta G_{\text{acid}}^{\text{a}}$.

Alcohols	$\text{CH}_3\text{CH}_2\text{CN}^{34}$	DMSO^{34}	iPrCN^{34}	MeCN^{34}
$\Delta G^{\circ}_{\text{acid}}$	367.4	366.4	367.9	365.2
1-Pentanol	367.6 (35°C)	-----	367.5 (26°C)	-----
1-Hexanol	367.4 (33°C)	-----	367.5 (26°C)	-----
1-Heptanol	368.1 (33°C)	366.7 (27°C)	368.0 (27°C)	-----
1-Octanol	367.7 (33°C)	365.5 (23°C)	-----	-----
1-Nonanol	368.0 (32°C)	366.7 (21°C)	368.0 (27°C)	-----
2-Methyl- 3-pentanol	-----	-----	-----	364.8 (30°C)
2-Methyl- 2-hexanol	-----	-----	-----	365.1 (28°C)
3,3-Dimethyl butanol	-----	-----	-----	365.0 (33°C)

a. Uncertainty of ± 0.2 kcal/mol.

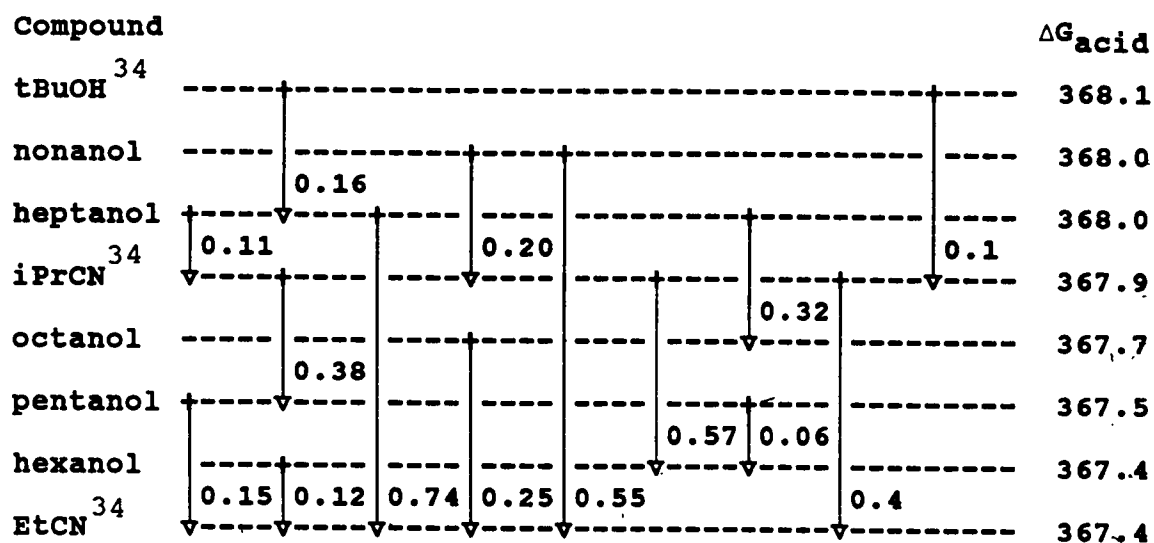


Figure 7. Acidity ladder generated from the equilibrium method at 25°C.

long chain alcohols were equilibrated with the carbon acids at 25°C.

This non-monotonic trend among the long chain alcohols' acidities could not be due to the alkoxides remaining a linear structure. The acidities would have decreased at a linear rate with increasing carbon length. Therefore, there must be something else that affects the acidities of the long chain alcohols and causes this non-monotonic trend. In order to determine the reason, a comparison of the equilibrium results with previous results from the literature was done.

A plot of the ionization potentials of these alcohols performed by Peel and Willett⁵⁵ against our results at 25°C, shown in Figure 8 (page 60), shows a linear trend up to C₄. The monotonic trend, however, is lost after C₆. It should be noted that the researchers who measured the ionization potentials of the alcohols, did not measure the ionization potentials of 1-octanol and 1-nonanol. Catalàn estimated those two alcohols' ionization potentials by performing an extrapolation of the ionization potentials^{55,57} against the Taft substituent parameters⁵⁶ of the alcohols, methanol to 1-heptanol. This is not a correct way to determine 1-octanol and 1-nonanol's ionization potentials. Too much error is involved when using the extrapolation method. The only appropriate way would be determine their ionization potentials experimentally.

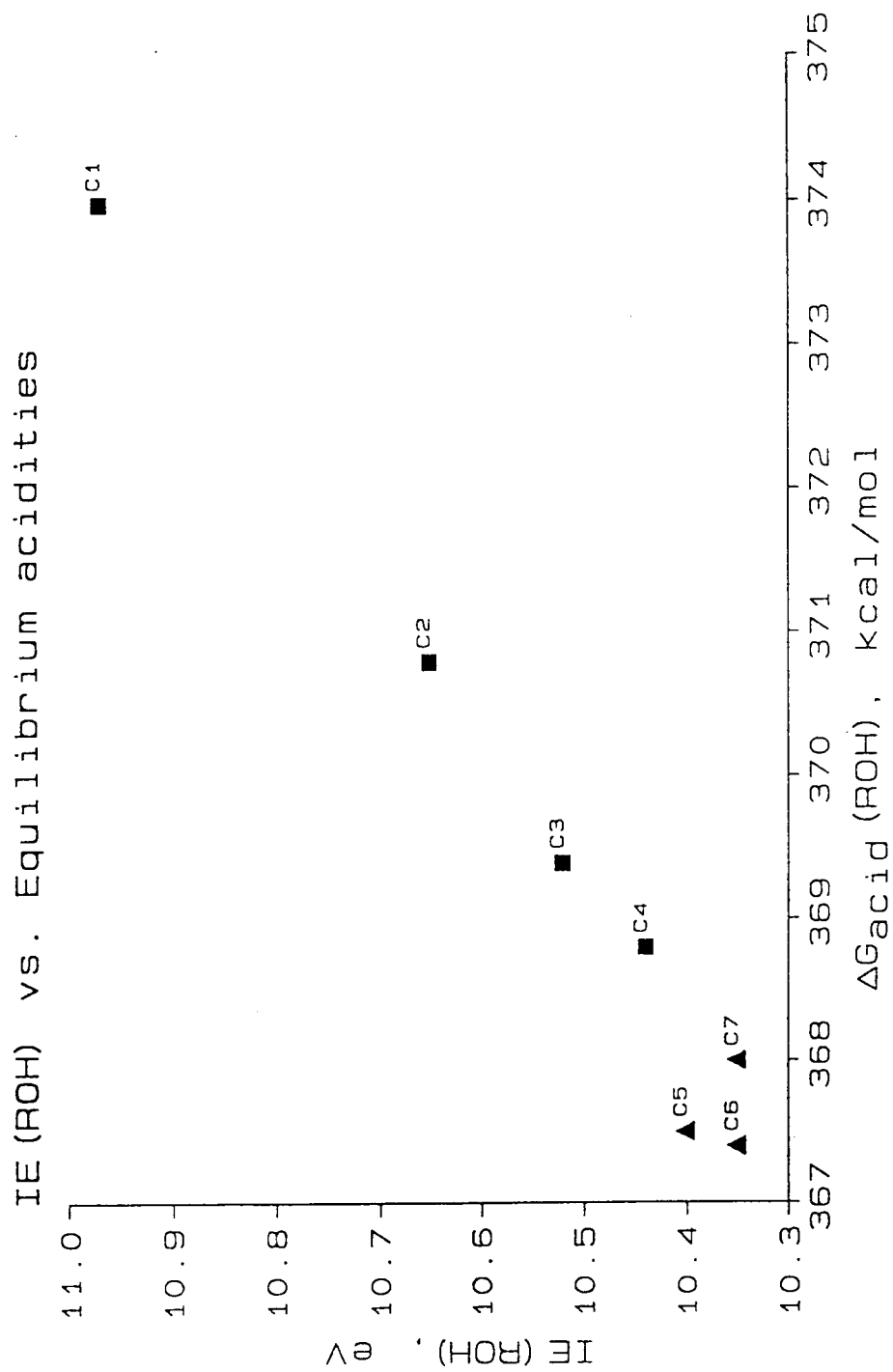


Figure 8. A plot of the primary alcohols' ionization potentials against their equilibrium acidities.

When the equilibrium results are compared to the results of Harrison⁴⁷ as shown in Figure 9 (page 62), there is a linear trend up to 1-butanol. Also, note that the branched alcohols are included in the linear trend. However, the longer chain alcohols deviate from the linear trend. 1-Pentanol and 1-hexanol are more strongly acidic by the equilibrium method than by the low energy CID method, relative to the smaller alcohols. Also, 1-heptanol, 1-octanol, and 1-nonanol are more weakly acidic by the equilibrium method than by the low energy CID method. These methods' dependent trends are indicating that the long chain alkoxides are not remaining linear. This might imply that the long chain alcohols are coiling. The equilibrium method would be more sensitive to a coiling effect, since the anions formed are in equilibrium with their neutral species. The acidity measurements are reflective of the free isolated anions. Because the neutral and the anionic species are in equilibrium with each other, the chances for the alkoxides to coil are increased in comparison to using the kinetic method. In the kinetic method, the anions of the neutral species are tied up the majority of the time as a dimer ion. At the point the dimer ion dissociates, the alkoxides might be existing in an equilibrium between linear and coiled structures. Therefore, the acidity measurements in the kinetic method would not represent either a linear or coiled structure of the alkoxides, but a mixture of the two.

low energy CID vs. equilibrium acidities

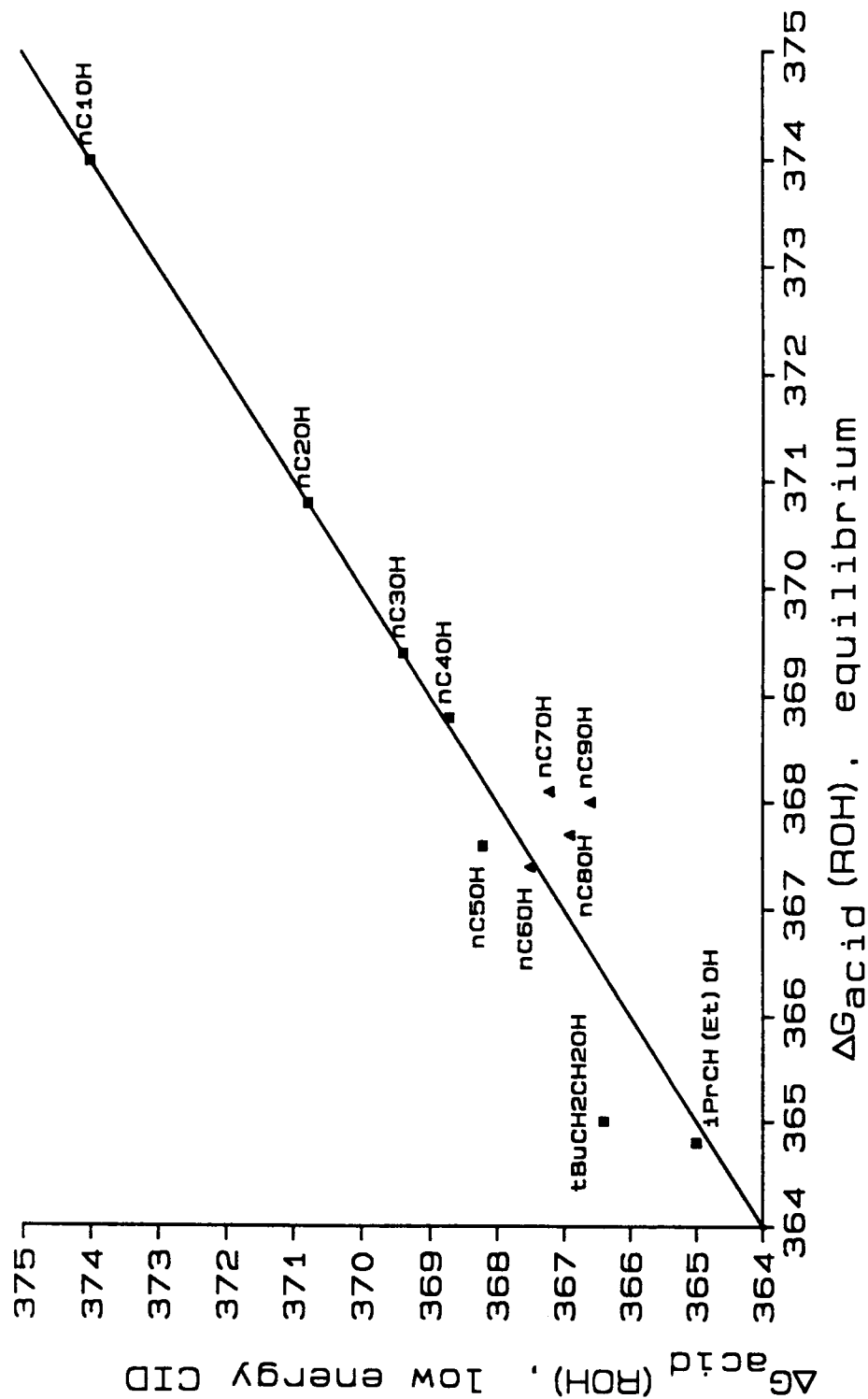


Figure 9. A plot comparing the alcohols' acidities using a low energy CID method to the equilibrium method.

Furthermore, the non-monotonic trend is still present when comparing the high energy CID results to the equilibrium results, as shown in Figure 10 (page 64). Here, the "effective" temperature is much higher than in the low energy CID. Note that the 1-heptanol is still removed from the trend among the long chain alcohols as in Figures 8 (page 60) and 9 (page 62).

The observation that the kinetic method does not show the irregularity in acidities of the long chain alcohols is due to how the average relative rate constants are calculated. The average relative rate constants attained by using the kinetic method are only an estimation. There is an assumption taken when calculating the measured acidities. It is assumed the vibrational frequencies of the hydrogen bonds in the dimer ion, ν_1 and ν_2 , are equal.⁴⁸ This assumption will work for molecules that remain linear upon dissociation from the dimer ion. This assumption will not work, however, when one of the molecules in the dimer ion is capable of coiling as in the long chain alcohols' case. A molecule that is capable of coiling will have a different ΔS value than a linear molecule, which will affect the vibrational frequencies in the dimer ion by an unknown amount. Consequently, because of the assumption made ($\nu_1 = \nu_2$), the ΔG_{acid} will not reflect the vibrational frequencies differences ($\nu_1 \neq \nu_2$).⁴⁸ If the vibrational frequencies had been included when calculating the average

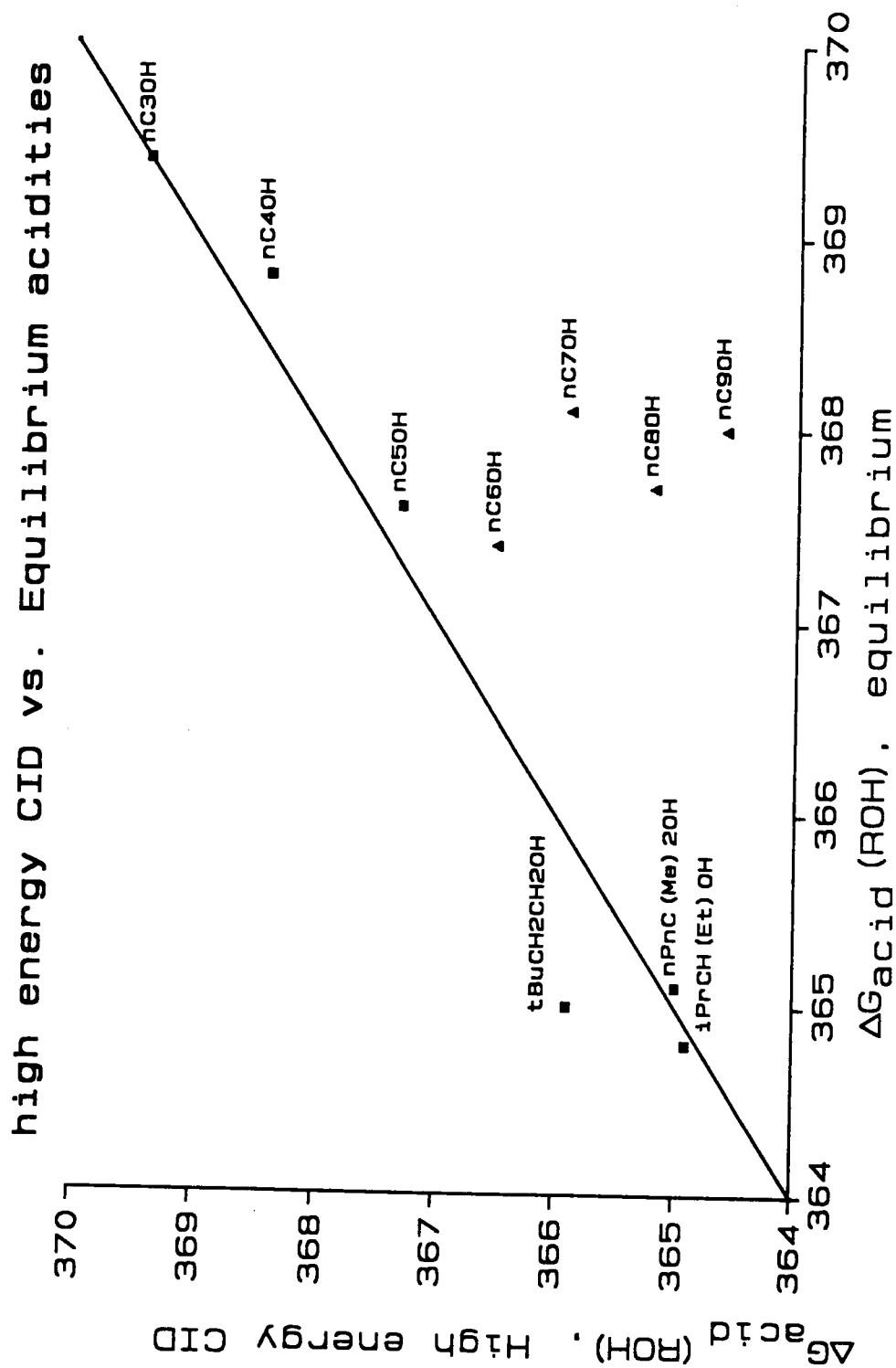


Figure 10. A plot comparing the alcohols' acidities using a high energy CID method to the equilibrium method.

relative rate constants, the acidity measurements would have been similar to the equilibrium method's.

The irregularity in the long chain alcohols' acidities found in our results might be due to a geometry strain when the alkoxides are cyclizing to form intramolecular hydrogen bonds. When the alkoxides are in the cyclic structures, the $\text{-CH}_3\cdots\text{O}$ bond could be strained when reaching a certain carbon length. For our case, 1-heptanol might be a long enough carbon chain to form the cyclic structure, but the geometry of the molecule could be strained. This could explain why 1-heptanol was less acidic than 1-octanol. After 1-heptanol, the carbon chain length is long enough that once the alkoxide is cyclized, the cyclic structure is not as strained and the acidity will reflect it. In fact according to the diol study, there was an irregular trend in acidity due to a geometry strain of the cyclic structures. The acidity trend of the diols was as follow: 1,4-butanediol > 1,5-pentanediol > 1,3-propanediol.⁵² This could explain why there was an strengthening in acidity after 1-heptanol.

Upon careful study of the long chain alcohols' acidities, the non-monotonic trend is similar to the trend found in Catalàn's literature study of the primary alcohols. He failed to notice this non-monotonic trend past 1-pentanol. This could indicate that the long chain alcohols are cyclizing. Upon deprotonation, the terminal methyl group can stabilize the oxygen anion by its polarizability

effect; thus, strengthening the acidity. If this is occurring in another homologous functional group series as well, the non-monotonic trend should also appear in longer carbon lengths. For example, if protonated primary alkylamines formed cyclic structures one would expect to observe a decrease in the basicities with increasing carbon length. The basicity of the alkylamines would show a deviation from the linear decrease in basicity of the alkylamines with increasing carbon chain length. However, Catalàn's literature study had shown a linear trend in the primary alkylamines' basicities. This indicates that the protonated primary alkylamines do not form cyclic structures, but remain linear. Therefore, it seems reasonable to believe this non-monotonic trend of the long chain alcohols' acidities are due to the alkoxides cyclizing and forming intramolecular hydrogen bonds. In order to determine if our results at 25°C are implying the alkoxides are cyclizing and forming intramolecular hydrogen bonds, the entropy effect must be explored.

The entropy value of the hydrogen-oxygen bond of an alcohol is $\Delta S = 22$ eu.³⁴ This is slightly less than what would be expected if the entropy was due to just the loss of the proton, 26.0 eu.³⁸ This is assuming the alkoxides are not cyclizing. By using this entropy value for the long chain alcohols at 25°C and $\Delta S = 25.5$ eu for propionitrile,³⁴ the long chain alcohols (1-pentanol and beyond) would be

more acidic than propionitrile. Furthermore, if it is assumed the long chain alkoxides are cyclizing, the long chain alcohols should still be more acidic than propionitrile. However, our results show that the long chain alcohols are less acidic than propionitrile.

In light of our results, it is difficult to predict which argument is correct: coiling effect or intramolecular hydrogen bonding. There is a need for further studies on the long chain alcohols, such as measuring the acidities at several consistent temperatures to determine accurately the experimental ΔS_{acid} and relative acidities. Also, theoretical calculation can be performed to see if either a coiling effect or intramolecular hydrogen bonding is in favor for the long chain alcohols to cyclize. Furthermore, a study of the long chain alcohols with an internal double bond could also help determine if the acidities are due to one of the two reasons by making the alkoxide too rigid to cyclize.

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