# Investigations of pressure-dependent ion-molecule chemistry using pulsed high pressure mass spectrometry

by Douglas Hale Williamson

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
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Abstract:
For years, one of the primary goals in the field of gas - phase ion chemistry has been a “bridging of the gap” between operative energetics in gas phase and solution phase chemistry. For accurate comparisons to be made between identical chemical systems in different solvent environments, gas - phase energetics must be studied under pressures high enough to ensure a thermal distribution of relevant energetics. In addition, many gas - phase kinetic and equilibrium processes display significant pressure - dependent behavior. The work presented here characterizes four studies that investigate the impact of buffer gas pressure and identity on chemical behavior. The first section examines buffer gas effects on kinetic processes operative in the electron capture behavior of azulene. It was found that, at conditions commonly employed in electron capture methods, thermal electron detachment (TED) processes display a positive temperature dependence that significantly lowers detection limits for low electron affinity compounds. The second section investigates the pressure dependence of the electron capture reaction of POC13. In this work, for the first time, the competitive dissociative and resonance EC product pathways were found to display a significant pressure dependence. This pressure dependence was modeled with Boltzmann energy distributions and RRK kinetic theory. The third section characterized a significant, pressure - dependent source of error in PHPMS studies of ion - molecule kinetics. Specifically, at low pressures, molecular flow conditions in the ion source lead to an enhancement of neutral reagent concentrations yielding inflated apparent rate constant measurements. Source parameters such as pressure and aperture dimensions were manipulated to characterize this phenomenon. The final study examined ion - molecule cluster equilibria in order to create a method for stabilizing low electron affinity compounds against TED and side reaction processes that ultimately limit detection limits for EC - based methods. To achieve this goal, the Lewis acid SiF4 was used to cluster low electron affinity compounds containing oxygen and this method has potential applications in explosives residue analysis as well as trace analysis work with electron capture mass spectrometry (ECMS).

# INVESTIGATIONS OF PRESSURE – DEPENDENT ION – MOLECULE CHEMISTRY USING PULSED HIGH PRESSURE MASS SPECTROMETRY

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of a thesis submitted by

Douglas H. Williamson

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Eric Grimsrud Eric Grimsrud 6/21/00
(Signature) (Date)

Approved for the Department of Chemistry

Eric Grimsrud Eric Grimsrud 6/21/00
(Signature) (Date)

Approved for the College of Graduate Studies

Bruce McLeod Bruce R. McLeod 6-27-00
(Signature) (Date)

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# ABSTRACT

For years, one of the primary goals in the field of gas – phase ion chemistry has been a "bridging of the gap" between operative energetics in gas phase and solution phase chemistry. For accurate comparisons to be made between identical chemical systems in different solvent environments, gas – phase energetics must be studied under pressures high enough to ensure a thermal distribution of relevant energetics. In addition, many gas - phase kinetic and equilibrium processes display significant pressure – dependent behavior. The work presented here characterizes four studies that investigate the impact of buffer gas pressure and identity on chemical behavior. The first section examines buffer gas effects on kinetic processes operative in the electron capture behavior of azulene. It was found that, at conditions commonly employed in electron capture methods, thermal electron detachment (TED) processes display a positive temperature dependence that significantly lowers detection limits for low electron affinity compounds. The second section investigates the pressure dependence of the electron capture reaction of $POCl_3$. In this work, for the first time, the competitive dissociative and resonance EC product pathways were found to display a significant pressure dependence. This pressure dependence was modeled with Boltzmann energy distributions and RRK kinetic theory. The third section characterized a significant, pressure – dependent source of error in PHPMS studies of ion – molecule kinetics. Specifically, at low pressures, molecular flow conditions in the ion source lead to an enhancement of neutral reagent concentrations yielding inflated apparent rate constant measurements. Source parameters such as pressure and aperture dimensions were manipulated to characterize this phenomenon. The final study examined ion – molecule cluster equilibria in order to create a method for stabilizing low electron affinity compounds against TED and side reaction processes that ultimately limit detection limits for EC – based methods. To achieve this goal, the Lewis acid $SiF_4$ was used to cluster low electron affinity compounds containing oxygen and this method has potential applications in explosives residue analysis as well as trace analysis work with electron capture mass spectrometry (ECMS).

# INTRODUCTION

The field of gas phase ion chemistry (GPIC) has experienced a period of remarkable growth over the past 30 years (1-5). As a result of this expansion, GPIC phenomena and mass spectrometric techniques currently find application in areas of science ranging from biochemistry to astrophysics.

Accompanying GPIC research into applied technology is the development of techniques probing ion molecule systems in search of theories bridging the gap between gas phase and solution phase chemical behavior. As Speranza has pointed out, there is currently much debate regarding the value of the intrinsic chemical information typifying GPIC research (6). One school of thought suggests that investigation of solvent - free ion - molecule behavior serves no useful purpose since solvent effects play such a large role in chemical reactivity. In contrast, many opine that direct comparison between gas - phase and solution chemistry is the only way to truly separate intrinsic reactivity from the solvation and ion - pairing effects that often dominate chemical behavior in condensed phases.

In order to draw proper comparisons between gas - phase and solution - phase chemistry, gas - phase data must be collected under the same classical kinetic, structural and stereochemical methodologies as the solution phase analogue where all relevant species are in a state of thermal equilibrium. In more formal terms, all gas phase species must have Boltzmann energy distributions for all degrees of freedom; i.e. the system must be in a state of thermal equilibrium with its environment (7).

Regardless of formation method, an isolated, gaseous ion is thermalized by either radiative emission or buffer gas collisional stabilization. Radiative relaxation processes are sometimes observed with complex molecules, however, collisional stabilization is the dominant relaxation mechanism for the majority of gas phase ions (6). To fully explain the role of buffer gas in ion - molecule reactivity, it is necessary to develop a model of gas phase energetics that accounts for the role of buffer gas on system kinetics and thermodynamics. Before addressing these issues, however, it is important to develop many unique features of ion - molecule reaction coordinates.

## Model of Gas Phase Ion - Molecule Reaction Energetics

In 1977, Brauman et al. (8) studied nucleophillic substitution kinetics reactions for a series of anionic nucleophiles and neutral substrates. While interpreting the data in terms of nucleophillicity, leaving group ability, and steric effects, Brauman and coworkers determined that traditional theories of reaction coordinate energetics were insufficient for proper characterization of observed kinetics. Of particular interest was the large variation in observed reaction rate constants - ranging from collisional to values almost beneath detection capabilities. While many ion - molecule reactions are slow due to entropic, dynamic, or steric effects, the chemical series of this particular study were, relatively speaking, structurally similar. It was not possible to explain these variations with past theories of gas phase reaction coordinate energetics. Particularly problematic was the $Cl^-$ / $CH_3Cl$ system where experimental $S_N2$ kinetics led directly to the proposal of a novel reaction coordinate.

Under traditional notions of reaction energetics, the $[Cl \circ CH_3 \circ Cl]^-$ transition state must be either the minima of an attractive potential energy surface or the maxima of a traditional reaction coordinate where reactants and products are separated by a relatively high energy transition state barrier. Simple attractive electrostatic forces between the nucleophillic anion and neutral substrate rule out the possibility of a traditional reaction coordinate with no attractive minima. Conversely, if the reaction proceeds through an intermediate representing the potential energy surface minima, then there are no barriers to transition state formation and the observed rate constant should be one - half the collisional rate constant for formation of the $Cl^- \circ CH_3Cl$ association species. However, the experimental rate constant for this system was about 0.3 % of the collisional rate constant which invalidates the possibility of a single intermediate with no formation barriers. In addition, the symmetry of this system suggests that a low - energy intermediate with formation barriers would only be possible on a potential energy surface containing three minima. The kinetic data could also be interpreted in terms of a double well potential energy surface that has become the accepted model for ion – molecule systems of this type. In Figure 1 (reproduced from Speranza (6)), a gas phase double well potential (Curve A) is seen to evolve from a solution phase potential energy surface (Curve C) as the degree of solvation is reduced. Figure 1 demonstrates the energetic variations occurring in different chemical reaction environments. In particular, the transition state moves from a high energy state, relative to reactants, to an energy that is roughly equal to that of the reactants. The quite dramatic variation in the kinetic data discussed previously can now be interpreted with respect to this new understanding of

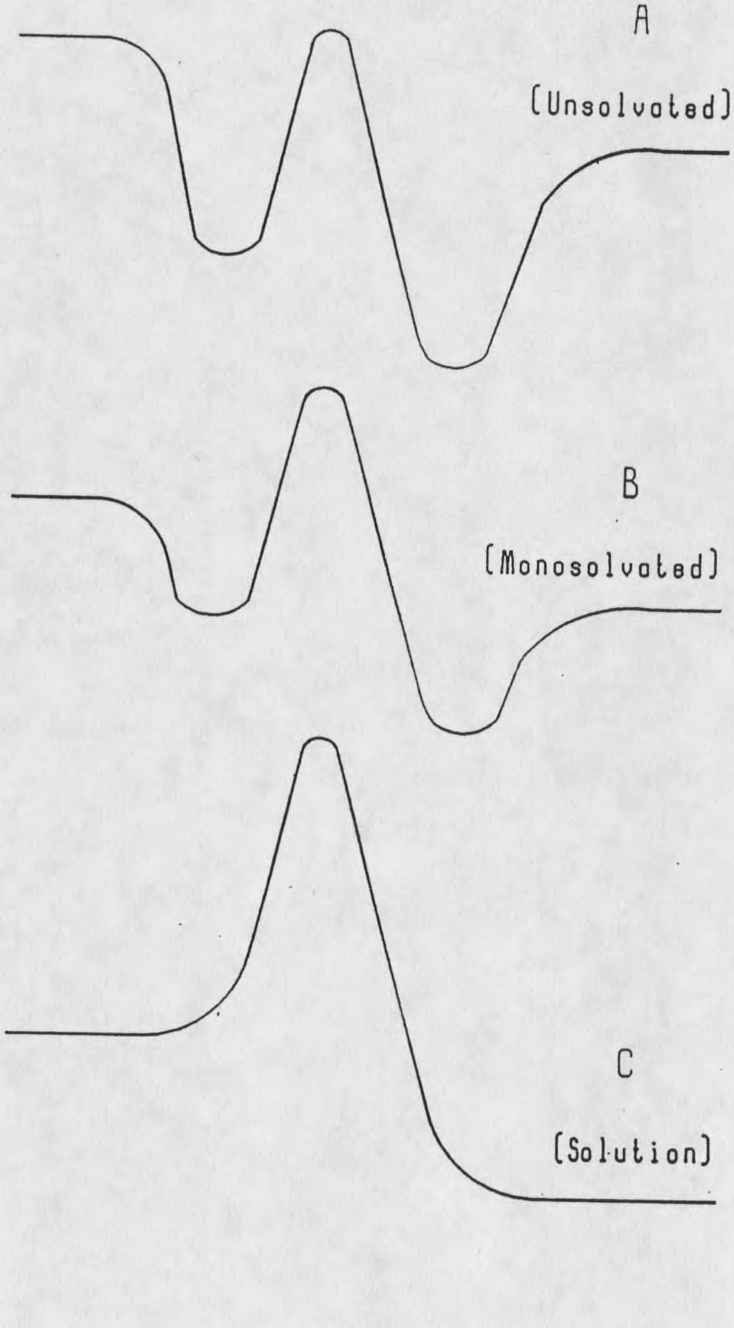

A
(Unsolvated)
B
(Monosolvated)
C
(Solution)

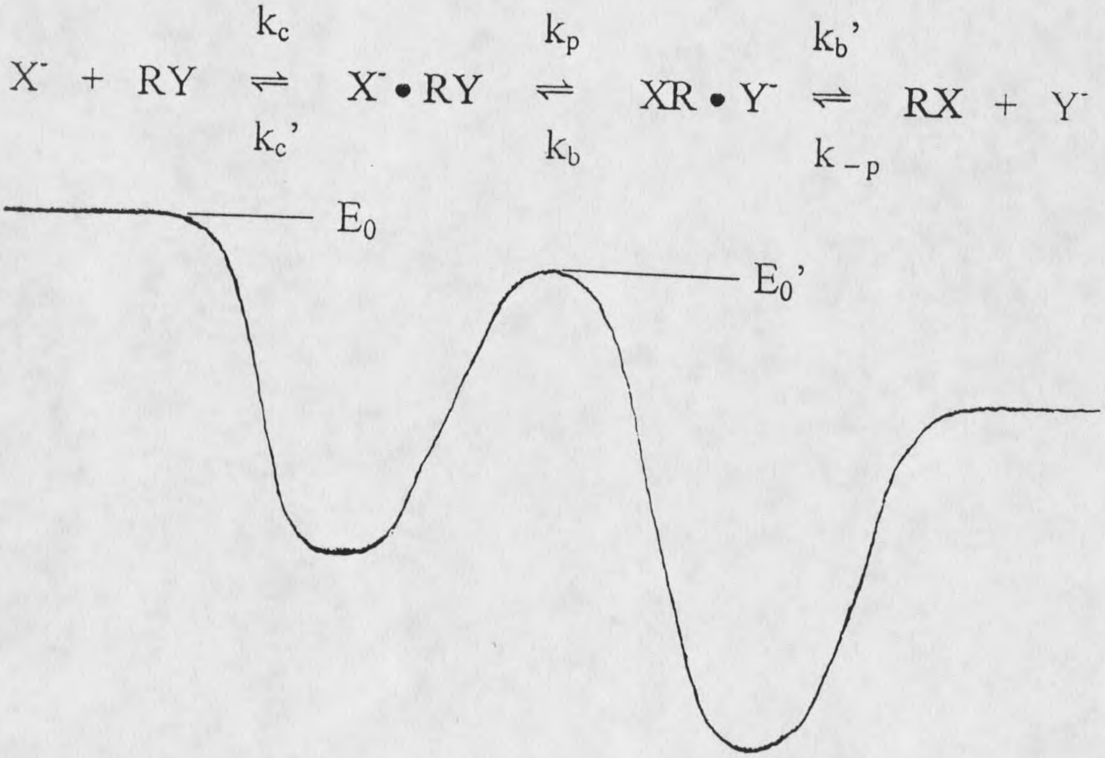
**Figure 1.** Potential energy surface for a reaction under unsolvated (Curve A) conditions, monosolvation of the ionic reactant (Curve B), and solution phase conditions (Curve C).

gas phase ion – molecule energetics where the rate of nucleophillic substitution can now be envisioned to vary as a function of relative central barrier height.

With this new insight, the kinetics of gas phase nucleophillic substitution reactions can be interpreted by the mechanism outlined in equation 1.

$$X^- + RY \underset{k_b}{\overset{k_c}{\rightleftharpoons}} X^- \circ RY \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} XR \circ Y^- \underset{k_c'}{\overset{k_b'}{\rightleftharpoons}} RX + Y^- \qquad (1)$$

In this reaction sequence, also outlined in Figure 2, $k_c$ represents the rate constant for formation of an ion / neutral association complex which, from this point, will be referred to as an entrance channel complex. The entrance channel complex is formed with an excess energy equal to the enthalpy of formation for the thermalized cluster species. Conversely, $k_b$ expresses the rate constant for unimolecular dissociation of the entrance channel complex back to reactants. Upon formation, the entrance channel complex, barring dissociation by $k_b$, isomerizes by passage through the transition state, $k_p$, to form the exit channel complex, $XR \circ Y^-$, which can either dissociate to form products, $k_b'$, or reisomerize to the entrance channel complex, $k_c'$. If $k_b > k_p$, then the overall reaction rate will be less than half of $k_c$ with relative values of $k_b$ and $k_p$ determining overall reaction rate. If $k_{-p}$ is assumed to be negligible, then the bimolecular rate constant is given by $k_{overall} = (k_c k_p) / (k_b + k_p)$. This assumption is valid, for these systems, because, for exothermic reactions, $k_b' > k_b$, and product formation is energetically favored if the two reactions are sufficiently similar entropically. For thermoneutral reactions, all rate



$$X^- + RY \underset{k_c'}{\overset{k_c}{\rightleftharpoons}} X^- \bullet RY \underset{k_b}{\overset{k_p}{\rightleftharpoons}} XR \bullet Y^- \underset{k_{-p}}{\overset{k_b'}{\rightleftharpoons}} RX + Y^-$$

**Figure 2.** Mechanism and potential energy surface for a representative gas phase nucleophillic displacement reaction.

constants lie below collisional levels indicating that $k_b' = k_b >> k_p$. Once the central barrier is overcome, the exit channel complex immediately dissociates to products making the assumption stated above valid for the Cl / $CH_3Cl$ system as well as general gas phase $S_N2$ reactions like $Cl^-$ / $CH_3Br$.

This model demonstrates that the overall reaction rate will vary as a function of relative dissociation and isomerization rates of the entrance channel complex. These rates vary as a function of the relative barrier heights, depicted in Figure 2 as $E_0$ and $E_0'$. If $E_0'$ is larger than $E_0$, the overall reaction rate will be slow with unimolecular decomposition back to reactants providing a dominant pathway to the entrance channel complex. Conversely, a small central barrier will result in the isomerization pathway becoming the dominant loss mechanism for the entrance channel complex. If the central barrier is comparable to the energy of the separated reactants, the impact on kinetic behavior is more difficult to interpret. In this case, the kinetics can be interpreted with statistical theories describing relative isomerization and dissociation rates in terms of the transition state associated with each competing kinetic pathway. The dissociation pathway proceeds through a relatively "loose" centrifugal bottleneck while the isomerization pathway proceeds through a relatively "tight" transition state configuration. As depicted in Figure 3, the dissociation pathway is favored entropically due to the higher state density associated with the centrifugal barrier configuration. This theory is supported by the observed negative temperature dependencies associated with this type of reaction.

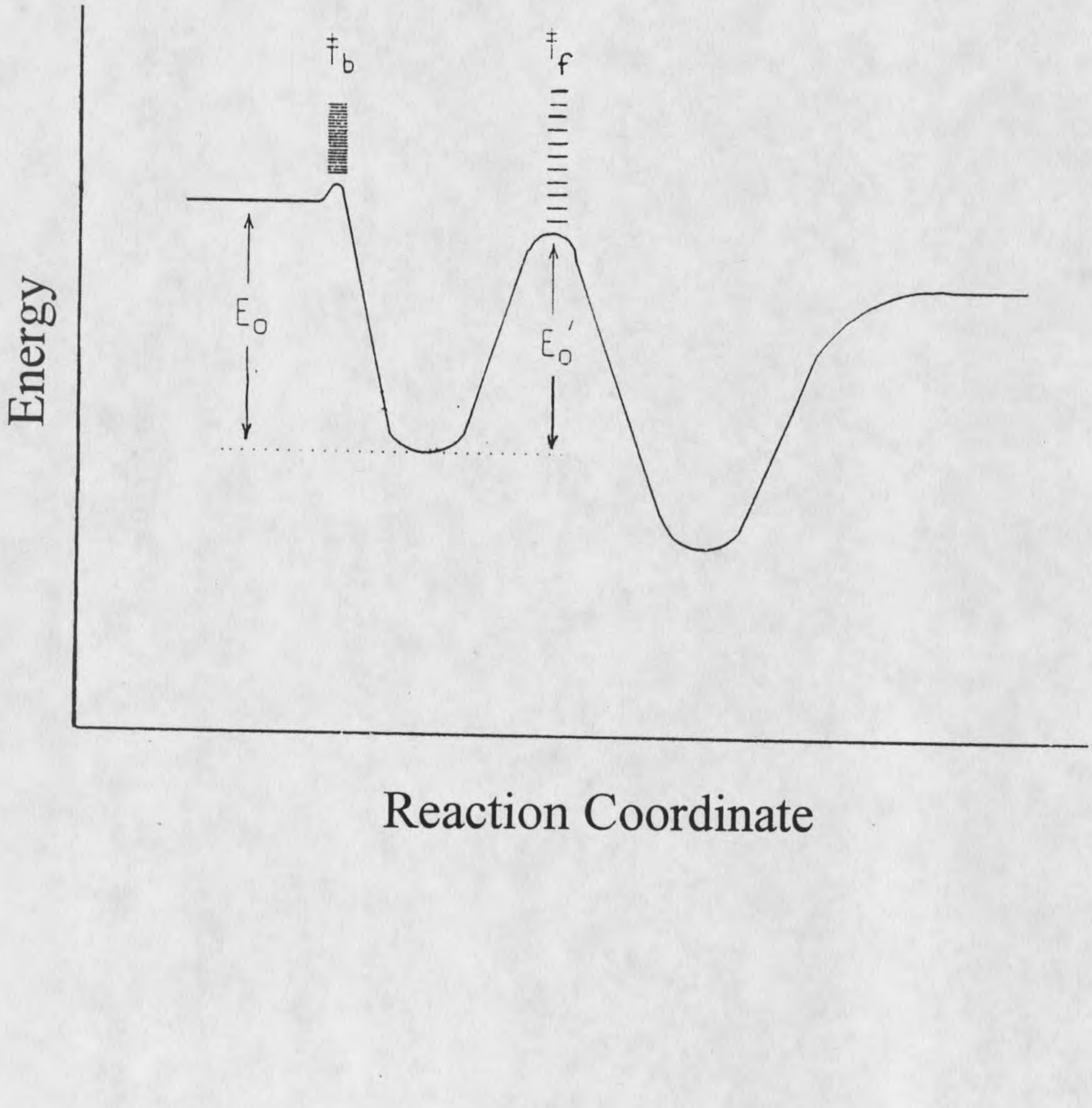

‡b
‡f
Eo
Eo'
Energy
Reaction Coordinate

**Figure 3.** Plot demonstrating qualitative energy level spacing between the two transition states operative in the gas phase $S_N2$ reaction coordinate.

## Model for Pressure Dependent Gas Phase Ion – Molecule Kinetics

The $S_N2$ reaction between $Cl^-$ and $CH_3Br$ has served as a gas phase prototype for comparison between experiment and theory (9-11). Experimentally, this reaction displays a negative temperature dependence and positive pressure dependence; it is the pressure dependence that will be the focus of the following discussion.

Under nonthermal conditions, the nascent entrance channel complex preferentially decomposes back to reactants due to favorable statistical factors for this process. However, if the complex undergoes enough buffer gas collisions to completely remove excess energy imparted to the complex prior to isomerization or dissociation, the energy distribution for the complex will assume a thermal distribution above the zero point energy of the reaction coordinate surface. In this case, reaction kinetics can be treated with traditional Arrhenius plots of Log ($k_{obs}$) vs. $T^{-1}$ which provide information regarding the magnitude of the central energy barrier. This scenario is often referred to as a high pressure limit of kinetic behavior (HPL) and it is under these conditions that direct comparison between gas phase and solution phase chemistry is valid.

In the HPL, dissociation of the thermal complex to reactants or isomerization to products will proceed through a thermal activation process described by simple transition state theory (TST) shown in equation 2 (12 - 13).

$$k = f \frac{kt}{h} \frac{Q^*}{Q_A Q_B} e^{-Eo/RT} \tag{2}$$

In this expression, $Q^*$, $Q_A$, $Q_B$ are the partition functions (electronic, vibrational and rotational) of the activated complex and reactants A and B, T is the temperature of the buffer gas, $E_0$ represents the transition state energy relative to the zero point energy of the entrance channel complex and $f$ is a transmission coefficient for passage through the transition state . This transmission coefficient is invoked to account for the possibility of a nascent exit channel complex reisomerizing through the central barrier to form the entrance channel complex. Barrier recrossing has been observed in trajectory calculations of gas phase $S_N2$ systems by Hase (14 - 18) and successfully employed to interpret kinetic data with TST modeling by Grimsrud and coworkers (10). The fraction of species crossing the transition state without recrossing is assumed to approach unity as the buffer gas pressure is increased (12).

Conversely, in a low pressure environment the entrance channel intermediate energy distribution will not be described by a Boltzmann distribution. When the kinetic time scale for a chemical intermediate is much smaller than the time between buffer gas collisions, the kinetics occur via a "chemical activation" process typifying low pressure limit (LPL) kinetic behavior. The method invoked for analysis of subsequent unimolecular kinetics, the RRKM (Rice, Ramsperger, Kassel, and Marcus) theory, is provided in equation 3 (19 - 20).

$$k(E) = \frac{G(E-E_0)}{hN(E)} \tag{3}$$

In this expression, $G(E-E_0)$ is the sum of vibrational and internal rotational quantum states for the transition state configuration at energies above the transition state barrier, $E_0$. N(E) is the density of states for, in the systems referenced here, the entrance channel complex of a double well potential energy surface. As portrayed in Figure 2, the fate of the entrance channel complex, in the absence of thermalizing buffer gas collisions, is described by the ratio of the isomerization and dissociation rate constants. This ratio is described by extending the RRKM treatment into equation 4.

$$\frac{k_p}{k_b} = \frac{G'(E - E_0' - E_{ROT})}{G(E - E_0)} \qquad (4)$$

In this expression, $\Delta E_{ROT}$ is a correction to the internal energy of the forward transition state allowing for angular momentum conservation. Relative rates of isomerization and backdissociation can be described by integration of equation 4 over an appropriate energy distribution (8,19). RRKM theory also assumes that the hyperthermal entrance channel complex energy is randomized to allow for statistical treatment of the unimolecular decomposition.

Due to varying degrees of collisional energy quenching, most ion - molecule reactions occur under conditions somewhere between the thermal and hyperthermal regimes described by RRKM and TST theories. This results from a partitioning of the entrance channel intermediate between thermal and hyperthermal energy distributions - each of which is characterized by unique rate constants for the dissociation and isomerization processes. The introduction of buffer gas collisions to this reaction sequence is demonstrated in equation 5 and Figure 4 which utilizes a generic $X^- + Y$ nucleophillic substitution reaction.

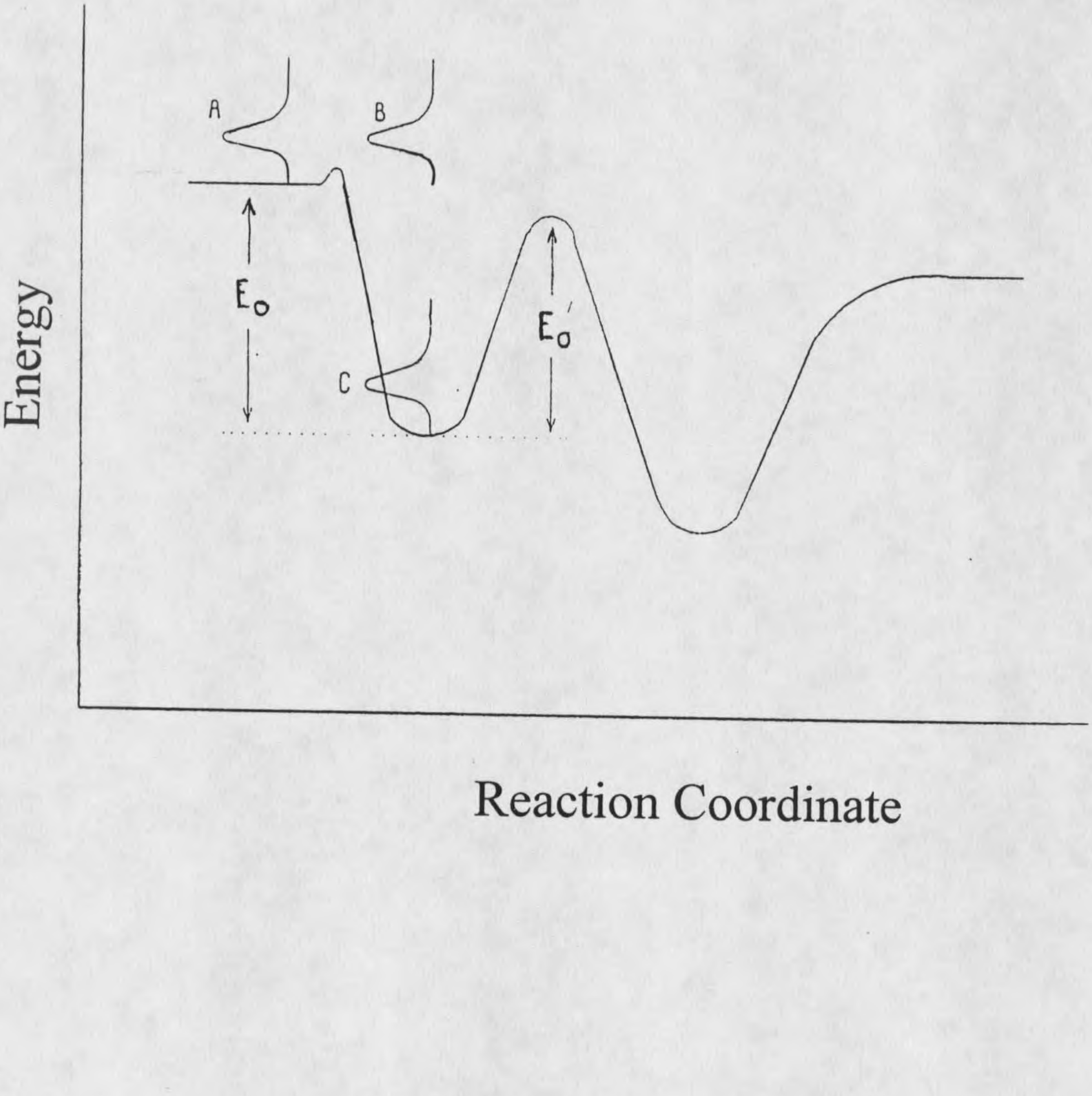


**Figure 4.** Reaction coordinate for the prototypical gas phase $S_N2$ reaction between $Cl^-$ / $CH_3Br$. Curve A represents the energy distribution for the reactants in thermal equilibrium with the buffer gas. Curve B represents the energy distribution for the entrance channel complex under conditions of "chemical activation." Curve C represents the energy distribution for a complex under conditions of "thermal activation."

$$\begin{tikzcd}
X^- + RY \arrow[r, shift left, "k_c"] & (X^- \circ RY)^* \arrow[l, shift left, "k_b"] \arrow[r, shift left, "k_p"] \arrow[d, "k_q{[M]}"] & XR \circ Y^- \arrow[l, shift left, "k_{-p}"] \arrow[r, shift left, "k_b'"] & RX + Y^- \arrow[l, shift left, "k_c'"] & (5) \\
& X^- \circ RY \arrow[ul, "k_b'"] \arrow[ur, "k_p'"'] & & &
\end{tikzcd}$$

In this sequence, the intermediate, $X^- \circ RY$, will be subject to either thermal activation (TST), chemical activation (RRKM) or a combination of processes depending on the operative experimental pressure. This reality obviates the need for explicit knowledge of pressure conditions prior to kinetic data interpretation. Most instrumental techniques have a limited pressure range and, therefore, many kinetic measurements are subject to significant pressure – related variation reflecting intrinsic entropic factors associated with the system of interest.

## Instrumental Methods Utilized in the Study of Gas Phase Ion Chemistry

Figure 5 shows a variety of ion – molecule instrumental techniques and the wide range of pressures available to investigators in the field. Noteworthy within this instrumental ensemble are the ion cyclotron resonance (ICR) techniques operating at pressures ranging from $10^{-2}$ Torr to $10^{-8}$ Torr (21 - 22) and the flow tube methods (FA and SIFT) which operate around 1 Torr and are most similar to the techniques utilized here. Another instrumental method, relevant to this work, is ion mobility mass spectrometry (IM - MS) which is capable of operating at pressures of approximately 1 atmosphere (23 – 28).

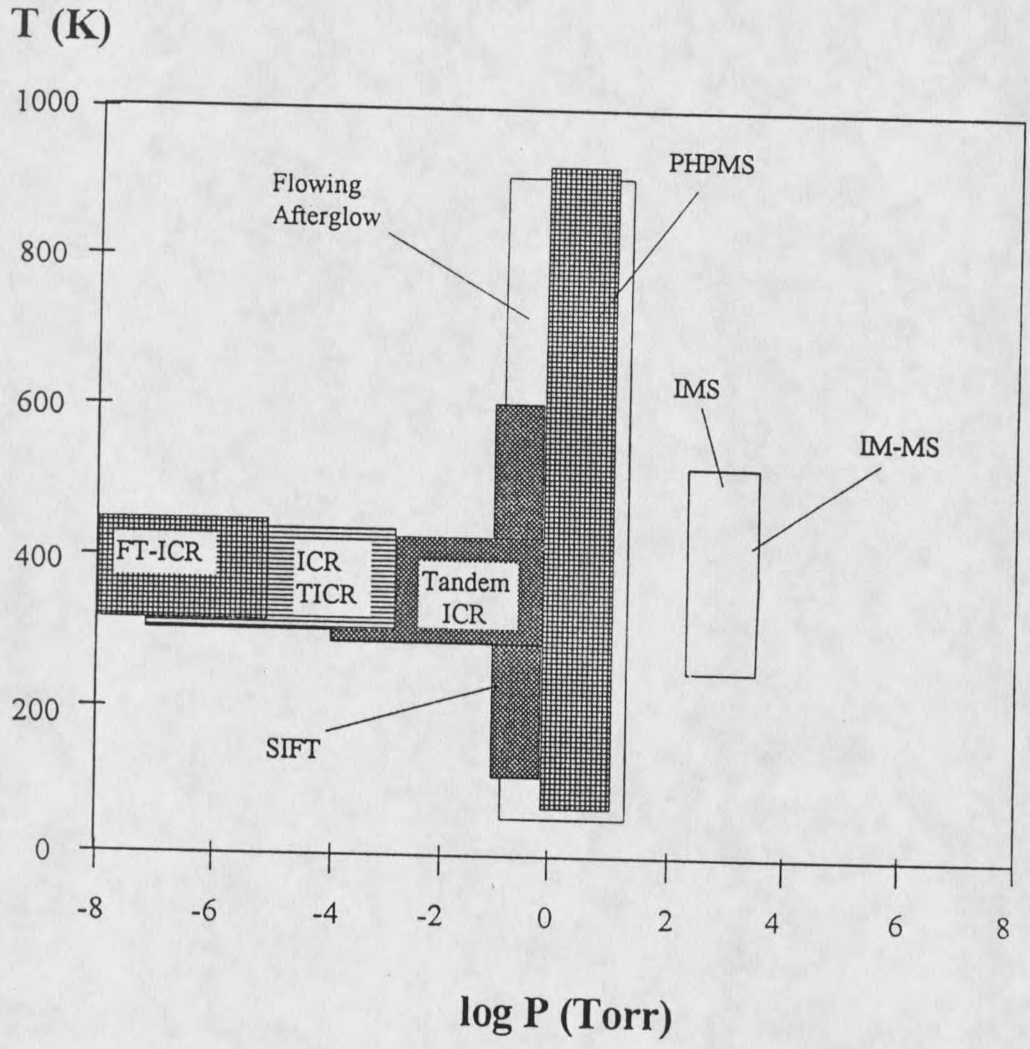


**Figure 5.** A survey of the primary instrumental methods used for the investigation of ion – molecule phenomena. The operative pressure range of this instrumentation spans approximately 11 orders of magnitude.

ICR methods, commonly employed in the study of ion – molecule chemistry under conditions of low pressure (<< 1 Torr), are responsible for a plethora of gas phase ion – molecule kinetic data. One key advantage associated with this technique is the ability to measure gas phase chemical kinetics as a function of reactant or product ion kinetic energy (29 – 32). However, due to low operating pressures, ICR methods collect data under hyperthermal conditions that complicate modeling of observed chemistry since ion energies are often poorly defined.

In flowing afterglow (FA) and selected ion flow tube (SIFT) instrumentation, ionization is achieved in a pure carrier gas, typically helium, by a hot cathode electron emitter (33). The resulting plasma, consisting of electrons, positive ions and a small amount of negative ions, is constrained to the carrier gas flow and charged particles are thermalized as they move away from the ionization region. Downstream from this ionization region, an ion source gas is added to the discharge afterglow to generate ions that will react further downstream with reagent gases to create the chemistry of interest. Like ICR methods, FA methods provide some degree of control over ion - molecule interaction energies enabling determination of energy dependent reaction kinetics (34 - 35). SIFT techniques are quite similar to the FA methods, but vary in the method of ion introduction. Specifically, in SIFT experiments, generated ions are mass – selectively passed to the flow tube through a quadrupole mass filter. This eliminates many background and secondary ion products that frequently interfere with proper data collection. Both of these techniques have a relatively narrow operating pressure range (between 0.5 and 1 Torr) that, in contrast to the ICR methods, makes them a mid –

pressure technique where thermalization of ionic reactants is possible and can lead to experimental energies defined by Boltzmann distributions.

As seen in Figure 5, the vast majority of instrumental methods operate below 10 Torr. However, one technique, currently enjoying extensive use in our laboratory, is ion mobility mass spectrometry (IM-MS) which operates at approximately atmospheric pressures (36-38). With IMS instrumentation, ions are formed in a source region lined with a $Ni^{63}$ radioactive foil. Periodically, ion packets are released from the source region, via a pulsed gate lens, and moved into the drift tube region where they are pushed along by an electric field running the length of the tube. At sufficiently high pressures, this drift region acts as a plasma chromatograph - separating the ions formed in the source region on the basis of mass and shape. Detection is achieved with a Faraday plate and, for some instruments, a mass spectrometer samples ion signal through a pinhole aperture in the Faraday plate. The salient feature of this instrument, with respect to this work, is its ability to monitor ion – molecule chemistry at pressures exceeding ICR and FA methods by anywhere from 3 to 11 orders of magnitude. These high - pressure conditions can have a dramatic impact on experimental measurements.

Although IMS instrumentation plays a role in some of the results presented here, most of the data was collected on a pulsed high pressure mass spectrometer (PHPMS) operating at pressures of around 1 to 10 Torr. In many ways, this method is analogous to FA techniques in terms of operational temperatures and pressures. However, the PHPMS samples ion wall currents generated by ambipolar diffusional processes following a stationary afterglow produced in the ion source. This instrument will be described in