J. Chem. Soc., Faraday Trans. 2, 1986, **82**, 2047–2052

Determination of the Absolute Rate Constant for the Reaction $O + NaO \rightarrow Na + O_2$ by Time-resolved Atomic Chemiluminescence at $\lambda = 589$ nm $[Na(3\,^2P_J) \rightarrow Na(3\,^2S_{1/2}) + h\nu]$

John M. C. Plane† and David Husain*

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP

We present the first laboratory measurement of the absolute second-order rate constant for the overall removal of $O(2\,^3P_J)$ by NaO:

$$O(2\,^3P_J) + NaO \xrightarrow{2a} Na(3\,^2S_{1/2}) + O_2 \quad (k_{2a}) \qquad (2)$$
$$O(2\,^3P_J) + NaO \xrightarrow{2b} Na(3\,^2P_J) + O_2 \quad (k_{2b})$$

$k_2 = k_{2a} + k_{2b}$. NaO was generated at known concentrations in the presence of an excess of He in a slow-flow system by titrating N_2O with Na derived from a heat-pipe oven *via* the reaction $Na + N_2O \rightarrow NaO + N_2$. Atomic chemiluminescence at $\lambda = 589$ nm $[Na(3\,^2P_J) \rightarrow Na(3\,^2S_{1/2}) + h\nu]$ subsequent to pulsed irradiation was then monitored in the time domain following reaction (2*b*). Analysis of the chemiluminescence profiles yielded $k_2(T = 573\ K) = (3.7 \pm 0.9) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The importance of this reaction in interpreting the mesopheric chemistry of sodium is considered in detail. An estimate of the branching ratio $\alpha = k_{2b}/(k_{2a} + k_{2b})$ from the present measurements of *ca.* 1% indicates a value considerably lower than that based on statistical considerations alone and used previously in computer models of the mesosphere.

The reactions

$$Na + O_3 \longrightarrow NaO + O_2 \qquad (1)$$

$$O + NaO \xrightarrow{2a} Na(3\,^2S_{1/2}) + O_2 \quad (k_{2a}) \qquad (2)$$
$$O + NaO \xrightarrow{2b} Na(3\,^2P_J) + O_2 \quad (k_{2b})$$

have long been recognised as critical in governing the distribution of atomic sodium in the 90 km region above the earth's surface (the mesosphere), the component of the air-glow emission due to the Na *D*-lines $[Na(3\,^2P_J) \rightarrow Na(3\,^2S_{1/2}) + h\nu, \lambda = 589$ nm] and *D*-line emission in meteoric trails. These two reactions were first proposed by Chapman[1,2] to account for such emission. They constitute a pair of processes in a larger scheme controlling the nature of the sodium layer, whose shape is now well characterised (peak at *ca.* 89 km, half-width at Na maximum *ca.* 8 km) by rocket-borne photometers[3] and

† Present address: Rosenstiel School of Marine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, Florida 33149, U.S.A.

LIDAR.[4-6] The peak Na abundances are established (4.1×10^3 and 5.7×10^3 cm^{-3}, day and night, respectively[7]), as are the free Na column densities.[8] The overall input source of sodium to the layer by meteor ablation has also been estimated in some detail.[9,10] This paper describes the first absolute rate measurement of reaction (2) by time-resolved atomic chemiluminescence at $\lambda = 589$ nm which, with our previously, recently reported absolute measurement of k_1 by the totally different method of time-resolved atomic resonance absorption at the same wavelength following pulsed irradiation,[11] enables computer models of the sodium layer,[12-20] hitherto largely constructed from estimated rate data, to be put on an experimental basis. The necessity for using experimentally measured rate constants to remove the ambiguities inherent in models of this mind is illustrated by examining the two very recent models described in ref. (13) and (14). Both models are able to account for the detailed features and the diurnal variations of the Na profiles that have been measured very accurately using LIDAR.[4-6] However, eight of the ten reactions which are common to the two models, coupling the species Na, NaO, NaO_2 and NaOH, are ascribed rate constants which are different by up to a factor of thirty. Indeed, the estimated value of k_2 in these models varies by a factor of four. There is thus a clear need for experimental determination of k_2. We have recently measured $k_1(500\ K) = (4^{+4}_{-2}) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1},[11] supporting the estimate of Kolb and Elgin[12] based on a simple electron-jump model and yielding values much larger than earlier estimates using H-atom analogues.[19] Our measurement is also in agreement with the recent measurement of Silver.[21] The value of k_2 is determined here by a new technique.

Experimental

The absolute rate constant, k_2, for reaction (2) overall was measured by monitoring the chemiluminescent production of $Na(3\,^2P_J)$ following reaction (2*b*) subsequent to the photochemical generation of $O(2\,^3P_J)$ arising from the flash photolysis of excess NaO. NaO itself was produced in known quantities at elevated temperatures by the titration process

$$Na + N_2O \rightarrow NaO + N_2 \qquad (3)$$

whose rate constant we have recently determined by time-resolved atomic resonance absorption spectroscopy [$k_3 = (1.9 \pm 0.3) \times 10^{-10} \exp(-1503/T)$ cm^3 $molecule^{-1}$ s^{-1}].[22] The apparatus employed is a development of the system which we have recently described in detail for the study of the reaction between $K + OH + He$[23] and subsequently modified for $Na + OH + He$,[24] but it does not require a spectroscopic source for optical excitation of a reactant or a product. Na was derived from the flow of He over sodium at elevated temperatures ($T = 603$ K) in a heat-pipe oven,[25] at which its vapour density is 7×10^{14} atoms cm^{-3},[26] and which can readily be calibrated empirically in the heat pipe by steady atomic resonance fluorescence at $\lambda = 589$ nm using phase-sensitive detection.[24] A flow of Na entrained in He (f_3) then enters a stainless-steel photochemical reactor at $T = 573$ K into which also enters two further flows, $N_2O + He$ (f_1) and He alone (f_2). The small quantity of N_2O from f_1 is immediately and completely converted (in milliseconds) by the excess of Na from f_3 into NaO *via* reaction (3). The residence time in the vessel is *ca.* 1-5 s. The initial compositions are calculated from the measured flows (f_1, f_2 and f_3) and the resulting Na concentrations calculated from the flows and small depletion due to reaction (3). These are much smaller than the vapour density of Na at the reactor temperature of $T = 573$ K.[26] The steady-state concentration of NaO in each experiment is subsequently calculated from the measured input and output mass flows of N_2O and NaO, respectively, and the diffusion of NaO out of the (effective) cylindrical reactor volume ($r = 2.25$ cm, $l = 2.9$ cm) using the 'long-time' solution of the diffusion equation

for a cylinder.[27] The diffusion coefficient of NaO in He is taken to be that of D(OH–He) = 1.15 $cm^2 s^{-1}$ (atmospheric pressure, $T = 573$ K) which we have reported[28] and which is a standard working approximation. The resulting value of [NaO] (steady-state) may readily be shown to be calculated to an accuracy of better than 20%. Thus, following the pulsed irradiation of NaO (steady-state) may readily be shown to be calculated to an accuracy of better than 20%. Thus, following the pulsed irradiation of NaO with an N_2 discharge, operating at atmospheric pressure attached to the reactor and described previously in detail,[23] a small quantity of $O(2\,^3P_J)$ is generated in the presence of a known excess of NaO (+Na, N_2 and He). Thus k_2 is determined by time-resolved atomic chemiluminescence at $\lambda = 589$ nm [$Na(3\,^2P_J) \rightarrow Na(3\,^2S_{1/2}) + h\nu$] with photon counting using this strong electric-dipole-allowed emission[29] following reaction (2b) as a spectroscopic marker for reaction (2) overall.

The present technique can be contrasted with a method involving monitoring the decay of $O(2\,^3P_J)$ directly by say, atomic resonance fluorescence at $\lambda = 130$ nm [$O(3\,^3S_1) \rightarrow O(2^3P_J) + h\nu$]. This would, of course, require the use of an atomic-oxygen optical excitation source operating at this wavelength. We have recently described measurements on time-resolved atomic resonance fluorescence in this type of system for ground-state iodine atoms at $\lambda = 178.3$ nm $\{I[5p^4 6s(^2P_{3/2})] - I[5p^5(^2P^0_{3/2})] + h\nu\}$.[30,31] Extension into the vacuum ultraviolet was achieved by attachment of the atomic iodine resonance source using N_2 for flushing the optical path external to the reactor and requiring no significant modification to the photomultiplier detection system, apart from employing the appropriate interference filter. Corresponding measurements on $O(2\,^3P_J)$ at $\lambda = 130$ nm would require, however, the design and construction of a new apparatus, especially with respect to the coupling of a vacuum u.v. photomultiplier detection system for photon counting, operating at room temperature, physically attached to a high-temperature stainless-steel reactor. This approach is clearly beyond the present experimental arrangement. Time-resolved chemiluminescence from $Na(3\,^2P_J)$ at $\lambda = 589$ nm using reaction (2b) provides a convenient means of avoiding such problems and permitting measurement of k_2. As would be expected, absolute densities of $Na(3\,^2P_J)$ generated in this system are difficult to estimate from the observed photon count rates. They are clearly low when calculated on the basis of a single pulsed measurement, and this accounts for the low estimate of the branching ratio in reaction (2) [$k_{2b}/(k_{2a} + k_{2b})$; see later].

Results and Discussion

Fig. 1 gives examples of the time-resolved chemiluminescence from $Na(3\,^2P_J)$ at $\lambda =$ 589 nm in digitised form (I_F, counts per channel, 256 channels) determined by photon counting and resulting from reaction (2b) following pulsed irradiation. The chemiluminescence marker indicates the decay of $O(2\,^3P_J)$ at different concentrations of NaO in the reactor. Placing [$Na(3\,^2P_J)$] in stationary state, we may readily show that the genuine chemiluminescence signal is given by

$$I_F(\lambda = 589\text{ nm})\,(t) = \frac{\Phi k_{2b}[\text{NaO}][O(2\,^3P_J)]_{t=0} \exp(-k't)}{1 + \sum k_Q[Q]/A_{nm}} \qquad \text{(i)}$$

where the symbols have their standard meaning.[23,24] k' is the pseudo-first-order decay coefficient for $O(2\,^3P_J)$ and is given by

$$k' = k_{diff} + k_2[\text{NaO}] \qquad \text{(ii)}$$

where $k_2 = k_{2a} + k_{2b}$; the fluorescence quenching term, $\sum k_Q[Q]/A_{nm}$, is negligible, and in any event does not effect the time dependence of the chemiluminescence. The signals are analysed to the form

$$I_F = \theta_1 + \theta_2 \exp(-k't) \qquad \text{(iii)}$$

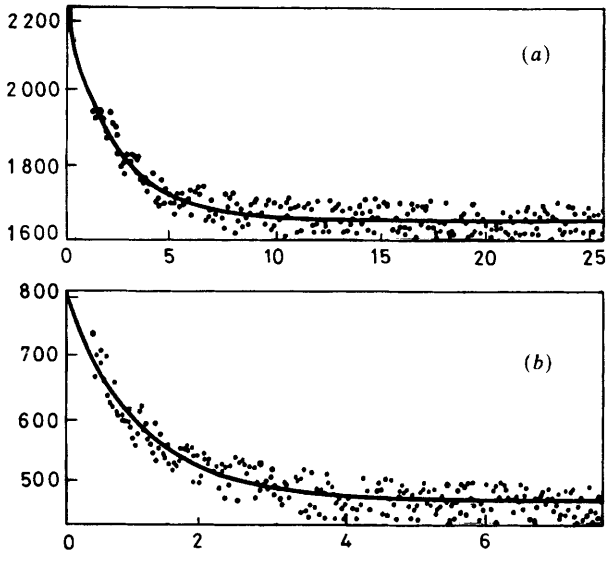

Fig. 1. Digitised time-variation of the light intensity (I_F, counts per channel) at $\lambda = 589$ nm indicating the decay of atomic chemiluminescence, $Na(3\,^2P_J) \rightarrow Na(3\,^2S_{1/2}) + h\nu$, resulting from the reaction between O and NaO following pulsed irradiation with monitoring of atomic sodium, derived from a heat-pipe oven by steady atomic resonance fluorescence coupled with phase-sensitive detection. {$T = 573$ K; $E = 45$ J; repetition rate 1 Hz; no. of individual experiments = 400; (——) $I_F = \theta_1 + \theta_2 \exp(-k't)$; $[He] = 9.6 \times 10^{17}$ atom cm^{-3}}.

	$[Na]/10^{13}$ atom cm^{-3}	$[N_2O]$ (initial)$/10^{13}$ molecule cm^{-3}
(*a*)	20	1.8
(*b*)	5.6	16

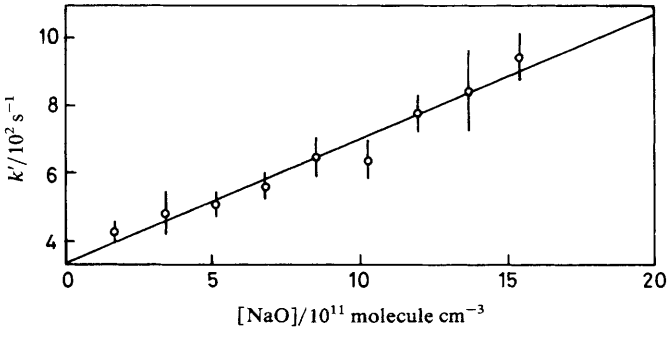

Fig. 2. Variation of the pseudo-first-order rate coefficient, k', for the decay of atomic oxygen, $O(2\,^3P_J)$, on reaction with NaO following pulsed irradiation and monitored by time-resolved atomic chemiluminescence at $\lambda = 589$ nm [$Na(3\,^2P_J) \rightarrow Na(3\,^2S_{1/2}) + h\nu$] ($T = 573$ K).

according to the LAMFIT procedure of Powell,[32] where θ_1 represents the effect of the steady background signal and the second term in eqn (iii) can be identified with eqn (i). Fig. 2 gives the variation of k' with [NaO], yielding $k_2(573\text{ K}) = (3.7 \pm 0.9) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, incorporating both the 2σ error in the slope and the confidence limits of the calculation of [NaO] (steady state) (see earlier). The small intercept in fig. 2 is consistent with the diffusion of $O(2\,^3P_J)$ out of the observation

region of the optics though $D[O(2\,^3P_J)—He]$ is difficult to quantify confidently as the boundary conditions for light collections[27] are more difficult to define than those for the volume of the reactor used in the calculation of [NaO] (steady state).

The earlier measured value of k_1,[11] and that of k_2 determined here, thus support those used in the recent model of Thomas *et al.*[13] The branching ratio, $\alpha = k_{2b}/(k_{2a} + k_{2b})$, not required for quantification of k_2 itself, is difficult to determine accurately from these measurements using the combination of the count rate at $\lambda = 589$ nm, the fraction of NaO photolysed, the fraction of the emitted light collected, the transmission of the interference filter and the quantum efficiency of the photomultiplier tube. Our estimate indicates $\alpha = 0.01$ as an upper limit, significantly lower than a value of one-third suggested by Bates and Ojha[33] on statistical considerations alone. Detailed experimental characterisation of the branching ratio α requires knowledge of a range of parameters clearly beyond the scope of the present measurements, including the light output from the pulsed initiation source together with the transmission of the CaF_2 optics employed, the absorption cross-section of NaO as a function of wavelength and calibration of the detection system using standard light-calibration techniques. The present measurement has yielded the absolute value of k_2, and this may now be incorporated into computer models for sodium profiles in the mesophere.

We thank St John's College, Cambridge, for a Research Fellowship held by J.M.C.P., during the tenure of which this work was carried out and Dr G. A. Jones of R.A.R.D.E. (Westcott, Bucks.) for helpful discussions.

References

1 S. Chapman, *Astrophys. J.*, 1939, **90**, 309.
2 S. Chapman, in *The Aurora and Airglow*, ed. E. B. Armstrong and A. Dalgarno (Pergamon, Oxford, 1955), p. 204.
3 R. G. H. Greer and C. Best, *Planet. Space Sci.*, 1967, **15**, 1857.
4 G. Megie and J. E. Blamont, *Planet. Space Sci.*, 1977, **25**, 1093.
5 M. R. Bowman, A. J. Gibson and M. C. W. Sandford, *Nature (London)*, 1969 **221**, 456.
6 L. Thomas, A. J. Gibson and S. K. Battacharrya, *J. Atmos. Terr. Phys.*, 1977, **39**, 1405.
7 B. R. Clemesha, D. M. Simonich, P. P. Bastista and V. W. J. H. Kirchhoff, *J. Geophys. Res.*, 1982, **87**, 181.
8 C. R. Burnett, W. E. Lammer, W. T. Novak and V. L. Slides, *J. Geophys. Res.*, 1972 **77**, 2934.
9 D. M. Hunten, R. P. Turno and O. B. Toon, *J. Atmos. Sci.*, 1980, **37**, 1342.
10 M. Gadsden, *Proc. Royal Meteorological Soc. Specialist Group* (Hertford College, Oxford, 6th April 1983).
11 D. Husain, P. Marshall and J. M. C. Plane, *J. Chem. Soc., Chem. Commun.*, 1985, 1216.
12 C. E. Kolb and J. B. Elgin, *Nature (London)*, 1976 **263**, 488.
13 L. Thomas, M. C. Isherwood and M. R. Bowman, *J. Terr. Atmos. Phys.*, 1983 **45**, 594.
14 V. W. J. H. Kirchhoff, *Geophys. Res. Lett.*, 1983 **10**, 721.
15 S. C. Liu and G. C. Reed, *Geophys. Res. Lett.*, 1979 **6**, 283.
16 N. D. Sze, M. W. W. Ko, W. Swider and E. Murad, *Geophys. Res. Lett.*, 1982 **9**, 1187.
17 W. J. Baggaley, *Nature (London)*, 1975, **257**, 567.
18 R. J. Thomas, *Planet. Space Sci.*, 1974, **22**, 175.
19 J. E. Blamont and T. M. Donahue, *J. Geophys. Res.*, 1964, **69**, 4093.
20 D. M. Hunetn, *Space Sci. Rev.*, 1967, **6**, 493.
21 J. A. Silver, M. S. Zhaniser and A. C. Stanton, *Proc. Int. Sympos. Chemical Kinetics* (Natl Bur. Stand. Gaithersburg, Maryland, U.S.A., June 1985).
22 D. Husain and P. Marshall, *Combust. Flame*, 1985, **60**, 81.
23 D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1465.
24 D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1619.
25 C. R. Vidal and J. Cooper, *J. Appl. Phys.*, 1969, **40**, 3370.
26 *JANAF Thermochemical Tables, Project Directors* D. R. Stull and H. Prophet, Natl Bur. Stand., U.S., NSRDS-NBS-37, (U.S. Government Printing Office, Washington, D.C., 2nd edn, 1971).
27 A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1934).
28 D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 713.

29 C. H. Corliss and W. R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, Natl Bur. Stand. Monogr. 53 (U.S. Government Printing Office, Washington, D.C., 1962).
30 D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1675
31 J. M. C. Plane and D. Husain, *J. Phys. Chem.*, 1986, **90**, 501.
32 M. J. D. Powell, personal communication cited in D. Husain and N. K. H. Slater, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 606.
33 D. R. Baates and P. C. Ohja, *Nature* (*London*), 1980, **286**, 790.

Paper 6/568; *Received* 21*st March*, 1986