

# Temperature Dependence of the Absolute Third-order Rate Constant for the Reaction between $\text{Na} + \text{O}_2 + \text{N}_2$ over the Range 571–1016 K Studied by Time-resolved Atomic Resonance Absorption Spectroscopy

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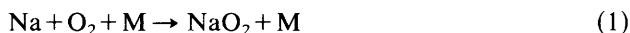
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We present a detailed investigation of the absolute third-order reaction rate constant ( $k_1$ ) for the process



measured over the temperature range  $T = 571\text{--}1016\text{ K}$ .  $\text{Na}(3^2\text{S}_{1/2})$  was generated by the pulsed irradiation of NaI vapour and monitored in the presence of  $\text{O}_2$  and  $\text{N}_2$  in the 'single-shot' time-resolved mode by atomic resonance absorption spectroscopy of the unresolved  $D$ -line doublet at  $\lambda = 589\text{ nm}$  [ $\text{Na}(3^2\text{P}_{1/2,3/2}) \leftarrow \text{Na}(3^2\text{S}_{1/2})$ ]. A new experimental system has been specially designed for this temperature-dependent investigation. The diffusion coefficient,  $D(\text{Na}\text{--}\text{N}_2)$ , has been measured in this temperature range, demonstrating a dependence on  $T^{1.52 \pm 0.24}$  and yielding a value of  $D(\text{Na}\text{--}\text{N}_2)$  at s.t.p. of  $0.15 \pm 0.05\text{ cm}^2\text{ s}^{-1}$ . A limited body of data from similar measurements in neon yields  $D(\text{Na}\text{--}\text{Ne})$  at s.t.p. =  $0.19 \pm 0.04\text{ cm}^2\text{ s}^{-1}$ . The data for  $k_1(\text{Na} + \text{O}_2 + \text{N}_2)$  within the temperature range 571–1016 K are described by the form  $k_1 = (1.11 \pm 0.08) \times 10^{-23} T^{-2.47 \pm 0.14}\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$ . However, for extrapolation to temperatures outside the measured regime the formalism of the unimolecular rate theory of Tröe, with a dependence of  $\langle \Delta E \rangle$  on  $T^{-0.7}$ , has been quantitatively employed to yield  $k_1(200\text{ K})$  and  $k_1(2000\text{ K}) = 8.8 \times 10^{-30}$  and  $6.8 \times 10^{-32}\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$ , respectively. The extrapolated rate data are of particular relevance to the role of reaction (1) in the mesosphere and in flames. A limited body of rate data is reported for the effect of neon in the analogue of reaction (1) yielding  $k_1(\text{Na} + \text{O}_2 + \text{Ne}) = (3.5 \pm 0.2) \times 10^{-31}$  and  $(2.7 \pm 0.1) \times 10^{-31}\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$  at  $T = 726$  and  $844\text{ K}$ , respectively.

Renewed interest has developed in the rate of the reaction



following the recent time-resolved resonance absorption measurements we have reported on atomic sodium,<sup>1</sup> leading to values of the absolute third-order rate constant,  $k_1$ , which were found to be approximately a thousand times greater than had previously been concluded from measurements on oxygen-rich flames.<sup>2–4</sup> Apart from fundamental considerations for association reactions, this interest has chiefly concerned two areas where sodium superoxide formation is now considered to play a prominent role, namely in modelling the chemistry of sodium in the upper atmosphere at *ca.* 90 km,<sup>5,6</sup> where  $\text{M} = \text{N}_2$  is of prime concern, and interpreting the chemistry of sodium in oxygen-rich flames.<sup>7,8</sup> In the case of sodium in the upper atmosphere, where it has been observed that there is thin layer of free metal atoms at a height of *ca.* 90 km above the earth's surface,<sup>9</sup> two recent models<sup>5,6</sup> indicate

that  $\text{NaO}_2$  is probably the major sink of free Na in the lower part of the mesosphere above 60 km and below 85 km. The ambient temperature of this region is *ca.* 200 K, far outside the range of temperature over which reaction (1) has been studied directly (724–844 K).<sup>1</sup> An accurate temperature extrapolation to these atmospheric conditions from values of  $k_1$  accessible through experiment is therefore highly desirable.

The detailed chemistry of sodium in oxygen-rich flames, including the mechanism involving a large set of reactions undergone by the minor constituents Na, NaO,  $\text{NaO}_2$ , NaOH, H, OH and O, together with both the values of rate constants of reactions critical in the mechanism and also bond energies of species containing alkali-metal atoms, is a matter of current controversy.<sup>7,8</sup> The paper of Hynes *et al.*<sup>8</sup> includes a concise review of this area. The results of recent investigations on the modelling of oxygen-rich flames seeded with sodium<sup>7,8</sup> indicate that NaOH is the major form in which Na is bound up in flames; however, there is current disagreement over whether this is the result of direct reaction between Na and OH radicals<sup>7</sup> or of rapid formation of  $\text{NaO}_2$  followed by further reaction with H and OH radicals to yield NaOH.<sup>8</sup> An accurate temperature extrapolation of  $k_1$ , in this case to flame temperatures between 1500 and 2400 K, would assist in resolving this controversy.

In this paper we describe the construction of a new experimental arrangement for investigating time-resolved resonance absorption measurements on  $\text{Na}(3^2S_{1/2})$ , generated by pulsed irradiation of NaI vapour at elevated temperatures. The resulting system may be contrasted with that employed in our earlier investigation of reaction (1) in which no significant temperature dependence of the rate was detected for the limited range  $T = 724\text{--}844\text{ K}$ .<sup>1</sup> This system includes a new high-temperature reactor and furnace for pulsed-irradiation studies, operating over a range of nearly 500 K, in this case 571–1016 K. Further developments include the construction of a very-high-intensity hollow-cathode atomic resonance source for monitoring  $\text{Na}(3^2S_{1/2})$  by resonance absorption, with a major improvement in the signal-to-noise ratio, as well as a new optical system and computer interfacing to the output of the photoelectric detection system. The resulting measurements have provided us with an important and relatively rare body of data, namely a set of recombination rate constants over a significant temperature range where these have been measured directly. This may be contrasted with the usual situation,<sup>10</sup> where low-temperature recombination-rate data are combined with high-temperature dissociation measurements (usually from shock tubes) through detailed balancing. Recombination rate constants are generally characterised by very small temperature dependences, therefore highly accurate dissociation rate constants, governed by relatively large activation energies, are necessary in order to combine both sets of data. However, whilst the temperature dependences of the recombination rate constants are small, these dependences reflect the combined roles of various fundamental aspects of the recombination process which become apparent in the extrapolation procedure itself (see later). The data from the present work have been used to extrapolate  $k_1$  to 200 and 2000 K by making use of the Tr  e formalism,<sup>10,11</sup> which can be tested more rigorously here than was possible in our previous measurements of the rate constants for the third-order reactions of K and Na with OH ( $M = \text{He}$ ).<sup>12,13</sup> We demonstrate that this procedure provides a satisfactory model for the recombination reaction between  $\text{Na} + \text{O}_2 + \text{N}_2$  over a wide temperature range.

## EXPERIMENTAL

The principle of the experimental arrangement for monitoring  $\text{Na}(3^2S_{1/2})$  in the ‘single-shot mode’ by time-resolved atomic resonance absorption of the unresolved doublet at

$\lambda = 589 \text{ nm}$  [ $\text{Na}(3^2P_{1/2,3/2}) \leftarrow \text{Na}(3^2S_{1/2})$ ],  $\lambda = 589.6$  and  $589.0 \text{ nm}$ ,  $gA = 0.9 \times 10^8$  and  $1.8 \times 10^8 \text{ s}^{-1}$ , respectively<sup>14</sup>] following the pulsed irradiation of NaI vapour above solid NaI at elevated temperatures<sup>15</sup> is essentially that given in our previous paper.<sup>1</sup> However, apart from the design of the quartz reaction vessel and flash lamp, there are many significant differences between the present system and that employed in the earlier kinetic investigations of both sodium and potassium atoms.<sup>1,16</sup>

Given the objective of rate measurements on transient sodium atoms across a wide temperature range, particular care was expended in the construction of the assembly comprising the reaction vessel and flash lamp within the oven designed for these measurements. The reaction vessel and flash lamp were supported parallel to each other within a cylindrical cavity drilled through twelve firebricks held within a metal case. Heating was provided by four heating elements of 750 W each, placed symmetrically within the firebrick construction. The large heat capacity of this system and the insulation provided by the firebricks, analogous to a domestic storage heater and in marked contrast to the use of externally wound heating tape employed previously,<sup>1</sup> ensures constancy of temperature adjusted by means of a Eurotherm 020 controller over a series of kinetic measurements at a given temperature ( $\pm 2^\circ \text{C}$ ) and only a relatively small temperature gradient along the length of the reactor itself ( $\pm 10^\circ \text{C}$ ). Temperature monitoring was carried out using thermocouples similarly placed about the reactor as described previously.<sup>1</sup> Temperatures  $> 1000 \text{ K}$  can be reached with this system and kinetic measurements at  $1016 \text{ K}$  are presented here; however, at such temperatures, reaction of NaI with the silica resulted in damage to the windows of the reactor with subsequent reduction in the optical transmission.

In contrast to the sealed microwave-powered discharge source of resonance radiation at  $\lambda = 589 \text{ nm}$  described in the earlier study,<sup>1</sup> the present system employed a high-intensity hollow-cathode source, based on the general principles of the design given by Bell *et al.*<sup>17</sup> but differing substantially in physical construction. The cathode was constructed from copper tubing, coiled into a cup and supported on a tungsten rod. The anode comprised a wide tube of copper foil surrounding the cathode and also mounted on a tungsten rod. The electrodes were sealed by fusion into the Pyrex body of the lamp, which also supported a flat Pyrex end window, for optical transmission, attached to the lamp by epoxy resin. This window could be removed for cleaning the electrodes and for addition of fresh sodium to the cathode, from which the metal slowly distilled to cooler parts of the lamp. A connection was made to the gas-handling line in order to admit a typical pressure of 15 Torr of krypton gas (1 Torr  $\approx 133 \text{ N m}^{-2}$ ). The lamp included a side arm for cooling in liquid nitrogen ( $-196^\circ \text{C}$ ) in order to reduce the pressure of krypton whilst striking the initial discharge. A stabilised power supply yielded an operating current of *ca.* 180 mA with a potential drop of *ca.* 270 V across the lamp. This may be compared with a commercial hollow-cathode source normally used for routine atomic absorption spectroscopic analysis and operating typically at say 8 mA. (We are deeply indebted to Mr C. J. Smith of the Glass-blowing Department of this Laboratory for the design and construction of this lamp.) The intense *D*-line doublet, deliberately unresolved in this system for the convenience of adherence to the Beer-Lambert law (see later), was optically isolated using a large grating monochromator (Hilger and Watts, Monospek 1000, focal length 1 m, 1200 lines per mm) at a large slit width (*ca.* 2.5 mm). As hitherto,<sup>1</sup> resonance absorption of the *D*-lines was monitored using an E.M.I. 9783B photomultiplier tube (700 V, Wallis power supply R53/6). A blocking filter (Wratten filter no. 21), mounted on the slit of this monochromator, limited any incident radiation of  $\lambda > \text{ca. } 530 \text{ nm}$ , hence reducing the effect of scattered light from the photoflash lamp operated up to an energy of *ca.* 300 J. The radiation from such a source has been approximated to that of a black body of temperature  $6500^\circ \text{C}$ .<sup>1,18</sup> The optical characteristics of the p.m. tube, the blocking filter and the flash lamp have been presented graphically in our earlier paper.<sup>1</sup> The signal-to-noise ratio of the unattenuated  $I_0$  signal with this overall arrangement is much greater than that observed previously,<sup>1</sup> typically 100:1 in these measurements. There is also a marked improvement in the elimination of the scattered light pulse using the larger monochromator compared with the smaller Grub Parsons M2 instrument used earlier,<sup>1</sup> resulting in rate measurements being made on a shorter timescale and permitting characterisation of faster atomic decay profiles.

The major development with the present system concerns data capture and analysis. The photoelectric signals representing time-resolved atomic resonance absorption at  $\lambda = 589$  nm following pulsed irradiation were amplified in the standard manner by means of a current-to-voltage converter employing a fast-settling operational amplifier.<sup>19</sup> The signals were captured in a transient recorder (Data Laboratories DL 902) storing 2048 data points, digitised to an accuracy of 1 part in 256, with a maximum sampling rate of 1 MHz, and employed in the A/B mode in order to measure the attenuated ( $I_{tr}$ ) and unattenuated ( $I_0$ ) signals on separate timescales. The transient recorder was interfaced (8PI0 parallel interface) to a microcomputer (Comart CP 200) to which the signals were transferred. The data were subsequently analysed by iterative fitting using a least-squares program to the form:

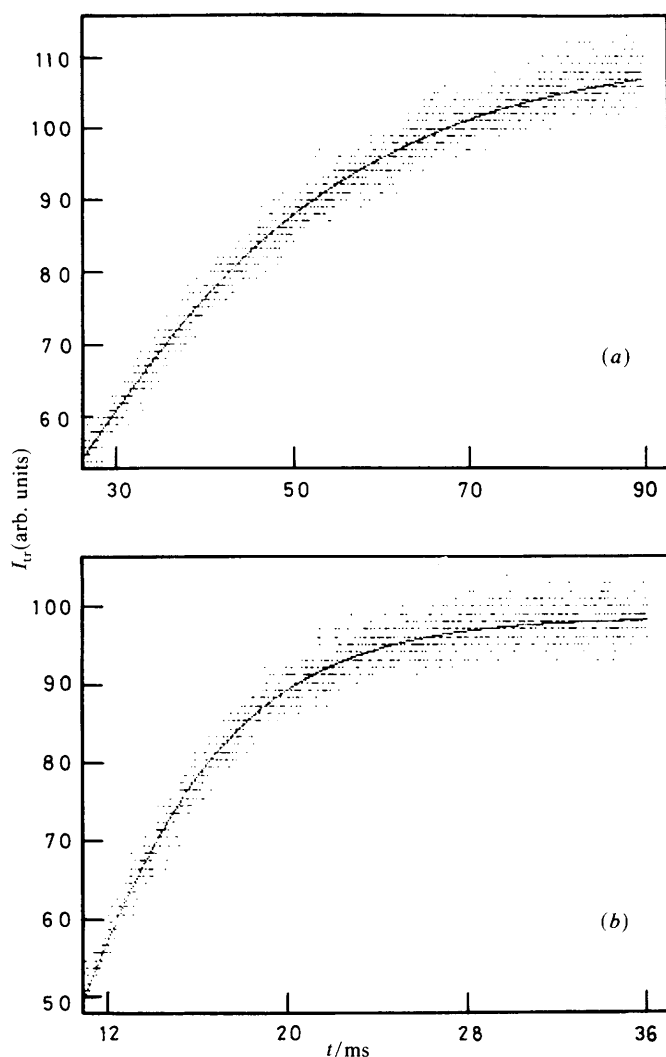
$$I_{tr} = I_0 \exp [-A \exp (-k't)] \quad (i)$$

where  $k$  is the pseudo-first-order rate coefficient for the decay of  $\text{Na}(3^2S_{1/2})$  and the prime object of the kinetic measurements.  $I_0$  is determined from the B sweep of the transient recorder in a time regime where  $\text{Na}(3^2S_{1/2})$  has been totally removed.  $A$  and  $k'$  are the parameters adjusted to minimise the mean-square deviation of the computed form of  $I_{tr}$  from the observed data points. Eqn (i) is, of course, simply the combination of the standard Beer-Lambert law with the first-order decay for  $[\text{Na}(3^2S_{1/2})]_r$ . We have previously determined<sup>1</sup> the 'curve-of-growth'<sup>20</sup> for the unresolved  $D$ -lines by atomic resonance absorption measurements coupled with phase-sensitive detection<sup>21</sup> on sodium vapour in equilibrium with solid sodium at elevated temperatures, and have demonstrated that the Beer-Lambert law may be employed for degrees of absorption of  $<40\%$ . Kinetic analyses on  $\text{Na}(3^2S_{1/2})$  are restricted to this regime. Computerised fitting of the data to the form of eqn (i) enjoys the advantage that the data points in the region where  $I_{tr}$  is close to  $I_0$  may be employed in the analysis. This may be contrasted with the standard first-order kinetic plots used previously for this type of investigation,<sup>1</sup> namely  $\ln [I_0/I_{tr}]$  against  $t$ , which is of slope  $-k'$  following eqn (i). Such points lie in the region of greatest scatter and so contribute little to the determination of  $A$  and  $k'$ . In addition, the fitting routine is 'robust' with respect to random fluctuations in the decay trace, and thus numerical smoothing as used in the earlier investigation<sup>1,22</sup> is not needed prior to the analysis here. All decay traces, including those presented here, were analysed without smoothing. Straight-line graphs of kinetic results were constructed using a routine which weighted points inversely to their variance and which provided statistical errors in both the slope and intercept.<sup>23</sup> Quoted errors represent one standard deviation. All materials were prepared essentially as described previously.<sup>1</sup>

## RESULTS AND DISCUSSION

### DIFFUSION OF $\text{Na}(3^2S_{1/2})$ IN $\text{N}_2$ AS A FUNCTION OF TEMPERATURE

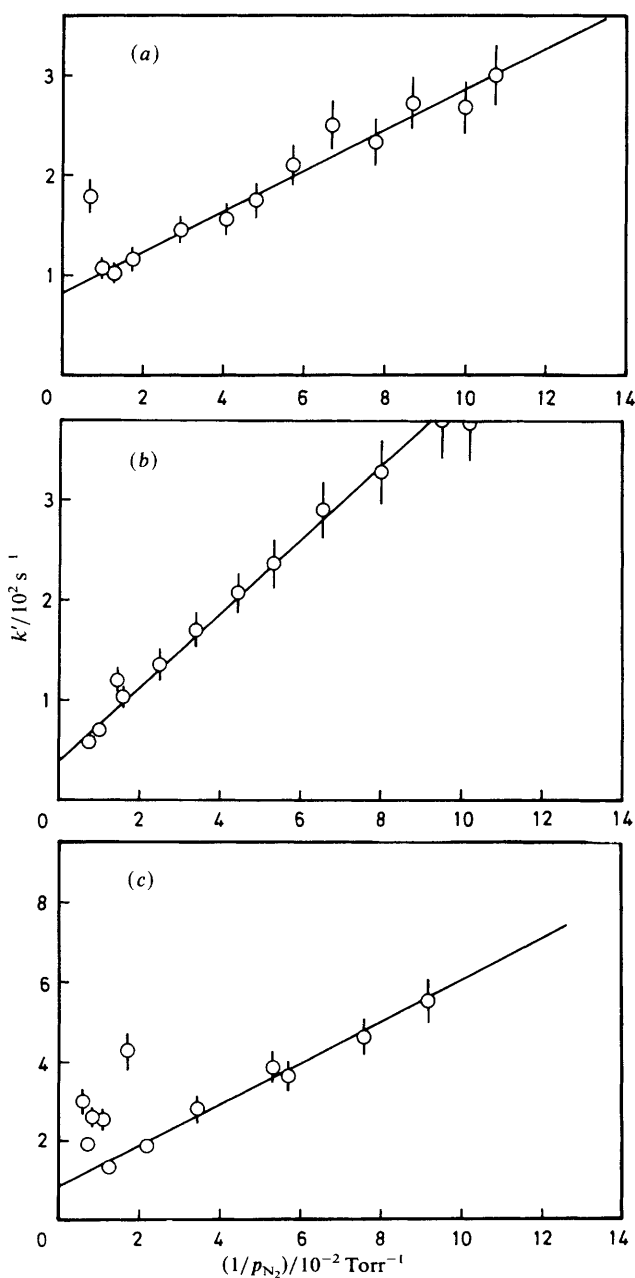
We have shown in our earlier investigations that the quantitative characterisation of diffusional removal rates of  $\text{Na}(3^2S_{1/2})$  in this type of system may be used as an internal kinetic standard.<sup>1</sup> In the present measurements the diffusional decay rate of  $\text{Na}(3^2S_{1/2})$  in  $\text{N}_2$  is studied in detail as a function of temperature. The quality of the raw data obtained can be seen in fig. 1, which shows the digitised time-variation of the transmitted light intensity, indicating the relatively slow decay of resonance absorption by ground-state sodium atoms following the ultraviolet pulsed irradiation of  $\text{NaI}$ <sup>24</sup> in the presence of  $\text{N}_2$  alone at  $T = 722$  K. This is in the middle of the temperature range employed here. The increasing rate with decreasing pressure of  $\text{N}_2$  can be seen by comparison of fig. 1(a) and (b). The quality of the computerised fit using eqn (i), yielding the first-order decay coefficient,  $k'$ , is also shown in fig. 1. Similar traces were obtained for the other temperatures employed, where the decay rate of  $\text{Na}(3^2S_{1/2})$  was monitored across a wide pressure range in each case. Fig. 2 shows the variation of  $k'$  with the reciprocal of the pressure of nitrogen, including the extremes of temperature used here, clearly demonstrating diffusional



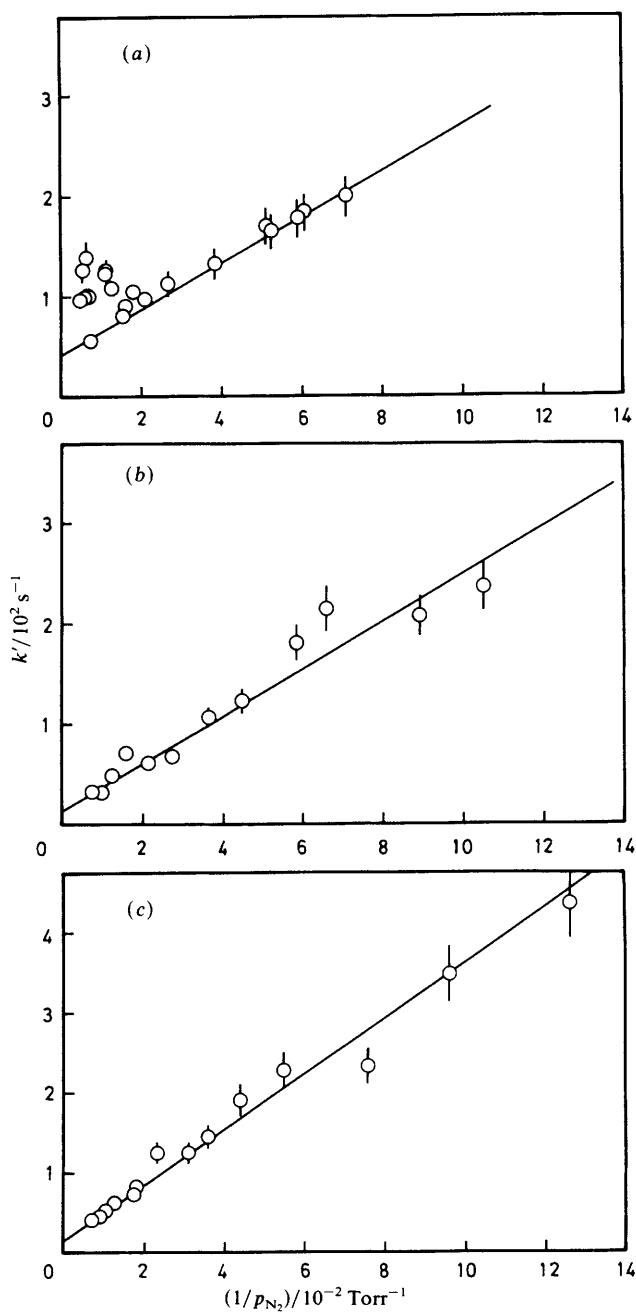
**Fig. 1.** Digitised time-variation of the transmitted light intensity ( $I_{tr}$ ) at  $\lambda = 589$  nm [ $\text{Na}(3^2P_J - 3^2S_{1/2})$ ] indicating the decay of resonance absorption by ground-state sodium atoms in the presence of  $\text{N}_2$  following the pulsed irradiation of NaI.  $E = 200$  J;  $T = 722$  K; the dots are digitised data points while the smoothed curve is a computerised fitting to the form  $I_{tr} = I_0 \exp[-A \exp(-k't)]$ .  $p_{\text{N}_2}/\text{Torr}$ : (a) 80.7; (b) 15.2.

loss. Fig. 3 illustrates diffusional removal of  $\text{Na}(3^2S_{1/2})$  at various temperatures, including those for conditions pertinent to fig. 1 for  $T = 722$  K. A limited number of measurements were carried out on the diffusional decay of  $\text{Na}(3^2S_{1/2})$  in neon at  $T = 725$  and  $845$  K, the results of which, analogous to those given in fig. 2 and 3, are presented in fig. 4.

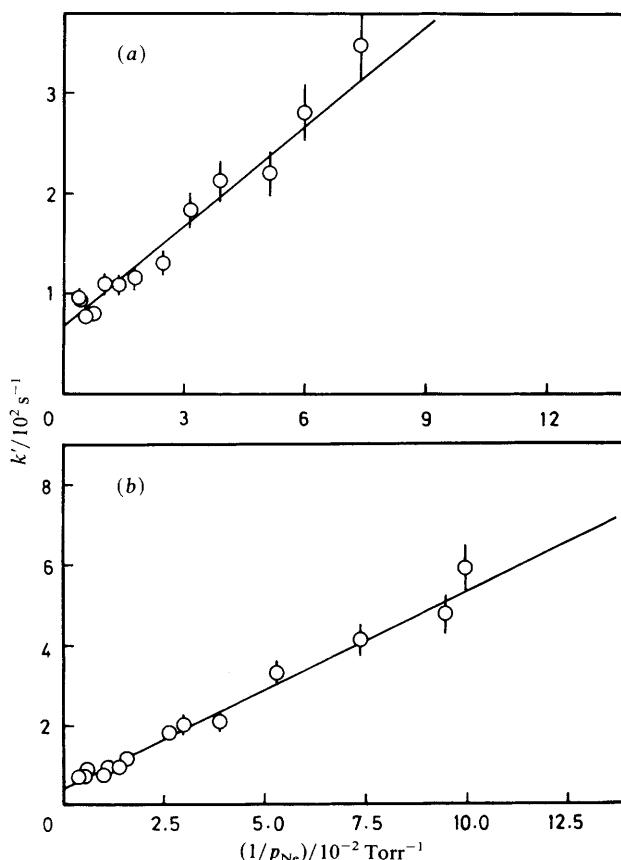
The absolute values of the diffusion coefficients for  $\text{Na}(3^2S_{1/2})$  can be derived from the values of  $k'$  indicated in fig. 2–4 with the simplified form of the ‘long-time



**Fig. 2.** Variation of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{Na}(3^2S_{1/2})$  derived by pulsed irradiation with the reciprocal of the pressure of  $\text{N}_2$  to obtain diffusional rate data at different temperatures.  $T/\text{K}$ : (a) 570; (b) 810; (c) 1016.



**Fig. 3.** Variation of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{Na}(3^2S_{1/2})$  derived by pulsed irradiation with the reciprocal of the pressure of  $\text{N}_2$  to obtain diffusional rate data at different temperatures.  $T/\text{K}$ : (a) 621; (b) 722; (c) 908.



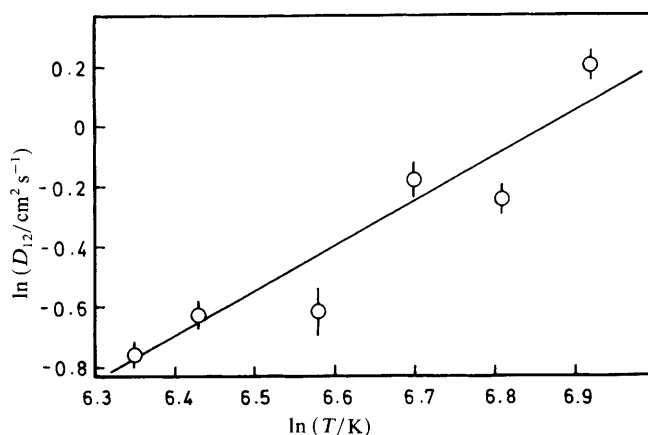
**Fig. 4.** Variation of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{Na}(3^2S_{1/2})$  derived by pulsed irradiation with the reciprocal of the pressure of Ne to obtain diffusional rate data at different temperatures.  $T/\text{K}$ : (a) 725; (b) 845.

solution' of the diffusion equation for a cylinder of length  $l$  and radius  $r$  ( $r = 1 \text{ cm}$ ), where  $l \gg r$  in this case:<sup>20,25</sup>

$$k' \approx 5.81 D_{12}/r^2. \quad (\text{ii})$$

$D_{12}$  [i.e.  $D(\text{Na-N}_2)$  or  $D(\text{Na-Ne})$ ] is, of course, inversely proportional to the pressure of the bath gas. Some erratic values of  $D_{12}$  generated from measurements with a new quartz reaction vessel were observed, possibly indicating that not all collisions of  $\text{Na}(3^2S_{1/2})$  with the walls result in 'sticking'. However, following a limited number of kinetic runs, a consistent series of plots of the type shown in fig. 2–4 were obtained. The slopes of these plots yielding  $D_{12}$  were derived from weighted least-squares analyses with data-point contributions according to the variances, so that the scattered data points for some measurements at high pressures of  $\text{N}_2$ , as indicated in fig. 2(c) and 3(a) for example, made little contribution to the computed value of the slope. Assuming a simple power dependence ( $n$ ) of  $D_{12}$  on temperature, which would be  $n = 1.5$  from considerations of simple gas-kinetic theory but which should be more complex when viewed in terms of the appropriate transport integrals involved in the Chapman-Enskog equation,<sup>26</sup> fig. 5 shows the variation of



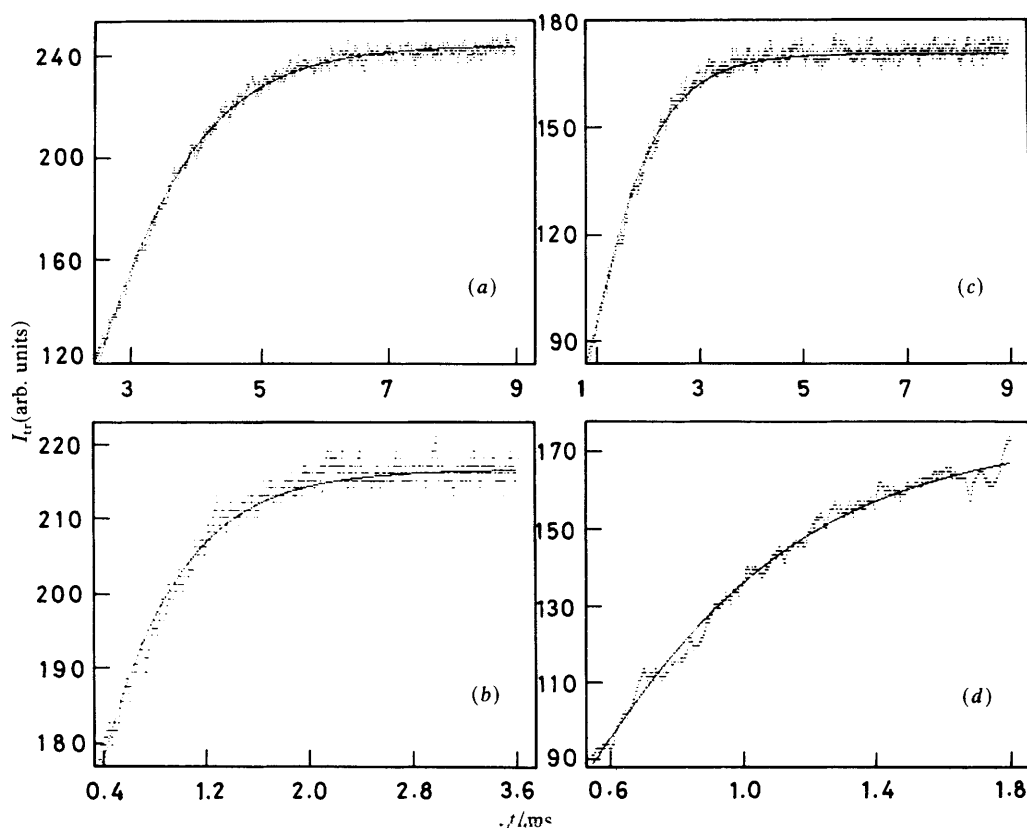


**Fig. 5.** Variation of the diffusion coefficient of sodium atoms,  $\text{Na}(3^2S_{1/2})$ , in molecular nitrogen as a function of temperature [ $\ln(D_{12})$  against  $\ln(T/K)$ ] in the range 570–1016 K.

$\ln[D_{12}(\text{Na}-\text{N}_2)]$  with  $\ln(T)$ , yielding  $n = 1.52 \pm 0.24$ . Extrapolation to s.t.p. yields  $D(\text{Na}-\text{N}_2) = 0.15 \pm 0.05 \text{ cm}^2 \text{ s}^{-1}$ . This constitutes a clear improvement on the values reported hitherto<sup>1</sup> (0.27 and  $0.21 \text{ cm}^2 \text{ s}^{-1}$ ) from the limited investigations at the two temperatures of 722 and 844 K. The result for  $D(\text{Na}-\text{N}_2)$  at s.t.p. obtained here may be compared with the estimates derived from simple collision theory employed by Carabetta and Kaskan<sup>2</sup> of  $0.192 \text{ cm}^2 \text{ s}^{-1}$  and the value of  $0.158 \text{ cm}^2 \text{ s}^{-1}$  used by Kolb and Elgin.<sup>27</sup> These diffusional rate measurements demonstrate that there is no significant contribution by the rapid reaction between Na and  $\text{I}_2$ .<sup>28</sup> Indeed, statistical-thermodynamic considerations indicate that, the kinetic effect of atomic recombination notwithstanding, iodine at the densities expected here on the basis of photodissociation would be in the atomic form at these temperatures. The data in fig. 4 yield values of  $D(\text{Na}-\text{Ne})$  of 0.17 and  $0.20 \text{ cm}^2 \text{ s}^{-1}$ , respectively, when extrapolated to s.t.p. on the assumption that  $n = 1.5$  from the slopes of the plots in fig. 4(a) and (b). We report  $D(\text{Na}-\text{Ne}) = 0.19 \pm 0.04 \text{ cm}^2 \text{ s}^{-1}$ . However, this result has not been obtained from measurements across a temperature range comparable to that used in the determination of  $D(\text{Na}-\text{N}_2)$ .

#### RATE OF $\text{Na} + \text{O}_2 + \text{N}_2$ AS A FUNCTION OF TEMPERATURE

The presence of a small quantity of oxygen and the resulting kinetic effect of reaction (1) ( $M = \text{N}_2$ ) on the decay of  $\text{Na}(3^2S_{1/2})$  can be seen in fig. 6, where the timescales are shortened by at least a factor of ten compared with those in fig. 1 for effectively the same temperature. Fig. 6(a) and (b) show the increase in the decay rate of  $\text{Na}(3^2S_{1/2})$  by varying the oxygen concentration at a fixed concentration of nitrogen. In these measurements  $[\text{N}_2]:[\text{O}_2]::ca. 1000:1$ , and hence the total pressure may be taken to be that of nitrogen. Fig. 6(c) and (d) indicate the increase in rate on increasing the concentration of  $\text{N}_2$  for a fixed concentration of  $\text{O}_2$ . We have, of course, shown earlier that, in the absence of  $\text{O}_2$ , the decay rate for  $\text{Na}(3^2S_{1/2})$  decreases with increasing pressure of  $\text{N}_2$  alone owing to diffusion. Diffusional corrections to the values of  $k'$  obtained by the curve-fitting procedure indicated in eqn (i) are required for the data of fig. 6(c) and (d) in order to extract the kinetic contribution to the decay from reaction (1). Such corrections are relatively small,



**Fig. 6.** Digitised time-variation of the transmitted light intensity ( $I_{tr}$ ) at  $\lambda = 589$  nm [ $\text{Na}(3^2P_J - 3^2S_{1/2})$ ] indicating the decay of resonance absorption by ground-state sodium atoms in the presence of  $\text{O}_2$  and  $\text{N}_2$  following the pulsed irradiation of NaI.  $E = 360$  J;  $T = 724$  K; the dots are digitised data points while the smoothed curve is a computerised fitting to the form  $I_{tr} = I_0 \exp[-A \exp(-k't)]$ .

	$[\text{N}_2]/10^{17}$ molecule $\text{cm}^{-3}$	$[\text{O}_2]/10^{14}$ molecule $\text{cm}^{-3}$
(a)	4.84	10.3
(b)	4.84	25.2
(c)	7.10	11.6
(d)	17.2	11.6

typically 10% or less of  $k'$ , and they are taken empirically and directly from data of the type given in fig. 2–4 and do not depend upon the interpretation yielding  $D(\text{Na}-\text{N}_2)$ . No diffusional corrections are necessary for the slopes of the plots of the type  $k'$  against  $[\text{O}_2]$  derived from data such as are given in fig. 6(a) and (b) because the total pressures, and hence the diffusional contributions to decay of  $\text{Na}(3^2S_{1/2})$ , are effectively constant.

Fig. 7 shows the variation of  $k'$  with  $[\text{O}_2]$  and  $[\text{N}_2]$  at the two extremes of temperature investigated here, namely 571 and 1016 K. Thus fig. 7(a) shows  $k'$  against  $[\text{O}_2]$  (fixed  $[\text{N}_2]$ ) and fig. 7(b)  $k'$  against  $[\text{N}_2]$  (fixed  $[\text{O}_2]$ ) for  $T = 570$  K with

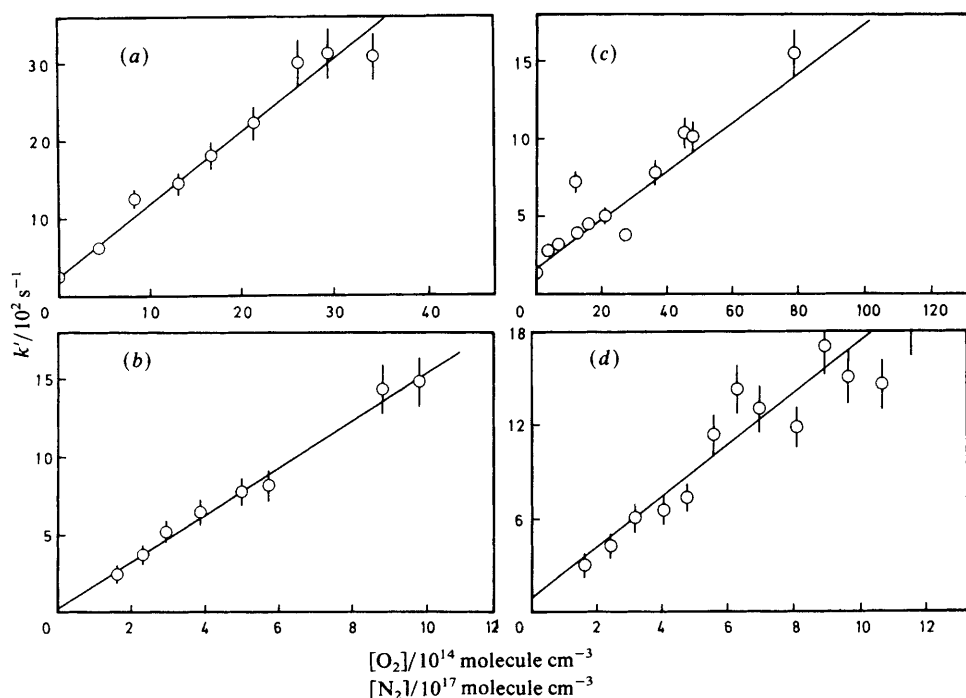


Fig. 7. Variation of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{Na}(3^2S_{1/2})$  in the presence of  $\text{O}_2$  and  $\text{N}_2$  at  $T = 571$  and  $1016$  K ( $x = \text{variable concentration}$ ).

	$T/\text{K}$	$[\text{O}_2]/10^{14} \text{ molecule cm}^{-3}$	$[\text{N}_2]/10^{17} \text{ molecule cm}^{-3}$
(a)	570	$x$	5.24
(b)	570	9.21	$x$
(c)	1016	$x$	2.96
(d)	1016	35.7	$x$

the analogous data for  $T = 1016$  K in fig. 7(c) and (d). Clearly,  $k'$  is kinetically first-order with respect to  $[\text{O}_2]$  and  $[\text{N}_2]$ . Similar pairs of plots to those presented in fig. 7 were obtained for the intermediate temperatures  $T = 624, 726, 810$  and  $844$  K which, of course, include the results for the conditions pertinent to fig. 6, the middle of the temperature range investigated.

The kinetic analysis yielding  $k_1$  extends the form given in our earlier paper,<sup>1</sup> namely

$$k' = k_{\text{diff}} + k_1[\text{O}_2][\text{N}_2] + k_2[\text{O}_2] \quad (\text{iii})$$

in a manner similar to that given in our measurements of the absolute third-order rate constant for the reaction between  $\text{K}(4^2S_{1/2}) + \text{O}_2 + \text{M}$ .<sup>16</sup> Empirically, it is found in the present measurements that the slope of the plot of  $(k' - k_{\text{diff}})$  against  $[\text{N}_2]$ , yielding  $k_1$  directly, is marginally although significantly smaller than that obtained by plotting  $k'$  against  $[\text{O}_2]$  (yielding  $k_1[\text{N}_2] + k_2$ ). Following quantitative arguments of the type presented for our previous kinetic measurements on  $\text{K}(4^2S_{1/2})$ ,<sup>16</sup> we may readily show that  $k_2$  is not a genuine rate constant for a second-order reaction

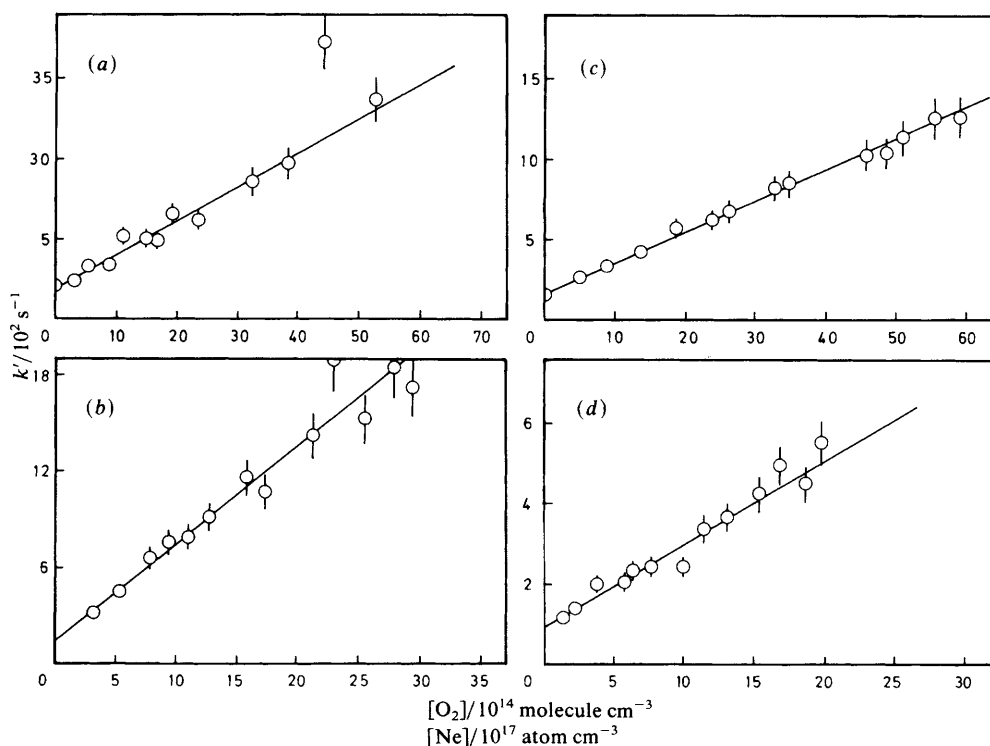
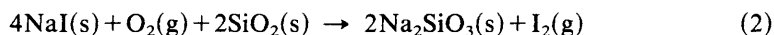


Fig. 8. Variation of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{Na}(3^2S_{1/2})$  in the presence of  $\text{O}_2$  and Ne at  $T = 726$  and  $844$  K ( $x$  = variable concentration).

	$T/\text{K}$	$[\text{O}_2]/10^{14} \text{ molecule cm}^{-3}$	$[\text{Ne}]/10^{17} \text{ atom cm}^{-3}$
(a)	726	$x$	4.55
(b)	726	17.6	$x$
(c)	844	$x$	4.58
(d)	844	7.8	$x$

between  $\text{Na}(3^2S_{1/2})$  and  $\text{O}_2$ . Apart from thermochemical considerations for atom abstraction<sup>29</sup> coupled with estimates of the temperature dependences of  $k_2$ , the effect of  $k_2$  can be almost eliminated, such as yielding a value of *ca.* 10% of that of  $k_1[\text{N}_2]$ , by the speed at which measurements are carried out. Note that all rate measurements described here were carried out at times following admission of the reaction mixture from the gas-handling line to the reactor which are long compared with heat transfer from the walls of the reaction vessel. The effective value of  $k_2$  increases with temperature and one may only speculate as to its source. One possibility is a slow reaction of the type



followed by rapid reaction of  $\text{Na}(3^2S_{1/2})$ , generated by pulsed irradiation, with  $\text{I}_2(\text{g})$ ,<sup>24</sup> which would be at a higher density than that resulting from iodine-atom recombination after photolysis of NaI. For the extreme examples of temperature, and hence of  $k_2$  (see above), the value of  $k_1$  derived, respectively, from the slope

**Table 1.** Absolute third-order rate constants for the reaction between  $\text{Na} + \text{O}_2 + \text{M}$  ( $\text{M} = \text{N}_2$  and  $\text{Ne}$ ) at various temperatures

$k_1/10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$T/\text{K}$
$\text{Na} + \text{O}_2 + \text{N}_2$	
$16.5 \pm 0.8$	571
$14.4 \pm 0.6$	622
$8.9 \pm 0.6$	724
$7.6 \pm 1.0$	810
$5.1 \pm 0.6$	906
$4.3 \pm 0.4$	1016
$\text{Na} + \text{O}_2 + \text{Ne}$	
$3.5 \pm 0.2$	726
$2.7 \pm 0.1$	844

and concentration indicated in fig. 7(a) is <10% greater than that using the analogous procedure with fig. 7(b) ( $T = 570 \text{ K}$ ). For the data of fig. 7(c) and (d), the difference is <20%, with a monotonic variation across the temperature range. All values of  $k_1$  quoted here result from the plot of  $(k' - k_{\text{diff}})$  against  $[\text{N}_2]$ , where the effect of  $k_2$  is totally eliminated. Similar considerations apply to the smaller body of data for  $\text{M} = \text{Ne}$  in reaction (1) for  $T = 726$  and  $844 \text{ K}$ , the relevant kinetic plots being given in fig. 8. The resulting values of the absolute third-order rate constants,  $k_1$ , for reaction (1) at the temperatures employed are given in table 1.

It is convenient to describe the small temperature dependence of rate constants for association reactions empirically in the form of a negative power of  $T$ . The results for  $k_1(\text{M} = \text{N}_2)$  are plotted in the form  $\ln(k_1)$  against  $\ln(T)$  in fig. 9, yielding a straight line of slope  $-2.47 \pm 0.14$ . Hence, for the temperature range 571–1016 K we may describe  $k_1$  in the form

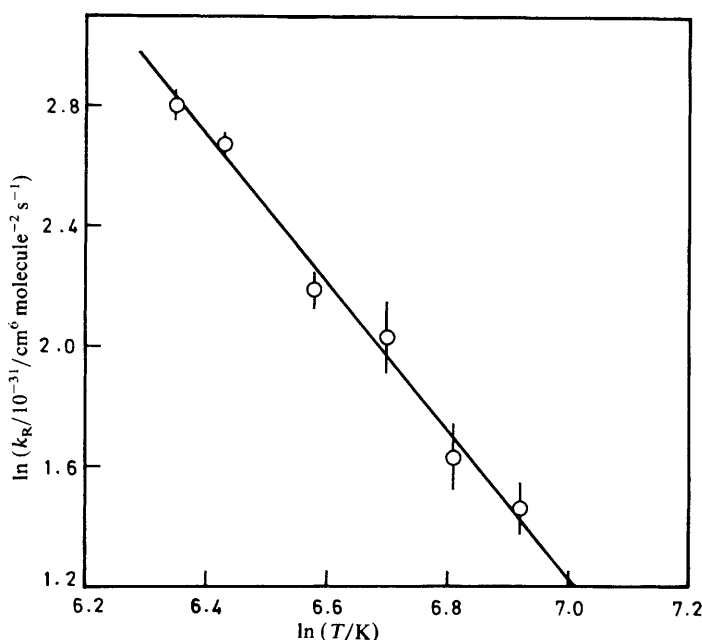
$$k_1(\text{Na} + \text{O}_2 + \text{N}_2) = (1.11 \pm 0.08) \times 10^{-23} T^{-2.47 \pm 0.14} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The error includes the 16 standard errors from the linear least-squares fit to the plot and is considered to be greater than any systematic experimental errors.

There is good agreement between the present results and the average value of  $k_1(\text{M} = \text{N}_2)$  for the temperatures 724 and 844 K reported hitherto of  $(1.0 \pm 0.24) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ .<sup>1</sup> The above expression for  $k_1$  from the present measurements yields values of  $9.6 \times 10^{-31}$  and  $6.6 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $T = 724$  and  $844 \text{ K}$ , respectively. The values of  $\text{M} = \text{Ne}$ , listed in table 1, indicate a significant reduction in the three-body recombination efficiency for this particular third body. The two data points for  $k_1(\text{M} = \text{Ne})$  may be used to estimate a value of  $n$  in the form  $k_1(\text{Na} + \text{O}_2 + \text{Ne}) = AT^{-n}$  of  $n = 1.7$ .

#### EXTRAPOLATION OF $k_1(\text{Na} + \text{O}_2 + \text{N}_2)$ OVER THE TEMPERATURE RANGE 200–2000 K

In view of the importance of reaction (1) for  $\text{M} = \text{N}_2$  in the mesosphere and in flames (see introduction), the data for  $k_1$  are extrapolated over the range 200–2000 K, the limits representing sensible conditions for the two respective environments. The extrapolation is carried out using the formalism of Tröe,<sup>10,11</sup> which is also described in some detail in our paper on the rate of reaction between  $\text{K} + \text{OH} + \text{He}$ .<sup>12</sup> Briefly,



**Fig. 9.** Variation of the absolute third-order rate constant ( $k_R$ ) for the recombination reaction  $\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$  as a function of temperature over the range 570–1016 K [ $\ln(k_R/10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$  against  $\ln(T/K)$ ].

the rate constant of a thermal unimolecular reaction in the limiting low-pressure range ( $k_0$ ) is expressed as the product of a strong-collision rate constant,  $k_0^{\text{sc}}$ , and a weak-collision efficiency,  $\beta_c$ , for the energy transfer:

$$k_0 = \beta_c k_0^{\text{sc}}. \quad (\text{iv})$$

Following the formalism of Tröe,<sup>10,11</sup> the strong-collision rate constant is expressed in the form

$$k_0^{\text{sc}} = \frac{Z_{\text{LJ}} \rho(E_0) RT \exp(-E_0/RT)}{Q_{\text{vib}}} F_E F_{\text{anh}} F_{\text{rot}} F_{\text{rot,int}} F_{\text{corr}} \quad (\text{v})$$

where the other symbols have their usual significance.<sup>10–12</sup> The strong-association rate constant  $k_{\text{rec},0}^{\text{sc}}$  may be obtained from  $k_0^{\text{sc}}$  in the standard manner *via* the equilibrium constant,  $K_{\text{eq}}$ :

$$k_{\text{rec},0}^{\text{sc}} = K_{\text{eq}} k_0^{\text{sc}}. \quad (\text{vi})$$

$k_0^{\text{sc}}$  represents an upper limit for the rate constant and must be multiplied by the collision efficiency,  $\beta_c$  ( $0 < \beta_c < 1$ ), whose temperature dependence is given by

$$\frac{\beta_c}{1 - \beta_c^{1/2}} = \frac{\langle \Delta E \rangle}{F_E RT} \quad (\text{vii})$$

where  $\langle \Delta E \rangle$  is the average energy transferred per collision. There is uncertainty about the exact temperature dependence of  $\langle \Delta E \rangle$ ,<sup>30–33</sup> although it is generally considered that the value of  $n$  in an expression of the form  $\langle \Delta E \rangle \propto T^n$  lies between *ca.* –1 and 0 for third bodies, M, other than helium, over a broad range of

**Table 2.** Extrapolation of rate data for the reaction  $\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$ 

input parameters for the $\text{NaO}_2$ molecule	
$R_{\text{Na}-\text{O}} = 2.07 \text{ \AA}$ , $R_{\text{O}-\text{O}} = 1.33 \text{ \AA}$ , $I_{\text{ABC}} = 4.78 \times 10^4 \text{ amu}^3 \text{ \AA}^6$ , $\nu_1 = 332.8 \text{ cm}^{-1}$ , $\nu_2 = 390.7 \text{ cm}^{-1}$ , $\nu_3 = 1080 \text{ cm}^{-1}$ , $E_0 = 170 \text{ kJ mol}^{-1}$	
data for $\text{Na} + \text{O}_2 + \text{N}_2$ at $T = 735 \text{ K}$	
$\sigma(\text{NaO}_2\text{-N}_2) = 4.5 \text{ \AA}$ , $\varepsilon(\text{NaO}_2\text{-N}_2)/k = 450 \text{ K}$ , $Z_{\text{LJ}} = 7.71 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , $E_z = 10.8 \text{ kJ mol}^{-1}$ , $K_{\text{eq}} = 1.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$	
$s = 3$ , $m = 2$ , $r = 0$ , $Q_{\text{vib}} = 4.44$ , $a = 0.989$ , $\rho(E_0) = 0.0677$ , $F_{\text{E}} = 1.070$ , $F_{\text{anh}} = 1.72$ , $F_{\text{rot}} = 19.86$ , $I^+/I = 68.0$ , $C_v = 0.0561$ , $\nu = 1.225$ , $k_{0^{\text{sc}}} = 2.17 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , $k_{\text{rec},0}^{\text{sc}} = 3.70 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , $\beta_c = 0.24$ , $\langle \Delta E \rangle = -3.15 \text{ kJ mol}^{-1}$	

temperatures (e.g. 200–7000 K<sup>30</sup>). We consider that the extrapolation for reaction (1) coupled with the present data for  $k_1$  may be used to estimate a value for  $n$  both within the uncertainties of the data themselves and the input parameters required for the calculation.

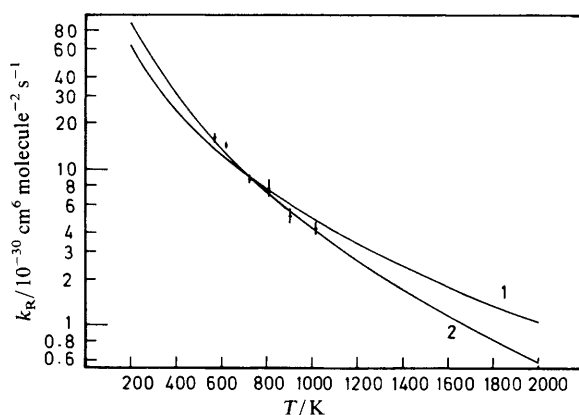
#### DATA INPUT FOR THE CALCULATIONS

Matrix-isolation studies on the  $\text{NaO}_2$  molecule using Raman and infrared spectroscopy show this to be an ion-pair species,  $\text{Na}^+\text{O}_2^-$ , with isosceles-triangular geometry.<sup>34</sup> The vibrational frequencies of the molecule together with the bond lengths required to evaluate the moments of inertia are given in table 2. The value of the  $\text{Na}-\text{O}_2$  bond dissociation energy is uncertain since estimates of this quantity are derived from kinetic modelling on flames where the resulting value itself depends, to some extent, on the model of the flame adopted. Nevertheless, two recent estimates<sup>7,8</sup> indicate that the bond energy is of magnitude *ca.*  $170 \text{ kJ mol}^{-1}$  (error  $\pm 20 \text{ kJ mol}^{-1}$ ), which is in accord with a crude estimate by Alexander<sup>34</sup> of  $150 \text{ kJ mol}^{-1}$ . We have therefore chosen to set  $E_0$  at  $170 \text{ kJ mol}^{-1}$ ; the exact value does not significantly affect the temperature extrapolation of  $k_1$  (see later). The choice of Lennard-Jones parameters used in estimating the reference collision frequency between  $\text{NaO}_2$  and  $\text{N}_2$  is entirely arbitrary. Fortunately, their choice is again not critical and we have selected 'reasonable' values of  $\sigma(\text{NaO}_2\text{-N}_2) = 4.5 \text{ \AA}$  ( $10 \text{ \AA} = 1 \text{ nm}$ ) and  $\varepsilon(\text{NaO}_2\text{-N}_2)/k = 450 \text{ K}$ , which yielded the best fit to the experimental data.

#### APPLICATION OF THE TRÖE FORMALISM

The formalism of Tröe is now applied to  $k_1(\text{Na} + \text{O}_2 + \text{N}_2)$ , treating  $\text{NaO}_2$  as a molecule consisting of three oscillators (*i.e.*  $s = 3$ ), two of which are lost during dissociation of  $\text{NaO}_2$ . The O—O stretch is, of course, preserved. In order to obtain an unbiased fit to the data in table 1 we have chosen to use the mid-point of the line in fig. 9 [*i.e.*  $\ln(k_1)$  against  $\ln(T)$ ], namely at  $T = 753 \text{ K}$ . The results of the calculation are shown in table 2, which reveals a sensible value of  $\beta_c$  at this temperature of 0.24, in good accord with the results of other recombination reactions where  $\text{N}_2$  is the third body.<sup>32</sup>

Particular mention should be made of the calculation of  $F_{\text{rot}}$ . This represents a major source of uncertainty in applying the formalism.<sup>35</sup> We have employed the improvement suggested by Tröe<sup>35</sup> for calculating  $F_{\text{rot}}$  at low temperatures by



**Fig. 10.** Extrapolation of the third-order rate constant ( $k_R$ ) for the reaction between  $\text{Na} + \text{O}_2 + \text{N}_2$  over the temperature range 200–2000 K indicating the effect of the dependence of  $\langle \Delta E \rangle$  with temperature, (●, experimental data points). (1)  $\langle \Delta E \rangle \propto T^0$ ; (2)  $\langle \Delta E \rangle \propto T^{-0.7}$ .

replacing the van der Waals potential with a Morse potential to describe the breaking of the  $\text{Na}-\text{O}_2$  bond and by replacing the quasi-diatomic centrifugal potential described in Tröe's original paper<sup>10</sup> (and in our previous papers on  $\text{K} + \text{OH} + \text{He}$  and  $\text{Na} + \text{OH} + \text{He}$ <sup>12,13</sup>) by a polyatomic model. We have also considered the role of loosening vibrations, which introduce zero-point barrier effects. Following the procedure described by Tröe<sup>35,36</sup> we find that the dissociating  $\text{NaO}_2$  molecule is not described adequately by 'loose' activated complex theory and that a full computer calculation<sup>36</sup> of the centrifugal barrier pattern is required with a 'looseness parameter' of  $1 \text{ \AA}^{-1}$ . This has a significant effect on the value of  $F_{\text{rot}}$  at low temperatures.

In order to calculate the variation of  $k_1$  with temperature, the extrapolation procedure was performed to yield the best fit through the data points given in table 1. We have examined the effect on the fit by varying (a) the Lennard-Jones' parameters describing the  $\text{NaO}_2-\text{N}_2$  collision, (b) the threshold energy  $E_0$ , corresponding to the  $\text{Na}-\text{O}_2$  bond dissociation energy, and (c) the values of  $n$  in the expression  $\langle \Delta E \rangle \propto T^n$ . The first two factors have little effect in matching the rather steep temperature dependence of  $k_1$  on  $T^{-2.47}$  that has been observed from the present data (fig. 9). However, the best fit to our data for  $k_1$  (table 1) was obtained using a value of  $n = -0.7$ . The result is illustrated on the semi-logarithmic plot of  $k_1$  against  $T$  in fig. 10. Although the absolute value of this exponent is greater than that of  $0.0 \pm 0.2$  suggested from the very recent measurements by Tröe and co-workers<sup>33</sup> on the collisional deactivation of highly vibrationally excited toluene molecules, a large body of other work<sup>30-32,35</sup> supports a value of  $n$  between  $-1$  and  $0$ . Thus setting  $n = -0.7$ ,  $E_0 = 170 \text{ kJ mol}^{-1}$  and other parameters as listed in table 2, we obtain the temperature extrapolation illustrated in fig. 10 [ $\ln(k_1)$  against  $T$  from 200 to 2000 K]. In order to demonstrate the improved quality of the fit to our present data achieved by taking  $n = -0.7$  instead of zero, a second curve is presented on fig. 10 for the case of  $\langle \Delta E \rangle = \text{a constant}$ .

The values of  $k_1(\text{Na} + \text{O}_2 + \text{N}_2)$ , extrapolated on the basis of  $\langle \Delta E \rangle \propto T^{-0.7}$  (fig. 10), are thus given by

$$k_1(200 \text{ K}) = 8.8 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_1(2000 \text{ K}) = 6.8 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$



These may be compared with the values of  $2.3 \times 10^{-29}$  and  $7.8 \times 10^{-32}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> for  $T = 200$  and  $2000$  K, respectively, based on the simple power dependence demonstrated graphically in fig. 9. The use of Tröe's extrapolation<sup>10,11</sup> in this context is clearly of greater importance for use in the mesosphere than in flames. The extrapolated value of  $k_1$  for  $T = 2000$  K is in accord with that used in the flame model employed by Hynes *et al.*<sup>8</sup> ( $10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> at  $2000$  K). However, the overall model is constructed from a mechanism involving 17 reactions, and until knowledge of the absolute fundamental rate constants for both the forward and backward steps in these processes is unequivocally established, the simplified model employing four reactions<sup>8</sup> should be viewed with some caution.

Finally we consider the relative efficiencies of the third bodies we have now studied in reaction (1), i.e. He, Ne, N<sub>2</sub> and CO<sub>2</sub>.<sup>12</sup> It is clear from eqn (iv) and (v) that, taking He as the reference bath gas,

$$\frac{\beta_c^M}{\beta_c^{\text{He}}} = \frac{k_0^M Z_{\text{LJ}}^{\text{He}}}{k_0^{\text{He}} Z_{\text{LJ}}^M} \quad (\text{viii})$$

The use of eqn (viii) reveals that the relative collision efficiencies in reaction (1) for He:Ne:N<sub>2</sub>:CO<sub>2</sub> are 1:0.9:1.9:3.9 at  $T = 724$  K, which may be compared with the ratio of the rate constants at this temperature<sup>12</sup> of 1:0.58:1.6:3.3. These relative efficiencies, in particular the perhaps unexpected smaller efficiency of Ne with respect to that of He, are in accord with a wide body of experimental data.<sup>37</sup> This lends additional support to the proposal<sup>11</sup> that the collisional efficiency,  $\beta_c$ , in both relative and absolute terms is largely independent of the nature of the reaction in which the bath gas (M) is acting as a third body.

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