The Kinetic Ion Mobility Mass Spectrometer: Measurements of Ion–Molecule Reaction Rate Constants at Atmospheric Pressure

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An instrumental method for measuring the rate constants of ion-molecule reactions in an atmospheric pressure buffer gas is described here. The instrument consists of an ion mobility spectrometer, a mass spectrometer, and an associated gas-handling plant. The rate constants are measured by two different operational modes of the instrument. One of these does not require mass spectrometric sampling of the reaction mixture and, therefore, completely avoids measurement errors that are commonly associated with aperture sampling of a high-pressure ionized gas. The application of this instrument to the S_N^2 nucleophilic displacement reactions of chloride anions with a series of alkyl bromides in nitrogen buffer gas at 640 Torr and 125 °C is described, and the results are compared with those obtained by others at lower pressure.

Introduction

The field of gas-phase ion chemistry has received much attention during the last 3 decades. Hundreds of research groups, spanning a wide variety of scientific interests from chemical physics to biochemistry, have contributed to the extensive literature in this area.¹⁻⁶ It is therefore somewhat surprising that our present understanding of the dynamics of ion-molecule reactions in the gas phase is limited to those physical conditions in which the total system pressure is relatively low, less than a few Torr. This is clearly due to the fact that the mature techniques presently used for studying ion-molecule reactions in the gas phase do not function at pressures higher than about 6 Torr. The ion cyclotron resonance (ICR) methods⁶ require operating pressures less than about 10⁻⁵ Torr, the flowing afterglow (FA) mass spectrometer⁷ and the selected ion flow tube (SIFT)⁸ perform optimally at pressures of about 1 Torr, and the pulsed e-beam high-pressure mass spectrometer (PHPMS) has been shown to perform well at pressures up to about 6 Torr.⁹ For several reasons, it is desirable that new versatile methods be developed for the study of ionmolecule reactions at elevated pressures. Perhaps the most compelling of these reasons is so that ion-molecule reactions will become more completely understood over the entire range of physical conditions in which they readily occur. Another more practical reason is to provide a firmer foundation for several currently important instrumental methods of analysis, including the atmospheric pressure ionization mass spectrometer (APIMS),¹⁰ the ion mobility spectrometer (IMS),¹¹ and the electron capture detector (ECD),¹² which are based on gas-phase ionic reactions in atmospheric pressure buffer gases.

Only a few attempts have previously been made at measuring rate constants of ion-molecule reactions in buffer gases near atmospheric pressure. In a series of articles by Collins, Lee, and co-workers, $^{13-17}$ the charge-transfer reactions of He₂⁺, Ne₂⁺, and Ar₂⁺ with a variety of atoms and small molecules were characterized in the noble buffer gases at total pressures up to about 2 atm. The experimental method for these measurements involved the initiation of ionization by an intense electron beam and the monitoring of either the fluorescence from excited N2⁺ that was produced by competitive reactions of the reagent ions with added N_2 or the optical absorption of UV light by Ar_2^+ . The results obtained by Collins et al. in these studies revealed a previously unknown effect of elevated buffer gas pressure on ion-molecule reactions. They found that at elevated pressures, a termolecular mechanism became operative which, along with the well-known bimolecular mechanism for these systems, resulted in overall reaction rates that significantly exceeded the expected Langevin/ADO collision rate. They explained these rate enhancements at very high pressures in terms of third-body encounters that changed otherwise glancing interactions of the ion and reagent neutral into inwardly spiraling orbits. Unfortunately, the experimental method of Collins et al. has not proven to be generally

applicable to the study of other ion-molecule reactions. Matsuoka and co-workers¹⁸⁻²¹ have also reported measurements of ion-molecule reactions at atmospheric pressure by a time-re-

solved atmospheric pressure ionization (TRAPI) mass spectrometer in which ionization was initiated by a pulsed X-ray source. While this approach could potentially be applied to many ionmolecule reaction systems, several formidable problems can be anticipated in its use for kinetic studies. These problems include the following: adiabatic expansion and cooling of the source gas in the region of the ion-sampling aperture of an APIMS can perturb the effective gas temperature and relative ion intensities in this region;²² diffusional loss of ions is very slow at atmospheric pressure, and therefore, "old" ions from previous pulse cycles will persist for times far greater than the time of one measurement cycle;¹⁸ the means by which ions are lost in the region of the ion-sampling aperture are not under tight experimental control and potentially involve several competing phenomena, including electron recombination, ion recombination, diffusion, migration, and ventilation.23

In the present study, we describe a new approach to the measurement of ion-molecule rate constants in an atmospheric pressure buffer gas that appears to offer a high level of applicability to negative and positive ion-molecule reaction systems. This instrument utilizes elements of the IMS and the APIMS which, as indicated above, have been used extensively for chemical analysis. In this instrument, the reaction of interest is made to occur in the ion drift region of an IMS where ion transport can be controlled and ion loss by recombination reactions is eliminated. With one of two operational modes of this instrument, MS measurements of the reaction mixture are unnecessary, and therefore, potential errors commonly associated with aperture sampling of a high-pressure buffer gas are completely avoided. With its second operational mode, mass spectrometric analysis of the ions is used along with the IMS. Hereafter, this instrument will be referred to as the kinetic ion mobility mass spectrometer (KIMMS).

In this first report of this instrument, we have chosen to describe its application to a series of $S_N 2$ nucleophilic displacement reactions involving the chloride anion and several alkyl bromides. This reaction system is of central importance to the field of physical organic chemistry and has been extensively studied in the gas phase by the ICR,²⁴ FA,²⁵ SIFT,^{26,27} and PHPMS^{28,29} techniques. In the gas phase, the rates of these reactions are thought to depend on the behavior of relatively short-lived ion-neutral intermediates. Hence, in the present measurements of these reactions by the KIMMS technique, the effect of increased collisional stabilization of these intermediates in an atmospheric pressure buffer gas will be of specific interest.

Experimental Section

Apparatus. The KIMMS consists of three major components, as shown in Figure 1. They are an ion mobility spectrometer (IMS), a mass spectrometer (MS), and a gas-handling plant (GHP). An expanded view of the source and detection ends of the IMS is provided in Figure 2.

The walls of the IMS are defined by a Pyrex glass tube, 40 cm in length and 9 cm in diameter. This tube is terminated at both



Figure 1. Diagram of the KIMMS apparatus: (a) stainless steel source gas dilution volume, (b) septum inlet, (c) needle valve, (d) N_2 source gas supply, (e) source and drift gas exhaust, (f) flow meter, (g) pressure transducer, (h) insulated box, (i) drift tube, (j) ion source, (k) Tyndall gate, (l) Faraday plate/MS aperture, (m) drift gas inlet, (n) universal joint, (o) electrostatic lens element, (p) quadrupole mass filter, (q) 6-in. diffusion pump, (r) first vacuum envelope, (s) channeltron electron multiplier, (t) second vacuum envelope, (u) 3-in. diffusion pump, (v) N_2 drift gas supply, (w) leak valve, (x) on/off valve, (y) fused silica capillary, (z) 4-L stainless steel dilution volume, (aa) N_2 gas supply.



Figure 2. Expanded view of the ion source and detection regions of the KIMMS: (a) drift field ring, (b) ceramic support post, (c) stainless steel tube, (d) ceramic insulators, (e) 15-mCi ⁶³Ni foil, (f) Teflon washer, (g) Tyndall gate, (h) Pyrex glass tube, (i) screen grid, (j) Faraday plate, (k) Macor washer, (l) Viton O-ring, (m) drift gas entrance port, (n) electrostatic lens element, (o) stainless steel spacer post, (p) quadrupole mass filter.

ends by glass-to-metal seals and stainless steel flanges. An electric field is generated along the length of the tube by 19 stainless steel rings (common hose clamps) that are strapped around the glass tube and are electrically connected via $1-M\Omega$ resistors. The detection end of the resistor chain is electrically grounded, while the ion source and the ring closest to the ion source are connected to a ±5000-V power supply (Model 205B-05R, Bertan Associates, Inc., Hicksville, NY). Therefore, the potential of the rings in front of the ion source decreases incrementally toward ground potential, and the potential of the rings behind the ion source float at ± 5000 V. Ions are created by a 15-mCi ⁶³Ni-on-Pt radioactive foil (New England Nuclear, Boston, MA) that is located inside a movable ion source (see Figure 2). Nitrogen gas flows continually through the ion source from a 1-L exponential dilution volume at a rate of about 50 mL min⁻¹. Following injection of a suitable compound into the dilution volume, the reagent ion of choice is created in the ion source (Cl⁻ is produced in the present study by dissociative electron capture to CCl_4).

Some of the ions formed in and near the source will drift under the influence of the electric field toward the detection end of the IMS and will thereby enter a counterflowing current of nitrogen gas, to be subsequently referred to as the drift gas. The drift gas enters the drift tube via two ports within the IMS-MS interface flange (Figure 2) with a flow rate of approximately 500 mL min⁻¹. Both the drift and source gases exit through the source flange of the IMS tube. Because of its greater flow rate, the drift gas sweeps the source gas with it so that the source gas is not expected to penetrate more than a few centimeters beyond the end of the ion source.

A movable Tyndall ion gate³⁰ is located about 0.5 cm in front of the ion source and consists of two vertical arrays of gold-plated stainless steel wire separated and electrically insulated by an 0.005-cm-thick Teflon washer (Figure 2). Each array (Graseby Ionics, Watford, UK) has wires of diameter, 0.01 cm, and separation, 0.1 cm, across a 3-cm circular opening. The gate is supported by two ceramic legs, and its potential is set equal to that corresponding to its position in the IMS drift field. The gate can be "closed" to the passage of ions by applying a 40-V potential difference between the two arrays and can be "opened" to the passage of ions by equalizing the potential difference. As will be described below, the Tyndall gate is operated in either a "continuously open" or a "pulsed" mode. In the pulsed mode, the gate is opened for brief periods (0.1-1 ms) about 10 times s⁻¹.

One means of ion detection is provided by a stainless steel Faraday plate that is located 23.7 cm from the Tyndall gate (Figure 2). The ion current at the Faraday plate is amplified by a fast operational amplifier set to a gain of 109 V/A. This signal is fed into a digital signal averager (Model 370, Nicolet Instruments, Madison, WI). By "pulsed mode" operation of the Tyndall gate with synchronous triggering of the signal averager, an ion arrival time spectrum is obtained. Temporal resolution of the Faraday current measurements is enhanced by the addition of a 3-cm-diameter, 0.025-cm-thick gold-plated stainless steel screen grid (Graseby Ionics, Watford, UK) in front of the Faraday plate. This screen grid is electrically insulated from the Faraday plate by a 0.0127-cm-thick Teflon washer and is maintained at a slightly higher potential appropriate for its position in the drift field. The screen grid capacitively decouples the Faraday plate from the approaching ion cloud, thereby reducing the magnitude of image charges.31

At the center of the Faraday plate is a 50-µm-diameter aperture which admits ions into the first vacuum stage of the mass spectrometer. The 50-µm aperture is at the center of a 1-cm-diameter, 25-µm-thick stainless steel disk (Optimation, Salem, NH) which is attached to the Faraday plate with an electrically conducting epoxy glue (TRA-DUCT 2924, TRA-CON Inc., Medford, MA). The Faraday plate is mounted on, but is electrically insulated from, the nose cone of the MS by a macor washer (Figure 2). Vacuum integrity is maintained by viton O-rings on either side of the macor washer. The Faraday plate has either a +9-V or a -9-V potential applied to it by a mercury battery to allow detection of positive or negative ions, respectively, in the mass spectrometer (since the quadrupole axis of our MS is grounded, the potential of the Faraday plate determines the ion energy during mass spectral analysis).

In order to reduce mechanical stress on the glass IMS tube, the IMS and the MS are mechanically connected by a universal joint (Figure 2). This joint consists of an aluminum flange with two large viton O-rings on either side to provide both flexibility and the vacuum seal. The O-rings are prevented from being fully compressed by two pairs of stainless steel posts also located on either side of the flange.

The entire IMS is enclosed in an insulated box and is temperature variable over a range from ambient to 175 °C. Heating is achieved with two 1550-W finned strip heaters and a temperature controller (Model CN9000A, Omega Engineering Inc., Stamford, CT). Both the drift gas and source gas are preheated by heater tapes prior to their entry into the IMS. The temperature of the drift gas is monitored by a Type J thermocouple located near the point at which the drift gas enters the IMS.

Regular grade nitrogen (Valley Welders, Billings, MT) was used as both the drift gas and source gas. This was purified by passing it through three traps in series: an oxygen-removing trap (Alltech Associates, Inc., Deerfield, IL), a molecular sieve (5A)/drierite/activated charcoal trap (Alltech), and an OMI-1-indicating purifier (Suppelco, Inc., Bellefonte, PA). Gas flow rates were monitored by using rotameters (Omega Engineering, Inc., Stamford, CT), and the pressure within the IMS was measured by using a Barocel pressure transducer (Type 622AB, Edwards, Wilmington, MA) that was located on the gas exit line.

The mass spectrometer has a two-stage vacuum envelope (Figure 1); the first stage is maintained at a pressure of 4×10^{-4} Torr against the leak through the Faraday plate aperture by a 6-in. diffusion pump. Six lens elements are used to focus the ions into the second vacuum envelope. The sixth lens element has an aperture of 3-mm diameter and is located on, but is electrically insulated from, a nose cone which leads to the second vacuum envelope. The second vacuum envelope is maintained at a pressure of 6×10^{-6} Torr by a 3-in. diffusion pump. In the second envelope, the ions are focused into a quadrupole mass filter and then detected by using a channeltron electron multiplier (Model 4039, Galileo Electro Optics Corp., Sturbridge, MA) operating in the pulsecounting mode. The ion pulses are amplified by using a preamplifier (Model F-100T, Modern Instrumentation Technology, Inc., Boulder, CO) and then sent to a rate meter (Model TC 525, Tennelec/Nucleus, Inc., Oak Ridge, TN).

The quadrupole mass filter has been adapted from a used GC/MS system (Finnigan, Model 3200) and is controlled by an MS data system (Vector One, Teknivent, Maryland Heights, MO) with a Zenith-386 SX microcomputer. The pressure in the first vacuum envelope is measured by using a Penning gauge (Model CP25-K, Edwards) and that of the second envelope by the ionization gauge of the original Finnigan 3200 GC/MS system.

The GHP (Figure 1) provides a means of accurately seeding the nitrogen drift gas with the reagent compound of interest at concentrations as low as a few parts per billion. The GHP has a 4-L stainless steel volume that is typically pressurized to about 2500 Torr with nitrogen. The pressure in this volume is measured by using a Barocel pressure transducer (Edwards). Small quantities of the reagent compound of interest are then injected into this volume through a septum inlet, thereby providing a first stage of dilution. This mixture then flows out of this volume through a 20-cm by 50- μ m internal diameter fused silica capillary at a rate of about 1.3 mL min⁻¹ (640 Torr, 125 °C) into the main stream of nitrogen drift gas, thereby providing a second stage of dilution. The exact rate of flow through the capillary is determined by monitoring the pressure drop in the 4-L volume as a function of time. The GHP is housed in an insulated box and is maintained at a temperature of 150 ± 5 °C by using two 1250-W finned strip heaters and a temperature controller.

Generation of the Reagent Ion. In order to study $S_N 2$ displacement reactions of Cl⁻ by the KIMMS technique, ideally only Cl⁻ ions would be generated in the ion source. However, a few other negative ions are also invariably created along with Cl⁻ due to the presence of impurities. As will be described below, most of these impurities are thought to be formed as a result of the radiation chemistry that is occurring in the source. Therefore, these impurities cannot be avoided, and their potential effects must be accounted for in the data analysis.

With the potential of the ion source set to -5000 V, the electric field in the vicinity of the ion source will cause a portion of the negative ions created in the source to drift toward the Tyndall gate. These ions can then be admitted to the drift region either continuously, by use of the open mode of the Tyndall gate, or periodically, by use of the pulsed mode of the Tyndall gate. In the drift region, the ions will migrate through the drift gas with a velocity, v_d , given by³²

$$v_d = KE \tag{1}$$

where E is the electric field strength and K is the ion mobility given by³²

$$K = \frac{3}{16} \frac{q}{N} \left(\frac{1}{m} + \frac{1}{M}\right)^{1/2} \left(\frac{2\pi}{k_B T}\right)^{1/2} \frac{1}{\Omega_{\rm D}}$$
(2)

q is the charge on the ion, N is the drift gas number density, m

TABLE I: Typical Conditions of the IMS

drift gas/flow rate	$N_2/525 \pm 13 \text{ mL min}^{-1}$
source gas/flow rate	$N_2/50 \pm 5 \text{ mL min}^{-1}$
temp	125 ± 5 °C
pressure	640 ± 10 Torr
drift field strength	194 V cm ⁻¹
Tyndall gate pulse width	0.2 ms
reaction length	23.7 cm
sweeps per IM spectrum	500
sweeps per MAIM spectrum	5000

is the mass of the ion, M is the mass of the drift gas molecules, $k_{\rm B}$ is Boltzmann's constant, and $\Omega_{\rm D}$ is the average ion-drift gas cross section. In the pulsed mode, the shape of an ion packet as it first enters the drift region is determined by the width of the pulse applied to the Tyndall gate. However, as this ion packet moves down the drift tube, additional broadening of the packet can occur, due to ion diffusion and possibly also due to mutual ion-ion Coulombic repulsion if the ion density is sufficiently high. The diffusion coefficient, D, of a given ion is related to the mobility of that ion by the Einstein relationship³²

$$D = \frac{Kk_BT}{q} \tag{3}$$

Under the experimental conditions used here (Table I), K for the Cl⁻ ion is measured to be $\sim 5.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and, by eq 3, D is $\sim 0.17 \text{ cm}^2 \text{ s}^{-1}$. The longitudinal spreading of an infinitely narrow packet of Cl⁻ ions by diffusion during its transport through the drift region is described by³²

$$s_{\rm d} = 2(Dt_{\rm d} \ln 2)^{1/2}$$
 (4)

where s_d is the standard deviation for the distribution of ions in the spreading ion cloud and t_d is the arrival time of Cl⁻ at the Faraday plate. Since t_d is 24.5 ms under the present conditions, s_d for diffusional spreading of the Cl⁻ ion packet is expected to be on the order of 0.1 cm, which is small in comparison with the length of the drift region, 23.7 cm. This calculation of s_d also indicates that diffusional spreading in the radial direction will also be relatively small. The effective diameter of an ion packet leaving the source is probably about 1 cm and is expected to increase no more than about 50% during its transport through the drift region. It is also important to note that if experimental conditions were used (relatively low drift field, for example) in which significant radial diffusion occurred during the transport of ions through the drift region so that only a fraction of the initial ions arrived at the Faraday plate, the efficiency of detection by the Faraday plate would still be expected to be the same for all ions. This is because small ions of high D will also be characterized by high K and low t_d so that the spreading of these smaller ions as described by eq 4 will be the same as that of larger ions of low $D.^{32}$

The average energy, KE_{ave} , of the ions in a drift field can be determined from the Wannier equation³²

$$KE_{ave} = \frac{3}{2}k_BT + \frac{1}{2}mv_d^2 + \frac{1}{2}Mv_d^2$$
 (5)

where the first term on the right side is the thermal kinetic energy and the next two terms represent the energy imparted by the drift field. Under the conditions of our experiment, the contribution of the drift field to KE_{ave} will be negligible and the energy of the ions will be essentially thermal. For example, the drift velocity of Cl⁻ is 965 cm s⁻¹ in 640 Torr of nitrogen at 125 °C in a field strength of 194 V cm⁻¹. While the thermal kinetic energy contribution to KE_{ave} is calculated to be 51.5 meV at this temperature, the energy imparted to this ion by the field is only 0.03 meV, i.e., less than 0.1% KE_{ave} .

The physical conditions of the IMS are listed in Table I. With the Tyndall gate open, the ion current at the Faraday plate is about 0.8 nA and the total ion signal reaching the detector of the mass spectrometer is about 20 000 counts s⁻¹. For the present study, 20 μ L of CCl₄ headspace vapor was added to the 1.0-L source gas dilution volume (Figure 1) so that Cl⁻ ions were created in the ion source by dissociative electron capture to CCl₄. The Cl⁻ arrival time spectrum in pure nitrogen drift gas is shown in Figure



Figure 3. Ion mobility spectrum of the reagent ions. The most intense signal at 24.5 ms is due to Cl^- , which is formed by electron capture to CCl_4 in the ion source. Other minor peaks are also observed; the origin of these is described in the text.



Figure 4. Mass spectrum of the reagent ions.

3 under the conditions listed in Table I except that a gate pulse width, t_g , of 0.5 ms was used. The major peak observed at drift time 24.5 ms is due to Cl⁻. The apparent signal at the origin (t = 0 ms) is not real but is due to radio-frequency (RF) pickup at the Faraday plate of the pulse applied to the Tyndall gate. The Cl⁻ peak has a distinctly broadened base that extends several milliseconds either side of the main peak. On the trailing side of this base, three distinct peaks, having drift times of 28.8, 30.0, and 33.1 ms, are also observed. The presence of ions other than Cl⁻ is also indicated in Figure 4, which is a low-resolution mass spectrum recorded while the IMS was momentarily switched to the continuous mode. In addition to the Cl⁻ isotopes at m/z =35 and 37, several ions in the mass range m/z = 50-100 are observed. The mass spectrum in Figure 4 yields no information as to which ions arrive under the various mobility peaks in Figure 3. However, by tuning the mass spectrometer to a specific ion and switching the IMS back to the pulsed mode, the arrival time spectrum of each ion in the mass spectrum can be determined, as illustrated in Figure 5.

The mass-analyzed ion mobility spectra (MAIMS) in Figure 5 provide a great deal of information concerning the peaks observed in the overall IMS spectrum shown in Figure 3. The small difference in mobility of the ³⁵Cl⁻ and ³⁷Cl⁻ isotopes can be noted in Figure 5, and this causes a slight asymmetry in the IMS peak for Cl⁻ in Figure 3. It is also noted in Figure 5 that essentially all of the Cl⁻ ions arrive between drift times of 23.0 and 25.3 ms and that no ions arrive at times shorter than 23.0 ms. Therefore, the broadening at the leading edge of the Cl⁻ peak in Figure 3 is not real but is due to capacitive effects of the Faraday plate/electrometer current measurements. This factor may also account for a portion of the broadening observed at the trailing edge of the Cl⁻ peak in Figure 3. The ion of m/z = 63 is thought to be $CI \cdot N_2$ formed in the free jet expansion of gas that occurs at the IMS-MS interface.³³ This is consistent with the observation in Figure 5 that its drift time coincides with that of the Cl⁻ ions. The ion of m/z = 71 is the cause of the peak at 28.8 ms in Figures 3 and 5 and, after consideration of the relative intensity of two chlorine isotope ions of m/z = 73 and 75, has been attributed to Cl-HCl. The fact that this ion appears as a distinct peak in Figure



Figure 5. Mass-analyzed ion mobility spectrum of several of the reagent ions.

5 indicates that it is formed in the ion source rather than in the drift region. Small amounts of HCl are undoubtedly produced in the ion source following the recombination of Cl⁻ with positive ions.³⁴ The ion of m/z = 81 is thought to be due to Cl⁻HCOOH. The peak in Figure 5 at 30 ms indicates that a significant portion of these ions are produced in the ion source. However, this ion is also observed in Figure 5 distributed between 24 and 30 ms, indicating that it is formed continuously in the drift region from the Cl⁻ ion. Therefore, this association of Cl⁻ with HCOOH in the drift region accounts for a portion of the apparent broadening of the Cl⁻ peak in Figure 3 between 26 and 30 ms. The ion of m/z = 95 is thought to be due to Cl⁻·CH₃COOH. The fact that this ion is observed in Figure 5 between drift times of 24 and 33 ms indicates that it is formed from Cl⁻ throughout the length of the drift tube, with a small amount of source production forming the peak at 33.1 ms. None of the ions shown in Figures 4 and 5 are observed prior to the addition of CCl₄ to the source gas, and all of these ions are observed when either CF₂Cl₂ or CFCl₃ is used instead of CCl4 for the generation of Cl-. A parallel study in our laboratory by a pulsed high-pressure mass spectrometer operating with 4 Torr of methane buffer gas has indicated that the acidic species, HCOOH and CH₃COOH, are formed by reactions of water vapor with radical hydrocarbon species that are absorbed on the walls of the ion source. In the IMS, these reactions apparently occur throughout the system. This is not surprising since all traces of water can not be removed from our gas supplies and the walls of our instrument undoubtedly accumulate a small amount of the radical species that are continuously generated by the ⁶³Ni ion source.

Determination of Rate Constants from Ion Mobility Spectra. If an alkyl bromide (RBr) is added to the drift gas, the reaction

$$Cl^- + RBr \xrightarrow{k_6} Br^- + RCl$$
 (6)

is expected to occur throughout the length of the drift region. Since the ionic product of this ion-molecule reaction is known to have a mobility that differs from that of the reagent ion, the occurrence of reaction 6 in the drift region will have a pronounced effect on the ion mobility spectrum observed when the Tyndall gate is operated in the pulsed mode. Several predictions of "modified" ion mobility (MIM) spectra for the case of reaction 6 are shown in Figure 6. These have been determined for the present experiments by using the analytical expression developed by Woo and Whealton^{35,36} which incorporates the pulse width applied to the Tyndall gate, diffusional spreading of the ions, and the separation of the Cl⁻ and Br⁻ ions in accordance with their known mobilities. These predictions clearly indicate that the shapes of the MIM spectra will depend strongly on the rate of reaction 6 and should, therefore, provide a means of experimentally determining k_6 .

In the present experiments, a mixture of the RBr of interest was made by pressurizing the GHP to 2500 Torr with nitrogen and then injecting the alkyl bromide through the inlet septum by using either a 500- μ L gas-tight syringe (for methyl bromide) or a 10- μ L gas-tight syringe (for ethyl bromide, isopropyl bromide, and *n*-butyl bromide). The contents of the GHP are then leaked into the main drift gas stream through the capillary (see Figure



Figure 6. Predictions for ion mobility spectra of Cl⁻ modified by reaction with CH₃Br in the drift region using the analytical model in refs 35 and 36. The following set of parameters has been used: Tyndall gate pulse width, 0.2 ms; drift tube length, 23.7 cm; Cl⁻ ion drift velocity, 965 cm s⁻¹; Br⁻ ion drift velocity, 865 cm s⁻¹; temperature, 125 °C; pseudofirst-order rate constants, k_6 [CH₃Br], (a) 0, (b) 20, (c) 60, (d) 100, (e) 160 s⁻¹.



Figure 7. Ion mobility spectra modified by the reaction, $Cl^- + CH_3Br \rightarrow Br^- + CH_3Cl$, using the following concentrations of CH_3Br in the drift tube: (A) none, (B) 1.29×10^{12} , (C) 2.60×10^{12} , (D) 5.27×10^{12} molecules cm⁻³.

1). While the ion mobility spectrum was altered immediately after the initial opening of the GHP, a period of several minutes was generally required for complete stabilization of the system. Before each measurement, about 20 μ L of CCl₄ headspace vapor was injected into the source gas dilution volume (as expected, the MIM spectra observed were not dependent on the exact amount of CCl₄ added as long as all of the electrons were converted to Cl⁻ ions). A MIM spectrum is then recorded. An additional aliquot of RBr was subsequently added to the GHP, and the above sequence of steps was repeated until 6–10 MIM spectra, over a wide range of RBr concentrations, had been obtained. In Figure 7, four representative spectra of this type for the case of R = CH₃ are shown, including the first (7A) for which no CH₃Br had been



Figure 8. (A) Reaction-modified IM spectrum obtained with 1.95×10^{12} CH₃Br molecules cm⁻³ in the drift tube and $t_g = 0.5$ ms. The numbered lines indicate the choice of data used in the area method for determining k_{6} , as explained in the text. (B) Mass-analyzed IM spectra of the Cl⁻ and Br⁻ ions under identical reaction conditions.

added and the last (7D) for which the concentration of CH₃Br is sufficiently high that almost all of the Cl⁻ has been converted to Br-. In parts B and C of Figure 7, intermediate concentrations of CH₃Br have resulted in the partial conversion of Cl⁻ to Br⁻. It is apparent in Figure 7 that the major changes in the IMS spectra caused by the addition of CH₃Br to the drift gas are, indeed, of the general type predicted in Figure 6. Also, it is noted in Figure 7 that the impurity ions having drift times of 28.1, 30.0, and 33.1 ms remain approximately constant in intensity as the concentration of CH₃Br is increased. This indicates that these ions do not react with CH₃Br and, therefore, do not participate in the production of Br⁻. It is also noted in Figure 7 that the experimentally observed mobility peaks are significantly broader than those predicted by the model of the experiment shown in Figure 6. This is not surprising since the model does not include several potentially complicating factors, 37,38 such as space-charge broadening of the peaks, imperfections in the drift fields and the Tyndall gate, and peak distortions by the detection system.

Due to the unknown contributions to peak broadening just mentioned, it was not possible to determine accurate values of k_6 simply by comparison of the shapes of measured MIM spectra with those derived from the model predictions shown in Figure 6. Therefore, the following method³⁹ of determining k_6 from MIM spectra was used. If $A(Cl^-)$ and $A(Br^-)$ are the respective areas of the Cl⁻ and Br⁻ peaks under a MIM spectrum, then the pseudo-first-order reaction rate constant, $\alpha = k_6[RBr]$, is given by

$$\alpha = \frac{1}{t_{\rm d}} \ln \left(\frac{A(\rm Cl^{-}) + A(\rm Br^{-})}{A(\rm Cl^{-})} \right)$$
(7)

where t_d is the drift time (and hence reaction time) of the Cl⁻ reagent ions (24.5 ms in Figure 7). The determination of $A(Cl^-)$ and $A(Br^-)$ requires knowledge of the distribution of these two ions under the overlapping portions of the MIM spectrum. This information was obtained using the parallel arrival time measurements shown in Figure 8. In this figure, a MIM spectrum (8A) and a MAIMS (8B) for the Cl⁻ and Br⁻ ions are shown for a given reaction condition. From the shapes of the MAIMS in Figure 8B and from the assumption that just outside the Cl⁻ peak the intensity of the Br⁻ peak will increase exponentially³⁹ with time, the approximations shown in Figure 8A for determination of the



Figure 9. Plot of α as determined from mobility spectra using the area method and eq 7 vs the concentration of CH₃Br in the drift tube. The straight line was determined by least-squares analysis of the kinetic data for which 20 s⁻¹ < α < 120 s⁻¹.

areas of the Br⁻ and Cl⁻ peaks were established. Line 1 is the background ion signal determined far away from any peaks. Lines 2 and 6 denote the boundary of the arrival time spectra of the reactant and product ions, respectively. The product ion arrival time data between lines 4 and 5 are fit to an exponential curve by using a least-squares routine. The derived curve is then extrapolated back to shorter drift times and at point 3, the minimum between the reactant and product peaks, is linearly extrapolated to the intersection of lines 1 and 2. Thus, the ion signal between lines 2 and 4 which lies above the extrapolated line is assumed to be due to the reactant ion, and that between lines 2 and 6 which is below the extrapolated line is assumed to be due to the product of k_6 by this method were reproducible under a given set of reaction conditions to within $\pm 20\%$.

A set of MIM spectra that include those shown in parts B–D of Figure 7 have been analyzed by using the area method just described, and the calculated values of α by eq 7 are plotted in Figure 9 as a function of the concentration of CH₃Br in the drift tube. A straight line is expected, intercepting the axes near the origin with the slope being equal to k_6 . The three data points at higher CH₃Br concentrations fall below the expected line. This can be attributed to the difficulty in measuring the area under the reagent ion peak when significant conversion to the product ion has taken place. Similar errors occur in the measurement of the area under the product ion peak when only a small amount of conversion has taken place. Consequently, the more accurate data are expected to be the midrange values ($20 \text{ s}^{-1} \le \alpha \le 120 \text{ s}^{-1}$). A least-squares fit of these midrange data points yields k_6 = $3.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Determination of Rate Constants by Ion Mobility-Mass Spectrometry Measurements. Another means of measuring k_6 was provided simply by operating the IMS in the continuous mode (Tyndall gate open) and using the mass spectrometer for measuring the relative amounts of reactant and product ions present at the end of the drift tube. In this approach, the reaction time was determined from pulsed-mode measurements of the Cl⁻ ion drift time, as described above. This method of k_6 measurement does not require that the mobilities of the reagent and product ions differ and, therefore, is of added interest to us in that it should increase the general applicability of the KIMMS technique.

The results obtained by this approach for the case of $R = CH_3$ are shown in Figure 10 where the same gaseous mixtures as used in Figure 9 have been used. First, the plot of log Cl⁻ intensity vs CH₃Br concentration is expected to have a slope equal to $-k_6t_d/2.3$, where t_d is the drift time of the Cl⁻ ion. This measurement of the diminution of the reagent ion intensity, alone, relies on high stability of the mass spectrometer over several hours. Nevertheless, a good straight line is obtained. A plot of log (Cl⁻/(Cl⁻ + Br⁻)) intensity ratio vs CH₃Br concentration is also expected to have a slope equal to $-k_6t_d/2.3$. While this means of treating the data does not require long-term stability of the mass spectrometer, it is vulnerable to detection mass bias effects if detection sensitivities to Cl⁻ and Br⁻ differ. Nevertheless, this



Figure 10. Log-linear plot of the $C\Gamma$ ion intensity (**m**) and the ratio of the ion intensities, $C\Gamma/(C\Gamma + Br^{-})$ (**A**), as a function of CH_3Br concentration in the drift tube, as determined from IM-MS measurements. The total ion signal, $C\Gamma + Br^{-}$, is also shown (*****). The straight lines were determined by least-squares analysis of the kinetic data.



Figure 11. Reaction-modified ion mobility spectra with 1.59×10^{12} CH₃Br molecules cm⁻³ in the drift tube using the following drift field strengths: (a) 194, (b) 183, (c) 171, (d) 159, (e) 148, (f) 136 V cm⁻¹. Note the increased conversion of reactants to products and increased diffusive spread with use of longer drift times.

method of treating the data also provides a good straight line in Figure 10 whose slope is essentially identical to that obtained from the measurements of Cl⁻ intensity, alone. The high level of agreement between the two slopes in Figure 10 suggests that the entire instrumental system is very stable and that the mass bias effects under the MS focusing parameters selected here are small. High stability and low mass discrimination is also evidenced by the relatively small fluctuations ($\leq 15\%$) in the sum of the Cl⁻ and Br⁻ ion signals, also plotted in Figure 10, as a function of CH₃Br concentration. From the slopes of both kinetic plots in Figure 10, k_6 for CH₃Br is determined to be 3.4×10^{-11} cm³ s⁻¹. This value is identical to that obtained above by analysis of MIM spectra. Determinations of k_6 from IM-MS measurements have also been found to be reproducible to within ±20%.

Effects of Drift Field Strength and Convection on Rate Constants. In our previous discussion of eq 5, it was shown that the amount of kinetic energy imparted to the Cl⁻ reagent ion by the drift field should be very small (less than 0.1%) relative to the average kinetic energy of the Cl⁻ ion at 125 °C. Therefore, we would not expect the rate constants determined by the KIMMS to be dependent on the magnitude of the drift field. This expectation was verified by experiments such as the one shown in Figure 11 where several MIM spectra have been recorded for a given reaction mixture using a variety of different electric field strengths, from 194 to 136 V cm⁻¹. With use of lower fields, the reaction time of the ions is increased so that progressively greater fractions of reaction are observed. A plot of $\ln ((A(Cl^{-}) + A (Br^{-})/A(Cl^{-}))$ vs the drift time of the Cl⁻ ion yields a straight line, as shown in Figure 12. According to eq 7, the slope of this line should be equal to $\alpha = k_6[CH_3Br]$. A least-squares fit to these data yields $\alpha = 59.2 \text{ s}^{-1}$, and since $[CH_3Br] = 1.59 \times 10^{12}$ cm⁻³, a rate constant of 3.7×10^{-11} cm³ s⁻¹ is calculated from these data. This value is in good agreement with those determined



Figure 12. Plot of $\ln ((A(Cl^-) + A(Br^-))/A(Cl^-))$ vs Cl⁻ drift time as determined from the reaction-modified IM spectra shown in Figure 11 using the area method. In accordance with eq 7, the slope of the line shown (obtained by least-squares analysis) should provide an independent determination of α .

TABLE II: Rate Constants, k_6 (cm³ s⁻¹), for the Reaction of Cl⁻ with MeBr, EtBr, i-PrBr, and n-BuBr at 125 °C

	present study, at 640 Torr		
	MIM ^a	IM-MS ^b	lit. ^c at 4 Torr
MeBr	3.4×10^{-11}	3.4×10^{-11}	8.8 × 10 ⁻¹²
EtBr	1.1×10^{-11}	1.3×10^{-11}	9.7×10^{-12}
i-PrBr	8.0×10^{-13}	7.6 × 10 ⁻¹³	6.2×10^{-13}
n-BuBr	2.2×10^{-11}	2.2×10^{-11}	2.0×10^{-11}

^aDetermined from reaction-modified ion mobility (MIM) spectra. ^bDetermined from ion mobility-mass spectrometry (IM-MS) measurements. ^cFrom ref 28 by PHPMS.

previously by varying the concentration of CH_3Br and, therefore, supports our expectation that the rate constants measured here are not affected by the drift field.

To determine whether the drift gas flow rate has a significant effect on the measured reaction rate constants, a series of studies of the CH₃Br reaction were made in which the drift gas flow rate was set to 270 mL min⁻¹ rather than its normal setting of 525 mL min⁻¹. Rate constants measured under these conditions from MIM spectra and by the IM-MS methods described above were 3.6×10^{-11} and 3.3×10^{-11} cm³ s⁻¹, respectively. These determinations are in excellent agreement with those given earlier and support our assumption that gas flow rates have little affect in the measured rate constant as long as the flow rate of the drift gas is in large excess of that of the source gas.

Results and Discussion

The reactions of Cl⁻ with methyl bromide (MeBr), ethyl bromide (EtBr), isopropyl bromide (i-PrBr), and *n*-butyl bromide (n-BuBr) were studied here under the conditions listed in Table I, and the rate constants for these reactions, determined from MIM spectra and from IM-MS measurements, are listed in Table II. All of these reactions are known to occur in the gas phase by the S_N2 nucleophilic displacement mechanism in which Br⁻ is produced as the only ionic product.²⁶ The potentially competitive E2 elimination mechanism is not possible for these reactions since it is endothermic by about 10 kcal mol⁻¹. Also listed in Table II are determinations of k_6 for these reactions at 125 °C by Caldwell et al.,²⁸ who used the PHPMS method with methane buffer gas at 4 Torr. While several other groups²⁴⁻²⁷ have also studied these reactions, only the report of Caldwell et al. included measurements at the temperature used in the present study.

It is apparent in Table II that very good agreement is obtained between the k_6 determinations by the MIM and IM-MS methods described in the Experimental Section for all four alkyl bromides studied here at 640 Torr total pressure. For each reaction, the difference in the measurements of k_6 by these two approaches is less than our estimates of the reproducibility of each measurement (±20%). It is also apparent that all of these S_N2 reactions are slow relative to their Langevin/ADO collision rate constants,⁴⁰ for which $k_{ADO} = 1.7$ (±0.3) × 10⁻⁹ cm³ s⁻¹ is expected. The



Figure 13. Energy coordinate for the nucleophilic displacement reaction of Cl⁻ with RBr where $R = CH_3$. This reaction is thought to proceed first by formation of an intermediate cluster ion, Cl⁻ RBr, and then by passage over a concerted transition state, \ddagger . The efficiency of the overall reaction is determined by a competition between the forward (k_p) and the reverse (k_b) reactions of the intermediate. Energies for the intermediates and transition state have been taken from ref 28.

observation that k_6 for the i-PrBr reaction is much slower than those of the other three alkyl bromides is consistent with the expectation that steric hindrance to $S_N 2$ nucleophilic attack will be greater for a secondary than a primary alkyl bromide.²⁶

The most interesting features of the data in Table II are noted upon comparing our results obtained at 640 Torr to those obtained by Caldwell et al.²⁸ at 4 Torr. For EtBr, i-PrBr, and n-BuBr, the rate constants measured at 640 Torr are essentially the same as those measured at 4 Torr. For each of these three cases, k_6 at the higher pressure is only 10-25% greater than at the lower pressure. Since differences of this magnitude are within the estimated uncertainties of the present measurements as well as those of Caldwell et al., we conclude that there is no detectable pressure dependence for the rates of these reactions over the pressure range from 4 to 640 Torr. For the case of MeBr, however, a significant pressure dependence for k_6 is indicated. Our measurement at 640 Torr is 3-4 times greater than that of Caldwell et al. at 4 Torr.

A significant pressure dependence for the reaction of MeBr with Cl⁻ and a lack of pressure dependence for the corresponding reactions of the other alkyl bromides can be rationalized in terms of additional observations reported by Caldwell et al.²⁸ and the double-well potential energy surface^{24,29} for these reactions shown in Figure 13. The reactions of Cl⁻ with RBr are thought to occur first through the formation of an intermediate ion-neutral complex, Cl⁻·RBr, and then by the passage of this intermediate over the concerted S_N2 transition state, **‡**. In this model, the rate of the overall reaction, k_6 , will be given by

$$k_6 = \frac{k_{\rm c}k_{\rm p}}{k_{\rm p} + k_{\rm b}} \tag{8}$$

where k_c is the Langevin/ADO collision rate constant for the formation of the intermediate, Cl⁻·RBr, and k_b and k_p are rate constants for the backward and forward reactions of Cl-RBr along the reaction coordinate. An additional and potentially important process that is not represented in Figure 13 is the collisional stabilization of the initially-formed excited species, (Cl-RBr)*. As symbolized in Figure 13, about 10 kcal mol⁻¹ of "chemical activation" energy will be imparted to (Cl-RBr)* by the association of Cl⁻ and RBr. If the rate of stabilizing collisions between the buffer gas and $(Cl^- \cdot RBr)^*$ is greater than k_b or k_p , this activation energy will be lost and the ion-neutral complex will be brought into thermal equilibrium with the buffer gas. In this case, $k_{\rm b}$ and $k_{\rm p}$ will assume different values characteristic of a thermalized Cl-RBr species. For a given reaction, it should be possible to change the system from one involving an excited intermediate, (Cl-·RBr)*, to one involving a thermalized intermediate, Cl-·RBr, by changing the pressure of the buffer gas from a low to a sufficiently high value. Over this pressure range, the rate of the overall reaction would be affected in accordance with eq 8, and with additional increases in pressure beyond that needed to thermalize the intermediate, no additional changes in the overall rate constant would be expected. It is therefore interesting to note that Caldwell et al.²⁸ reported that for the cases where R = Et, i-Pr, and n-Bu, the intermediate Cl-RBr species was observed to be in thermal equilibrium with their buffer gas at 4 Torr

pressure, at least for experiments performed in the lower end of their temperature range (303 K). With use of higher temperatures, this equilibrium reaction favors the reactants, as expected, so that the relative concentration of CI-RBr was too low to be reliably monitored in the PHPMS experiments of Caldwell et al. Nevertheless, it is likely that the intermediates for the cases, R = Et. i-Pr. and n-Bu, were also brought into thermal equilibrium with the buffer gas in their experiments at higher temperatures, including 125 °C. Therefore, the observations made here that the k_6 values for R = Et, i-Pr, and n-Bu at 640 Torr are essentially the same as those measured by Caldwell et al. at 4 Torr might have been expected.

For the case of R = Me, however, Caldwell et al. observed that the intermediate species, (Cl-MeBr)*, was never in thermal equilibrium with the reaction system at 4 Torr. Therefore, they concluded that the intermediate, (Cl-MeBr)*, was not fully stabilized by collisions with the 4-Torr buffer gas and that the rate constants, $k_{\rm b}$ and $k_{\rm p}$, reflected those of a partially activated (Cl-MeBr)* species that had experienced partial but not complete stabilization by collisions. For the specific case of MeBr shown in Figure 13, additional internal energy in the ion complex might be expected to increase $k_{\rm h}$ more than it does $k_{\rm h}$ because dissociation back to reactants will be entropically favored relative to forward motion over the tight transition state, ‡.^{24,28} Evidence for this expectation is provided by the fact that k_6 for the case of R = Me has been shown to decrease with an increase in the temperature of the buffer gas.²⁸ Since the buffer gas pressure used in the present study is more than 2 orders of magnitude greater than that used by Caldwell et al., it is reasonable to suggest that collisional stabilization of (Cl-MeBr)* is complete in the present study. This is expected to reduce the ratio of $k_{\rm b}$ to $k_{\rm p}$ in the present study and, in accordance with eq 8, would explain an increased k_6 for this reaction at the higher pressure.

Conclusion

The kinetic ion mobility mass spectrometer (KIMMS) has been shown here to provide a means of investigating ion-molecule reactions under ambient pressure conditions. The method is expected to be applicable to the study of any ion-molecule reaction provided that the reagent ion of interest can be created in a high-pressure ion source and that it will be immune to reaction with ubiquitous buffer gas impurities, such as water. Although the initial use of the KIMMS instrument related here has involved only one choice of temperature (125 °C), pressure (640 Torr), and buffer gas (nitrogen), variations of these parameters are expected to be easily accomplished in future applications of the KIMMS to studies of positive and negative ion-molecule reactions at elevated pressures.

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References and Notes

- (1) Franklin, J. L. Ion-Molecule Reactions, Part I, Kinetics and Dynamics; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1979.
- (2) Franklin, J. L. Ion-Molecule Reactions, Part II, Elevated Pressures and Long Reaction Times; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1979
- (3) Bowers, M. T. Gas Phase Ion Chemistry; Academic Press: New York, 1979; Vol. I.
- (4) Bowers, M. T. Gas Phase Ion Chemistry; Academic Press: New York, 1979; Vol. II.
- (5) Bowers, M. T. Gas Phase Ion Chemistry; Academic Press: New York, 1984; Vol. III.
- (6) Lehman, T. A.; Bursey, M. M. Ion Cyclotron Resonance Spectrometry; Wiley-Interscience: New York, 1976.
- (7) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. Adv. At. Mol. Phys. 1969, 5, 1-56.
- (8) Adams, N. G.; Smith, D. In Techniques for the Study of Ion Molecule Reactions; Farrar, J. M., Saunders, W., Eds.; John Wiley and Sons, Inc.: New York, 1988; pp 165-220.
- (9) Kebarle, P. Techniques for the Study of Ion Molecule Reactions; Farrar, J. M., Saunders, W., Eds.; John Wiley and Sons, Inc.: New York, 1988; pp 221-286.
- (10) Carroll, D. I.; Dzidic, I.; Horning, E. C.; Stillwell, R. N. Appl. Spectrosc. Rev. 1981, 17, 337-406.
- (11) Carr, T. W. Plasma Chromatography; Plenum Press: New York, 1984
- (12) Zlatkis, A.; Poole, C. F. Electron Capture, Theory and Practice in Chromatography; Elsevier: New York, 1981. (13) Lee, F. W.; Collins, C. B.; Waller, R. A. J. Chem. Phys. 1976, 65,
- 1605-1615.
 - (14) Collins, C. B.; Lee, F. W. J. Chem. Phys. 1978, 68, 1391-1401.
 - (15) Collins, C. B.; Lee, F. W. J. Chem. Phys. 1979, 71, 184-191.
 (16) Collins, C. B.; Lee, F. W. J. Chem. Phys. 1980, 72, 5381-5389.
- (17) Collins, C. B.; Lee, F. W.; Tepfenhart, W. M.; Stevefelt, J. J. Chem.
- Phys. 1983, 78, 6079-6090. (18) Matsuoka, S.; Nakamura, H.; Tamura, T. J. Chem. Phys. 1981, 75, 681-689
- (19) Matsuoka, S.; Nakamura, H.; Takaaki, T. J. Chem. Phys. 1983, 79, 825-830.
 - (20) Matsuoka, S.; Nakamura, H. J. Chem. Phys. 1988, 89, 5663-5669.
 - (21) Matsuoka, S.; Ikezoe, Y. J. Phys. Chem. 1988, 92, 1126-1133.
 (22) Zook, D. R.; Grimsrud, E. P. J. Phys. Chem. 1988, 92, 6374-6379.
- (23) Gobby, P. L.; Grimsrud, E. P.; Warden, S. W. Anal. Chem. 1980, 52, 473-482
- (24) Olmstead, W. N.; Brauman, J. I. J. Am. Chem. Soc. 1977, 99, 4219-4228.
- (25) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. Can. J. Chem. 1976, 54, 1643-1659.
- (26) Depuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. J. Am. Chem. Soc. 1990, 112, 8650-8655.
- (27) Viggiano, A. A.; Paschkewitz, J. S.; Morris, R. A.; Paulson, J. F. J. Am. Chem. Soc. 1991, 113, 9404-9405.
- (28) Caldwell, G.; Magnera, T. F.; Kebarle, P. J. Am. Chem. Soc. 1984, 106, 959-966.
 - (29) Hirao, K.; Kebarle, P. Can. J. Chem. 1989, 67, 1261-1267
- (30) Mason, E. A.; McDaniel, E. W. Transport Properties of Ions in Gases; John Wiley & Sons, Inc.: New York, 1988; p 55.
- (31) Spangler, G. E.; Cohen, M. J. In Plasma Chromatography; Carr, T. ., Ed.; Plenum Press: New York, 1984; Chapter 1.
- (32) Revercomb, H. E.; Mason, E. A. Anal. Chem. 1975, 47, 970-983.
 (33) Siegel, M. W.; Fite, W. L. J. Phys. Chem. 1976, 80, 2871-2881.

 - (34) Grimsrud, E. P.; Knighton, W. B. Anal. Chem. 1982, 54, 565-570.
 - (35) Woo, S. B.; Whealton, J. H. Phys. Rev. 1969, 180, 314-318. (36) Keller, G. E.; Sullivan, M. R.; Kregel, M. D. Phys. Rev. 1970, 1,
- 1556-1558.
 - (37) Spangler, G. E.; Collins, C. I. Anal. Chem. 1975, 47, 403-407.

 - (38) Glasser, M. L. J. Appl. Phys. 1988, 63, 4823-4831.
 (39) Woo, S. B.; Whealton, J. H. Phys. Rev. 1971, 4, 1046-1051.
 - (40) Su, T.; Bowers, M. T. In Gas Phase Ion Chemistry; Bowers, M. T.,
- Ed.; Academic Press: New York, 1979; Vol. I, Chapter 3.