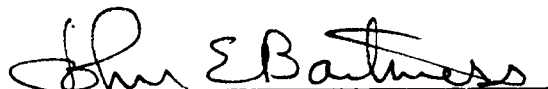


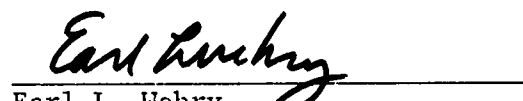
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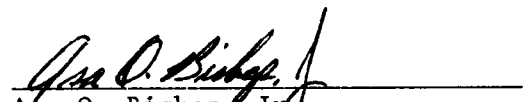
I am submitting herewith a dissertation written by Deborah Ann Thomas entitled "Ion Cyclotron Resonance Mass Spectrometry: 1) Gas-Phase Ion/Molecule Studies. 2) Comparison of Detection Modes for Ion Abundance Measurements." I have examined the final copy of this dissertation for form and content, and recommend that it be accepted for the degree of Doctor of Philosophy, with a major in Chemistry.

  
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Vice Provost  
and Dean of The Graduate School

ION CYCLOTRON RESONANCE MASS SPECTROMETRY: 1. GAS-PHASE ION/MOLECULE  
STUDIES 2. COMPARISON OF DETECTION MODES FOR ION ABUNDANCE  
MEASUREMENTS

A Dissertation  
Presented for the  
Doctor of Philosophy  
Degree  
The University of Tennessee, Knoxville

Deborah Ann Thomas

May 1991

### Dedication

To: Casey C. Grimm - my loving and supportive better half, who made sure I finished this dissertation.

To: Ann E. and John M. Thomas, Mildred B. Grigsby, Amy E. Thomas and Sarah L. Thomas - my loving family, for teaching me early the value of an education and for standing by me as I pursued one.

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## Abstract

Ion cyclotron resonance mass spectrometry (ICR-MS) is one of the most widely used techniques for studying gas-phase ion/molecule reactions. Physical organic properties such as basicity and acidity are often measured. This technique has been applied to two studies: measuring the gas-phase acidity of the conjugate acids of some frequently used bases in organic synthesis and determining the structures of the isomeric (M-H) anions of methyl nitrite and nitromethane. In addition a comparison is made between the different detection modes available to ICR-MS; slow passage (SP), rapid scan (RS) and Fourier transform (FT).

Choice of solvent and counter ion can influence the reaction in organic synthesis. To study the intrinsic properties of compounds, measurements are made in the gas-phase in the absence of these effects. The gas-phase acidities of hexamethyldisilazane, trimethylsilanol, triethylsilanol, diisopropylamine and 2,2,6,6-tetramethylpiperidine are reported here. The gas-phase reactivity of all the anions except hexamethyldisilazide parallel their reactivity in the solution phase. Hexamethyldisilazane is a much stronger acid than anticipated and semi-empirical and *ab initio* calculations suggest some possible rehybridization which may be controlled by the counter ion. Further work is being pursued in this area.

The isomeric (M-H) anions of methyl nitrite, nitromethane and formyl hydroxamate are studied here by means of MS/MS experiments,

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## Chapter 1

### Introduction

#### A. Introduction to Mass Spectrometry and Mass Spectrometers

Mass spectrometry is a microanalytical technique that resolves molecular ions and ionic fragments produced from an analyte based on their mass-to-charge ( $m/z$ ) ratio. The mass spectrum usually includes a molecular ion peak and characteristic fragment ion peaks that together make up a fingerprint of the analyte.<sup>1-4</sup> Mass spectrometry has found wide usage ranging from studies of the fundamentals of gas-phase ion chemistry to the analytical application of sequencing peptides. Although there are a variety of instruments, all mass spectrometers contain three major components; an ion source, a mass analyzer and a detector.<sup>1-4</sup> They are classified according to their construction. For example, there are magnetic sector instruments, quadrupole instruments, time-of-flight instruments and ion traps. As an introduction to the techniques employed for these studies, brief overviews of gas-phase ion/molecule reactions, sector instruments and ion cyclotron resonance mass spectrometers are given.

J. J. Thompson using his modified cathode ray tube reported the first gas-phase ion/molecule reaction. He observed an ion at mass-to-charge ( $m/z$ ) = 3 and speculated that it could be  $H_3^+$ .<sup>5</sup> In 1925, after studying the behavior of the ionization products of hydrogen at varying pressures, it was proven that  $H_3^+$  was being produced by the reaction of  $H^+$  with  $H_2$ .<sup>6</sup> Hogness and Harkness made the first in-depth

study of an ion/molecule system. In 1928, they studied the reactions of both the positive and negative ions of iodine observing both charge transfer from the atomic ions to the molecular ions and also the formation of  $I_3^+$  from the reaction of  $I_2^+$  and  $I_2$ .<sup>6</sup> During the next few decades, physicists measured ionization potentials, appearance potentials and bond dissociation energies utilizing mass spectrometry. The only reported ion/molecule reaction during this time was the observation that the hydronium ion is a product of the reaction between ionized water and neutral water. Renewed interest in the subject arose when  $CH_5^+$ , a pentavalent carbon compound, was observed by several researchers during the 1950's. Since that discovery, the field of gas-phase ion/molecule reaction studies has grown remarkably.<sup>6</sup>

Many classes of chemical reactions have been studied in the gas-phase, such as substitution and elimination reactions which are mechanistically comparable to solution phase reactions.<sup>7</sup> Gas-phase ion/molecule reaction studies allow the intrinsic behavior of the reactants to be studied without interfering solvent effects. Hence comparisons between gas-phase and solution phase observations often give insight into the driving forces of some chemical reactions. For example, one of the most startling early studies was Brauman and Blair's demonstration that for a series of simple alcohols the order of acidities in the gas-phase is the reverse of the order in solution phase because of solvent effects.<sup>7,8</sup>

The initial studies of gas-phase ion/molecule reactions were performed on conventional sector instruments, which were not always ideally suited to the studies undertaken which sometimes required high pressures and long reaction times. Therefore instrumental modifications such as addition of high-pressure ion sources were made; and new instruments such as ion cyclotron resonance mass spectrometers were developed.

In a sector instrument, the ion source, mass analyzer and detector are spatially separated. The purpose of an ion source is to vaporize and ionize the analyte of interest and introduce it into the mass analyzer.<sup>1-4</sup> There are several different types of ion sources, the most common of which is an electron ionization (EI) source. In this source the gaseous analyte is bombarded with a stream of electrons produced from a filament. Although the energy of the electrons can be controlled, typical operating conditions utilize 70 eV electrons to ensure sufficient energy to cause reproducible ionization. In the near collisions between an analyte molecule and an electron, excess energy is imparted to the analyte causing fragmentation. Some molecules do not give molecular ions under such energetic conditions.<sup>1-4</sup> To circumvent this problem, ion sources that produce analyte ions with lower internal energies have been developed. One such source is the chemical ionization (CI) source. The CI source employs a background gas that plays a role in the ionization process. The CI gas is ionized by electron ionization and then further ion/molecule reactions with the gaseous analyte produces analyte

cations. Alternatively, the CI gas can serve as a bath gas to thermalize the electrons so in the negative ion mode electron capture by the analyte can occur. In general CI usually produces a more intense molecular ion and fewer fragment ions than EI.<sup>1-4</sup> The need for both of these sources to have gaseous analytes greatly limits the number of compounds that can be studied, so alternative vaporization and ionization methods have been developed to deal with heavier, less volatile samples. Sample probes capable of quick, localized heating, like the direct chemical ionization probe or the direct insertion probe, can vaporize the sample inside an EI or CI source. New ionization methods include fast atom bombardment, secondary ion mass spectrometry, laser desorption and plasma desorption.<sup>1,4,9</sup>

The second major component of a sector mass spectrometer is the mass analyzer. Mass analyzers employ electric and/or magnetic fields to measure the different  $m/z$  ratios formed in the ion source.<sup>1-3,9</sup> In a magnetic field the flight path of an ion is deflected depending on its  $m/z$  ratio in a manner that is described by equation 1, where  $B$  =

$$m/z = B^2 r^2 / (2V) \quad (1)$$

magnetic field strength,  $r$  = radius of curvature, and  $V$  = accelerating voltage applied to the ion in the ion source. A magnetic sector disperses ions based on their momentum. Mass scanning is generally accomplished by scanning the magnetic field or the accelerating voltage.<sup>1-4</sup> To achieve double-focusing conditions and higher mass resolution, electrostatic analyzers are employed sequentially with magnetic sectors. This arrangement allows both momentum and energy

focusing to occur. Electrostatic analyzers employ electric potential differences between two parallel plates to focus ions of a given energy.<sup>1-3,9</sup>

The third major component of a sector mass spectrometer is the detector. Most sector instruments employ either a Faraday cup collector or an electron multiplier to measure the currents caused by ions striking the surface of the detector.<sup>1,3</sup>

There are several kinds of ion traps. One of the most common is the ion cyclotron resonance mass spectrometer (ICR-MS). The foundation of modern ICR-MS lies in the cyclotron principle developed by Lawrence and Livingston.<sup>10</sup> Stated most simply, the cyclotron principle describes the motion of ions in crossed electric and magnetic fields. (Eq. 2) An ion of a given  $m/z$  ratio will follow a circular orbit

$$\omega_c = zqB/m \quad (2)$$

perpendicular to the magnetic field, the frequency of which depends on the  $m/z$  ratio. This is the cyclotron frequency,  $\omega_c$ , of the ion.<sup>1,9,11-19</sup> Sommer, Thomas and Hipple were the first to apply the cyclotron principle to mass analysis in the development of the omegatron in 1950.<sup>4,11,20-23</sup> Ions are created in the center of the ion trap and excited to larger orbits by the application of an external radiofrequency (rf) field whose frequency matches the cyclotron frequency of the ion being studied. Ions with a large enough radius of orbit strike a fixed collector and generate a signal.<sup>4,18,11,20-23</sup> Nearly fifteen years later the first ICR-MS was produced by Wobschall.<sup>11,24</sup> It contained the drift cell which has an ion source

and a drift region where the external rf was applied.<sup>7,11,14,17,24</sup> The drift cell was necessary to avoid space charge effects caused by the ionizing electron beam.<sup>11-14,16-18</sup> Although drift cells are still used for some applications,<sup>25</sup> most ICR mass spectrometers now employ the trapped ion cell with pulsed grid modulation invented by McIver<sup>1,7,9,11,12,19,26-29</sup> (Fig. 1). This cell allows for trapping times longer than with a drift cell; and with the pulse sequence, time resolved studies can be more accurate. In this cell a series of accurately timed pulses generate the ions, eject selected ions if desired and detect the ions. This pulse sequence gives the temporal separation that is unique to ion traps<sup>9,7,11,12,24,26-29</sup> (Fig. 2).

Along with changes in the cell design there have been changes in the detector. The first detector was a physical one that measured ions striking a surface.<sup>4,7,11,16,20-23</sup> However, marginal oscillators which detect power absorption at a single frequency<sup>4,7,11-14,16-18,27-30</sup> were soon dominant, but this required scanning the magnetic field which was time consuming.<sup>4,15</sup> The development of the capacitance bridge detector was important in furthering ICR mass spectrometry. The capacitance bridge detector measured the image current produced on a cell plate by the coherent motion of a packet of ions.<sup>1,7,9,15,26,31</sup> Now the excitation frequency could be swept while the magnetic field was held constant. In the rapid scan technique, the excitation rf was swept while the detector "listened". If the excitation rf matched a cyclotron frequency, the detector recorded this match.<sup>1,9</sup>

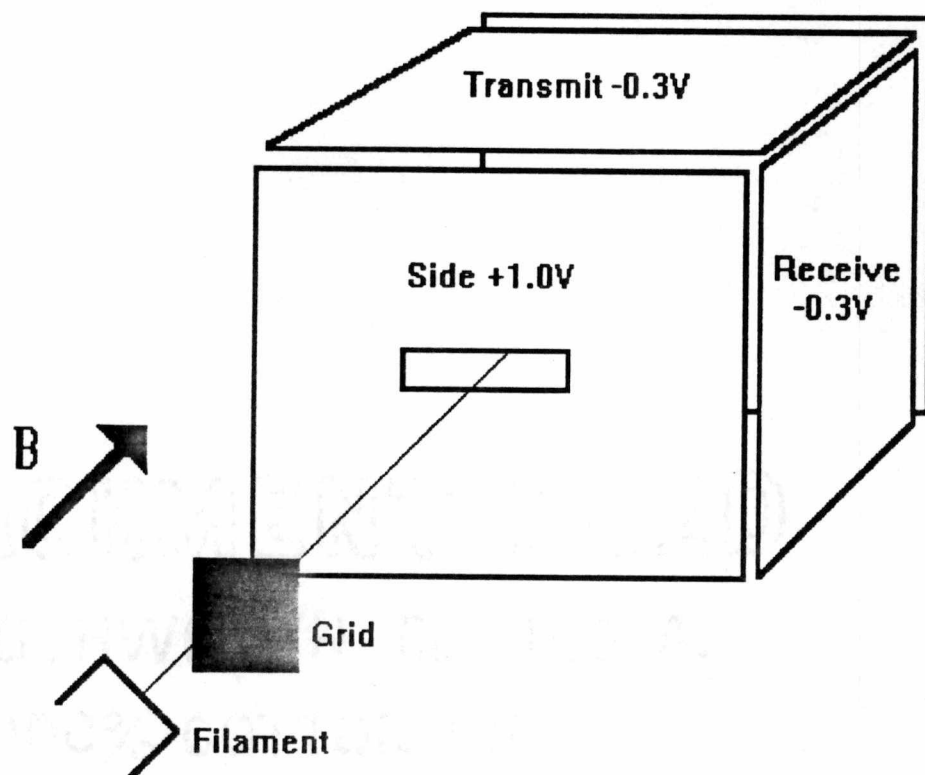


Figure 1.

The Cubic Ion Cell.

Voltages shown are for trapping positive ions.

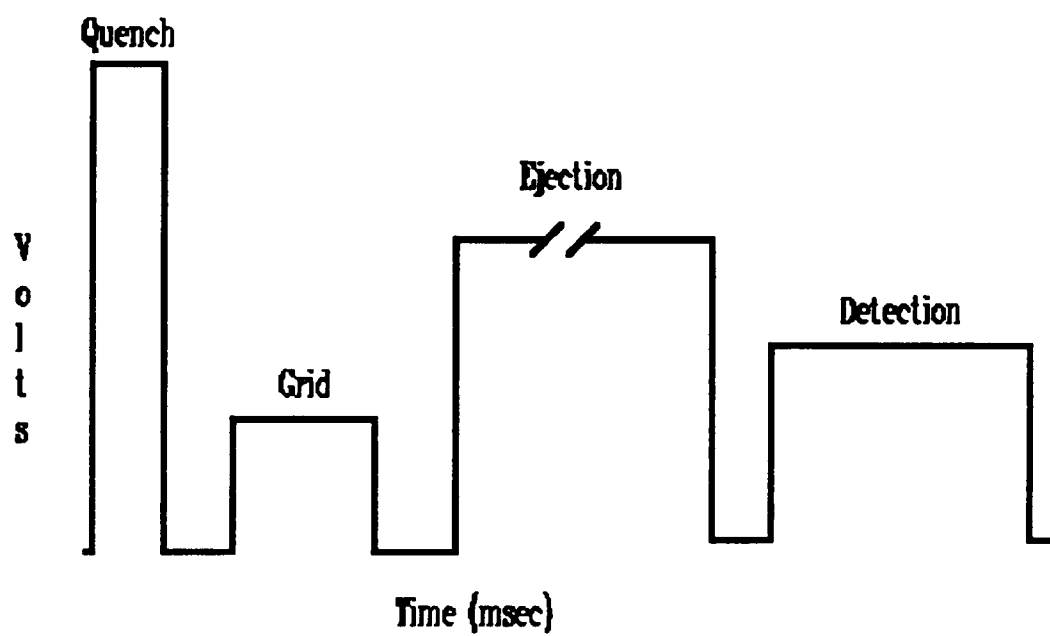


Figure 2.  
The Pulse Timing Sequence.

The pulses are either dc voltages applied directly to the cell plates (quench and grid) or dc pulses used to trigger other events (detection and ejection). The repetition rate of the pulse sequence is variable, which allows for time-resolved studies to be performed.

About the same time that the capacitance bridge detector was introduced, Fourier transform (FT) detection was also being developed. In the FT method, all ions are simultaneously excited by a "chirp", or fast sweep, of frequency and then simultaneously detected. This information is digitized and subjected to a FT to generate a frequency spectrum, or a mass spectrum.<sup>1,4,7,9,15,19,30-36</sup>

There are several comparisons that can be made between sector instruments and ICR instruments. These include the multiplex advantage of FT-ICR-MS, mechanical and operating differences and dynamic range.<sup>1,9,36</sup> The sector instruments previously described have one thing in common; most of them are scanning instruments.<sup>9</sup> This fact implies that only one  $m/z$  ratio is resolved at a given time even though ions are constantly being produced. Although this detection scheme applies to the majority of sector instruments, some employ photographic plates, multichannel electron multipliers or photodiode arrays to detect a window of ions simultaneously.<sup>1,36,37</sup> However, photographic detection is cumbersome and multichannel analyzers are expensive.<sup>9</sup> ICR-MS was initially developed as a scanning technique, but with the application of FT detection methods it is a technique in which all ions are detected simultaneously. Not only is this a more efficient method than rapid scan or slow passage detection, it is also

experimentally much faster than either of these. An entire spectrum can now be obtained in the time previously required per data point. This advantage becomes very useful in signal averaging.<sup>1,9,15,36</sup> However, data workup can be very time consuming for the FT experiment.

The mechanical simplicity of ICR mass spectrometers is a major advantage for this technique. The vacuum system does not have to be nearly as extensive as for sector instruments. In ICR-MS there are no slits to reduce ion transmission and there are no ion optics to focus.<sup>1,9,15</sup> However, FT MS experiments require operating under high vacuum and this limits the type of ionization methods that can be used. Recently, ionization methods like FAB have been interfaced to FT mass spectrometers using quadrupoles to inject the ions into the ion trap.

The dynamic range of sector instruments employing electron multipliers is on the order of  $10^6$  while for ICR instruments using the capacitance bridge detector the dynamic range is only  $10^3$ .

## B. Description of the Bartmess Ion Cyclotron Resonance

### Mass Spectrometer

The ion cyclotron resonance mass spectrometer (ICR-MS) used in these studies is described in detail here (Fig. 3). The heart of the spectrometer is the  $2 \times 2.5 \times 2.5 \text{ cm}^3$  ion trap (Fig. 1). The ion cell is composed of six plates. The side plates are biased with a small dc voltage to trap ions in the direction parallel to the magnetic field. The two other sets of plates are used in ion excitation and detection.



The rf used to excite or eject ions from the cell is applied to the pair transmitter plates 180° out of phase on opposite plates. The pair of receiver plates is part of the capacitance bridge detector. The entire assembly is enclosed in the five liter analyzer manifold, where the vacuum is produced by a Balzers TPU 110 Turbomolecular pump backed by an Alcatel 2008A mechanical pump. The vacuum system is on a track that enables the insertion of the cell into the center of an electromagnet, or the withdrawal of the cell for purposes of baking the instrument to clean it. Pressure is measured with a Huntington Mech. Labs / Bayard-Alpert ionization gauge used in conjunction with a Granville-Phillips series 270 gauge controller. The ionization gauge pressure readings can be calibrated with a MKS Baratron type 146 capacitance manometer. After a 10 hour bakeout at 100°C the analyzer pressure is typically in the low nanoTorr region. When in operation the analyzer manifold is located within the 2-3/4" pole gap of a Varian 9" diameter, 1.4 T electromagnet that is usually operated near 1 T to avoid overheating at higher field strengths. Samples are admitted to the analyzer region via Varian 951-5106 variable sapphire leak valves. The foreline region of the instrument is kept at a pressure of a few microTorr by a 2" CVC, VMF-21, air-cooled diffusion pump backed by another roughing pump. Samples are subjected to several freeze-pump-thaw cycles to degas them prior to introducing them into the analyzer region. When necessary, there is a solids probe inlet just below the cell, but it is difficult to control the pressure of a solid analyte. If a sample has insufficient vapor pressure to be

leaked into the analyzer region, thermally heating the sample and instrument can alleviate the problem. Usually the cell, foreline and sample are externally heated to moderate temperatures, less than 80°C.

It is important that the pulse sequence be accurately timed. All the pulse circuitry and some voltages are controlled by a dedicated IBM-PC through Tecmar Labmaster interface boards. A typical pulse sequence (Fig. 2) includes a quench pulse, a grid pulse, variable delay with possible ion ejection and a detect pulse. The quench pulse ejects all ions in the cell prior to beginning an experiment. The grid pulse turns on and off the electron beam by using dc voltages to either allow the beam to enter the cell or to deflect the beam so it does not enter the cell. The delay time is variable; ions can be stored from a few milliseconds to several seconds. If desired, selected ions or mass windows can be ejected by application of appropriate rf voltages to the transmit plates during this delay time. The detect pulse begins the frequency sweep that excites all the ions in the cell. This sequence is repeated several times for the purposes of signal-averaging in the rapid scan and FT experiments. For ions that are of low intensity the instrument can operate in the unquenched mode where the quench pulse is not used. The dc voltages on the cell plates are manually tuned prior to final data acquisition. The excitation rf is generated by a Rockland frequency synthesizer that is controlled by the IBM-PC. In addition to it, there is a Wavetek frequency generator that is used in some of the double resonance, or ion ejection, studies. Ions are detected by a capacitance bridge

detector. The analog signal is both digitized and stored in the IBM-PC memory and output to a Tektronix 5110 oscilloscope. The stored data can be manipulated prior to either visual output onto a Tektronix 4006-1 CRT or hardcopy generation on a Tektronix 4662 interactive digital x-y plotter.

Phil Geracci and John Bartmess developed the software that runs the experiments and manipulates the data.<sup>38</sup> During the course of this work, modifications were made that correct for errors in ion ejection pulses for double resonance experiments. Extensive software modifications and minor hardware modifications were also made to upgrade the instrument to a FT-ICR-MS. These changes are discussed in detail in Chapter 4 of this dissertation.

### C. Description of Tandem Mass Spectrometer

The VG ZAB-EQ mass spectrometer used for the nitromethane/methyl nitrite work is a hybrid instrument with extended geometry for high mass analysis. It is a reverse geometry instrument with quadrupoles as the third analyzer (Fig. 4). There are multiple ion sources available including electron ionization/chemical ionization (EI/CI), field desorption (FD) and fast atom bombardment (FAB). In addition there are several sample introduction systems including a Hewlett-Packard gas chromatograph (GC), a heated reference inlet, a direct insertion probe (DIP) and a direct chemical ionization (DCI) probe. The discussion here describes the portions of the instrumentation used in these studies.

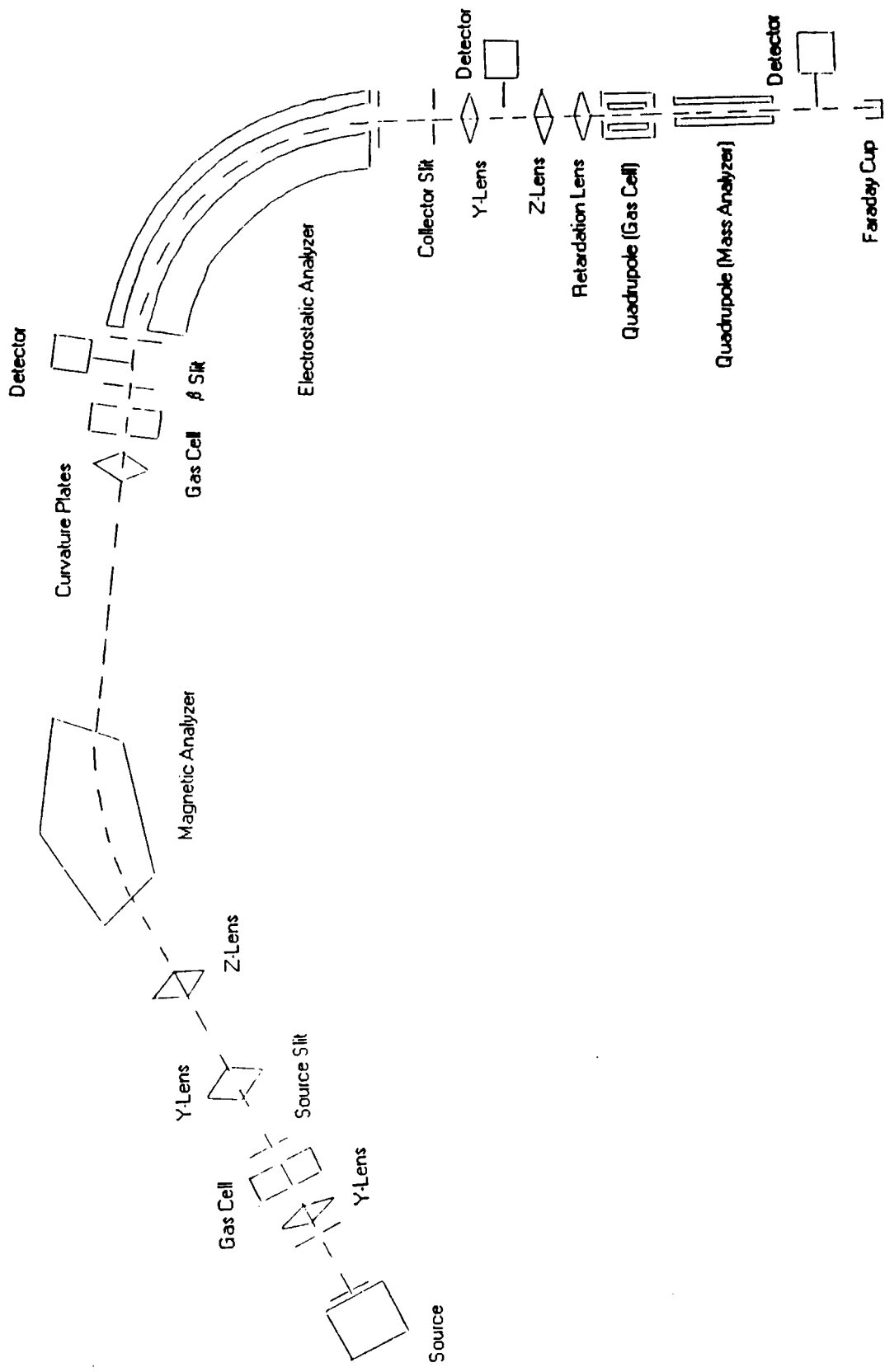


Figure 4.  
Block Diagram of the VG ZAB Mass Spectrometer.

Negative ion chemical ionization (NCI) experiments were performed using the VG combined EI/CI source. Samples were either introduced via the reference inlet or the DCI probe. The data were collected using the 11-250J VG data system. The instrument was operated in the double focusing mode for the NCI experiments. In addition mass analyzed ion kinetic energy spectroscopy experiments were performed. These experiments are described in detail in Chapter 3.

#### D. Scope of Dissertation

This dissertation consists of two distinct parts. The first portion will be concerned with gas-phase studies performed primarily using the ICR-MS. This part will include a study done on the gas-phase acidity of some synthetically interesting bases. It will also include a study performed on the structures of the isomeric (M-H) anions of nitromethane and methyl nitrite.

The second part of this dissertation will be concerned with modifying the ICR-MS to include FT detection and the subsequent studies performed employing the modified instrument. It will include a comparison of the different modes of data collection - slow passage, rapid scan and Fourier transform - on some typical gas-phase ion/molecule reaction systems.

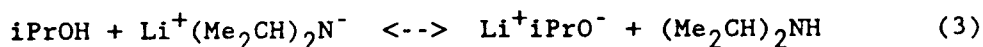
## Chapter 2

### The Intrinsic (Gas-Phase) Basicity of Some Anionic Bases Used in Synthesis

#### A. Introduction

Salts of many strong anionic Brønsted bases are commonly utilized for deprotonation of substrates, such as butyllithium, lithium diisopropylamine, potassium hydride, etc. Chemists tend to use the strongest base available to ensure deprotonation on the first attempt, with modification to reduce nucleophilicity only when necessary. In the common solvent systems used for such work, however, the nature and concentration of the counterion, solvent, and chelating agents will appreciably alter the intrinsic reactivity of the bases. It would therefore be useful to know the intrinsic basicity of such species, relative to various acidic functional groups, in order to analyze the effect of these perturbations on the reactivity.

Fraser and coworkers<sup>39-43</sup> have measured equilibrium ion-pair acidities of a number of these salts in tetrahydrofuran, with lithium as a counterion (eqn. 3). Although a complete scale of such acidities,



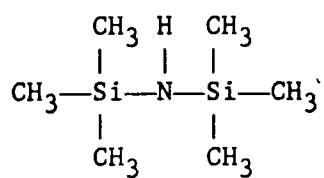
including a wide variety of functional groups such as ketones, esters, nitriles, etc., has not been published, quantitative data for a number of lithioamide bases are available,<sup>44-49</sup> and can be used to determine an ordering of acidities. For example, Bordwell and coworkers,<sup>47-49</sup> have constructed an extensive scale of  $\text{pK}_a$ 's in DMSO solvent.

Therefore a study of the gas-phase acidities of the conjugate acids of some of the anionic bases commonly used in synthetic chemistry (Fig. 5), specifically hexamethyldisilazane 1, di-isopropylamine 2, 2,2,6,6-tetramethylpiperidine 3, and triethylsilanol 4, has been undertaken. These intrinsic acidities, relative to the acidities of many of the functional groups utilized in solution,<sup>47-49</sup> will provide the framework against which one can estimate the counterion and solvent effects which may control the thermochemistry in solution.

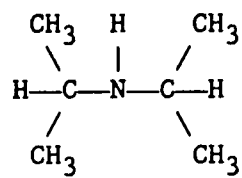
### B. Experimental

Acidities were determined using the ion cyclotron resonance (ICR) spectrometer,<sup>29,30,50</sup> with a capacitance bridge detector operated in rapid scan mode<sup>51-53</sup> that was described in Chapter 1. Neutral gas pressures were measured using a Bayard-Alpert style ionization gauge, and calibrated against a capacitance manometer to obtain true pressures.

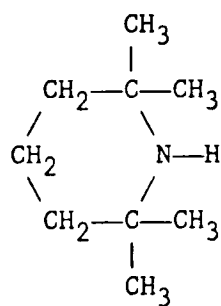
Hexamethyldisiloxane, hexamethyldisilazane 1, diisopropylamine 2, 2,2,6,6-tetramethylpiperidine 3, triethylsilanol 4 and the known acids were used as obtained commercially, except for the oximes which were sublimed prior to use. Their purities were checked by gas chromatography using either a column of Carbowax 20M or SE-30 on acid-washed Chromosorb W with a thermal conductivity detector and by the ICR mass spectra. Fluoride ion was generated by electron ionization (4.2 eV) on nitrogen trifluoride at ca.  $5 \times 10^{-7}$  torr partial pressure. Methoxide was generated by electron ionization on methyl nitrite.<sup>54-56</sup>



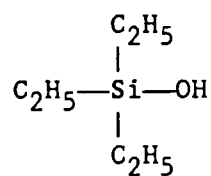
1



2



3



4

Figure 5.

Structures of Conjugate Acids of Commonly Used Synthetic Bases.

### C. Results

The acidities of these conjugate acids were determined in one of two ways: either by equilibrium measurements or by bracketing experiments. In the equilibrium method the unknown acid (AH) is reacted with a known acid (BH) (eqn. 4) and when the ratio of the



anions is constant, equilibrium is assumed to be established. An equilibrium constant can be written for equation 4 (eqn. 5). All the

$$K = \frac{[AH][B^-]}{[A^-][BH]} \quad (5)$$

necessary values to calculate K can obtained from an ICR experiment. The peak heights in the mass spectrum are assumed to be directly proportional to the concentration of the anionic species and the neutral concentrations are obtained from the ion gauge pressure of the neutral calibrated with a capacitance manometer. Once K is measured, the free energy of the system can be calculated using equation 6. The

$$\Delta G = -RT \ln(K) \quad (6)$$

temperature is known to be 305K.<sup>57</sup> This value gives the relative acidity difference, so by using the known acid's  $\Delta G_{\text{acid}}$ , the absolute acidity can be calculated. In the gas-phase, the larger  $\Delta G_{\text{acid}}$  is the weaker acid. Since most thermochemistry is reported as enthalpies, it is convenient to convert from free energy to enthalpy by using equation 7 and estimating the entropy from statistical mechanics.

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

In the bracketing method the anion of the unknown acid (AH) is reacted sequentially with a series of known acids (BH,CH) as in

equations 8 and 9. When two known acids are found close in acidity

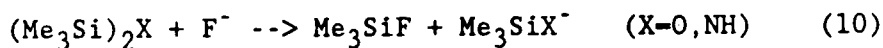


where one undergoes proton transfer and the other doesn't, the acidity of the unknown acid is assumed to lie between the two known acids.

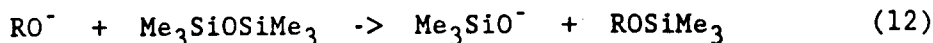
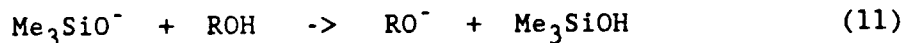
Once again, it is useful to convert to  $\Delta H$  as described above.

Using the usual gas-phase equilibrium techniques<sup>58</sup> described above, the acidity of hexamethyldisilazane 1 was determined to be 0.1 kcal/mol weaker than that of ethanethiol. Similarly, triethylsilanol 4 is 0.6 kcal/mol weaker in acidity than pyrrole. Diisopropylamine 2 is 0.1 kcal/mol weaker than pyridine, and 2,2,6,6-tetramethylpiperidine 3 is 0.5 kcal/mol stronger an acid than diisopropylamine 2. These values are presented in Table 1.

Trimethylsilanol and trimethylsilylamine are not readily available, so their conjugate anions were generated by fluorodesilylation<sup>59</sup> (eq. 10) of the corresponding disilylether and



disilylamine compounds. The acidities were then determined by the bracketing method described above. A serious problem in the present work was found to be the generation of the  $\text{Me}_3\text{SiX}^-$  anions ( $\text{X}=\text{O}, \text{NH}$ ) not only by fluoride but also by the anions of the standard acids (eqns. 11 and 12). This cycle results in the continued presence



of the  $\text{Me}_3\text{SiO}^-$  anion in the mass spectrum, even after the

Table 1.

Gas-Phase Acidities of Some Weak Acids Determined in this Work.

| Acid                                 | Method <sup>a</sup> | $\Delta G_{\text{acid}}^b$ | $\Delta H_{\text{acid}}^c$ | Source of Data <sup>d</sup>              |
|--------------------------------------|---------------------|----------------------------|----------------------------|------------------------------------------|
| (iPr) <sub>2</sub> NH                | Eq.                 | 382.8±0.4                  | 390.7±0.4                  | 0.1 weaker than pyridine                 |
| TMP <sup>e</sup>                     | Eq.                 | 382.3±0.4                  | 390.2±0.4                  | 0.5 stronger than iPr <sub>2</sub> NH    |
| Me <sub>3</sub> SiNH <sub>2</sub>    | Br.                 | 371.0±5.0                  | 379.4±5.0                  | Between MeOH, tBuOH                      |
| Me <sub>3</sub> SiOH                 | Br.                 | 357.5±4.0                  | 365.4±4.0                  | Between Me <sub>2</sub> C=NOH, tBuCH=NOH |
| Et <sub>3</sub> SiOH                 | Eq.                 | 351.5±2.3                  | 359.4±2.3                  | 0.6 weaker than pyrrole                  |
| (Me <sub>3</sub> Si) <sub>2</sub> NH | Eq.                 | 349.7±2.3                  | 357.6±2.3                  | 0.1 weaker than EtSH                     |

a. Eq. - equilibrium measurement; Br. - bracketing between two acids of known reactivity

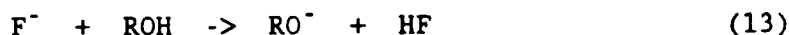
b. Units are kcal/mole. Uncertainties are absolute values. Data are referenced to the acidity scale in Refs. 62 and 63.

c. Units are kcal/mole. Calculated from an entropy of acidity estimated from statistical mechanics.<sup>58</sup> The -OH and -NH groups next to Si are taken as free rotors.

d. Known acid(s) used to determine relative acidity.

e. 2,2,6,6-tetramethylpiperidine

thermochemical threshold for reaction (11) becoming exothermic is exceeded. Double resonance ejection of  $\text{RO}^-$  halts reaction (12), and the near-collision rate disappearance of  $\text{Me}_3\text{SiO}^-$  is taken as an indication that reaction (11) has become exothermic. The cycle is further complicated by the reaction (eq. 13):



being exothermic for R larger than neopentyl. Care was taken that production of  $\text{RO}^-$  by this method was not mistaken for reaction (11).

#### D. Discussion

The gas-phase acidities of the dialkylamines are in the expected polarizability order of  $\text{di-Me} < \text{di-iPr} < \text{di-Me}_3\text{Si}$ .<sup>60</sup> An early report of the acidity of  $\text{Et}_2\text{NH}$  being comparable to that of water<sup>8,61</sup> is consistent with the present results. As indicated by the data in Table 2, a single trimethylsilyl group strengthens the acidity of methane by  $27 \pm 4$  kcal/mol,<sup>62</sup> of water by  $26 \pm 5$  kcal/mol, and of ammonia successively by  $25 \pm 6$  kcal/mol and  $21 \pm 7$  kcal/mol. Saturation effects occur when the combined effects of two substituents are less than the two separately. The uncertainties of these values are too large to draw conclusions concerning saturation effects<sup>63,64</sup> in the amine, but it can be seen that the  $\text{Me}_3\text{Si-}$  group has a fairly constant anion stabilizing effect, regardless of the atom type. Since a single trimethylsilyl group strengthens the acidity of methane by 27 kcal/mol, addition of two more of these groups would approximately

Table 2.

## A Gas-Phase Acidity Scale of Groups of Synthetic Interest.

| Acid                              | $\Delta G_{\text{acid}}^b$ | Acid                                 | $\Delta G_{\text{acid}}^b$ |
|-----------------------------------|----------------------------|--------------------------------------|----------------------------|
| MeH                               | $408.6 \pm 1.2$            | tBuOH                                | 368.0                      |
| nBuH                              | $407.1 \pm 2.6$            | 1,3-Dithiane                         | 366.8                      |
| tBuH                              | $405.7 \pm 2.6$            | CH <sub>3</sub> C                    | 365.2                      |
| NH <sub>3</sub>                   | $396.1 \pm 0.7$            | CH <sub>3</sub> CO <sub>2</sub> Me   | 365.1                      |
| H <sub>2</sub>                    | $394.2 \pm 0.1$            | CH <sub>3</sub> COCH <sub>3</sub>    | 361.9                      |
| Me <sub>2</sub> NH                | $389.2 \pm 0.6$            | Et <sub>3</sub> COH                  | 364.3                      |
| H <sub>2</sub> O                  | $384.1 \pm 0.2$            | Me <sub>3</sub> SiOH                 | $357.5 \pm 4^c$            |
| (iPr) <sub>2</sub> NH             | $382.8 \pm 0.4^c$          | Et <sub>3</sub> SiOH                 | $351.5^c$                  |
| TMP <sup>d</sup>                  | $382.3 \pm 0.4^c$          | (Me <sub>3</sub> Si) <sub>2</sub> NH | $349.7^c$                  |
| Me <sub>3</sub> SiCH <sub>3</sub> | $381.6 \pm 2.9$            | Phenol                               | 342.3                      |
| MeOH                              | 374.0                      | MeCO <sub>2</sub> H                  | 341.5                      |
| Me <sub>3</sub> SiNH <sub>2</sub> | $371.0 \pm 5.0^c$          |                                      |                            |

a. All data from Refs. 65 and 66 unless otherwise noted.

b. Units are kcal/mole. Values are  $\pm 2.3$  kcal/mol absolute,  $\pm 0.2$  kcal/mol relative to other acids, unless otherwise stated.

c. This work.

d. 2,2,6,6-tetramethylpiperidine.

give a  $\Delta G_{\text{acid}}$  of 330 kcal/mol for  $(\text{Me}_3\text{Si})_3\text{CH}$  which would make that the most acidic localized carbon acid known.

If the gas-phase acidities of a number of these alkyl- and dialkylamines are plotted against their gas-phase basicities, a linear correlation is seen (Fig. 6,  $r = 0.980$ ,  $\Delta G_{\text{acid}} = -0.74 \Delta G_{\text{base}} + 547.8$ ). A similar correlation has been noted for the gas-phase acidity and basicity of alcohols;<sup>67</sup> the slope in that case is comparable to this data at -0.75. This implies that the alkyl groups are stabilizing both positive and negative charges, consistent with polarizability being a major mode of this stabilization.

$\text{Et}_3\text{SiOH}$  is a stronger acid in the gas-phase than  $\text{Me}_3\text{SiOH}$  by  $6.0 \pm 2.5$  kcal/mol, again consistent with polarizability effects.<sup>60</sup> For comparison,  $\text{Et}_3\text{COH}$  is likewise a stronger acid than  $\text{Me}_3\text{COH}$  by  $3.7 \pm 0.3$  kcal/mol.<sup>65,66</sup> However, as a base (protonation to form a cation),  $\text{Me}_3\text{SiOSiMe}_3$  is ca. 8 kcal/mol weaker than  $\text{Me}_3\text{C-O-CMe}_3$ ,<sup>68</sup> and  $\text{Me}_3\text{SiOH}$  is comparable to  $\text{Me}_3\text{COH}$  in basicity,<sup>69,70</sup> indicating that the trimethylsilyl group is not interacting with charged sites solely by polarizability (which would be the case if the silyl compounds differed from the carbon compounds by a constant amount), but also as a polar electron accepting group. Taft and coworkers<sup>67</sup> have separated the polar effect (I) and the polarizability effect (P) of various substituents, using the difference between the effect of the substituents on the gas-phase acidities and basicities. Applying that same analysis<sup>67</sup> to the present data, the values obtained in Table 3 show that the trialkylsilyl groups have about the same electron

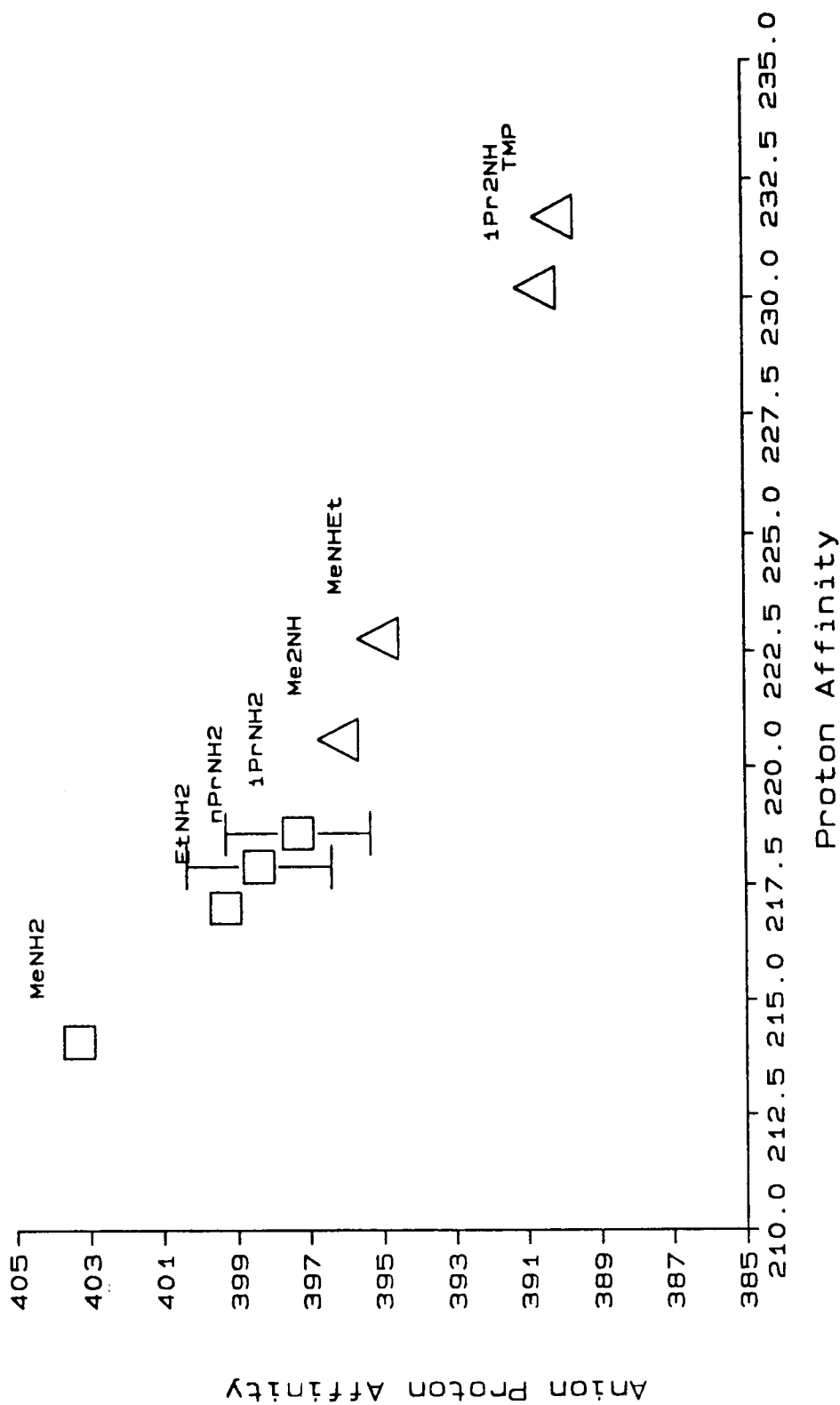


Figure 6.  
Gas-Phase Basicities vs. Gas-Phase Acidities  
for Alkyl- and Dialkylamines.

Table 3.

Polar I and Polarizability P Values<sup>a</sup>

| Group                             | I     | P     |
|-----------------------------------|-------|-------|
| Et <sub>3</sub> Si-               | -3.3  | 19.2  |
| Me <sub>3</sub> Si-               | -2.1  | 14.4  |
| Me-                               | (0.0) | (0.0) |
| Et-                               | 1.5   | 4.7   |
| tBu-                              | 2.3   | 8.5   |
| CF <sub>3</sub> CH <sub>2</sub> - | -13.3 | 3.3   |
| PhCH <sub>2</sub> -               | -2.8  | 7.6   |

a. Ref. 67 or present work (see text).

accepting ability, in the polar sense, as the benzyl group, and are about twice as polarizable as both benzyl and tert-butyl groups. Although the polarizability result seems reasonable, the polar effect is remarkable; trialkylsilyl has usually been considered a polar electron-donating group<sup>71,72</sup> based on its electronegativity and  $\sigma_I$  value. It does have a slightly positive  $\sigma_R^-$  value,<sup>71,72</sup> however, indicating that it is capable of resonance stabilization of negative charge under the proper circumstances. Utilizing the master equation for prediction of XOH acidities in the gas-phase given by Taft and coworkers (eq. 14),<sup>73</sup> with the  $\sigma$  constants for the  $\text{Me}_3\text{Si}-$  group,<sup>72</sup>

$$\delta\Delta G^\circ_{(g)} = (-23.4 \pm 0.8)\sigma_\alpha + (73.4 \pm 0.9)\sigma_F + (72.8 \pm 2.0)\sigma_R \quad (14)$$

yields a calculated gas-phase acidity for  $\text{Me}_3\text{SiOH}$  of 367.6 kcal/mol, over 10 kcal/mol weaker than observed experimentally. It would appear that the  $\sigma$  constants for  $\text{Me}_3\text{Si}-$ , obtained from cationic data, are not appropriate for the present anionic systems. This greater than expected effect of the trimethylsilyl group on stabilization of nitranions and oxyanions has been examined using semi-empirical molecular orbital calculations. The relative gas-phase enthalpies of acidity ( $\Delta H_{\text{acid}}$ ) for  $\text{Me}_2\text{NH}$  and **1** have been calculated using the MNDO and AM1 methods.<sup>74-78</sup> These methods in general result in localized anions being too high in energy,<sup>74-78</sup> and for the present case predict **1** to be only 7 kcal/mol more acidic than dimethylamine, disagreeing with the experiment by 32 kcal/mol. However, an intriguing result for the anion of **1** is found: while the geometries for  $\text{Me}_2\text{NH}$ ,  $\text{Me}_2\text{N}^-$ , and **1** are much as expected, with approximately tetrahedral geometry at

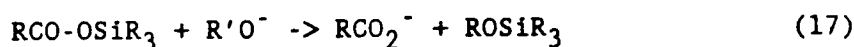
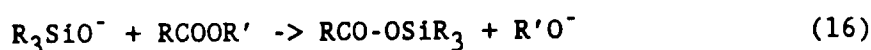
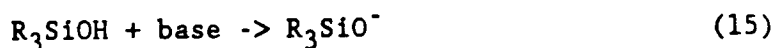
nitrogen, the deprotonation product of **1** has a linear Si-N-Si structure! The HOMO of the anion in this case is 1.7 eV more bound than for  $\text{Me}_2\text{N}^-$ . These results are being further pursued at the *ab initio* level by John Bartmess and John Bloor to explore this apparent rehybridization.

Turning to the comparison with solution-phase reactivity of these anions, in all solvents for which data is available,<sup>39-43,46-48</sup> **1** is at least 10  $\text{pK}_a$  units (14 kcal/mol) more acidic than the dialkylamines. This parallels the relative acidities in the gas-phase, where **1** is 32 kcal/mol stronger as an acid than **2** and **3**. The reduction in the size of the substituent effect (8 kcal/mole difference) on going to solution is attributable to partial stabilization of the anion in solution by the counterion and solvent, in addition to an attenuation in the polarizability effect, from charge delocalization by the solvent and counterion. What is more pertinent in comparing the gas-phase and solution phase data are the relative acidities of compounds of synthetic interest, such as ketones, alkynes, nitriles, etc. with the basicity of the anionic species examined here. In the gas-phase, it has been previously noted that methoxide will deprotonate all carbonyl compounds, nitriles, acetylenes, and most benzylic sites in the gas-phase.<sup>79</sup> The anions of **2** and **3** are intrinsically only 8 kcal/mol stronger as bases than methoxide. The only simple acids that fall between the amines and methanol are toluenes with electron-donating groups attached, such as *p*-dimethylamino-toluene. Thus methoxide and the anions of these amines

should behave intrinsically almost identically. The preference for the use of the amine anions in solution is obviously due to their decreased nucleophilicity, for steric reasons.

In the gas-phase, the conjugate base of 1 will not deprotonate simple ketones (other than  $\text{CF}_3\text{COCH}_3$ ), nitriles, esters, or alkyl-substituted terminal alkynes.<sup>58</sup> 1 is more acidic than  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\text{pK}_a$  9.2) in aqueous solution<sup>80</sup> and is comparable in acidity to ethanethiol ( $\text{pK}_a$  10.61) in aqueous solution.<sup>80</sup> Hence a reversal in reactivity is seen in going from the solution phase to the gas-phase. In organic solvents, however, the conjugate base of 1 readily deprotonates ketones<sup>46</sup> and esters.<sup>44,45</sup> The lithium counterion (THF solvent) must therefore stabilize the enolate anion more than the amide anion, to shift the equilibrium by at least 17 kcal/mol! This also implies that proper choice of solvent and/or counterion will allow considerable selectivity in this case. An example is the relative basicities of the sodium salt of 1 vs. the lithium salt; the latter resulted in only  $\gamma$ -deprotonation of an  $\alpha,\beta$  unsaturated ketone, but the sodium salt deprotonated an adjacent simple ketone in the same molecule.<sup>81</sup> Although kinetic control may be invoked as the difference here, the counterion may be controlling the equilibria at the stage of the initial proton transfer, since the site of the conjugated enone is comparable in intrinsic acidity to the amide anion.<sup>82</sup>

The anions of the trialkylsilanols have been used in solution not primarily as strong bases, but rather as nucleophiles which are the synthetic equivalent of  $\text{O}^-$  (eqns. 15-18).<sup>83</sup> The observed basicity in



vs.



that  $R_3SiO^-$  does not deprotonate the  $\alpha$ -H of esters in solution, is consistent with the anion's weak basicity in the gas-phase.

### E. Conclusions

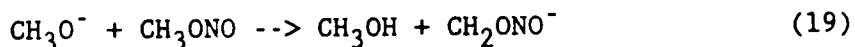
Knowledge of the intrinsic reactivity of species of this type, plus observing how this can be subsequently modified by solvation and counterions, allows the chemist better control and selection of the available reaction pathways. It has been shown that the observed reactivity of dialkylamide anions in solution is consistent with their intrinsic reactivity, but that hexamethyldisilazide anion appears to have its solution phase reactivity modified considerably by the counterion. Further exploration of counterion effects on the reactivity of the conjugate base of 1, or possibly of species of the type  $Me_3Si-NHR$ , where R = some bulky alkyl group, would be of interest. The latter species should be intrinsically just a little weaker in acidity than any ester or ketone, so that counterion control might tune its reactivity through the range of synthetic interest.

## Chapter 3

### The Structures of the (M-H) Anions of the $\text{CH}_3\text{NO}_2$ Isomers of Methyl Nitrite and Nitromethane

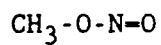
#### A. Introduction

Methyl nitrite ( $\text{MeONO}$ , 5) is commonly used in chemical ionization (CI) mass spectrometry (MS) and ion/molecule reaction studies as a source of methoxide, which is generated by thermal electron dissociative attachment.<sup>54-56</sup> Methoxide reacts with methyl nitrite to produce an (M-H) anion at 60 u. (Eqn. 19) Previously, this ion has

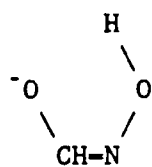


been represented<sup>84</sup> as a dipole stabilized carbanion (6).<sup>85-88</sup> Based on the gas-phase acidities of methanol<sup>65</sup> and the acidities of other compounds that form known dipole stabilized anions,<sup>85-88</sup> however, it seems that reaction 19 should be considerably endothermic. If anion 6 is envisioned in the most favorable geometry for most dipole stabilized anions, with the lone pair of electrons of the carbanion syn to a transoid nitrosyl group,<sup>85-88</sup> then there is a lone pair of electrons on the nitrosyl group close to the carbanion. Such a structure should be destabilized relative to a carbonyl stabilized carbanion. In this study, alternative structures have been considered for the (M-H) anion at 60 u (Figure 7).

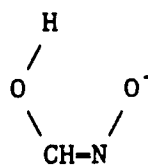
There are two chemical possibilities which may explain the presence of the anion at 60 u despite the apparent endothermicity of its formation. First, neutral methyl nitrite might be rearranging in



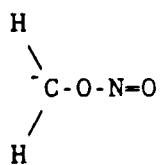
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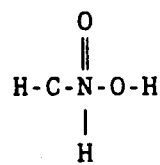
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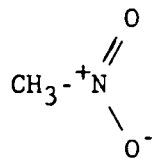
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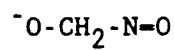
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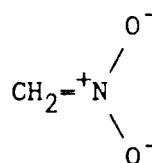
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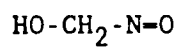
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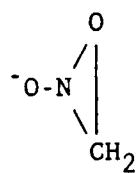
12



8



13



14

Figure 7.

Structures of Isomers of Methyl Nitrite and their (M-H) Anions.

the vacuum system to nitromethane ( $\text{MeNO}_2$ , 7). Deprotonation of nitromethane by methoxide is 24 kcal/mol exothermic and, therefore, a plausible reaction. Second, the (M-H) anion of methyl nitrite may not be the straightforward deprotonation product, but rather a rearranged structure. There are other possible isomers of  $\text{CH}_2\text{NO}_2^-$  that could be reasonably accessed in such a rearrangement. These include the rapidly interconvertible anions 9 and 10 from neutral formyl hydroxamate, 11, and nitrosomethoxide, 12, from unstable nitrosomethanol, 13. The calculated barrier for rearrangement of the neutral species, methyl nitrite to nitromethane, has been shown to be 53 kcal/mol<sup>89,90</sup> and calculated at a very high level of CI to be 67 kcal/mol.<sup>91</sup> This high energy barrier implies that the neutral rearrangement is probably not occurring, but the anion rearrangement may be occurring. Therefore, the structures of the 60 u anions from methyl nitrite, nitromethane and several isomers have been examined.

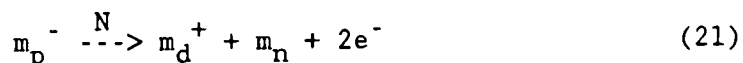
The information that is readily available from an electron ionization mass spectrum is, under favorable circumstances, the molecular weight of the compound and limited structural information from the fragmentation pattern. Distinguishing isomeric compounds can be difficult without additional experiments. Therefore, three approaches are employed here to overcome this difficulty: mass spectrometry/mass spectrometry (MS/MS) experiments, ion-molecule reaction studies and molecular orbital calculations.

Mass spectrometry/mass spectrometry experiments provide additional structural information over a single stage mass

spectrometry experiment.<sup>92</sup> In these experiments the ion of interest is isolated and further studied. One such MS/MS experiment is the mass-analyzed ion kinetic energy spectrometry (MIKES) experiment which is employed in this study. Here, the ion of interest, called the parent, or precursor, ion, is isolated by setting the magnetic sector of a reverse geometry mass spectrometer to pass only the corresponding  $m/z$ . The electrostatic analyzer is then scanned to facilitate detection of any ions, called daughter, or product, ions, arising from dissociation of the parent ion in the field free region between the magnet and electrostatic analyzer. If no techniques are used to induce this dissociation, any observed daughter ions would be the result of metastable transitions. Frequently, collision-induced dissociation (CID) is used to encourage fragmentation of the parent ion in the second field free region. This process is described by reaction 20, where  $m_p^+$  is the parent ion;  $m_d^+$  is a daughter ion;  $m_n$  is



a neutral fragment; and  $N$  is a collision gas such as  $\text{He}$ .<sup>92</sup> The only functional difference between a metastable transition and CID is the presence of  $N$ . These processes occur in the field-free region between the magnet and electrostatic analyzer. Another possible process is charge inversion described by reaction 21.<sup>92</sup> If isomeric parent ions



are observed under any of these conditions to give different daughter ion spectra, then one can conclude that the parent ions have different structures.<sup>92</sup>

Several reagents have been discovered that are selective for specific types of gas-phase ions. For example, DePuy studied the gas-phase addition reactions of a series of carbanions with several neutral reagents.<sup>93</sup> By observing the products of reactions of these neutral reagents with an anion of unknown structure, one can determine if this anion behaves like a carbanion. In addition, deuterium exchange behavior can be indicative of structure. Protons bound to heteroatoms such as nitrogen or oxygen, will undergo rapid deuterium exchange with D<sub>2</sub>O or MeOD. Lastly a measurement of gas-phase acidity and/or basicity can also give insight into an ion's structure.

Molecular orbital calculations can be very helpful in determining the energetics of different structures and of rearrangements between isomeric possibilities. *Ab initio* calculations are the most accurate and informative. For anions, the best basis set is the 6-31+G//6-31+G which employs diffuse orbitals. The expense of *ab initio* calculations, however, requires that they are employed judiciously. Alternatively, semi-empirical programs can give helpful insights into reaction and structure energetics within their limitations. For example, the MNDO<sup>74-76</sup> method and AM1<sup>77,78</sup> method both do not perform well when N-O bonds are involved. A newer calculation method, the PM3 Hamiltonian,<sup>94</sup> does a slightly better job and was employed for this study.

The goal of this work is to determine the structures of the isomeric (M-H) anions produced by loss of one proton from methyl nitrite. This goal is accomplished by using MS/MS, reactivity and molecular orbital calculations.

## B. Experimental

The negative ion chemical ionization (NICI) mass spectra and mass-analyzed ion kinetic energy spectrometry (MIKES) spectra were obtained using a VG ZAB-EQ instrument with reverse geometry controlled by a VG 11-250J computer system as described in Chapter 1. Ammonia was used as the chemical ionization (CI) gas for nitromethane experiments (where proton abstraction by  $\text{NH}_2^-$  was necessary to form the (M-H) anion); either methane or nitrogen (where the nonreactive CI gas thermalized the electrons) was used as the CI gas for methyl nitrite experiments; and methane was used as the CI gas for formyl hydroxamate experiments. Typical CI gas pressure was  $1.5 \times 10^{-4}$  Torr. For MIKES experiments with collision induced dissociation (CID), helium was used at 1-5 microTorr, giving 50-80% reduction of the parent peak. Experiments were run at 6kV accelerating potential. All gases were reagent grade.

The ion/molecule work was performed using the home-built pulsed ion cyclotron resonance (ICR) mass spectrometer that was described in Chapter 1. Data were obtained by the rapid scan technique.<sup>51-53</sup> Nitrogen trifluoride,  $\text{NF}_3$ , which produces fluoride upon electron ionization was used to generate the (M-H) anion of nitromethane.

Methyl nitrite was synthesized in an ICR tube by mixing isoamyl nitrite and methanol<sup>56</sup> in about a 1:3 ratio. The existence of methyl nitrite in the vapor phase above this mixture was confirmed by FT-IR analysis of the head space gas; and the FTIR spectrum obtained agreed with the published spectrum.<sup>95</sup> Also, based on vapor pressure data,<sup>96</sup>

the percent composition of the vapor above an equimolar mixture of the constituents would be 98.5% methyl nitrite, 1.4% methanol and less than 0.1% isoamyl nitrite and isoamyl alcohol. No O-H stretch was observed in the gas-phase FTIR spectrum. Formyl hydroxamate was synthesized according to the literature method<sup>97</sup> as described here. Fifteen mL of distilled water and 12 mL of absolute ethanol were added to a 250 mL round bottom flask fitted with a condenser. Seven g of hydroxylamine hydrochloride were slowly added until completely dissolved by stirring. The solution was cooled to 8°C and 25 mL of 10N NaOH solution was slowly added to the flask maintaining the temperature below 20°C. The mixture was allowed to warm to room temperature (about 30°C). Then 8.1 mL of ethyl formate was added dropwise. The solution was clear at this point and was stirred under N<sub>2</sub> for 1.5 hrs. Then the flask was cooled with an ice bath as 10.5 mL of concentrated HCl was added. A gas evolved. The pH was 6 according to tests with pH paper. The mixture was evacuated using a rotary evaporator for 1.5 hrs. until a yellow sludge remained. One-hundred mL of absolute ethanol was added and the solution was evaporated to dryness. Then the crystals were extracted with two aliquots of 100 mL of boiling ethyl acetate. Upon cooling to just below boiling, the NaCl crystals would fall out of solution and the liquid was decanted to an erlenmeyer flask. The solution was allowed to boil until it began to look cloudy, and then cooled to room temperature. It was placed in a freezer overnight. The crystals were separated from the cold ethyl acetate by suction filtration, then washed twice with cold ethyl acetate and once with

diethyl ether. The melting point of the white crystals was 76-78°C. Starting materials and other chemicals were obtained from commercial sources and were not further purified.

### C. Results and Discussion

From an ICR time study (Table 4), the rate constant,  $k$ , for the appearance of the 60 u anion from methyl nitrite 5 is  $3.3 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , and for the appearance of 46<sup>-</sup> ( $\text{NO}_2^-$  from a nucleophilic displacement of methoxide on MeONO),  $k = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The rate for production of 60<sup>-</sup> is about 12% efficient relative to the trajectory-calibrated ADO rate constant<sup>98</sup> of  $2.7 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The ratio of the intensities of 60<sup>-</sup>/46<sup>-</sup> is about 1/5, consistent with earlier drift cell ICR results.<sup>84</sup>

The negative ion chemical ionization (NICI) mass spectra of all molecules are summarized in Table 5. The three neutral isomers yield different product ions, but this does not indicate different structures for the 60<sup>-</sup> ion from each neutral. For nitromethane 7, the base peak is 60<sup>-</sup>, from proton abstraction by amide. Also present are peaks at 46 daltons ( $\text{NO}_2^-$ ), 107 daltons [ $(\text{M}+\text{NO}_2\text{H})^-$ ], and 121 daltons [ $(2\text{M}-\text{H})^-$ ]. For methyl nitrite 5, the spectrum is much more complicated. The 60<sup>-</sup> peak is present, but there are several more intense peaks in the spectrum: 31 daltons ( $\text{CH}_3\text{O}^-$ ), 85 and 87 daltons (from residual isoamyl alkoxide<sup>56</sup>), and also peaks at 101, 119 and 176 daltons. The NICI mass spectrum of formyl hydroxamate 11 has the base

Table 4.

Time Study of Methyl Nitrite in the ICR Mass Spectrometer.<sup>a</sup>

| Delay time (msec) | Height of NO <sub>2</sub> <sup>-</sup> (mV) | Height of MeONO <sup>-</sup> (mV) |
|-------------------|---------------------------------------------|-----------------------------------|
| 50                | 71                                          | 18                                |
| 100               | 84                                          | 23                                |
| 150               | 102                                         | 23                                |
| 200               | 100                                         | 24                                |
| 250               | 123                                         | 29                                |
| 300               | 127                                         | 26                                |
| 400               | 129                                         | 27                                |
| 500               | 129                                         | 27                                |

a - Ionization gauge pressure for this experiment = 1.1  $\mu$ Torr.

Table 5.

The NCI Mass Spectra of Methyl Nitrite, Nitromethane  
and Formyl Hydroxamate.

| Compound                 | Anion mass(% of base peak) |         |          |                                                            |
|--------------------------|----------------------------|---------|----------|------------------------------------------------------------|
| Methyl Nitrite 5         | 60(35%) <sup>a</sup>       | 31(35%) | 46(100*) | 85(100*)<br>87(100*)<br>101(40%)<br>119(100*)<br>176(100*) |
| Nitromethane 7           | 60(100%)                   |         | 46(15%)  | 107(15%)<br>121(20%)                                       |
| Formyl<br>Hydroxamate 11 | 60(100%)                   | 42(30%) | 44(65%)  | 72(35%)                                                    |

a-The 60 u peak was a small fraction of the total signal under the conditions used and represents less than 1% of the base peak at 87u.

\*-Offscale, >100%

peak at 60 daltons, the (M-H) anion produced by proton loss, with other peaks at 42 daltons ( $\text{CON}^-$ ), 44 daltons ( $\text{CH}_2\text{ON}^-$ ) and 72 daltons.

To gain structural information about the  $60^-$  ions, MIKES experiments on the  $60^-$  ion from each of the neutral precursors were performed; these data are summarized in Table 6. The MIKES experiments under four different conditions - CID with and without charge inversion, and no CID with and without charge inversion - were attempted. The most useful information was obtained from the experiments without charge inversion. For these experiments, the presence of a peak at 58 daltons (nominally  $\text{O}=\text{C}-\text{N}-\text{O}^-$ ) in the methyl nitrite 5 spectrum and its absence in the nitromethane 7 spectrum leads to the conclusion that the two anions have different structures. Bursey and coworkers<sup>99</sup> came to the same conclusion for methyl nitrite and nitromethane, using MIKES to examine the same anions. They report positive fragments for both ions, which were not observed under our experimental conditions. Their negative fragment MIKES results are essentially the same as observed here.

To determine if the (M-H) anion of methyl nitrite rearranges to nitrosomethoxide 12, MIKES experiments were performed on the  $60^-$  anion from formyl hydroxamate 9,10. Under CID conditions the (M-H) anions from formyl hydroxamate and methyl nitrite give the same fragment ions. The relative intensity of the  $42^-$  fragment is larger, however, in the CID/MIKES spectrum of formyl hydroxamate than in that of methyl nitrite. The metastable ion MIKES spectra also differ: in the spectrum of  $60^-$  generated from methyl nitrite, the  $42^-$  fragment is present,

Table 6.

NICI/MIKES Spectra  
of Nitromethane, Methyl Nitrite and Formyl Hydroxamate<sup>a</sup>

|                     | Nitromethane           | Methyl<br>Nitrite             | Formyl<br>Hydroxamate         |
|---------------------|------------------------|-------------------------------|-------------------------------|
| No CID -            |                        |                               |                               |
| no charge inversion | 60(s)                  | 60(s), 58(m),<br>42(m)        | 60(s), 58(w)                  |
| charge inversion    | No peaks               | No peaks                      | Not attempted                 |
| CID -               |                        |                               |                               |
| no charge inversion | 60(s), 59(s),<br>42(m) | 60(s), 59(m),<br>58(m), 42(w) | 60(s), 59(m),<br>58(m), 42(s) |
| charge inversion    | No peaks               | No peaks                      | Not attempted                 |

a- Intensities noted by (s) - strong, (m) - medium, (w) - weak

while it is not observed in the spectrum of  $60^-$  from the formyl hydroxamate. These differences imply that all three ions have different structures.

Results from a number of ion/molecule reactions provide further insight into the structures of the anions. The  $\Delta G_{\text{acid}}$  of nitromethane 7 has been measured to be  $350 \pm 2$  kcal/mol.<sup>65</sup> Bracketing experiments (Table 7) performed on  $60^-$  from methyl nitrite yield an apparent  $\Delta G_{\text{acid}}$  of  $361 \pm 4$  kcal/mol ( $\Delta H_{\text{acid}} = 368 \pm 4$  kcal/mol using  $T = 305\text{K}$ <sup>57</sup> and  $\Delta S = .023$  kcal/mol from statistical mechanics). This difference in the proton affinity of the anions of the two compounds also leads to the conclusion that the anions have different structures.

Deuterium exchange has been used to evaluate the number and type of exchangeable hydrogens in an anion.<sup>100-103</sup> The  $60^-$  anions from methyl nitrite and nitromethane 8 do not undergo facile deuterium exchange with methyl alcohol- $d_4$ , while the  $60^-$  anion from formyl hydroxamate 9,10 shows one exchange. The apparent reaction of the ion from formyl hydroxamate may not be due to an ion/molecule reaction, but to neutral-neutral exchange of methyl alcohol- $d$  with the oxygen and nitrogen bound protons of formyl hydroxamate prior to formation of the  $60^-$  anion. Nevertheless, the presence of one deuterium after deprotonation is consistent with structures 9 or 10, and not with 6, 8, or 12 which should exchange either two hydrogens or no hydrogens.

The  $60^-$  ion from methyl nitrite shows deuterium exchange of two hydrogens with benzyl alcohol- $d_1$ , which has an acidity close to that of the conjugate acid of the  $60^-$  anion from methyl nitrite. It is

Table 7.

Gas-phase Acidity Bracketing of the 60<sup>-</sup> u Anion from Methyl Nitrite.

| Compound                          | $\Delta H_{\text{acid}}^a$ | Result                                     |
|-----------------------------------|----------------------------|--------------------------------------------|
| Isopropyl Alcohol-Od <sup>b</sup> | 368.8 $\pm$ 2              | Not reactive with 60 u                     |
| Benzyl Alcohol-Od <sup>b</sup>    | 363.4 $\pm$ 2              | Some decrease, 60 u $\rightarrow$ 107 u    |
| Acetoxime                         | 359.1 $\pm$ 2              | 60 u $\rightarrow$ 72 u, oxime more acidic |

a-Values are kcal/mol from ref. 65.

b-Deuterated on oxygen.

neutralized by 1,1,1-trifluoroethanol- $d_1$ , with no exchange. The  $60^-$  ion from nitromethane **8** does not undergo deuterium exchange with benzyl alcohol- $d_1$ , but exchanges two hydrogens with 1,1,1-trifluoroethanol- $d_1$ . Thus the  $60^-$  ions from nitromethane, methyl nitrite and formyl hydroxamate all show distinctive behavior on deuterium exchange.

The two deuterium exchanges seen for the  $60^-$  from methyl nitrite with benzyl alcohol- $d_1$  are consistent with the ion having structure **6**, where there are two hydrogens equivalent to the original proton that was removed, but can also be rationalized in terms of structure **12**. It can be speculated that deuteron transfer occurs from the alcohol to the oxyanion in **12**, followed by deprotonation by benzyloxide still in the ion/molecule complex to give structure **10** (estimated acidity of  $\text{HOCH}_2\text{NO}$  is  $348 \text{ kcal/mol}^{104}$ ). The ion **10**, on collision with a second benzyl alcohol- $d$ , can undergo a second deuterium exchange at carbon. In contrast, if **12** collides with methyl alcohol- $d$ , simple proton transfer is  $13 \text{ kcal/mol}$  endothermic. The reaction to form **10** is exothermic, but involves proton transfer from carbon. This can have an appreciable barrier<sup>105</sup> and thus may be too slow to observe with methyl alcohol- $d$ . The greater well depth<sup>106</sup> for the  $\text{PhCH}_2\text{O}^- \cdots \text{DOCH}_2\text{NO}$  complex would explain its faster reaction for deuterium exchange.

The results from several other gas phase reactions diagnostic for various carbanion-type structures are given in Table 8. In double resonance experiments<sup>7</sup> a reactant ion is ejected from the ICR cell and the subsequent changes in the spectrum are noted for reaction connectivity. For example if the ion at  $60^- \text{ u}$  is ejected from the cell

Table 8.

Gas-Phase Reactions of Anions from Nitromethane,  
Methyl Nitrite and Formyl Hydroxamate.

| Neutral<br>Reagent            | 60 <sup>-</sup> from<br>CH <sub>3</sub> NO <sub>2</sub> | 60 <sup>-</sup> from<br>CH <sub>3</sub> ONO | 60 <sup>-</sup> from<br>HC(-O)NHOH | Reference |
|-------------------------------|---------------------------------------------------------|---------------------------------------------|------------------------------------|-----------|
| N <sub>2</sub> O              | No reaction                                             | No reaction                                 | Not attempted                      | 107       |
| CO <sub>2</sub>               | No reaction                                             | No reaction                                 | Not attempted                      | 93,107    |
| CS <sub>2</sub>               | 60 u -> 92 u                                            | No reaction                                 | Not attempted                      | 93        |
| OCS                           | No reaction                                             | No reaction                                 | Not attempted                      | 93        |
| MeSSMe                        | 60 u -> 106 u                                           | No reaction                                 | No reaction                        | 108       |
| C <sub>6</sub> F <sub>6</sub> | 60 u -> 207 u                                           | No reaction                                 | Not attempted                      | 109       |

and another peak also disappears from the spectrum, it is concluded that the other peak is a product of a reaction involving  $60^-$  u. Double resonance was used here to confirm that the peaks of interest are formed by reaction of  $60^-$  with the neutral reagents. Several reagents have been discovered that react with specific types of anions. They include  $N_2O$ ,<sup>107</sup>  $CO_2$ ,<sup>93,107</sup>  $CS_2$ ,<sup>93</sup>  $OCS$ ,<sup>93</sup> dimethyldisulfide,<sup>108</sup> and perfluorobenzene.<sup>109</sup> Neither  $60^-$  from methyl nitrite or from nitromethane **8** reacts with  $N_2O$ ,  $CO_2$ , or  $OCS$ . For  $CS_2$  and the  $60^-$  anion from nitromethane, an addition of sulfur is observed to give an anion at 92 u; the  $60^-$  ion from methyl nitrite does not react in this manner. The  $60^-$  ion from nitromethane also reacts with dimethyldisulfide to give a characteristic ion at 106 daltons ( $60^- + SCH_3 - H$ ); the  $60^-$  ion from methyl nitrite does not. For perfluorobenzene and  $60^-$  from nitromethane, a product ion at 207 daltons ( $60^- + C_6F_6 - 2HF$ ) appears. Figure 8 indicates a possible mechanism for production of this ion. The (M-H) anion of methyl nitrite does not react with perfluorobenzene. The  $60^-$  anion from formyl hydroxamate **9,10** does not react with dimethyldisulfide.

*Ab initio* calculations with the Gaussian 86 program employing the 6-31+G//6-31+G basis set<sup>110,111</sup> were done on a number of the anions of interest here, plus their corresponding conjugate acids. Correlation energy probably will make some difference in the relative energies of these structures, due to the appreciably different bonding types involved. At an uncertainty level of about 5 kcal/mol, however, it is believed that the pre-Hartree-Fock level calculations given here are

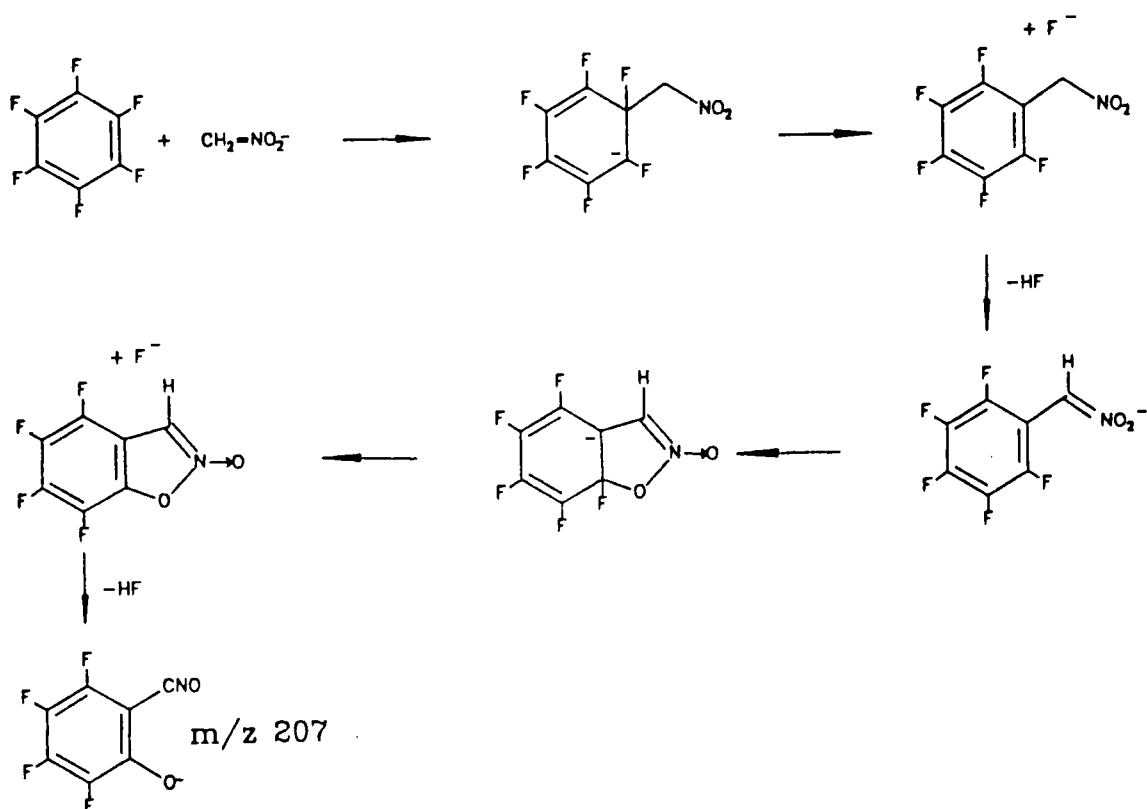


Figure 8.  
Possible Mechanism for Production of 207 u  
in the Reaction of  $C_6F_6$  with Nitromethane.

sufficient to guide an interpretation of the energetics. As shown in Tables 9 and 10, the calculations indicate that deprotonation of methyl nitrite 5 by methoxide to form anion 6 is 25 kcal/mol endothermic. This calculated acidity of 5 (405 kcal/mol) is close to that observed experimentally for dimethyl ether (407 kcal/mol).<sup>112</sup> In both  $\text{CH}_3\text{OCH}_2^-$  and 6, the carbanion is attached to an oxygen atom, so polar effects should be comparable. There is no possibility of any extra "dipolar stabilization" in  $\text{CH}_3\text{OCH}_2^-$ . In view of the similarity in acidity therefore, it is unlikely that there is any dipolar stabilization involved in the (M-H) anion of 5. In absolute energies, carbanion 6 is the least stable, then methyl nitronate 8 and nitrosomethoxide 12 are comparable and 51 kcal/mol more stable than 6. Finally, 9 and 10 are 30 kcal/mol more stable than 8 and 12. For the conjugate acids, the calculations place methyl nitrite at -1.8 kcal/mol (more stable) from nitromethane, while experimentally it is less stable by +2.0 kcal/mol.<sup>113</sup> The calculated acidity of nitrosomethanol 13 agrees well with the observed bracketed acidity of the conjugate acid of  $60^-$  from methyl nitrite, though note that no zero point energy correction has been applied, to convert the calculated  $\Delta E$  to  $\Delta H$ .<sup>110,111</sup> The calculations thus support 12 as the structure of  $60^-$  from methyl nitrite.

One further line of information arises from linear free energy relationships. The acidity of  $\text{HOCH}_2\text{N}=\text{O}$  as an alcohol can be predicted from the  $\rho_I$  for the gas phase acidities of  $\text{RCH}_2\text{OH}$ .<sup>58</sup> Using a revised value of  $\rho_I$  of 20.3 kcal/mol<sup>65</sup> and  $\sigma_I(\text{NO}) = 0.37$ ,<sup>71</sup> a  $H_{\text{acid}}$  of 364.5

Table 9.

*Ab initio* Calculations on (M-H) Anions from Isomers of  $\text{CH}_3\text{NO}_2$ .

| Neutral Species                       |    | $\Delta\Delta E_f^a$ | Anion                                   |      | $\Delta\Delta E_f^a$ | $\Delta E_{\text{acid}}^b$ | $\Delta H_{\text{acid exp.}}$ |
|---------------------------------------|----|----------------------|-----------------------------------------|------|----------------------|----------------------------|-------------------------------|
| $\text{CH}_3\text{NO}_2$              | 7  | (0.0)                | $\text{CH}_2=\text{NO}_2^-$             | 8    | (0.0)                | 351.8                      | 356.4 <sup>c</sup>            |
| $\text{CH}_3\text{ON}\ddot{\text{O}}$ | 5  | -1.8                 | $^-\text{CH}_2\text{ON}\ddot{\text{O}}$ | 6    | 51.3                 | 405.0                      |                               |
| $\text{HOCH}_2\text{NO}$              | 13 | -13.1                | $^-\text{OCH}_2\text{NO}$               | 12   | -0.2                 | 364.7                      | (368) <sup>d</sup>            |
| $\text{OCHNHOH}$                      | 11 | -46.8                | $^-\text{OCH}=\text{NOH}$               | 9,10 | -30.5                | 368.1                      |                               |

a=6-31+G//6-31+G, Gaussian 86. All values are kcal/mol relative to first compound in the column.

b= $\Delta E(\text{anion}) - \Delta E(\text{neutral}) + 365.7$  kcal/mol.

c=Ref. 65.

d=this work.

Table 10.

Calculated Thermochemistry for Possible 60<sup>-</sup> u Anion Structures.

| Reaction                                                                 | $\Delta E^a_{\text{rxn}}$ |
|--------------------------------------------------------------------------|---------------------------|
| MeO <sup>-</sup> + MeONO -> MeOH + <sup>-</sup> CH <sub>2</sub> ON=O (6) | +25                       |
| MeOH + CH <sub>2</sub> =NO <sub>2</sub> <sup>-</sup> (8)                 | -26                       |
| MeOH + <sup>-</sup> OCH <sub>2</sub> N=O (12)                            | -26                       |
| MeOH + <sup>-</sup> OCH=NOH (9)                                          | -57                       |

a=6-31+G//6-31+G, Gaussian 86, kcal/mol

kcal/mol is calculated, quite close to the observed acidity of  $368 \pm 4$  kcal/mol for the  $60^-$  from methyl nitrite and the calculated  $\Delta E_{\text{acid}}$  of 364.8 kcal/mol.

Based on all these lines of argument, it is concluded that the  $60^-$  anion from methyl nitrite has structure 12. There are two reasonable mechanisms for formation of 12. As shown in Figure 9, path A involves initial formation of 6 in an ion/molecule complex, followed by unimolecular rearrangement through a cyclic intermediate 14, which breaks the ring N-O bond to give the final oxyanion 12. It might be argued that 14 could just as easily cleave a C-O bond to open to 8, of stability comparable to 12. To examine this point, semi-empirical molecular orbital calculations were used to explore the reaction pathways postulated here. These were employed due to the prohibitive cost of investigating reaction surfaces of this complexity with *ab initio* calculations. Most existing semi-empirical methods are notorious for not obtaining reasonable energies when dealing with N-O bonds: the MNDO method<sup>74-76</sup> calculates methyl nitrite to be -40 kcal/mol (more stable) from nitromethane (experimental: +2 kcal/mol less stable), while AM1,<sup>77,78</sup> an improved version of MNDO, results in methyl nitrite being -22 kcal/mol from nitromethane. These methods are clearly not appropriate to the present problem. The recent PM3 Hamiltonian,<sup>94</sup> however, places methyl nitrite +6.8 kcal/mol from nitromethane, in the right direction and of the right order of magnitude. Thus this newer method<sup>114</sup> is used to examine various reasonable pathways on the reaction surface. For the isomerization of

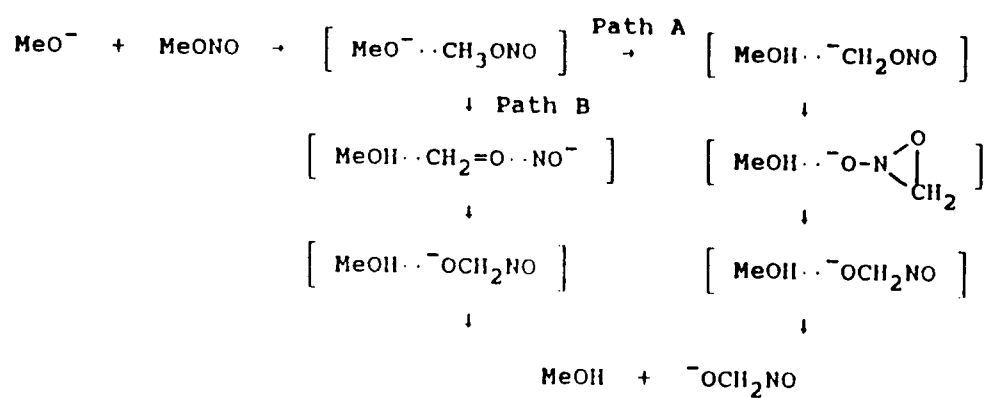


Figure 9.  
Formation of the Rearranged Anionic Structure  
for the (M-H) Anion from Methyl Nitrite.

$\text{CH}_2\text{ONO}$  ( $\Delta H_f(\text{PM3}) = -10.7 \text{ kcal/mol}$ ) to  $\text{OCH}_2\text{NO}$  ( $\Delta H_f(\text{PM3}) = -38.7 \text{ kcal/mol}$ ), a barrier of  $7.6 \text{ kcal/mol}$  is found. The geometry of the transition state is roughly that of 14, but with the nitrogen of the NO group  $2.0 \text{ \AA}$  from both the C and the O in the nominal three member ring. This is not an exact transition state (based on one negative frequency) since the C-O-N bond angle in 6 was simply reduced until a maximum in energy was found, at  $89.5^\circ$ . Structure 14 at the PM3 level is not an intermediate; no stable point could be found on the reaction surface for such a cyclic structure, using any reasonable bond lengths. No simple transition state for the isomerization of 6 to 8 could be found, either, but based on an extensive survey of geometries it is thought that any pathway must involve a minimum  $\Delta H > 50 \text{ kcal/mol}$ . This is consistent with the need to break a C-O bond, costing energy, before the  $\text{CH}_2$  group can rotate, to stabilize the charge by resonance delocalization. For the isoelectronic neutral system,  $\text{NH}_2\text{ONO}$  rearranging to  $\text{NH}_2\text{NO}_2$ , a barrier of  $22 \text{ kcal/mol}$  has been calculated at the MCSF/6-31G\*\*//4-31G level.<sup>115</sup>

Another more likely mechanistic possibility is path B in Figure 9, an  $\text{E}_2$  type elimination in the ion/molecule complex, followed by nucleophilic addition of  $\text{NO}^-$  to the carbonyl group. The net reaction to free  $\text{NO}^-$  and formaldehyde is estimated to be exothermic by  $-3.8 \text{ kcal/mol}$ ,<sup>65</sup> but if the  $\text{NO}^-$  bonds to the formaldehyde to give 12, the reaction enthalpy is about  $-26 \text{ kcal/mol}$ . In such a complex, there is no simple pathway for the intermediates formaldehyde and  $\text{NO}^-$  to go to  $\text{CH}_2=\text{NO}_2^-$ . The  $\text{E}_2$  pathway B seems more likely than the rearrangement

pathway A for energetic reasons, as well. Based on the *ab initio* calculations, plus a reasonable estimate of the complexation energy of -15 kcal/mol for methanol plus  $^-\text{CH}_2\text{ONO}$ , the ion/molecule complex for the nonrearranged  $\text{MeOH}\cdots^-\text{CH}_2\text{ONO}$  is about 10 kcal/mol endothermic, relative to the reactants methoxide and methyl nitrite. This energy barrier would have to be overcome by rearrangement of the carbanion during proton transfer, which seems unlikely. In contrast, the  $\text{E}_2$  pathway should be mechanistically facile, and result in a product ion/molecule complex considerably more stable than the reactants. For  $\text{MeOH}\cdots^-\text{OCH}_2\text{NO}$ , an estimate for the complex is about 45 kcal/mol more stable than the reactants, thus providing the driving force for the reaction. All points on path B should be exothermic, relative to the reactants.

#### D. Conclusions

Different fragmentation and reactivity pathways indicate that the structures of the (M-H) anions from nitromethane, methyl nitrite and formyl hydroxamate are not the same. For the (M-H) anion from methyl nitrite the structures outlined in Table 10 have been considered. All but 12 have been ruled out because of calculated energetics, reactivity and fragmentation experiments. No distinctive reaction of the alkoxide structure expected for 12 was found, other than its apparent proton affinity.

These results raise a serious question regarding the practice of measuring approximate acidities by the bracketing method. Were such a

test applied here, the acidity obtained for methyl nitrite would be wrong by at least 25 kcal/mol. It is imperative that the structure of anions produced in this fashion be verified by the various reaction techniques available.

## Chapter 4

### Instrumentation Modifications and Experimental Studies for Detection Mode Comparisons

#### A. Introduction

As part of this investigation, the home-built ion cyclotron resonance mass spectrometer (ICR-MS) has been upgraded to include Fourier transform (FT) detection capabilities by the addition of an IonSpec system. The IonSpec system contains three parts: a universal host controller for communication with the IBM PC, a synthesizer programmer to control the Rockland frequency synthesizer, and a transient digitizer for data collection. The original design of the spectrometer was described in Chapter 1. In order to accommodate FT detection both hardware and software modifications were necessary.

For the hardware portion, the key differences between the rapid scan (RS) and the FT experiments are the generation of the excitation frequency and the data acquisition. In the RS experiment, the Rockland frequency synthesizer is controlled directly by the IBM PC, but because of the need for a fast frequency "chirp" in the FT experiment, additional hardware is necessary and provided by the synthesizer programmer (SP) of the IonSpec system. For data acquisition in the RS experiment, the 30 kHz A/D converter on the Tecmar Lab Master board and the IBM PC memory are sufficient. However, in the FT experiment the requirement for a fast (2 MHz) A/D converter and accompanying fast

memory must be met by the transient digitizer (TD) in the IonSpec system. These modifications are described in detail below.

Although the software is based on programs originally written by Phil Geraci, John Bartmess and Rick Hunter, major modifications were necessary. The majority of the modifications are in the experimental control and data manipulation programs. Data manipulation is limited for two reasons. 1) The number of spectra that are accessible at the same time is limited because it is impossible to have more than two arrays dimensioned at 64K with the current PC-1 computer and the 640K DOS memory limitation. 2) The time required to perform calculations can quickly become excessive for more than 32K data points. Therefore, one program, FTMAIN, was developed primarily for experiment control and data collection, and other programs were developed to perform data manipulations with the intention of using an IBM PS/2 system to do these calculations. The programs are described in detail below.

#### B. Hardware Modifications

The nature of a Fourier Transform (FT) detection scheme requires several special electronic devices. The Nyquist theorem<sup>116</sup>, which states that signal sampling must occur at a rate that is at least twice the frequency of the signal, imposes strict requirements on the analog-to-digital (A/D) conversion rate and accompanying hardware. For FT-MS, signals in a 1 Tesla field and cubic cell generally have a frequency in the 25-1000 kHz range. This range necessitates a 2 MHz A/D converter and computer memory that can store the digital values at

that rate. In addition it is desirable to excite all the ions simultaneously. In reality this is accomplished by a frequency "chirp"; that is, a frequency sweep that lasts for approximately 1 msec. This requires careful control of the Rockland frequency generator.

Figures 9 and 10 are block diagrams of the configurations used for the RS and FT experiments, respectively. In the next few paragraphs descriptions of the individual components not described in Chapter 1 will be given, followed by a summary of the overall system.

**B.1 - IBM PC** The IBM PC is the interface between the user and the instrument. For control of instrumental parameters and data acquisition, Tecmar boards were installed in two expansion slots in the chassis of the IBM PC. The first board is the Tecmar Lab Master board. This board contains a 16-channel A/D converter, a 2-channel D/A converter, 24 input/output (I/O) lines and five timer/counters.<sup>117</sup> A 30 kHz A/D converter is employed in the RS experiment for data acquisition and in both experiments for sampling voltage levels that represent several experimental parameters. The analog signal may be sampled as single ended input, pseudo differential input or true differential input. The RS experiment uses single ended input.<sup>118</sup> The Lab Master A/D circuitry provides 12 bit resolution.<sup>117,118</sup> The RS and FT experiments employ 8 of the I/O lines and one of the timers for the pulse generation necessary for the time-resolved experiment.<sup>118</sup> The Lab Master timing/counting circuitry uses an AMD 9513 integrated chip and contains a 1MHz oscillator for the AMD 9513.<sup>117</sup> Timer 1 pre-

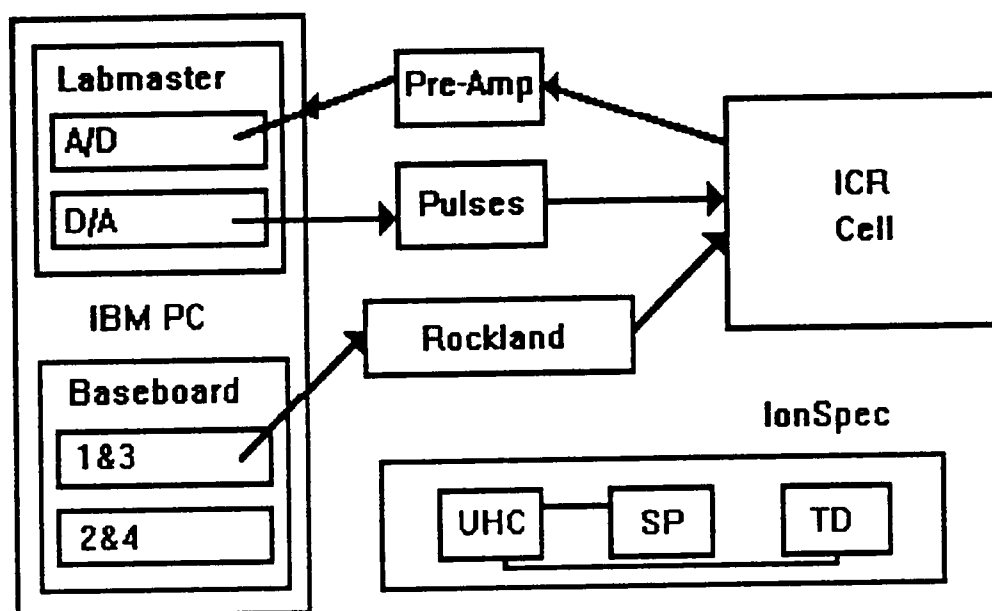


Figure 10.

Block Diagram of System Configured for Rapid Scan Experiment.

(See text for definitions of abbreviations.)

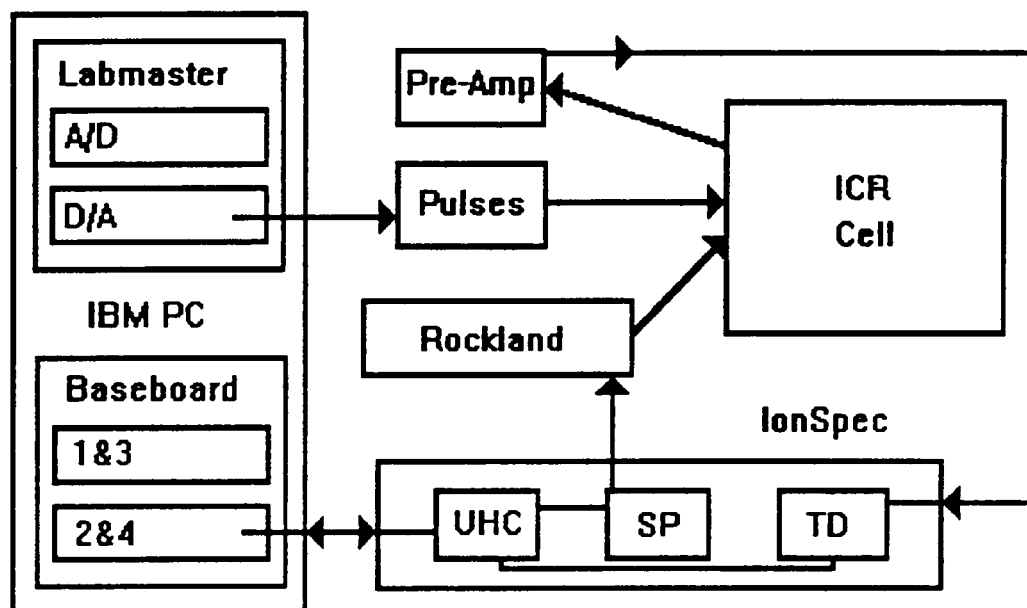


Figure 11.

Block Diagram of System Configured for Fourier Transform Experiment.

(See text for definitions of abbreviations.)

over 1 MHz in 1 msec is shown in Figure 14. For this spectrum 1000 steps of 1 kHz were taken at an amplitude of 9000 mV. However, the output was taken from the 1 V p-p output from the Rockland instead of the variable output. One thing that must be noted is that the "chirp" does not cover the entire programmed range and the relatively constant peak-to-peak voltage is over a more limited range. The ideal waveform would be a square-wave for frequency vs. amplitude. The observation that the discrete nature of the frequency sweep caused the excitation frequency amplitude to over the range scanned was made very early by McIver and others.<sup>122-124</sup> To characterize the cause of the ripples (the smaller deviations within the frequency sweep) and skirts (the large deviations at the edges of the sweep), the frequency sweep parameters were varied. The number of steps seemed to have the greatest influence on the resolution and general waveform, and hence a trade-off is made; while fewer steps allow for a faster chirp, they also produce a poorer excitation waveform. Therefore, the programmed frequency range was always started at least 15kHz lower than the lowest desired frequency and extended to at least 15kHz higher than the highest desired frequency, and all chirps were set for 1 msec duration. A 1 msec duration always corresponds to 1000 steps, and the increment is set accordingly. The timing for the start of the A/D converter is very important. To generate the spectra of the frequency "chirps", the A/D converter was triggered to begin at the beginning of the frequency "chirp" and the RF signal was input to the TD. However, for an actual FT experiment, it is desirable to begin the A/D

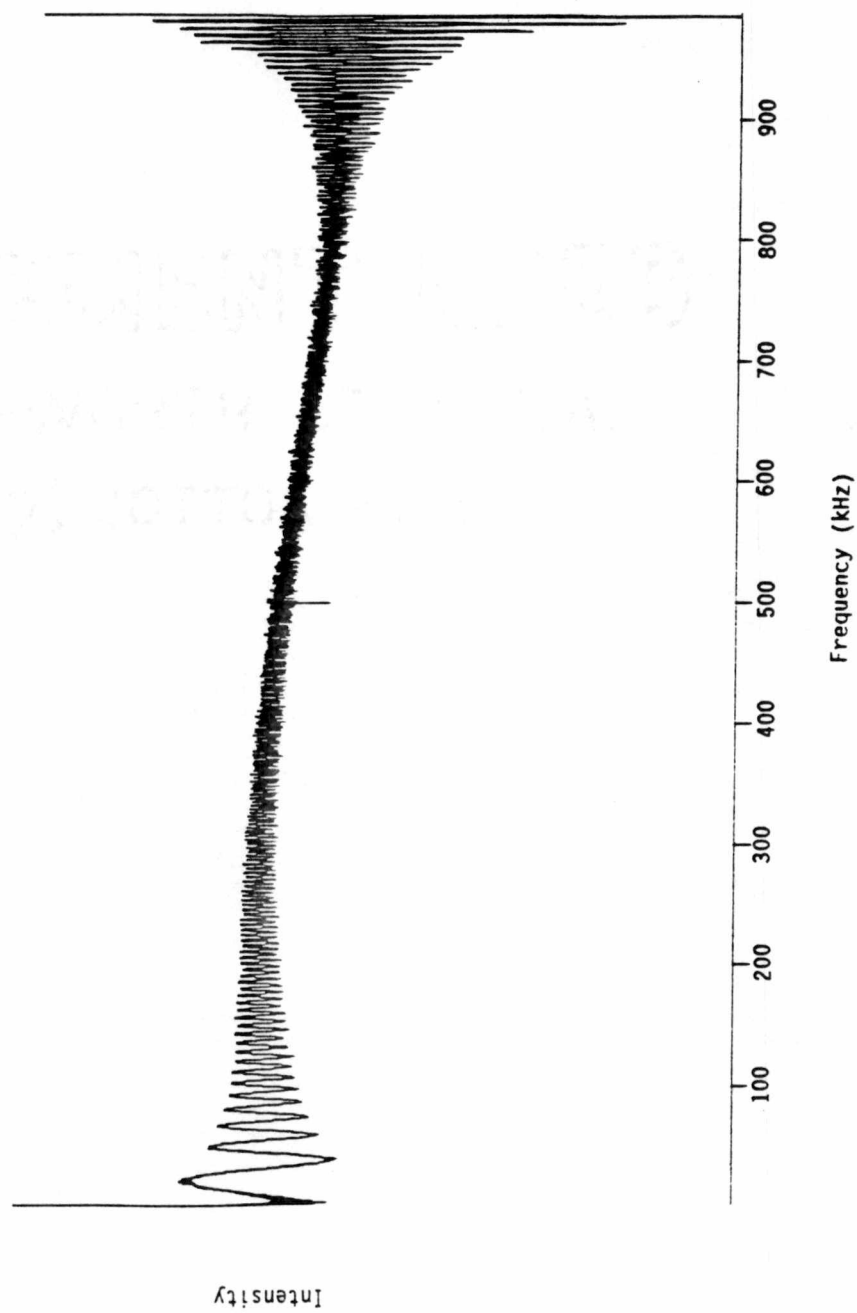


Figure 14.

Magnitude Mode FT Spectrum of Excitation Frequency "Chirp".

conversions at a short, but precisely known, time after the end of the frequency chirp to prevent the acquisition of residual rf noise. The IonSpec system provides a way to begin the A/D conversions 512 nsec after the ENDCHIRP status signal is activated. To test this operation a simple RC circuit was constructed that generates a voltage ramp when the switch is closed (Figure 15). The output of this circuit will be dependent on time and is triggered with the detect pulse which also begins the frequency "chirp". The test was performed in two ways: 1) to begin with the start of the frequency "chirp" and 2) to begin 512 nsec after the end of the frequency "chirp". The results are shown in Figure 16. A point can be related to a time relative to the beginning of the A/D conversion because of the precise sampling intervals. As can be seen, the timing is performing as expected. More discussions on the RF excitation frequency characteristics with respect to the observed spectrum are in Chapter 5.

**B.3 - RF Amplifier** The RF Amplifier (RF Amp) may be added to the Rockland circuitry to boost the amplitude of the excitation frequency. In an FT experiment, the fast frequency sweep requires much larger peak-to-peak amplitudes to deposit the same power in the ions as in a RS experiment. With the RF Amp the range of available voltages is 0-80 V p-p, and without the RF Amp the range is 0-10 V p-p. The characterization of programmed amplitudes versus observed amplitudes at the cell is given in Figure 17. With the RF Amp the calculated correlation from a least-squares fit is 0.995 with a slope of 0.966 volts at cell per volts programmed. Without the RF Amp, the calculated

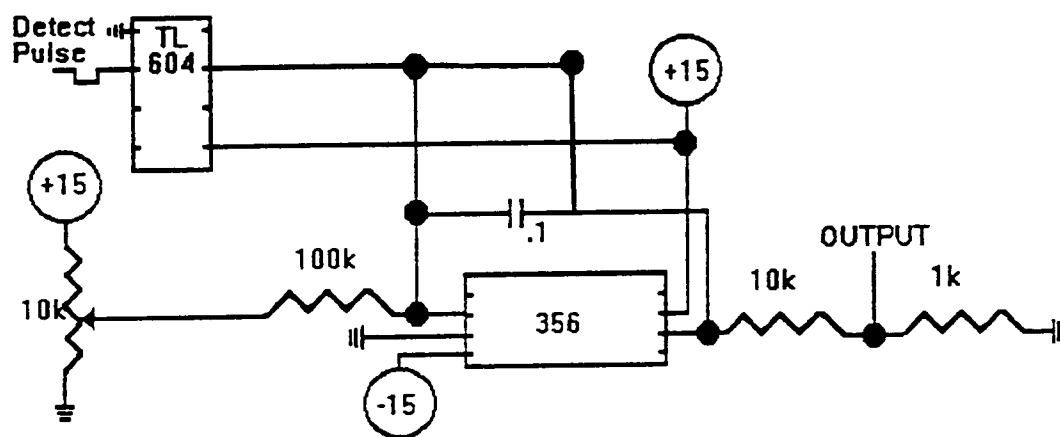


Figure 15.  
RC Timing Circuit.

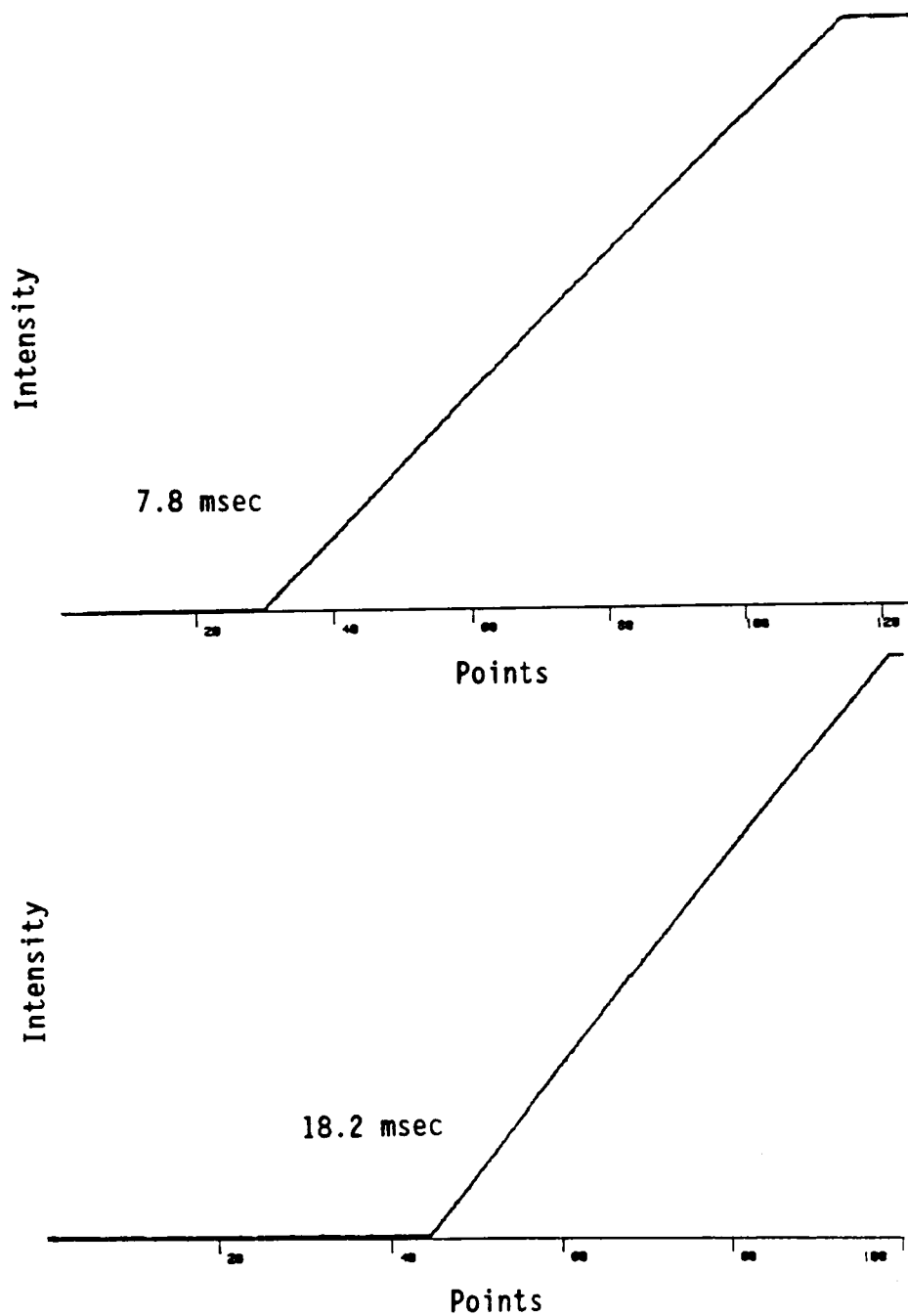


Figure 16.

Timing Circuit Results.

(Top = Begin A/D with "chirp", Bottom = Begin A/D 512 nsec after "chirp", please see text.)

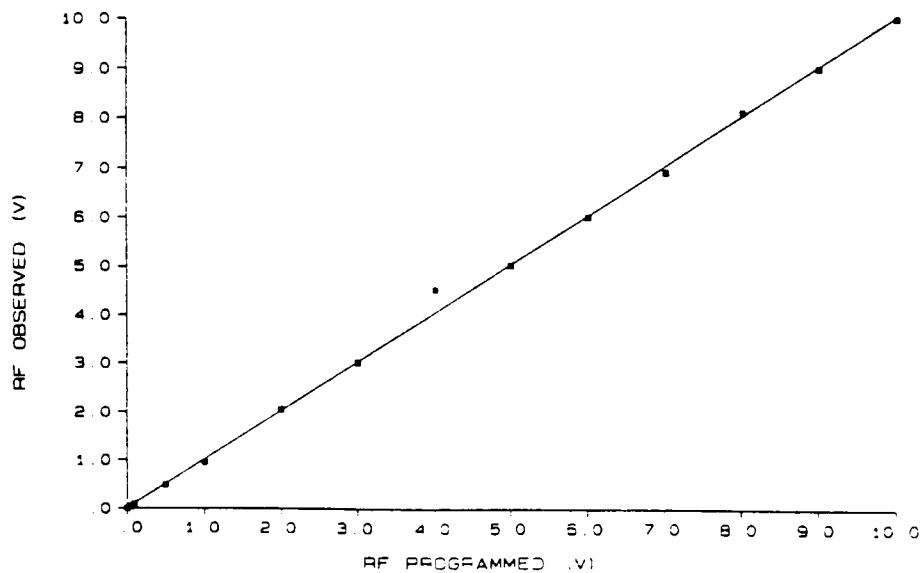
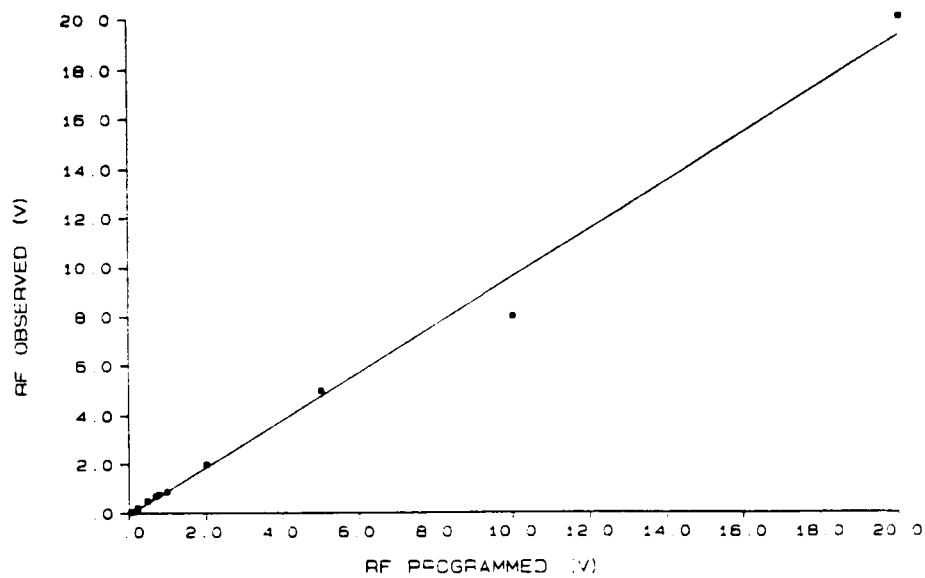


Figure 17.

Programmed Excitation Frequency Amplitudes vs. Observed  
Amplitudes at the Cell.

(Top = with RF Post Amp, Bottom = without RF Post Amp, please see text)

correlation from a least squares fit is 0.999 with a slope of 1.00 volts at cell per volts programmed.

**B.4 - Summary** The remainder of the hardware was left virtually unchanged. The key differences between the rapid scan experiment and the FT experiment are the generation of the excitation frequency and the data acquisition. In the rapid scan experiment, the Rockland frequency synthesizer is controlled directly through the IBM PC, but because of the need for a fast frequency "chirp" in the FT experiment, it is controlled by the SP of the IonSpec system. For data acquisition in the RS experiment, the 30 kHz A/D converter provided by the Tecmar Lab Master board and the computer memory are sufficient. However, in the FT experiment, the need for a 2 MHz A/D converter and accompanying fast memory, must be met by the TD in the IonSpec system.

To mechanically change to the FT setup from the RS setup, there are two things that must be done. First, the input to the Rockland frequency synthesizer must be changed from the IBM PC cable to the IonSpec system cable. Second, the output of the detector preamplifier must be changed from the IBM PC to the TD in the IonSpec system.

### C. Software Modifications

The software is largely derived from programs written by Phil Geraci, Rick Hunter and John Bartmess. It is composed primarily of two divisions: experimental control and data manipulation/overlay. The source code is a combination of FORTRAN code and assembly code. This

section will give a description of the major modifications in the software.

C.1. - Outline of Software FTMAIN is the name of the main program that executes the FT experiments. The flow of FTMAIN is outlined in the Appendix. The Main menu has five options: 1) perform an unquenched FT experiment, 2) perform a quenched FT experiment, 3) manipulate data, 4) plot data, 5) save or read data files. Each of these options will display new menus and a response of 99 will return to the main menu. If values are changed in any of the menus that make the parameters different from their state when the data was acquired, a warning message will be displayed.

C.2. - Experiment Setup Some of the parameters that must be set in the FT experiment include number of scans, RF amplitude, mass range, sampling rate for the A/D and pulse timing. (See Table 11.) These parameters are accessible through either the FT Experiment Quenched Mode or FT Experiment Unquenched Mode menus. Once the user has set the programmable parameters, the computer must do calculations to generate information needed by the IonSpec system and for pulse generation. After setup is complete, the FORTRAN code calls a series of Assembler code programs to perform the experiment. Upon completion of an experiment, the IonSpec system transfers the data to the IBM PC.

C.3 -Data Manipulation The data received by the IBM PC is the time domain signal (TDS); to obtain mass or frequency information from the TDS, the FT of the data must be taken. Equation 21 describes the TDS

Table 11.

## Programmable Parameters and Common Values.

| Parameter      | Range of Common Values | Comments                                                              |
|----------------|------------------------|-----------------------------------------------------------------------|
| magnetic field | 0.7 - 1.1 Tesla        | The magnetic field must be set by hand, but is used for calculations. |
| # of A/D pts.  | 4096-16384 points      | Must be multiple of 2. Not > 32768.                                   |
| # of scans     | 10-100 scans           | > 100 may overload memory.                                            |
| Hz increment   | 1-50,000 Hz            | Usually set to give 1 msec chirp.                                     |
| RF amplitude   | 1000-3000 mV           | See Chapter 5.                                                        |
| Low mass       | 30-100 amu             | Also changes high frequency. Must obey Nyquist theorem.               |
| High mass      | 50-200 amu             | Also changes low frequency.                                           |
| Low frequency  | 1-500 kHz              | Also changes high mass.                                               |
| High frequency | 10-1000 kHz            | Also changes low mass. Must obey Nyquist theorem.                     |
| Sampling rate  | 1-2000 ksps            | Must obey Nyquist theorem.                                            |
| Detect width   | 1-8 msec               | Should be as long as chirp.                                           |
| Grid width     | 5-30 msec              | See Chapter 5.                                                        |
| Detect delay   | 10-2000 msec           | "Reaction" time.                                                      |

for a single component, where  $\omega_0$  = resonant frequency,  $\tau$  = relaxation

$$f(t) = 1/2(\pi)K\cos\omega_0 t \exp(-t/(\tau)) \quad 0 < t < T \quad (21)$$

time and T is acquisition time. For a multicomponent system, the TDS consists of the sum of eqn. 21 for each component.<sup>125</sup> The Fourier transformation of the summation yields the frequency domain spectrum. The Fast Fourier Transform (FFT), introduced by Cooley and Tukey in 1965, is an algorithm that efficiently computes the FT of a data set.<sup>126</sup> The FT spectrum consists of two components, one derived from the portion of the spectrum that is in-phase with the excitation frequency and one that is 90° out-of-phase with the excitation frequency. The in-phase component is the dispersion spectrum and the out-of-phase component is the absorption spectrum.<sup>116</sup> Equations 22 and 23 describe each component:<sup>116</sup>

$$D(\omega) = (\omega_0 - \omega)(\tau)^2 / [1 + (\omega_0 - \omega)^2(\tau)^2] \quad (22)$$

$$A(\omega) = \tau / [1 + (\omega_0 - \omega)^2(\tau)^2] \quad (23)$$

However, to obtain either of these spectra, the phase spectrum must first be determined. If this information is not available, the data is usually reported as either the magnitude mode or the power spectrum. Equations 24 and 25 describe these spectra:<sup>116</sup>

$$M(\omega) = ([A(\omega)]^2 + [D(\omega)]^2)^{.5} \quad (24)$$

$$P(\omega) = [M(\omega)]^2 \quad (25)$$

In general, magnitude mode spectra are reported in FT-ICR-MS.

To improve the appearance and/or ability to obtain information from the frequency domain spectrum, several digital processes have been developed. The two most notable are apodization, or windowing,

and zero-filling. Apodization is performed on the TDS prior to performing the FT. It generally reduces the skirts (or side lobes) associated with large peaks which arise from the finite acquisition time. This process enables small peaks which may be next to large peaks to be detected.<sup>116</sup> A number of apodization functions have been proposed including: Rectangle, Hamming, and Blackman-Harris 3-term.<sup>116</sup> There have been several studies undertaken to determine the best window for the experiment being performed. Aarstol and Comisarow<sup>116,125</sup> proposed that selection of the apodization function should be determined by the dynamic range required, but they recommended that the Blackman-Harris 3-term window should be the standard choice for FT-ICR-MS.<sup>116,125</sup> The form of the Blackman-Harris 3-term window is given in equation 26.

$$BH(t) = 0.42423 - 0.49755\cos(2\pi t/T) + 0.07922\cos(4\pi t/T) \quad (26)$$

For quantitative work, Brenna and Creasy proposed the Noest-Kort function (eqn. 27).<sup>127</sup>

$$M = M * C \quad (27)$$

where:

$$M = 0.430 + 0.843\cos(\pi t) - 0.239\cos(2\pi t) + 0.043\cos(5\pi t) - 0.602U \quad (28)$$

$$C = 0.5 \exp(t/\tau - (t/\tau)^2 / (4 \ln 2)) \quad (29)$$

$$\begin{aligned} U &= (1-4t) \text{ for } 0 < t < 1/4 \\ &= (3-4t) \text{ for } 3/4 < t < 1 \\ &= 0 \text{ elsewhere} \end{aligned}$$

$\tau$  = translational relaxation constant

The other common data manipulation prior to taking the FT of the data set is zero-filling. The FT of the TDS produces  $N/2$  complex data

points (N=number of A/D points) because of the restraint of the Nyquist theorem.<sup>116</sup> The discrete frequencies are spaced  $1/T$  Hz (T=data acquisition time) apart.<sup>116</sup> If only the absorption spectrum (which deals with the real amplitude vs. frequency) or dispersion (which deals with the complex amplitude vs. frequency) is employed, effectively half of the data is not reported. Magnitude mode uses both the imaginary and real components.<sup>116</sup> However, if the TDS is extended by adding N zeroes after the last experimental data point, the FT of this data set now results in N complex data points being recovered. In addition, the discrete frequencies are  $1/(2T)$  Hz apart, because the effective sampling period has been doubled.<sup>116</sup> For quantitative work Mitchell and DeLong propose multiple zero-fills in order to obtain discrete peak heights closer to the continuous peak heights.<sup>116,128</sup> Manipulation of the TDS is done through the Data Manipulation Menu. If more than one scan has been acquired, signal-averaging may be done. A plot of the signal-to-noise (S/N) ratio versus the square root of the number of scans for FT detection is shown in Figure 18. This data was collected using the intensity of the 83 amu signal from the  $\text{CHCl}_2^+$  from chloroform as the signal. The ionization gauge pressure of chloroform was near  $4 \times 10^{-6}$  Torr, the electron energy etc. The noise level was calculated using an algorithm that calculates the standard deviation of the data and discards all points greater than 3 times that deviation. This process is repeated five times. The last standard deviation is taken as the level of the noise. The data is linear with respect to the square root of the number of scans below about 100

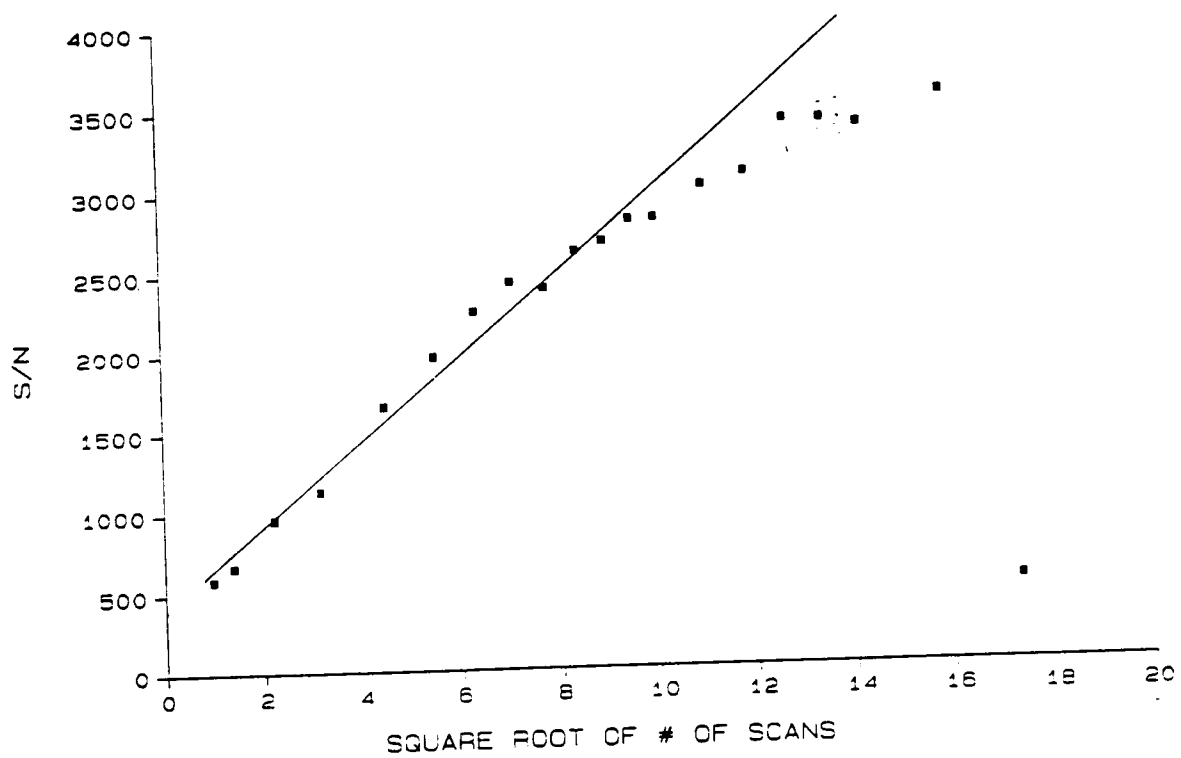


Figure 18.

Signal-to-Noise Ratio Versus the Square Root of the Number of Scans

scans. The deviation from linearity for points where more than 100 scans are acquired is believed to arise from artifacts such as overflow in the TD memory. Theoretically, for a 9 bit signal being accumulated in a 16 bit memory location, 128 scans could be acquired. If the overflow in the memory is excessive, the digitized waveform begins to appear like a square wave (Fig. 19), and the subsequent FT produces a spectrum with strong peaks at the odd harmonics of the base frequency. This phenomenon was observed for the experiment using 300 scans. In addition, low frequency noise (1-3kHz) in the present system is often much more intense than the signal. The source of this noise remains unidentified. A high-pass filter has not been employed because of the wide bandwidth of the experiment and because of the possible loss of phase information. This noise problem could contribute to the premature deviation from linearity.

Also in this menu, the number of zero-fills to perform is set, an apodization function may be selected, and either the absorption mode or magnitude mode spectrum may be chosen. Because all data acquisition is performed on an early IBM PC with limited RAM of 640 Kbytes and relatively slow computation speed of 5 MHz, the program is limited to data sets of 64K. Hence, if 32K of data are collected, only one zero-fill may be performed. In addition, it should be noted that the larger the TDS, the longer the computation time for calculating both apodizations and FT's. In general, 16K of data are acquired. With no zero-fills and no apodization, computation time is 24 sec. With 1 zero-fill and no apodization, computation time is 45 sec. With 1 zero-

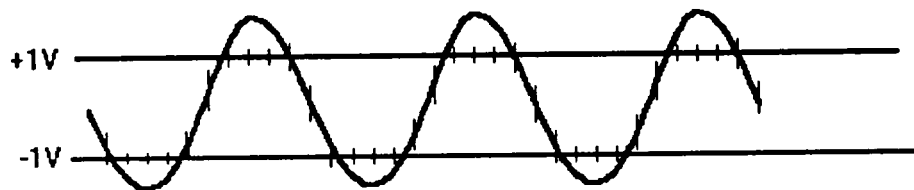


Figure 19.

Digitized Overranged Sine Wave Appears Like Square Wave.

fill and a Blackman-Harris 3-term apodization, computation time is 79 sec. This effect of excessive computation time prompted us to write separate programs for such manipulations as dividing one spectrum by another, calculating S/N ratios and segmenting the TDS prior to FT. These programs are generally run on an IBM PS/2 (16 MHz Model 50). However, the system is still not ideal, because it requires writing and reading several files to disk.

The plotting of the data is done through the Plotting menu. The data can be plotted as a mass or frequency spectrum within the range of interest; or a selected portion of the data buffer can be plotted linearly with respect to frequency. As described in Chapter 1 plots are done on a Tektronix 4006-1 CRT and hardcopy plots are generated on a Tektronix 4662 interactive digital x-y plotter. For publication quality spectra, modifications of the original plotting routines and some data manipulation was done by J. Bartmess for visual output to a VGA or hardcopy generation on a Hewlett-Packard LaserJet Printer.

For reading and writing to the disk and other parameter manipulations, access is gained through the Reading or Saving Jbuff menu. This menu allows the operator to 1) read or save data files to disk, or 2) read or save parameter files to disk, or 3) recall raw data stored immediately after the experiment, or 4) view the values of the data buffer by a screen dump, or 5) change parameters that are used in experiments and data manipulation, but are not available through other screens, such as the debug flag.

C.3 - Summary The software modifications are quite extensive. The IBM PC setup limits the capabilities of an individual program. It is impossible to have more than two arrays dimensioned at 64K; this limits the number of spectra that are accessible at once. In addition, the time required to perform calculations can quickly become excessive for more than 32K data points. However, the software designed here will collect the required data and perform simple calculations. For more extensive calculations additional programs have been written for use on an IBM PS/2 which has a much faster clock speed and hence reduces the time required to perform calculations.

To switch between rapid scan and FT detection requires the switching of two cables - the Rockland input and signal output. In addition the operator must switch from the ICRRUN program to the FTMAIN program.

#### D. Slow Passage

From the ICR equation (eq. 2, p. 5) it can be seen that the mass-to-charge ratios can be scanned in at least two ways. The magnetic field can be scanned at a constant excitation frequency, or the excitation frequency can be scanned at constant magnetic field strength. In the earlier designs of the ICR mass spectrometers, a marginal oscillator detector was employed while the magnetic field was scanned. In such a scheme, the ion being detected was excited and it completely relaxed before the next ion was excited. This mode of operation has been called slow passage.

For the studies done in Chapter 5, the slow passage mode of our home-built ICR spectrometer was resurrected to permit comparisons between all three modes of possible detection. Attempts were made to operate the experiment under computer control by stepping the excitation frequency by several Hertz and acquiring several scans at each interval. However, because of difficulties in tuning the signals, much of the data was acquired under analog mode. In this mode, the excitation frequency was held constant while the magnetic field was swept over  $\pm 0.1$  Tesla. The capacitance bridge detector output was directly recorded on an x-y plotter or could be observed on the Tektronix 5110 oscilloscope. The pulses were generated using the old pulse box which was not computer-controlled.

To switch to the analog mode for the slow passage experiment from the setup for rapid scan, the pulse timing cables must be exchanged, the Rockland frequency synthesizer must be taken out of remote (the frequency and attenuation must be manually set), and the magnet must be set to sweep.

### E. Conclusions

This chapter has described the modifications that were necessary to setup the ICR mass spectrometer to acquire data in all three available modes: slow passage, rapid scan (no modifications) and Fourier transform. While the modifications for the Fourier transform experiment were quite extensive, switching effectively between all three modes is not very difficult. It only requires switching a couple

of cables and changing the software. With the spectrometer able to operate in all three modes, comparison of the observed signals from known chemical systems is intended to see if the signal intensities vary depending on the type of detection scheme used.

## Chapter 5

### Comparison of Detection Modes for Ion Abundance Measurements in Ion Cyclotron Resonance Mass Spectrometry

#### A. Introduction

There are three modes of detection available for ion cyclotron resonance mass spectrometry (ICR-MS): slow passage (SP), rapid scan (RS) and Fourier transform (FT). One of the primary uses of ICR-MS is to measure gas-phase physical-organic properties such as basicity or rate constants, which require accurate ion abundance measurements. To date there has been no study to determine if the type of detection mode will affect the results. For this reason, as detailed in Chapter 4, the existing system has been equipped to perform these experiments.

Certain events during detection are fundamentally different for each mode. The first step of detection is to excite the ions to a larger orbital radius; following this translational excitation the ions relax to the center of the cell. Different paths exist for this translational relaxation.<sup>116</sup> For instance, the ions could undergo ion/neutral collisions that knock them out-of-phase with the coherent ion packet so they are not detected.<sup>116</sup> One of the fundamental differences in the three detection modes is the time, relative to this relaxation, in which the ions are detected. In the SP experiment, only the absorbance is detected. In other words the detector is only "listening" while the ions are being excited. In the RS experiment, both the absorbance and emission are being detected. The detector is

on throughout the frequency sweep, so that as the excitation frequency passes through the resonant frequency, the absorbance is observed; but after the excitation frequency passes by the resonant frequency, the emission is observed. In the FT experiment, only emission is observed since the ions are excited prior to turning on the detector. Another fundamental difference between the detection modes is the multiplex advantage of the FT detection scheme.<sup>116</sup> In FT experiments, all the ions generated with each pulse cycle are detected simultaneously. This multiplex advantage is often reflected in signal-averaging, since the detection time for the entire spectrum has been reduced tremendously. In RS experiments, all the ions generated with each pulse cycle are detected individually as the excitation frequency sweeps through their resonant frequency. In SP experiments, only one frequency is determined per pulse cycle, so hundreds of pulse cycles are needed to compile enough data to construct a spectrum. In light of these differences, there are some questions that can be raised. First, in the rapid scan experiment the time for detection can be several hundred milliseconds long; are the ion populations changing during this time-frame? Second, in the FT method, the ions are detected before they have a chance to translationally relax; does this affect the ion abundances? Finally, if the experimental parameters, particularly pressure, change with time, then the SP experiment could suffer.

In addition to the fundamental issues outlined above, there are several experimental parameters that affect the quantitation of ion

abundances in the ICR cell. They can be characterized as experimental conditions and data manipulations. Some of the experimental conditions investigated include the excitation rf characteristics, grid pulse duration, filament current, and emission current. The data manipulations that are available for FT data are extensive, but only a limited number were investigated: division by the excitation magnitude spectrum, apodization and segmented FT calculation. For the comparison of detection methods in ICR MS, three systems were studied. The isotope ratios from  $\text{CHCl}_2^+$  were measured as a function of experimental parameters and in some cases as a function of data manipulation techniques. After experimental conditions were determined that lead to the most accurate ratios, the gas-phase basicities of two sets of compounds were measured in an attempt to study some of the more fundamental issues such as whether the detection mode perturbs the equilibrium in ion/molecule studies. The selection of which pairs of compounds to study was carefully made. To measure equilibrium ratios properly, each set of compounds was selected so that the compounds had gas-phase basicity values within a few kcal/mole of each other. Then, one system was chosen so that the difference in mass was relatively small and the other so that the difference in mass was relatively large. It was anticipated that the latter experiment would show manifestations of the fundamental questions outlined above.

## B. Isotope Ratio Measurements

B.1. Introduction Isotope ratio measurements were performed on the

$\text{CHCl}_2^+$  fragment from chloroform for the purpose of determining how experimental parameters and data manipulation affected the quantitation of ion abundances. As mentioned above, excitation rf characteristics, filament current, grid pulse duration and emission current were studied. In addition comparisons were made on the same set of data for zero-filling, apodization, division by the excitation magnitude spectrum and segmented FT calculations. The goal is to determine the best circumstances to use for acquisition of quantitative data when the correct answer is not known *a priori*.

**B.2. Experimental** The ICR mass spectrometer described in Chapters 1 and 4 was used to acquire the data in the quenched mode with detect delays of 100 msec. The grid width, emission current, filament current and excitation rf amplitude were varied according to the experiment. Typical operating pressures were  $3\text{-}5 \times 10^{-7}$  Torr as read on the ionization gauge. Chloroform was obtained from commercial sources and was not further purified. All FT spectra were calculated in the magnitude mode.

**B.3. Excitation rf characteristics** The excitation rf characteristics, such as amplitude and waveform, directly affect the magnitude of the detected signals.<sup>116,129,130</sup> In an ideal system, the magnitude of the detected signals is directly proportional to the excitation rf amplitude, until the ions are ejected from the cell. For FT experiments, several excitation methods have been proposed: 1) "burst" excitation (an intense rf excitation at one frequency) which was used in the first FT experiment,<sup>32,129</sup> 2) "chirp" excitation, or a fast

frequency sweep,<sup>33</sup> 3) "impulse" excitation which utilizes a very short dc pulse,<sup>131</sup> 4) random or pseudo-random time-domain noise<sup>116</sup> which is impractical because of the extensive calculations involved, and 5) Stored Waveform Inverse FT (SWIFT) method, which requires additional electronics devices and computer capabilities.<sup>132,133</sup> Although the SWIFT method generally produces the best (with respect to waveform) excitation waveform, most FT ICR-MS is performed using the "chirp" excitation, because of its inherently simpler implementation. For the FT experiments in this study, the "chirp" method was employed.

In the chirp method of excitation the frequency is swept very quickly, usually over several hundred kHz in 1 msec (Figure 14, p. 69). The skirts (the large amplitude errors at the beginning and end of the frequency sweep) and in-band ripples (the smaller amplitude errors within the excitation frequency range) are caused by the discrete steps used to generate the spectrum<sup>129</sup> and can have maximum amplitude errors of 17% of the average amplitude.<sup>122,123</sup> It has also been reported, and observed here, that the number of steps and the duration of the frequency sweep has a marked effect on the excitation waveform.<sup>129</sup> In general, the excitation waveform is closer to ideal with more steps and longer duration; however, to maintain the simultaneous excitation, there is a trade-off. Two methods, division of the signal spectrum by the excitation spectrum<sup>123,124,129</sup> and application of an algorithm proposed by Noest and Kort,<sup>122,123</sup> have been used to correct for this effect. The division method has been employed for manipulation of some of the data.

In addition to the waveform affecting the quantitation of ion abundances, the amplitude of the excitation rf can affect peak ratios within a spectrum.<sup>134-137</sup> One theory proposed to explain this effect is based on z-axis oscillation (the movement of the ions parallel to the magnetic field) excitation and possible ejection.<sup>136,138</sup> There are reports that the effect can be mass-discriminatory<sup>134,136</sup> and is worse for transient excitations, such as the "chirp" method.<sup>136</sup> This effect can be reduced by increasing the trapping plate voltage and decreasing the excitation amplitude.<sup>134-136</sup> Recently suggestions have been made for new cell designs, including the use of wire mesh screens in front of the cell plates, that may minimize this effect.<sup>139</sup> Another theory for the sometimes large errors in ion abundances measured with large excitation rf amplitudes is based on space-charge effects.<sup>140</sup> The effect of excitation rf characteristics is studied here for all three modes of detection in the isotope ratio measurements.

The results for the studies of the excitation rf characteristics are presented in Figures 20-23. In Figure 20, where the intensity of the signal at mass 83 vs. the rf amplitude is plotted, it can be observed that the relationship between the magnitude of the observed signal and the magnitude of the excitation rf is linear in the range of 0-3000 mV rf peak-to-peak amplitude. It is assumed that above 3000 mV of excitation rf, the ions are absorbing enough translational energy that they are being ejected from the cell. The theoretical ejection voltage for ions in a 2.54 cm cell and excitation time of 1 msec in a 1.3T field is 2.4 V p-p, slightly less than what is observed.<sup>116</sup> The

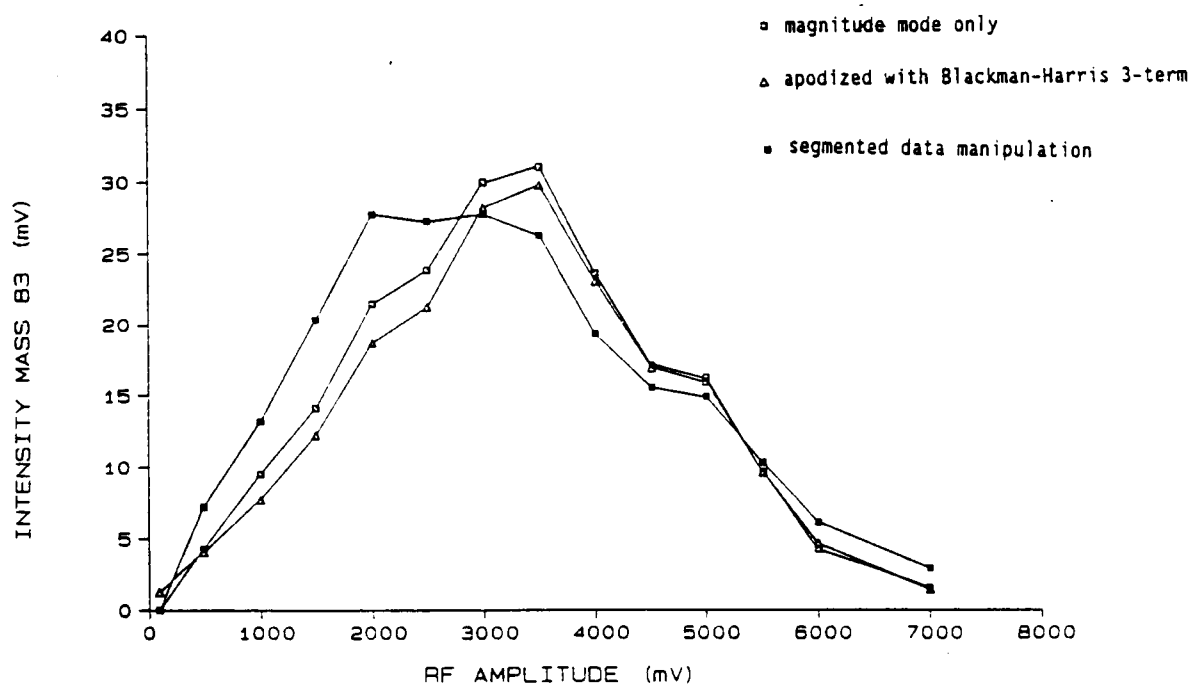


Figure 20.

Intensity of 83 amu vs. Excitation Rf Amplitude with FT detection.

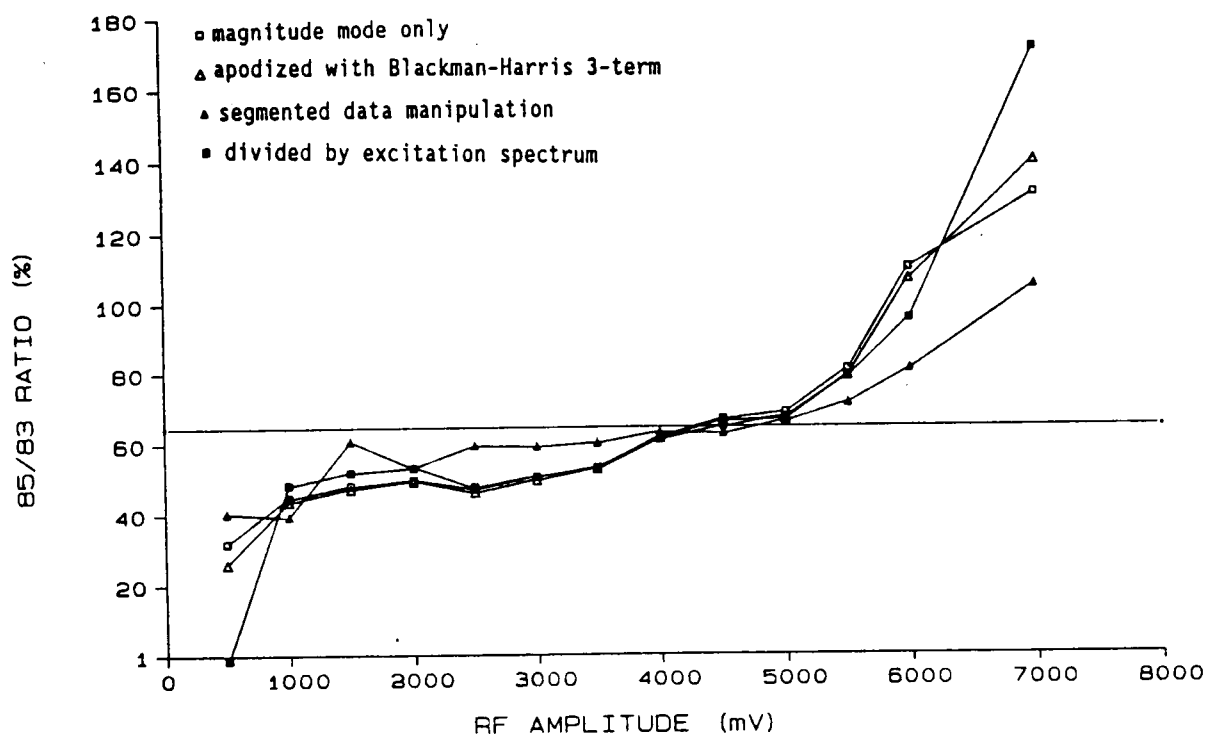


Figure 21.

Isotope Ratio of 85/83 vs. Excitation Rf Amplitude FT Detection.

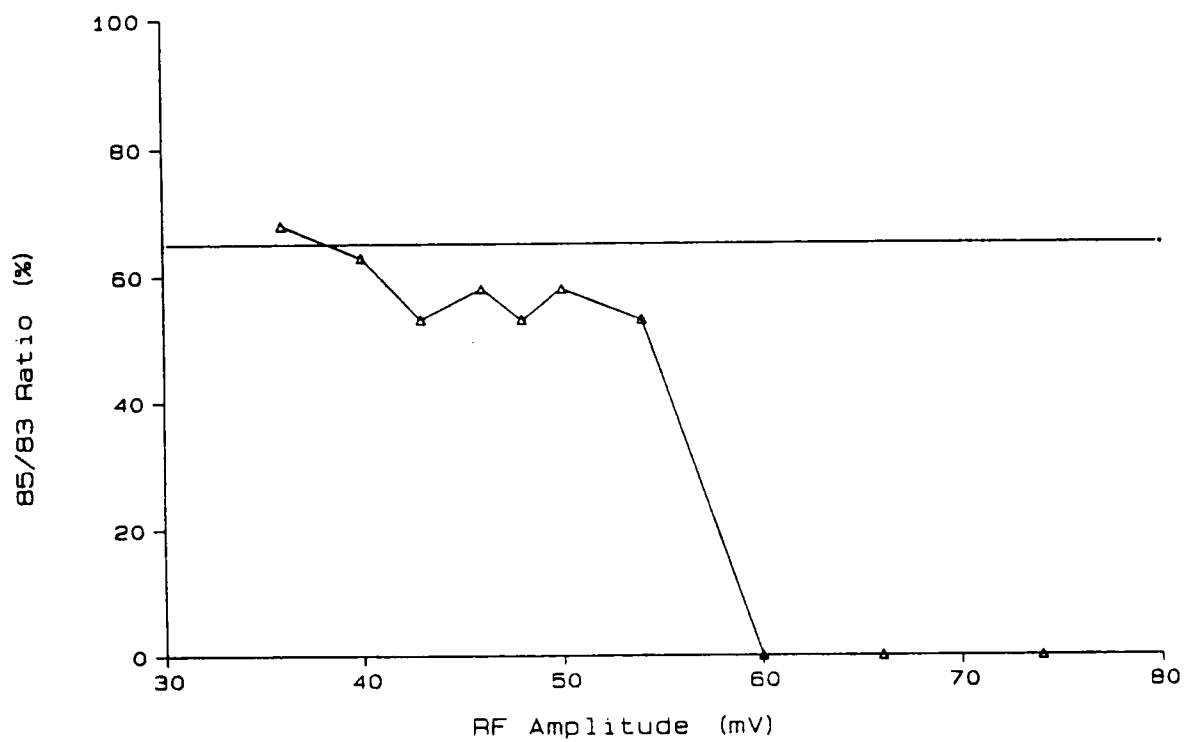


Figure 22.

Isotope Ratio of 85/83 vs. Excitation Rf Amplitude

Slow Passage Detection

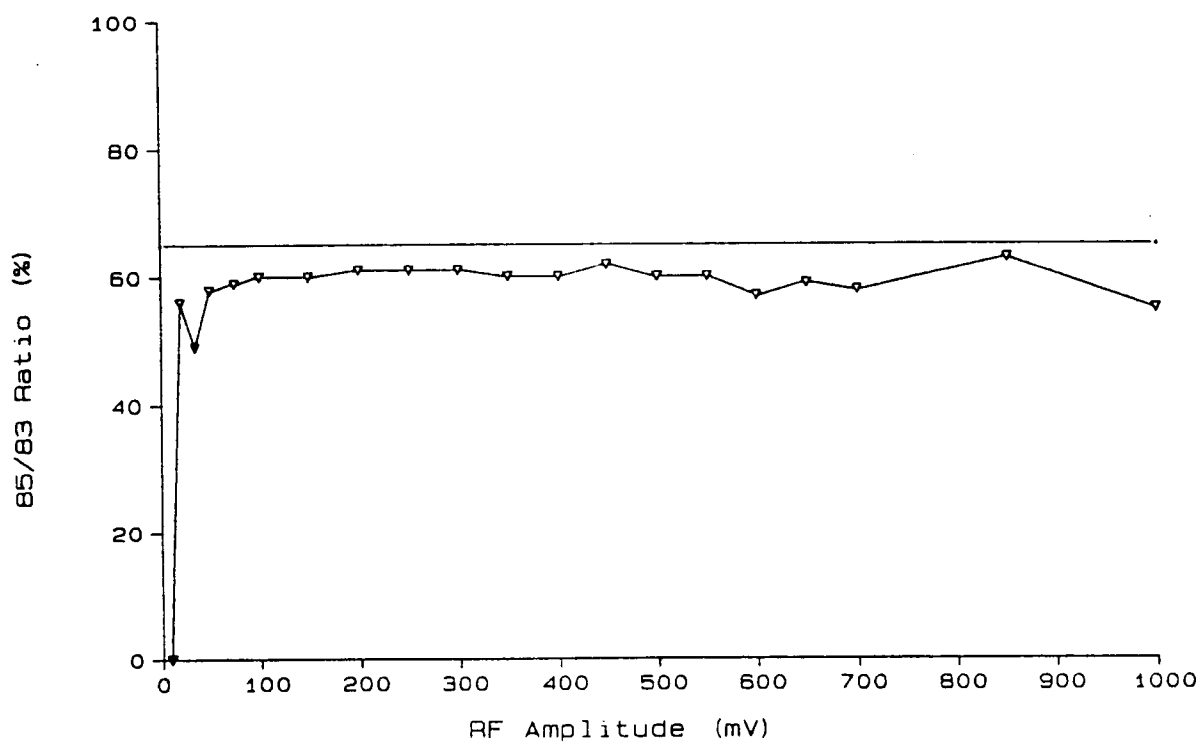


Figure 23.

Isotope Ratio of 85/83 vs. Excitation Rf Amplitude

Rapid Scan Detection.

higher experimental value could be related to the bandwidth of the excitation rf. In the above calculations, it has been assumed that the bandwidth is larger than the time for excitation.

In order to check the accuracy of the measured ion abundances, it is helpful to look at the measured isotope ratios (Fig. 21-23). There are two assumptions made concerning EI and isotopic abundances. One is that the cross-section for ionization is essentially the same for isotopes of the same molecule of close molecular weight, and the second is that enough ions are sampled to get a statistical distribution. In these experiments approximately 10,000 ions are detected per pulse cycle. The FT data presented in Figure 21 show a sloping plateau for rf values from about 1000 mV to 5000 mV of excitation rf. All lines are slightly lower than the theoretical value at 65%, until they begin to climb around 5500 mV. Figure 22 presents data from a similar slow passage experiment. The first two points are close to the theoretical values, but then the line falls to a plateau that is well below the theoretical value. The rapid scan data are displayed in Figure 23. Compared to the FT and SP data, the RS signal appears to be much less affected by the changes in rf amplitude. However, the plateau portion of the graph is again below the theoretical value. The deviation from theoretical could arise from ejection of the higher mass ion,<sup>134,136</sup> but this seems unlikely for ions so close in mass. Another possibility currently under study in R.C. Dunbar's group is the possibility of space-charge effects<sup>140</sup> (see discussion on Number of Ions below.). One conclusion that can be drawn

from these data is that all the detection methods generally report the 85/83 ratio as slightly less than the 65% expected theoretically.

While this result is disappointing in its accuracy, it is reassuring that under optimal conditions, all three methods yield similar ratios.

**B.4 - Number of Ions** There are two variables that combine to determine the number of ions produced during the grid pulse: grid pulse duration and emission current (which is indirectly related to the filament current). For a typical experiment an estimation of the number of ions being formed is calculated as follows. The cross section,  $\sigma$ , will be defined as the number of ions formed divided by both the number of electrons and number of target molecules per  $\text{cm}^2$ . The number of electrons can be calculated from the emission current and grid pulse duration. If the emission current is  $1 \mu\text{A}$  and the grid pulse duration is  $0.010 \text{ sec}$ , the number of electrons is  $6 \times 10^{10}$ . The number of target molecules per  $\text{cm}^2$  can be calculated from the pressure,  $0.4 \mu\text{Torr} \times 1/3$  baratron factor for  $\text{CHCl}_3$ ; the volume of the electron beam;  $0.600 \text{ cm}^3$  and the area of the electron beam,  $0.315 \text{ cm}^2$ . If  $\sigma$  is estimated to be  $1.6 \times 10^{-16} \text{ cm}^2$  for a  $70\text{eV}$  process, then the number of ions is  $8 \times 10^4$ . As the above calculations show, the number of ions is directly dependent on the grid pulse duration and the emission current, which is related in an indirect way to the filament current. The grid pulse duration is the time during which electrons are admitted to the ICR cell and primary ion formation is occurring. It has been reported for FT experiments that longer grid pulse durations decrease the error in ion abundance measurements.<sup>135,141</sup> However, other sources report more

accuracy with low ion densities.<sup>142</sup> The overlapping effects of grid pulse duration, filament current and emission current could explain these differences. If the first study was conducted at very low ion densities, errors in the measurements of small signals would be more apparent at the shorter grid pulse durations. The effects of these variables are studied here in the isotope ratio measurements. (Fig. 24-26) Measurements were taken under two conditions: varying the grid pulse duration and constant number of ions. The experimental parameters that were not varied were: magnetic field at 13.3 T, in FT scan 210-270 kHz and in RS scan 215-272 kHz.

Figure 24 is data collected by FT detection and RS detection at constant filament current while varying the grid pulse duration. While both lines show a negative slope, the FT data show a much more pronounced effect as the grid pulse duration is extended. Generally, the best data are at shorter grid pulse durations. The second set of RS data was taken under conditions that attempted to keep the number of ions constant by varying the emission current and grid pulse duration so that their product was a constant, either 56  $\mu\text{C}$  or 160  $\mu\text{C}$ . Figure 25 plots the grid pulse duration versus the isotope ratio at constant emission current; both lines have a slightly negative slope indicating shorter grid pulse durations are desirable. In addition the line corresponding to the lower emission current is more accurate. For the data where the filament current is plotted versus the isotope ratio, (Fig. 26) the best results are obtained at lower filament currents and for the data collected at lower emission currents. These

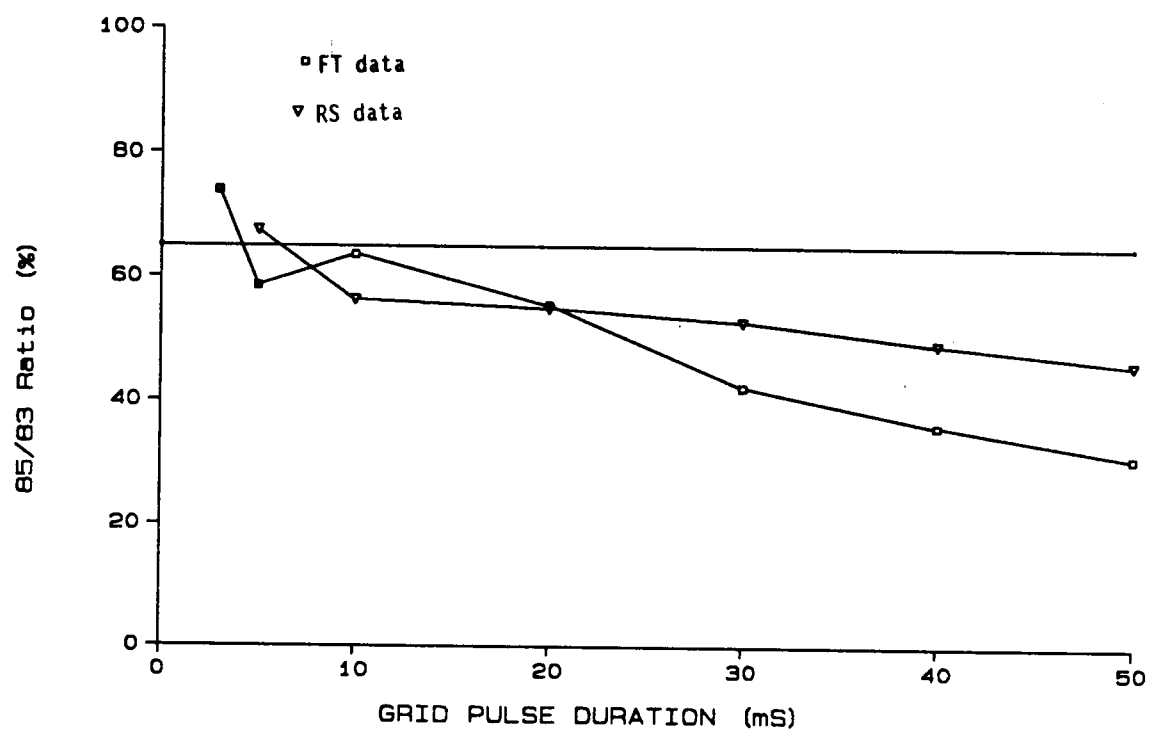


Figure 24.  
Isotope Ratio 85/83 vs. Grid Pulse Duration  
at Constant Filament Current.

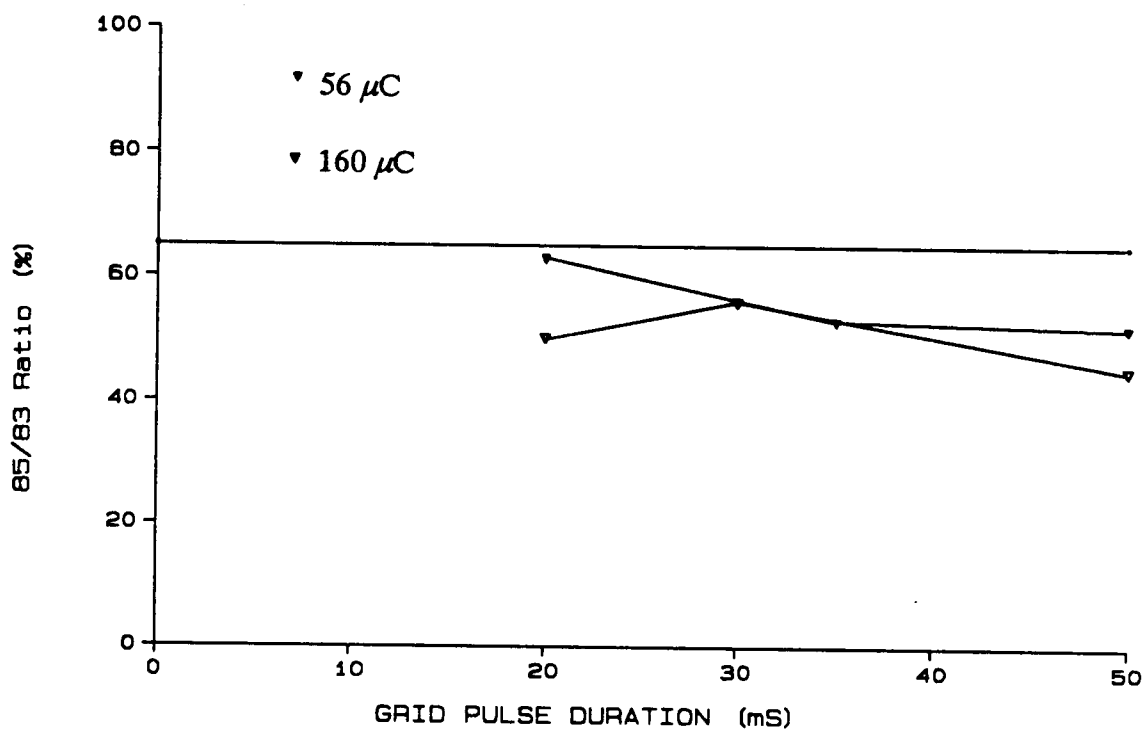


Figure 25.  
Isotope Ratio 85/83 vs. Grid Pulse Duration  
at Constant Emission Currents.

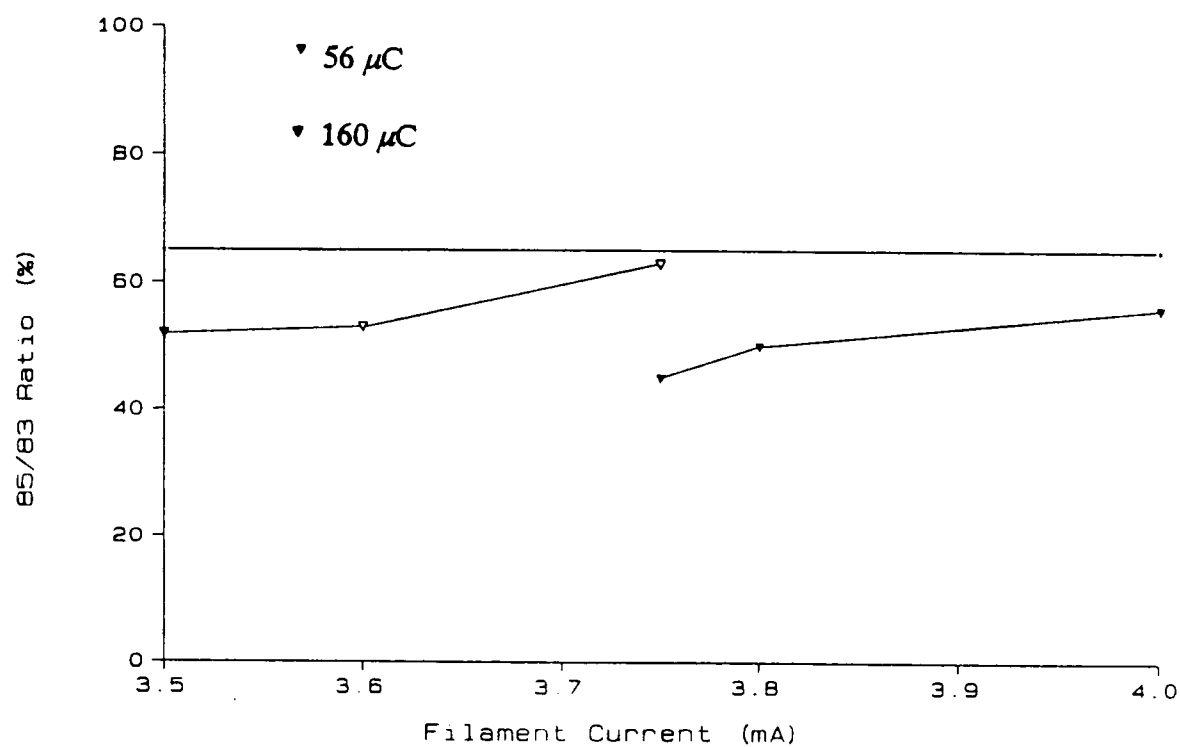


Figure 26.  
Isotope Ratio  $^{85}/^{83}$  vs. Filament Current with Constant  
Number of Ions.

results suggest that it is the number of ions in the cell that are affecting the isotope abundance ratios. A conclusion that can be drawn from the observed data is that the best conditions for collecting data are with relatively short grid pulse durations and relatively low emission currents. However, these conditions will probably not give the best sensitivity, since the S/N ratio will decrease because of the smaller number of ions being generated under these conditions. Also, in comparing the RS data and the FT data, both detection methods seem to be more accurate with the lower number of ions, although the RS data do not appear to be as affected by this condition as the FT data.

**B.5 Trapping Plate Voltages** The trapping plate voltages are the dc voltage levels imposed on the plates to restrict the drift of ions parallel to the magnetic field. Recent reports show that peak ratios can be distorted by variations in the trapping plate voltages.<sup>141</sup> Gross and coworkers recommend the use of high trap plate voltages (larger than 0.74V).<sup>142</sup> The plate voltage levels interact with the z-axis ejection also mentioned under excitation rf amplitudes.<sup>135,136</sup> While no definitive data were collected to examine this phenomenon, data were generally collected at trapping plate voltages of 1.8-2.2 V. One of the effects of lowering the trapping plate voltage is that the ions will physically spread out more, possibly reducing space charge effects. Another possible effect is that ions with extra translational energy may overcome the dc potential and escape from the cell, thus perturbing quantitation of ion abundances.

**B.6 - Data Manipulations** For any method using digitized data, proper data manipulation is critical. Several algorithms have been suggested that aid in the extraction of information from the available data, besides zero-filling and apodization, which were discussed in Chapter 4. Some of the new transform methods proposed include: a zoom transform, which increases the number of data points across a peak;<sup>143</sup> a linear prediction method, which avoids the intensity errors introduced by different relaxation constants;<sup>144</sup> and a maximum entropy method, which is used for very small data sets.<sup>145</sup> This study did not investigate any of these methods.

Another source of error in ion abundance measurements arises from the fact that different ions have different translational relaxation rate constants. As mentioned in the introduction, ions are excited to a larger orbital radius in order to facilitate detection. Relaxation from this excitation primarily occurs through ion/neutral collisions, and hence the signal strength decays as a function of them. These translational relaxation rate constants may be different for different ions. Two methods have been proposed to extract the initial amplitudes and translational relaxation rate constants from a FT data set: linear prediction and segmented FT.<sup>123,128,144,146</sup> In the linear prediction method, the data is fit to a model using a least-squares procedure. After the first fit, the frequency and relaxation constants are known, but a second least-squares procedure must be performed to obtain the phase and initial amplitude information.<sup>144</sup> The segmented FT method divides the existing data set into overlapping segments starting at

well-defined times. The FT for each segment is calculated and the natural logs of the magnitude of the peaks of interest are plotted against the offset time (Fig. 27).<sup>128</sup> The y-intercept can be assumed to be the amplitude at time zero and the slope contains information for calculating the relaxation constant.<sup>128</sup> For even more accurate determinations, the data can be extrapolated back to the beginning of the detection sequence.<sup>128</sup> Only the segmented FT method was studied here.

The data from the experiments of the intensity (or ratio) versus the excitation rf amplitude shown in Figures 20 and 21 were further manipulated. The data in Figure 20 are plotted on three lines, one for magnitude mode FT calculations, one for the same data but with a Blackman-Harris apodization and one for the same data but with the segmented FT performed on it. Of the three lines the most accurate one and the one least sensitive to the changes in the rf amplitude is the segmented FT line. At the extremes, the apodization results fall slightly below the simple FT calculations. In Figure 21, an additional line for manipulation by division by the excitation spectrum is added to the graph. Once again, the best results appear to be from the segmenting procedure. The division procedure appeared to have only a slight effect if any on the results and worsens the accuracy at the extremes. While data manipulations could aid in extracting valuable information from the data set, only minor improvements were observed here.

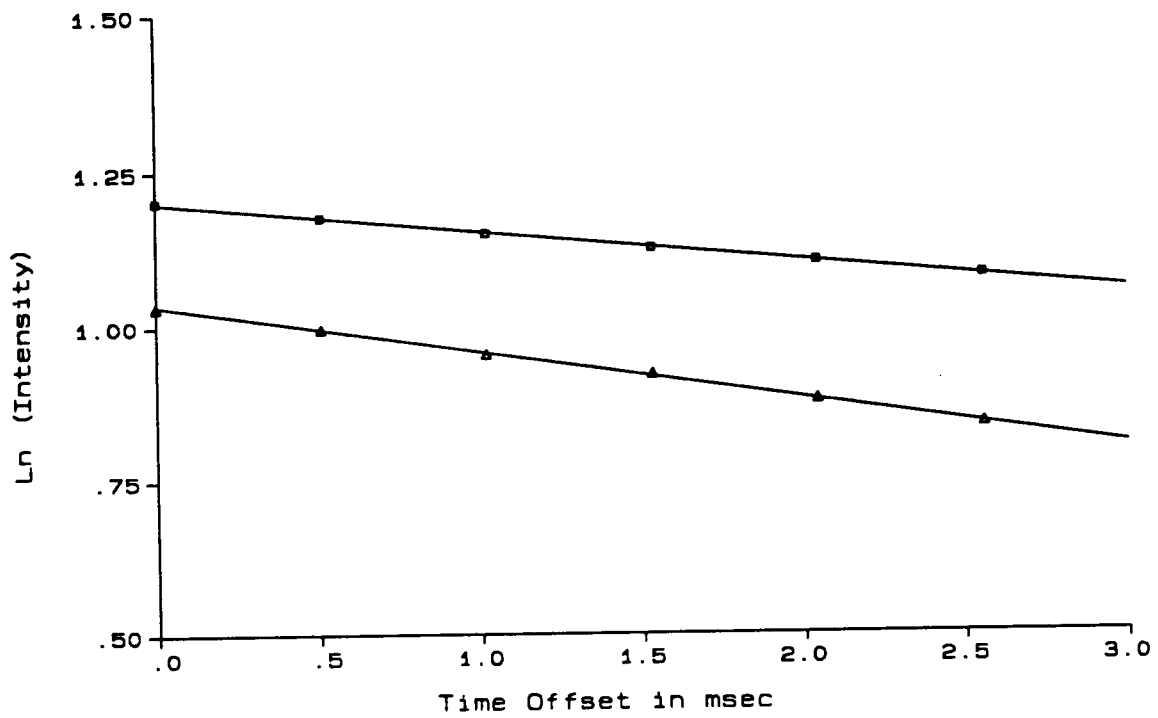


Figure 27.  
Segmented FT Data.

**B.7 -Conclusions** The isotope ratio measurements have been used to identify some of the operational parameters that give the most accurate ion abundance measurements. These parameters appear to be the same for all detection methods, although the sensitivity of the methods to the parameters does vary. The general guidelines discovered here include operating at excitation rf amplitudes near (but below) the ejection level, operating under conditions that lowers the ion density in the cell (low filament current, low emission current and short grid pulse durations), and using appropriate data manipulations such as division by the excitation spectrum or segmenting of the data.

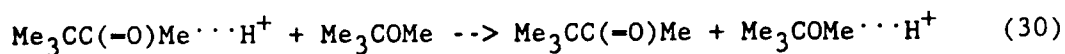
### C. Basicity Measurements

**C.1 Introduction** ICR MS is commonly used for measuring gas-phase physical-organic data, such as rate constants and equilibrium constants. Concerns about the possibility that the choice of detection method could perturb the ion/molecule system under study prompted some preliminary work looking at gas-phase basicity. The relative basicities of pinacolone vs. t-butyl methyl ether and bromobenzene vs. methanol have been studied.

**C.2 Experimental** The ICR MS described in Chapters 1 and 4 was employed. All chemicals were obtained from commercial sources. The purities of the pinacolone and t-butyl methyl ether were checked by gas chromatography. Sample pressures were measured using an ionization gauge and were calibrated with a capacitance manometer. The experimental conditions for the slow passage experiments were:

electron energy = 25 eV, excitation rf frequency = 200 kHz, excitation rf amplitude = 25 mV and a five minute magnet sweep from 11.25 to 13.75 Tesla (or 86 to 105 daltons). The experimental conditions for the rapid scan experiments on the methanol system were: electron energy = 25 eV, rf amplitude = 400 mV, mass scan from 200-30 amu (85 - 563 kHz) at a magnetic field of 11.0 Tesla. The RS experimental conditions for the pinacolone experiments were: electron energy = 25 eV, rf amplitude = 200 mV (except as noted), mass scan from 110-78 amu (246-174 kHz), and magnetic field = 12.5 Tesla. The experimental conditions for the FT experiments on the methanol system were: electron energy = 25 eV, rf amplitude = 7000 mV (except as noted), mass scan from 26 - 330 amu (50 - 650 kHz), and magnetic field = 11.0 Tesla. The experimental conditions for the FT experiments for the pinacolone experiments were: electron energy = 25 eV, rf amplitude = 5000 mV, mass scan from 78 - 109 amu (175 - 245 kHz), and magnetic field = 12.5 Tesla.

**C.3 Results** The results of the equilibrium measurements for the experiments with pinacolone and t-butyl methyl ether are presented in Table 12. Two different sets of data were collected. The first set gives a  $\delta\Delta G_{\text{base}}$  of -0.88 kcal/mol for reaction 30, suggesting that the t-butyl methyl ether is slightly more basic than the pinacolone.



The  $\pm 0.2$  kcal/mol error generally associated with these types of equilibrium experiments,<sup>58,147</sup> encompasses all the experimental scatter seen here. The literature  $\Delta G_{\text{base}}$  values are 194.5 kcal/mol for

Table 12.

## Equilibrium Results for Basicity Measurement

## Pinacolone vs. t-Butyl Methyl Ether

| Mode | RF amp | Emiss I <sup>a</sup> | 101/89 <sup>b</sup> | K <sup>c</sup> | $\Delta G^d$ | Manipulation   |
|------|--------|----------------------|---------------------|----------------|--------------|----------------|
| SP   | 25     | e                    | 4.2                 | 4.4            | -0.88        | SP data        |
| RS   | 200    | e                    | 3.9                 | 4.1            | -0.84        | RS data        |
| FT   | 5000   | e                    | 3.7                 | 3.9            | -0.81        | Mag. Mode only |
| RS   | 50     | 2.4                  | 3.4                 | 4.2            | -0.85        | RS data        |
| RS   | 100    | 2.4                  | 3.5                 | 4.4            | -0.88        | RS data        |
| RS   | 200    | 2.4                  | 3.2                 | 4.0            | -0.82        | RS data        |
| RS   | 100    | 1.2                  | 3.5                 | 4.4            | -0.85        | RS data        |
| FT   | 1500   | 2.4                  | 3.6                 | 4.5            | -0.89        | Mag. Mode only |
| FT   | 3000   | 2.4                  | 5.8                 | 7.2            | -1.2         | Mag. Mode only |
| FT   | 4500   | 2.4                  | 1.7                 | 2.1            | -0.44        | Mag. Mode only |
| FT   | 3000   | 1.2                  | 2.6                 | 3.2            | -0.69        | Mag. Mode only |
| FT   | 1500   | 2.4                  | 4.4                 | 5.5            | -1.0         | Mag. Mode/div. |
| FT   | 4500   | 2.4                  | 1.7                 | 2.1            | -0.44        | Mag. Mode/div. |
| FT   | 3000   | 1.2                  | 3.0                 | 3.7            | -0.77        | Mag. Mode/div. |

a-measured in  $\mu A$ .

b=peak height ratios.

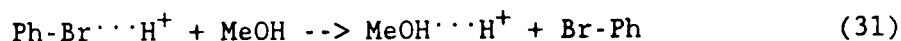
c=equilibrium constant for reaction 30.

d=calculated from the equilibrium constant for reaction 30.  
values are in kcal/mol.

e=not measured, but constant for these experiments.

pinacolone<sup>68</sup> and 194.4 kcal/mole for t-butyl methyl ether.<sup>68</sup> The second portion of the data in Table 12 was collected under various operating conditions. As concluded in Part B of this chapter, the  $\Delta G_{\text{base}}$  values that are the most reproducible were acquired under conditions of low emission current and/or excitation amplitudes near 3000 mV (close to ejection levels). Fairly large deviations from the correct value (-0.88 kcal/mol) are observed if the rf amplitude is too large or too small, especially if the emission current is also relatively high. The RS data was not as affected by the changes in experimental parameters, which also agrees with the observations made in Part B.

The results of the experiments for equilibrium basicity measurements between methanol and bromobenzene are summarized in Table 13. (reaction 31) The deviation between individual experiments is much



greater here than for the pinacolone versus t-butyl methyl ether experiment. Especially troublesome is the different signs attached to the measured  $\Delta G_{\text{base}}$  values. For the RS experiments, reaction 31 as written would be exothermic, and for the FT experiments, it would be endothermic. The  $\Delta G_{\text{base}}$  literature values<sup>68</sup> reported are 174.6 kcal/mol for bromobenzene and 174.1 kcal/mol for methanol. These values would suggest that reaction 31 as written would be +0.5 kcal/mol endothermic. Several factors could be contributing to the unreliable results obtained in the RS experiment. The longer detection period required to scan over a wider mass range may be allowing the

Table 13.

## Equilibrium Results for Basicity Measurement

## Methanol vs. Bromobenzene

| Mode | RF amp | Emiss I <sup>a</sup> | 157/33 <sup>b</sup> | K <sup>c</sup> | $\Delta G^d$ | Manipulation   |
|------|--------|----------------------|---------------------|----------------|--------------|----------------|
| RS   | 400    | 1.6                  | 3.4                 | 1.3            | -0.16        | RS data        |
| RS   | 200    | 1.6                  | 3.0                 | 1.2            | -0.11        | RS data        |
| FT   | 7000   | 1.6                  | 1.2                 | 0.5            | +0.41        | Mag. Mode only |
| FT   | 5000   | 1.6                  | 0.7                 | 0.3            | +0.72        | Mag. Mode only |
| FT   | 9000   | 1.6                  | 1.5                 | 0.6            | +0.30        | Mag. Mode only |
| FT   | 7000   | 0.8                  | 1.0                 | 0.4            | +0.54        | Mag. Mode only |
| FT   | 7000   | 0.8                  | 1.0                 | 0.4            | +0.54        | Mag. Mode/div. |

a-measured in  $\mu A$ .

b-measured peak height ratios.

c-equilibrium constant for reaction 31.

d-calculated from the equilibrium constant for reaction 31.  
values in kcal/mol.

reaction to continue as the detection is occurring. To explore this possibility some calculations have been done using the ADO trajectory rate constant. The results show for an endothermic reaction,  $k_{\text{traj}} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  and for the reverse reaction,  $k_{\text{traj}} = 2.3 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ . Here the scan was from high to low frequency, and with rate constants that would permit several collisions to occur per detection period, the low mass ion abundance could be changing during the detection. This would increase the methanol value and make the basicity value appear smaller or even inverted from the real situation. In an FT detection scheme, all the ions are excited simultaneously and then detected simultaneously. There would not be any opportunity for one ion to experience a longer reaction period than the other. The results taken for the FT show reasonable values under the determined experimental parameters (at low emission current and rf amplitudes near ejection level). The rf amplitudes in this FT experiment are much greater than in the previous experiment because of the wider frequency chirp. It has larger skirts and amplitude deviations (from an ideal rectangle) than the narrower chirp that could contribute to the deviations. However, if this were true, the division by the excitation spectrum should have an effect, but it does not. The scatter within the FT experiments is probably caused by other artifacts like the excitation rf amplitude and ion density.

**C.4 - Conclusions** Several conclusions can be drawn from these two equilibrium studies. The first one is that, as predicted by the

isotope ratio measurements, the RS experiment is in general not as affected by changes in experimental parameters as the FT experiment. The second one is that the measurements over narrow mass ranges (frequency ranges) agree very well for the three detection modes. Finally, there may be some artifacts generated in the wide mass range measurements, causing a disparity between the RS results and the FT results. One possibility to overcome this problem would be to scan sections of interest of the spectrum only, and therefore avoid the longer detection period in RS and the poorer excitation characteristics in FT. Further studies should be done on this experiment, such as using an electrometer to detect total ion currents during a quench pulse. For example, if the electrometer were connected to a side plate and instead of the usual detection pulse, a quench pulse was used, all the ions trapped in the cell would impinge on the side plate and could be detected. In order to extract individual ion currents, an ejection pulse for that ion could be applied to the cell just prior to the quench pulse. The difference in the two signals would be the intensity of the ejected ion.

#### D. Conclusions

The purpose of this chapter is two-fold: first to determine general operating conditions that are suitable for all three detection modes and second to compare some gas-phase equilibrium measurements in a preliminary attempt to identify discrepancies between the different detection modes. The best operating conditions for each mode include

using excitation rf amplitudes that are close to ejection levels and using low ion numbers. It should be noted that these conditions will not always give the best sensitivity. It is also shown that there are virtually no discrepancies between the different detection modes when narrow mass ranges are scanned, but some discrepancies appear between the RS results and the FT results when wide mass ranges are scanned. Further studies are needed to pursue this observation.

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## APPENDIX

## APPENDIX

The following is a description of program hierarchy within the FT programs.

### FTMAIN

#### I. FT experiment Unquenched Mode.

- A. Screen\* - Displays programmable parameters on screen
  - 1. Voltage\* - Gets voltage levels for this experiment
  - 2. Plcnt\* - Orders pulses by time
  - 3. Smprate\* - Converts code for sampling rate to decimal
- B. Response\* - Queries programmer for new parameter value
  - 1. Rfdb\* - Converts RF amplitude in mV to db
  - 2. Rate\* - Converts decimal sampling rate to closest code
- C. TDINIT\* - Initializes memory in TD
- D. Setup\* - Sets up experimental parameters
  - 1. K2jpul\* - Gets pulses
  - 2. Tecpl\* - Readies pulses for passing to PULFT\*
  - 3. Rfdb\* - Converts Rf amplitude in mV to db
- E. PULFT\* - Actual data collection routine
- F. Voltage\* - Gets voltage levels for this experiment
- G. TDRDO\* - Reads data buffer in TD memory into PC memory

#### II. FT experiment Quenched Mode.

A-G. (Same as #1 above.)

### III. Data Manipulation.

A. Datman\* -Displays data manipulation menu; does calculations

1. Average on/off - Turns signal averaging on/off-
2. Number of zerofills - Selects number of zerofills to do
3. Hamming apodization on/off
4. Blackman-Harris apodization on/off
5. Absorption mode FT results
6. Magnitude mode FT results
7. Perform calculation - Does all steps selected above
  - a. Apod\* - Calculates apodizations
  - b. Transform\* - Calculates transforms

### IV. Data Plotting - Does plotting to CRT and/or plotter

A. Bfpl\* - Displays plotting parameters for editing

1. Set low mass
2. Set high mass
3. Doplot\* - Does a mass plot to CRT, here
  - a. Xyz\* - Outputs to CRT or plotter, multiple calls
  - b. Bufmm\* - Finds minimum and maximum points in buffer
  - c. Width\* - Calculates FWHM for largest peak in range
  - d. Cnt2mv\* - Converts A/D counts to mV
  - e. Endplot\* - Writes text below spectrum
4. Doplot\* - Does a mass plot on CRT and plotter, here
  - a-e. (Same as #3)
5. (Not available)
6. Set low frequency

7. Set high frequency
8. Doplot\* - Does a frequency plot on CRT
  - a-e. (Same as #3)
9. Doplot\* - Does a frequency plot on CRT and plotter, here
  - a-e. (Same as #3)
10. Set starting point
11. Set ending point
12. Doplot\* - Does a point plot on CRT, here
  - a-e. (Same as #3)
13. Doplot\* - Does a point plot on CRT and plotter, here
  - a-e. (Same as #3)

V. Data saving and/or reading.

A. Savread - Saves or reads data/parameters to/from disk

1. Read file from disk
  - a. Datainfo\* - Displays relevant information about file
2. Save file to disk
  - a. Datainfo\* - Displays relevant information about file
3. Screen dump buffer - Dumps data buffer to screen
4. Recall buffer - Recalls last data stored on c: drive
5. Store buffer - Stores current data to c:
6. Change parameters - Allows some parameters not otherwise accessible to be changed, like debug flag
7. Save parameters to disk
8. Read parameters from disk
  - a. Readpara\* - Reads parameters from disk

9. Display information table

a. Datainfo\* - Displays relevant information about file

\* - self standing subroutine, if name is all capital letters then it is an assembly language routine.

## VITA

Deborah Ann Thomas, daughter of Ann E. and John M. Thomas, was born in Columbus, IN, on June 3, 1963. She began her elementary school education at Allisonville Elementary School in Indianapolis, since her family had moved there in 1965. In 1973, her family moved to Noblesville, IN, where she attended Stony Brook Elementary School and Noblesville Junior High School. In 1977, her family moved to Pell City, AL, where she graduated from Pell City High School in 1981.

She attended Transylvania University in Lexington, KY, on a National Merit scholarship. While there, she was a member of the field hockey, swimming and softball teams. She was a member of Chi Omega sorority. While at Transylvania University, she received the American Institute of Chemists Award in her senior year, was a member of Omicron Delta Kappa and was recognized in *Who's Who in American Colleges and Universities*. During her last semester of undergraduate education, she participated in the Argonne National Laboratory Student Research program, where she worked with Dr. Zoltan Nagy on an electrochemical project. She graduated *cum laude* with a Bachelor of Arts degree with majors in chemistry and computer science in 1985.

The following summer she participated in the Summer Science Alliance research program at the University of Tennessee - Knoxville, where she worked on a computer project with Dr. John Bartmess. After that summer she enrolled in graduate school at the University of Tennessee. While at UTK, she received an ARCO fellowship and awards for outstanding graduate teaching assistant during the years 1986-

1990. In 1986, she was appointed a student operator in the UTK Center for Mass Spectrometry. She was concurrently a teaching assistant for general chemistry and laboratory assistant for the graduate-course in electronics.

She has recently joined the staff of the Coordinated Instrumentation Facility at Tulane University in New Orleans, LA, where she moved with her husband, Dr. Casey C. Grimm.