

Rate constants for the reactions of O^+ with N_2 and O_2 as a function of temperature (300–1800 K)

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We have studied the rate constants for the reaction of O^+ with N_2 over the temperature range 300–1600 K and the reaction of O^+ with O_2 over the range 300 to 1800 K. The results are in good agreement with previous measurements made up to 900 K. The rate constant for the O^+ reaction with N_2 shows a minimum in the temperature range 1100–1300 K. The increase above this temperature is due to $N_2 v=2$ becoming populated. The rate constant for $O^+ + O_2$ shows a minimum in the 800–1100 K range. Comparing to previous drift tube measurements allows the rate constant for $O_2 (v>0)$ to be derived. The $v>0$ rate constant is approximately five times larger than the $v=0$ rate constant. © 1997 American Institute of Physics. [S0021-9606(97)00909-4]

INTRODUCTION

During the 1960's and 1970's there was considerable interest in ionospheric chemistry.^{1–3} In particular, reactions that convert atomic ions, especially O^+ , to diatomic ions were found to be extremely important in controlling the electron density in the ionosphere. This stems from electron–ion recombination being extremely slow for atomic ions and very fast for diatomic ions.⁴ Numerous studies^{5–13} were made to understand the important reactions in this conversion; the two most important were found to be



and



The ionospheric temperature range is very broad (a few hundred to a few thousand Kelvin), so it becomes necessary to measure these reactions over as wide a temperature range as possible.¹⁴ Two studies of these reactions were made at temperatures up to 900 K.^{7,8} From low temperatures up to 900 K the rate constants were found to decrease with increasing temperature. At the time of these two studies, it was impractical to increase the temperature range further. Therefore, in order to obtain information on how these reactions would proceed at even higher temperatures, alternative approaches were needed. The simplest experimental method to obtain information pertinent to higher temperatures was to study the reactions in a drift tube. This method was well suited to study the effect of translational energy and success-

fully increased the range over which the translational temperature could be studied to well over 10 000 K.^{10–12} However, this approach did not help in increasing vibrational and rotational temperatures beyond 900 K. This is important since at the 900 K limit, O_2 and N_2 are mainly in the ground vibrational states. Schmeltekopf *et al.*^{5,6} studied reaction (1) at 300 K translational and rotational temperature as a function of vibrational temperature of N_2 by exciting the N_2 in a microwave discharge. They found that vibrational energy strongly affected the reactivity, showing the need for true temperature measurements.

Recently, we have constructed a flowing afterglow to study ion molecule reactions at temperatures from 300 to 1800 K.¹⁵ This range covers ionospheric temperatures under most situations. In this paper we report kinetics measurements of reaction (1) up to 1600 K and reaction (2) up to 1800 K.

EXPERIMENT

The measurements were made in a high temperature flowing afterglow. This apparatus has been described in detail recently¹⁵ and just a brief description is given here. Ions are created by electron impact in the upstream, cooled section of a ceramic flow tube. A helium buffer carries the ions downstream where the flow tube is heated by a commercial furnace. After the gases have reached the equilibrium temperature,¹⁶ the reactant gas is added. The bulk of the gas is pumped by a Roots blower, a small fraction is sampled; the ions are analyzed by a quadrupole mass filter and detected by an electron multiplier. The decay of the primary ion signal as a function of the reactant neutral gas concentration yields the rate constant. The only significant change in the instrument since the detailed description was published has been to slightly lengthen the flow tube upstream of the furnace. This allowed for measurements up to 1800 K by increasing the distance between the hot zone and the sealing gaskets and o-rings. Two minor changes included the use of a turbopump on the ion lens region and a separate pump for the vacuum box.

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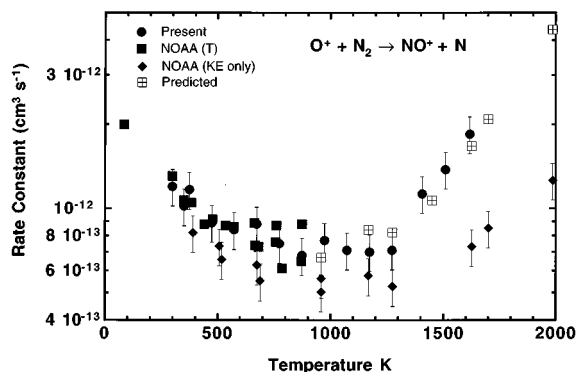


FIG. 1. Rate constants for the reaction of O⁺ with N₂. The NOAA temperature data are from Lindinger *et al.* (Ref. 8) and the drift tube data from Albritton *et al.* (Ref. 11). The predicted values are described in the text.

The O⁺ ions were made from O₂ for the O₂ reaction and from a mixture of O₂ and CO for the N₂ reaction. The CO was added to react with metastable O⁺.¹⁷ This could not be done in the O₂ reaction, since C⁺ was made in the process and C⁺ reacts with O₂ to form O⁺.¹⁷ For the O₂ reaction more O₂ source gas was added to rid the system of metastables. Sufficient O₂ and CO were added to ensure that the production of O⁺ was complete before the reactant inlet. The helium was passed through a liquid nitrogen trap to reduce the water vapor concentration, and the reactant neutrals were used without further purification. O⁺ was a relatively minor ion, O₂⁺ being the major one. No attempt to measure the product ions was made except to confirm the appearance of products known from other results. We estimate the error in the measurements as ±25% and ±15% for the total and relative error, respectively.

RESULTS

O⁺+N₂

Figure 1 shows the rate constants for the reaction of O⁺ with N₂ as a function of temperature. The rate constants are very small, reaction occurring on the order of 1 in 10³ collisions. At low temperature the rate constants decrease with temperature and show a minimum in the 1100–1300 K range before rising steeply at higher temperature. The results are in excellent agreement with the previous measurements made at temperatures up to 900 K. Shown are the data from the NOAA laboratory.⁸ The results of Chen *et al.*⁷ are similar.

Several drift tube studies were made of this reaction.^{10–12} Plotted in Fig. 1 are the data of Albritton *et al.*,¹¹ the most recent and thorough drift tube measurement. The other studies are similar, except that the rate constants near the minimum in the Albritton *et al.* study are slightly smaller. The drift tube data were taken as a function of ion kinetic energy and converted to effective translational temperature by KE=1.5 *kT*. The drift tube data agree with the present data within experimental uncertainty up to 1300 K. Above 1300 K the present thermal results increase much faster than the drift tube results, in which only the ion translational energy is increased.

TABLE I. Fractions of N₂ and O₂ that are vibrationally excited at various temperatures.

Temperature (K)	Population N ₂ (<i>v</i> >0)	Population N ₂ (<i>v</i> =2)	Population O ₂ (<i>v</i> >0)
500	0.001	0	0.01
600	0.003	0	0.02
700	0.008	0.0001	0.04
800	0.01	0.0002	0.06
900	0.02	0.0005	0.08
1000	0.03	0.001	0.10
1100	0.04	0.002	0.13
1200	0.06	0.003	0.15
1300	0.07	0.005	0.17
1400	0.09	0.007	0.20
1500	0.10	0.010	0.22
1600	0.12	0.013	0.24
1700	0.14	0.016	0.26
1800	0.15	0.019	0.28

Comparing drift tube results to pure temperature results allows information on internal energy dependences of the reactivity to be derived.¹⁸ Any difference in rate constant at the same translational temperature is due to internal energy. For the reaction of N₂ with O⁺ this means the N₂ internal energy. The good agreement between the pure temperature and kinetic energy data at low temperatures (<1000 K) shows that N₂ rotational energy has at most a small role in controlling the reactivity, since only a small fraction of N₂ is vibrationally excited.

The difference at the same translational temperature between the drift tube studies and the present results at high temperature is due to N₂ vibrations becoming excited in the thermal experiments. Table I shows the population of N₂ in vibrationally excited states as a function of temperature. N₂ (*v*=1) is already populated to a small extent by 1000 K, yet no clear enhancement in the rate constant is observed until 1300 K. Since there is only a relatively small difference in the *v*=1 population between 1200 and 1300 K, the data suggest that the increase may in fact come from a large rate enhancement for the *v*=2 state which changes in population by almost a factor of 2 over this temperature range.

The speculation that the increase is due to *v*=2 is confirmed by the experiments of Schmeltekopf *et al.*^{5,6} In their experiment, the reactants' translational and rotational temperatures were fixed at 300 K while the N₂ vibrational temperature was varied from 300 to 6000 K by means of a microwave discharge. The measured rate constants increased slightly from 1000–1200 K and dramatically above that. From their data they derived vibrational state specific rate constants for *v* from 0–11. They found the *v*=1 rate constant to be about the same as the *v*=0 rate constant. The rate constant for *v*=2 increased by about a factor of 40 from the *v*=0 and 1 values. The rate constant continued to increase for higher *v*'s until a value close to the collisional value was reached for *v*=6. This shows that the increase in our pure temperature data is due almost exclusively to *v*=2, present in only small abundance.

The two nonthermal experiments can be combined to

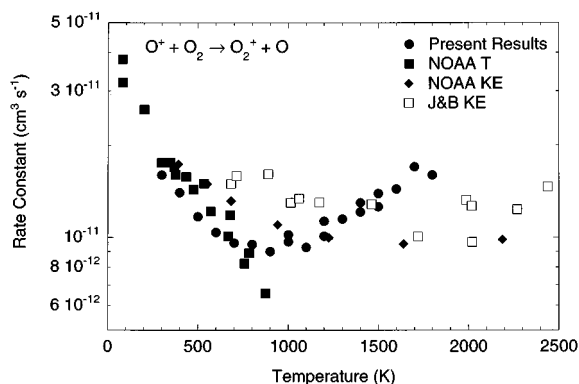


FIG. 2. Rate constants for the reaction of O^+ with O_2 . The NOAA temperature data are taken from Lindinger *et al.* (Ref. 8) and Ferguson (Ref. 19). The NOAA kinetic energy data are from McFarland *et al.* (Ref. 10) and J&B refers to drift tube work of Johnsen and Biondi (Ref. 12).

compare with the present data. The NOAA vibrational temperature data were reported relative to the 300 K rate constant. Scaling these data points to the drift tube translational temperature ($T_{\text{vib}}=T_{\text{trans}}$) rather than scaling to the 300 K rate constant allows a thermal rate constant to be predicted with both vibrational and translational effects included. This ignores the effects of rotational excitation (shown above to be at most a small effect). This also assumes that the translational energy dependences of the vibrationally excited species are the same as that for $v=0$. The results of this prediction are shown in Fig. 1. Very good agreement is found. Unsatisfactory agreement is obtained (not shown) if the vibrational temperature data are plotted relative to the 300 K rate constant. This shows that both vibrational and translational energy are important in controlling the rate constant in this temperature range and that the assumption of similar translation dependences for different states is reasonable. The reason for the strong increase at $v=2$ is at present unexplained.

$O^+ + O_2$

Figure 2 shows the rate constants for the reaction of O^+ with O_2 as a function of temperature. The rate constants are small, although they are about a factor of 10 larger than those for the O^+ with N_2 reaction. At low temperature, the rate constants decrease with temperature and show a minimum in the 800–1100 K range before rising at higher temperature. Error bars of $\pm 25\%$ are shown. Several previous studies of the temperature dependence of this reaction have been made. At NOAA, the reaction was studied from 100 to 900 K.^{8,9,19} Chen *et al.*⁷ studied the reaction from 300 to 700 K. The most recent NOAA results are shown in Fig. 2, the other results being in good agreement with them. The present data agree with the previous study within 15% at all temperatures except 900 K. At 900 K the present results are 27% higher than the NOAA results, still within the combined uncertainty.

In addition to the temperature studies, several drift tube studies have been made.^{10–12} The results from the two

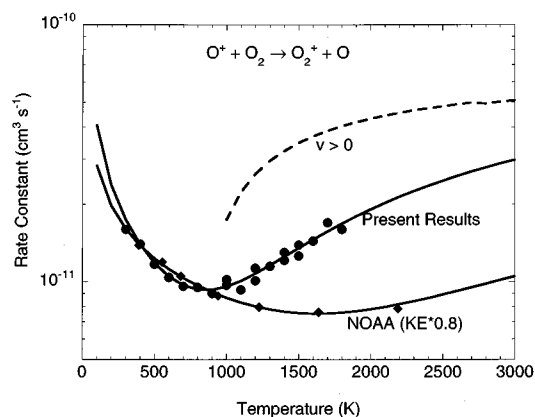


FIG. 3. Rate Constants for the reaction of O^+ with O_2 . The NOAA kinetic energy data are from McFarland *et al.* (Ref. 10). The solid lines through the data represent fits to the expression $k=A_1(300/T)^n+A_2 \exp(-E_a/kT)$. The derivation of the rate constants for O_2 ($v>0$) is described in the text.

NOAA studies are essentially the same, and the McFarland *et al.*¹⁰ data taken in a helium buffer are plotted in Fig. 2 as well as the Johnsen and Biondi¹² data. At low translational temperatures, the rate constants taken in the drift tube studies are slightly larger than those found for the pure temperature dependence at most effective temperatures. This is especially true for the data of Johnsen and Biondi. However, the main difference between the data is that the minimum in kinetic energy (outside the range of the data plotted in Fig. 2) is much broader and occurs at higher translational temperatures (~ 1600 K) than the minimum for the pure temperature data. The pure temperature rate constants also increase much faster with increasing temperature than do the drift tube data. These differences are due to the O_2 vibrations becoming excited at high temperatures.²⁰

The slight offset between the pure temperature and kinetic energy data makes a direct derivation of the internal energy dependence of the reaction slightly complicated. In order to facilitate this comparison we scaled the drift tube data so that the present results and the drift tube data coincide at the lowest translational temperature studied, namely, 400 K. Figure 3 shows this comparison including only the present results and the data from McFarland *et al.* for simplicity. The scaling factor for the drift tube data is 0.8, or a 20% offset, which is within the uncertainty of either data set.

In order to facilitate the derivation of vibrational energy effects, the two data sets are fit to the following expression:

$$k=A_1(300/T)^n+A_2 \exp(-E_a/kT), \quad (3)$$

where A_1 , A_2 , n , and E_a are adjustable constants. The results of this fitting are shown in Fig. 3 as solid lines and, as can be seen, are very accurate representations of the data. The values of the constants are listed in Table II. Below the minimum in the pure temperature data, there is excellent agreement between the present results and the scaled drift tube results. This shows that O_2 rotations do not play a major role in controlling the reactivity. At temperatures above the minimum, the pure temperature data clearly lie above the drift tube data. The separation occurs at a temperature where the

TABLE II. Fitting parameters for the reaction of O⁺ with O₂ to the expression, $k = A_1(300/T)^n + A_2 \exp(-E_a/kT)$. The fits are to the scaled drift tube data. To reproduce the original data multiply the A factors by 1.25.

	A_1 (cm ³ s ⁻¹)	n	A_2 (cm ³ s ⁻¹)	E_a (kJ mol ⁻¹)
Drift tube data	1.6×10^{-11}	0.52	5.5×10^{-11}	56.8
Temperature data	1.7×10^{-11}	0.77	8.54×10^{-11}	28.8

O₂ vibration starts to become excited (see Table I), indicating that excited O₂ vibrations increase the reactivity.

From the two fits and the O₂ vibrational population as a function of temperature, it is possible to derive the rate constants for vibrationally excited O₂. The rate constant at a given temperature can be written as

$$k(T) = \sum k_i \cdot \text{pop}(i), \quad (4)$$

where, $k(T)$ is the measured rate constant as a function of temperature, k_i is the rate constant for a particular vibrational state, and $\text{pop}(i)$ is the population of that state. We take k_0 as the drift tube data, assume that all vibrationally excited O₂ reacts at the same rate, and derive the fraction of O₂ that is vibrationally excited from the known temperature. The results are shown in Fig. 3 and represent the translational temperature dependence of the $v > 0$ rate constant. The data show an initial rise that probably has to do with the fact that below 1200 K the drift tube data and the present results are similar and therefore the derivation depends on a small difference between two large numbers. At 1200 K and above, the present data continue to rise but at a much slower rate, roughly paralleling the translational temperature dependence for $v = 0$, i.e., the drift tube data, but a factor of 4–5 larger.

On the basis of thermochemistry we know that the O⁺ reaction with O₂ ($v'' = 0$) can produce O₂⁺ in states from $v' = 0-7$ and the O⁺ reaction with O₂ ($v'' = 1$) can produce O₂⁺ in states from $v' = 0-8$.²¹ Table III lists the Franck–Condon factors for these states.^{21,22} Frequently, charge transfer is fastest when the process is energy resonant.²³ Therefore, in order to compare Franck–Condon factors it is useful to compare the product states for O₂⁺ (v') for the O₂ ($v'' = 1$) reaction to the O₂⁺ ($v' - 1$) for the O₂ ($v'' = 0$) reaction. In this way the energy resonances are approximately equal. The last column in Table III makes such a comparison. As v' in-

TABLE III. Franck–Condon factor for the O₂⁺(X²Π_g)–O₂(X³Σ_g⁻) system. The last column is the ratio of Franck–Condon factors for states with comparable energy gaps.

$v'O_2^+$	F.C.F. O ₂ ($v'' = 0$)	F.C.F. O ₂ ($v'' = 1$)	F.C.F. O ₂ ($v'' = 1, v''$)/ F.C.F. O ₂ ($v'' = 0, v' - 1$)
0	0.188	0.270 0	
1	0.365	0.081 390	0.432 93
2	0.291	0.045 02	0.12
3	0.123	0.260 2	0.89
4	0.029 77	0.234 9	1.9
5	0.004 145	0.089 06	3.0
6	0.000 31	0.016 76	4.0
7	1.03e-05	0.001 574	5.1
8		5.809 0e-05	5.6

creases the energy gap becomes smaller, and finally for $v' = 7$ and 8 for O₂ ($v'' = 0$) and O₂ ($v'' = 1$), respectively, the energy gap reduces to a few tens of wave numbers. For these near resonant products states and the two next closest resonant states, the Franck–Condon factor ratio is in the 4–5.6 region, values very close to the experimental rate constant ratio. While this agreement may be fortuitous, it does provide a simple explanation for the rate constant increase. If the above explanation is true, the product states will be highly vibrationally excited, a result that can be checked experimentally in a beam apparatus.²⁴ The exact nature of the rate increase awaits a detailed molecular dynamics calculation beyond the scope of this study.

CONCLUSIONS

The rate constants for the reactions of O⁺ with N₂ and O₂ have been measured for the first time at temperatures up to 1800 K. The results clearly show that drift tube studies do not model kinetics at high temperature adequately. The problem arises mainly from the fact that vibrations are not excited in drift tube measurements. However, combining the present high temperature data with previous drift tube results allows rate constants for vibrationally excited molecules to be derived. The present measurements confirm the observation of Schmeltekopf *et al.* that N₂ ($v = 2$) increases the O⁺ with N₂ rate constant by a factor of 40 over the N₂ ($v = 0$) rate constant. For the reaction of O⁺ with O₂ we find that O₂ vibrations increase the rate constant by a factor of 5 over the ground state. Rotations are shown to play a minimal role in controlling the reactivity for both these reactions.

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