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New Apparatus for the Study of Ion−Molecule Reactions at Very High Pressure (25−700 Torr): A Turbulent Ion Flow Tube (TIFT) Study of the Reaction of SF_6^- + SO_2

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A new instrument, the turbulent ion flow tube (TIFT), has been developed for studying ion−molecule reactions up to atmospheric pressure. The instrument is based on the turbulent flow neutral reactor developed by Seeley et al.,[8] and it operates under turbulent rather than laminar flow conditions. The TIFT is currently designed to operate at room temperature over a pressure range from approximately 20−750 Torr, although higher pressures are possible with minor modifications. In this initial report, 300 K rate constants and product distributions, measured from 25 to 700 Torr, are presented for the reaction of SF_6^- with SO_2. Both the rate constants and product distributions for this reaction are independent of pressure, and the present results are consistent with previous measurements made at <1 Torr.

Introduction

Gas-phase ion chemistry under conditions of very high pressure has been the subject of review by Knighton and Grimsrud.[1] The very high pressure range is somewhat arbitrarily defined by those authors as the region between 0.01 and 10 atm, representing a pressure regime beyond the well-characterized “high pressure” range (0.1−5 Torr). The use of the term “high pressure” to describe such low pressures is common in mass spectrometry, and the convention will be followed here.

There are several reasons why it is important to study gas-phase ion chemistry in the very high pressure regime. (1) Processes that are not observed at lower pressures can become the dominant processes at higher pressures. This is especially applicable for some analytical instruments that operate at atmospheric pressure such as the atmospheric pressure ionization mass spectrometers. (2) Performing kinetic measurements within the high pressure limit ensures that all species along the reaction coordinate are thermally equilibrated with the buffer gas. This allows the observed rate constants of ion−molecule reactions to be rigorously interpreted in terms of candidate mechanisms and potential energy surfaces for that reaction. (3) Weak chemical interactions between ions and buffer gas molecules in the very high pressure range may alter both the potential energy surfaces and the rate constants of ion−molecule reactions. (4) Very slow reactions can be studied easily at very high pressure. We estimate that the present instrument can measure rate constants 3−5 orders of magnitude slower than conventional flow tube experiments.

To date, there have been few ion kinetics measurements in the very high pressure region. Knighton and Grimsrud[2] cite only 15 papers in the literature in which gas-phase ion−molecule reaction rate constants or equilibrium constants have been determined by techniques using buffer gas pressures in this pressure regime. The lack of data in this pressure regime is due largely to a lack of experimental capabilities. Some of the instruments used at lower pressure are simply not adaptable to the very high pressure region, e.g., ICR-MS. Recently, several instruments have been developed by Grimsrud and co-workers to study ion−molecule reactions in the very high pressure range. These include the ion mobility spectrometer[3−5] and the photodetachment-modulated electron capture detector.[6]

Knighton and Grimsrud have suggested that the fast flow technique long used for studying gas-phase ion−molecule reactions could be adaptable to the very high pressure range. In the past, flow tube experiments, all of which are based on laminar flow dynamics, have only been used to study gas-phase ion−molecule reactions up to 5 Torr. It is difficult to measure ion−molecule rate constants at significantly higher pressures in the standard laminar flow tube designs for several reasons, e.g., reactions times become too long, vacuum systems cannot handle the gas load, mixing the reactant species is problematic, and many ion sources are not efficient at high pressure. Seeley et al.[8] have recently described an apparatus based on turbulent flow dynamics for studying radical reactions in the very high pressure regime. Instruments of this type have used chemical ionization for detecting neutral kinetics. We have adapted the turbulent flow design and constructed a new turbulent flow tube instrument for studying ion−molecule reactions in the very high pressure range.

In this report, we present details of the new apparatus, including measurements of the key parameters such as ion velocity and mixing distance. We also present reaction rate constants and product distributions for the reaction of SF_6^- with SO_2, measured over the pressure range from 25 to 700 Torr.

Experimental Section

Apparatus. The new turbulent ion flow tube (TIFT) is shown schematically in Figure 1. The stainless steel flow tube measures 102 cm in length and 2.54 cm in diameter and is pumped by a high-volume Busch pump (117 ft^3 min^{-1}). The pressure in the tube is measured using an MKS 1000 Torr capacitance manometer and can be varied from approximately 20−750 Torr by throttling the gate valve on the main pumping line. The upper

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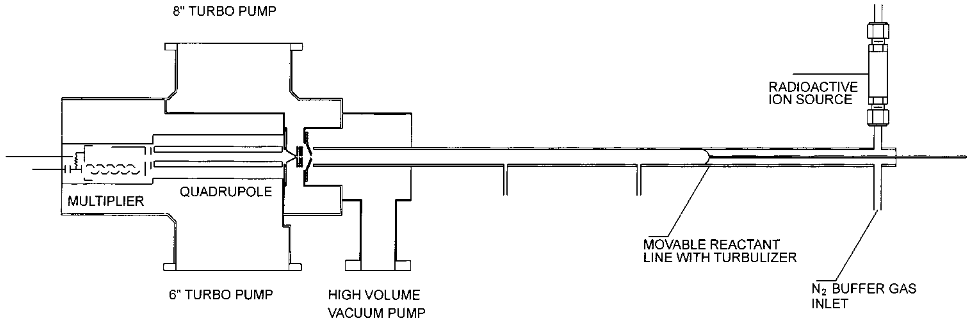

Figure 1. Schematic of the new turbulent ion flow tube (TIFT).

pressure limit is currently set by a pressure relief valve, which prevents large gas flows from over-pressurizing the system in the event the exit valve is inadvertently closed. In principle, the instrument could operate at much higher pressures. The buffer gas, N_2, is obtained from the gas delivery port of a high pressure liquid N_2 dewar. The standard ion flow tube gas, helium, is not used because the flow rates needed to obtain turbulent flow are excessive, and hence, the cost of helium prohibits its routine use.

The flow tube contains an ion source and a moveable neutral reactant inlet that are described below. All flows are monitored with calibrated MKS mass flow meters. The flow tube is terminated by a blunt sampling cone on which an orifice 50 μm in diameter is mounted. The detection system consists of two chambers. The sampling chamber contains a set of three aperture lenses and a skimmer for focusing and collimating the ion beam. Typically, the sampling cone and the first and third lens elements operate with $\leq$10 V, while the second lens element and skimmer operate with 50−80 V applied. The skimmer serves as the pumping aperture into the detector chamber where ions are analyzed using an Extrel C-150 quadrupole mass spectrometer and a ETP electron multiplier. The sampling and detector chambers are each pumped by a 550 L s^{-1} Varian Turbo pump. The detector pump is backed by the sampling chamber pump, which is backed by an oil-free scroll pump. Pressure in the sampling chamber ranges from 1.3×10^{-5} to 5.8×10^{-4} Torr when the flow tube is varied from 30 to 725 Torr. The pressure in the detector chamber varies from 1.9×10^{-7} to 2.4×10^{-6} Torr over this range of flow tube pressures.

Ions are produced by passing a precursor gas through a Nuclecel in-line ionizer (NRD), a tube measuring 2.5 in. in length and 0.25 in. in inner diameter that contains Polonium (^{210}Po) metallic foil. This results in a relatively gentle ion source since much of the ionization comes from secondary electrons that are thermalized by the high pressure of the buffer gas. This is confirmed by the present experiments where the SF_6^-/SF_5^- ratio is a good indicator of electron energy. Achieving significant ion signal from the source requires passing large gas flows through the in-line ionizer. Typically, flows of 50 L min^{-1} are required; however, only a very small percentage of this flow (10^{-3} to 10^{-6} %) is actual precursor source gas. The remainder is N_2 buffer gas. An additional buffer flow, typically 20 L min^{-1}, is introduced into the flow tube via another inlet, as shown in Figure 1. The flow of N_2 into the tube from both inlets can be varied to achieve the desired source conditions and flow dynamics.

The flow characteristics of gas in a tube are particularly dependent upon the Reynolds number, N_R,[9]

$$N_R = \frac{2a\,\bar{u}\rho}{\mu} \quad (1)$$

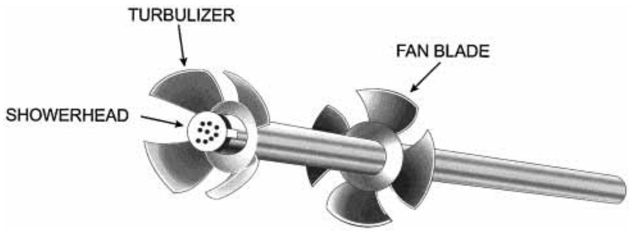

Figure 2. Schematic of the movable inlet, which includes several attachments to promote eddy formation. A stationary stainless steel fan-blade centers the inlet in the turbulent core of the flow tube and promotes eddy formation upstream of the reactant. An additional fan-shaped Teflon “turbulizer” and stainless steel “showerhead” ensure proper mixing of the reactants.

where a is the internal radius of the flow tube, $\bar{u}$ is the average gas velocity, ρ is the gas density, and μ is the gas viscosity coefficient. The Reynolds number represents the ratio of inertial forces to viscous forces in the flow tube. Low values of N_R correspond to laminar flow conditions, characterized by streamlined fluid convection, while large values of N_R correspond to turbulent flow conditions, which is characterized by a multitude of eddies with rapidly oscillating trajectories. Empirically, it has been found that laminar flow is stable at $N_R < 2000$ and that turbulent flow is stable at $N_R > 3000$.[7] Conditions between $2000 < N_R < 3000$ are often classified as “transitional” because oscillations between turbulent and laminar flow can be observed under controlled conditions. For the typical N_2 flow rates noted above, Reynolds numbers of over 4000 are achieved, well into the turbulent flow regime.

Neutral reactant gas is introduced into the flow tube via a moveable 0.25 in. diameter stainless steel inlet line that runs along the radial center of the flow tube. To ensure adequate mixing of the reagents, several attachments have been added to the tip of the moveable inlet to promote eddy formation. A schematic of the inlet is shown in Figure 2. First, a stationary stainless steel fan-blade has been attached several inches upstream from the end of the inlet. This serves both to keep the inlet centered in the turbulent core of the flow tube and to promote eddy formation upstream of the reactant line. Second, a fan-shaped Teflon “turbulizer”, as developed by Seeley et al.,[8] is attached to the tip of the movable injector. Finally, a 0.25 in. diameter stainless steel “showerhead” has been added to the very tip of the inlet, offset by approximately 2 mm, directly in the path of the neutral reagent flowing from the inlet. This causes the gas to be sprayed out of several holes and also redirected from the center line into the turbulizer.

In characterizing their turbulent flow reactor, Seeley et al.[8] concluded from flow visualization studies that with the Teflon turbulizer alone the reactant concentrations appeared radially homogeneous 5 cm downstream of the movable inlet when either the pressure was below 10 Torr or N_R was above 700. In the present experiment, the actual mixing distance in the flow tube has been determined by measuring rates at several reaction distances. This end correction determination takes into account the mixing time of the neutral reactant. End corrections were examined at 100 and 300 Torr, and in both cases, the rates measured at many reaction distances (25−77 cm) were within 3% of each other, indicating the end corrections are negligible at both 100 and 300 Torr. In general, we have found that the additional showerhead and stationary fan blade inlet line attachments provide more complete mixing of the reactants than that achieved by using only the turbulizer.

Seeley et al.[8] also investigated the issue of reactant wall interactions leading to interference in determining rate constants. Through modeling and experimental tests, they concluded that the frequency of reactant wall interactions decreases rapidly with increasing pressure and that within the turbulent flow regime, wall losses are at least an order of magnitude smaller than in the low pressure laminar regime. Since ions are lost with every collision with the wall, the persistence of ions down the length of the flow tube supports this assertion and the present technique should be well suited to studying ion−radical reactions.

Determination of Rate Constants. The experimental approach taken to determine the rate constant, *k*, for the general reaction

$$A^{\pm} + B \rightarrow C^{\pm} + D \tag{2}$$

is to monitor the decrease in the $A^{\pm}$ ion count rate as a function of the flow rate of the neutral reactant gas, B, into the flow tube. Because B is present in large excess, pseudo-first-order kinetics apply, and the reaction rate equation in this case is expressed as

$$\ln([A^{\pm}]_0/[A^{\pm}]) = k\tau[B] \tag{3}$$

The reaction time, τ, is related to the average ion velocity, v_i, and the reaction distance, z, by $\tau = z/v_i$. The ion velocity depends on the dimensions of the flow tube, the identity of the carrier gas, and the carrier gas temperature, pressure, and flow rate. In this apparatus, the ion velocity can be measured by inserting electrodes into the flow tube's two additional ports, pulsing each of the electrodes separately, and measuring the ion arrival times. The ion velocity is then calculated by dividing the distance between the two pulsing electrodes by the difference in the two arrival times. The ratio of the ion velocity to the buffer velocity, v_b, where

$$v_b = Q/\pi a^2 \tag{4}$$

and a is the flow tube radius and Q is the volumetric flow rate of buffer gas in the tube, was determined as a function of N_R at several different pressures. These results are shown in Figure 3. In laminar flow ($N_R < 2000$), v_i/v_b decreases from 2 to 1.3. The value of 2 is the value expected at the maximum of the parabolic velocity profile characteristic of laminar flow, demonstrating that little mixing of the ions occurs at high pressures in the absence of turbulence. In the turbulent flow regime ($N_R > 3000$), v_i/v_b has a value of ≤ 1.2. The turbulent velocity profile in the central portion of the tube is significantly flatter than the laminar profile. The central core is the only portion sampled by the mass spectrometer. The ion velocity could not be measured above 300 Torr with the existing pulse generator. A larger voltage pulse (>100 V) is required for ion velocity measurements at higher pressures since making a significant perturbation to the ion signal depends on the ratio of the electric field to the number density. However, there is no obvious pressure dependence in the value of v_i/v_b over the range of pressures examined. In practice, the instrument is operated at $4500 < N_R < 5000$ where v_i/v_b is approximately 1.10. The flow velocities and ion reaction times obtained under typical operating conditions are shown in Figures 4a,b, respectively, as a function of pressure. Note that the flow velocities are linear as a function of $1/P$ since we normally change the pressure by throttling the

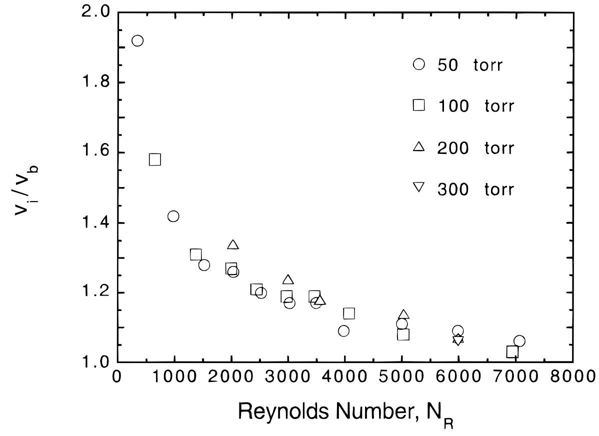

Figure 3. Ratio of ion velocity to buffer velocity, v_i/v_b, as a function of Reynolds number, N_R, at pressures of 50, 100, 200, and 300 Torr.

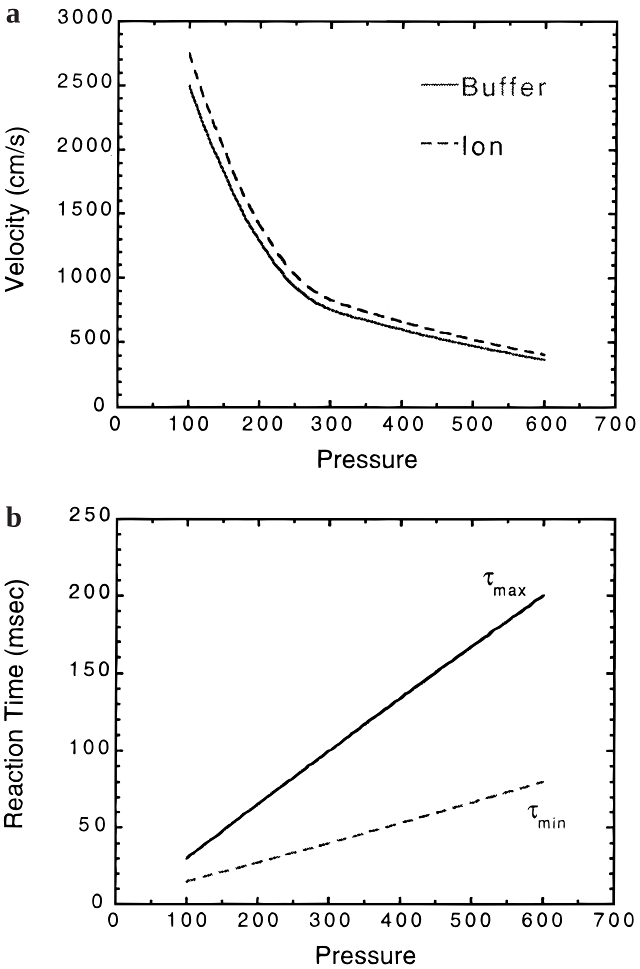

Figure 4. (a) Flow velocities as a function of pressure for typical operating conditions of $4500 < N_R < 5000$. Note that flow velocities are linear as a function of $1/P$. (b) Minimum and maximum ion reaction times as a function of pressure for typical operating conditions of $4500 < N_R < 5000$. The range of reaction times corresponds to the range of distances that can be achieved using the movable inlet.

exhaust valve while keeping the flow rate constant. The ion reaction times involved in this experiment are relatively long, which often necessitates the use of very dilute neutral reactant gas mixtures. For fast reactions, mixtures of $<0.1\%$ in N_2 are used routinely.

Although the general scheme outlined above for measuring reaction rates works well, we find that the time required to stabilize the different neutral reactant gas flow concentrations becomes a practical consideration at higher pressures. Small flow rates take considerable time to flush the inlet line at high pressure since a large quantity of gas resides in the inlet line. Stable reactant flows are more easily achieved by adding a N_2 reactant flush gas mixed as closely as possible to the reactant line. The flow rates are 10−1000 times as large as the reactant flow. In the future, kinetics may be measured by varying the distance of the inlet, and thus the reaction time, rather than by varying the neutral reactant concentration.

In considering the errors associated with the new TIFT apparatus, we note that Seeley et al.[8] have argued previously that the largest potential error associated with operating in turbulent flow conditions is related to determining the turbulent core velocity. However, because the ion velocity can be well characterized in this apparatus as compared to a neutral apparatus, this is not expected to be a major source of error. Another potentially large source of error involves unknown mixing of the reactants. Again, this is not thought to be a significant factor in this apparatus because end corrections can be measured directly and were found to be negligible (less than a few percent). What remains are the usual errors associated with flow tube measurements of rate constants,[10] e.g., errors associated with measuring total and reactant flow rates, pressure, temperature, and reactant mixture concentrations. Because it is often necessary to use very dilute reactant mixtures, we suspect preparation of these mixtures leads to the single largest source of error in this experiment. Absolute errors in the rate measurements are estimated to be on the order of 25%, while the relative errors are estimated to be 15%. These errors are the same as we report for our other ion flow tubes.[11,12]

Pressure-dependent product distributions can be obtained for some ion−molecule reactions using the TIFT. Because this instrument is more similar to a flowing afterglow than to a SIFT, the ability to obtain product distributions may not be general; particular experimental conditions need to be met in order to obtain product information. First, the reactant ion has to be produced cleanly in the ion source, meaning only trace amounts of other reactive ions are formed simultaneously. Parent ions that can be formed with the radioactive ion source are good candidates. Second, it is imperative that impurity levels in the flow tube be reduced to the lowest levels possible since the instrument is extremely sensitive to fast reacting impurities. Finally, it is important to be able to distinguish and account for other chemistry that may be occurring in the flow tube. For example, there may be other ions present in the flow tube that react to yield similar products as that from the reactant ion of interest. Alternatively, secondary chemistry may occur, either between the product ions and the neutral reactant gas or between the product ions and the source gas. Because reaction times in this instrument can be relatively long, even very slow reactions can affect the observed product distributions. In practice, product branching fractions were determined by recording the product ion count rates as a function of the neutral reactant flow rate. To reduce the effects of secondary reactions between the product ions and the neutral reactant, product distributions were determined at low neutral reactant concentrations. In addition, the effects of these secondary reactions were accounted for by extrapolating the measured branching fractions to a neutral reactant flow rate of zero. The product distributions obtained thus far were then corrected for the products of other reactive ions present simultaneously in the flow tube. To reduce the effects of mass discrimination, the product distributions were determined at low mass resolution; no further correction was made for mass discrimination. As an additional note, we considered the possibility that mass bias may exist in the extraction/sampling region given that Zook and Grimsrud[13] report heavy ions are sampled more efficiently in a high pressure instrument and that this is related to the lens voltages in the extraction/sampling region. However, this sampling deficiency does not appear to be a problem with the current system and operation of extraction lenses. Comparing the reactant ion signal loss to the sum of the product ion signals yields a maximum absolute uncertainty in the branching fractions of 25%. The relative error is estimated to be 10%.

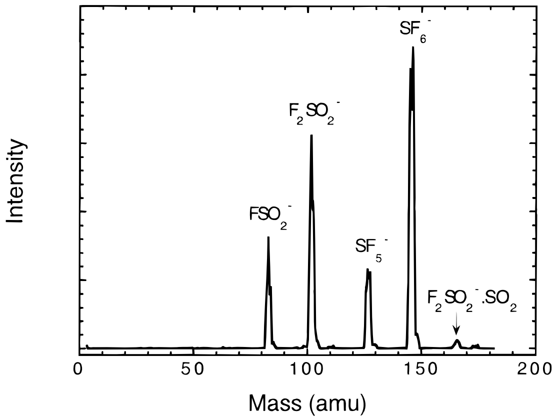

Figure 5. Typical mass spectrum obtained for the reaction of $SF_6^- + SO_2$ at 100 Torr.

Results and Discussion

As a first study to show the capabilities of the TIFT, we chose the previously characterized reaction of SF_6^- with SO_2, in part because SF_6^- is easily formed in the radioactive source and is not easily hydrated. As shown in previous studies at <1 Torr,[14−16] this reaction yields three product ions:

$$\begin{aligned} SF_6^- + SO_2 &\rightarrow SF_5^- + FSO_2 \qquad (5) \\ &\rightarrow FSO_2^- + SF_5 \\ &\rightarrow F_2SO_2^- + SF_4 \end{aligned}$$

A typical mass spectrum obtained at 100 Torr is shown in Figure 5, illustrating that the same ionic products are formed in the very high pressure region. Two examples of kinetics data obtained at 100 Torr are shown in Figure 6.

Rate constants were determined from data sets similar to that shown in Figure 6a, where a large percentage of the primary SF_6^- ion signal is depleted by reaction with SO_2. Total rate constants are shown in Table 1 for pressures from 25 to 700 Torr. The overall rate constant is not pressure dependent, and the reaction proceeds at approximately 75% of the collision rate, consistent with previous measurements made at <1 Torr.[14−16] Interestingly, Ferguson has noted that the rate of reaction 5 varies with kinetic energy, decreasing an order of magnitude at 0.6 eV and then increasing again.

Product distributions were determined from kinetics data sets such as that shown in Figure 6b, where only a small percentage

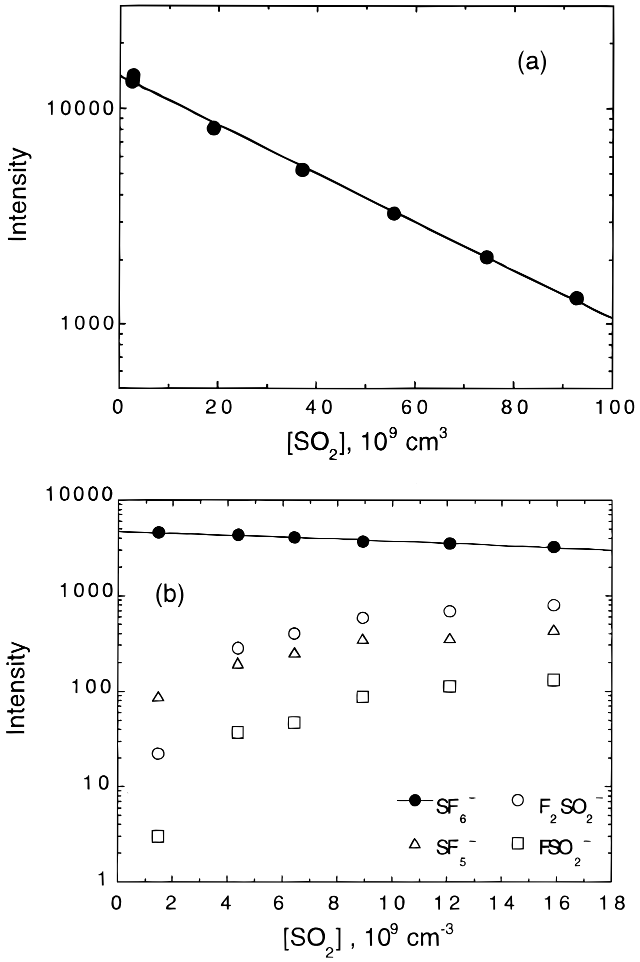

Figure 6. Kinetics data for reaction of $SF_6^- + SO_2$ at 100 Torr. (a) Data showing large depletion of primary ion signal used for determining reaction rate constants. (b) Data showing small depletion of SF_6^- signal used for determining product distributions.

TABLE 1: Rate Constants and Product Ion Distributions for the Reaction of SF_6^- with SO_2, Measured at 300 K from 25 to 700 Torr

pressure (Torr)	rate (10^{-9} cm^3 s^{-1})[a]	branching fractions		
		$SF_5^- + FSO_2$	$F_2SO_2^- + SF_4$	$FSO_2^- + SF_5$
<1	1.0[b]	0.26[c]	0.54[c]	0.20[c]
25	1.1	0.26	0.60	0.14
50	1.1	0.23	0.57	0.20
100	1.1	0.23	0.63	0.14
200	1.0	0.23	0.60	0.17
300	1.1	0.22	0.60	0.18
500	1.1	0.24	0.61	0.15
700	0.99	0.23	0.57	0.20

[a] $k_c = 1.4 \times 10^{-9}$ cm^3 s^{-1}, as calculated by the method of Su and Chesnavich.[18,19] [b] References 14−16. [c] Reference 16.

of the primary ion was reacted with SO_2 in order to reduce the effect of secondary reactions. In addition, the flow of SF_6 was kept extremely small. This low flow rate is feasible since the SF_6 electron attachment rate constant is more than 2 orders of magnitude greater than reaction 5.[17] As shown in Table 1, the product distributions for reaction 5 are independent of pressure from 25 to 700 Torr within our experimental uncertainty. These results are in good agreement with the previous measurements made at <1 Torr. Ferguson has noted that, like the rate constants, the branching fractions for reaction 5 vary dramatically with energy.[14] At low E/N, $F_2SO_2^-$ is the dominant product ion while FSO_2^- and SF_5^- are major products at high E/N. The combination of the present results and the energy dependence results may indicate that the lifetime of the complex is exceedingly short and that the increase in pressure does not result in collision of the buffer with the collision complex before it falls apart.

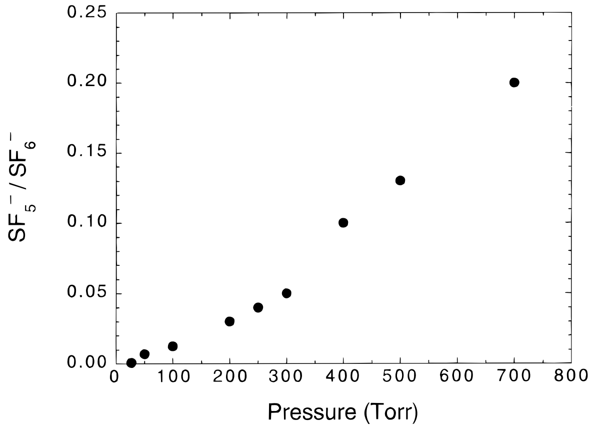

Figure 7. Ratio of SF_5^- to SF_6^- in the absence of SO_2, as a function of pressure, demonstrating larger percentage of SF_6^- fragmentation upon sampling with increasing flow tube pressure.

In measuring product distributions for reaction 5 at pressures above 200 Torr, several complications arose. First, the SF_5^- signal that appears at the detector is not only a product of the $SF_6^- + SO_2$ reaction; some results from breakup of SF_6^- during sampling. The amount of SF_5^- resulting from electron attachment to SF_6 is well-known (0.07%).[17] While this does account for the amount of SF_5^- observed at 25 Torr, it does not account for the much larger fraction observed at higher pressures. We were unable to change the SF_5^- to SF_6^- ratio by introducing the SF_6 source gas either upstream or downstream of the in-line ionizer, indicating electrons from the radioactive source are indeed thermalized. The amount of SF_5^- resulting from breakup of SF_6^- increases with increasing pressure, as shown in Figure 7 where the SF_5^- to SF_6^- ratio in the absence of SO_2 is shown. This increase suggests SF_6^- is partially dissociating upon sampling. Although we have been able to effect the SF_6^- to SF_5^- ratio by changing the lens voltages, we could not completely eliminate this problem without reducing the ion signal to unworkable levels. For the branching ratio measurements, a background of SF_5^-, representing that due to breakup of SF_6^-, is subtracted from the SF_5^- signal. Although this becomes a relatively large correction at 500 Torr and above, we were still able to obtain reasonable data at these higher pressures, as evidenced by the flatness of the branching ratio with pressure.

Another complication with measuring product distributions above 200 Torr involved interfering secondary reactions between the products of reaction 5 and the SF_6 source gas. Because the reaction time is relatively long at high pressures, even very slow secondary reactions can be observed in this apparatus. In this case, the $F_2SO_2^-$ product was found to react slowly with SF_6:

$$F_2SO_2^- + SF_6 \rightarrow SF_5^- + F_3SO_2 \qquad (6)$$

The unwanted effect of this secondary reaction was reduced by using a 1% SF_6 mixture through the in-line ionizer rather than using neat SF_6.

Secondary reactions between SO_2 and the SF_5^- and $F_2SO_2^-$ products from reaction 5 were also observed:

$$SF_5^- + SO_2 \rightarrow F_2SO_2^- + SF_3 \quad (7)$$

$$F_2SO_2^- + SO_2 \rightarrow FSO_2^- + FSO_2 \quad (8)$$

Our qualitative observations are consistent with the measurements of Streit[15] who has previously reported a rate constant for reaction 7 equal to 6×10^{-10} cm^3 s^{-1}, while reaction 8 was reported to be slow. The secondary chemistry indicates that FSO_2^- is the terminal negative ion in this system.

Summary

A new instrument has been developed for studying ion−molecule reactions in the very high pressure range. It is currently designed to operate at room temperature over a pressure range from approximately 20−750 Torr. Higher pressures are possible with minor modifications. The instrument is based on the turbulent flow neutral reactor developed by Seeley et al.,[8] and it operates under turbulent rather than laminar flow conditions.

In this initial report, 300 K rate constants and product distributions, measured from 25 to 700 Torr, are presented for the reaction of SF_6^- with SO_2. Both the rate constants and product distributions for this reaction are independent of pressure, and the present results are consistent with previous measurements made at <1 Torr.

This apparatus is complementary to other ion−molecule kinetics instruments. The TIFT, along with only a small number of other instruments,[3−6] can study ion−molecule reactivity up to atmospheric pressures. It is the only fast flow instrument, which means the distinct advantages of fast flow techniques are maintained, e.g., allowing reactions with unstable neutrals to be studied. The very high pressure instruments should allow new types of reactivity to be studied. Several examples are evident. Extremely slow reactions should be able to be studied with a rate constant limit of 10^{-17} molecules^{-1} cm^3 s^{-1} easily achievable. Knighton and Grimsrud have shown that high pressures can change reaction rates by allowing the buffer to interact with the collision complex.

Presently, the TIFT instrument is only operable at room temperature. However, the ability to vary temperature has always played a major role in our laboratory, and an upgrade is in progress to add temperature variability (298−900 K) to this instrument. This will require preheating the gas with an Omegalux airflow heater. The pressure range will also be extended to approximately 2 atm. The TIFT compliments the other fast flow instruments in our laboratory, allowing for studies of ion−molecule reactions over a wide range of conditions. With the combination of a high-temperature flowing afterglow and a selected ion flow drift tube, studies over an extended temperature range of 80−1800 K can be made. Studies over a kinetic energy range of 0.01−0.5 eV can also be made.

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