

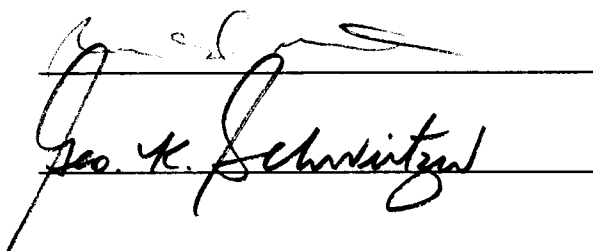
To the Graduate Council:

I am submitting herewith a thesis written by Catherine Ann Crowder entitled "Gas-Phase Ion Chemistry: 1. Electron Impact Generation of Anions 2. Diol Acidities 3. Isotope Effects on Electron Transfer Equilibria." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.



John E. Bartmess, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



Vice Provost
and Dean of the Graduate School

GAS-PHASE ION CHEMISTRY: 1. ELECTRON IMPACT GENERATION
OF ANIONS 2. DIOL ACIDITIES 3. ISOTOPE EFFECTS
ON ELECTRON TRANSFER EQUILIBRIA

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Catherine Ann Crowder

May 1989

DEDICATION

The author wishes to dedicate this work to her family: Carol and Lamar Royer, Carolyn Crowder, Tom Crowder, Telli dog, Fats the cat and the late Burton E. Crowder and Bucky dog.

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ABSTRACT

The use of ion cyclotron resonance mass spectrometry has permitted the investigation of several problems concerning gas-phase ion chemistry.

The first is a way to generate a large selection of low energy anions by electron impact for use in studying gas-phase ion/molecule reactions. Dissociative attachment is a useful process for doing this, yet few cases are known in which anions can be produced from precursor molecules with large enough cross sections to make them feasible sources of ions in mass spectrometers. A design strategy for predicting the structure of a precursor molecule that could undergo dissociative attachment with a large cross section is elucidated. We propose the structure $\text{Ar-N=N-CR}_2\text{G}$, which can undergo dissociative attachment resulting in the formation of the $\text{R}_2\text{C=G}^-$ carbanion. This precursor molecule is successful in giving the desired carbanions when the G group is either a nitro or perfluoroalkyl group.

The gas-phase acidities of a series of diols are determined. By comparing the acidities of the diols with the acidities of comparable monoalcohols, it appears that the diols do form cyclic structures of varying degree by intramolecular hydrogen bonding.

Isotope effects on the electron transfer equilibria of $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ and $\text{Ph}^{14}\text{NO}_2/\text{Ph}^{15}\text{NO}_2$ have been investigated. The results for the $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ system are in line with solution phase results which favor the formation of the light ion. The results for the $\text{Ph}^{14}\text{NO}_2/\text{Ph}^{15}\text{NO}_2$ system favor neither ion giving an equilibrium constant

of essentially one, explaining solution-phase results that are solvent/counterion dependent. A correlation between bond shortening and lengthening upon anion formation and values for the gas-phase equilibrium constants is discussed.

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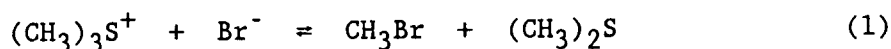
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CHAPTER I

ION CYCLOTRON RESONANCE MASS SPECTROMETRY

A. Introduction

By examining ion/molecule reactions in different solvents it has been noted that a change in solvent can alter the nature and extent of a reaction. For example, the equilibrium constant for reaction (1) is 290 in dimethylformamide and 3.6 in an 80% by weight mixture of methanol and



water.¹ Similarly, the carbon alkylation reaction of sodium β -naphthoxide with benzyl bromide will not occur when the solvent is formamide or dimethylsulfoxide but is 84% complete when the solvent is water.¹ The effect of solvent polarity on the rates of substitution reactions for alkyl halides is well known.² A solvent that stabilizes ions well will increase the rate of ionization in $\text{S}_{\text{N}}1$ reactions. A polar solvent will also increase the rate of a $\text{S}_{\text{N}}2$ reaction when the nucleophile is a neutral molecule but will slow it down when the nucleophile carries a negative charge.² The strength of an acid or base is also solvent dependent. In aqueous solution both perchloric acid and hydrogen chloride are fully ionized and considered strong acids. In anhydrous formic acid perchloric acid is still fully ionized but hydrogen chloride is not; in fact it is now considered a weak acid. When sulfuric acid is the solvent, carboxylic acids are considered bases, whereas in aqueous solution they are weak acids.³ If structure-reactivity relationships could be observed in the absence of solvent,

considerable insight into what controls these changes in reactivity might be gained. This is possible by investigating ion/molecule reactions in the gas phase, where the intrinsic properties of a system can be studied. In 1970 Brauman and Blair⁴ reported the reversal of the strengths of a series of aliphatic alcohols in the gas-phase relative to aqueous solution. This report caused chemists to re-evaluate their thoughts concerning the structure and reactivity of compounds and paved the way for more extensive gas-phase investigations. One of the most useful techniques for investigating gas-phase ion/molecule chemistry is Ion Cyclotron Resonance (ICR) mass spectrometry. This technique was used for all the studies carried out for this thesis and will be described in this chapter.

B. The Ion Cyclotron Resonance Phenomenon

When a moving charged particle is subjected to a magnetic field perpendicular to its path, the particle will move in a circular orbit. The angular frequency (ω) of this circular motion, or cyclotron frequency, is given by equation (2); where B = magnetic field strength, q = charge on particle, and m = mass of particle.⁵

$$\omega = qB/m \quad (2)$$

Equation (2) can be rearranged to yield the following equation (3).

$$m/q = B/\omega \quad (3)$$

From equation (3) one can see that if the magnetic field strength remains constant, then the m/q relationship will vary with the inverse

of the frequency. When the frequency of an applied radio frequency (rf) field matches an ion's cyclotron frequency, then the ion is said to be in resonance and can be detected. This idea is called the cyclotron principle.⁶ The first instrument developed to use this idea analytically was the omegatron. It was developed in 1950 by Sommer, Thomas, and Hipple at the National Bureau of Standards and was used to measure the mass of the proton.⁷ Modern ion cyclotron resonance mass spectrometers can be used for high resolution mass detection as well, but can also be used to investigate a variety of gaseous ion/molecule reactions. This is done by a technique known as double resonance. This technique allows one to determine the source of product ions by identifying the reactant ions in ion/molecule collisions. Double resonance can be accomplished in two ways. If the ion/molecule reaction rate depends on kinetic energy, then irradiation of the reactant ion at its resonance frequency will cause a change in the product yield. The other way of determining the relationship between product and reactant ions is by ion ejection. In this technique the reactant ion is irradiated at its cyclotron frequency with enough power to cause it to strike the sides of the cell before it has time to react, thereby causing a decrease in the product yield.^{8,9}

C. Instrumentation

The ICR spectrometer used for this research is controlled by an IBM PC personal computer using Tecmar Labmaster interface boards. A block diagram of the spectrometer is illustrated in Figure 1 (p 4). The static ion trap (McIver cell), where the ion chemistry takes place, is

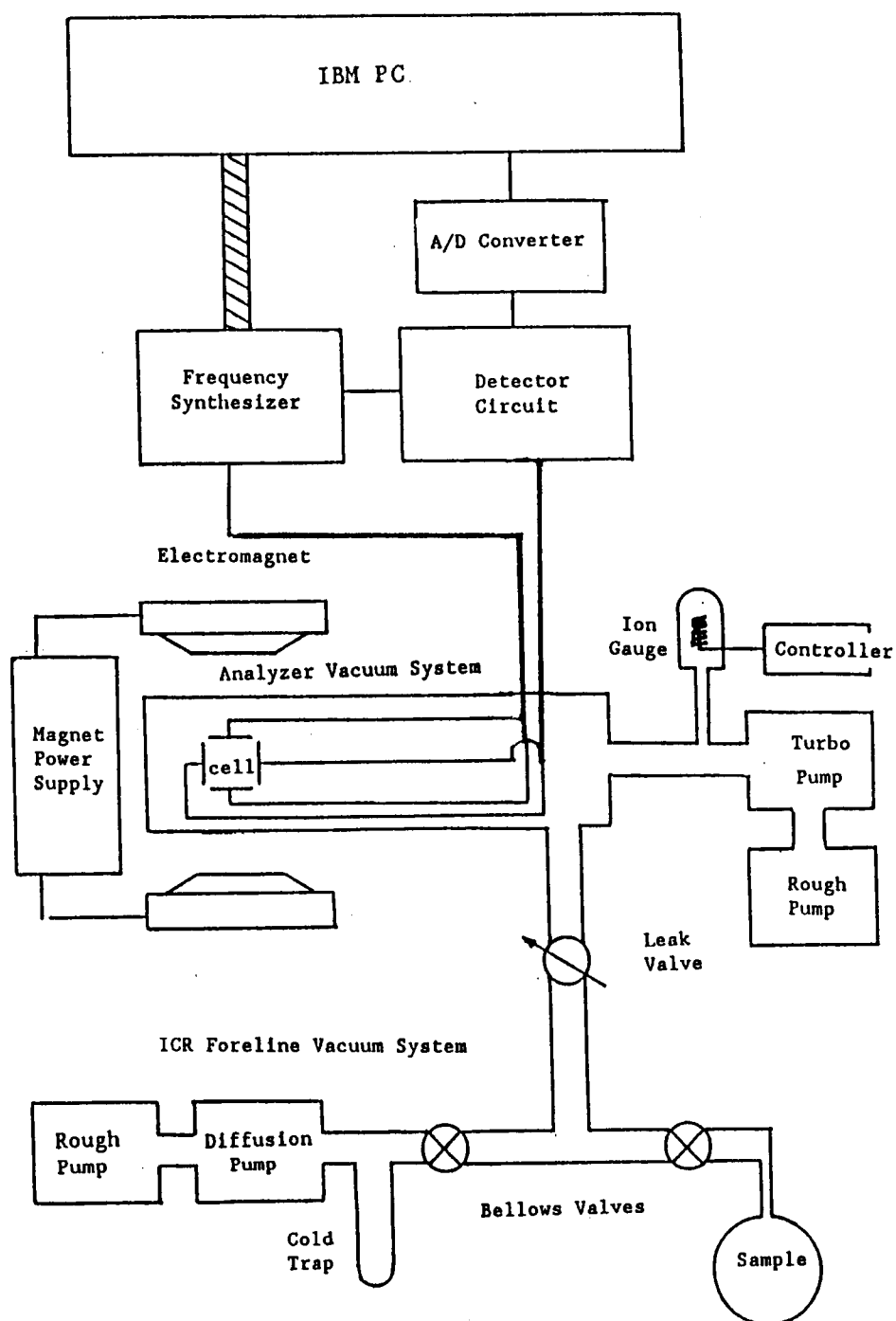


Figure 1. Block diagram of the ICR spectrometer. ¹⁰

located within a five liter analyzer manifold. The analyzer manifold is pumped by a Balzers TPU 110 Turbomolecular pump, backed by an Alcatel 2008A mechanical pump. The pressure is measured by a Huntington Mech. Labs / Bayard-Alpert ionization gauge used in conjunction with a Granville-Phillips gauge controller series 270. Following an overnight bakeout at 100°C the analyzer region of the spectrometer has a typical base pressure of 1×10^{-9} torr. The analyzer manifold is located between the poles of a Varian 9", 14 kG electromagnet that is typically operated at 10 kG. Samples are admitted to the analyzer region through Varian 951-5106 variable sapphire leak valves. Volatile samples are degassed by a freeze-pump-thaw cycle on the foreline manifold before being admitted to the analyzer region. The foreline manifold has a pressure of 1×10^{-6} torr and is pumped by a 2" CVC, VMF-21, air cooled diffusion pump. Ions are brought into resonance by sweeping the rf field using a Rockland frequency synthesizer controlled by the IBM PC. Ions are detected by using a capacitance bridge detector. Ion signals are digitized into the PC, and can also be observed on a Tektronix 5110 oscilloscope. Data can be output using a Tetronix 4662 interactive digital x-y plotter.

D. Ion Generation and Detection

Ions in the ICR cell are generated by electron impact on neutral gases. A neutral gas is leaked into the McIver cell and positive and negative ions are produced in an electron beam. The electron beam is generated by a hot rhenium filament that is not in contact with the cell, and accelerated by an electric field. The electron beam is

switched by the grid. When the voltage on the grid is more negative than that of the filament the electron beam cannot enter the cell. The reverse situation allows the electron beam to enter the cell. The electron beam current is monitored by the electron collector that is located opposite the filament. The ions that are formed are traveling at very high speeds and must be trapped in order to be detected. The ions are trapped in the McIver cell,¹¹ which is shown in Figure 2 (p 7). The ions in the cell are trapped in three directions by magnetic and electric fields. The magnetic field restrains the motion of the ions in a direction perpendicular to the magnetic field and causes them to move in circular orbits. Ions are trapped in the direction parallel to the magnetic field by weak electric fields ($\pm 1V$) applied to plates at opposite ends of the trap. The voltages can be changed on these plates depending on whether positive or negative ions are being trapped. Ions can be trapped up to several minutes in this way. During this time ion/molecule reactions can take place. In order to detect the ions an rf signal is applied to the upper and lower plates of the cell and is swept in frequency. When the applied rf of the signal generator matches the ions' cyclotron frequency, resonance occurs.¹² This resonance produces an image current on the cell plates that unbalances the capacitance bridge of the detector. This signal is then amplified and sent through a filter that removes the background rf. The signal can then be observed using an oscilloscope and is digitized into the PC's memory.

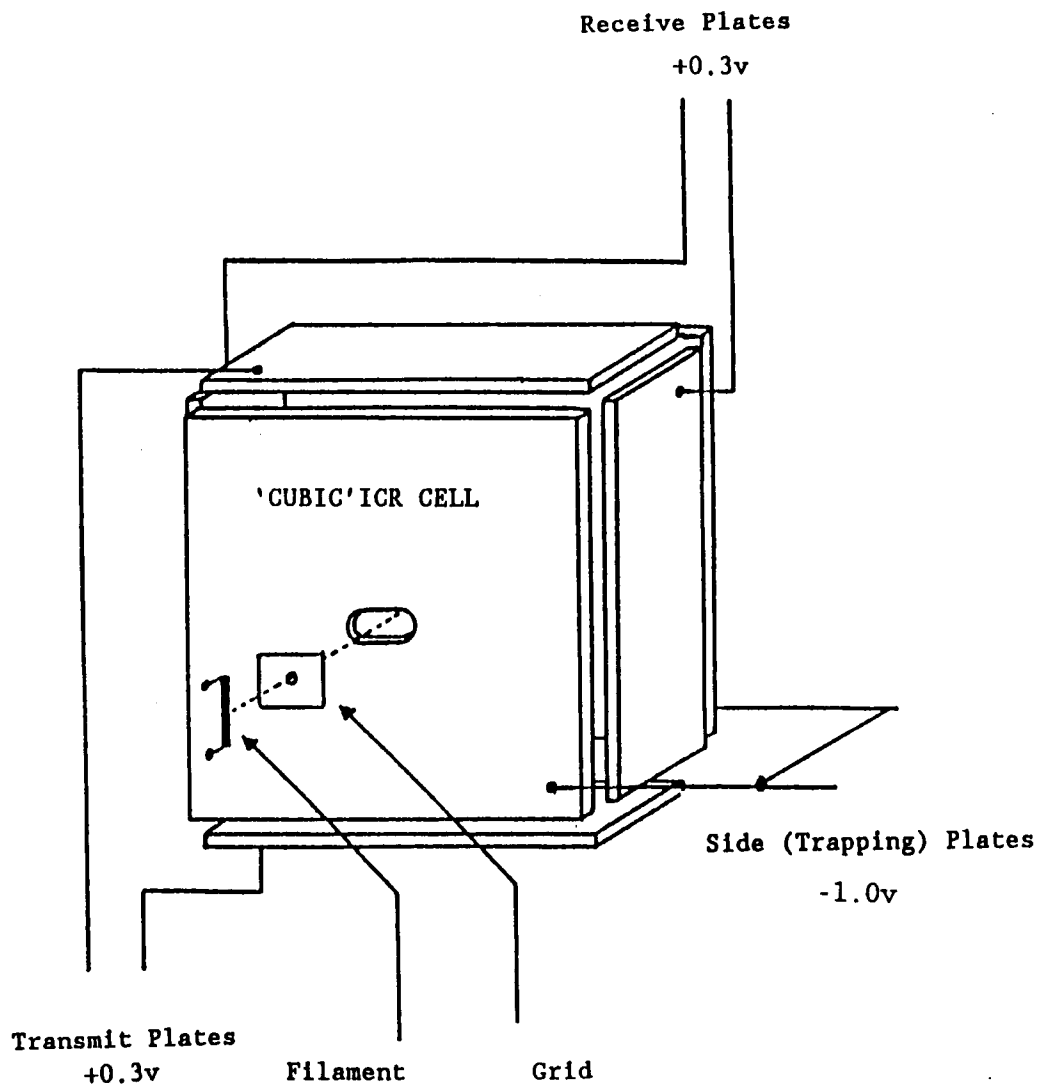


Figure 2. The McIver cell. Voltages are set to trap negative ions.¹⁰

E. Modes of Operation/Equilibrium Studies

The ICR spectrometer can be operated in two modes, unquenched and quenched. In the unquenched mode the ions, once formed, remain in the cell until they become neutralized by random collisions with neutrals and/or the cell walls. In the quenched mode, ions are allowed to remain in the cell after they are formed only for a specified period of time. After that period of time has elapsed the ions are expelled from the cell by biasing one side plate to a voltage opposite that of the ions' charge. When this happens the ions are no longer trapped and become neutralized by collisions with the cell wall. The unquenched mode is used to determine whether an ion is present at any reaction time by allowing its concentration to build up. A sample unquenched spectrum of isoamyl nitrite is shown in Figure 3 (p 9). The quenched mode is used to study the kinetics of a reaction over time. This mode is especially useful when doing equilibrium studies to determine thermodynamic data.^{6,12} The equilibrium constant, K_{eq} , can be determined for reaction (4). The value for K_{eq} can be obtained using equation (5).



$$K_{eq} = [B^-][AH]/[A^-][BH] \quad (5)$$

The ratio of $[AH]/[BH]$ is the ratio of the pressures of the neutral molecules.¹³ The pressures of the neutral molecules are measured using an ion gauge and a Baratron type 146 capacitance manometer. The ion gauge and the Baratron manometer are calibrated to give identical readings for the N_2 molecule. Molecules with ionization cross sections larger than N_2 will produce ion gauge readings higher than their true

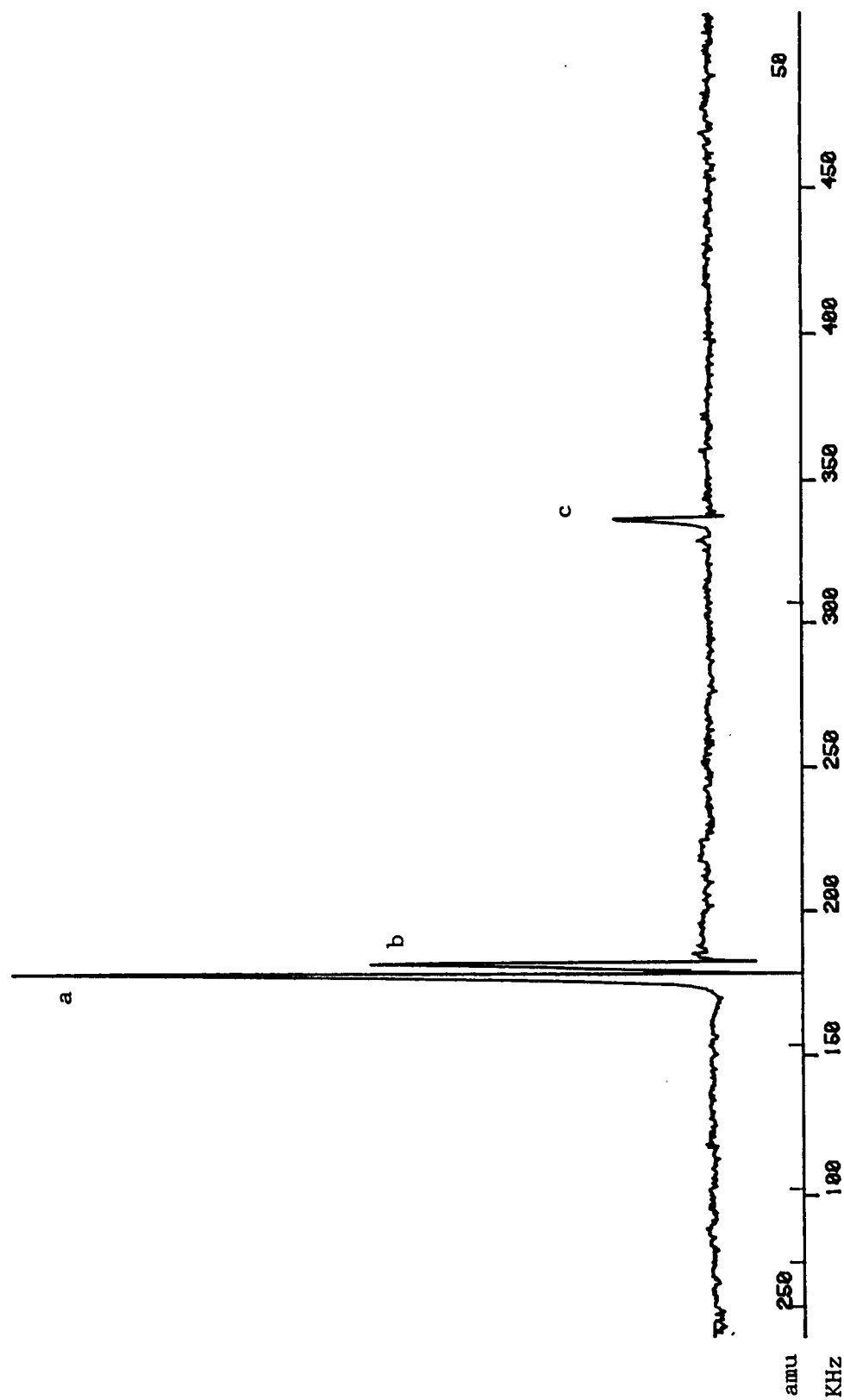


Figure 3. Unquenched mass spectrum of isoamyl nitrite. Where
 $a = C_5H_{11}O^+$ $b = C_5H_9O^+$ $c = NO_2^+$

pressure. This effect occurs because the ion gauge measures ion current, and the ion current will be greater for the molecule with the larger ionization cross section. The reverse is true for molecules with ionization cross sections smaller than N_2 . The calibration factor for correcting the ion gauge pressure is found by plotting the ion gauge readings versus Baratron manometer readings at several different pressures. The relationship is linear, with an intercept of zero. The slope is equal to the calibration factor (B/I), which is the quantity that the ion gauge pressure is multiplied by to obtain the true pressure. In lieu of doing the calibration measurements, a calibration factor can be calculated using an empirical method based on the polarizability of the molecule.¹⁴ In order to determine the ratio of the ions $[B^-]/[A^-]$ at equilibrium, the ratio of their intensities in millivolts are plotted versus time in milliseconds. At long times, when the ratio of ion concentrations is constant, the reaction is assumed to be at equilibrium. The value for the equilibrium concentration of ions, $[B^-]/[A^-]$, is used in equation (5) (p 8). The free energy of the reaction can be calculated from the equilibrium constant by using equation (6). This method of obtaining thermodynamic data has been used

$$\Delta G = - RT \ln K_{eq} \quad (6)$$

to determine gas-phase acidities and basicities for a number of different compounds and will be explained in greater detail in Chapter III.

CHAPTER II

ELECTRON IMPACT GENERATION OF ANIONS

A. Introduction

The behavior of gaseous charged particles in electric and magnetic fields has been studied since the turn of the century. The study of positive ions has progressed at a much more rapid pace than that of negative ions, the reason being that negative ions are much more difficult to produce in the gas phase than positive ions. The most common way of producing either kind of ion in the gas phase is by electron impact. In this technique a beam of electrons at a specified energy is transmitted through a neutral gas to produce ions. For a more detailed description of how this is accomplished in the ICR spectrometer see Chapter 1 of this thesis.

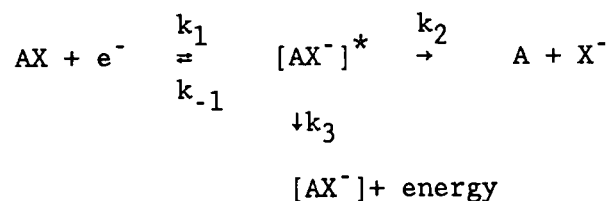
To produce a positive ion, the incident electron must remove an electron from its orbit around the neutral molecule. This process is represented by equation (7), where AX represents any neutral molecule.¹⁵



This process is always endothermic making it possible to remove an electron from any molecule by varying the electron energy.¹⁶

Most neutrals do not efficiently make negative ions. To make negative ions by electron impact, the electron must first be captured by the neutral molecule. Electron capture proceeds according to the Franck-Condon principle, taking place through a vertical transition between two potential energy surfaces. The ion is formed in a state of

electronic and vibrational excitation. Once this excited molecular ion has been formed there are numerous channels available for release of its excess energy.¹⁷ These channels are represented in the following scheme.



k_1 =electron attachment
 k_{-1} =autodetachment
 k_2 =dissociative attachment
 k_3 =non-dissociative attachment

The attachment of an electron to a neutral molecule to produce a stable negative ion is either a dissociative (k_2) or non-dissociative (k_3) process, with autodetachment (k_{-1}) as the competing process. The last is the process by which the captured electron departs from the excited molecular anion, returning it to the original neutral molecule. Resonance non-dissociative electron attachment occurs at very low electron energies, approximately 0 to 2 electron volts and results in the formation of a parent negative ion. The excess energy of the excited parent anion is lost through collisions within the cell and/or through radiative emission. The process of dissociative attachment, or dissociative resonance capture, is the process of most interest, since it can lead to a variety of different anions, depending on the neutral precursor. This process takes place between 0 and 15 electron volts, producing a low energy stable anion, providing there is a suitable dissociative channel available.^{16,18}

Various dissociative channels of a molecule AX are shown in Figure 4 (p 14). Figure 4-a shows the potential energy curve for the neutral molecule AX and the excited molecular anion $[AX^-]^*$. The potential energy curve for $[AX^-]^*$ in this case is a repulsive one. Electrons with energies between E_1 and E_2 are most likely to be captured by the neutral molecule according to the Franck-Condon principle. The Franck-Condon region of the curve is denoted by horizontal lines. Once the excited molecular anion is formed it can either dissociate or autodetach. The autodetachment region is denoted by the vertical lines between the two potential energy curves. Dissociation results in the formation of a neutral or radical and a negative ion. Figure 4-b is an example of a potential energy curve that has an attractive region outside of the Franck-Condon and autodetachment regions. This attractive region of the potential energy curve does not greatly influence the autodetachment or dissociative processes but can lower the probability of the formation of X^- by favoring AX^- . Figure 4-c represents a potential energy curve for $[AX^-]^*$ in which an attractive region is located within the Franck-Condon region where non-dissociative attachment can compete with autodetachment and dissociative attachment. If an electron with energies between E_7 and E_6 is captured by a molecule AX both autodetachment and dissociative attachment are possible. Between the energies of E_5 and E_6 electron attachment to produce AX^- is possible. This is a non-dissociative product that can be formed within the Franck-Condon region. Another channel for dissociative attachment is represented in Figure 4-d. This channel involves the formation of X^- by a non-radiative transmission from a bound state of AX^- to a repulsive

≡ FRANK - CONDON REGION
 III AUTOIONIZATION REGION

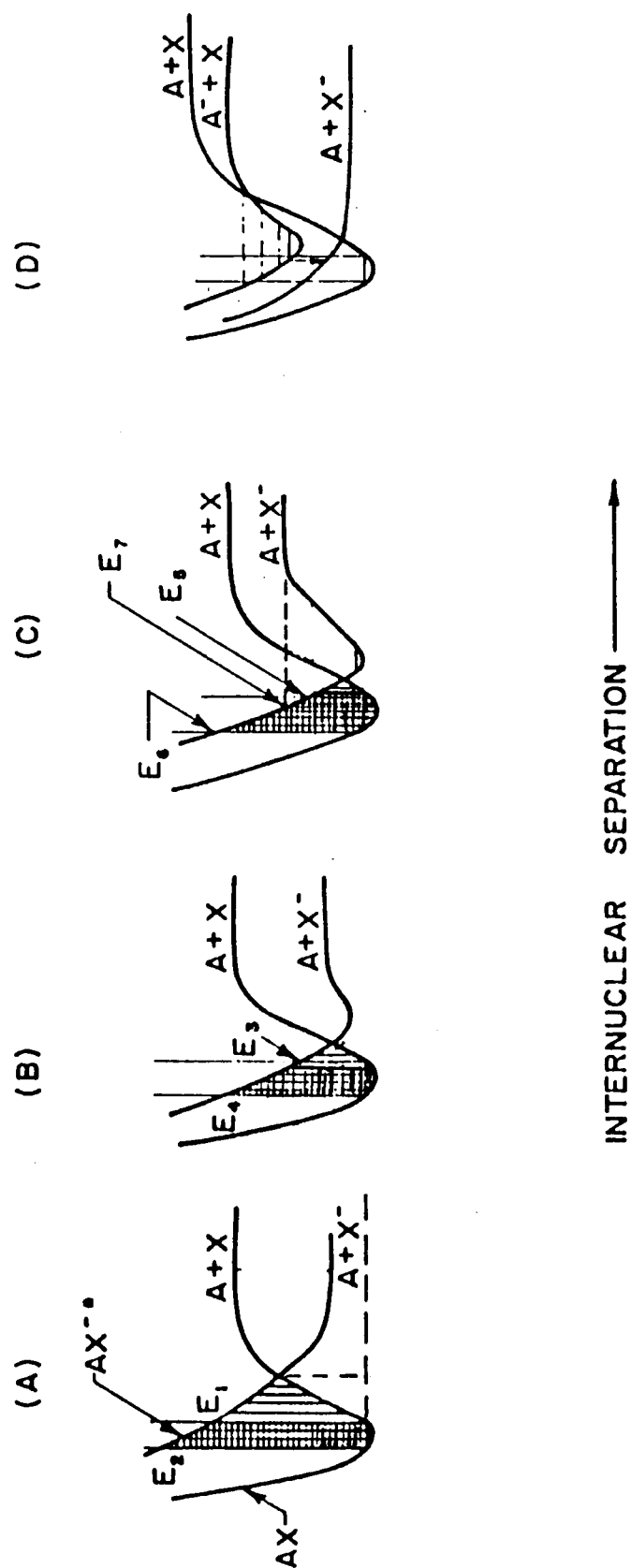


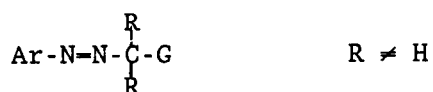
Figure 4. Potential energy diagrams for various modes of dissociative electron attachment.^{1/}

state of the molecule that results in the formation of X^- by dissociation.^{17,19}

It would be ideal, in terms of the study of gas phase ion/molecule chemistry, to be able to design a molecule that would undergo the dissociative attachment process giving desired anions, with large cross sections for production by electron impact. It is the objective of this research to find a rational scheme for predicting the structure of a precursor molecule that could make the above possibility a reality. To produce these low energy anions by dissociative attachment in the gas phase with large cross sections (high probability of formation) it is proposed that the precursor molecule meet the following conditions:

1. The lowest unoccupied molecular orbital must be below zero electron volts (bound), and the excited state $[AX^-]^*$ must live long enough to dissociate.
2. There must be a suitable low energy dissociative channel (weak bonds).
3. The anion produced must be stable with respect to autodetachment.

The proposed precursor molecule has the following structure.



Upon dissociative attachment, the above molecule would yield the $\text{R}_2\text{C}=\text{G}^-$ carbanion plus $\text{ArN}=\text{N}^{\cdot}$, which could then break apart to yield $\text{Ar}^{\cdot}$ and N_2 . In this system G is a good electron accepting group such as nitro or acetyl. The pi system of the arylazo moiety captures the electron and the azo bonds form a weak link which can dissociate. Table I (p 16)

TABLE 1

PHENYL DIAZO COMPOUNDS PROPOSED FOR INVESTIGATION
OF DISSOCIATIVE PROPERTIES

Precursor Molecule	Expected Anion
$\text{C}_6\text{H}_5\text{-N=N-C(CH}_3)_2\text{-NO}_2$	$(\text{CH}_3)_2\text{C=NO}_2^-$
$\text{C}_6\text{H}_5\text{-N=N-C(CH}_3)_2\overset{\text{O}}{\parallel}\text{CH}_3$	$(\text{CH}_3)_2\text{C=COCH}_3^-$
$\text{C}_6\text{H}_5\text{-N=N-C(CH}_3)_2\overset{\text{O}}{\parallel}\text{C(CH}_3)_2$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C=COCH}_3^-$
$\text{C}_6\text{H}_5\text{-N=N-SO}_2\text{Ph}$	$\text{C}_6\text{H}_5\text{SO}_2^-$
$\text{C}_6\text{H}_5\text{-N=N-C(CF}_3)_2\text{CF}_2\text{CF}_2\text{CF}_3$	$(\text{CF}_3)_2\text{C}^-\text{CF}_2\text{CF}_2\text{CF}_3$
$\text{p-NO}_2\text{-C}_6\text{H}_4\text{-N=N-C(CH}_3)_2\overset{\text{O}}{\parallel}\text{C(CH}_3)_2$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C=COCH}_3^-$
$\text{C}_6\text{H}_5\text{-N=N-C(CH}_3)_2\overset{\text{O}}{\parallel}\text{C-H}$	$(\text{CH}_3)_2\text{C=CHO}^-$

lists the phenyldiazo compounds that were investigated to test the validity of the dissociative parameters. Table II (p 18) lists other compounds that were used for the investigation of dissociative properties.

B. Experimental Section

1. Instrumentation

A Varian T-60A nuclear magnetic resonance spectrometer was used to obtain proton spectra. A Jeol FX90Q Fourier Transform nuclear magnetic resonance spectrometer was used to obtain carbon-13 spectra. Spectra were determined for compounds dissolved in deuterated chloroform or deuterated dimethyl sulfoxide. Tetramethylsilane was used as the internal standard. Melting points were determined using a Laboratory Devices Meltemp. Electron impact studies were carried out using the ion cyclotron resonance mass spectrometer described in Chapter I. MNDO (Modified Neglect of Diatomic Differential Overlap) calculations using a modification of the (QCMP004) micro computer program were done on an IBM PC.²⁰

2. Method

Pulsed ion cyclotron resonance spectrometry was used to generate and detect anions at neutral precursor pressures ranging from 1 to 10 microtorr, depending on the volatility of the sample. The quenched mode was used with a grid length of 40 milliseconds and a delay time of 100 milliseconds. The radio frequency amplitude, trapping voltage, and filament current were set to give maximum signals. The electron energy was varied from a nominal +0.5 V to -70.0 V at the above conditions.

TABLE II
 COMMERCIALY AVAILABLE COMPOUNDS INVESTIGATED FOR
 THEIR DISSOCIATIVE PROPERTIES

Precursor Molecule	Desired Anion
Acetanilide	PhNH^-
Acetic Anhydride	CH_3COO^-
Azo-bis-isobutyronitrile	$(\text{CH}_3)_2\text{CCN}^-$
Benzene sulfonyl chloride	$\text{PhSO}_2^- + \text{Cl}^-$
Benzoyl bromide	Br^-
Benzoyl chloride	Cl^-
Benzoyl cyanide	CN^-
Benzoyl fluoride	F^-
Isoamyl nitrite	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{O}^-$
Methyl benzoate	CH_3O^-
Nitromethane	NO_2^-
Di-tert-butylperoxide	$(\text{CH}_3)_3\text{CO}^-$

3. Compounds

Acetanilide, acetic anhydride, azo-bis-isobutyronitrile, benzenesulfonyl chloride, benzoyl bromide, benzoyl chloride, benzoyl cyanide, isoamyl nitrite, methyl benzoate, nitromethane and di-tert-butyl peroxide were purchased from Aldrich Chemical Company. The sample of 2-phenylazo-perfluoro-2-methyl-2-pentane was donated by B. Smith of Dupont. Samples of 2-phenylazo-2-nitropropane, phenylazo-benzenesulfinate, 2-methyl-2-phenylazo-2,4-pentanedione and 2-methyl-2-p-nitrophenylazo-2,4-pentanedione were successfully synthesized in the laboratory. The syntheses of 2-methyl-2-phenylazopropanal and 3-methyl-3-phenylazobutanone were unsuccessful.

2-Phenylazo-2-nitropropane $\text{PhN}=\text{NC}(\text{Me})_2\text{NO}_2$

1. A 500-mL three-necked round-bottomed flask was equipped with a magnetic stirring bar, a 125-mL dropping funnel and a reflux condenser. The flask was charged with 10.6 mL (0.12 mol) of aniline and 115 mL of 50% fluoboric acid. The flask was immersed in an ice bath. A solution of 9.0 g (0.13 mol) of sodium nitrite dissolved in 36 mL of water was added dropwise with stirring over a period of one hour. The product was collected by suction filtration on a Buchner funnel. The crude product was washed with 20 mL of 50% fluoboric acid, twice with absolute ethanol and then with diethyl ether. A white solid, phenyl diazonium tetrafluoroborate (20.5 g), was obtained in 95% yield. The crystals were used in the next step without further purification.²¹

2. A 250-mL three-necked round-bottomed flask was equipped with a magnetic stirring bar, a powder funnel, and a reflux condenser. The flask was immersed in an ice bath and charged with 50 mL of a 1 M

sodium hydroxide solution and 4.45 mL (0.05 mol) of 2-nitropropane. Phenyl diazonium tetrafluoroborate (10.5 g, 0.05 mol) was slowly added with stirring over a period of 45 minutes. A dark yellow-red oil was separated from the aqueous solution. The aqueous layer was extracted with three 20-mL portions of diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by gravity filtration, and the excess solvent was removed completely under reduced pressure on a rotary evaporator. The resulting dark yellow-red oil gave the following absorptions in the proton magnetic resonance spectrum (CDCl_3) δ : 1.94 (s, 6H, CH_3), 7.40 - 7.94 (complex, 5H, aromatic). The proton decoupled C-13 spectrum gave δ : 23.430 (CH_3), 112.594 (C, quat), 123.274, 129.775, 132.727, 151.173 (C, aromatic). The literature boiling point is $98^\circ\text{C}/0.07\text{ mm}$.^{22,23}

2-Methyl-2-phenylazo-2,4-pentanedione $\text{PhN}=\text{NC}(\text{Me})(\text{COMe})_2$

In a manner similar to that for the synthesis of 2-phenylazo-2-nitropropane, 2-methyl-2-phenylazo-2,4-pentanedione was prepared with the following exception: in the second step, 5.82 mL of 3-methyl-2,4-pentanedione was substituted for 2-nitropropane. The resulting orange oil gave the following absorptions in the proton NMR spectrum (CDCl_3) δ : 1.52 (s, 3H, CH_3), 2.18 (s, 6H, CH_3), 7.10-7.80 (complex, 5H, aromatic) and in the C-13 spectrum δ : 18.419 (CH_3), 28.306 (2, CH_3), 114.226 (C, quat.), 122.732, 129.422, 132.077, 151.878 (C, aromatic), 204.075 (2C, carbonyl). Literature references^{24,25,26} give $\text{PhNHN}=\text{C}(\text{Me})(\text{COMe})$ as the product for this reaction, but NMR indicates the structure given in Table I (p 16).

2-Methyl-2-p-nitrophenylazo-2,4-pentanedione $\text{NO}_2\text{-C}_6\text{H}_4\text{N=NC(Me)(COMe)}_2$

The synthesis of 2-methyl-2-p-nitrophenylazo-2,4-pentanedione was carried out in a manner similar to that of 2-methyl-2-phenylazo-2,4-pentanedione with the following exceptions: it was carried out half scale and in step one 8.29 g of p-nitroaniline was substituted for aniline and in step two 2.33 mL of 3-methyl-2,4-pentanedione was used. The resulting red oil gave the following absorptions in the proton NMR ($\text{d}_6\text{-DMSO}$) δ : 2.0 (s, 3H, CH_3), 2.41 (s, 6H, CH_3), 7.40 (d, 2H, $\text{J}=9.0$, aromatic), 8.15 (d, 2H, $\text{J}=9.0$, aromatic), 3.25 water impurity (10%). Again literature references^{24,25,26} indicate the formation of the hydrazone as the product, but NMR indicates the azo compound to be the correct structure.

Phenylazobenzenesulfinate $\text{PhN=NSO}_2\text{Ph}$

Phenylazo-benzenesulfinate was synthesized in a manner similar to that for 2-phenylazo-2-nitropropane. In step two the sodium salt of benzenesulfinic acid (8.21 g) was substituted for 2-nitropropane, and a 1M HCl solution was used in place of the 1M NaOH solution. The product was collected by suction filtration on a Büchner funnel and recrystallized from a 50:50 mixture of hexanes and methanol. The resulting yellow crystals gave a melting point of 162°C and the following absorption in the proton NMR (CDCl_3) δ : 6.90-8.35 (complex, aromatic).

2-Methyl-2-phenylazopropanal $\text{PhN=NC(Me)}_2\text{CH=O}$

1. Into a 250-mL three-necked round-bottomed flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer were placed 8.1 mL of acetone, 100 mL of methanol, and 9.8 mL of phenylhydrazine.

The mixture was refluxed for 15 minutes. Glacial acetic acid (2.5 mL) was added dropwise, and the solution refluxed for 45 minutes. To the warm solution, cold distilled water was added until a permanent cloudiness resulted. The solution was cooled in an ice water bath. The solid was collected by suction filtration using a Büchner funnel and washed with 20 mL of distilled water containing 1 mL of glacial acetic acid. The product was immediately recrystallized by dissolving it in hot methanol. Distilled water was added until permanent cloudiness appeared. The solution was cooled overnight in the refrigerator. The crystals were isolated by suction filtration on a Buchner funnel and washed with cold dilute methanol. The resulting pale yellow crystals, acetone phenylhydrazone^{27,28}, gave a melting point of 27-30 °C and the following absorptions in the proton NMR (CDCl₃) δ : 1.81 (s, 3H, CH₃), 2.00 (s, 3H, CH₃) 6.62 - 7.40 (complex, 5H, aromatic), 4.63 water impurity. The crystals were used without further purification.

2. A 150-mL 3-necked round-bottomed flask was fitted with a reflux condenser, dropping funnel, magnetic stirrer and dry nitrogen inlet. Sodium metal (0.06 g) was placed into the flask, and 50 mL of absolute ethanol was added dropwise under a nitrogen atmosphere with stirring. When solution was complete, 4.04 mL of ethyl formate was added all at once through the dropping funnel. After stirring for 15 minutes, 7.4 g of acetone phenylhydrazone dissolved in absolute ethanol was added dropwise over a period of 30 minutes. The solution was refluxed for one hour. The ethanol was removed by simple distillation. The crude product was washed with distilled water and extracted with diethyl ether. The combined organic layers were dried over anhydrous magnesium

sulfate. The magnesium sulfate was removed by gravity filtration, and the ether removed completely under reduced pressure on a rotary evaporator. The resulting yellow oil gave absorptions in the proton NMR spectrum identifying it as starting material (acetone phenylhydrazone). The above procedure was repeated with the reflux time lengthened from one hour to 19.5 hours. The result was the recovery of acetone phenylhydrazone.

3-Methyl-3-phenylazobutanone $\text{PhN}=\text{NC}(\text{Me})_2\text{COMe}$

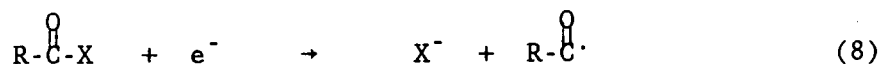
1. Acetone phenylhydrazone was prepared in the exact manner as it was in the attempted synthesis of 2-methyl-2-phenylazopropanal.
2. A 500-mL three-necked round-bottomed flask equipped with a magnetic stirring bar, dry nitrogen inlet, reflux condenser, and septum was charged with 200 mL of dry diethyl ether and 7.00 mL diisopropylamine and cooled to $-78\text{ }^{\circ}\text{C}$. Butyllithium (1.6 M, 31.3 mL) was added slowly over a period of 20 minutes and the solution was stirred for one hour. The temperature was raised to $0\text{ }^{\circ}\text{C}$ and the solution was stirred for another hour. The temperature was returned to $-78\text{ }^{\circ}\text{C}$, and 7.88 g of acetone phenylhydrazone dissolved in diethyl ether was added dropwise over an hour. The color of the solution changed from clear to orange to dark orange. Upon the addition of acetic anhydride (4.72 mL) the solution turned yellow. The solution was stirred overnight and allowed to come to room temperature. Distilled water was added to the solution and extracted with diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by gravity filtration, and the ether removed under reduced pressure on a rotary evaporator. The resulting yellow oil could not be

identified as the desired product and appeared to be a mixture of starting materials. The procedure was tried again substituting acetyl chloride (3.55 mL) for the acetic anhydride and then again using 7.11 mL of the chloride. The results were the same as those obtained using acetic anhydride.

C. Results and Discussion

Table III (p 25) lists the precursor molecules that successfully underwent dissociative attachment to give the desired anions, as well as those that did not. Plots of ion intensity as a function of electron energy for the successful systems can be found in Figures 5-10 (p 26,27,28,31,32,33).

Looking at the results for the systems represented by equation (8),



it is noted that all the precursor molecules of the form RCOX, gave the desired anions (Figures 5 (p 26), 6 (p 27), and 7 (p 28)), with the exceptions of benzoyl fluoride, acetanilide and phenyl acetate. These results were not entirely unexpected, since we previously proposed above that a precursor molecule should have a bound LUMO. According to MNDO calculations performed on a series of precursor molecules, it was found that the benzoyl fluoride, acetanilide and phenyl acetate had LUMO's that were not bound. Results of these MNDO calculations can be found in Table IV (p 29). It should be noted from this table that acetic anhydride also has an unbound LUMO, but does give the desired anion. This suggests that a bound LUMO is not necessarily a requirement for

TABLE III
SUCCESSFUL AND UNSUCCESSFUL SYSTEMS

Precursor Molecule	Desired Anion	Anion Formed
$\text{PhN}=\text{NC}(\text{CH}_3)_2\text{NO}_2$	$(\text{CH}_3)_2\text{C}=\text{NO}_2^-$	yes
$\text{pNO}_2\text{C}_6\text{H}_5\text{N}=\text{NC}(\text{CH}_3)(\text{COCH}_3)_2$	$\text{CH}_3\text{COC}(\text{CH}_3)=\text{COCH}_3^-$	yes
$\text{PhN}=\text{NC}(\text{CF}_3)_2\text{CF}_2\text{CF}_2\text{CF}_3$	$(\text{CF}_3)_2\text{C}^-\text{CF}_2\text{CF}_2\text{CF}_3$	yes
PhCOCN	CN^-	yes
PhCOCl	Cl^-	yes
PhCOBr	Br^-	yes
CH_3NO_2	NO_2^-	yes
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{ONO}$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{O}^-$	yes
$(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{CO}^-$	yes
$(\text{CH}_3\text{CO})_2\text{O}$	CH_3COO^-	yes
$\text{PhN}=\text{NSO}_2\text{Ph}$	PhSO_2^-	no
$\text{PhN}=\text{NC}(\text{CH}_3)(\text{COCH}_3)_2$	$\text{CH}_3\text{COC}(\text{CH}_3)=\text{COCH}_3^-$	no
PhCOF	F^-	no
PhSO_2Cl	PhSO_2^- or Cl^-	no
CH_3CONHPh	PhNH^-	no
$\text{CH}_3\text{CO}_2\text{Ph}$	CH_3COO^-	no
$\text{NCC}(\text{CH}_3)_2\text{N}=\text{NC}(\text{CH}_3)_2\text{CN}$	$(\text{CH}_3)_2\text{C}=\text{CN}^-$	no

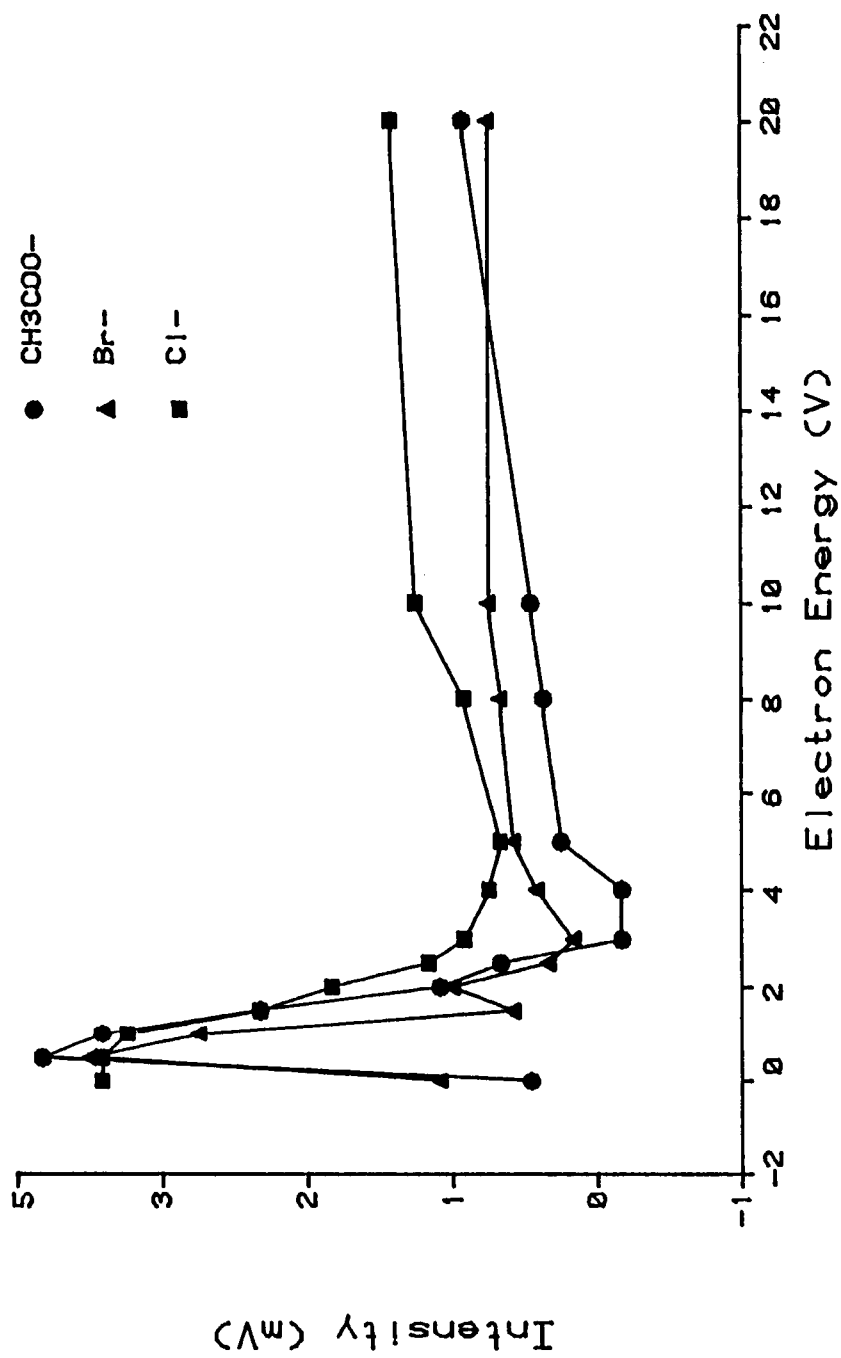


Figure 5. Plots showing anion formation from the following precursor molecules: (CH₃CO)₂O, PhCOBr, PhCOCl.²⁹

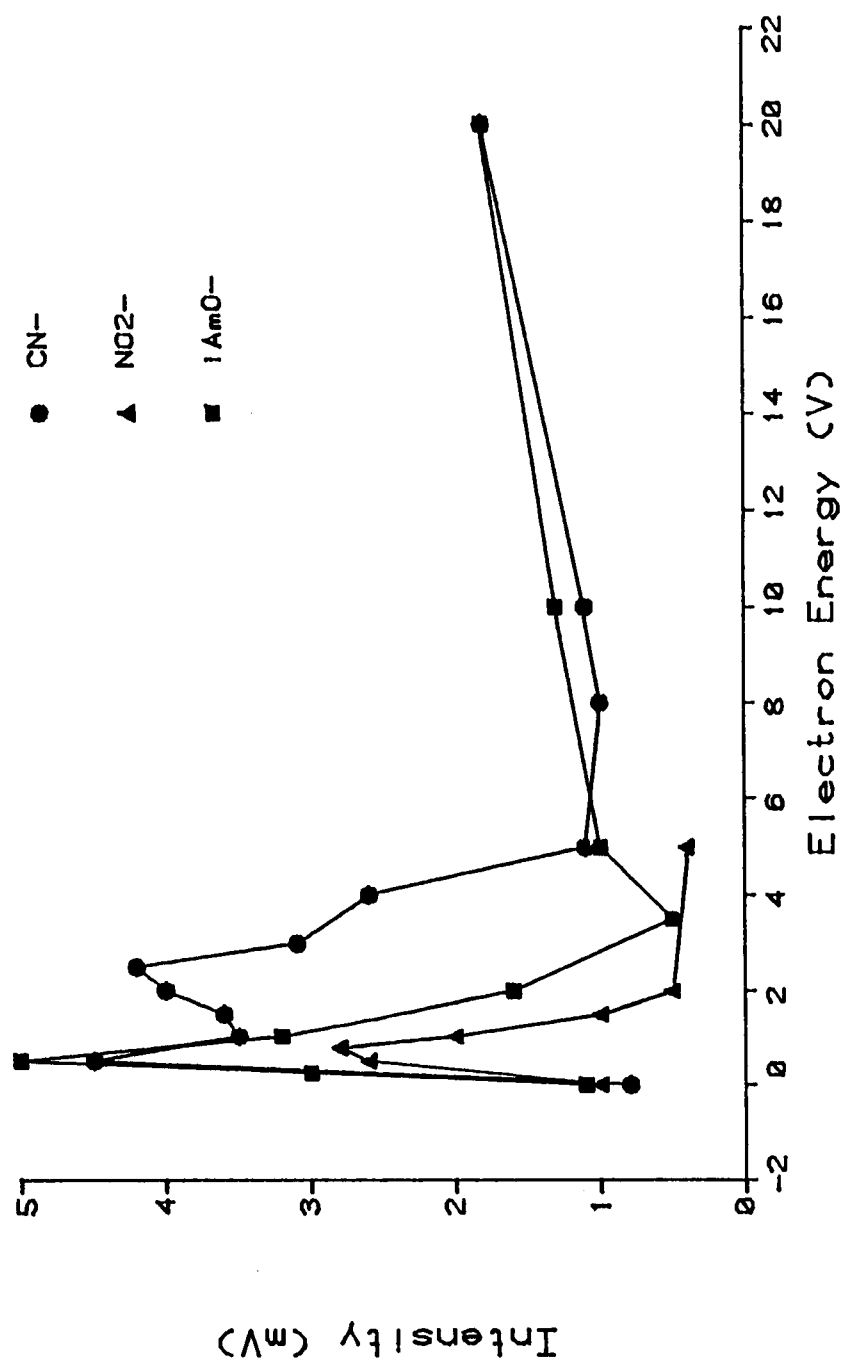


Figure 6. Plots showing anion formation from the following precursor molecules: $(\text{CH}_3)\text{CHCH}_2\text{CH}_2\text{ONO}$, PhCOCN , CH_3NO_2 .

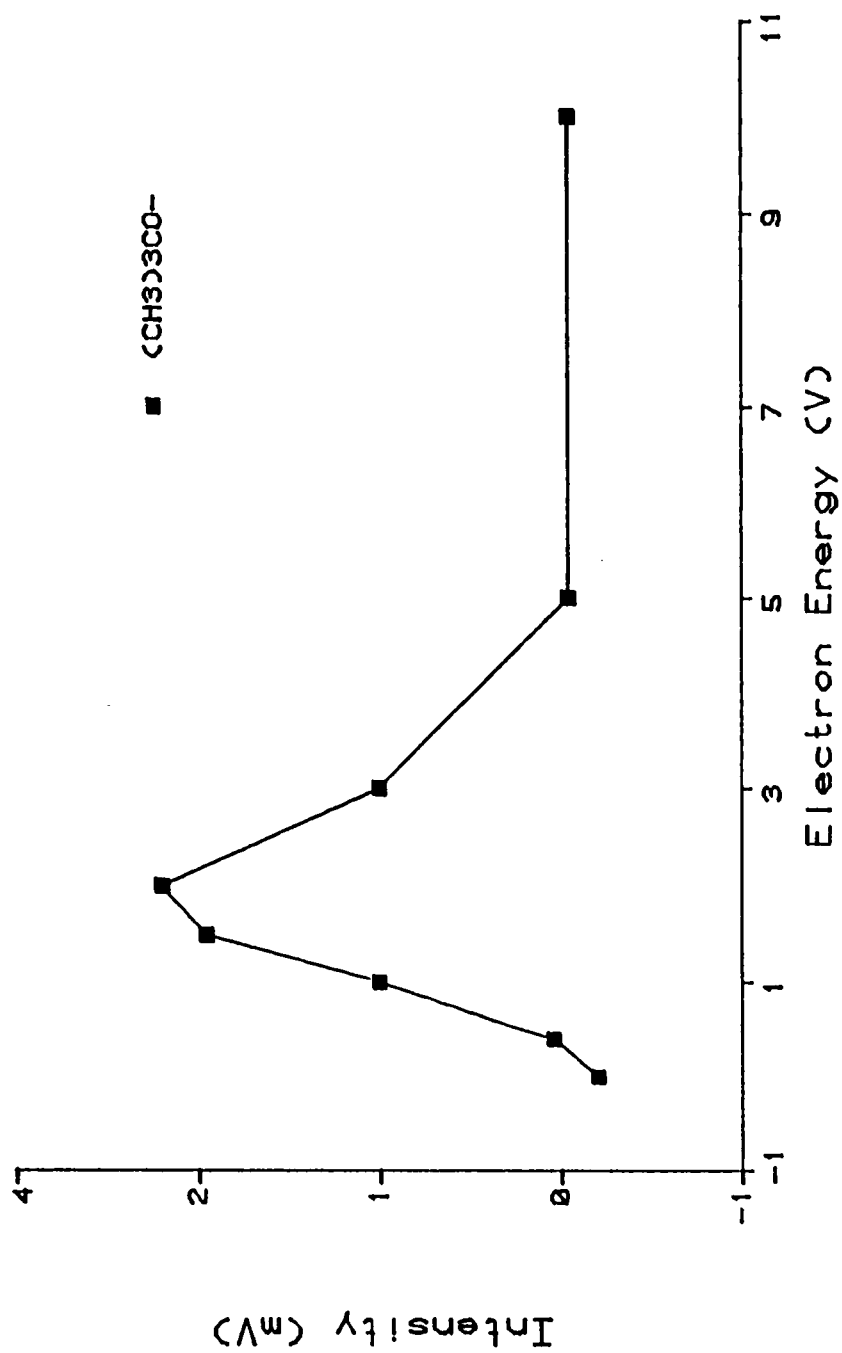


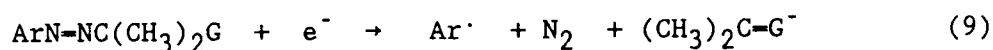
Figure 7. Plot showing anion formation from the precursor molecule:
 $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$.

TABLE IV
CALCULATED VALUES FOR THE LUMO'S OF SELECTED MOLECULES
BY MNDO CALCULATIONS

Molecule	LUMO
PhN-NH	-0.530 eV
PhN-NCH ₂ COCH ₃	-0.647 eV
PhN-NCH ₂ NO ₂	-1.17 eV
(CH ₃ CO) ₂ O	+0.392 eV
CH ₃ COC1	-0.071 eV
CH ₃ COCN	-0.442 eV
CH ₃ COF	+0.259 eV
CH ₃ CONHPh	+0.128 eV
CH ₃ COOPh	+0.0375 eV
NCC(CH ₃) ₂ N=NC(CH ₃) ₂ CN	-0.167 eV

dissociative attachment, but does increase the probability of dissociative attachment by producing the excited molecular anion at a lower energy. This low energy excited molecular anion is less likely to undergo autodetachment than a higher energy species, thereby increasing the probability of dissociative attachment.

For the systems represented by equation (9), involving the



phenylazo group as part of the precursor molecule, it was found that 2-phenylazo-2-nitropropane and 2-phenylazo-perfluoro-2-methyl-2-pentane gave copious amounts of the desired anions (Figures 8 (p 31) and 9 (p 32)). However these precursor molecules contain G groups (nitro or perfluorohexyl) that are capable of dissociative attachment on their own. In these cases, the phenylazo group provided the dissociative ability for the molecule but not necessarily the electron capture aspect. It is also noted that the diacetyl compound (2-methyl-2-phenylazo-2,4-pentanedione) with the parent phenyl group failed to give the desired anion, whereas the diacetyl compound with a nitro group at the para position of the phenyl ring gave large amounts of the desired anion as shown in Figure 10 (p 33). This result indicates that it is possible to tune the precursor structure as needed with ring substituents in order to vary the lifetime of the excited molecular anion, and by so doing to increase the probability of dissociative attachment. The successful synthesis of either 2-methyl-2-phenylazopropanal or 3-methyl-3-phenylazobutanone would have proved the viability of the proposed precursor structure. Formation of the desired anion

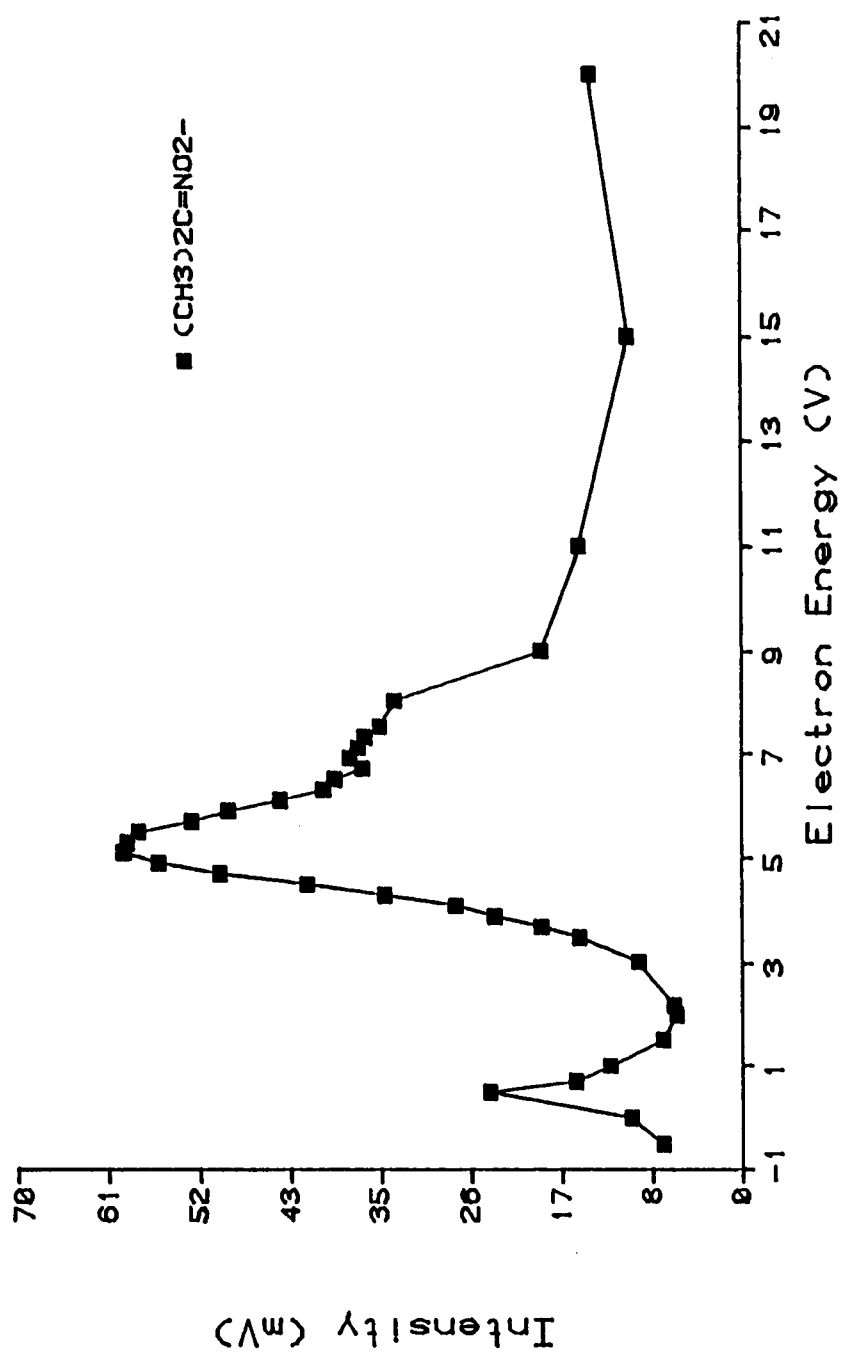


Figure 8. Plot showing anion formation from the precursor molecule $\text{PhN}=\text{NC}(\text{CH}_3)_2\text{NO}_2$.

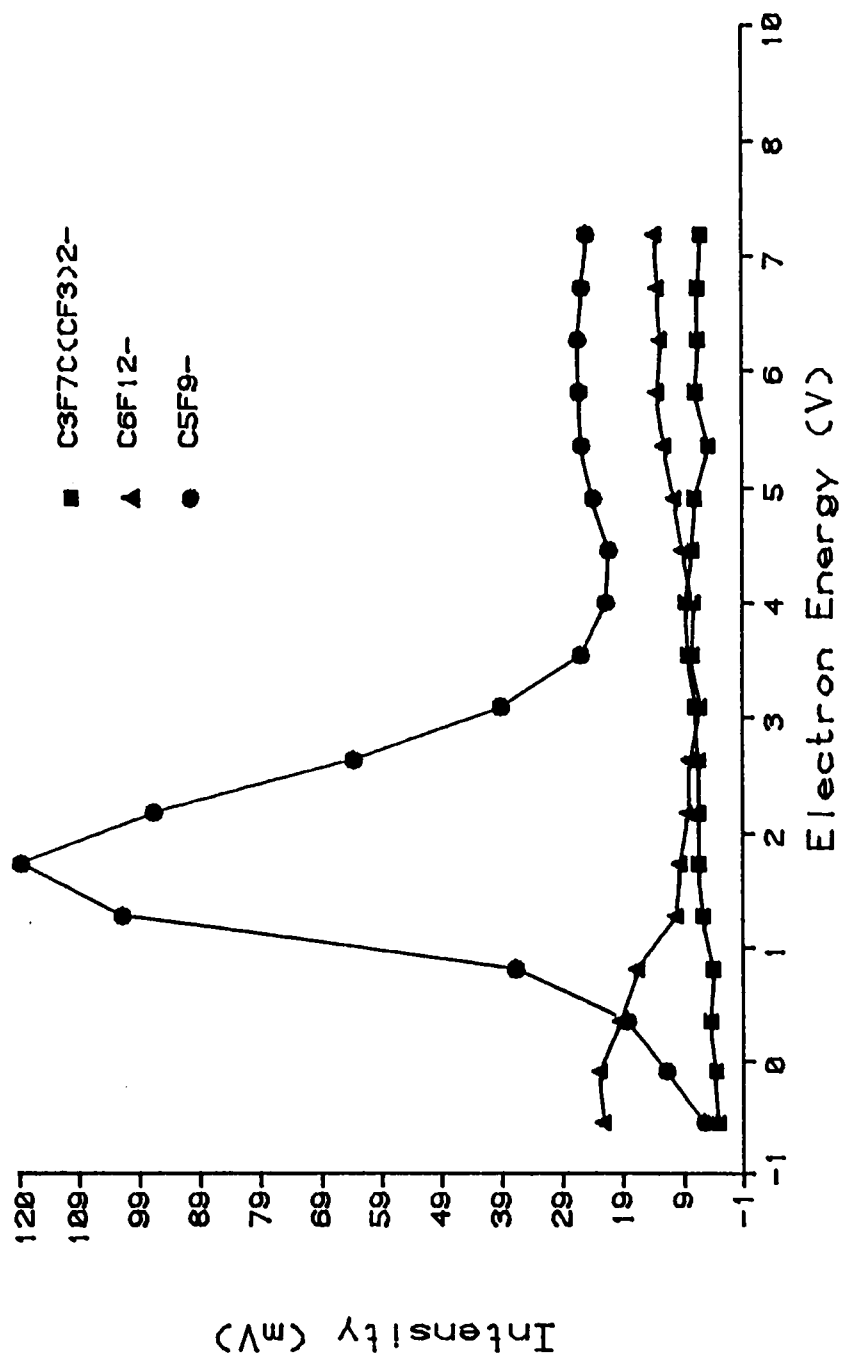


Figure 9. Plots showing anion formation from the precursor molecule:
 $\text{PhN=NC(CF}_3)_2\text{CF}_2\text{CF}_2\text{CF}_3$.

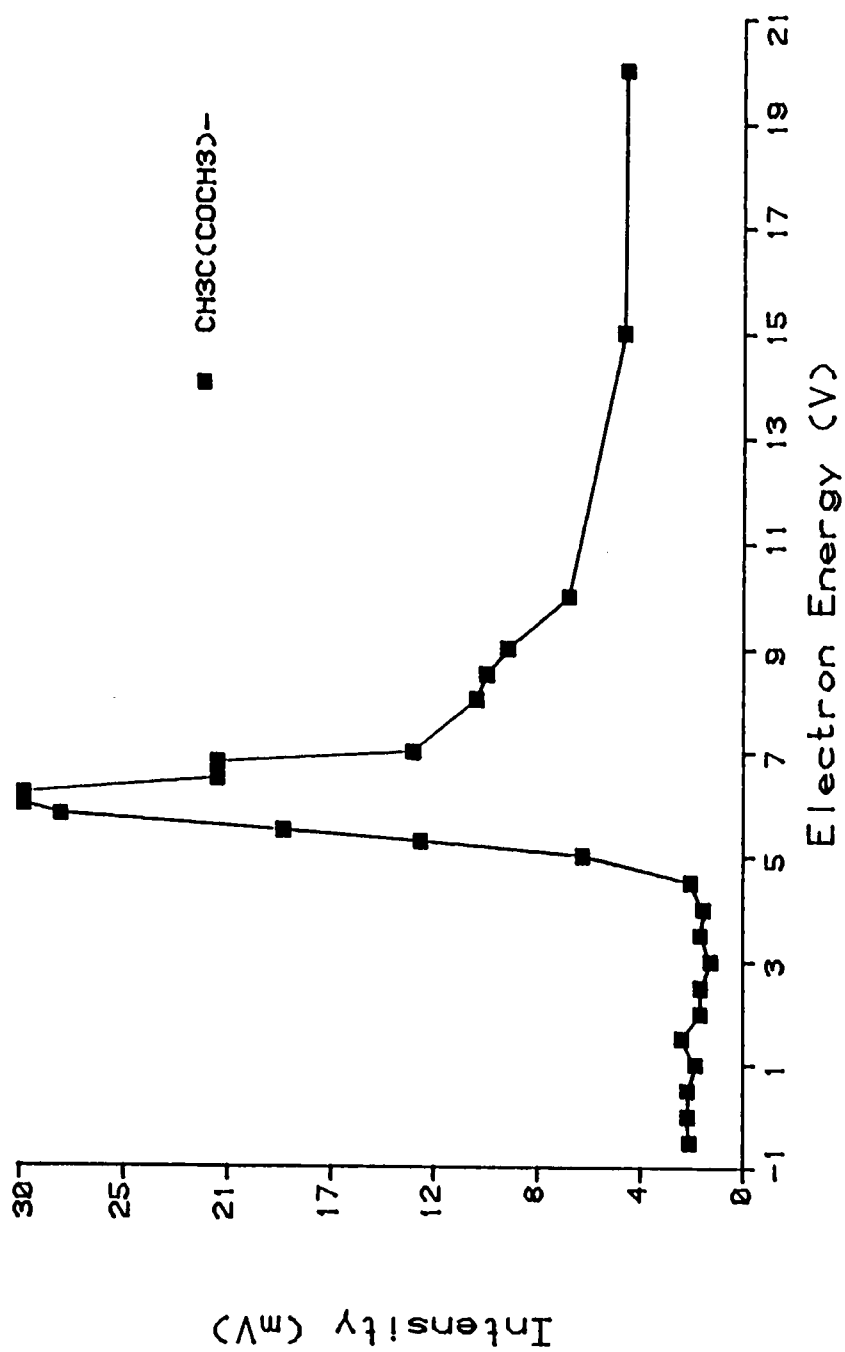


Figure 10. Plot showing anion formation from the precursor molecule:
 $\text{pNO}_2\text{-C}_6\text{H}_4\text{-N=NC(CH}_3\text{)(COCH}_3\text{)}_2$.

would have indicated that the phenylazo group was responsible for the electron capture ability of the molecule as well as for the dissociative ability of the molecule, since CH_3CHO or CH_3COCH_3 are not known to undergo dissociative attachment on their own.

To determine the validity of the parameters suggested for dissociative attachment, Table V (p 35) was constructed. This table consists of those experimental systems for which LUMO values were available and for which ΔH_{rxn} could be calculated. From this table it appears that the requirement for a precursor molecule to have a bound LUMO, in order to undergo dissociative attachment, is not always a valid one. This conclusion is evidenced by the ability of acetic anhydride to undergo dissociative attachment to form the desired anion. It also appears that a reaction does not have to be exothermic in order to successfully produce anions; however, the endothermicity of the reaction must be small. This idea makes sense because excited molecular anions formed under low energy conditions are more likely to undergo dissociative attachment. The more excess energy a molecular anion has, the more likely the excited molecular anion will be to lose the added electron through autodetachment. This results in the failure of the system to give the desired product anion. In conclusion it appears that the design strategy for the precursor molecule, and its dissociative attachment, are valid for certain cases. Those cases being ones in which G is a good electron accepting group and in which the further option of tuning the π energy of the phenylazo ring with substituents is possible when the desired anion is not detected initially.

TABLE V
SUMMARY TABLE FOR THE DISSOCIATIVE ATTACHMENT PROCESS

System	ΔH_{rxn}^a	Anion produced	LUMO ^b bound
$\text{PhN=NCH}_2\text{NO}_2 + e^- \rightarrow \text{Ph}^\cdot + \text{N}_2 + \text{CH}_2=\text{NO}_2^-$	-69 kJ/mol	yes	yes
$\text{CH}_3\text{COCl} + e^- \rightarrow \text{CH}_3\text{CO}^\cdot + \text{Cl}^-$	-7 kJ/mol	yes	yes
$(\text{CH}_3\text{CO})_2\text{O} + e^- \rightarrow \text{CH}_3\text{CO}^\cdot + \text{CH}_3\text{CO}_2^-$	+28 kJ/mol	yes	no
$\text{CH}_3\text{COCN} + e^- \rightarrow \text{CH}_3\text{CO}^\cdot + \text{CN}^-$	+29 kJ/mol	yes	yes
$\text{CH}_3\text{NO}_2 + e^- \rightarrow \cdot\text{CH}_3 + \text{NO}_2^-$	+29 kJ/mol	yes	yes
$\text{CH}_3\text{CO}_2\text{Ph} + e^- \rightarrow \text{CH}_3\text{CO}^\cdot + \text{PhO}^-$	+92 kJ/mol	no	no
$\text{CH}_3\text{COF} + e^- \rightarrow \text{CH}_3\text{CO}^\cdot + \text{F}^-$	+172 kJ/mol	no	no
$\text{CH}_3\text{CONHPh} + e^- \rightarrow \text{CH}_3^\cdot + \text{PhNH}^-$	+196 kJ/mol	no	no

^a ΔH_{rxn} values were calculated for each system using the equation $\Delta H_{\text{rxn}} = (\sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}})$. Values for $\Delta H_{\text{reactants}}$ and $\Delta H_{\text{products}}$ were obtained from references 30 and 31.

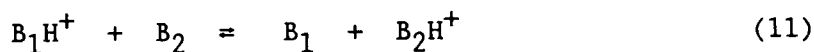
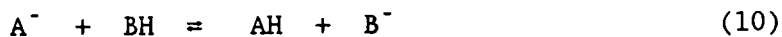
^bMNDO calculations.

CHAPTER III

DIOL ACIDITIES

A. Introduction

The gas-phase acidity or basicity of a compound is a function of the structure of the anion or cation formed. The ability of a compound to produce ions capable of forming intramolecular hydrogen bonds results in the formation of a more stable anion or cation than expected. This increased stability of the ion would be reflected in a stronger acidity or basicity (a lower value for ΔG_{acid} or a higher value for ΔG_{base}) than expected for that particular compound. This possibility of intramolecular hydrogen bonding by certain molecules in the gas phase has led to the investigation of their acidities or basicities. This investigation was done to determine the energetics of such interactions. When discussing the acidity of a compound, one is referring to a study done in the negative ion mode, and when discussing basicity one is referring to a study done in the positive ion mode. Either the acidity or basicity of a compound can be determined by evaluating the thermodynamic data that are available for the following proton transfer equilibria (10) and (11).^{13,32} The abbreviations BH, AH, B₂, and B₁



refer to neutral acids or gases. The equilibrium constants K_{eq} , for the above reactions, (10) and (11), can be determined experimentally, and the value for the Gibbs free energy obtained from these data as was

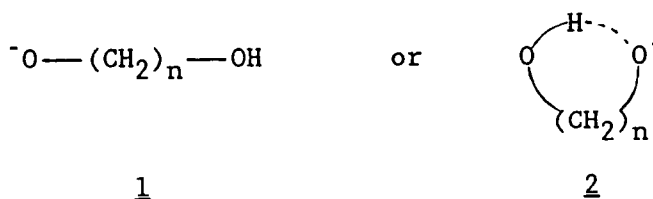
described in Chapter I. Values for other thermodynamic data, such as the enthalpy and entropy changes for a particular equilibrium, can be derived from this information and from that available in the literature.

Yamdagni and Kebarle³³ investigated the gas-phase basicity of a series of α,ω -diaminoalkanes, $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ ($n=2$ to $n=7$), by studying the proton transfer reaction shown by equation (11) (p 36), where B_1 represents an alkyl amine and B_2 represents an α,ω -diaminoalkane. It was expected that the diaminoalkane would produce a positive ion capable of forming a proton bridge via a cyclic structure, as opposed to maintaining the open chain structure of the neutral. If this assumption were correct, the basicity of the diaminoalkane would be greater than that of a similar monoamine where one of the amino groups of the diaminoalkane was replaced by a methyl group. When the basicities (ΔG) and proton affinities (ΔH) of the α,ω -diaminoalkanes were evaluated, this prediction was confirmed. It was found that the proton affinities of the α,ω -diaminoalkanes were greater than those of the corresponding monoalkanes by up to 20 kcal/mol for the diaminoalkanes where $n=3$ or larger, indicating the release of additional energy due to the cyclization of the α,ω -diaminoalkanes. When the proton transfer reactions of the diaminoalkanes were studied at different temperatures, the equilibrium constant showed considerable temperature dependence, indicating that the proton transfer reaction was occurring with significant entropy change. Again this was evidence for the cyclization of the cations of the α,ω -diaminoalkanes. The calculated entropy loss for the cyclization of the diaminoalkanes reached a maximum when the

ring size could accommodate a hydrogen bond of linear geometry. This geometry became possible when the α,ω -diaminoalkane ring contained six members, including hydrogen.

The formation of intramolecular hydrogen bonding in the gas-phase has also been confirmed for other bifunctional compounds. Morton and Beauchamp³⁴ investigated a series of α,ω -dimethoxyalkanes, $\text{CH}_3\text{O}(\text{CH}_2)_n\text{OCH}_3$ ($n=2$ to $n=6$). They found evidence for intramolecular hydrogen bonding showing a preference for an eight membered ring ($n=5$). A ring of this size would accommodate a linear hydrogen bond.³⁵ Similar results were reported for other bifunctional species such as amino alcohols^{34,35} and diketones³⁸. But what is the behavior of bifunctional compounds in the negative ion mode?

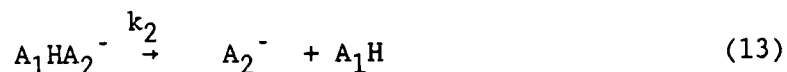
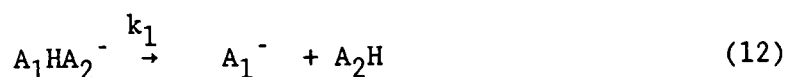
We have chosen to investigate the acidity of a series of aliphatic diols, $\text{HO}(\text{CH}_2)_n\text{OH}$ ($n=2$ to $n=5$), using Ion Cyclotron Resonance Mass Spectrometry. We would like to know the structure of the anion of these diols. Do they form a cyclic structure 2 or maintain the entropically favored straight chain structure 1?



Thermodynamic data obtained from the proton transfer reaction (10) (p 36) can indicate the structure of the anion. In this proton transfer reaction A^- is the anion of the diol and BH is a neutral monofunctional acid. The equilibrium constant, K_{eq} , for the proton transfer is measured experimentally, and the other thermodynamic data are obtained as described

in the results and discussion section of this chapter. It is known from the energetics of a few alkoxide-alcohol clusters that the formation of a symmetric intermolecular hydrogen bond is worth approximately 22 kcal/mol in enthalpy and about 15 kcal/mol in Gibbs free energy.³⁹ If the anion of the diol is cyclizing by the formation of intramolecular hydrogen bonds one would expect the diols to be more acidic by up to 15 kcal/mol in ΔG_{acid} than for monoalcohols of comparable molecular size.

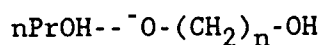
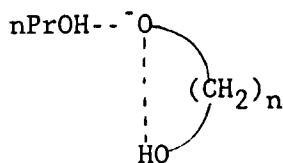
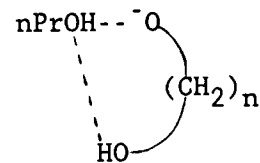
Some work on this problem has already been done by Houriet, Tabet, and Tchapla.⁴⁰ Their work differs from ours in the method employed. They studied the dissociation of proton-bound dimers whereas we studied proton transfer reactions. Instead of an ICR, they used a double sector mass spectrometer of reverse geometry, a ZAB-2F, operated in the mass-analyzed ion kinetic energy spectrometric (MIKES) mode. This spectrometer was equipped with a high pressure chemical ionization source, into which a binary mixture of alcohols was added at a 1:1 ratio at pressures of approximately 10^{-2} torr. The reactant gas was $\text{N}_2\text{O}/\text{CH}_4$ (1/10) and was added up to pressures of about 1 torr. Source temperatures were approximately 180°C . The dimer ion, once made, was then selected by the magnetic sector of the instrument and the metastable ions were detected by the electrostatic analyzer (ESA). In this method the branching ratio (12)/(13) (p 40) is taken as a measure of the equilibrium constant for $\text{A}_1\text{H} + \text{A}_2^- \rightleftharpoons \text{A}_1^- + \text{A}_2\text{H}$. This method results in the formation of two products as shown in equations (12) and (13) (p 40), where A_1H is 1-propanol and A_2H is a diol.⁴¹



The concentrations of the decomposition products can be directly related to their respective rate constants of formation as shown by equation (14), where I equals ion intensity and the ΔG_{acid} values are scaled to known values for monoalcohols. This relationship

$$\ln I(A_1^-)/I(A_2^-) = \ln k_1/k_2 \propto \delta\Delta G_{\text{acid}}/RT \quad (14)$$

is based on the assumption that k_1 and k_2 behave in an identical manner as functions of the internal energy of the system. This assumption is justified by the use of narrow time/energy domains due to the use of metastable ions, and by the similarity between the kinds of bonds being broken in the dissociation of the proton bound dimers. However, if competitive rearrangements and/or dissociations are possible, the quantification of results can be altered.⁴² There is some question as to the structure of the dimer ion in these studies when dealing with diols. The dimer ion could have any of the following structures 3, 4, or 5

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which upon dissociation could lead to different product distributions and different ΔG_{acid} values. We are doing our acidity studies using Ion Cyclotron Resonance Mass Spectrometry, which does not involve the formation of dimer ions and their consequent dissociation, to validate the results of Houriet and co-workers as well as to report the acidities of some diols not included in the work of Houriet and co-workers.

B. Experimental Section

1. Compounds

Samples of 2,2-dimethyl-1,3-propanediol and 1,5-pentanediol were purchased from Aldrich Chemical Company. Ethylene glycol was purchased from Fisher Chemical Company, and 1,4-butanediol was purchased from Eastman Chemical Company. All diols were used as received with the exception of 1,5-pentanediol, which was distilled prior to use. The anilines used as standard acids were distilled, and the oximes were sublimed prior to use.

2. Method

The ion cyclotron resonance spectrometer described in Chapter 1 was used in the quenched mode to obtain the equilibrium data. The electron beam was on for 40 ms. Delay times were varied from 100 ms upward to 3000 ms while scanning masses 40 amu through 120 amu. Isoamyl nitrite was used as an electron impact generated source of isoamyl alkoxide, which then deprotonated the neutral diols. Samples of the diols were admitted into the hot spectrometer (350K - 365K) approximately sixteen hours prior to the collection of data in order to obtain stable pressures. The ion gauge pressure of the isoamyl nitrite was kept in

the region of 2×10^{-7} torr (ion gauge). Neutral pressures of the diols and equilibrating acids were varied with a total ion gauge pressure ranging from 6×10^{-6} torr to 1×10^{-5} torr depending on combinations and acidities.

C. Results and Discussion

Table VI (p 43) lists the thermodynamic data for the diol systems obtained by ion/molecule reaction equilibrium studies (single temperature) using Ion Cyclotron Resonance Mass Spectrometry. The equilibrium studied is represented by equation (15). The temperature at



AH = Diol

BH = Aniline, p-fluoroaniline, m-fluoroaniline or
pivaldehyde oxime

which the equilibria were studied, the acid used to equilibrate the diol, values for the equilibrium constant and the $\delta\Delta G_{\text{acid}}$ values for each equilibrium studied are given in Table VII (p 44). The $\delta\Delta G_{\text{acid}}$ values were obtained using equation (16). The ΔG_{acid} values were then derived from equation (17). In order to report a value for ΔH_{acid} using

$$\delta\Delta G_{\text{acid}} = -RT \ln K_{\text{eq}} \quad (16)$$

$$\Delta G_{\text{acid}}(\text{AH}) = \Delta G_{\text{acid}}(\text{BH}) + \delta\Delta G_{\text{acid}} \quad (17)$$

$$\Delta G_{\text{acid}} = \Delta H_{\text{acid}} + T\Delta S_{\text{acid}} \quad (18)$$

equation (18), ΔS_{acid} must be known. The most accurate way of determining a value for ΔS_{acid} is by doing temperature-dependent studies on a system at equilibrium, and from that data constructing a van't Hoff plot of the

TABLE VI
THERMODYNAMIC DATA OBTAINED BY ICR^a

Diol	ΔG_{acid}	ΔH_{acid}	ΔS_{acid}
1,2-ethanediol	360.9	364.7	10.7
1,3-propanediol	355.8	356.8	2.8
2,2-dimethyl-1,3-propanediol	358.3	359.3	2.8
1,4-butanediol	354.6	355.8	3.8
1,5-pentanediol	355.5	256.9	3.8

^aUnits are in kcal/mol for ΔG_{acid} and have an experimental error of ± 2 kcal/mol. Units for ΔH_{acid} are in kcal/mol and ΔS_{acid} are in cal/molK (eu).

TABLE VII
EXPERIMENTAL CONDITIONS AND RESULTS FOR EQUILIBRIUM STUDIES

Diol	BH	Temp.	K_{eq}	$\delta\Delta G^a$
1,2-ethanediol	aniline	359 K	0.078	1.8
1,3-propanediol	p-fluoroaniline	343 K	5.7	-1.2
2,2-dimethyl-1,3-propanediol	aniline	356 K	3.0	-0.77
1,4-butanediol	pivaldoxime	365 K	5.4	-1.2
1,5-pentanediol	m-fluoroaniline	361 K	0.11	1.6

^aUnits are in kcal/mol. A negative sign indicates that acid BH is more acidic than acid AH; a positive sign indicates the opposite.

log of the equilibrium constant versus the reciprocal of the temperature. A value for ΔH_{acid} can then be obtained from the slope of the line of the van't Hoff plot, while $\Delta S_{\text{acid}}/R$ is the intercept. However, it is difficult to do temperature studies in the ICR spectrometer because it is limited to a 100 °C temperature range, with an upward temperature maximum of 120 °C. We are already operating at 80 °C, so little range is available. Therefore, the ΔS_{acid} values must be approximated using equation (19), where $\Delta S_{\text{acid}}(\text{mono})$ is equal to 22.0 cal/molK, the value estimated by statistical mechanics for the corresponding monoalcohol.¹² A value for ΔS_{cycl} was obtained from the

$$\Delta S_{\text{acid}}(\text{diol}) = \Delta S_{\text{acid}}(\text{mono}) + \Delta S_{\text{cycl}} + \Delta S_{\sigma}^{\circ} \quad (19)$$

work done by Yamdagni and Kebarle on the cyclization of the comparably sized α,ω -diaminoalkanes.³³ To a first approximation it is assumed to be a good estimate for the cyclization of the diol system. In equation (19), ΔS_{σ} represents the term for the change in rotational entropy of the system as the diol forms its anion, and is equal to $-R \ln(\sigma_{\text{products}}/\sigma_{\text{reactants}})$ where σ is the symmetry number.¹³

Looking at the ΔG_{acid} values obtained for the diols versus the monoalcohols of comparable structure and molecular weight (Table VIII, p 46), it is observed that the diols are considerably more acidic than the corresponding monoalcohols by up to 12.7 kcal/mol in ΔG_{acid} . This increased acidity can be attributed to the formation of intramolecular hydrogen bonds in the anions of the diols. Maximum stability (12.7 kcal/mol) of the intramolecular hydrogen bond was found for 1,4-butanediol, which can form a seven membered ring. This is

TABLE VIII
COMPARISONS OF DIOL ACIDITIES MEASURED BY ICR WITH COMPARABLE
MONOALCOHOLS^a

Diol	ΔG_{acid}	Monoalcohol	ΔG_{acid}^b	$\delta \Delta G_{\text{acid}}$
1,2-ethanediol	360.9	1-propanol	369.4	8.5
1,3-propanediol	355.8	1-butanol	368.4	12.6
2,2-dimethyl-1,3-propanediol	358.3	tBuCH ₂ OH	366.0	7.7
1,4-butanediol	354.6	1-pentanol	367.3	12.7
1,5-pentanediol	355.5	1-hexanol	366.5	11.0

^aAll units are in kcal/mol.

^bSee reference 30.

comparable to the 15.3 kcal/mol for symmetric intermolecular hydrogen bonds.³⁹ A seven membered ring can accommodate a linear hydrogen bond and was therefore expected to give maximum stability to the diol anion. The increased acidity of all the diols relative to the monoalcohols implies some degree of intramolecular hydrogen bonding for all the diol anions studied. The intramolecular hydrogen bonding in the anions of aliphatic diols forming rings smaller than six members and greater than seven members is only a weak proton bridge. This partial hydrogen bonding in the diol anions containing less than seven members is probably due to the ring strain induced by an OHO bond angle of less than 180° . The presence of methyl substituents on diols forming small anionic rings appears to result in additional eclipsing strain in the ring, as well as reducing the strength of the hydrogen bond due to the polarizability of the methyl groups. This results in a weaker acidity relative to an unsubstituted diol capable of forming the same size ring. Such is the case with the 2,2-dimethyl-1,3-propanediol, which showed an increase in ΔG_{acid} of 2.5 kcal/mol when compared with the ΔG_{acid} value for 1,3-propanediol. When the size of the ring formed by the intramolecular hydrogen bonding of the diol anion exceeds seven members a linear hydrogen bond is still possible. However, now the stabilizing effect of this geometry is counteracted by the decreased entropy of restricting the long carbon chain, making only partial hydrogen bonding possible. Results for the anions of diols capable of forming rings with more than eight members could not be obtained using ICR due to the low vapor pressure of these diols. However, Houriet *et al.*⁴⁰ were able to experiment with aliphatic diols ($n=3$ to $n=12$) using the

MIKES method, and verified the aforementioned assumptions for larger rings. They also found 1,4-butanediol to have the largest increase in apparent acidity for the diols tested, relative to monoalcohols of comparable molecular weight and structure, with decreases in $\delta\Delta G_{\text{acid}}$ values for rings smaller than seven members and in rings with more than eight members.

Table IX (p 49) compares the results for the diols that were tested by both ICR and MIKES. The MIKES results parallel those obtained by ICR, with respect to the direction of the acidities of the three diols, showing the order 1,4 > 1,5 > 1,3. However, the magnitude of the ΔG_{acid} values for the three diols studied by both methods show the values reported by the ICR method to be more acidic than those reported by the MIKES method in all cases.

This discrepancy in ΔG_{acid} values for the diols indicates some doubt as to the validity of the assumptions made by Houriet and coworkers concerning the dissociation of proton bound dimers involving members containing more than one functional group. When deriving equation (14) (p 40) from equation (20), (which is derived from the expression for k as the unimolecular rate constant and refers to the rate constants k_1 and k_2 for equations (12) and (13) (p 40)), the following assumptions were made: (1). $Q_1 = Q_2$ (2). $Q_1^*/Q_2^* \approx \nu_1/\nu_2$ where

$$\ln k_1/k_2 = \ln Q_1^*Q_2/Q_2^*Q_1 + \Delta\epsilon_o/RT \quad (20)$$

Q =the partition function of the dimer ion

Q^* =the partition function for the activated complex

$\Delta\epsilon_o$ =the difference in activation energies for reactions (12) and (13)

TABLE IX
COMPARISONS OF ΔG_{acid} VALUES OBTAINED BY ICR AND MIKES^a

Diol	ICR	MIKES ^b	$\delta\Delta G_{\text{methods}}$
1,3-propanediol	355.8	363.1	7.3
1,4-butanediol	354.6	359.5	4.9
1,5-pentanediol	355.5	359.9	4.4

^aAll units are in kcal/mol.

^bSee reference 10.

ν_1 and ν_2 are the vibrational frequencies of the hydrogen bonds in the dimer ion and $\nu_1 = \nu_2$. By making these assumptions, equation (20) (p 48) is reduced to equation (21), which is similar in form to

$$\ln k_1/k_2 = \Delta\epsilon_o/RT \quad (21)$$

equation (14) (p 40). If all of these assumptions are valid for the diols as they were for the monoalcohols then a plot of $\ln k_1/k_2$ versus ΔG_{acid} would result in a straight line with a slope equal to $1/RT$, where T is not the temperature of the ion source, but the effective temperature of the collisionally activated dimer ions that undergo unimolecular dissociation in a certain region of the mass spectrometer. The effective temperature of the dimer ion is a measure of its internal energy and is determined by the ion's structure.⁴¹

If the values for $\ln k_1/k_2$ of the three diols studied by the MIKES method are plotted against the diol acidities obtained by ICR a straight line is not obtained, as shown in Figure 11 (p 51). It should also be noted that the points for the diols do not lie on the line for the monoalcohols. This result means that some of the assumptions leading to equation (21) are not valid in the case of the diols. It seems that the most likely source of error in the series of assumptions made in deriving equation (21) is in assuming that the vibrational frequencies, ν_1 and ν_2 , are approximately equal. The vibrational frequencies should differ since the monoalcohol of the dimer is restricted to a chain structure whereas the diol is assumed to be cyclized by hydrogen bonding of unknown structure as was illustrated on page 40 of this thesis. Overall, it seems that the assumptions made to validate equation (21)

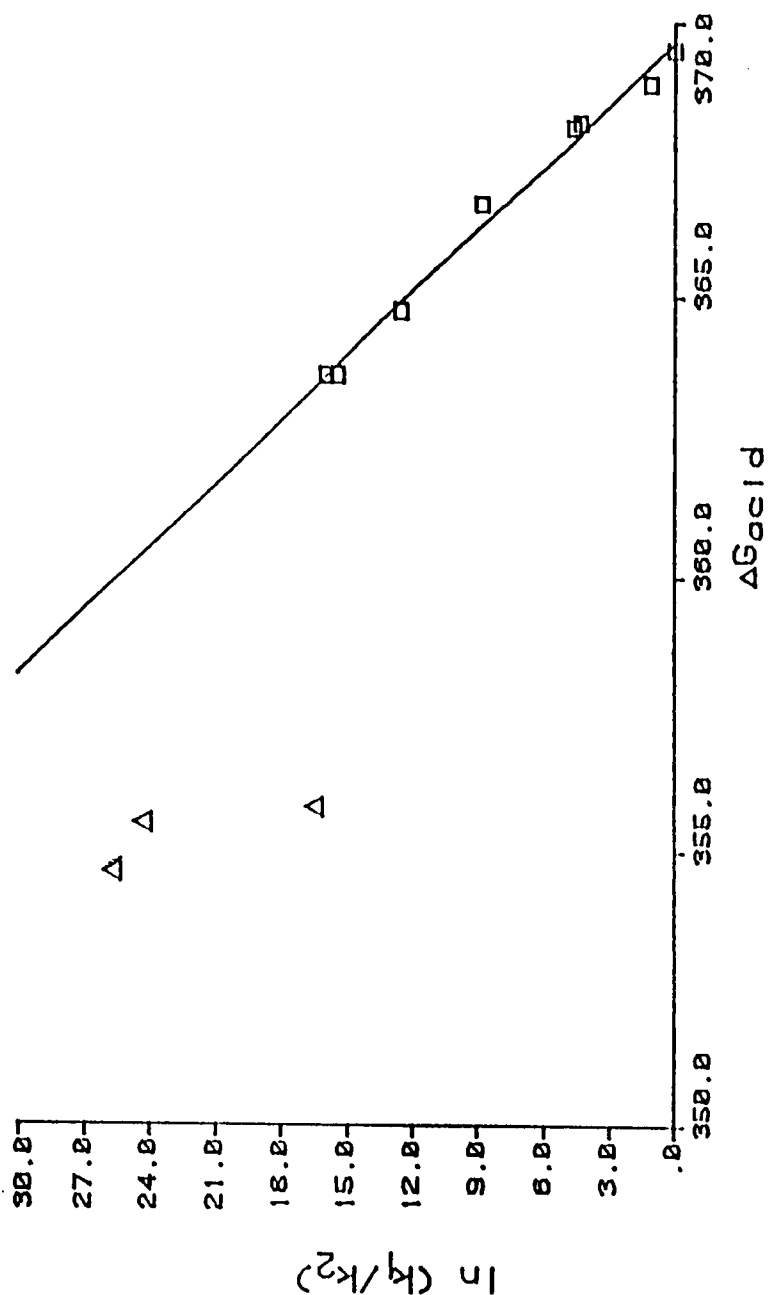


Figure 11. Plot of branching ratios for selected diols and monoalcohols vs. ΔG_{acid} values. The plot represents a comparison of data for the diols (Δ), and the monoalcohols ($\square$). The $\ln k_1/k_2$ values were obtained from references 40 and 42. The ΔG_{acid} values for the diols were obtained experimentally and those for the monoalcohols from reference 30.

seem to work qualitatively but not quantitatively. It would appear that a mathematical correction for the differences in the hydrogen bond frequencies of the two species making up the dimer ion would bring the ΔG_{acid} values for the diols obtained using MIKES into line with those obtained using ICR.

CHAPTER IV

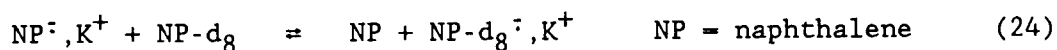
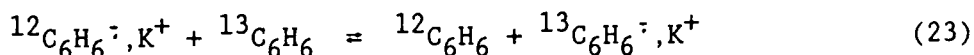
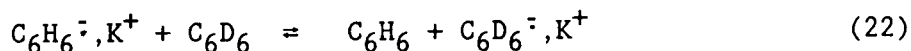
ISOTOPE EFFECTS ON ELECTRON TRANSFER EQUILIBRIA

A. Introduction

Ever since atoms of the same element were found to exist in different isotopic forms, chemists have been interested in separating them for their applications to the fields of energy and the life sciences. The chemical and physical similarities between isotopes make the separation of isotopes difficult. Isotopes have similar chemical and physical properties but may undergo the same chemical reactions at different rates due to their different masses. A water solution containing both ^2H and ^1H can become enriched in the deuteriated species by passing an electric current through the solution. The ^2H water molecules are decomposed at a lower rate than the ^1H water molecules such that more ^1H molecules are lost as gas causing the water molecules left behind to be enriched with the ^2H isotope. Separations can also be achieved by use of phase-exchange reactions where the concentration of one isotope in one phase is favored. Such is the case with ammonia where the ^{15}N isotope is concentrated in the aqueous phase and ^{14}N isotope is concentrated in the gaseous phase.⁴³ Gaseous diffusion is used to separate isotopes of higher mass. This method was developed during World War II to separate ^{235}U from the predominant ^{238}U form of uranium for use in the atomic bomb. In this process ^{235}U was obtained as the gaseous hexafluoride which diffused faster than the ^{238}U hexafluoride. By repeating the process many times separation was accomplished.⁴⁴ There is now evidence that isotopes can be separated

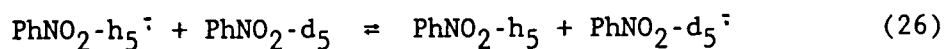
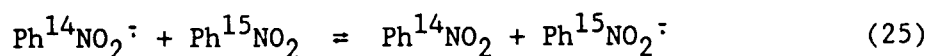
chemically by taking advantage of their differing electron affinities. Stevenson and coworkers separated the ^{15}N and ^{14}N isotopes of nitrobenzene in this way. They started with nitrobenzene (0.37% ^{15}N) dissolved in liquid ammonia and added potassium metal to this solution as a source of electrons. It was found that the ^{15}N nitrobenzene molecules were more likely to pick up the electrons and form radical anions than the molecules of ^{14}N nitrobenzene. After the ammonia was evaporated from the solution and the neutral nitrobenzene distilled, the potassium salt of nitrobenzene enriched in ^{15}N was left behind. This salt was then chemically treated to return it to neutral nitrobenzene. This process was repeated sixteen times to produce a sample of nitrobenzene that was 99% ^{15}N nitrobenzene.^{45,46}

Electron spin resonance spectroscopy (ESR) was used by Stevenson and coworkers to probe the solution-phase electron transfer equilibria of several isotopic systems. Those isotopic systems are shown below by reactions (22), (23), and (24). It was found that the solution-phase electron affinity of benzene (22) decreased upon replacement of the hydrogens with deuteriums.⁴⁷ This was also the case with naphthalene (24).⁴⁸ Similar results were obtained for benzene when ^{12}C was replaced with ^{13}C (23).⁴⁷ In all cases the light ion was favored regardless of solvent, giving values for the equilibrium constants of less than one. The solvents used were tetrahydrofuran (THF) and dimethoxyethane (DME).



Such equilibria result in the enrichment of the neutral. It was then speculated that this would always be the case when a light atom was replaced with its heavy isotope in a molecule where the atom being replaced had been located at a position of high spin and charge density.⁴⁸ However, when the ^{14}N atom in nitrobenzene was replaced with ^{15}N , in solution, the electron equilibrium favored the heavy ion. It was found that this effect could be reversed by changing the counterion from potassium to sodium in liquid ammonia.⁴⁶

The question arises from Stevenson's work as to the cause of the diminished or enhanced electron affinities of the isotopically labeled species. How much of this effect is inherent in the structure of the radical anion and how much is due to solvent or counterion effects? Gas-phase studies using ion cyclotron resonance mass spectrometry were undertaken to probe this question. In the gas-phase the intrinsic equilibrium constant can be determined, and the free energy changes of the electron transfer can be calculated as described in Chapter I, part E, of this thesis. Two systems were studied. In one system the ^{14}N radical anion of nitrobenzene was equilibrated with ^{15}N nitrobenzene (25). In the other system the radical anion of deuteriated nitrobenzene was equilibrated with nitrobenzene (26).



Intrinsic differences in the systems are postulated to arise from differences in the electronic effects and zero point energies of the radical anions.⁴⁸

B. Experimental Section

1. Compounds

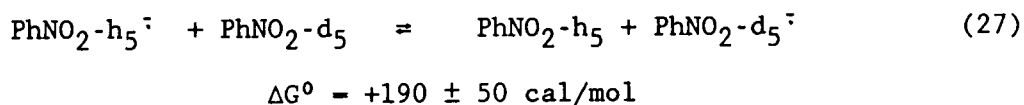
Nitrobenzene was purchased from Fisher Chemical Company. Samples of d_5 -nitrobenzene and ^{15}N -nitrobenzene were donated by G.R. Stevenson of Illinois State University. Samples were used without further purification - the ICR spectrum showed no impurities.

2. Method

The ion cyclotron resonance mass spectrometer described in Chapter I was used to obtain gas phase equilibrium constants for the PhNO_2 - h_5/PhNO_2 - d_5 and $\text{Ph}^{15}\text{NO}_2/\text{Ph}^{14}\text{NO}_2$ systems. The vapor from a premixed solution of PhNO_2 - h_5/PhNO_2 - d_5 ($50\mu\text{l}/100\mu\text{l}$ or $50\mu\text{l}/50\mu\text{l}$) was admitted to the ICR with a combined neutral pressure of approximately 7×10^{-6} torr, ion gauge. Two separate samples were used for the $\text{Ph}^{15}\text{NO}_2/\text{Ph}^{14}\text{NO}_2$ system due to a shortage of sample. Each pure sample was admitted through a leak valve. Pressure ratios of 1:1 and 2:1 were used with a total neutral pressure of 7×10^{-6} torr (ion gauge). Relative ion gauge sensitivities for the two isotopes were assumed to be the same. The ICR was operated in the quenched mode with a 40 ms grid at detection times ranging from 100 ms to 1000 ms. The electron energy was kept at a minimum (0-1 eV) and the filament current (3.5 A) and trapping voltages (-1.0 V) set to give maximum signal intensities.

C. Results and Discussion

The gas-phase results for the $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ system and the $\text{Ph}^{14}\text{NO}_2/\text{Ph}^{15}\text{NO}_2$ systems are shown in Table X (p 58). The results for the $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ system were in line with solution-phase results for similar systems. The equilibrium favored the formation of the light



ion (27). Gas-phase studies on isotopic proton-transfer systems have also produced results that favor the light ion. Reported secondary isotope effects for deuterium substitution into CH_3X^- ($\text{X} = \text{O}, \text{NH}, \text{S}$) for the acidity of CH_3XH ranged from 100 to 170 cal/mol per D, whereas in the electron transfer system of $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ the value was 40 cal/mol per D.⁴⁸ The secondary isotope effects of proton transfer can be compared with those for electron transfer. In each case redistribution of electron density through the C-H/C-D bonds is expected to stabilize the effect of the extra electron. For CH_3X^- , electron density is drawn into the C-H/C-D antibonding orbitals causing the C-H/C-D bonds to weaken favoring the formation of the light ion.⁴⁷ The magnitude of the secondary isotope effect for the CH_3X^- system is expected to be larger than that for the $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ system since hyperconjugation of the C-H/C-D bonds is possible whereas in the $\text{PhNO}_2\text{h}_5/\text{PhNO}_2\text{-d}_5$ system only poor s-p overlap of the C-H/C-D bonds is possible with the aromatic π system. Semi-empirical molecular orbital calculations (AM1) performed on the nitrobenzene neutral and the nitrobenzene radical anion (Table XI, p 59) show a shortening of the

TABLE X
EQUILIBRIUM CONSTANTS AND FREE ENERGIES OF ELECTRON TRANSFER

<u>electron transfer</u> from to		T(K)	K _{eq}	ΔG^{0a} (cal/mol)
PhNO ₂ -h ₅	PhNO ₂ -d ₅	305	0.73	190 ± 50
Ph ¹⁴ NO ₂	Ph ¹⁵ NO ₂	305	1.02	-12 ± 12

^aExperimental error was determined by multiple experiments.

TABLE XI

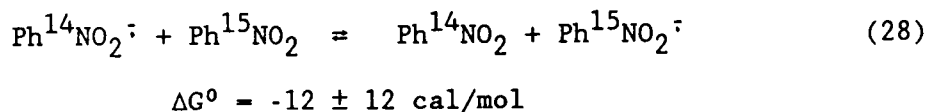
MOLECULAR ORBITAL CALCULATIONS (AM1). BOND LENGTHS (Å) OF
NITROBENZENE AND OF NITROBENZENE ANION RADICAL^a

Parameter	PhNO ₂	PhNO ₂ ⁻	δ bondlengths
N - O	1.2021	1.2275	+0.0254
C - N	1.4862	1.4145	-0.0717
C _i - C _o	1.4046	1.4324	+0.0278
C _o - C _m	1.3932	1.3814	-0.0118
C _m - C _p	1.3953	1.4064	+0.0111
C _o - H	1.1034	1.0989	-0.0045
C _m - H	1.0008	1.0992	+0.0984
C _p - H	1.1011	1.0951	-0.0060

^a See reference 48.

C-H bonds on electron attachment; whereas in benzene and naphthalene, similar calculations indicate that the C-H/C-D bonds lengthen upon formation of the radical anion. In both cases equilibrium favors the formation of the light ion. This result implies that more than first order causes are responsible for the gas-phase results obtained for the $\text{PhNO}_2\text{-h}_5/\text{PhNO}_2\text{-d}_5$ system. However, calculations do indicate a zero point energy difference that favors the formation of the light ion.⁴⁸

An equilibrium constant of 1.02 was measured for the $\text{Ph}^{14}\text{NO}_2/\text{Ph}^{15}\text{NO}_2$ system (28), indicating a similarity in the electron affinities of the two isotopes. Repeated measurement in the ICR spectrometer did not alter the results.⁴⁸ The nitrogen atom in



nitrobenzene is bound to three other atoms and has a p orbital that is part of the π system. The effects of increasing electronic charge on conjugated systems has been studied by Khatkale and Devlin using IR and Raman spectroscopy. The system they studied involved the reduction of tetracyanoethylene to its radical anion. Results indicate that multiple bonds are weakened (lengthened) and single bonds are strengthened (shortened) on formation of the radical anion.⁵⁰ It appears that in the $\text{Ph}^{14}\text{NO}_2/\text{Ph}^{15}\text{NO}_2$ system bond lengthening and shortening effects around the nitrogen atom cancel, leading to the value for the gas-phase equilibrium constant of essentially one. Confirmation comes from calculations (Austin model one (AM1)) that indicate a lengthening of the nitrogen-oxygen bonds and a shortening of the nitrogen-carbon bonds.

This would explain the results obtained in solution. Since there are no intrinsic effects ($K_{eq} \approx 1$) favoring the formation of the heavy or light ion the direction of the equilibrium is influenced by the polarity of the solvent and/or the size of the counterion, making it possible to tune the system for the formation of the desired isotopic ion.

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VITA

Catherine Ann Crowder was born in Saint Louis, Missouri on July 23, 1951. She moved with her family to Knoxville, Tennessee in 1958 where she attended West Hills Elementary School and Bearden High School. She graduated from high school in June of 1969 and then entered the University of Tennessee, Knoxville and in December of 1973 received a Bachelor of Science degree in Elementary Education. She then taught elementary school in Memphis, Tennessee and Atlanta Georgia.

In the fall of 1981 she re-entered the University of Tennessee, Knoxville and in December of 1984 received a Bachelor of Arts degree in Chemistry. She then began study toward a Masters degree in Chemistry supported by a graduate teaching assistantship. This degree was awarded in May of 1989. During this time she received awards for excellence as a graduate teaching assistant, most notably the C. W. Keenan Outstanding General Chemistry Graduate Teaching Assistant Award and The University of Tennessee Chancellor's Graduate Teaching Assistant Award. She is a member of the American Chemical Society and the American Society for Mass Spectrometry.