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Rate coefficient for the reaction $N + NO$

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Abstract. Evidence has been advanced that the rate coefficient for the reaction $N + NO \rightarrow N_2 + O$ has a small positive temperature dependence at the high temperatures (900–1500 K) that prevail in the terrestrial middle and upper thermosphere by Siskind and Rusch (1992), and at the low temperatures (100–200 K) of the Martian lower thermosphere by Fox (1993). Assuming that the rate coefficient recommended by the Jet Propulsion Laboratory evaluation (DeMore et al., 1992) is accurate at 300 K, we derive here the low temperature value of the activation energy for this reaction and thus the rate coefficient that best fits the Viking 1 measured NO densities. We find that the fit is acceptable for a rate coefficient of about $1.3 \times 10^{-10}(T/300)^{0.5}\exp(-400/T)$ and better for a value of about $2.5 \times 10^{-10}(T/300)^{0.5}\exp(-600/T) \text{ cm}^3 \text{ s}^{-1}$.

Introduction

The reaction

is the major loss process for odd nitrogen in the thermosphere of Venus, Earth, and Mars. A temperature-independent rate coefficient for (1) of $3.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ over the temperature range 200–400 K [Lee et al., 1978] has been recommended by the Jet Propulsion Laboratory (JPL) evaluation for many years [e.g., DeMore et al., 1992], and this value has generally been used in models for temperatures outside this range as well. Recently, Siskind and Rusch [1992] published a study of NO in the terrestrial thermosphere, in which they considered the effects of the newly revised rate coefficient [DeMore et al., 1990] for the reaction

on the densities and solar cycle variation of NO. They found that use of the revised rate coefficient results in increased production of NO and leads to a significant discrepancy in the measured and model NO densities. They suggested that this discrepancy could be resolved if the rate coefficient for (1), k_1 , has a weak positive temperature dependence, which would indicate the presence of a small activation barrier. Assuming the recommended value of k_1 to be accurate at room temperature, Siskind and Rusch [1992] found that the terrestrial NO data could be better fitted by their models if the rate coefficient for the temperature

range of interest, about 900–1500 K, were given by $1.6 \times 10^{-10}\exp(-460 \pm 60/T) \text{ cm}^3 \text{ s}^{-1}$. This value is similar to the laboratory value of Clyne and McDermid [1975] ($8.2 \times 10^{-11}\exp(-410 \pm 120/T) \text{ cm}^3 \text{ s}^{-1}$), which was rejected by the JPL evaluators. Recently, Davidson and Hanson [1990] carried out high-temperature laboratory measurements of the rate coefficient for reaction (1), and their recommended value, $7.12 \times 10^{-10}\exp(-787/T) \text{ cm}^3 \text{ s}^{-1}$, also suggests the presence of a small activation barrier.

In an independent study of odd nitrogen in the Martian thermosphere Fox [1993] suggested that the model NO densities could be brought into agreement with the values measured by Viking [Nier and McElroy, 1976] only if the total production rate of odd nitrogen were increased or the total loss rate were decreased. Generally, Martian model NO densities have been found to be substantially lower than the measured values [McElroy et al., 1976; Yung et al., 1977; Krasnopolsky, 1993]. Since the total production rate of odd nitrogen on Mars is fairly well constrained, we concluded that the recommended rate coefficient for (1) does not apply to the temperatures (100–200 K) that prevail in the Martian lower thermosphere. We found that adoption of a temperature-dependent rate coefficient like those reported by Clyne and McDermid [1975] or Davidson and Hanson [1990] brings our model into substantial agreement with the measurements. We made no attempt to optimize the value of the rate coefficient, and our study did not address the sensitivity of the density profile to the value of the rate coefficient. Moreover, the temperature profile that was adopted in the previous investigation was not that derived from Viking measurements, but a fit to an analytical functional form designed to reproduce the Viking measured CO_2 densities over a large altitude range [Fox and Dalgarno, 1979].

We consider here whether the Martian NO density profiles can provide more information about the low

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Figure 1. Temperature profiles derived from Vikings 1 and 2 mass spectrometer data. The Viking 1 profile was used in this work. Figure is from *Nier and McElroy* [1977]

temperature rate coefficient for reaction (1). Assuming that the JPL recommended value is accurate at 300 K, we derive a best fit for E_a/R and thus for k_1 to the NO densities from Viking 1. We assume a rate coefficient of the form $A \times (T/300)^{0.5} \exp(-E_a/RT)$, where E_a is the activation energy and $A \times (T/300)^{0.5}$ is the preexponential (Arrhenius) factor. We have chosen to include the temperature dependence of the preexponential factor explicitly because in the low temperature regime a

small change in temperature can be a large fraction of the absolute temperature. Since the accuracy of the data and model do not permit fine-tuning, we tested values of E_a/R from 100 to 800 K in increments of 100 K. The preexponential factor for each value of the activation temperature was then fixed by the requirement that the value of k_1 be $3.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 300 K.

Calculations and Results

The temperature profiles derived from the Viking 1 mass spectrometer data are shown in Figure 1 [*Nier and McElroy*, 1977]. The Viking 1 NO densities were reported in the altitude range from about 128 to 145 km, where the reported temperatures are about 110–160 K [*Nier and McElroy*, 1976]. We have constructed a low solar activity model of the Martian thermosphere-ionosphere, in which we compute the densities of 12 ions and 5 minor neutral constituents over the altitude range 100 to 400 km. This model is based on measured density profiles of CO_2 , N_2 , CO , Ar , and O_2 from the Viking 1 mass spectrometer [*Nier and McElroy*, 1976]. The O densities were derived from model calculations of the O_2^+ and CO_2^+ densities, which were measured by the retarding potential analyzer on the Viking spacecraft [*Hanson et al.*, 1977]. The model is described fully by

Figure 2. Model profiles of odd nitrogen species compared to Viking measurements. The squares are measured densities of NO from *Nier and McElroy* [1976] and *McElroy et al.* [1976] and are approximately the size of the original data points. The solid curves are the density profiles for the rate coefficient for (1) that we propose best fits the measurements, $2.5 \times 10^{-10} (T/300)^{0.5} \exp(-600/T) \text{ cm}^3 \text{ s}^{-1}$. The short dashed curves are for a rate coefficient of $1.3 \times 10^{-10} (T/300)^{0.5} \exp(-400/T) \text{ cm}^3 \text{ s}^{-1}$, which also gives acceptable agreement with the data. The long-dashed curve is the NO density profile for the temperature independent value for k_1 of $3.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ recommended by *DeMore et al.* [1992].

Figure 3. Arrhenius plots ($\log k_1$ vs. $10^4/T$) for the analytical expressions derived for some of the measurements and models over the temperature range of validity for each study. The dot-short-dashed curve labeled "D&H" refers to the high temperature measurements of Davidson and Hanson [1990], the dashed curve labeled "C&M" to the measurements of Clyne and McDermid [1975], the short-dash-long-dash curve labeled "Lee" to the measurements of Lee *et al.* [1978] (which are recommended by the JPL evaluation [DeMore *et al.*, 1992]). The dot-long-dashed curve labeled "S&R" is the rate coefficient derived from the terrestrial thermosphere model of Siskind and Rusch [1992]. The solid curve is the value from 100 to 200 K derived in this work.

Fox and Dalgarno [1979, 1983] and by Fox [1993]. The smoothed temperature profile [cf. Fox and Dalgarno, 1979] was used in computing the background neutral densities, but for the odd nitrogen species, the actual temperatures shown in Figure 1 were employed.

Figure 2 shows the computed densities of $N(^4S)$ and NO compared to the measured NO densities from Viking 1. The size of the squares, which represent the measured NO densities, is about the same as that with which the original Viking data was presented and represents the approximate error bars involved. The long-dashed curve shows the poor fit to the NO densities that is obtained with the recommended temperature-independent value for k_1 , $3.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The short-dashed curve is the fit obtained for $k_1 = 1.3 \times 10^{-10} (T/300)^{0.5} \exp(-400/T) \text{ cm}^3 \text{ s}^{-1}$ and can be seen to provide acceptable agreement with the data. Better agreement, however, is obtained for $k_1 = 2.5 \times 10^{-10} (T/300)^{0.5} \exp(-600/T) \text{ cm}^3 \text{ s}^{-1}$, as the solid curve shows. The former value is similar to that derived for high temperatures by Siskind and Rusch [1992]. The computed NO densities for an activation temperature of 600 K are still slightly too small, but further increases in E_a/R above 600 K do not improve the agreement substantially. In this altitude range and for these small values of k_1 , loss of NO is controlled by the charge trans-

fer reactions

rather than by (1). Furthermore, the values of the pre-exponential factor become unacceptably large for values of E_a/R greater than about 600 K.

Discussion and Conclusions

One might argue that the discrepancy in the terrestrial NO densities could be rectified if the recently revised rate coefficient for (2) were assumed to be incorrect. Certainly this cannot resolve the problem with Martian thermospheric NO, where, because the O_2 mixing ratio in the thermosphere is very small, about 1×10^{-3} [Nier and McElroy, 1977], (2) is not important. Moreover, the model NO values on Mars are too small, whereas the model values for Earth are too large. Siskind and Rusch [1992] argue that the JPL recommended rate coefficient may apply to low temperatures but that a second channel opens up at high temperatures [Cohen, 1991], causing the rate coefficient to increase. We suggest here that also at temperatures

that are lower than those in the terrestrial middle atmosphere, the recommended rate coefficient is inadequate and that the temperature dependence of (1) extends to very low temperatures as well. This may have important implications also for odd nitrogen in the terrestrial lower thermosphere.

In Figure 3 we present an Arrhenius plot of the analytical expressions for the rate coefficients for (1) as derived from the measurements by Davidson and Hanson [1990], Clyne and McDermid [1975], and Lee *et al.* [1978] (that recommended by DeMore *et al.* [1992]) compared to those derived from the model calculation of Siskind and Rusch [1992] and in this work. Each rate coefficient is shown over the temperature range of validity stated by the investigators. There appears to be general agreement between the measured and model rate coefficients over a broad temperature range, except for the temperature-independent value at low temperatures. The evidence for a temperature dependence in the rate coefficient seems compelling.

Thus there are now two independent model studies of the thermospheres of two different planets, in addition to the measurements of Clyne and McDermid [1975] and Davidson and Hanson [1990], that suggest that the temperature-independent value of the rate coefficient for reaction (1) recommended by the JPL evaluators for the temperature range 200–400 K does not apply to temperatures outside this range. It is hoped that this study and that of Siskind and Rusch [1992] will encourage measurement of this rate coefficient over a wider range of temperatures, both above and below the 200–400 K range appropriate to the terrestrial middle atmosphere.

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References

- Clyne, M. A. A., and I. S. McDermid, Mass spectrometric determinations of the rates of elementary reactions of NO and of NO₂ with ground state N atoms, *J. Chem. Soc. Faraday Trans. 1*, **71**, 2189, 1975.
- Cohen, N., A brief review of the five nitrogen-oxygen neutral species reactions at high temperatures, *Rep. ATR-90(8512)-1*, The Aerosp. Corp., Los Angeles, Calif., 1991.
- Davidson, D. F., and R. K. Hanson, High temperature reaction rate coefficients derived from N-atom ARAS measurements and excimer photolysis of NO, *Int. J. Chem. Kinet.*, **22**, 843, 1990.
- DeMore, W. B., S. P. Sander, D. M. Golden, M. J. Molina, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, evaluation number 9, *JPL Publ. 90-1*, 217 pp., 1990.
- DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, evaluation number 10, *JPL Publ. 92-20*, 240 pp., 1992.
- Fox, J. L., The production and escape of nitrogen atoms on Mars, *J. Geophys. Res.*, **98**, 3297, 1993.
- Fox, J. L., and A. Dalgarno, Ionisation, luminosity and heating of the upper atmosphere of Mars, *J. Geophys. Res.*, **84**, 7315, 1979.
- Fox, J. L., and A. Dalgarno, Nitrogen escape from Mars, *J. Geophys. Res.*, **88**, 9027, 1983.
- Hanson, W. B., S. Sanatani, and D. R. Zuccaro, The Martian ionosphere as observed by the Viking retarding potential analyzers, *J. Geophys. Res.*, **82**, 4351, 1977.
- Krasnopolsky, V. A., Photochemistry of the Martian atmosphere (mean conditions), *Icarus* **101**, 313, 1993.
- Lee, J. H., J. V. Michael, W. A. Payne, and L. Stief, Absolute rate of the reaction of N(⁴S) with NO from 196–400 K with DF-RF and FP-RF techniques, *J. Chem. Phys.*, **69**, 3069, 1978.
- McElroy, M. B., T. Y. Kong, Y. L. Yung, and A. O. Nier, Composition and structure of the Martian upper atmosphere: Analysis of results from Viking, *Science*, **194**, 1295, 1976.
- Nier, A. O., and M. B. McElroy, Structure of the neutral upper atmosphere of Mars: Results from Viking 1 and Viking 2, *Science*, **194**, 1298, 1976.
- Nier, A. O. and M. B. McElroy, Composition and structure of Mars upper atmosphere: Results from the neutral mass spectrometers on Viking 1 and Viking 2, *J. Geophys. Res.*, **82**, 4341, 1977.
- Siskind, D. E., and D. R. Rusch, Nitric oxide in the middle to upper thermosphere, *J. Geophys. Res.*, **97**, 3209, 1992.
- Yung, Y. L., D. F. Strobel, T. Y. Kong, and M. B. McElroy, Photochemistry of nitrogen in the Martian atmosphere, *Icarus*, **30**, 26, 1977.
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