Determination of the Absolute Second-order Rate Constant for the Reaction $Na + O_3 \rightarrow NaO + O_2$

David Husain,* Paul Marshall, and John M. C. Plane

The Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.

The absolute second-order rate constant for the reaction $Na + O_3 \rightarrow NaO + O_2$ (k_1) has been determined by time-resolved atomic resonance absorption spectroscopy at λ = 589 nm [$Na(3^2P_J) \leftarrow Na(3^2S_{1/2})$] following pulsed irradiation, coupled with monitoring of O_3 by light absorption in the ultra-violet; this yields $k_1(500\ K) = 4\ (+4,-2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, resolving large differences for various estimates of this important quantity used in modelling the sodium layer in the mesosphere.

The fundamental reaction (1) is considered to be the main process for the removal of atomic sodium in the layer *ca.* 90 km above the earth's surface, and its magnitude is critical for modelling this layer in terms of such species as Na, NaO, NaO_2, O_3, and O.[1] It is perhaps not surprising that k_1 has not been measured experimentally hitherto on account of difficulties in monitoring, quantitatively and simultaneously, atomic sodium and ozone at what are necessarily elevated temperatures. Estimates of k_1 for such models, usually derived from the modification of rate data for reactions of H and N with O_3,[2,3] have varied by *ca.* three orders of magnitude. Thus,

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

values of k_1 of 1.5×10^{-13},[4] 6.5×10^{-12},[5] and 1×10^{-13} cm^3 molecule^{-1} s^{-1} [6,7] based on these analogues have been employed for temperatures in the region of *ca.* 200 K. A more recent estimate of k_1 reported by Kolb and Elgin[8] using an electron jump model for collision has yielded $k_1(200\ K) = ca.\ 3.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and this has been applied to later calculations of mesospheric profiles.[1] An experimental measurement of k_1 is clearly required to resolve this large variation in these estimates.

We have described in detail two experimental systems[9,10] for the kinetic study of $Na(3^2S_{1/2})$, generated by pulsed irradiation of sodium halide vapour at elevated temperatures, and monitored by time-resolved atomic resonance absorption of the unresolved doublet at λ = 589 nm [$Na(3^2P_J) \leftarrow Na(3^2S_{1/2})$] in the presence of stable molecules. The more sophisticated of these two systems,[10] incorporating direct computer interfacing, has been significantly modified to permit spectroscopic monitoring of low concentrations of O_3 during kinetic measurements on atomic sodium. The result is shown in Figure 1. $Na(3^2S_{1/2})$ is thus monitored on a time scale

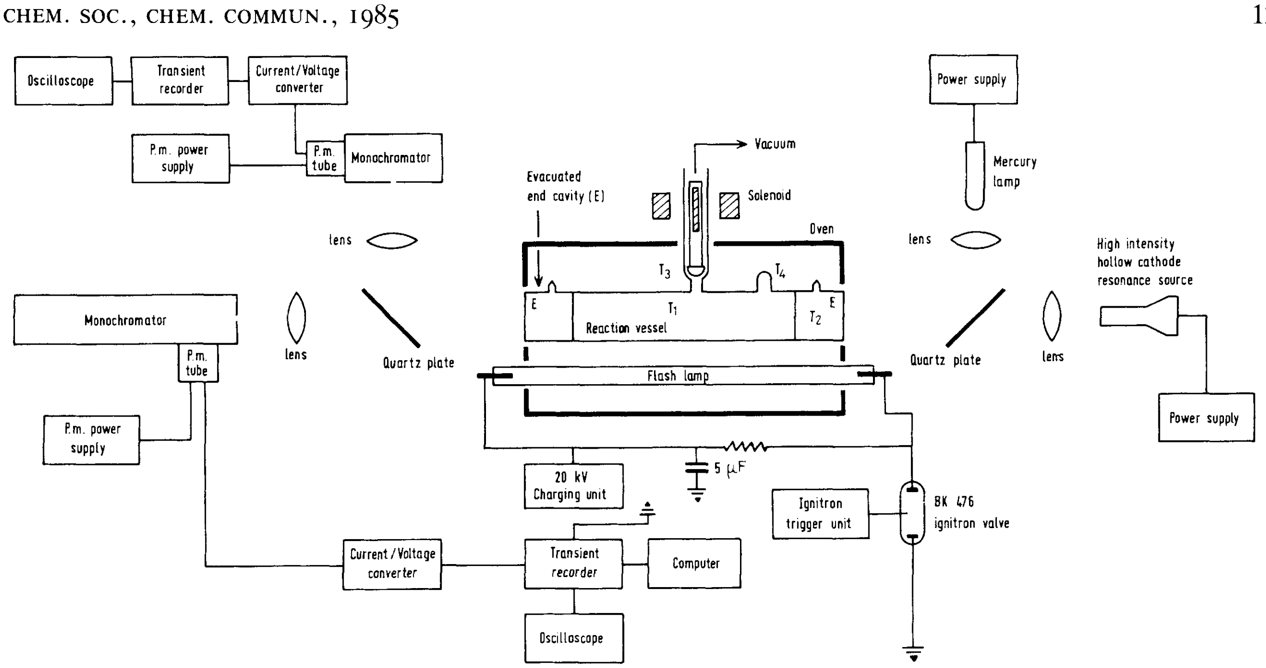

Figure 1. Block diagram of the apparatus for the kinetic study of the reaction between Na + O_3 at elevated temperatures by time-resolved atomic resonance absorption spectroscopic monitoring of $Na(3^2S_{1/2})$ in the single-shot mode at λ = 589 nm $[Na(3^2P_J) \leftarrow Na(3^2S_{1/2})]$ following pulsed irradiation coupled with simultaneous monitoring of O_3 by light absorption in the ultra-violet.

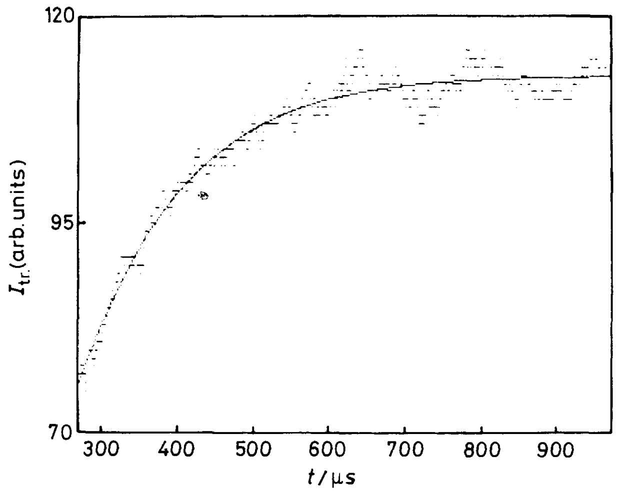

Figure 2. Digitised time-variation of the transmitted light intensity ($I_{tr.}$) at λ = 589 nm $[Na(3^2P_J)–Na(3^2S_{1/2})]$ indicating the decay of resonance absorption by ground-state sodium atoms in the presence of O_3 following pulsed irradiation. {E = 810 J; T = 500 K; p(total with He) = 80 Torr; $[O_3]$ = 1.9 × 10^{13} molecules cm^{-3}; :: digitised data points; smoothed curve, computerised fitting to the form $I_{tr.} = I_0\exp[-A\exp(-k't)]$}.

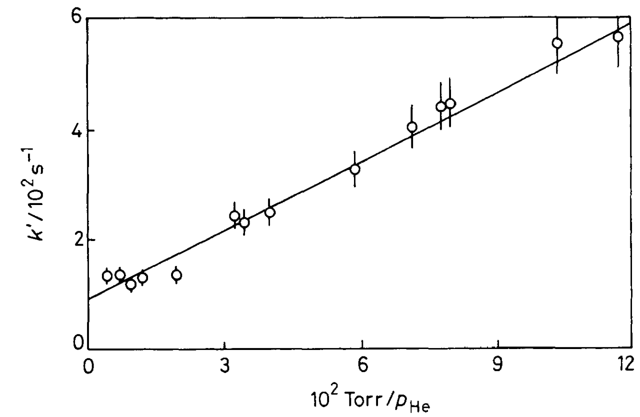

Figure 3. Variation of the pseudo-first-order rate coefficient (k') for the decay of $Na(3^2S_{1/2})$ following pulsed irradiation with $p(He)^{-1}$ to obtain diffusional rate data at T = 500 K.

of milliseconds and microseconds; O_3, which slowly decays on a time scale of *ca.* 1—5 seconds, is monitored on entry to the reactor by light absorption at λ = 253.7 nm derived from a mercury lamp [σ (λ = 253.7 nm) for O_3 = 1.1 × 10^{-17} cm^2][11] and recorded electronically (Figure 1) at the time of pulsed irradiation. Thus, $[O_3]$ at this time is less than that on entry to the reactor, involving degrees of light absorption in the range *ca.* 0.5—1%, but is effectively constant throughout the short decay of $Na(3^2S_{1/2})$.

Figure 2 shows a typical decay trace for $[Na(3^2S_{1/2})]$ in the presence of O_3 and excess of He following pulsed irradiation of NaI vapour at 500 K. This can be fitted by computer to the form of equation (2), where the symbols have their usual meaning,[10] and where k', the first-order decay coefficient for Na, is the object of experimental interest, and is given by equation (3). The system is sensibly free from kinetic

$$I_{t.} = I_0\cdot\exp[-A\cdot\exp(-k't)] \quad (2)$$

$$k' = k_{diff.} + k_1\cdot[O_3] \quad (3)$$

complexity as shown from the very slow diffusional loss of Na in He alone (Figure 3) which may be analysed as hitherto[9,10] yielding the value of D(Na–He) (1 atm, 500 K) = 0.94 ± 0.06 cm^2 s^{-1} in agreement with the data reported by Silver.[12] Extrapolation assuming a dependence of D on $T^{3/2}$ gives D(Na–He) (s.t.p.) = 0.38 ± 0.03 cm^2 s^{-1}. The quality of Figure 2 should be regarded with caution as the scattered light component has been subtracted from the overall decay profile and the resonance absorption signal represents a small difference between large quantities. Values of k' for $[O_3]$ = 0, 1.9 × 10^{13}, and 3.8 × 10^{13} molecule cm^{-3} were found to be 140 ± 20, (8.2 ± 1.0) × 10^3, and (1.3 ± 0.3) × 10^4 s^{-1}, respectively. The effect of the recombination of Na + O_2 + He, where O_2 results from the decomposition of O_3, is negligible in this system.[9,10] Using equation (3), this yields k_1 (500 K) = 4 (+4,−2) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, close to the hard-sphere collision frequency and clearly involving no significant activation energy and supporting the higher estimate of Kolb and Elgin.[8] The large error quoted for k_1 arises principally from the division of $(k' - k_{diff.})$ by $[O_3]$ calculated from a low degree of light absorption. The present result for k_1 demonstrates the dangers inherent in employing rate data for Na based on analogous reactions of H atoms.

We thank the Ministry of Defence for a research grant, to whom we are also indebted, together with the S.E.R.C., for a Studentship held by P.M. 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. Finally, we express our gratitude to Dr D. E. Jensen and Dr G. A. Jones of R.A.R.D.E., Westcott, Bucks. for their continued encouragement of this work.

Received, 22nd May 1985; Com. 704

References

1 L. Thomas, M. C. Isherwood, and M. R. Bowman, *J. Atmos. Terr. Phys.*, 1983, **45**, 587.
2 F. Kaufman, *Ann. Geophys.,* 1964, **20**, 106.
3 K. Schofield, *Planet. Space Sci.,* 1967, **15**, 643.
4 J. E. Blamont and T. M. Donahue, *J. Geophys. Res.*, 1964, **69**, 4093.
5 D. M. Hunten, *Space Sci. Rev.,* 1967, **6**, 493.
6 T. L. Brown, *Chem. Rev.,* 1973, **73**, 645.
7 W. J. Baggaley, *Nature (London)*, 1975, **257**, 567.
8 C. E. Kolb and J. B. Elgin, *Nature (London)*, 1976, **263**, 488.
9 D. Husain and J. M. C. Plane, *J. Chem. Soc., Faraday Trans. 2,* 1982, **78**, 163.
10 D. Husain, P. Marshall, and J. M. C. Plane, *J. Chem. Soc., Faraday Trans. 2,* 1985, **81**, 301.
11 'The Stratosphere: Present and Future,' NASA Reference Publication, eds R. D. Hudson and E. I. Reed (NASA Goddard Space Flight Center, U.S.A., 1980).
12 J. A. Silver, *J. Chem. Phys.*, 1984, **81**, 5125.