

## RATE CONSTANT FOR THE REACTION $\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$ UNDER MESOSPHERIC CONDITIONS

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### Summary

Measurement of the absolute third-order rate constant  $k_R$  for the reaction constituting the major sink for atomic sodium under mesospheric conditions, namely  $\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$ , has been extended to lower temperatures (415 - 1016 K) by the method of time-resolved atomic resonance spectroscopy at  $\lambda = 589 \text{ nm}$  ( $\text{Na}(3^2\text{P}_J) \leftarrow \text{Na}(3^2\text{S}_{1/2})$ ). This has facilitated extrapolation of the measured rate data over a wide temperature range using the Tröe formalism of unimolecular rate theory to the temperature of the 90 km region, namely about 200 K. For the range  $T = 200 - 2000 \text{ K}$ ,  $k_R$  ( $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ) can then be fitted to the expression

$$\ln k_R = -0.3225(\ln T)^2 + 2.133 \ln T - 69.211$$

The resulting value of  $k_R(200 \text{ K})$  is found to be about three times greater than expected on the basis of recent measurements derived from atomic-laser-induced fluorescence experiments using a fast flow reactor, further substantiating the role of  $\text{NaO}_2$  as a major sink.

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### 1. Introduction

The reaction



is considered to be the major sink for atomic sodium in the region 80 - 105 km above the Earth's surface [1 - 4]. Following our recent measurements [5] on the absolute rate of reaction (1) in the limited temperature range 724 - 844 K by time-resolved atomic resonance absorption spectroscopy following pulsed irradiation, there has been renewed experimental interest in direct studies of this process. This has arisen because those direct measurements clearly demonstrated that the earlier-reported values of  $k_R$  derived from monitoring atomic sodium in oxygen-rich flames were very low on account of complications resulting from flame equilibria [6, 7]. Whilst the

magnitude of  $k_R$  concerns the role of reaction (1) in such flames [8, 9], its effect in the 90 km region is crucial. Indeed, whilst the temperature dependence of the third-order recombination reaction (1) is expected to be and is found to be small over a limited temperature range (see below), this dependence is, nevertheless, critical for the extrapolation of  $k_R$  to temperatures appropriate to mesospheric conditions (about 200 K). For this reason, reaction (1) was re-investigated by the present authors [10] using time-resolved atomic resonance absorption spectroscopy with a new experimental system over the temperature range 571 - 1016 K, where the temperature dependence was both described empirically for the region investigated and was extrapolated to both mesospheric and flame temperatures by means of the Tr oe formalism of unimolecular reaction rate theory [11 - 14]. Simultaneous with that work, Silver *et al.* [15] have investigated  $k_R$  for reaction (1) over the temperature range 320 - 698 K by laser-induced atomic fluorescence on a fast flow reactor. Whilst there is sensible agreement in the measured rate data by the two techniques for  $T \approx 700$  K, the results for  $k_R$  reported by Silver *et al.* are lower than those obtained at the lower temperatures by time-resolved atomic absorption spectroscopy and imply, in particular, significantly lower values for mesospheric conditions. For this reason, we have extended our measurements [10] to  $T = 415$  K, which is close to the lower limit attainable with the present system, in order to obtain a significant overlap in the temperature ranges employing the two methods and to investigate the relatively large temperature dependence implicit in combining the data over the range of about 320 - 1016 K. The present data at lower temperatures are still found to be significantly higher and no major difference in the nature of the Tr oe extrapolation to that obtained hitherto is obtained. The rate data are compared in detail and the significance of the results to mesospheric conditions is considered.

## 2. Experimental details

A description of the experimental arrangement has been given in previous publications [10, 16, 17] including details of the lamp and vessel assembly, and the high intensity high current hollow cathode source of the atomic resonance radiation at  $\lambda = 589$  nm ( $\text{Na}(3^2\text{P}_J) \rightarrow \text{Na}(3^2\text{S}_{1/2}) + h\nu$ ) [18]. In brief,  $\text{Na}(3^2\text{S}_{1/2})$  was generated by the pulsed irradiation of NaI vapour [19] in the presence of  $\text{O}_2$  and excess  $\text{N}_2$  and monitored photoelectrically in the "single-shot mode" by time-resolved atomic resonance absorption at  $\lambda = 589$  nm. The resonance absorption signals were amplified without distortion [20], captured, digitized and stored in a transient recorder and transferred to a microcomputer for analysis using the form

$$I_{\text{tr}} = I_0 \exp\{-A \exp(-k't)\} \quad (2)$$

where the symbols have their usual meaning.  $k'$  is the overall first-order coefficient for the decay of  $\text{Na}(3^2\text{S}_{1/2})$  and is the object of the kinetic analysis.

Equation (2) represents the combination of the first-order kinetic decay of  $\text{Na}(3^2\text{S}_{1/2})$  and the standard Beer-Lambert law for the unresolved D-line doublet whose use in this context has been shown to be valid for degrees of light absorption less than about 40% [5]. This is certainly the case here where the degree of light absorption is less than 10% for measurements at the lowest temperature investigated ( $T = 415$  K). Diagrams demonstrating the nature of the raw data, namely examples of the digitized time variation of the computerized output indicating the transmitted light intensity  $I_{\text{tr}}(\lambda = 589 \text{ nm})$  following pulsed irradiation, have been given in previous publications. In this paper we shall proceed directly to values of  $k'$  derived from such computerized output.

### 3. Results and discussion

Figure 1 summarizes the rate data for the middle of the three temperatures investigated here ( $T = 470$  K). Thus, Fig. 1(a) shows the variation of  $k'$  versus  $[\text{O}_2]$  for fixed  $[\text{N}_2]$  and Fig. 1(b) shows the variation of  $(k' - k_{\text{diff}})$  versus  $[\text{N}_2]$  for fixed  $[\text{O}_2]$ . In general, the decay coefficient for  $\text{Na}(3^2\text{S}_{1/2})$  can be expressed in the form

$$k' = k_{\text{diff}} + k_{\text{R}}[\text{O}_2][\text{N}_2] \quad (3)$$

$k_{\text{diff}}$  represents the first-order decay coefficient for the loss of the  $\text{Na}(3^2\text{S}_{1/2})$  atoms in the presence of  $\text{N}_2$  alone, where diffusion dominates removal [10] and can be described by the approximate form of the long-time solution of the diffusion equation for a long cylinder [21, 22]:

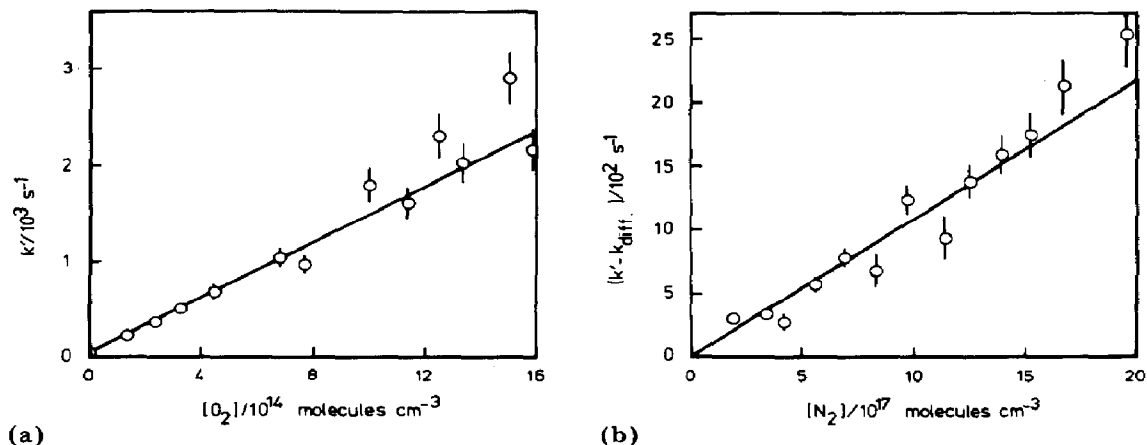


Fig. 1. Variation of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Na}(3^2\text{S}_{1/2})$  monitored by time-resolved atomic resonance absorption spectroscopy at  $\lambda = 589 \text{ nm}$  ( $\text{Na}(3^2\text{P}_J \leftarrow 3^2\text{S}_{1/2})$ ) in the "single-shot mode" following pulsed irradiation in the presence of  $\text{O}_2$  and  $\text{N}_2$  ( $T = 470$  K;  $E = 560$  J): (a)  $k'$  vs.  $[\text{O}_2]$  ( $[\text{N}_2] = 7.0 \times 10^{17}$  molecules  $\text{cm}^{-3}$ ); (b)  $(k' - k_{\text{diff}})$  vs.  $[\text{N}_2]$  ( $[\text{O}_2] = 5.6 \times 10^{14}$  molecules  $\text{cm}^{-3}$ ).

TABLE 1

Absolute third-order rate constants  $k_R$  for the reaction between Na + O<sub>2</sub> + N<sub>2</sub> determined by time-resolved atomic resonance absorption spectroscopy (errors, 1σ)

$T$ (K)	$k_R$ ( $\times 10^{-31}$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	$T$ (K)	$k_R$ ( $\times 10^{-31}$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )
415	21.4 ± 3.1 <sup>a</sup>	622	14.4 ± 0.6 <sup>b</sup>
470	19.7 ± 1.4 <sup>a</sup>	724	8.9 ± 0.6 <sup>b</sup>
570	15.7 ± 0.7 <sup>a</sup>	810	7.6 ± 1.0 <sup>b</sup>
571	16.5 ± 0.8 <sup>b</sup>	906	5.1 ± 0.6 <sup>b</sup>
		1016	4.3 ± 0.4 <sup>b</sup>

<sup>a</sup> This work.

<sup>b</sup> From ref. 10.

$$k_{\text{diff}} \approx \frac{5.81D_{12}}{r^2} \quad (4)$$

where  $D_{12} = D(\text{Na}-\text{N}_2)$  and  $r = 1$  cm for the present reactor. We have shown previously that

$$D(\text{Na}-\text{N}_2) = \left\{ (0.15 \pm 0.05) \frac{760}{p} \right\} \left( \frac{T}{273} \right)^{1.52 \pm 0.24} \quad (\text{cm}^2 \text{ s}^{-1}) \quad (5)$$

( $p$  is in torrs) which is in sensible accord with a wide range of other measurements [23]. On this basis, we may calculate  $k_{\text{diff}}$  for the conditions of Fig. 1(a), for example, as  $44_{-17}^{+23}$  s<sup>-1</sup>, which is small and fortuitously agrees with the measured intercept ( $44 \pm 6$  s<sup>-1</sup>). This procedure may be applied to each data point for the variation of  $k'$  versus  $[\text{N}_2]$  where the small contribution from  $k_{\text{diff}}$  to  $k'$ , compared with  $k_R[\text{O}_2][\text{N}_2]$ , may be so calculated or determined empirically, as was the case, from the variation of  $k'$  in N<sub>2</sub> alone at the appropriate temperature. Figure 1(b) shows the resulting plot of  $(k' - k_{\text{diff}})$  versus  $[\text{N}_2]$  ( $[\text{O}_2] = 5.6 \times 10^{14}$  molecules cm<sup>-3</sup>;  $T = 470$  K). The slopes of both plots, obtained by weighted-least-squares analyses, yield values of  $k_R$  ( $T = 470$  K) of  $(20.4 \pm 1.0) \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (Fig. 1(a)) and  $(19.0 \pm 1.0) \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (Fig. 1(b)). Table 1 gives the values of  $k_R$  derived from the series of investigations for the full temperature range 415 - 1016 K using the present experimental system. Good agreement can be seen for the two measurements at 570 K employing the present apparatus.

Figure 2 shows the data of Table 1 presented logarithmically for graphical convenience. The full line shows the Tröe extrapolation performed as described previously and fitted to the data of Table 1. As hitherto, essentially four adjustable parameters were employed for the best fit to the data:  $E_0$  (170 kJ mol<sup>-1</sup>),  $\sigma_{\text{LJ}}$  (4.5 Å),  $\epsilon/k$  (550 K) and  $n$  (-0.35) for  $-\langle \Delta E \rangle \propto T^n$  where the symbols have their standard meaning within the context of unimolecular rate theory. No major differences are found for these parameters compared with those employed earlier. In the present investigation, it was found that the variation of  $k_R$  with  $T$  was better fitted by the form  $-\langle \Delta E \rangle \propto T^{-0.7}$  compared with  $T^0$ . Sensitivity tests on these four parameters were

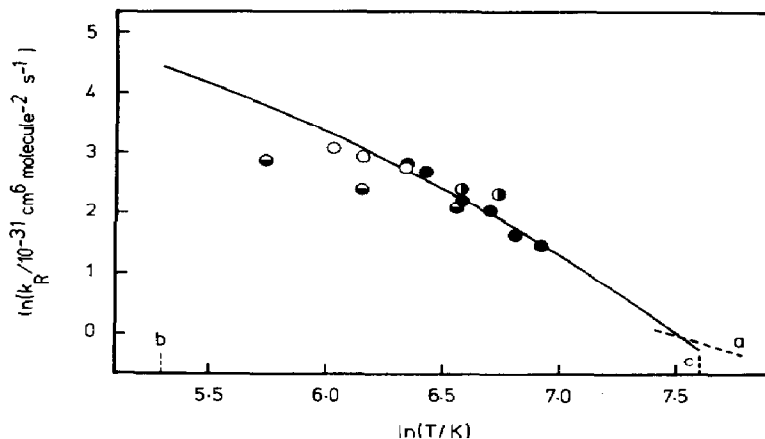


Fig. 2. Data for the absolute third-order rate constant  $k_R$  for the reaction  $\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$  ( $b = 200$  K;  $c = 2000$  K; see text for details):  $\circ$ , this work (time-resolved atomic resonance absorption spectroscopy following flash photolysis);  $\bullet$ , Husain *et al.* [10] (time-resolved atomic resonance absorption spectroscopy following flash photolysis);  $\bullet$ , Husain and Plane [5] (time-resolved atomic resonance absorption spectroscopy following flash photolysis);  $\ominus$ , Silver *et al.* [15] (fast flow reactor plus laser-induced atomic fluorescence); ---, a, Hynes *et al.* [9] (flame modelling); —, Tröe unimolecular rate theory extrapolation ( $-\langle \Delta E \rangle \propto T^{-0.35}$ ).

carried out following the procedure of Kaufman [24]. They reveal that the calculation of the recombination rate constant is most sensitive to  $\sigma_{LJ}$  and least sensitive to the nature of the temperature dependence of  $\langle \Delta E \rangle$ . The above parameters lead to the following results for the calculation at  $T = 735$  K, which is the middle of the temperature range:  $Z_{LJ} = 8.25 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{sc,0} = 2.33 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{rec,0} = 3.96 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ,  $-\langle \Delta E \rangle = 2.85 \text{ kJ mol}^{-1}$  and  $\beta_c = 0.23$ . The full curve in Fig. 2, representing the resulting Tröe extrapolation based on the above data, can be fitted empirically to the form

$$\ln\{k_R (\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})\} = -0.3225[\ln\{T (\text{K})\}]^2 + 2.133 \ln\{T (\text{K})\} - 69.211 \quad (6)$$

over the range 200 - 2000 K. The Tröe extrapolation based on the present data thus yields the following values for  $k_R$  pertinent to mesospheric and flame conditions:  $k_R(200 \text{ K}) = (8.3^{+3.1}_{-2.2}) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $k_R(2000 \text{ K}) = (7.9^{+1.7}_{-1.4}) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . These errors are calculated by combining the sensitivity of the input parameters with their estimated uncertainties ( $E_0$ , 15%;  $\sigma_{LJ}$ , 30%;  $\epsilon/k$ , 30%;  $n$ , 50%).

The present Tröe extrapolation through a range of data points for  $k_R$  from 415 to 1016 K may be contrasted with that of Patrick and Golden [25] which was not constrained through any set of measurements but was compared with data for reaction (1) then available [5]. Patrick and Golden chose an arbitrary but reasonable set of data for  $\sigma_{LJ}$ ,  $\epsilon/k$  and hence  $Z_{LJ}$  (see above), together with  $E_0$  ( $D(\text{Na}-\text{O}_2) = 163.2 \text{ kJ mol}^{-1}$  following ref. 9

and an invariance of  $\langle \Delta E \rangle$  with temperature. They further assumed that  $\beta = 0.3$  for  $N_2$  at  $T = 300$  K. (Unfortunately, the paper also includes errors (about 40%) in the calculation of the moments of inertia of  $NaO_2$ .) In the present paper, these quantities are adjustable variables optimized to fit the range of measured data points (see above). This can be seen particularly in the case of  $D(Na-O_2)$  which Jensen [8] has shown to lie in the range  $170 \pm 25$  kJ mol<sup>-1</sup>, and the value of  $n$  for the form  $\langle \Delta E \rangle \propto T^n$ . Patrick and Golden's modelling [25] leads to values of  $k_R$  which are significantly lower in absolute terms generally than those measured and presented in Fig. 2; the values show a smaller dependence of  $k_R$  on  $T$  than found here and pass through the datum point of Silver *et al.* [15] only for  $T = 300$  K (e.g.  $k_R(500 \text{ K}) = 1.1 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> [15];  $k_R(500 \text{ K}) = 8.65 \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> [25]).

Figure 2 includes the measured data reported by Silver *et al.* [15] which are clearly lower in magnitude and less sensitive to temperature than observed in the present set of investigations. On the basis of the data points as shown, Silver *et al.* report  $k_R = (1.9 \pm 0.4) \times 10^{-30} (T/300)^{-(1.1 \pm 0.5)}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> for the restricted temperature range 300 - 700 K. Extrapolation outside this range, a procedure not adopted by Silver *et al.* [15] would yield  $k_R(200 \text{ K}) = (3.0 \pm 1.1) \times 10^{-30}$  and  $k_R(2000 \text{ K}) = (2.4^{+5.0}_{-1.7}) \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-1</sup> s<sup>-1</sup>;  $k_R(200 \text{ K})$  is lower by a factor of about 3 than that obtained by extrapolation here and  $k_R(2000 \text{ K})$  is higher by a similar factor. Figure 2 also shows the data for  $k_R$  of Hynes *et al.* [9] from modelling of oxygen-rich flames seeded with sodium. Estimates of  $k_R$  from diffusion flames [26 - 28] are significantly higher than either the values derived from the present measurements or those from time-resolved laser-induced atomic fluorescence measurements [15] which are the lowest reported. This difference remains and is not resolved by the particular Tr e modelling employed by Patrick and Golden [25]. It must be emphasized that the Tr e modelling employed here is anchored on nine data points for  $k_R$  as a function of temperature. An alternative empirical procedure, totally independent of unimolecular reaction rate theory modelling, is to employ the observed phenomenological linear relationship between  $\ln(k_R)$  and  $\ln\{T(\text{K})\}$  [10] yielding a value of  $k_R(200 \text{ K})$  sensibly in accord with our value for this quantity obtained here using the Tr e formalism. Either by using a Tr e extrapolation on the rate data or by empirical extrapolation, reaction (1) is clearly seen to support the role of  $NaO_2$  as a major sink in the 90 km region.

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