Planet. Space Sci. 1967. Vol. 15, pp. 1777 to 1780. Pergamon Press Ltd. Printed in Northern Ireland

ENERGY DEPENDENCE OF REACTIONS O^+ WITH N_2, O_2—I

DRIFT TUBE MEASUREMENTS

D. K. BOHME, P. P. ONG and J. B. HASTED
University College London, London, England
and
L. R. MEGILL
Institute for Telecommunication Sciences and Aeronomy
Environmental Science Services Administration, Boulder, Colorado, U.S.A.

(*Received* 29 *June* 1967)

Abstract—Rate constants for $O^+ + O_2 \rightarrow O_2^+ + O$, (1) and $O^+ + N_2 \rightarrow NO^+ + N$, (2) have been measured with the drift tube technique, using ground state O^+ ions. The energy variation for (1) is slight from 0·07 eV (2×10^{-11} cm^3 sec^{-1}) to 0·2 eV (3×10^{-11} cm^3 sec^{-1}) but it rises almost linear with energy to 9×10^{-10} cm^3 sec^{-1} at 20 eV. The rate for (2) rises almost linear with energy from 7×10^{-13} cm^3 sec^{-1} at 0·07 eV to 3×10^{-10} cm^3 sec^{-1} at 10 eV.

In discussing the theory of the *F*-region of the atmosphere it is necessary to know the rate coefficients for those reactions which convert atomic ions into molecular ions. Because of the constitution of the atmosphere the two most important reactions of this type are

$$O^+ + O_2 \rightarrow O_2^+ + O \tag{1}$$

and

$$O^+ + N_2 \rightarrow NO^+ + N \tag{2}$$

These two reactions have been measured near room temperature by a number of workers.(1–3) The *F*-region of the ionosphere, however, has temperatures varying from about 750°K near sunspot minimum to about 1200°K near sunspot maximum.(4,5) During magnetic storms the temperature of the *F*-region may rise even higher. Temperatures as high as 2500°K have been reported.(6)

Recently Kaneko, Megill and Hasted(7) have reported a technique for measuring the rates for reactions such as (1) and (2) in the energy region of interest. The system consists of an ion source, followed by a mass selector, which injects ions into a differentially pumped drift tube. The drift tube contains the reactant gas and (if needed) a buffer gas. The energy of the ions is controlled by adjusting the electric field in the drift tube. The ions are sampled at an exit aperture at the back of the drift tube, mass analysed and counted. From the ratio of the count rates and knowledge of the gas partial pressures and drift field it is possible to calculate both the rate for the conversion process and the mean energy of the ions. A more detailed account of the analysis is available in Ref. 7.

At the time the original experiment was performed, it was discovered that the input ion beam contained an unspecified number of excited ions. However, rates for reaction (1) were obtained and published.(7) Reliable values for reaction (2) were unavailable because of the competing and apparently fast charge exchange between excited O^+ and N_2.

The equipment described in Ref. 7 has been modified by substituting an ion source in which the energy of the ionizing electrons can be controlled and narrowed, so that a beam of ground state ions is assured.

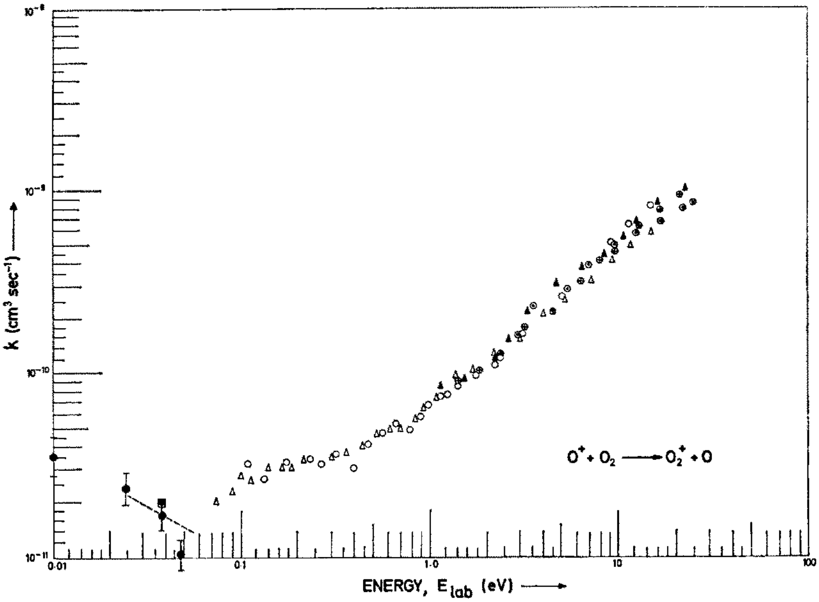

FIG. 1. IMPACT ENERGY DEPENDENCE OF RATE FOR $O^+ + O_2 \rightarrow O_2^+ + O$.
Points with error bars are afterglow measurements described in Part II of this paper. Broken line represents afterglow measurements of Ref. 12. Open square is Ref. 3, and full square Ref. 13.

Drift technique Gas total pressures and proportions of O_2 (torr)	 (%)	Ion source Electron energy (eV)	Symbol
0·90	0·92	26·0	○
0·70	0·91	26·5	⊙
0·70	0·91	27·5	⊕
0·90	0·92	33·5	△
0·66	0·92	31·0	▲

In addition a quadrupole mass spectrometer has been substituted for the ion sampling radio-frequency mass spectrometer, allowing higher mass resolution. A more detailed description of the modifications will be available in connection with the reporting of experimental results not primarily of aeronomic interest.

The temperature variation of rate for reaction (1) is shown in Fig. 1. This rate was reported in Ref. 7 but the measurements have been repeated with ground state ions; additional data from Part II of this paper are also displayed. The rate is virtually independent of energy over an appreciable range.

An experiment to measure the rate for reaction (2) has been performed using the equipment briefly described above. The energy variation of rate is shown in Fig. 2. Errors and comparison with previous measurements are discussed in Part II of this paper. As can be seen, the rate is roughly proportional to energy above 300°K. This means that even for the lowest *F*-region temperatures the appropriate rate is at least twice that measured for

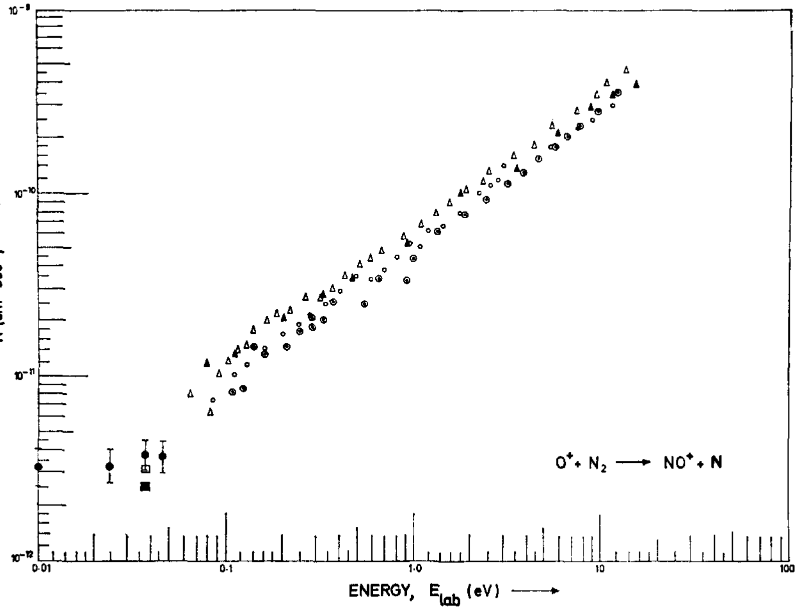

FIG. 2. IMPACT ENERGY DEPENDENCE OF RATE FOR $O^+ + N_2 \rightarrow NO^+ + N$.
Points with error bars are afterglow measurements described in Part II of this paper. Open square is Ref. 3 and full square Ref. 13.

Drift technique Gas total pressures and proportions of N_2 (torr)	(%)	Ion source electron energy (eV)	Symbol
0·85	1·01	25·2	○
0·79	2·19	25·5	⊙
0·79	2·19	35·0	△
0·85	1·01	25·0	▲

room temperatures. In addition, since there is a considerable diurnal variation in temperature, a similar diurnal variation in the appropriate rate will occur.

These results are of importance to *F*-region theory since they show that a considerable diurnal variation of recombination rate can be expected because of temperature changes in the atmosphere. This effect is additional to that due to excited oxygen ion production in the daytime(7) and to effects caused by increasing the vibrational temperature of the N_2(8,9)

These measurements will be of special importance in discussing recombination processes above the auroral zone where electric fields of some magnitude may be present.(10) In addition, if the theoretical model for red arcs presented by Megill and Carleton(11) is correct, recombination will be greatly enhanced, especially at the beginning of the event, because of the greatly increased ion energy.

REFERENCES

1. LANGSTROTH, G. F. O. and HASTED, J. B., *Discuss. Faraday Soc.* **33**, 298, (1962).
2. DICKINSON, P. H. G. and SAYERS, J., *Proc. Phys. Soc. Lond.* **76**, 137, (1960).
3. FERGUSON, E. E., FEHSENFELD, F. E., DUNKIN, D. B., SCHMELTEKOPF, A. L. and SCHIFF, H. I., *Planet. Space Sci.* **12**, 1169 (1964).
4. JACCHIA, L. G., *Rev. Mod. Phys.* **35**, 973 (1963).

5. Harris, I. and Priester, W., *J. atmos. Sci.* **19**, 286 (1962).
6. Muliarchik, T. M., translated title, *Spectral, Electrophotometrical, and Radar Researches of Aurorae and Airglow*, No. 1, Academy of Sciences Moscow, 41–42 (1959).
7. Kaneko, Y., Megill, L. R. and Hasted, J. B., *J. chem. Phys.* **45**, 3741 (1966).
8. Thomas, L. and Norton, R. B., *J. geophys. Res.* **71**, 227 (1966).
9. Schmeltekopf, A. L., Fehsenfeld, F. C., Gilman, G. I. and Ferguson, E. E., *Planet. Space Sci.* **15**, 401 (1967).
10. Swift, D. W., *J. geophys. Res.* **68**, 2131 (1963).
11. Megill, L. R. and Carleton, N. P., *J. geophys. Res.* **69**, 101 (1964).
12. Smith, D., Copsey, M. J. and Fouracre, R. A., *Private communication* (1966).
13. Copsey, M. J., Smith, D. and Sayers, P. J., *Planet. Space Sci.* **14**, 1047 (1966).

Резюме—Константы скорости для $O^+ + O_2 \rightarrow O_2^+ + O$, (1) и $O^+ + И_2 \rightarrow ИO^+ + И$, (2) были измерены техникой дрейфовой трубки с использованием ионов O^+ в основном состоянии. Вариация энергии для (1)—не бопьше от 0,07 эв.(2×10^{-11} см^3 сек$^{-1}$) до 0,2 эв. (3×10^{-11} см^3 сек$^{-1}$), но она возрастает почти линеарно с энергией до 9×10^{-10} см^3 сек$^{-1}$ на 20 эв. Скорость для (2) возрастает почти линеарно с энергией от 7×10^{-12} см^3 сек$^{-1}$ на 0,07 эв. до 3×10^{-10} см^3 сек$^{-1}$ на 10 эв.