Investigations of gas phase ion-molecule reactions at elevated pressures using ion mobility-mass spectrometry
by Kris E Sahlstrom

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University


Abstract:
The field of gas phase ion chemistry has undergone rapid expansion during the last three decades. This has resulted in an increased need for experiments designed to elucidate the mechanisms, kinetics and thermochemistry of ion molecule reactions in the gas phase. Due to instrumental limitations, the vast majority of experimental methods operate under buffer gas pressures of less than a few Torr. Analytical methods operating at high pressures and support for theoretical models of ion-molecule reactivity are two areas that would benefit from the results from experimental methods operating under very high buffer gas pressure conditions. An Ion Mobility-Mass Spectrometer (IM-MS) has been constructed in our laboratory and has previously been applied to the study of simple substitution and clustering reactions. Modifications of the original IM-MS have increased the range of electric field strength and buffer gas pressure and have allowed the investigation of chemical systems between 300 and 1100 Torr. Rate constants for the thermal electron detachment of azulene" and for the reaction of chloride ion with methyl bromide have been measured over this pressure range. These investigations, and the reaction of chloride ion with isopropylbromide at atmospheric pressure, are the subject of this thesis work. Significant differences were observed in the behavior of these reactions when compared to results from experimental methods operating at lower buffer gas pressures. It has been determined that rate constants for the detachment of thermal electrons from azulene are inversely dependent on buffer gas pressure due to interaction of the anion with buffer gas molecules. Rate constants for the reaction of chloride ion with methylbromide were observed to increase with increased buffer gas pressure and the lifetime of the reaction intermediate was found to be in the low picosecond range. Investigations of the reaction of chloride ion with isopropylbromide revealed a change in mechanism on going from low to high buffer gas pressures. Direct bimolecular nucleophilic substitution is operative at low pressures while indirect unimolecular decomposition of the reaction intermediate was observed at high buffer gas pressures. The kinetic parameters and thermodynamic properties of this reaction at one atmosphere pressure were determined.

# INVESTIGATIONS OF GAS PHASE ION-MOLECULE REACTIONS AT ELEVATED PRESSURES USING ION MOBILITY - MASS SPECTROMETRY

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A thesis submitted in partial fulfillment
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APPROVAL

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Kris E. Sahlstrom

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 P. Grimsrud _____ 8/8/97
Date

Approved for the Department of Chemistry

David M. Dooley _____ 8/11/97
Date

Approved for the College of Graduate Studies

Robert Brown _____ 8/11/97
Date

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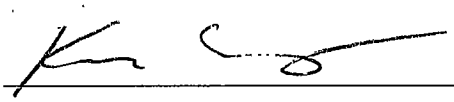
Signature 

Date 8-11-97

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# ABSTRACT

The field of gas phase ion chemistry has undergone rapid expansion during the last three decades. This has resulted in an increased need for experiments designed to elucidate the mechanisms, kinetics and thermochemistry of ion molecule reactions in the gas phase. Due to instrumental limitations, the vast majority of experimental methods operate under buffer gas pressures of less than a few Torr. Analytical methods operating at high pressures and support for theoretical models of ion-molecule reactivity are two areas that would benefit from the results from experimental methods operating under very high buffer gas pressure conditions. An Ion Mobility-Mass Spectrometer (IM-MS) has been constructed in our laboratory and has previously been applied to the study of simple substitution and clustering reactions. Modifications of the original IM-MS have increased the range of electric field strength and buffer gas pressure and have allowed the investigation of chemical systems between 300 and 1100 Torr. Rate constants for the thermal electron detachment of azulene$^-$ and for the reaction of chloride ion with methyl bromide have been measured over this pressure range. These investigations, and the reaction of chloride ion with isopropylbromide at atmospheric pressure, are the subject of this thesis work. Significant differences were observed in the behavior of these reactions when compared to results from experimental methods operating at lower buffer gas pressures. It has been determined that rate constants for the detachment of thermal electrons from azulene$^-$ are inversely dependent on buffer gas pressure due to interaction of the anion with buffer gas molecules. Rate constants for the reaction of chloride ion with methylbromide were observed to increase with increased buffer gas pressure and the lifetime of the reaction intermediate was found to be in the low picosecond range. Investigations of the reaction of chloride ion with isopropylbromide revealed a change in mechanism on going from low to high buffer gas pressures. Direct bimolecular nucleophilic substitution is operative at low pressures while indirect unimolecular decomposition of the reaction intermediate was observed at high buffer gas pressures. The kinetic parameters and thermodynamic properties of this reaction at one atmosphere pressure were determined.

# INTRODUCTION

The field of Gas Phase Ion Chemistry (GPIC) has undergone a period of very rapid growth in the past three decades (1-5). This has been the result of the ongoing and increasingly swift development of the electronic and vacuum technologies required for the instrumentation used in this field. This evolution has resulted in an unprecedented increase in the number of experiments and analytical applications based on processes occurring in the gas phase. Knowledge of the chemical and physical processes occurring in these gas phase environments is often essential in these applications. Thus, theoretical and experimental investigations to determine fundamental kinetic and thermochemical parameters for processes occurring in the gas phase are vital and have attended the rapid development of GPIC.

While literally thousands of papers have been published concerning ion-molecule (IM) reactions at low (< 5 Torr) buffer gas pressures, less than 20 papers have been published in which IM reactions have been investigated by instrumental methods that use buffer gases in the very high pressure (VHP) range (6 - 20). (For convenience, buffer gas pressure ranges will be divided into the low pressure (LP) range, between $10^{-7}$ and $10^{-5}$ Torr, the high pressure (HP) range, between 0.1 and 5 Torr and the very high pressure (VHP) range, between 100 Torr and 10 atmospheres buffer gas pressure). This is not due to a lack of interest in processes occurring at higher pressures, but rather due to instrumental difficulties encountered at these pressures. This lack of knowledge concerning IM reactions at VHP is an important motivation for developing new, reliable methods for investigating IM reactions under conditions of VHP.

In response to this need, a new instrumental method has been developed in our laboratory which incorporates the advantages of Ion Mobility Spectrometry (IMS) and Mass Spectrometry (MS) and which shall be referred to hereafter as Ion Mobility - Mass Spectrometry (IM-MS). This instrument has previously been successfully applied to the study of simple bimolecular reactions (10) and cluster equilibria (11). Modifications to the original IM-MS have since expanded its utility to include the investigation of IM reactions over the pressure range of 300 to 1100 Torr. Rate constants for the thermal electron detachment of azulene$^-$ ($Az^-$) and for the reaction of chloride ion with methyl bromide ($Cl^-/CH_3Br$) have both been measured over this pressure range. These investigations, and the reaction of chloride ion with isopropylbromide ($Cl^-$/*i*-PrBr), are the subject of this thesis work.

Motivations for Investigating Ion Molecule Reactions at Elevated Pressures

Important motivations for the study of GPIC at VHP are the establishment of a sound experimental foundation for theories of IM reactivity at very high pressures and for models of solvation and intrinsic structure-stability and structure-reactivity relationships. Also, some of the most sensitive analytical methods used in the environmental, forensic and biological sciences rely on processes occurring in the gas phase under very high buffer gas pressures (21 - 23). Clearly, it is vital that the chemical and physical processes occurring in VHP buffer gases be understood.

Experimental Support for Theoretical Models of Ion-Molecule Reactivity

The development of instrumental methods and the expansion of computing capabilities has helped catalyze the growth of theoretical models attempting to more accurately describe IM reactivity. One of the most significant theoretical advances in GPIC and one that underlies all gas-phase nucleophilic bimolecular substitution ($S_N2$) reactions is the "double well" description of an IM reaction coordinate proposed by Brauman et al. (24) and shown in Figure 1. This reaction coordinate was invoked to explain the inefficiency of exothermic $S_N2$ reactions having low or negative activation energies. A typical $S_N2$ reaction that exhibits this behavior is the $Cl^-/CH_3Br$ reaction system given in detail below and also shown in Figure 1.

$$Cl^- + CH_3Br \underset{k_b}{\overset{k_c}{\rightleftharpoons}} Cl^-(CH_3Br)^* \xrightarrow{k_p} (Cl \cdot CH_3Br)^{\ddagger} \longrightarrow Br^-(CH_3Cl) \longrightarrow Br^- + CH_3Cl \qquad (1)$$

$k_b'$, $k_q[M]$, $k_p'$

$Cl^-(CH_3Br)$

Even though the activation barrier for this reaction is ~ -2.0 kcal $mol^{-1}$ below the energy of the reactants, the reaction proceeds to products with only about 1% efficiency, i.e. only about 1 out of every 100 collisions results in the formation of products. The reason for this inefficiency, and the motivation for studying reactions such as these at higher buffer gas pressures, can be understood by following the progress of this reaction along the reaction coordinate in Figure 1.

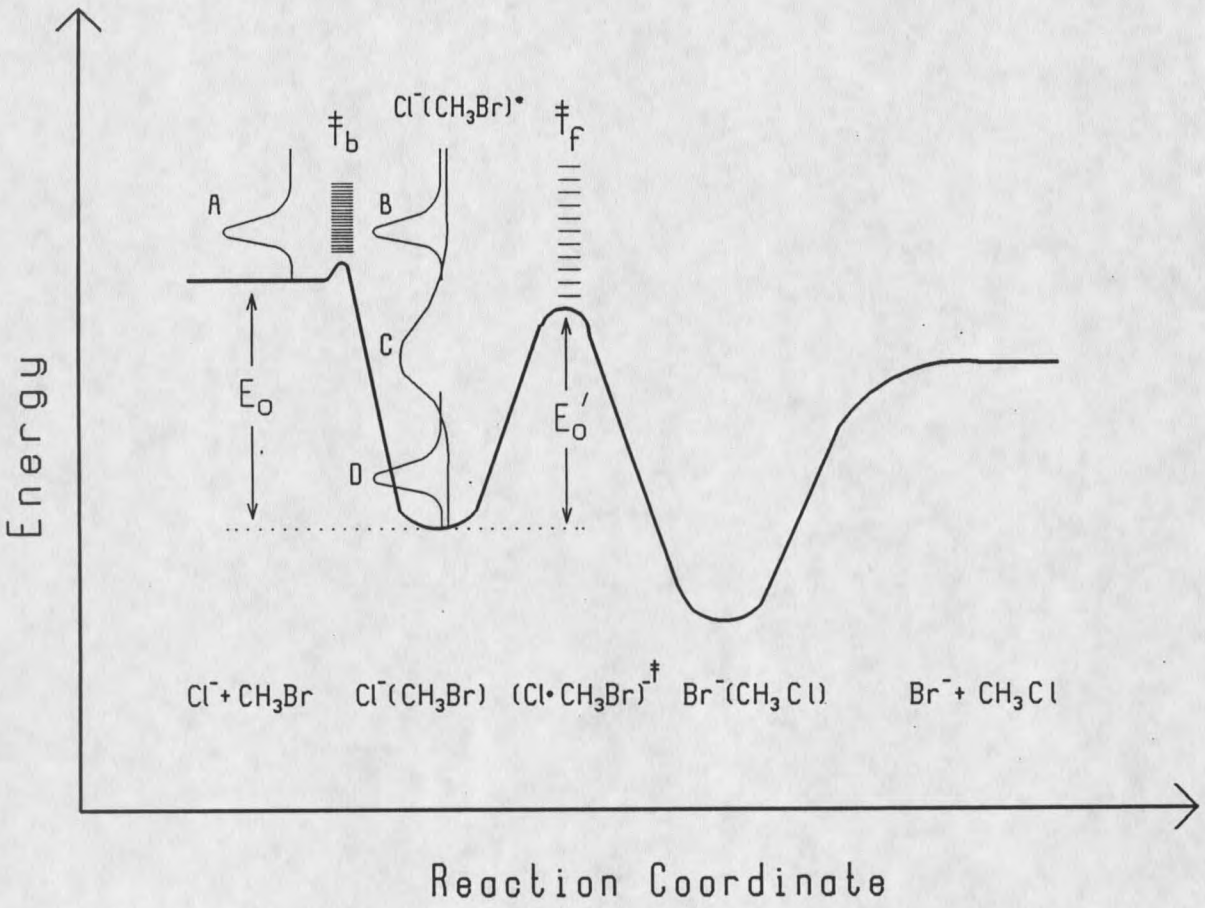


**Figure 1.** Reaction coordinate diagram for a typical gas phase $S_N2$ nucleophilic displacement reaction. Curve A represents the energy distribution function for the reactants in thermal equilibrium with the buffer gas. Curve B represents the distribution function for entrance-channel complexes at low pressure, curve C for an incompletely thermalized ensemble of complexes and curve D for the ion complexes at high pressure (completely thermalized). Other major points are discussed in the text.

The reactants, with a total energy distribution represented by curve A in Figure 1, come together with a collisional rate, $k_c$, described by conventional ADO theory (1), and form entrance channel ion-complexes, $Cl^-(CH_3Br)$. This interaction involves an energy barrier due to the centrifugal forces in the $Cl^-(CH_3Br)$ rotating ion complex, represented in Figure 1 by the first transition state, $\neq_b$. The inefficiency of the reaction is a result of competition between passage over the transition state ($\neq_f$) to products and dissociation back over the centrifugal barrier to form reactants. The observed rate constant for reaction sequence 1 depends on the magnitude of the rate constants for these two reaction pathways as shown in equation 2.

$$k_{observed} = k_c\left(\frac{k_p}{k_b + k_p}\right) \qquad (2)$$

where $k_p$ and $k_b$ also represent $k_{p'}$ or $k_{b'}$ in reaction sequence 1. The expression in parenthesis, $k_p/(k_b + k_p)$, describes the efficiency of reaction; i.e., any reaction where $k_p$ is large, ($k_b$ can be ignored) is limited by the collisional rate constant, $k_c$. Conversely, any reaction where $k_p$ is small is limited by the isomerization of entrance channel complexes over the transition state to form exit channel ion-complexes. The magnitude of the unimolecular rate constants in reaction sequence 1 is a function of the energy of the entrance channel ion-complexes. The ion complexes are initially formed with an excess internal energy equal to the exothermicity of the association reaction, represented by the species $Cl^-(CH_3Br)^*$ in Figure 1 (curve B), and are said to be chemically activated. These chemically activated complexes can dissociate backwards to reactants, $k_b$, isomerize over the transition state to form exit channel ion-products, $k_p$, or

collisions with the buffer gas can remove the excess internal energy to form the ion-complex represented by the species $Cl^-(CH_3Br)$. These species, referred to as thermalized ion-complexes (having thermal energy), can also form reactants or products with rates characterized by the different rate constants, $k_b'$ and $k_f'$.

Whether an $S_N2$ reaction proceeds through chemically activated or thermal-energy ion-complexes depends on the average lifetime of the ion-complex and on the pressure of the surrounding buffer gas. If the average lifetime of the ion-complex is much shorter than the average time between collisions of buffer gas molecules (low buffer gas pressure), then the ion-complexes will retain much of their chemical activation energy, characterized by rate constants $k_i$. A chemical system operating under these conditions is said to be in its low pressure limit (LPL) of kinetic behavior. If the average ion-complex lifetime approaches that of the time between collisions (intermediate buffer gas pressure), then a fraction of the ion-complexes will lose their excess energy by collisions with the buffer gas molecules. The total energy distribution of the ion-complexes under these conditions might be expected to resemble curve C in Figure 1. Finally, if the average ion-complex lifetime is very long relative to the time between collisions with buffer gas molecules (very high buffer gas pressure), all of their chemical activation energy will be quenched by the buffer gas. The total energy distribution of these thermal-energy ion-complexes will then be determined by the temperature of the buffer gas, represented by the Boltzman distribution curve D in Figure 1. Under these conditions, reaction sequence 1 will proceed through the thermal-energy ion-complexes characterized by rate constants $k_b'$ and $k_p'$. A reaction is said to be operating in its high pressure limit (HPL) of

kinetic behavior if the pressure of the buffer gas is high enough (or the lifetime of the ion-complex is long enough) to effectively thermalize all the ion complexes.

There are two fundamental theories for determining rate constants ($k_i$) for the chemically activated and thermal-energy entrance channel ion-complexes (25 - 27). The theory treating the unimolecular dissociation of the chemically activated species is referred to as RRKM (Rice, Ramsperger, Kassel and Marcus) and that for the thermal-energy species is the Transition State Theory (TST). The general expression for the unimolecular rate constant of a system in its LPL of kinetic behavior is given by equation 3

$$\text{RRKM:} \qquad k(E) = G(E - E_0) / hN(E) \tag{3}$$

where $G(E - E_0)$ is the sum of the vibrational and internal rotational quantum states for the transition state (forward or backward) in the energy range $E - E_0$ and $N(E)$ is the density of states for the entrance channel ion-complex. At a specific energy level (Figure 1), the ratio of the forward and backward rate constants is given by

$$\text{RRKM:} \qquad \frac{k_p}{k_b} = \frac{G'(E - E_0' - \Delta E_{rot})}{G(E - E_0)} \tag{4}$$

where $\Delta E_{rot}$ is a correction for the internal energy of the forward transition state to allow for conservation of angular momentum. The rate constants given here are micro-rate constants characteristic of a specific energy level; equation 4 must be integrated over an appropriate energy distribution function (i.e. ref. 25, p 240) to arrive at the overall ratio of rate constants for chemically activated reaction 1. The inefficiency of reaction 1 ($k_p/k_b < 1$) is due to the

greater number of states in the entropically favored (loose) reverse direction (dissociation) as compared to isomerization over the entropically less-favored (tight) forward transition state (Figure 1).

When an IM reaction is brought to its HPL of kinetic behavior, the unimolecular rate constant for dissociation of the ion-complex can be determined by TST, shown in Equation 5.

$$\text{TST:} \qquad k = f \frac{kT}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-E_0/RT} \tag{5}$$

Here, $Q^{\ddagger}$, $Q_A$, $Q_B$ are the partition functions (electronic, vibrational, translational and rotational) of the activated complex and of reactants A and B, respectively, T is the temperature of the buffer gas and $f$ is the transmission coefficient. The transmission coefficient is introduced to allow for the possibility of exit-channel complexes isomerizing back over the transition state and re-forming entrance channel ion-complexes. It is essentially that fraction of species crossing the transition state that go on to form products and is assumed to be unity under conditions of high buffer gas pressure (26).

While statistical methods (RRKM) of interpreting the kinetics of some reactions have been very successful (28, 29), recent theoretical and experimental evidence have indicated non-statistical (non-RRKM) behavior for some simple IM reactions. Theoretical calculations have revealed such non-statistical behavior as vibrational mode-specific rate enhancements (30 - 31), de-coupling of intra-molecular ion-complex vibrational modes (33), translational versus internal reactant energy rate differences (34) and vibrational excitation of reaction products (35).

These theoretical results have also found support in recent experiments. Graul and Bowers (36 - 37), using Mass Spectrometer based methods (~ 0.1 Torr), measured the kinetic energy distribution of the $Cl^-(CH_3Br)^*$ ion-complex dissociation products and found vibrationally excited products. Viggiano, et al. (38), using a selected ion flow tube (~ 0.5 Torr), found that the rate constant for reaction sequence 1 did not depend on reactant internal energy, implying a de-coupling of the vibrational modes in the ion-complex. These theoretical and experimental results imply that statistical theories might not adequately describe some chemical systems. These uncertainties could be eliminated, and the kinetics of reaction could be reliably interpreted, if such systems could be brought to their HPL of kinetic behavior. Also, the interpretation of IM reaction kinetic data is simplified if the reaction can be brought to its HPL of kinetic behavior. In the HPL, theoretical analysis of the kinetic data requires only knowledge of the reactants and the forward, rate-determining transition state, no knowledge of entrance channel complexes or of the reverse transition state is required.

Well-established instrumental methods for investigating IM reactions, such as Ion Cyclotron Resonance and Mass Spectrometry, operate at low buffer gas pressures. Under these conditions, the ion-complexes are not expected to undergo collisions with the buffer gas and so are in their LPL of kinetic behavior. Other instrumental methods operate at high buffer gas pressures (Flowing Afterglow and Selected Ion Flow Tube) where it is difficult to predict whether or not an IM reaction is in the LPL or HPL of kinetic behavior. The IM-MS was developed in response to the need for instruments operating at very high buffer gas pressures that could force a reaction to its HPL of kinetic behavior. Also, by comparison with reaction

kinetics obtained using lower pressure methods, techniques at very high pressures could indicate whether an IM reaction was at or approaching its HPL of kinetic behavior.

Determinations of Intrinsic Chemical Behavior: Support for Models of Solvation

Theorists and physical organic chemists are interested in experimental methods that can reproduce, in the gas phase, reactions of interest in solution, so that the effects of solvation and ion-pairing on the intrinsic properties of the species involved can be determined. Two reviews of the use of GPIC as a tool for elucidating information about reactions in solution can be found written by Speranza (39) and by Bartmess (40). For this application of GPIC experiments to be valid, they must study isolated ions that have the same distribution of internal energy as in solution phase, i.e. a thermal distribution, which can be guaranteed only with complete thermalization of reacting species. While many experimental methods operating at buffer gas pressures less than about 5 Torr, such as the selected-ion flow tube (SIFT), ion cyclotron resonance (ICR) and the pulsed electron high pressure mass spectrometer (PHPMS) provide valuable information about the structure and stability of ionic intermediates, they may provide only phenomenological rate and mechanistic information rather than information characteristic of thermal (as in solution phase) species.

The effect of solvation on the reaction coordinate for a typical $S_N2$ reaction can be seen in the three curves in Figure 2, reproduced from Speranza (39). Curve A in Figure 2 is similar to that in Figure 1, discussed earlier, while curves B and C show the effects of increased solvation. The dramatic change in the rates of some IM reactions occurring in solution phase

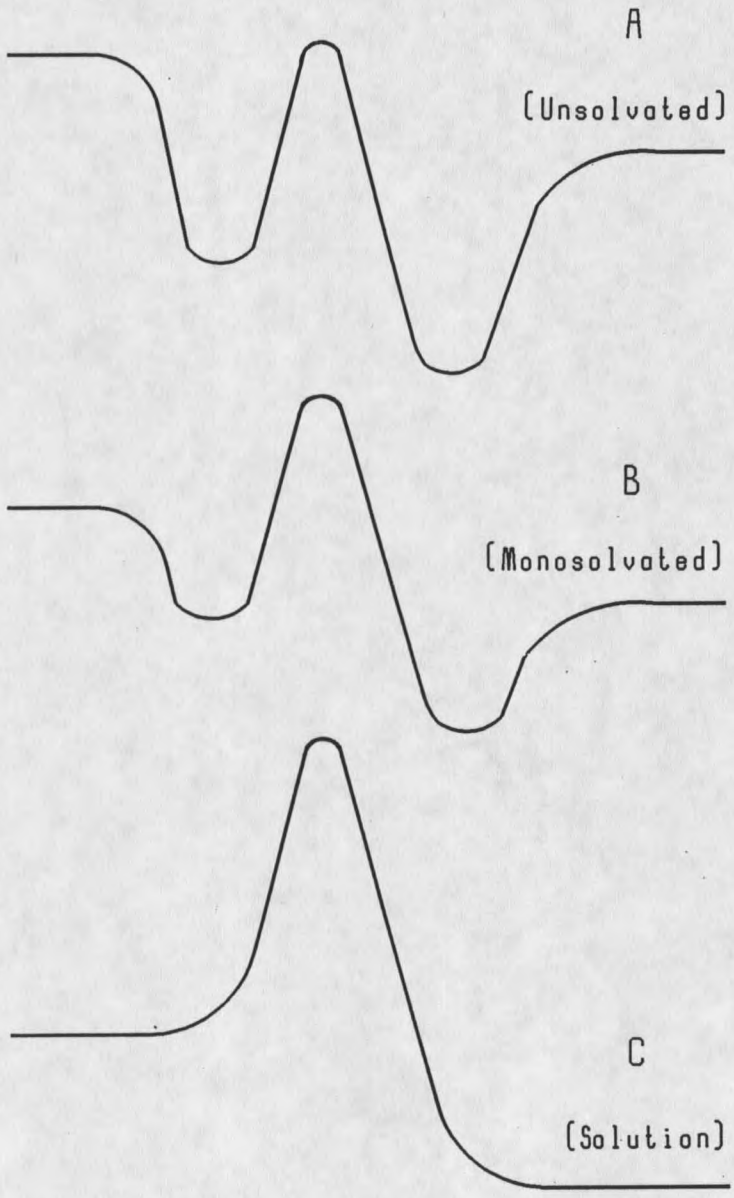


**Figure 2.** Reaction coordinate diagrams for the same reaction carried out in the gas phase with an unsolvated (curve A) or monosolvated (curve B) ionic reactant, or carried out in solution (curve C).

compared to the same reaction in the gas phase can be traced to the large change in the central barriers shown in Figure 2. It should be noted that large differences in reaction rates in gas phase compared to solution phase have been found only in the case of ionic (IM) reactions. For example, the rate constant for the Diels-Alder dimerization of cyclopentadiene is essentially the same in hexane or ethanol and is only three times larger than in the gas phase (41). However, it has been found that the simple $S_N2$ reaction, reaction 1, proceeds 15 orders of magnitude faster in the gas phase than in methanol (42).

Experiments carried out in the gas phase have also supported theories of reaction mechanisms determined from solution phase experiments. For example, it was long believed that the higher reactivity of the iodide ion relative to other halide ions in nucleophilic $S_N2$ reactions in solution was a consequence of the increased ability of the more polarizable iodide ion to more readily supply electron density near the substrate (24). However, studies in aproptic solvents and more recently in the gas phase have shown that the higher reactivity of the iodide ion is due to its lower degree of solvation (lower central barrier), rather than to effects caused by its higher polarizability.

The effects of solvation on the kinetics of IM reactions have been investigated by Bohme et al. (43) in their study of the reaction of $F^-$ with $CH_3Br$ and $CH_3Cl$ and of $Cl^-$ with $CH_3Br$. They found that the rate constant for the bare (unsolvated) anion (near collisional for $F^-$ and $\approx$ 1% collisional for $Cl^-$) was decreased by three orders of magnitude with the addition of just one solvent molecule to the anion and was too slow to measure with the addition of two or more solvent molecules. In aqueous solution, the rate constant for these reactions is slower by

another 15 to 16 orders of magnitude. It was also noted that the rate constant for the reaction of $Cl^-$ with $CH_3Br$ in the gas phase measured using their flowing afterglow apparatus (~ 5 Torr buffer gas pressure) was approximately twice the rate constant of the same reaction also measured in the gas phase, but using instead a pulsed ICR operating at much lower buffer gas pressures (~ $1 \times 10^{-5}$ Torr). Recent measurements by Giles and Grimsrud (10) using IM-MS (640 Torr pressure) have resulted in a rate constant for this reaction which is higher than that obtained using the flowing afterglow method. Thus, it is evident that the rate constants for IM reactions are not only different in solution and in gas phase, but are also dependent on the buffer gas pressure.

Furthering our understanding of the theory of IM reactions and providing support for models of solvation are important uses of VHP instrumental methods. Perhaps a more practical application of this technology, and an increasingly vital one, is the need to develop a better understanding of IM processes underlying some of the most sensitive analytical methods in use today.

Support for Sensitive Analytical Methods

Analytical methods operating in the VHP range can be extremely sensitive and find widespread use in the detection of trace quantities of explosives, narcotics, environmental pollutants, and for characterizing biological samples. They include Ion Mobility Spectrometry (IMS), Atmospheric Pressure Ionization Mass Spectrometry (APIMS) and Electron Capture Detection (ECD) for use with Gas Chromatography (GC). As discussed in the preceding sections, the rate constants obtained from investigations of IM reactions under low pressure

conditions are not necessarily applicable when applied to ionic reactions operating at high pressures. For example, work carried out by Knighton et al. (45) has shown that the APIMS spectra of $C_7F_{14}$ were significantly altered by the addition of water or methanol at partial pressures that may also be found in the buffer gases used in the detection methods mentioned above. The APIMS spectra were altered by the formation of molecular anions clustered with the added water or methanol. It is expected that the formation of clustered species at higher pressures, particularly at low temperatures, would significantly effect the response in these detection schemes to the analyte due to the change in stability of the clustered anion. In addition, work by Mock et al. (46) in which the rate constant of thermal electron detachment of the azulene molecular anion, $Az^-$, was measured using the Photo-Detachment Modulated-ECD (PDM-ECD) at two atmospheres pressure yielded a rate constant three times lower than that measured by Kebarle et al. (47) using a PHPMS at 5 Torr pressure. Further measurements of the rate constants of $Az^-$ thermal electron detachment have been carried out and reported herein using IM-MS. The results of this work revealed that the rate constants of thermal electron detachment at ~ one atmosphere pressure are higher than that reported by Mock but lower than that measured by Kebarle. This implies that increased buffer gas pressures might result in a larger equilibrium concentration of azulene adducts that are more stable than the unclustered anion. The effects and implications of azulene electron detachment using IM-MS will be discussed in more detail later.

The formation of adducts and dimers at the very high buffer gas pressures in IMS has been observed to significantly alter ion mobility spectra. Eiceman et al. (48) reported peak

distortion and baseline perturbations in the ion mobility spectra of butyl acetate isomers. Fragmentation of the iso-, tert- and sec- butyl acetate isomers and declustering of the n-butyl acetate isomer from the dimer to the monomer ions was observed at high (160 °C) temperatures. Preston et al. (49) observed the change in reduced ion mobility as a function of neutral reagent concentration in the ion mobility spectra of DPM/acetone (DPM = 3-(3-methoxypropoxy)propanol (dipropylene glycol monomethyl ether), acetone/water and pyridine/water. A decrease in the reduced mobility (longer observed drift times) as the neutral reagent (acetone or water) concentration was increased was attributed to the establishment of a clustering equilibrium in the drift tube. It was also possible to determine the thermodynamic constants for these clustering reactions by measuring the change in reduced mobility as a function of neutral reagent. Thermodynamic constants for the dimerization of pyridine were determined in this manner. Investigations of this type reveal the uncertainties inherent in the interpretations of ion mobility spectra. Clearly, these complicating effects of VHP buffer gases need to be investigated and understood.

## Instrumental Methods for Investigating IM Reactions in the Gas Phase

The temperature and pressure ranges used in IM-MS and in other instrumental methods in GPIC are illustrated in Figure 3 (39). It is evident from Figure 3 that most techniques for investigating IM use low to high buffer gas pressures where chemically activated, rather than thermalized, ion-complexes are likely. A brief review of the instrumental methods illustrated in Figure 3 will reveal some of the advantages and disadvantages of methods operating under low and high buffer gas pressures.