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Much Improved Upper Limit for the Rate Constant for the Reaction of O_2^+ with N_2

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The rate constant for the reaction of O_2^+ with N_2 to produce NO^+ plus NO has been measured at 423, 523, and 623 K in a turbulent ion flow tube. Much improved upper limits for this reaction at the three temperatures are 2, 4, and 10 × 10^{-21} cm^3 s^{-1}, respectively. These results should render this reaction irrelevant when modeling all plasmas involving atmospheric gases.

The reaction of O_2^+ with N_2,

$$O_2^+ + N_2 \rightarrow NO^+ + NO \tag{1}$$

is known to be slow[1−8] despite the fact that it is exothermic by 89.4 kJ mol^{-1}.[9] Previous studies have found the rate constant for reaction 1 to be immeasurably slow. The most stringent limit showed that the rate constant is less than 2×10^{-18} cm^3 s^{-1} at 300 K.[4] However, because N_2 is the most abundant atmospheric neutral and O_2^+ does not react rapidly at low pressure with any other relatively abundant atmospheric neutral, e.g., H_2O, O_2, CO_2, Ar,[1,8] reaction 1 may have an impact on atmospheric modeling if the rate constant is as fast as listed above. This recently became clear when a model of atmospheric sprites (a special form of upward moving lightning from clouds to the bottom part of the ionosphere) showed NO^+ production by reaction 1.[10] That model adopted a value of 1×10^{-17} cm^3 s^{-1} for the rate constant, almost as low as the best limit.[11,12] Note that at higher pressures and lower temperatures, O_2^+ can cluster to most atmospheric gases.[1,8]

In recent studies in our laboratory, a nearly pure O_2^+ signal was observed at the end of a turbulent ion flow tube when an N_2 buffer was used.[13−16] This clearly showed that the reaction was slower than the previously published limits. Therefore, the recent understanding that the previous limits for this reaction did not render reaction 1 negligible provided the motivation either to measure the actual rate constant or to at least substantially decrease the upper limit. In this short note, new measurements are reported that reduce the upper limit by about 3 orders of magnitude.

The measurements were made in the Air Force Research Laboratory turbulent ion flow tube. This instrument is the only such instrument designed to study ion chemistry and has been described in detail previously.[16,17] Only pertinent details to the present measurements are given here. Ions were created in a corona discharge in a sidearm to the flow tube. The source was separated from the flow tube by a 1 mm orifice. The small size of the orifice was important in preventing N_2 backstreaming into the source. Upon exiting the ion source, the ions were carried downstream through a 2.54 cm diameter flow tube by a large flow of N_2 obtained from liquid N_2 boil-off. The ions were sampled through a nose cone and skimmer into a quadrupole mass spectrometer. The entire instrument can be heated to 350 C.

For these experiments, pure He and Ar were tried as source gases, as well as dilute mixtures of each noble gas with O_2 added. In all cases, O_2^+ was the dominant positive ion (after sufficient baking) at pressures less than 100 Torr and temperatures above 150 C. Below this temperature and at higher pressures, increasing amounts of proton hydrates were formed by the well know sequence of reactions,[1,8,18]

$$O_2^+ + H_2O + N_2 \rightarrow O_2^+(H_2O) + N_2 \tag{2}$$

$$O_2^+(H_2O) + H_2O \rightarrow H_3O^+(OH) + O_2 \tag{3}$$

Reaction 3 was followed by a fast switching reaction with another H_2O or by thermal decomposition so that H_3O^+, and $H_3O^+(H_2O)$ were the most abundant impurities. Because it was not possible to rid the TIFT of H_2O, the present measurements were performed at temperatures above 150 °C, where reactions 2 and 3 were less important. The maximum pressure at which an almost pure O_2^+ signal was found varied with temperature. During the course of the measurements, pressure was varied from 30 to 200 Torr, with the reported values (best limits) taken at 90, 150−200, and 80 Torr for temperatures of 423, 523, 623 K, respectively.

The experiment simply consisted of measuring the $[O_2^+]$:$[NO^+]$ ratio while minimizing the proton hydrates. First-order kinetics was applicable because the ion concentration was more than 10 orders of magnitude less than the N_2 concentration. Therefore, the rate constant for reaction 1 was given by

$$k = \ln \frac{[O_2^+]_0}{[O_2^+]}/[N_2]\tau = \ln \frac{[O_2^+] + [NO^+]}{[O_2^+]}/[N_2]\tau \tag{4}$$

where τ is the reaction time which had been previously measured.

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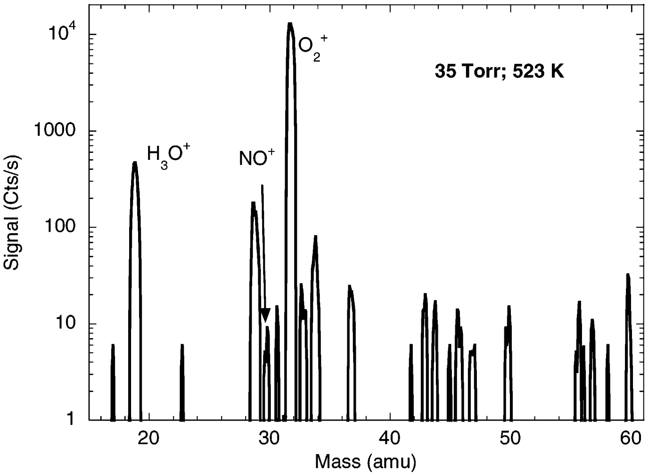

Figure 1. Mass spectrum taken at 35 Torr and 523 K.

A complication resulted because (1) NO is produced in discharges involving O_2 and N_2 and (2) O_2^+ is known to react rapidly with NO to produce NO^+; the rate constant is $\sim 4.5 \times 10^{-10}$ cm^3 s^{-1} at all temperatures.[19] To lower the previous limit for reaction 1, less than 5 ppbV of NO could be present in the flow tube. Various source conditions were tried and the ones that yielded the best $[O_2^+]$:$[NO^+]$ ratio included low corona voltage (<800 V), high flow of source gas, and no added O_2. It became clear that high voltages led to more NO^+, which indicated increased NO production in the source at higher energy. Under certain conditions, the NO^+ signal approached that of O_2^+. The high source gas flow helped prevent N_2 backstreaming into the source, and no O_2 limited high energy neutral oxygen species, such as O, O_3, and $O_2(^1\Delta)$. Obviously, this implies that the O_2 impurity in the buffer gas and/or the source gas was enough to ensure O_2^+ was the dominant ion in the flow tube. Ar^+, He^+, N^+, N_2^+, and O^+ all react with O_2 to produce O_2^+. O_2^+ was by far the dominant ion and any potential precursor was absent. This shows that O_2^+ is not produced along the length of the flow tube and can be considered as a point source for the purposes of this paper.

Figure 1 shows a sample mass spectrum taken at 35 Torr and 523 K over a relatively wide mass range. It shows that the O_2^+ peak was 40 times the next largest peak, H_3O^+, which resulted from reactions 2 and 3 followed by thermal decomposition of the cluster species. An ion at 29 amu was the next largest, possibly $C_2H_5^+$ or N_2H^+, also from impurities. The NO^+ peak is clearly small. Under our conditions, there is no known chemistry that would result in substantial NO^+ loss. Therefore, the impurities ions either stemmed from reaction with O_2^+ or were produced in the source and therefore were not tied to loss of NO^+ in the flow tube. Under conditions with more H_2O, NO^+ core ions could be converted to proton hydrates by reactions involving higher order water clusters. The impurity ion signals, therefore, may be added to the O_2^+ signal in the rate constant derivation. Doing so will lower the rate constant. Because upper limits are being reported, the conservative approach was to not include the impurities in the analysis and the numbers reported reflect that approach.

Although the spectrum shown in Figure 1 shows only a small amount of NO^+, it does not represent the reported rate constant limit. The reaction time for the data shown in the figure is about 20 ms, yielding a rate constant about 10 times the reported limit. To get the best limits, repetitive mass scans over the narrow range of 29−33 amu were averaged to increase the statistics for the small NO^+ peak. More efficiently data were taken by sitting alternatively on both peaks (O_2^+ and NO^+) and accumulating for 100's of seconds. The best limit had an NO^+ count rate of less than 0.3 count s^{-1}.

TABLE 1: Limits for the Reaction of O_2^+ with NO at Various Temperatures

temp (K)	rate constant upper limit (cm^3 s^{-1})
423	2×10^{-21}
523	4×10^{-21}
623	1×10^{-20}

Table 1 gives upper limits measured at three temperatures. These are assumed to be upper limits and not true rate constants because the limit decreased with decreasing corona voltage indicating that some NO was still produced. The lowest rate constants were measured with a corona voltage so low that the discharge was barely lit and on the verge of extinguishing. Therefore, reducing NO production further by this technique was not possible. The different limits at different temperatures are believed to be indicative of the cleanliness of the ion source and flow tube and not real. The increasing limits may, in fact, reflect an improvement with time (more outgassing) because the data were taken from high to low temperature. Repeated runs were not made because these limits are already low enough to ensure the rate is unimportant. The best limit indicates that the NO concentration in the flow tube was less than 4 pptV and is 3 orders of magnitude smaller than the previous best value.

Because these measurements were made at slightly higher temperatures than relevant for most regions of the atmosphere, some discussion of the potential temperature dependence is warranted. The limits show Arrhenius behavior and would indicate even lower values at normal atmospheric temperatures (200−300 K). Alternatively, many ion−molecule reactions have negative temperature dependences.[1,8] Years of experience indicate that a T^{-2} dependence would be quite large for a reaction involving only diatomics. Assuming this dependence, a maximum value of 1×10^{-20} cm^3 s^{-1} is obtained for a temperature of 200 K. For application to the atmosphere, this can conservatively be taken as the upper limit. The one region that is often colder than this is the summer mesopause region, but enough NO exists there to make reaction 1 irrelevant.[20] The same analysis indicates an upper limit of 4×10^{-21} cm^3 s^{-1} at 300 K.

In summary, the upper limit for the reaction of O_2^+ with N_2 to produce NO^+ is much lower than previous reported. The present study reduces the limit by 2−3 orders of magnitude and renders the reaction unimportant for modeling purposes. This work continues to show that improvements are needed in our understanding of ionospheric chemistry, in part through new instrumentation.[21]

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