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Investigation of the Reaction of O_3^+ with N_2 and O_2 from 100 to 298 K

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The kinetics of the reaction of O_3^+ with N_2 and O_2 have been studied at 100 and 298 K in a variable temperature-selected ion flow tube (VT-SIFT). The rate constants for O_3^+ reacting with N_2 measured in the VT-SIFT are slow, proceeding at $<5 \times 10^{-13}$ cm^3 s^{-1} at both temperatures, in disagreement with recent measurements by Cacace et al.[1] of the total rate constant of ca. 1.7×10^{-10} cm^3 s^{-1} at 298 K. However, a $N_2O_3^+$ intermediate postulated to be involved in the reaction has been observed at 100 K, in agreement with the previous experimental and theoretical results. Rate constants for the reaction of O_3^+ with O_2 at 100 and 298 K have also been measured in the VT-SIFT. The O_2 reaction rate constants are 3.1×10^{-10} and 2.9×10^{-10} cm^3 s^{-1} at 100 and 298 K, respectively, which are ca. half of the Langevin collision rate constant. Discrepancies between the current results and those of Cacace et al. in regard to the rate constants measured and the N_2O^+ product ions observed are discussed in light of newer data for the O_3^+ chemistry and the contributions of excited-state species. [Cacace, F.; et al. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1938.]

Introduction

Cacace et al.[1] have recently investigated the reaction of O_3^+ with N_2 as a possible source of N_2O, a major atmospheric precursor of NO_x pollutants and a pernicious greenhouse gas. They have found that this reaction produced either N_2O or N_2O^+ with a total rate constant of approximately 1.7×10^{-10} cm^3 s^{-1}. At this rate, they speculate that this reaction may produce a significant amount of N_2O in the atmosphere, most notably near power lines, in corona discharges and during thunderstorms. This source is not presently accounted for in current atmospheric models; thus, it could have a substantial impact on simulations.

Cacace et al. have proposed the mechanism given by eqs 1 and 2 for O_3^+ reacting with N_2. The reaction proceeds through a $N_2O_3^+$ ($m/z = 76$) reaction intermediate, where channels (1)

$$O_3^+ + N_2 \leftrightarrow [N_2O_3]^+ \xrightarrow{k_1} N_2O^+ + O_2 \qquad (1)$$

$$\xrightarrow{k_2} O_2^+ + N_2O \qquad (2)$$

and (2) are 4.2 and 22.9 kcal mol^{-1} exothermic, respectively. Rate constants for reactions 1 and 2 were estimated to be ca. 1.4×10^{-11} and 1.6×10^{-10} cm^3 s^{-1}, respectively, as measured in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. In a separate experiment using a ZAB multisector mass spectrometer, ions at $m/z = 32$, 44, and 76 were generated in their chemical ionization (CI) source using a 5% mixture of O_3 in O_2 with N_2. These ions have been postulated to be O_2^+, N_2O^+, and $[N_2O_3]^+$, respectively. The collisionally activated dissociation (CAD) mass spectra of these ions are consistent with this assignment, demonstrating that the ion at mass 76 can be attributed to $[N_2O_3]^+$. Also, the CAD spectrum for the peak at 76 amu agrees with the CAD spectrum from a CI experiment for O_2^+ reacting with N_2O, suggesting that the $N_2O_3^+$ formed has an $[N{-}N{-}O{\cdots}O{-}O]^+$ arrangement. Furthermore, reionization of the neutrals produced in the CAD experiment from $N_2O_3^+$ shows a major peak at $m/z = 44$ that indicated that some of the CAD events generate N_2O intact.[1]

Consistent with their experimental results, density functional theory (DFT) calculations performed by Cacace et al. indicate that two stable $[N_2O_3]^+$ structures exist that are connected by a transition state with a 10.6 kcal mol^{-1} barrier. These structures require that the N_2 moiety be bound to a terminal O atom.[1] In addition, previous ab initio calculations by Snyder and Sapse have shown that ion−dipole bonding of N_2^+ to the central O atom with O_3 in a C_{2v} symmetry does not produce a stable structure.[2]

Due to the potential importance of this reaction in atmospheric chemistry, the kinetics of the reaction of O_3^+ with N_2 have been studied further in the AFRL variable temperature-selected ion flow tube (VT-SIFT) under thermalized conditions. This distinction is important as Cacace et al. have noted that excited states may be generated in their experiments. Different sources of O_3^+ have been used in the VT-SIFT, and temperature-dependent studies of the kinetics have been made. The reaction of O_3^+ with O_2 has also been studied because of its relative importance to the N_2 reaction. The results of this study are reported at temperatures of 100 and 298 K.

Experimental Section

The VT-SIFT apparatus[3] is briefly described as it pertains to these experiments. Electron impact ionization on a supersonic expansion of O_2 (99.999% pure, AGA) with 40 psig backing pressure behind a 0.2 mm nozzle produces O_3^+ ions, presumably through the clustering reaction of O^+ with O_2. Identical results have been obtained using a 5% O_3 in O_2 mixture[4] in the stagnation chamber where O_3 can be ionized directly. For

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simplicity, pure O_2 expansion has been used for most of the experiments discussed here. The ions produced are mass selected with a quadrupole mass spectrometer and injected into a fast flow of helium (99.997% pure, AGA) buffer gas that is introduced through a Venturi inlet. Breakup of the O_3^+ into O_2^+ occurs upon injection into the flow tube so the source conditions have been adjusted to minimize this dissociation during injection. Unfortunately, the process cannot be eliminated entirely. The least amount of breakup results in approximately equal amounts of O_3^+ and O_2^+.

The buffer gas is passed through a liquid nitrogen cooled sieve trap to remove water vapor. Passing liquid nitrogen through copper lines surrounding the flow tube cools the flow tube to 100 K for the low temperature study. Nitrogen (99.999% pure, AGA) is introduced at one of two inlets downstream from the ion injection point and is allowed to react for a previously measured reaction time of approximately 3−7 ms to obtain the rate constants under pseudo-first-order kinetics conditions. Residual reactant ions and any product ions are sampled by an aperture in a blunt nose cone, then mass analyzed with a second quadrupole mass spectrometer, and detected with an electron multiplier. The instrument is interfaced with a desktop computer that controls the data acquisition. Rate constants measured in this manner have relative errors of ±15% and absolute errors of ±25%.[3]

Results and Discussion

Parts a and b of Figure 1 show mass spectra measured at 298 K in the VT-SIFT with and without N_2 added. In the absence of N_2 gas, $O_2^+$and O_3^+ are the only ions present. As mentioned above, O_2^+ arises from collisions of O_3^+ with the helium buffer gas upon injection. Both internal energy and translational energy can lead to the dissociation process. In the spectra in Figure 1, comparable amounts of O_2^+ and O_3^+ are found. This is the best ratio of these two ions attained in our apparatus because using lower injection energies leads to a complete loss of signal. In the presence of N_2, a small signal due to N_2^+ is found. This signal comes from a small fraction (1%) of electronically excited O_2^+ reacting with N_2.[5] Thus, in the present experiments, addition of N_2 comprising about 1% of the total gas flow to the flow tube changes the spectra to an almost a negligible extent. Particularly relevant is the fact that neither a peak for $N_2O_3^+$ ($m/z = 76$) nor N_2O^+ ($m/z = 44$) is observed, despite higher operating pressures than in the CI experiments of Cacace et al. The authors do note that no $N_2O_3^+$ signal was observed in the FT-ICR experiments.[1]

The total rate constant for the O_3^+ reaction with N_2 measured in the VT-SIFT is $<5 \times 10^{-13}$ cm^3 s^{-1} at 298 K. It cannot be ruled out that a small amount of O_2^+ is produced via reaction 2, which would be masked by the signal from dissociation of O_3^+ upon injection. However, the kinetics occur at the limit of the capabilities of the VT-SIFT; thus, the reported rate constant represents the upper limit that can be detected. The current value is in serious disagreement with the rate constant measured by Cacace et al. in their FT-ICR, i.e., 1.7×10^{-10} cm^3 s^{-1}. [1] In response to the present results, the authors have stated that the FT-ICR rate constant should be viewed as phenomenological, strictly providing an explanation for the formation of the $N_2O_3^+$ and N_2O^+ ions created in their CI source.[6] The authors further noted that the phenomenological rate constant decreases when the ionizing electron energy is lowered and approaches zero when the O_3^+ ions are cooled according to a thermalizing technique based on a short, high-pressure Ar pulse invariably utilized in previous works when measuring thermal rate constants in the FT-ICR.[6] The current kinetics measurements in the VT-SIFT, on the other hand, reflect the thermal reaction rate constant. The participation of excited electronic states as well as vibrational excitation in the FT-ICR experiments is reasonable considering that the four lowest doublet states of the O_3^+ cation lie in an energy range of 2 eV and the two lowest states are nearly degenerate.[7,8] Consequently, the discrepancy is strictly because of the different conditions under which the rate constants have been measured in the FT-ICR vs the VT-SIFT; i.e., the large rate constants observed in the FT-ICR experiments[1] may be due to the presence O_3^+ excited-state species.

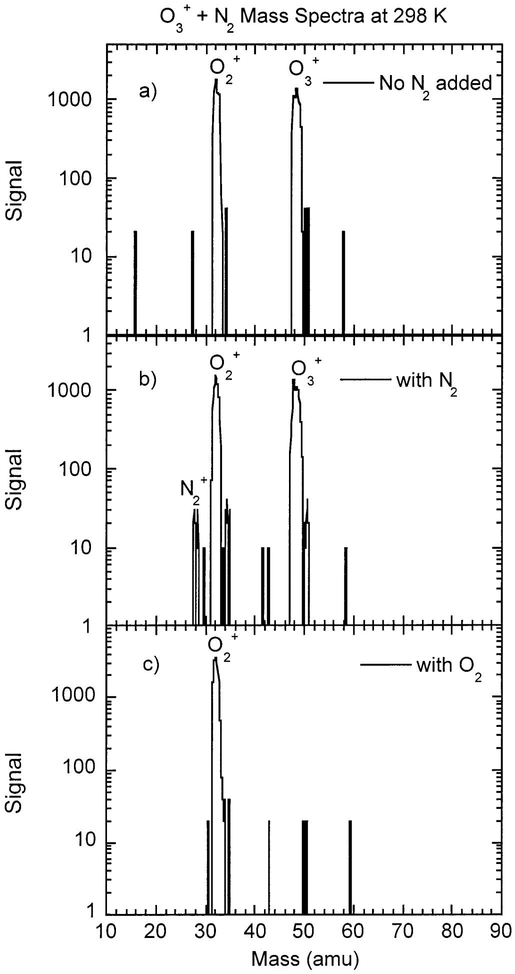

Figure 1. Mass spectra for the reaction of O_3^+ with N_2 at 298 K as measured in a variable temperature-selected ion flow tube (VT-SIFT). The spectra have been taken with (a) no reactant gas in the flow tube, (b) with N_2 added to the flow tube, and (c) with O_2 added to the flow tube.

The ion selected at 48 amu in the VT-SIFT source region is most likely O_3^+ because of its breakup into O_2^+ upon injection. However, to rule out the remote possibility that the remaining ion at 48 amu was not SO^+ (possibly formed from trace sulfur impurities in the source region from experiments performed months earlier), O_2 has been added to the flow tube. Charge transfer of O_3^+ with O_2 is exothermic but SO^+ charge transfer is endothermic,[9,10] so that SO^+ will be unreactive with O_2. Adding O_2 to the flow tube confirms that the ion at $m/z = 48$ is O_3^+ because it is entirely consumed by O_2, producing O_2^+ as seen in Figure 1c at 298 K. The rate constants for the reaction of O_3^+ with O_2 are 3.1×10^{-10} and 2.9×10^{-10} cm^3 s^{-1} at 100 and 298 K, respectively, which are almost half of the Langevin collision rate constant.

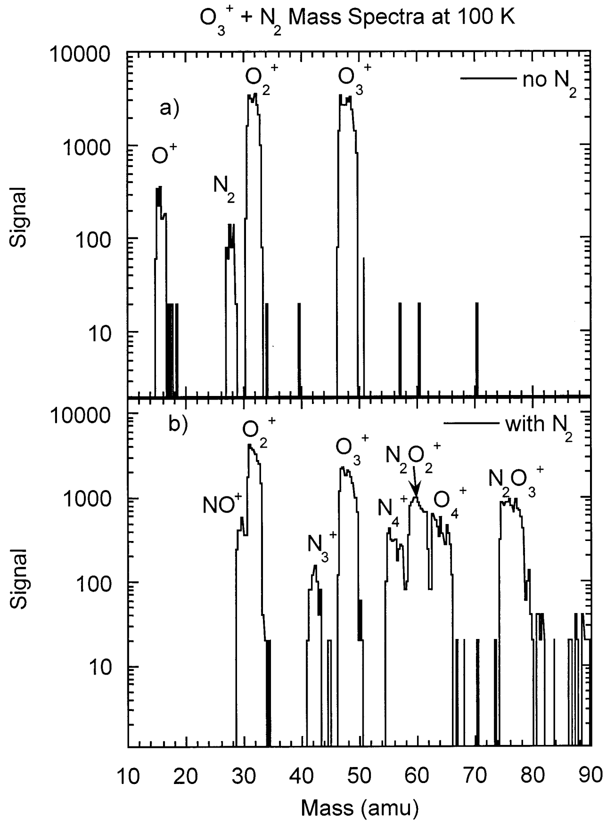

Figure 2. Mass spectra for the reaction of O_3^+ with N_2 at 100 K as measured in a variable temperature-selected ion flow tube (VT-SIFT). The spectra have been taken with (a) no reactant gas in the flow tube and (b) with N_2 added to the flow tube.

To further verify that the differences between the FT-ICR measurements[1] and the current VT-SIFT measurements are not due to the reaction of different isomers of O_3^+, Gaussian 98W calculations have been performed.[11] Several optimizations have been performed at the MP2(Full)/6-31G(d) level of theory with different starting points such as the geometry of neutral O_3 with C_{2v} symmetry, as well as a linear structure. Only one stable isomer of O_3^+ has been found having C_{2v} symmetry, which agrees with the previous calculations of the energy levels of O_3^+.[8,12] This result indicates that the O_3^+ ions studied in the two experiments are the same isomer, even though the source chemistry is different.

To increase the likelihood of observing the $N_2O_3^+$ complex in the VT-SIFT, the reaction of O_3^+ with N_2 has also been studied at 100 K. Parts a and b of Figure 2 show mass spectra taken at 100 K both with and without N_2 added. The O_3^+/O_2^+ ratio is smaller than at room temperature because the longer reaction time allows for more O_3^+ to react with the small O_2 impurity in the He buffer at 100 K. A peak is observed at mass 76, verifying that $N_2O_3^+$ is stable. This complex must be weakly bound because it is only observed in small abundance (~25% of the original O_3^+ signal with a maximum amount of N_2 added) and only observed at low temperature. No N_2O^+ at mass 44 is observed. The NO^+ ions arise from the reaction of N_2 with O^+ [5,13] that is created by the dissociation of O_3^+ during injection. O_4^+ is seen in Figure 2b with only N_2 added because of the 0.001% of O_2 impurity present in the N_2 supply. This ion presumably arises from the reactions of O_2^+, $N_2O_2^+$, and maybe $N_2O_3^+$ with the trace amount of O_2.[5] Nevertheless, it is clear that the ion with $m/z = 76$ arises from N_2 in the presence of O_3^+; thus, the stability of the weakly bound $N_2O_3^+$ complex has been confirmed at 100 K in agreement with the results of Cacace et al.[1] Figure 3 shows typical kinetics data measured at 100 K. The $N_2O_3^+$ signal increases with increasing N_2 flow with a concomitant decrease in the O_3^+ signal. Even at 100 K where the complex is stable, the total rate constant for the reaction of O_3^+ with N_2 is approximately 1.1×10^{-13} cm^3 s^{-1}.

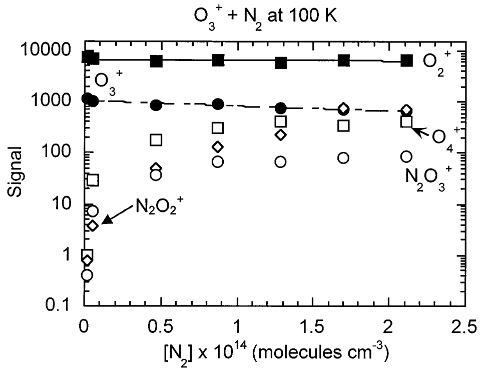

Figure 3. Kinetics data for the reaction of O_3^+ with N_2 at 100 K as measured in a variable temperature-selected ion flow tube (VT-SIFT). The ion signal is plotted vs the concentration of N_2 where the symbols are defined as follows: (●) O_3^+, (■) O_2^+, (○) $N_2O_3^+$, (□) O_4^+, and (◇) $N_2O_2^+$.

Although it is clear that thermal O_3^+ does not react rapidly with N_2, N_2O^+ is made in the CI source in the experiments of Cacace et al.[1] A likely source of this ion is excited-state reactions. In further tests by Cacace and co-workers, the intensity of the $N_2O_3^+$ peak drops significantly as the pressure of O_3 in the CI source is increased. Decreasing the energy of the ionizing electrons in the CI produces a similar decrease in the $N_2O_3^+$ signal.[6] In addition, the observation of N_3^+ formed in the CI mass spectrum[1] is known to involve the reaction of N_2^+ in a long-lived electronically excited state with N_2, further indicating that excited species are formed in the CI source. Consequently, it is clear that excited-state ions are generated in the CI source of Cacace and co-workers.

To test for the possibility of excited species using the VT-SIFT, O_3^+ has been injected directly into an N_2 buffer. In this experiment, the first collisions of O_3^+ with N_2 involve electronically, vibrationally, and translationally hot O_3^+. Most of the either electronically or vibrationally excited O_3^+ decomposes into O_2^+ upon injection. However, a small amount of the ions (around 1−2% of the total ions observed) is converted into N_2O^+. This amount may be somewhat higher as the N_2 buffer contains 0.001% O_2, as discussed earlier, and the reaction of N_2O^+ with O_2 is fast.[1,5] Nevertheless, this observation is consistent with the Cacace measurements showing N_2O^+ is produced in their ion source with O_3, N_2, and O_2 present.[1] The results also support the assertion that the reactions of excited species contribute to the N_2O^+ ion signal observed previously by Cacace et al.

The proposed scheme for N_2O formation in the atmosphere will be important only under certain conditions. First, O_3^+ ions must be produced. Reaction 1 must be faster than the competing reaction of O_3^+ with O_2. However, the present VT-SIFT experiments establish that reaction 1 is slow and that the charge-transfer reaction of O_3^+ with O_2 is fast over a wide temperature range. These results indicate that any O_3^+ that is formed will react rapidly with the O_2 present in air rather than with N_2. In addition, because O_3^+ reacts at close to the collision rate with O_2, the phenomenological rate constant corresponding to O_3^{+*} reacting with N_2 relevant to conditions prevailing in an atmospheric discharge plasma, where excited ions are generated, would have to be close to the collision rate to compete with the O_2 reaction and produce N_2O in substantial amounts. This mechanism would require substantial excited-state production of O_3^+, which may be difficult in these highly energetic environments considering the small 0.6 eV bond energy of O_3^+.[7,14] Thus, the current results do not support the contention that N_2O may be formed in the atmosphere from O_3^+ and N_2 and that the atmospheric impact of the reaction of O_3^+ with N_2 would be minimal under thermalized conditions.

However, the conditions in atmospheric plasmas and coronas will have localized nonequilibrated regions relative to the bulk atmosphere, where a high *local* concentration of O_3 may arise under conditions involving energetic ionizing electrons. At this point, electronically and vibrationally excited species should be abundant. In these concentrated areas, the conditions prevailing in the CI source of the multisector mass spectrometer of Cacace et al.[1] may be more representative of these nonequilibrium systems.

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