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A reexamination of the temperature dependence of the reaction of N^+ with O_2

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Abstract

The rate constants for the reaction of N^+ with O_2 have been measured as a function of temperature (200–1400 K) in a selected ion flow tube (SIFT) and high temperature flowing afterglow (HTFA). The datasets agree well with each other and the rate constants exhibit little temperature dependence. This is in contrast to two previous experiments at elevated temperature that reported the rate constant increased with temperature up to 1000 K. A small part of the difference is explained by the absence of a thermal transpiration correction in the original measurements. The new data implies that rotational and translational energy both have little influence on the reactivity. The equivalent nature of the two types of energy is expected from studies on other systems. Vibrational excitation appears to increase the rate constants to near collisional. The branching ratios measured in the SIFT are in good agreement with previous drift tube results and show that rotational and translational energy have little effect on the individual channels. (Int J Mass Spectrom 223–224 (2003) 397–402)
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Keywords: Selected ion flow tube; High temperature flowing afterglow; Rate constant

1. Introduction

N^+ is formed in the ionosphere [1,2] and is mainly lost by reaction with O_2. The reaction forms three products,

$$N^+ + O_2 \rightarrow O^+ + NO + 2.3\ \text{eV},$$
$$N^+ + O_2 \rightarrow NO^+ + O + 6.7\ \text{eV},$$
$$N^+ + O_2 \rightarrow O_2{}^+ + N + 2.5\ \text{eV}. \qquad (1)$$

Due to the importance of reaction (1) in the ionosphere, it has been studied by many techniques [3–18]. Since ionospheric temperatures can reach 1800 K [19], reaction (1) was one of the first reactions studied in both the NOAA and AFRL high temperature flowing afterglow (HTFA). The AFRL data [15] and those from the NOAA study showed excellent agreement up to 900 K [18] with the rate constants increasing with increasing temperature. The previous HTFA rate constants reach a plateau at temperatures above 1000 K at a value approximately equal to the collision rate. In contrast, drift tube studies show no kinetic energy dependence on the rate constant, which are about 50% of the collisional value [9,18]. Thus, the temperature studies and drift tube studies showed agreement with

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similar experiments but not with the other type of study. The difference was attributed to internal energy effects, i.e., kinetic energy did not influence the rate constants but some combination of electronic excitation of N^+ and rotational and vibrational energy of O_2 caused the rate constants to increase.

In writing a recent review on internal energy dependencies derived from comparisons of the HTFA data to kinetic energy data [19], it became clear that this reaction was an anomaly. Most of the difference between the temperature and kinetic energy data for reaction (1) had to be assigned to rotational energy. No other reaction of the dozens studied had a similar dependence on rotational energy. In all other cases involving species that do not have large rotational constants, rotational energy either behaved similarly to translational energy or had a negligible influence on reactivity. The unusual nature of the results prompted us to reexamine the kinetics in both the HTFA and selected ion flow tube (SIFT) in our laboratory. The SIFT data includes the first temperature dependence of the branching ratio and the combined data sets cover the temperature range from 200 to 1400 K.

2. Experimental

Both the SIFT and HTFA experimental apparatuses have been discussed in detail previously [19–21]. Therefore, only details pertinent to the present measurements are discussed here. In the SIFT, N^+ was made from N_2 in an electron impact ion source, mass selected, and injected into the flow tube. A small water impurity resulted in about 5% of the N^+ signal being converted to H_2O^+, which is known to react with O_2 exclusively by charge transfer [22]. Rate constants and branching ratios are measured in the usual manner [19–21] except that the branching ratios are corrected for the $O_2{}^+$ resulting from the H_2O^+ reaction. This correction is small, on the order of a few percent or less. The rate constant errors are estimated to be ±25 and 15% in absolute and relative value in both the HTFA and SIFT.

The HTFA has had a number of modifications since our first publication on this reaction [19,23]. The changes to the apparatus will be emphasized here. The ceramic flow tube has been replaced by a quartz flow tube, thereby limiting the maximum temperature to 1400 K. A thermal transpiration correction to the determination of the flow tube pressure has been added to the data analysis. The flow tube pressure is measured by an external capacitance manometer, which is maintained at 318 K and is connected to the flow tube with 0.25 in diameter tubing. The temperature gradient across this gas-filled tube leads to the development of a pressure gradient, i.e., thermal transpiration. The equation developed by Takaishi and Sensui [24] and discussed by Poulter et al. [25] was used to correct for thermal transpiration. When lower pressures are used, the thermal transpiration correction is larger. The old temperature data did not take this into account but measurements over the last several years have. This correction increases with increasing temperature and decreases with increasing pressure. The correction to the rate constant, which involves two pressure terms (one in the density and one in the ion velocity), is typically less than 10–15%.

Another large change is the addition of a second roots pump to the vacuum box. The improved pumping results in considerably less contamination from the firebrick surrounding the furnace from reaching the flow tube. Therefore, the mass spectra are much cleaner. The last major change involves moving the ion source off axis into a tee at the upstream end of the flow tube. The source region is now separated from the main flow tube by a replaceable diaphragm to control the source pressure. For these experiments, the source pressure is several times the flow tube pressure. This reduces the amount of source gas needed to make sure the source chemistry is complete before the reaction zone and reduces the amount of UV light reaching the flow tube from the ion source. The previous source had been baffled to prevent the UV light from entering the reaction region.

In the HTFA experiments, He^+ and He metastables were made in the source from a thoriated iridium filament biased at 130 V. N_2 was added downstream of the

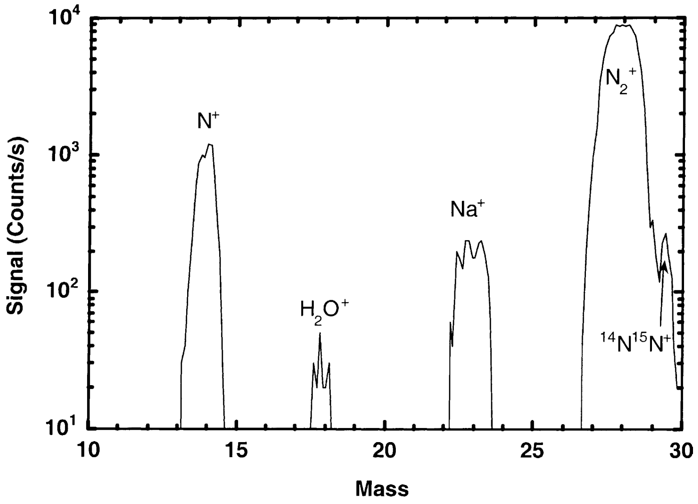

Fig. 1. Mass spectra without reactant at 1100 K.

filament but still in the ion source region. Metastable He atoms reacted with N_2 to make N_2^+, while He^+ makes both N^+ and N_2^+. An example of the spectra is shown in Fig. 1, taken at 1100 K. The spectra is very clean compared to those obtained in the older version of the HTFA. The main ion is N_2^+, followed by N^+. The other two ions visible are Na^+, formed from impurities in the flow tube walls, and a small H_2O^+ impurity peak. The presence of N_2^+ did not disturb the rate constant measurements since it reacts slowly with O_2 to form O_2^+. Na^+ is unreactive.

3. Results and discussion

Rate constants for reaction (1) are shown in Fig. 2 as a function of temperature, including the present HTFA and SIFT results, a previous drift tube measurement [8], and the two previous studies at high temperature [15,18]. The previous HTFA study is plotted with and without the thermal transpiration correction. The drift tube study shown in Fig. 2 is in good agreement with two other studies that are not shown for simplicity [4,9]. The drift tube studies show rate constants that are independent of kinetic energy. The SIFT data show no discernible temperature dependence from 200 to 550 K in agreement with the drift tube results. The present HTFA results show a temperature dependence essentially equal to our relative error limits, i.e., very small. The two previous studies at high temperature found rate constants that increased with increasing temperature up to 1000 K, in contrast to the present study. Above this temperature, the previous HTFA study found a leveling off at the collision rate. Thus, the temperature studies presented here are in disagreement with the previous ones.

Part of the discrepancy is due to thermal transpiration as can be seen in Fig. 2 [25]. However, this is only a small part of the disagreement. Due to the disagreement between the two sets of HTFA data, a number of checks were performed on the present HTFA data. Pressure, He flow rate, N_2 source gas flow, electron bias voltage, and emission current were all varied with no influence in the rate constants within experimental error. These are the only easily changeable parameters. Nothing could be found that would increase the rate constants. The SIFT data are in excellent agreement with the new HTFA measurements in the overlapping range and both new data sets lack a strong temperature dependence.

In addition to remeasuring the rate constants for reaction (1), the original HTFA data have been

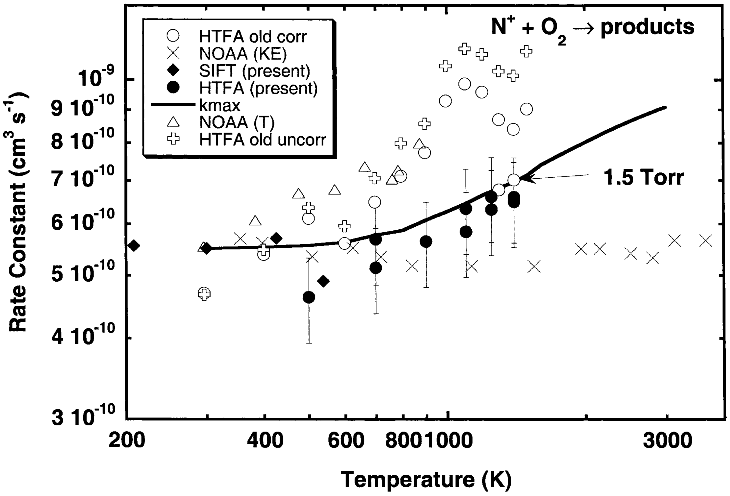

Fig. 2. Rate constants for the reaction of N^+ with O_2. The SIFT (present) and HTFA (present) points are from this study. The NOAA kinetic energy (KE) data are from McFarland et al. [8], the temperature data NOAA (T) are from Lindinger et al. [18] The HTFA old corr and HTFA old uncor refers to the published HTFA data [15] with and without the thermal transpiration correction. The error bars are ±15% on the present HTFA data. The old HTFA data taken at 1.5 Torr are indicated by an arrow.

reexamined. Data run at 1300 and at 1400 K have both been taken at elevated pressure (1.5 Torr vs. 1 Torr). The high pressure points are indicated with an arrow in Fig. 2 and agree with the present measurements. They are shown in the figure as the small circles on the solid line. The difference between the 1 and 1.5 Torr rate constants probably results from incomplete source chemistry at the lower pressure. In other words, not enough N_2 was added to quench all the He^+ and He^* before the beginning of the reaction zone in the low pressure data. Because He^+ reacts with N_2 to produce both N^+ and ${N_2}^+$, insufficient N_2 will lead to a situation where He^+ is the dominant ion at the start of the reaction zone and N^+ and ${N_2}^+$ are dominant at the end of the reaction zone, i.e., at the mass spectrometer. Therefore, the disappearance of N^+ with the addition of O_2 was due to He^+ reacting with O_2 rather than N_2 as well as from the reaction of N^+ with O_2. The reaction of He^+ with O_2 is faster that for N^+ and proceeds with a rate constant equal to those in the plateau region of the previous measurements [22]. Notes indicated that the amount of N_2 added in the previous experiments was marginal, but no mass spectra exist to check for the presence of He^+. Also the instrument has been sufficiently modified so that reproducing the previous conditions is not practical. It is not possible to speculate if this was also a problem in the NOAA temperature data as well.

Due to the above problem, we also measured selected points for O^+ and ${N_2}^+$ reacting with O_2. The rate constants were very slightly lower than the original values mainly due to the thermal transpiration correction. The small differences are not enough to change any of the original conclusions. No measurements of N^+ reactions with other neutrals have been made in the HTFA.

From a chemical dynamics viewpoint, the new data are easier to interpret. The old data required rotational energy to drive the reactivity much more efficiently than translational energy. No other system studied to date shows such a behavior [19]. Most systems studied show that rotational and translational energy have the same influence on reactivity. The drift tube data overlap within the error with the new HTFA data except at the highest temperatures. The good agreement between the SIFT and HTFA data with drift tube data imply that neither rotational nor translational energy have a large influence on the rate constants. At higher temperatures, the HTFA data are larger than the drift tube data although just slightly above the 15% relative error limits shown in Fig. 2. This indicates that vibrational excitation probably promotes reactivity. The line in Fig. 2 labeled k_{max} is calculated by taking the $v = 0$ rate constant as the drift tube data and assuming that the rate constants for vibrationally excited O_2 react at the collision rate. The line is in excellent agreement with the present data. This agreement suggests that O_2 ($v \geq 0$) reacts at close to the collision rate, but the small differences between the datasets makes definitive conclusions impossible.

In the SIFT experiments, the branching ratios were also measured. These are shown in Fig. 3 as function of rotational plus translational energy along with a previous drift tube study [4]. The main product accounting for about half the reactivity is charge transfer, O_2^+, followed by NO^+ at about 40% and then O^+ at less than 10%. None of the channels has a large energy dependence in the range of the present experiments although at high energy the drift tube measurements show that charge transfer becomes more important at the expense of the other channels. The same trends at high energy have also been found in a beam experiment [13]. The good agreement between the drift tube and SIFT experiments indicates that both rotational and translational energy do not change the branching ratio within our uncertainty (±3% for the minor channel and ±6% for the other two channels). The absence of an effect of different forms of energy on the branching ratios lends further support to the accuracy of the new values of the rate constants.

4. Conclusions

In summary, the rate constants for the reaction of N^+ with O_2 were remeasured at high temperature. The present measurements disagree with two previous high temperature studies, including one from this laboratory. However, agreement is now found with drift tube measurements and the derived internal energy dependencies are no longer anomalous. The error in the previous measurements is attributed in part to the absence of a thermal transpiration error and, more importantly, to incomplete source chemistry. When combined with the drift tube studies, the present measurements show that neither translational nor rotational energy appreciably affects the rate constant. This combination of measurements also provide evidence that one quantum

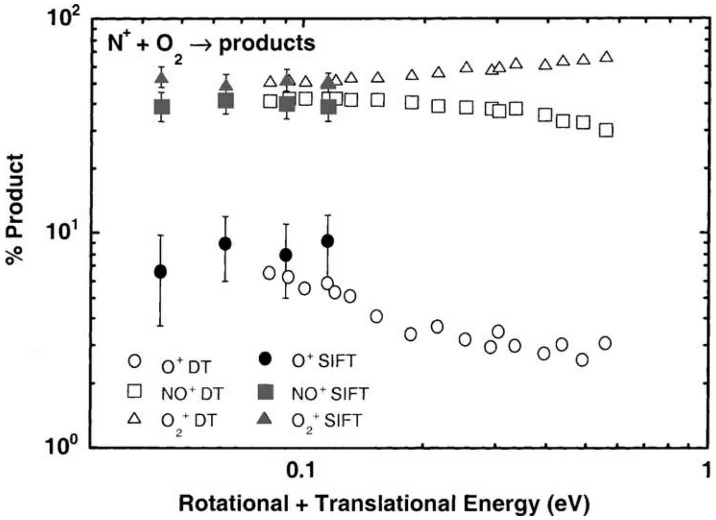

Fig. 3. Branching fractions for the reaction of N^+ with O_2 as a function of average rotational and translational energy. Solid points refer to the present SIFT experiments and open points refer to the flow drift tube study at NOAA [4].

of vibrational energy in O_2 increases the rate constant to the collision rate. Branching ratios were also measured as a function of temperature for the first time and found not to depend significantly on temperature, suggesting that the same mechanism is occurring over the entire temperature range. Detailed theoretical calculations by Irle and Morokuma [26] to explain these measurements are underway will be reported in the future.

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