

ON THE TEMPERATURE DEPENDENCE OF THE REACTION $O + NO \rightarrow NO_2^*$

WILLIAM E. SHARP

Space Physics Research Laboratory, University of Michigan, Ann Arbor, MI 48109, U.S.A.

(Received 14 July 1983)

Abstract—The published data on the temperature dependence of the radiative combination of atomic oxygen with nitric oxide at pressures near 1 torr is examined. Arguments are advanced to suggest that radiation near the cut-off wavelength ($\sim 3875\text{\AA}$) is coming from the unstabilized activated complex, NO_2^* . At 4000\AA a positive activation energy of 1 kcal mole^{-1} is deduced. Application of this temperature dependence with the rate coefficient at 5200\AA is made to airglow measurements in aurora. The deduced NO concentration is about 10^9 cm^{-3} , in general agreement with that deduced from the measured NO^+/O_2^+ ratio as well as an auroral model prediction.

INTRODUCTION

There is an apparent continuum emission in the visible wavelengths from the Earth's atmosphere that is considered to come from the association of atomic oxygen (O) and nitric oxide (NO) [Krassovsky, 1951].



The emission is a series of extremely diffuse, overlapping bands [Paulsen *et al.*, 1970], which have intensities that are a fraction of a Rayleigh/Ångstrom. Gadsden and Marovich [1973] have reported the wavelength distribution and intensity from a comprehensive analysis of ground-based observations at non-auroral latitudes. Observations by rocket-borne and satellite instruments of the emission profile have shown the emission to be centered at altitudes near 95 km [Baker and Waddoups, 1967; Greer and Best, 1967; Donahue, 1970; Witt *et al.*, 1976]. Ground-based observations at auroral latitudes show continuum emission levels that are enhanced over non-auroral latitude levels by up to a factor of 10 [Gattinger and Jones, 1974; Dick, 1970]. Rocket observations show the emission profile peak to vary with altitude [Sharp, 1978; Witt *et al.*, 1981]. The altitude profiles of the emission are potentially useful for deducing the NO concentrations provided the appropriate emission rate constant is known and information is available concerning the density of O. Some of the studies noted above have attempted to do this. However, they have pointed out that the required rate coefficient is not available at temperatures other than room temperature, and that the pressure dependence of the reaction is important at altitudes below 90 km. The purpose of this note is to report a deduction of the temperature dependence of the effective two body association rate

constant from published data. This temperature dependent rate coefficient is then used with a continuum emission profile reported by Sharp [1978] to deduce NO concentrations in an aurora.

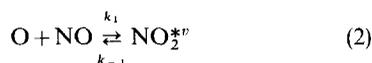
REVIEW

The onset of NO_2 emission is near 3875\AA (above the NO_2 bond energy) and extends into the infra-red. At pressures above 1 torr the integrated emission rate is independent of both pressure and the nature of the carrier gas. In addition, the integrated emission rate increases as the temperature is lowered. Below 1 torr the integrated emission rate decreases with decreasing pressure and reaches a constant value below about 2.5×10^{-4} torr. The peak of the spectral distribution shifts to the blue as the pressure is lowered; thus on decreasing from 1 torr to 2.5×10^{-4} torr, the 6000\AA region of the spectrum decreases by about a factor of 10, whereas near 4000\AA , there is a decrease of less than a factor of 2 (see review by Kaufman (1973)).

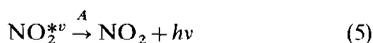
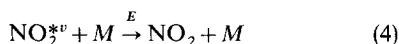
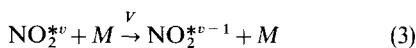
Two models of the recombination process have been advanced to explain the various observations. Keyser *et al.* [1968] advanced an energy transfer mechanism for the complex formed in two body recombination. When a third body is involved in the process (above 2.5×10^{-4} torr), its role is the stepwise vibrational relaxation of the collision complex. Golomb and Brown [1975] postulate a radical molecule complex mechanism in which a heteromolecular dimer is formed with the carrier gas molecule. Atomic oxygen then reacts with the dimer to form excited or ground state NO_2 .

The mechanism which best fits the observational data with the least number of free parameters is that of

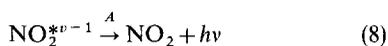
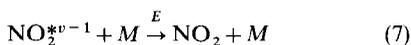
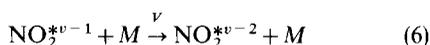
Keyser *et al.* [1968]. The process is outlined in the following steps (see Kaufman, 1973).



where the equilibrium constant $K_e = k_1/k_{-1}$ and NO_2^{*v} is the electronically excited complex formed on vibrational level v . Several processes now occur.



followed by a repeat for the new vibrational level;



where vibrational quenching V , electronic quenching E and A are assumed the same for each vibrational step and the back reaction k_{-1} is assumed much faster than the loss rate reactions. The collision complex is at equilibrium with O and NO. The intensity of the radiation emitted is then given by

$$I_\lambda(T, M) = k_\lambda(T, M) [\text{O}] [\text{NO}] \quad (9)$$

where

$$k_\lambda(T, M) = AK_e(T) \left\{ 1 + \frac{V[M]}{(E+V)[M]+A} + \dots \left(\frac{V[M]}{(E+V)[M]+A} \right)^{n-1} \right\} \quad (10)$$

n is the number of vibrational levels contributing to the radiation; $n = 1 + [(v_0 - v)/\Delta v_v]$ with $v_0 = 25,806 \text{ cm}^{-1}$, the threshold energy of the emission, v the frequency of the emitted radiation and Δv_v the average vibrational energy transferred, $500\text{--}1000 \text{ cm}^{-1}$ in O_2 [Cody, 1972]. Near the threshold wavelength of the emission, $\lambda \approx 3875 \text{ \AA}$ [Paulsen *et al.*, 1970; Fontijn *et al.*, 1964], there should be little pressure dependence (i.e. $n \approx 1$). This explains the choice of $v_0 =$ threshold energy. Therefore when $v_0 - v < \Delta v_v$, the emission at (or very near) this wave number, v , may come from the unstabilized collision complex at all pressures and temperatures. At 4000 \AA , $n \approx 2$ and probably only half of the chemiluminescence is coming from the unstabilized complex in a high pressure environment.

The temperature dependence of the emission is then confined to the equilibrium constant $K_e(T)$ and the

quenching rate E and V . At high pressure, the temperature dependence of the emission rate is a mixture of the temperature dependence of $K_e(T)$ and the quantity in the brackets of (10).

ANALYSIS

The temperature dependence of the total emission rate between 4000 \AA and 2μ can be placed on an absolute scale at room temperature by combining the data of Fontijn *et al.* [1964] for the visible and near i.r. with Golde *et al.* [1973] for the i.r. The reason for the combination is that Fontijn *et al.* underestimated the i.r. contribution above 8000 \AA . Golomb and Brown [1975] studied the temperature dependence of the light emission reaction at pressure of 1 torr. Although their emission rates were integrated only over $4000\text{--}8000 \text{ \AA}$, the resulting temperature dependence followed the same rate of change as does the total "3-body" rate constant between 353 and 187°K [Whytock *et al.*, 1976]. These rates of change are normalized to the Fontijn and Golde value and are shown in Fig. 1. The absolute emission rate of Vanpee *et al.* [1971] for 360 K is also plotted and is on the same line as the "3-body" rate. All of these are for O_2 as the third body. It can be concluded from the independent measurements and the temperature study measurements that the integrated emission rates of the Fontijn *et al.* [1964] and Golde *et al.* [1973] combination and Vanpee *et al.* [1971] are

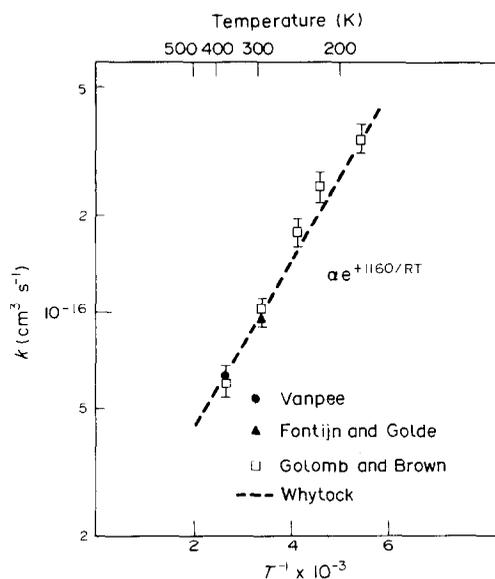


FIG. 1. THE INTEGRATED EMISSION RATE COEFFICIENT AS A FUNCTION OF TEMPERATURE FOR PRESSURES NEAR 1 TORR SHOWING A NEGATIVE ACTIVATION ENERGY OF $1.16 \text{ kcal mole}^{-1}$.

accurate both relative to one another and in an absolute sense.

The behavior of the spectral distribution as a function of temperature is less clear. At pressures above 1 torr and for temperature increases of over 1000 K there is substantial shift to the red of the distribution above 6000 Å [Vanpee *et al.*, 1971]. A comparison of the spectral shapes of Golde *et al.* [1973] with Vanpee *et al.* [1971] in the i.r. indicates relatively more i.r. emission at higher temperatures. The intensity distribution in the visible region between 5000 and 6000 Å changes little over a temperature range of ~200 to 1200 K [Golomb and Brown, 1975; Hartunian *et al.*, 1966]. No change in the cut-off wavelength has been seen with increasing temperature [Vanpee *et al.*, 1971]. Thus the spectral distribution below 6000 Å measured by Vanpee *et al.* and Fontijn *et al.*, will be assumed accurate and the intensity kinetics of the wavelength region (4000 Å) near cut-off will be examined.

Figure 2 shows the measured spectral distribution of the differential emission rate between 4000 and 6000 Å for three temperatures at 1 torr. The 1900 K data are from a high temperature flame [Vanpee *et al.*, 1971] and were only given in intensity units. The spectrum was normalized at 6000 Å to that value that would result if the rate of intensity drop between 296 and 360 K persisted to 1900 K. However, normalizing to 296 or 360 K would not alter the conclusions. The error bars on the data represent the estimates as reported by the authors. From this data it is observed that at 4250 Å and

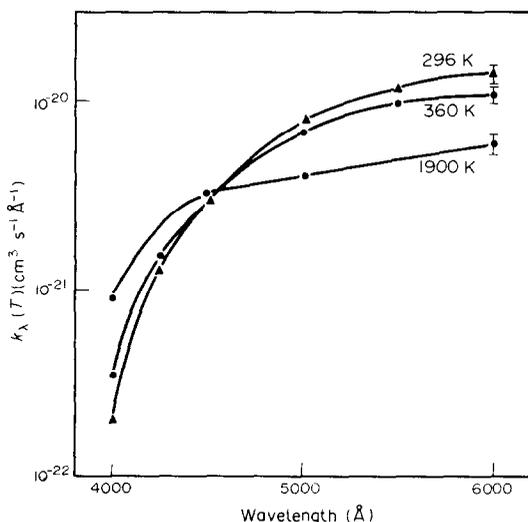


FIG. 2. THE DIFFERENTIAL EMISSION RATE COEFFICIENT AS A FUNCTION OF WAVELENGTH FOR THREE TEMPERATURE MEASUREMENTS AT 1 torr. 296 K by Fontijn *et al.* (1964); the 360 and 1900 K by Vanpee *et al.* (1971).

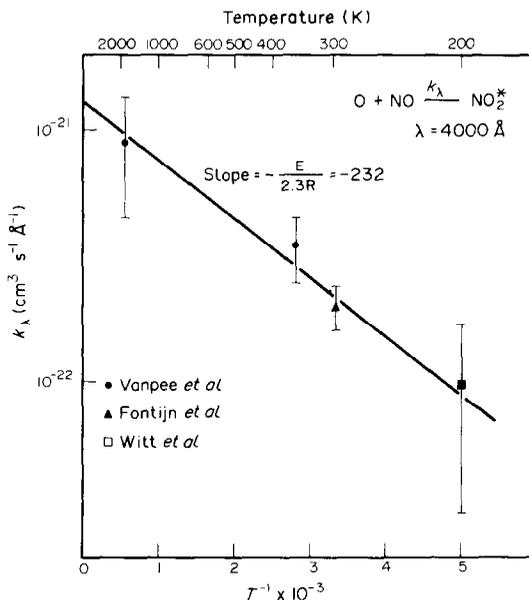


FIG. 3. THE INFERRED DIFFERENTIAL EMISSION RATE COEFFICIENT AT 4000 Å AS A FUNCTION OF TEMPERATURE.

Data are from Fig. 2 except for 200 K which is deduced from atmospheric measurements [Witt *et al.*, 1976].

4000 Å the trend for the emission rate is to increase with increasing temperature (i.e., has a positive activation energy). This positive activation energy is postulated to be identifiable with the initial bimolecular reaction.

A rate at 200 K was inferred in the following manner from data gathered in the atmosphere near the mesopause [Witt *et al.*, 1976]. At 100 km (pressure $\approx 10^{-4}$ torr) the volume emission at 5360 Å was deduced from measurements, along with measurements of the NO concentrations. Using a mean oxygen concentration from a compilation of a number of experiments [Offerman *et al.*, 1981] a rate of $(1.3 \pm 0.9) \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ is deduced for 5360 Å. It is reasonable to extrapolate this to 4000 Å using the low pressure spectral distribution of Becker *et al.* [1967]. This results in $k = (1 \pm 0.7) \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$.

Figure 3 is an Arrhenius plot of these data points. The error bars incorporate the reported accuracies as well as the precision of reading the data from the graphs. The straight line on the graph has a slope representing a positive activation energy of $E_A = 1 \text{ kcal mole}^{-1}$. This estimate is a lower limit in as much as a portion of the emission may be coming from the collision stabilized NO_2 .

APPLICATION

The two body recombination rate coefficient for 5200 Å is required to interpret our airglow data base

TABLE 1. [NO] FOR NASA 26.029 DERIVED USING $k_{5200\text{\AA}}(T)$

H (km)	T (K)	k_{5200} ($\text{cm}^{-3} \text{s}^{-1} \text{\AA}^{-1}$)	I_{5200} ($\text{ph}/\text{cm}^{-3} \text{s}^{-1} \text{\AA}^{-1}$)	[O] cm^{-3}	[NO] $\times 10^{+9} \text{cm}^{-3}$		
					Measure	Ions	Theory
100	200	6×10^{-22}	0.34	$11 \times 10^{+10}$	5.1	1.9	1.5
105	230	11	0.30	8	3.4	3.5	1.8
110	280	20	0.12	5.4	1.1	3.1	1.2
115	360	35	0.06	3.7	0.46	1.8	0.8

[Sharp, 1978]. At a temperature of 296 K and pressure of 1 torr the differential rate is $(1.0 \pm 35\%) \times 10^{-20} \text{cm}^3 \text{s}^{-1} \text{\AA}^{-1}$ [Fontijn *et al.*, 1964]. The pressure dependence of the spectral distribution [Cody, 1972; Becker *et al.*, 1967] suggests that the differential rate at 5200Å decreases to the low pressure rate by a factor of about 6.5. Therefore an estimate of the low pressure differential rate is:

$$k_{5200\text{\AA}}(296 \text{ K}) = (1.5 \pm 0.5) \times 10^{-21} \text{cm}^3 \text{s}^{-1} \text{\AA}^{-1}. \quad (11)$$

The temperature-dependent differential rate coefficient at 5200Å can be written

$$k_{5200\text{\AA}}(T) = (9 \pm 3) \times 10^{-21} \times \exp - 1060/RT \text{cm}^3 \text{s}^{-1} \text{\AA}^{-1}. \quad (12)$$

Above 100 km the collision complex is not quenched. Therefore the NO concentration is given by equation (9) with k_λ given by (12). The calculated densities are shown in Table 1. Included also are the estimates of [NO] from the measured $[\text{NO}^+]/[\text{O}_2^+]$ as discussed by Sharp [1978] and a theoretical calculation based on the parameters of the same aurora [Gerard and Rusch, 1979]. If there is a pressure contribution to the rate, k_λ , at 100 km, then the photometrically determined [NO] would be reduced. Given that the accuracies of determining NO by each method is probably no better than $\pm 50\%$, the agreement is remarkable.

CONCLUSION

The analysis of the emission rate coefficient of NO_2^* at high pressure near the cut-off wavelength has resulted in an estimate of the temperature dependence of the unquenched activated complex. This temperature dependence is found to have a positive activation energy of about 1 kcal mole $^{-1}$ which is consistent with bimolecular formation.

This analysis also suggests that this activation energy can be determined in a laboratory experiment by examining the wavelength region near the cut-off wavelength as the temperature is varied for the association of oxygen and nitric oxide even at high

pressure. Alternatively, a simultaneous measurement of I_λ , [O], [NO] and T in the atmosphere can accomplish the same result.

Acknowledgment—I appreciate many discussions with Professor Donald Stedman. This work was supported by NASA Grant NGR 23-005-360.

REFERENCES

- Baker, D. J. and Waddoups, R. O. (1967) *J. geophys. Res.* **72**, 4881.
- Becker, K. H., Groth, W. and Thran, D. (1967) *Chem. Phys. Lett.* **15**, 215.
- Cody, R. J. (1972) Mechanism of the chemiluminescent recombination of O and NO. Ph.D. Thesis, University of Pittsburgh.
- Dick, K. A. (1970) *J. geophys. Res.* **75**, 5605.
- Donahue, T. M. (1970) *J. geophys. Res.* **75**, 5605.
- Fontijn, A., Meyer, C. B. and Schiff, H. I. (1964) *J. chem. Phys.* **40**, 64.
- Gadsden, M. and Marovich, E. (1973) *J. atmos. terr. Phys.* **35**, 1601.
- Gattinger, R. L. and Vallence Jones, A. (1974) *Can. J. Phys.* **52**, 2343.
- Gérard, J.-C. and Rusch, D. W. (1979) *J. geophys. Res.* **84**, 4335.
- Golde, M. F., Roche, A. E. and Kaufman, F. (1973) *J. chem. Phys.* **59**, 3953.
- Golomb, D. and Brown, J. H. (1975) *J. chem. Phys.* **63**, 5246.
- Greer, R. G. H. and Best, G. T. (1967) *Planet Space Sci.* **15**, 1857.
- Hartunian, R. A., Thompson, W. P. and Hewitt, E. W. (1966) *J. chem. Phys.* **44**, 1765.
- Kaufman, F. (1973) The air afterglow revisited, in *Chemiluminescence and Bioluminescence* (Edited by Cornier, M. J., Hercules, D. M. and Lee, J.). Plenum, New York.
- Keyser, L. F., Kaufman, F. and Zipf, E. C. (1968) *Chem. Phys. Lett.* **2**, 523.
- Krassovsky, V. I. (1951) *Doklady Nauk S.S.S.R.* **78**, 669.
- Offerman, D., Friedrich, V., Ross, P. and Zahn, U. Von (1981) *Planet. Space Sci.* **29**, 747.
- Paulsen, D. E., Sheridan, W. F. and Huffman, R. E. (1970) *J. chem. Phys.* **53**, 547.
- Sharp, W. E. (1978) *J. geophys. Res.* **83**, 4373.
- Vanpee, M., Hill, K. D. and Kineyo, W. R. (1971) *AIAA Journal* **9**, 135.
- Witt, G., Dye, J. E. and Wilehl, N. (1976) *J. atmos. terr. Physics* **38**, 223.
- Witt, G., Rose, J. and Llewellyn, E. J. (1981) *J. geophys. Res.* **86**, 623.
- Whytock, D. A., Michael, J. V. and Payne, W. A. (1970) *Chem. Phys. Lett.* **43**, 466.