Probing Trapped Ion Energies Via Ion-Molecule Reaction Kinetics: Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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The kinetic energy-dependent $Ar^+ + N_2$ ion-molecule reaction has been used as a chemical "thermometer" to determine the kinetic energy of ions produced by electron ionization and trapped by using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The rate constant for this reaction obtained on the FTICR mass spectrometer was compared to previous work, which allowed a kinetic energy estimate to be made. In addition, the effects of varying parameters such as trapping voltage and pressure on ion kinetic energy were investigated. No evidence of the differing reactivity of higher energy electronic states of Ar^+, such as $^2P_{1/2}$, was observed and the results of a model of this system are presented that support this observation. Pressure studies revealed that with an average of as few as 13 ion-molecule collisions, Ar^+ ions are collisionally relaxed to an extent unaffected by additional collisions. Based on recent variable temperature selected ion flow drift tube measurements, FTICR ion energies are estimated to be slightly above thermal. (*J Am Soc Mass Spectrom 1992, 3, 727–733*)

Fourier transform ion cyclotron resonance (FTICR) methods have become quite popular in mass spectrometry, primarily because of their ability to trap ions for relatively long times. Thus, FTICR instruments have frequently been used to study ion-molecule reactions [1–9]. Physical quantities abstracted from such experiments include relative and absolute reaction rate constants [2, 5], proton transfer equilibrium constants [1, 4], electron affinities [7], and ionization potentials [3, 6, 8, 9]. Because such quantities may strongly depend on ion kinetic energy, development and assessment of schemes to estimate kinetic energies are of great importance.

There has been considerable interest in the kinetic energy of ions produced in FTICR mass spectrometers [10–13], and determinations of these energies are still the subject of much debate. Another class of instruments used for the study of ion-molecule reactions is based on the flow drift tube [14]. One such example is the selected ion flow tube (SIFT) [15]. In the SIFT technique ions are not stored, but reactions are investigated by varying the pressure of the neutral reactant contained in a relatively high pressure ($\sim$ 0.5 torr) buffer gas in the flow tube. Discrepancies between rate constants determined by FTICR and SIFT or other flow drift tube variants are frequently observed, and these are often ascribed to the presence of translationally

excited ions in the FTICR mass spectrometer. There exist at least six cases in which the difference between reported flow tube rate constants and FTICR rate constants has been reconciled by assigning an "effective" ion temperature of 500–1000 K to ions in the FTICR instrument [16, 17]. This argument is based on the fact that conventional FTICR reaction cells typically have potentials higher at the trapping plates than at the center of the cell, as shown in the SIMION [18] plot in Figure 1. Thus ions formed at or near the trapping plates will be translationally excited toward the center of the cell [19] and will initially have velocities characteristic of temperatures above thermal.[1] However, assignment of ion temperatures in the 500–1000 K range, in an effort to achieve agreement between FTICR and SIFT data, can minimize consideration of some fundamental aspects of FTICR, such as ion motion and relaxation in the analyzer cell.

Measurement of ion kinetic energy in an FTICR mass spectrometer can be approached in several ways. One technique that has been used successfully is ICR kinetic energy spectroscopy or kinetic energy release [20, 21]. This method measures the kinetic energy of the products of either exoergic ion-molecule reactions or selected ion photodissociation studies to infer electronic state information. The technique is not applicable for the measurement of near-thermal kinetic

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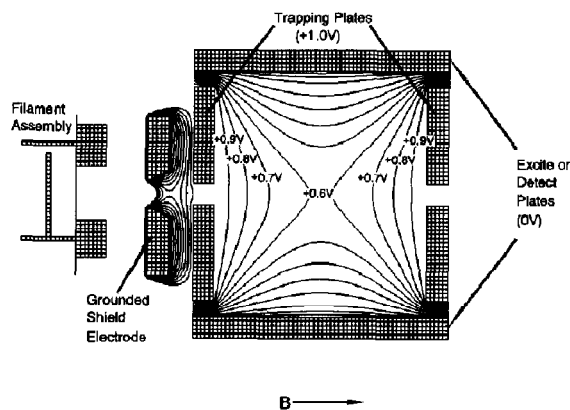[1]Newer cell designs with screened trapping plates greatly reduce this effect [19].

Figure 1. Equipotential lines in a standard cubic ion cyclotron resonance cell computed by SIMION. Trapping potential is 1.0 V, the potential applied to the filament assembly is 5.0 V, and other electrodes are at 0 V.

energies due to inefficient ion trapping for cell potentials below 100 meV. A second approach for measurement of the kinetic energy of ions in an ICR cell has employed ion time-of-flight determinations [22]. Pulsing the trapping potential to zero for increasingly longer periods of time and measuring the resulting ion intensity decay curve allowed ion kinetic energies to be evaluated. Unfortunately, this technique can be susceptible to stray potentials on the trapping plates or incompletely shielded potentials from the filament assembly.

Several chemical methods for measuring ion kinetic energies were discussed at a recent NATO conference [23].[2] The systems proposed for study included proton transfer equilibria, negative ion equilibria, and the charge exchange reaction of Ar^+ with N_2. The latter reaction seemed most convenient for the present study because of the simplicity of both the reaction and reactants. Furthermore, this reaction has been extensively studied and considerable data exist on its energy dependence. It can be studied with relative ease in FTICR mass spectrometers as well as in quadrupole ion traps (work presented in a companion paper by Basic et al. [24]).

In this article, the $Ar^+ + N_2$ reaction rate constant obtained in an FTICR mass spectrometer is compared to determinations in previous work where the reaction was studied as a function of kinetic energy. Although this ion-molecule reactivity approach to estimating ion energies may tend to average time-dependent ion motion and kinetic energies, the comparison does allow a crude estimate of FTICR ion kinetic energy to be made. More important, however, studies of this system permit the relative assessment of ion energies resulting from differing experimental conditions. Parameters may then be adjusted to reduce or minimize ion kinetic energy for situations in which low-energy ions

are critical. In addition, an indication of the average number of collisions necessary to produce varying degrees of thermalization can be obtained by examination of the reaction rate constant over a range of total pressures.

Experimental

All experiments reported here were carried out on a Nicolet (now Extrel FTMS, Madison, WI) FTMS-1000 system [Nicolet 1280 computer and vacuum controlling electronics, Oxford 3T (Oxford Instruments Limited, Oxford, England) superconducting magnet, vacuum chamber pumped by a 300 L/s oil diffusion pump]. The actual pumping speed of this system as used for data presented here was somewhat less than 300 L/s, because the main gate valve that isolates the vacuum chamber from the pump was partially closed (reproducibly to a 1/4 open position). Operation with a partially closed valve was beneficial because it greatly reduced pressure fluctuations and the system factor (defined below). Typical background pressures were in the low 10^{-9} torr region even with the valve partially closed. The basic principles of FTICR and details regarding this instrument can be found elsewhere [25–27].

Ion-molecule reactions are examined in the FTICR instrument by observing the time dependence of the intensity of reactant ions in a constant pressure of reactant gas. Rate constant extraction from the raw data ultimately involves division by the pressure of the neutral reactant; therefore, determination of this pressure is crucial for accurate ion-molecule reaction rate constant measurements. Pressure was monitored by an ionization gauge[3] mounted approximately 1.5 m from the ICR cell, external to the magnetic field. The pressure readings taken from the ionization gauge were corrected by two multiplicative factors. The first factor corrected the ionization gauge for sensitivity differences of different gases. This factor was measured by plotting simultaneous ionization gauge and capacitance manometer (MKS Baratron 200 Series, Type 270A, MKS Instruments, Inc., Burlington, MA) pressure readings on a sample of trapped gas. A sensitivity correction factor for each gas used in this work was obtained from the slope of these plots. The second factor corrected the ionization gauge readings for the difference in pressure between the ionization gauge and the ICR cell. This factor is called the system factor, f_{sys}, and is defined by

$$f_{sys} = \frac{P_{cell}}{P_{ion\ gauge}} \qquad (1)$$

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[2]For a complete summary of the Panel Discussion see ref 23.

[3]The ion gauge used here employed a standard thoria-coated nude ionization gauge filament, model RF-TI from Huntington Laboratories, Inc., Mountain View, CA, with a model 274 025 Digital Ionization Gauge Controller, Granville-Phillips Company, Boulder, CO.

The system factor was evaluated by performing three separate experiments. The first measurement involved the *kinetic energy-independent* [28] reaction

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad (1)$$
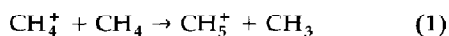
This most-studied ion-molecule reaction was used for calibration purposes in the present study. Raw data for this reaction are shown in Figure 2. The pressure dependence of the rate constant for this reaction was also investigated; the results are shown in Figure 3. Also indicated in Figure 3 is the average of numerous previously published values [29].[4] The system factor was obtained by dividing the average observed rate constant by the average literature rate constant. A second system factor determination was performed by connecting the capacitance manometer to a hollow stainless steel tube (i.d. = 10 mm) and inserting the tube through the solids probe inlet port into the vacuum chamber so that the open end of the tube was within a few millimeters of the cell. The ratio of the capacitance manometer reading to the *sensitivity corrected* ionization gauge reading was interpreted as the system factor. The final determination involved placing a second ionization gauge at the location of the ICR cell, in place of the cell, *in the absence of a magnetic field*. The ratio of the readings of the ion gauge at the cell position to those of the normal ion gauge (both readings independently sensitivity corrected and on a system with the gate valve adjusted to the 1/4 open position) yielded the system factor. All three experiments produced a system factor quite close to 2.0 (2.0, 2.0, and 1.9 for the kinetic energy-independent study, the Baratron and hollow solids probe versus the
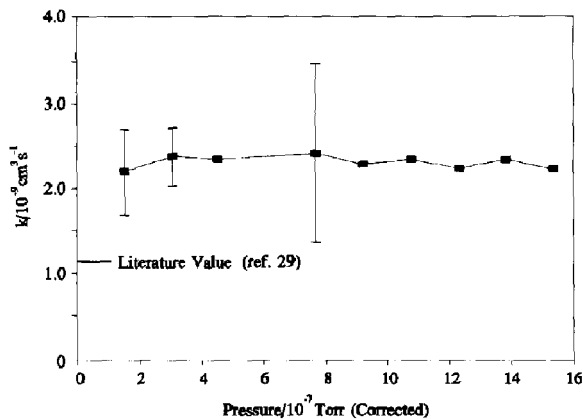
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[4]The rate constant used is an average of 20 reported values (1.13 × 10^{-9} cm³ s⁻¹) [29].

Figure 3. Reaction rate constant as a function of pressure for the $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ reaction. Error bars shown are the 95% confidence limits of the mean for multiple determinations.

ion gauge, and the ion gauge versus ion gauge with no magnetic field, respectively). These data indicate that the pressure at the cell was twice as high as the pressure at the ionization gauge, and a system factor of 2.0 has been applied to all pressure measurements (and thus the rate constants derived by using them) presented in this work.

As mentioned above, the *kinetic energy-dependent* charge exchange reaction,

$$Ar^+ + N_2 \rightarrow N_2^+ + Ar \qquad (2)$$
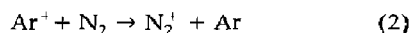
was investigated for the determination of ion energies. For this reaction, ions were formed by electron ionization and then allowed a "relaxation period," usually around 100 ms, during which they underwent approximately 10 ion-molecule collisions, lost excess kinetic energy, and relaxed along the z (magnetic field) axis to the center of the FTICR cell, where detection efficiency has been shown to be the highest [30, 31]. This relaxation period precludes the observation of any kinetic energy or electronic energy effects on the reactivity of Ar^+ ions during the first 100 ms after ion formation. However, such a relaxation period was necessary to avoid an initial increase in ion intensity due to the collisional relaxation of ions to the center of the cell. As discussed later, only after this period of time could reproducible exponentially decaying Ar^+ signals, indicative of a pseudo-first-order reaction, be obtained.

A nominal electron energy of 16 V was used for electron ionization. The typical trapping voltage was 1 V, but effects of the trapping voltage on ion energy were examined over the range 0.5–5 V. The effect of collisional cooling on ion energy was also investigated by varying the total pressure over the range from 4.0×10^{-7} to 2.0×10^{-5} torr with the Ar/N_2 pressure ratio varied independently from 10 to 0.20. All gases were of ultrahigh purity grade and were used as obtained.

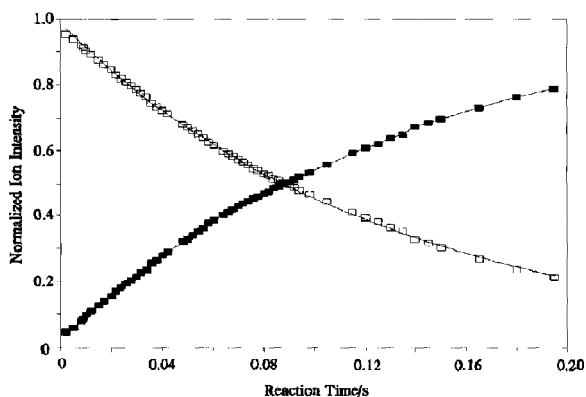**Figure 2.** Typical data obtained for the kinetic energy-independent reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ used to obtain the system factor, f_{sys}, estimate. Empty rectangles represent the normalized signal due to CH_4^+ ions, filled rectangles that due to CH_5^+ ions. These data were collected at a methane pressure of 2.9×10^{-7} torr (corrected).
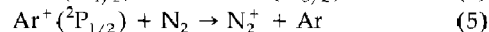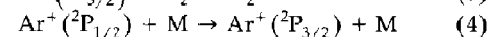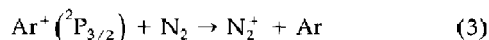
The ion transient response signals consisted in most cases of 16 K data points, were obtained in the broadband mode, and encompassed frequencies that corresponded to the mass range of 17.3–1000 u (The lower limit was set by the maximum analog-to-digital converter rate possible with our electronics.) This precluded the direct observation of ions with masses 16 and 17 (i.e., CH_4^+ and CH_5^+ from the kinetic energy-independent study); however, increasing the excitation frequency to above 2.667 MHz excited these ions and they could be observed as "reflected peaks" around 17.6 and 18.6 u [32]. These ions could also be observed by using the heterodyne detection mode. Ion frequencies were mixed with a carrier frequency of 3.135 MHz. Sum and difference frequencies resulted from this mixing and the selection of the difference frequency by a suitable low-pass filter resulted in frequencies for masses 16 and 17 that were lower than 2.667 MHz and could be observed directly. Both methods yielded the same rate constant for reaction 1, and consequently the "reflection technique" was more commonly employed due to its simplicity.

For reaction 2, Ar^+ and N_2^+ ions were formed by electron ionization. The N_2^+ ions formed by the electron beam as well as those produced by reaction 2 must be removed continually by single frequency excitation at the N_2^+ cyclotron frequency to prevent the reverse of reaction 2 from taking place (exothermic for N_2^+ formed in excited vibrational levels) [33]. Because only Ar^+ ions are present in the cell after this ejection (with the exception of a small amount of H_2O^+), ion loss must be carefully monitored. Normalization to account for nonreactive Ar^+ ion loss was not possible; for each pressure and trapping voltage, the electron beam current and/or beam length was adjusted so that little or no Ar^+ signal loss was seen when no N_2 was present in the chamber. Ion energies were extracted from the rate data by comparison with flow drift tube and variable temperature selected ion flow drift tube (VT-SIFDT) results for the kinetic energy dependence of the rate constant of reaction 2.

Results and Discussion

Ar^+ ions produced by electron ionization in the 15–17 eV range should have $^2P_{1/2}$ and $^2P_{3/2}$ states populated in a statistical 1:2 ratio based on the total angular momentum quantum numbers. Hamdan et al. [16] have shown that both states are produced by electron ionization and the reactivity (for charge transfer with N_2) of the higher energy $J = 1/2$ state is approximately three times that of the $J = 3/2$ state at collision energies below 0.2 eV. However, they also reported that the $J = 1/2$ state has a quenching rate constant that is nearly equal to the reaction rate constant. Kinetic modeling of this reaction system without the inclusion of an additional buffer gas was performed by

using the following reactions:

$$Ar^+\left(^2P_{3/2}\right) + N_2 \rightarrow N_2^+ + Ar \tag{3}$$
$$Ar^+\left(^2P_{1/2}\right) + M \rightarrow Ar^+\left(^2P_{3/2}\right) + M \tag{4}$$
$$Ar^+\left(^2P_{1/2}\right) + N_2 \rightarrow N_2^+ + Ar \tag{5}$$

The rate constants used [16] were $k_3 = 1.1 \times 10^{-11}$ cm^3 s^{-1}, $k_4 = 3.2 \times 10^{-11}$ cm^3 s^{-1}, and $k_5 = 3.6 \times 10^{-11}$ cm^3 s^{-1}. The possibility of spin conversion from the $J = 3/2$ state to the $J = 1/2$ state through collisions with neutrals was neglected. The results of the modeling are shown in Figure 4.

This model shows that, while minor deviations from the exponential fit do occur at longer times, the primary effect of the higher energy spin state is an increase in reactivity at short reaction times. The rate constant for the $Ar^+(^2P_{3/2})$ reaction is only 3% lower than that for the total Ar^+ reaction. As shown in Figure 4, the largest deviation of the total Ar^+ signal from an exponential fit is observed for reaction times less than 100 ms. This time period corresponds to the relaxation period which was always implemented in our work to allow collisional relaxation of ions to the center of the cell. Because our data collection began after this time period, we did not observe any curvature due to the difference in reactivity of the two spin states when the $\ln(Ar^+)$ signal was plotted as a function of reaction time.

The charge exchange reaction (reaction 2) was used to estimate ion temperatures or kinetic energy, as well as to investigate the effects of various experimental parameters on ion energy. Typical data for reaction 2 are shown in Figure 5. Figure 6 shows the increase in ion signal that was observed when no relaxation delay was implemented. Note that there was no observed growth of N_2^+, because N_2^+ was continually ejected by
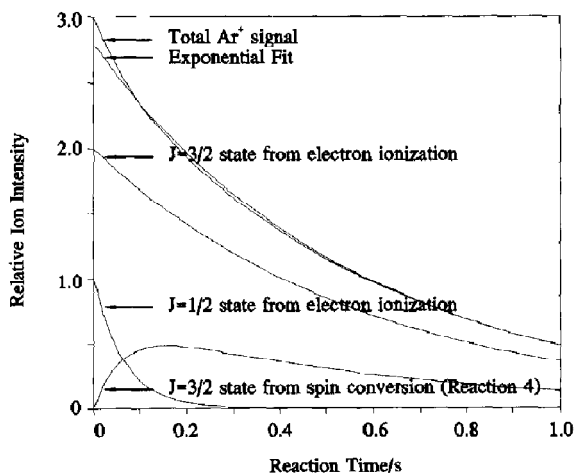

Figure 4. Ar^+ intensities as a function of time predicted by a model (see text) of the $Ar^+ + N_2$ system based on rate constants from ref 16 and pressures of 2×10^{-6} torr of each gas. The major contribution of the $J = 1/2$ state to Ar^+ decay is for reaction times less than 100 ms.
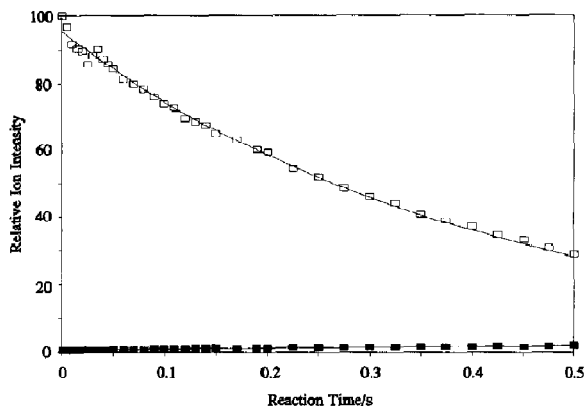
Figure 5. Data for the kinetic energy-dependent reaction $Ar^+ + N_2 \rightarrow Ar + N_2^+$ taken with 100 ms relaxation delay. These data were obtained with pressures of 2×10^{-6} torr of each gas. The filled rectangles are H_2O^+ and the empty rectangles are Ar^+ relative intensities.

Figure 7. Rate constant as a function of pressure for the kinetic energy-dependent $Ar^+ + N_2$ reaction. The total pressure is plotted on the abscissa. The total pressure was varied over the range from 4.0×10^{-7} torr to 2.0×10^{-5} torr, with the ratio of Ar/N_2 independently ranging from 10–0.20. No dependence of the rate constant on total pressure was observed within the 95% confidence limits of the mean for multiple determinations shown.

a single frequency cyclotron resonance ejection to prevent the possible reverse charge exchange reaction from occurring. Under the ejection conditions used, it can be estimated that the ejected ion struck the ICR cell plate in 100 μs after formation. Given the (corrected) pressure of 4.0×10^{-6} torr, an estimate of 0.01 collisions during this time can be made (see ref 12 for a similar calculation). A small quantity of m/z 18 formed with time from the charge transfer reaction between Ar^+ and trace quantities of H_2O.

The results of a pressure dependence study of the rate constant for reaction 2 are shown in Figure 7. In this study, the total pressure was varied over the range from 4.0×10^{-7} to 2.0×10^{-5} torr with various Ar/N_2 pressure ratios ranging from 10–0.20. Error limits indicate the 95% confidence limits of the mean of multiple determinations (n = 4 to 32) at a constant total pres-
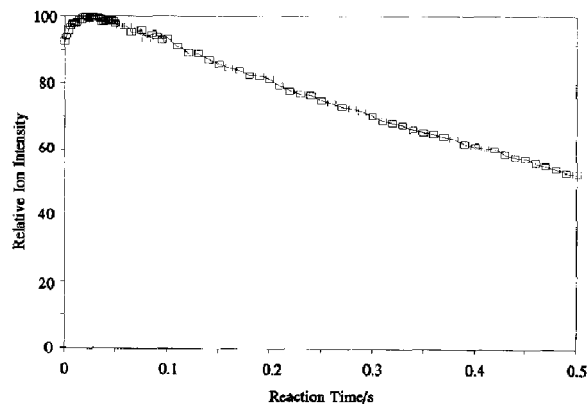

Figure 6. Data for the kinetic energy-dependent reaction $Ar^+ + N_2 \rightarrow Ar + N_2^+$ taken without the standard 100 ms relaxation delay. These data were obtained with pressures of 2×10^{-6} torr of each gas. The increase in intensity at short reaction times is due to the relaxation of the ion cloud toward the center of the cell where detection efficiency is the highest.
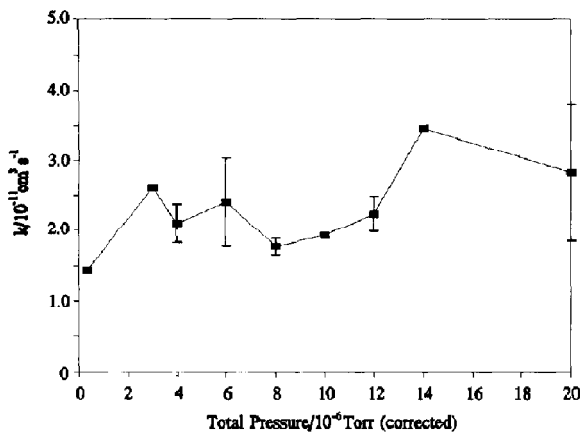
sure. The larger fluctuations in these data are probably due to the relatively slow rate of the reaction, which requires operation in a pressure region somewhat high by FTICR standards. Clearly, there is no significant effect of total pressure on the rate constant. Therefore, one may conclude that the 100 ms delay (discussed above) used to allow ions to relax to the center of the cell is also sufficient to allow the thermalization of ions formed with higher than thermal kinetic energies. Kinetics data for this reaction could not be collected without the relaxation delay because of the observed effect on the ion intensity illustrated in Figure 6. However, because the total pressure (corrected both for gas sensitivities as well as for a system factor of 2.0) was usually 4.0×10^{-6} torr or higher, one many use a Langevin [34] cross section to estimate that, with an average of as few as 13 collisions, Ar^+ ions were collisionally cooled to a kinetic energy that could not be reduced by additional collisions.

Because the trapping voltage is believed to be a major cause of translationally excited ions [35], its effect on the charge exchange reaction rate constant was also examined. The results of this study are shown in Figure 8. The data were obtained at constant argon and nitrogen pressures. As the trapping voltage was varied, the electron ionizing time and/or current were systematically adjusted to produce approximately the same signal intensities (and presumably approximately the same number of ions) at each trapping voltage. Data are shown for trapping voltages between 0.3 and 5 V. Error limits indicate 95% confidence limits of the mean for multiple determinations (n = 3 to 8) at a single trapping voltage. The results show no dependence of the rate constant on the trapping voltage. Thus the results of both the pressure and trapping
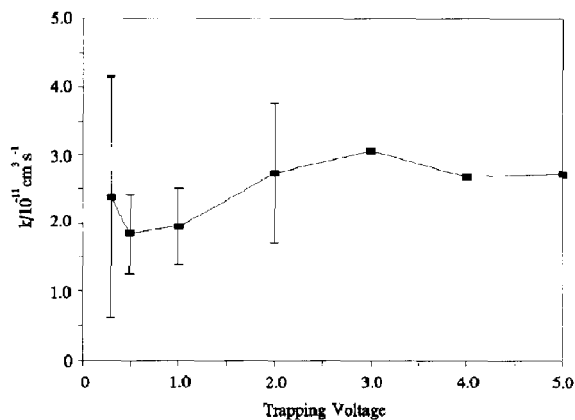
Figure 8. Rate constant as a function of trapping voltage for the kinetic energy-dependent reaction $Ar^+ + N_2$. All determinations were performed with 6×10^{-6} torr of argon and 6×10^{-6} torr of nitrogen. Shown are the 95% confidence limits of the mean of multiple determinations.

voltage studies indicate that even though ions may be formed with considerable excess kinetic energy, within the first 100 ms after formation they rapidly undergo collisional relaxation to the center of the cell.

An "effective" ion temperature may be extracted from this work by averaging all the rate constant determination results and comparing them to the flow drift tube work of Dotan and Lindinger [36]. Our average value for the charge exchange reaction coefficient is $(2.4 \pm 0.2) \times 10^{-11}$ cm^3 s^{-1} {in good agreement with $(2.2 \pm 0.2) \times 10^{-11}$ cm^3 s^{-1} determined in earlier ICR studies [37]}. By comparison to the flow drift tube data (Figure 3 of ref 36), one obtains a center of mass kinetic energy, K.E.$_{cm}$, of 0.065 ± 0.010 eV.

K.E.$_{cm}$ is defined by

$$K.E._{cm} = 1/2 \mu v_r^2 \tag{2}$$

where μ is the reduced mass of the colliding pair and v_r^2 is the square of the relative velocity. One can then solve for v_r^2 because μ is easily obtained from the ion and neutral masses. The square of the relative velocity is related to ion and neutral temperatures by [38]

$$v_r^2 = 3k(T_n/m_n + T_i/m_i) \tag{3}$$

if one assumes that the colliding neutrals and ions have separate Maxwell-Boltzmann distributions of velocities about temperatures T_n and T_i, respectively.[5] The temperature of the ICR cell as measured with a resistive temperature device was 375 K. By using this for T_n, which is the temperature of N_2 molecules, one obtains a temperature of 690 ± 190 K for T_i, the temperature of the Ar^+ ions. This result seems suspiciously high.

Bowers and co-workers [39] calculated the tempera-

ture for ions generated along the trapping potential surface by approximating this surface with

$$V_z = (V_t/2)(z^2 + 1) \tag{4}$$

where z is the distance along the z (magnetic field) axis with the origin at the center of the cell, and V_T is the applied trapping voltage. Assuming a thermal distribution for the neutral species and integrating over all z points of ion formation, their group estimated the velocities of ions to be only 50% greater than thermal for a 1 V trapping voltage *in the absence of any thermalizing collisions*. It is doubtful that the temperature of the Ar^+ ions would be almost twice the neutral temperature after 10 collisions with argon atoms or nitrogen molecules.

Alternately, one may compare the obtained rate constant to the more recent VT-SIFDT work of Viggiano et al. [40]. They investigated the kinetic energy dependence of the $Ar^+ + N_2$ reaction by varying the drift voltage at constant temperature as well as the temperature at constant drift voltage. While some uncertainties remain in their interpretation, the results showed that, at lower K.E.$_{cm}$ values, the effect of varying the temperature on the rate constant was not equivalent to the effect produced by altering the drift voltage. They concluded that increased temperatures probably led to an increase in the rotational energy of N_2. When plotted as a function of total energy, their rate constant data showed that, with a rotational contribution of kT, all points (Figure 3 of ref 40) fell on the same curve. Comparing the present FTICR data with that from the VT-SIFDT instrument indicates that the total energy for the reaction in the ICR cell is in the range 0.080–0.10 eV, which is defined as the average center of mass kinetic energy plus the average rotational energy. Again by using 375 K for T_n and subtracting kT_n (the rotational energy of N_2) from the total energy range given above, one obtains 0.048–0.068 eV for K.E.$_{cm}$. These kinetic energies correspond to an "effective" temperature (by using equation 3) of 545 ± 190 K for the Ar^+ ions. Although still somewhat high, this range does encompass the thermal value.

Conclusions

Measurements of the kinetic energies of ions produced in an FTICR instrument are crucial to the interpretation of data obtained from ion-molecule reactions. Several conclusions can be obtained from the present study. First, electronic states of Ar^+ of energy equal to or higher than that of $^2P_{1/2}$, if present, react with the same rate constant as $^2P_{3/2}$ or are rapidly relaxed. Second, no additional collisional cooling was observed after the 100 ms relaxation period, indicating that by that time, ions have been translationally cooled to a level which is unaffected by additional collisions. The value of this kinetic energy plateau is still not well defined; however, based on recent VT-SIFDT measurements, it is believed to be only slightly above thermal.

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[5]This result, derived by us in a manner similar to that of Kennard [38(a)] yields the same result as the equations presented by McFarland [38(b)].

The initial growth of ion intensity, which was avoided in our work by including the relaxation period, could itself serve as a "thermometer," indicating that ions have reached thermalization when the ion intensity maximizes. Because the detection efficiency has been shown to be position-dependent, and the average position in the trapping well is kinetic energy-dependent, one can conclude that the detection efficiency is itself dependent on the kinetic energy, with a maximum efficiency observed when the kinetic energy is at a minimum. Finally, the pressure-dependence study indicates that the Ar^+ ions are collisionally relaxed with as few as 13 collisions.

The assignment of temperatures to trapped ions depends heavily on the assumption that the ions have a Maxwell-Boltzmann distribution of velocities. Current experiments being performed in this laboratory have allowed some of the previously mentioned problems associated with the time-of-flight kinetic energy measurements in an FTICR mass spectrometer to be overcome. Although not yet complete, experiments utilizing this modified time-of-flight technique support the assumption of a Maxwell-Boltzmann distribution of velocities for the ions.

Acknowledgments

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