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Kinetic Investigation of the Reaction between $Na + O_2 + M$ by Time-resolved Atomic Resonance Absorption Spectroscopy

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A kinetic investigation has been carried out on ground-state sodium atoms, Na (3^2S), generated by the ultraviolet pulsed irradiation of NaI vapour at the temperatures $T = 724$ and 844 K, and monitored by time-resolved atomic resonance absorption in the "single-shot" mode at $\lambda = 589$ nm ($3^2P_J \leftarrow 3^2S$). In the presence of the gases He, N_2 and CO_2 alone, the atoms exhibit diffusional decay with removal at the walls of the vessel. The variation of the decay of Na (3^2S) as a function of the pressure of these gases, coupled with the use of the "long-time" solution of the diffusion equation for a cylinder, yields the following average diffusion coefficients (corrected to s.t.p.): $D_{Na-He} = 0.25$, $D_{Na-N_2} = 0.24 \pm 0.3$ and $D_{Na-CO_2} = 0.30$ cm^2 s^{-1}. The third-order reactions between $Na + O_2 + M$ (M = He, N_2 and CO_2) were investigated at $T = 724$ and 844 K, the rate constants indicating no significant temperature variation. The following third-order absolute rate constants for these processes for the range $T = 724$–844 K are reported:

$$k(M = He) = (6 \pm 1) \times 10^{-31}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

$$k(M = N_2) = (1.0 \pm 0{,}24) \times 10^{-30}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}$$

$$k(M = CO_2) = 2 \times 10^{-30}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1},$$

the datum for CO_2 being reliable to within a factor of two. The data are compared with those from analogous measurements for other metal atom reactions of the type $X + O_2 + M$ and are found to be of comparable magnitude. By contrast, the present results are *ca.* three orders of magnitude greater than those reported hitherto from flame measurements.

The third-order recombination of atomic sodium with molecular oxygen

$$Na + O_2 + M \rightarrow NaO_2 + M \tag{1}$$

is a reaction not only of fundamental kinetic interest but of relevance to flames containing alkali atoms[1,2] and to the role of atomic sodium in the upper atmosphere at heights in the region of 90 km.[3–6] However, the rates of reaction (1), particularly for specific third bodies (M), are not established and, indeed, have only been the subject of limited kinetic investigation of flames.[1,2] Carabetta and Kaskan[2] have reported an average overall third-order rate constant for the temperature range $T = 1420$–1600 K for an $H_2 + O_2 + N_2$ flame. This involved extracting rate data attributed to reaction (1) from the complex equilibria arising from the standard, rapid bimolecular reactions in a hydrogen + oxygen flame, using steady atomic resonance absorption measurements on alkali metal atoms along the flow of the flame. The sparsity of kinetic information on reaction (1) may be seen by reference to the review of Kaufman[7] where rate data for these reactions were estimated by analogy with data for atomic hydrogen.

In this paper, we describe a kinetic investigation of reaction (1) at the temperatures $T = 724$ and 844 K for the third bodies M = He, N_2 and CO_2, using time-resolved atomic-resonance absorption spectroscopic measurement on sodium atoms following their generation by pulsed photodissociation. These measurements have involved an experimental system similar to that employed by Davidovits and coworkers for rate measurements of the reactions between alkali elements, including Na, with halogens[8-12] but with various modifications to most aspects of their experimental arrangement. Absolute third-order rate constants for reaction (1) are reported for the specific third bodies $M = He$, N_2 and CO_2 at $T = 724$ and 844 K and these are compared with the results from flame measurements and recently reported absolute rate data for reactions analogous to reaction (1) using other metal atoms. Measurements are also reported for the diffusion of ground-state atomic sodium in the presence of these third bodies and the appropriate diffusion coefficients are also reported.

EXPERIMENTAL

Ground-state sodium atoms, $Na(3s^2S_{1/2})$, were studied by time-resolved atomic resonance absorption of the sodium-D lines at $\lambda = 589.6$ and 589.0 nm $[Na(3^2P_{1/2,3/2} \leftarrow 3^2S_{1/2})]$[13] ($gA = 0.90 \times 10^8$ and $1.8 \times 10^8\ s^{-1}$, respectively)[14] following the flash photolysis of sodium iodide. The experimental arrangement is shown in fig. 1. The apparatus incorporates aspects of the system described by Cross and Husain[15] for time-resolved atomic resonance absorption studies of $Pb(6^3P_0)$ in the "single-shot" mode following pulsed irradiation, with modified aspects of the system described by Edelstein and Davidovits.[10]

Dealing firstly with the contrast between the decay measurements of the present system and those of Edelstein and Davidovits,[10] this work employed the single-shot mode following the pulsed generation of the atoms ($E = 125$ J) in contrast with the experiments of Edelstein

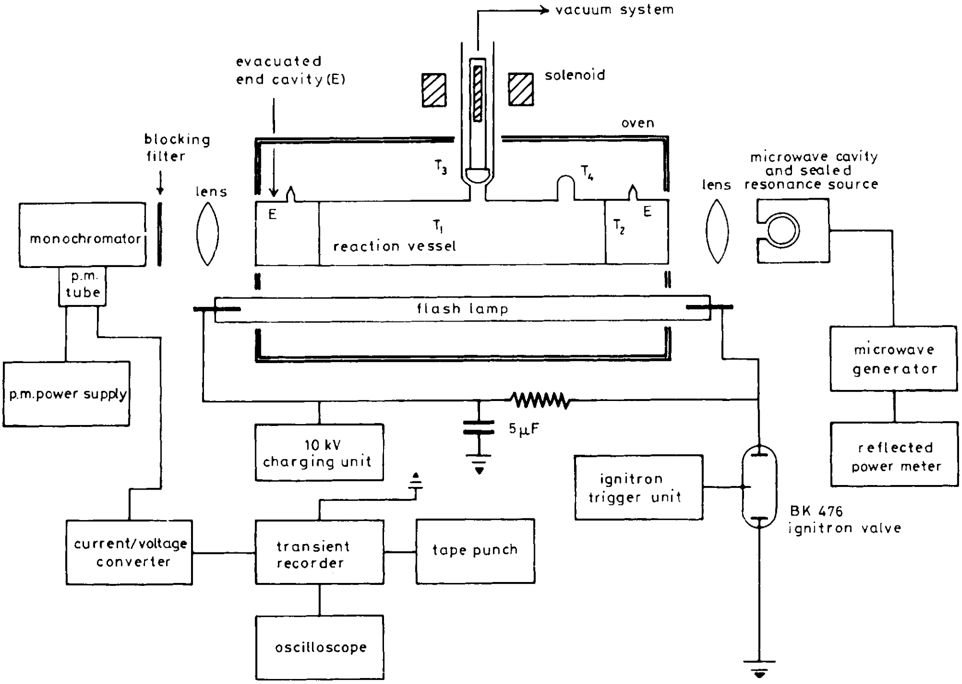

FIG. 1.—Block diagram of the apparatus for the kinetic study of $Na(3^2S)$ by time-resolved attenuation of atomic resonance radiation in the "single-shot" mode.

and Davidovits[10] who employed low-energy repetitive pulsing ($E = 0.125$ J, 50 Hz) on a static system. These workers[10] used a signal averaging technique with XY-output in order to make measurements of degrees of resonance absorption of *ca.* 5% and less, to ensure adherence to the Beer–Lambert law for their experimental conditions. It must be emphasised that for the purpose of time-resolved kinetic measurements, the only experimental requirement is the linearity in the logarithmic form of the "curve-of-growth" {ln [ln (I_0/I_{tr})] against ln c, where the symbols have their usual significance}, preferably with a slope of unity corresponding to the Beer–Lambert, or to some modified but determined form.[16] Detailed adherence of the measured light absorption to the correct oscillator strength is *not* required, and hence the use, for example, of the unresolved pair of sodium-D lines which yielded, empirically, a logarithmically constructed curve-of-growth of slope unity is all that is necessary. Edelstein and Davidovits[10] did not carry out curve-of-growth measurements but implicitly assumed, correctly, that such a logarithmic plot would be linear and of slope unity for a degree of light absorption of 5% or less. However, in this work, a curve-of-growth is required in order to use degrees of light absorption considerably higher than this when carrying out time-resolved measurements in the single-shot mode.

The curve-of-growth for the transition $Na(3^2P_{1/2,3/2} \leftarrow 3^2S_{1/2})$ was determined by measuring the extent of light absorption by atomic sodium in equilibrium with solid sodium in the temperature range $T = 380$–480 K. An apparatus similar to that described by Cross and Husain[17] was constructed employing chopping of the sodium resonance radiation (Phillips spectral lamp Na 93122) coupled with phase-sensitive detection. Considerable care was taken with the control of temperature in the cell, which included evacuated end compartments, and measurements were made with both rising temperature and falling temperature. With sodium vapour at particle densities commensurate with this temperature range (and certainly above it), particular care must be taken to minimise attack by sodium on the heated vessel and especially on the end windows. This is seen by a reduction in the I_0 signal. Quartz is badly attacked and so Pyrex glass must be used. Fig. 2 shows the curve-of-growth in logarithmic form for the unresolved doublet (Grubb Parsons "M2" monochromator, E.M.I. p.m. tube 9783 B). This is given here in the form ln [ln (I_0/I_{tr})] ($\lambda = 589$ nm) against -10^3 K/T, the abscissa being thus presented so as to yield an increasing linear measure of the logarithm of the sodium atom concentration. Absolute atomic densities of sodium may be calculated from the thermodynamic data given in the JANAF tables;[18] however, for the present purposes, we are only concerned with the slope of fig. 2 which is equivalent to a plot of ln [ln (I_0/I_{tr})] against ln [Na]. Inspection of the data in fig. 2 shows that, within experimental error, the Beer–Lambert law is obeyed (*i.e.* the slope is unity) for degrees of light absorption of *ca.* 40% and less and hence single-shot mode experiments may be carried out provided such a degree of light absorption is not significantly exceeded in the kinetic analysis of decay traces. In kinetic terms, this simply means that the overall first-order rate coefficient for the decay of $Na(3^2S)$ (k') may be derived from the slope of the (computerised) plot of ln [ln (I_0/I_{tr})] ($\lambda = 589$ nm) against time. This may readily be seen by reference to the Beer–Lambert law $\{I_{tr} = I_0 \exp(-\varepsilon cl),\ c = [Na(3^2S)]\}$, and to the first-order decay $[Na(3^2S)]_t = [Na(3^2S)]_{t=0} \exp(-k't)$. The single-shot measurements overcome the need for signal averaging and, further, dispense with the need for a slow flow system, kinetically equivalent to a static system as described for various time-resolved resonance absorption measurements carried out in this laboratory.[19] By comparison, the experiments of Davidovits and coworkers[8–12] employ repetitive pulsing (50 Hz) on a closed, static system with the assumption of no significant change in chemical composition during a series of repetitive pulses from which is derived a single decay trace.

More stringent considerations of the material employed apply to the construction of the spectroscopic resonance source for the time-resolved measurements. In these experiments, we employ a microwave-powered spectroscopic source in order to achieve a high I_0 signal-to-noise ratio in the pulsed measurements, principally in order to overcome standard difficulties encountered with scattered light from the photoflash. We have demonstrated hitherto that curve-of-growth resonance absorption measurements on atomic lead[17] and tin[20] derived using hollow cathode resonance sources[17,20] give rise to γ-values in the modified Beer–Lambert law $[I_{tr} = I_0 \exp(\varepsilon cl)^{\gamma}]$[16] which are equal, within experimental error, to those derived

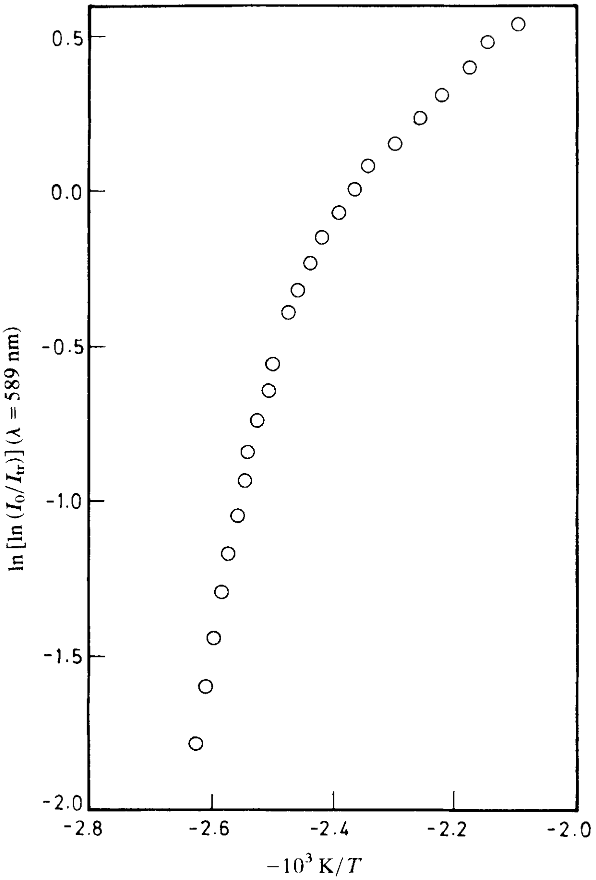

FIG. 2.—Experimental "curve-of-growth" in logarithmic form for the absorption of resonance radiation at $\lambda = 589$ nm [$Na(3^2P_J) \leftarrow Na(3^2S)$] by sodium atomic vapour in equilibrium with solid sodium in the temperature range $T = 380$–480 K.

empirically in pulsed experiments on $Pb(6^3P_0)$[17] and $Sn(5^3P_0)$[21,22] and which employed microwave-powered sources, despite expected differences in the light output characteristics for these two types of spectroscopic sources. The resonance source involved the use of a microwave cavity similar to the E.M.I. C111 device (incident power = 60 W) employed hitherto, for example, in the kinetic study of $Pb(6^3P_0)$[15] but utilising a sealed source of sodium with added krypton ($p_{Kr} \approx 1.6$ Torr, 1 Torr = 133 N m^{-2}) for operating the microwave discharge, essentially following the design of Bell *et al.*[23] and made in this laboratory. The sodium resonance lamps were constructed by careful, repetitive fractional distillation of sodium under good vacuum (*ca.* 10^{-5} Torr) into an ampoule constructed from pre-1960 Pyrex glass. This material was accidentally discovered to be sufficiently resistant to sodium, unlike standard modern Pyrex glass which appeared to absorb the sodium completely on distillation. The resulting microwave-powered sealed lamps, of which a number were constructed, are highly intense, suitably stable during experiments and characterised by operating lifetimes of hours. These devices may readily be changed on deterioration. [We are heavily indebted to Mr. C. J. Smith of the Glass Blowing Department of this Laboratory for his considerable assistance in the construction of these resonance sources, without which the single-shot measurements on $Na(3^2S)$ would not be feasible using an apparatus of the type shown in fig. 1.]

A full comparison of the reactor employed here (fig. 1) with that used by Edelstein and Davidovits[10] is not possible as these authors restrict their description to the general features of the system. The reaction vessel and the flash lamp (fig. 1) were constructed of quartz, permitting photolysis in air optics to $\lambda \gtrsim 200$ nm. At the temperatures employed in these kinetic measurements ($T = 724$–844 K), no serious deterioration in the quartz, as evidenced by a reduction in the I_0 signal, due to attack by sodium generated from the photolysis of NaI was observed. The temperature within the furnace was established (±8 K) by using evacuated end chambers (fig. 1, E) to reduce significant temperature variations along the reaction vessel and to prevent condensation on the end windows of the reaction vessel itself. The temperature was measured at various points by means of thermocouples (T_1–T_4, fig. 1). As in the experiments of Davidovits and Edelstein,[10] we employ a ground plug connecting the reaction vessel to the vacuum line, magnetically controlled for the inlet and pumping of reactant gases whose pressures were measured in the room-temperature vacuum apparatus with the plug open. The magnetic valve was independently heated and maintained at a temperature (as measured at T_3) a few degrees (*ca.* 10 K) above that of the reaction vessel to prevent significant condensation from the NaI in the reactor on to the plug. The small, sealed inlet at T_4, comprising a quartz–Pyrex seal, permits transfer into the reaction vessel of solid sodium iodide by breaking and re-sealing, this area being served by a seperately wound furnace. The temperature of the reaction vessel is taken as the average of T_1 and T_2 but high absolute accuracy is not critical as the temperature dependence of the recombination process (1) is small (see later). Indeed, Carabetta and Kaskan,[2] from their flame measurements, report a mean value of k_1 for the temperature range $T = 1420$–1600 K. Vapour pressures for sodium iodide at the reactor temperatures employed may be taken from Cogin and Kimball[24] who report the temperature variation to be given by $\log_{10} p_{\text{mm}}(\text{NaI}) = 12.525 - 11.895(1000/T) + \frac{5}{2}\log_{10}(1000/T)$, the latter term being included to allow for differences in the heat capacities of gaseous and crystalline NaI. In fact, neither the absolute vapour pressure employed in these experiments nor the absolute sodium atomic density generated on photolysis are critical provided the degree of resonance light absorption analysed is less than *ca.* 40%. Analysis of the first-order kinetic decays of $Na(3^2S)$ (see later) only, of course, requires knowledge of relative values of $[Na(3^2S)]_t$ in a given decay. Davidovits and Brodhead[25] have characterised the absorption spectrum of NaI in the ultraviolet. This molecule exhibits a broad absorption spectrum from $\lambda \approx 200$ nm up to $\lambda \approx 390$ nm, with a maximum in the region of $\lambda = 220$ nm. Whilst the potential curves of NaI[25] clearly indicate the production of both ground-state iodine atoms, $I(5^2P_{3/2})$, and the electronically excited $I(5^2P_{1/2})$ on photolysis in this region of the spectrum, consideration of the appropriate collisional quenching data for this atomic state[26] and also more importantly, consideration of the removal of $Na(3^2S)$ in these experiments leads to the conclusion that $I(5^2P_{1/2})$ has no significant effect on the processes investigated here.

Time-resolved resonance absorption at $\lambda = 589$ nm by Na (3^2S), generated on photolysis, was monitored photoelectrically with the same combination of monochromator and photomultiplier tube as employed in the curve-of-growth calibration. Reduction in the effect of scattered light from the photoflash was effected by means of a blocking filter (Kodak, Wratten filter no. 21). Fig. 3 shows the spectral characteristics of the relevant optical components. The flash lamp is approximate to a black-body radiator of temperature 6500 °C (6773 K) following Christie and Porter.[27] Optical isolation of the resonance transition at $\lambda = 589$ nm is effected by means of the monochromator. Most of the spectral response of the p.m. tube employed (E.M.I. 9783 B) and the low-wavelength component ($\lambda < 550$ nm) of the light output from the flash are blocked by the filter. Hence, good time-resolved resonance absorption signals may be obtained despite the use of the p.m. tube at a wavelength where its quantum efficiency is only *ca.* 2.5%. The p.m. tube is, of course, insensitive to scattered light from the photoflash at $\lambda \gtrsim 650$ nm (fig. 3).

Hence, with the overall system indicated in fig. 1, $Na(3^2S)$ was generated by the photolysis of NaI in the presence of excess buffer gas, depending on the particular third body under investigation, and monitored photoelectrically in the single-shot mode by resonance absorption using the p.m. tube as indicated (E.M.I. 9783 B, p.m. voltage 800 V, Brandenburg p.m. power supply). The photoelectric output signal was amplified without distortion using a

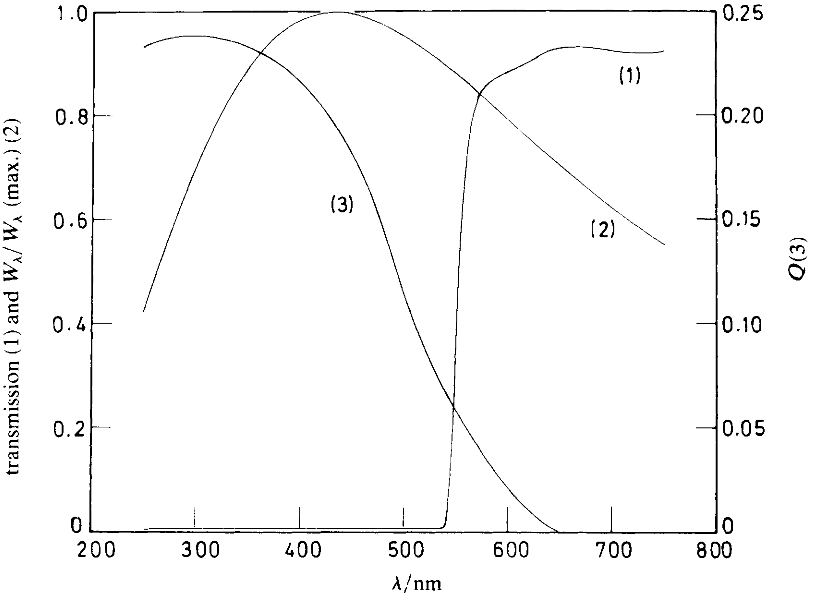

FIG. 3.—Wavelength sensitivity of components employed in the optical detection system of the experimental arrangement for monitoring ground-state sodium atoms at $\lambda = 589$ nm [$Na(3^2P_J) \leftarrow Na(3^2S)$] using attenuation of atomic resonance radiation in the "single-shot" mode following pulsed irradiation. (1) Transmission curve of Wratten filter no. 21; (2) "black-body curve ($W_\lambda/W_{\lambda(\max)}$)" for $T = 6500$ °C for the flash lamp; (3) quantum efficiency of E.M.I. p.m. tube 9783 B.

current-to-voltage converter,[28] captured and digitised in a transient recorder (Data Laboratories DL 905) employed in the "A/B" mode in order to record $I_{tr}(t)$ and I_0(steady) on different time bases, and transferred onto paper tape (Data Dynamics punch 1133) in ASCII code for direct input into the University of Cambridge IBM 370 computer. The oscilloscope (fig. 1) is employed purely for the purpose of visual display of the data.

MATERIALS

For the curve-of-growth measurements, sodium metal was vacuum distilled into a cold side arm in the Pyrex vessel used for generating vapour pressures of atomic sodium at defined elevated temperatures. NaI (solid) was vacuum distilled before use. All other materials (He, Kr, N_2, O_2 and CO_2) were prepared essentially as previously described.[22,29] Gaseous mixtures added to the solid NaI in the reaction vessel were prepared on a vacuum system in the standard manner.

RESULTS AND DISCUSSION

DIFFUSIONAL REMOVAL OF $Na(3^2S)$

The present investigation on the rate of removal of $Na(3^2S)$ by reaction (1) is carried out employing relatively low pressures of O_2 and an excess of the third body, M. Hence the diffusional contribution to the decay rate is governed by the pressure of the third body and this is first investigated by the measurement of k' as a function of p_M in the absence of O_2. Diffusional removal to the walls of the reaction vessel will be manifest by a linear relationship between k' and $1/p_M$.

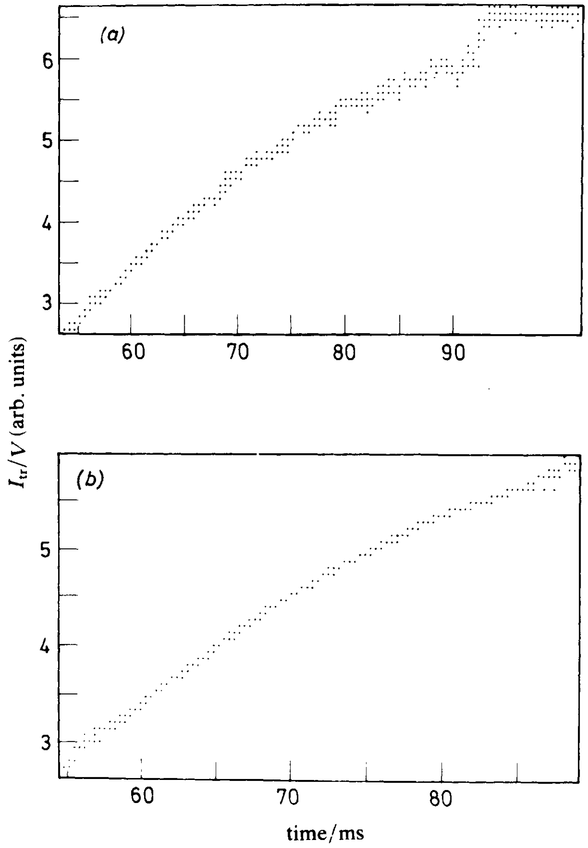

FIG. 4.—Digitised time-variation of the transmitted light intensity at $\lambda = 589$ nm [$Na(3^2P_J \rightarrow 3^2S)$] indicating the decay of resonance absorption by ground-state sodium atoms in the presence of N_2 following the pulsed irradiation of NaI. $E = 125$ J; $T = 724$ K; $p_{N_2} = 100.1$ Torr. (*a*) Rate data with the switch from the "A" to "B" time base of the transient recorder at $t = 92.4$ ms; (*b*) smoothed output for the data of the "A" time base.

Alternatively, the measured first-order decay coefficient, k', in the absence of O_2 may be taken as an empirical correction, *i.e.* the blank, in determining the contribution of reaction (1) to the total, measured value of k'. Fig. 4(*a*) shows an example of the raw data for the digitised time-variation of the computerised output of the photoelectric signal at $\lambda = 589$ nm, indicating the decay of resonance absorption by $Na(3^2S)$ in the presence of N_2. The presentation of the rate data in fig. 4(*a*) illustrates the use of the two time bases of the "A/B" mode, the latter displaying the steady I_0 signal. The output is presented for the long-time component of the decay, in this instance, on account of line saturation in the resonance absorption signal at shorter time. Of course, in the presence of O_2, when the decay of atomic sodium due to reaction (1) is rapid compared with that indicated in fig. 4(*a*) (see later), line saturation effects are shifted to considerably shorter time scales. Fig. 4(*b*) shows the smoothed data, following Savistsky and Golay,[30] of the time-dependent component in fig. 4(*a*), namely, the data from the "A" time base, yielding $I_{tr}(t)$. Purely for contrast at this stage, fig. 5(*a*) and (*b*) indicate the effect

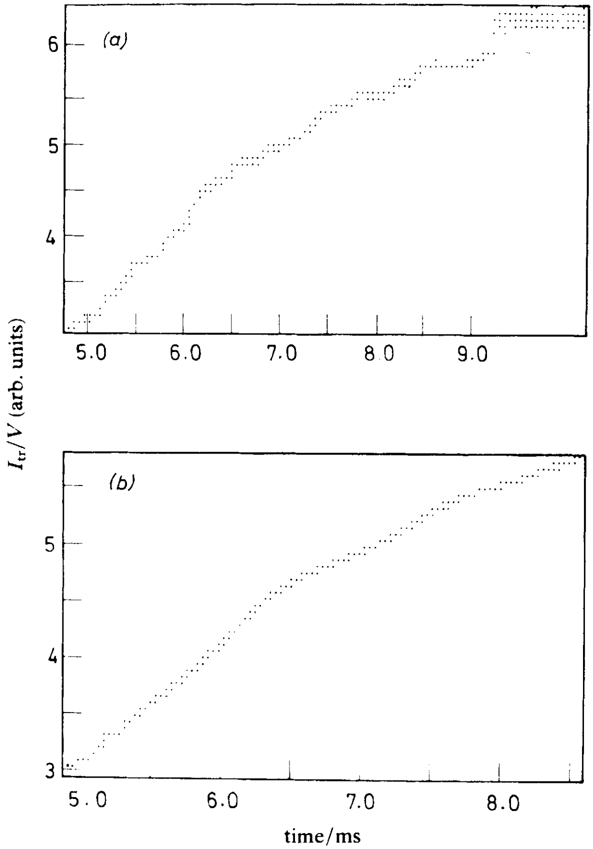

FIG. 5.—Digitised time-variation of the transmitted light intensity at $\lambda = 589$ nm [$Na(3^2P_J \rightarrow 3^2S)$] indicating the decay of resonance absorption by ground-state sodium atoms in the presence of N_2 and O_2 following the pulsed irradiation of NaI. $E = 125$ J; $T = 724$ K; $p_{N_2} = 100.5$ Torr; $p_{O_2} = 20.2$ mTorr. (*a*) Raw data with the switch from the "A" to "B" time base of the transient recorder at $t = 9.24$ ms; (*b*) smoothed output for the data of the "A" time base.

on the decay of $Na(3^2S)$ of the presence of a small pressure of O_2 at essentially the same pressure of N_2. Fig. 6(*a*) shows the first-order kinetic plot for the data of fig. 4(*b*), *i.e.* $\ln[\ln(I_0/I_{tr})]$ ($\lambda = 589$ nm) against time, for the decay of $Na(3^2S)$ in the presence of N_2 alone at the lower temperature employed in these studies ($T = 724$ K). The slope of this plot then yields the first-order decay coefficient, k'. Whilst some of the first-order decays indicate an extent of resonance absorption >40% at shorter times, decaying, of course, into the region where the curve-of-growth indicated clear adherence to the Beer–Lambert law (see earlier), the first-order plots are good across the range investigated. The standard error in the slope of fig. 4(*a*) is 0.3% and, in the intercept, 0.6%. k' was determined as a function of the pressure of nitrogen for $T = 724$ and 844 K. The results are presented in fig. 7(*a*) and (*b*) in the form k' against $1/p_{N_2}$, clearly indicating removal by diffusion as the dominant process in the absence of O_2. One may readily show that the contribution to the removal of $Na(3^2S)$ by atom–atom recombination at typical atomic densities encountered in these measurements, and which are of the order

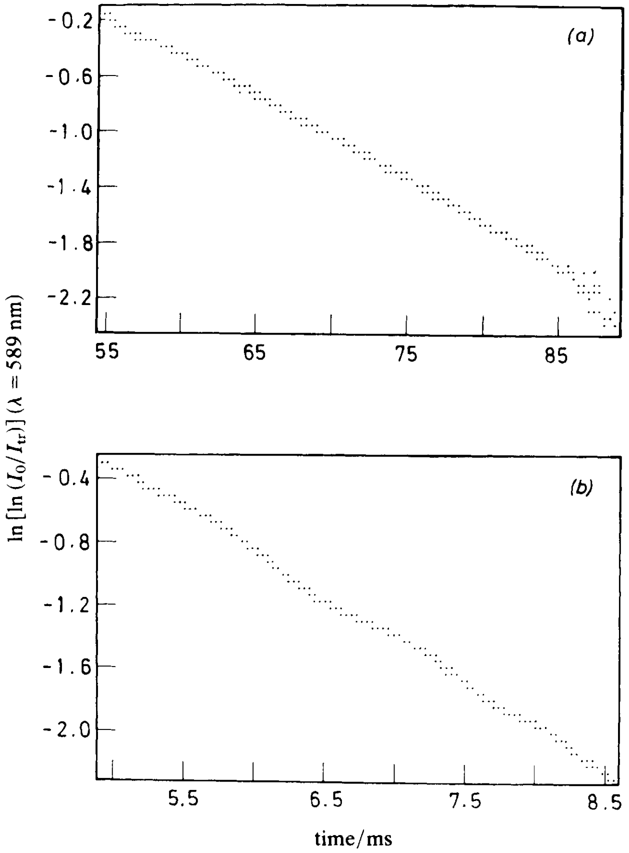

FIG. 6.—Typical pseudo-first-order plots for the decay of ground-state sodium atoms, generated from the pulsed irradiation of NaI, obtained by monitoring atomic resonance absorption at $\lambda = 589$ nm [$\mathrm{Na}(3^2P_J \leftarrow 3^2S)$]. $E = 125$ J; $T = 724$ K; first-order plots constructed from the smoothed digitised data of the "A" time base of the transient recorder. (*a*) $p_{\mathrm{N}_2} = 100.1$ Torr, $p_{\mathrm{O}_2} = 0$ Torr; (*b*) $p_{\mathrm{N}_2} = 100.5$ Torr, $p_{\mathrm{O}_2} = 20.2$ mTorr.

of 10^{10} particles cm^{-3} as estimated from "Doppler–Doppler" line absorption at the resonance transition,[31] is negligible using an assumed physically realistic recombination rate constant. Hence, the values of k' may be taken directly from fig. 7(*a*) and (*b*) to correct for the removal of $\mathrm{Na}(3^2S)$, principally by diffusion, when the atomic decay is monitored in the presence of O_2. Similar plots were constructed at the two temperatures for the decay of $\mathrm{Na}(3^2S)$ in the presence of He and of CO_2. Whilst the slopes of such plots are reproducible, a larger variation in the relatively small values of the intercepts was observed. The average value of an intercept of the plot of the type shown in fig. 7 is of the order of $50\ \mathrm{s}^{-1}$. This, coupled with the value of the rate constant for the reaction between $\mathrm{Na} + \mathrm{I}_2$ reported by Edelstein and Davidovits,[10] would arise from a pressure of molecular iodine of *ca.* 10^{-6} Torr. However, diffusional removal is clearly dominant and, within experimental error, k' in fig. 7, for example, is identified with k_{diff}. For instance, for the data in fig. 7(*a*), the ratio of the intercept to the mean value of k' measured in the range indicated in the plot is *ca.* 5%. In turn, k_{diff} may be described by the

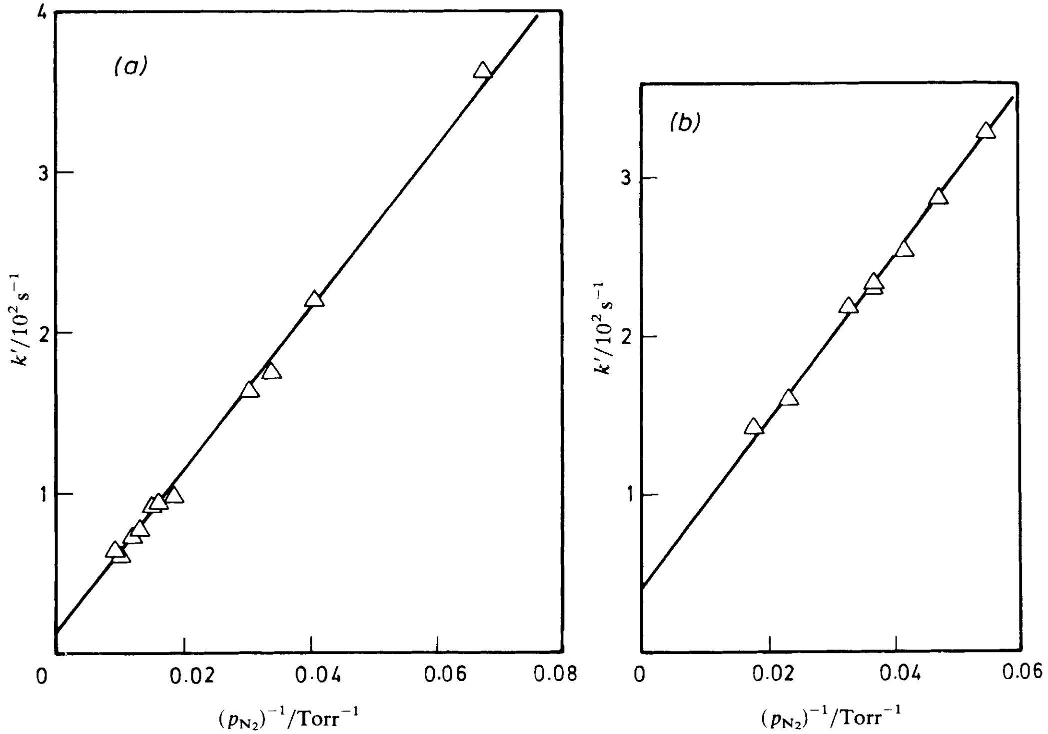

FIG. 7.—(*a*) Variation of the first-order rate coefficient (k') for the decay of Na(3^2S) derived by pulsed irradiation with the reciprocal of the pressure of N_2 to obtain diffusional rate data ($T = 724$ K). (*b*) Variation of the first-order rate coefficient (k') for the decay of Na(3^2S) derived by pulsed irradiation with the reciprocal of the pressure of N_2 to obtain diffusional rate data ($T = 844$ K).

"long-time" solution of the diffusion equation for a cylinder[31,32]

$$k_{\text{diff}} = \left(\frac{\pi^2}{l^2} + \frac{2.41^2}{r^2}\right) D_{12} \qquad \text{(i)}$$

$$\approx \frac{5.81}{r^2} D_{12} \qquad \text{(ii)}$$

as $l^2 \gg r^2$ ($r = 1$ cm in this system). The slopes of fig. 7(*a*) and (*b*) yield values of D_{12} at the appropriate temperatures which, following the standard $T^{3/2}$ dependence, may be used to estimate values of $D_{\text{Na-N}_2}$ at s.t.p. of 0.27 ± 0.01 and 0.21 ± 0.01 cm^2 s^{-1} (2σ), respectively. This may be compared with the value employed by Carabetta and Kaskan[1] of $D_{\text{Na-N}_2}$(s.t.p.) = 0.192 cm^2 s^{-1}, estimated by means of a simple collision theory approach. The average values for the diffusion coefficients for atomic sodium in the upper atmosphere of 1.0×10^5 and 4.2×10^4 cm^2 s^{-1} employed by Kolb and Elgin[6] for heights of 90 and 85 km, respectively, where the total particle densities (M) are reported as 0.63×10^{14} and 1.52×10^{14} particles cm^{-3}, respectively, would yield $D_{\text{Na-N}_2}$(s.t.p.) = 0.158 cm^2 s^{-1} for an average temperature of 180 K.[33] The implicit use of this value was presumably estimated on similar considerations of kinetic theory.[6] Similar linear plots of k'

against $1/p_M$ were obtained for the decay of Na(3^2S) in the presence of He and CO_2 at temperatures of 724 and 844 K. The plots were also used for empirical correction on the data in the presence of O_2 to extract the first-order contribution of reaction (1) from k' (overall). However, despite the good linear plots which then yielded physically realistic values for D_{Na-M} when extrapolating the diffusion data from $T = 844$ K to s.t.p. to give $D_{Na-He} = 0.25 \pm 0.02$ and $D_{Na-CO_2} = 0.30 \pm 0.01$ cm^2 s^{-1}, the values extrapolated to s.t.p. from the data for $T = 724$ K were found to be high ($D_{Na-He} = 0.83 \pm 0.02$ and $D_{Na-CO_2} = 1.15 \pm 0.01$ cm^2 s^{-1}). Mechanistic speculation on the variation of the diffusional removal rate in these two gases is not especially fruitful. It is, however, clear that diffusional removal is dominant and the appropriate correction to k' by k_{diff} may be made empirically at the relevant temperatures to extract the contribution to k' due to reaction (1). It is also worth emphasising that the diffusional behaviour of Na(3^2S) and the magnitudes of the diffusion coefficients generated from the use of the diffusion equation, in reasonable accord with values expected from simple gas kinetic theory, constitute a sensitive test of the present system. The observed diffusional rates for atomic sodium not only provide an internal kinetic check of the present rate measurements but also justify the neglect of any serious complications arising from the photochemistry of sodium iodide.

$Na + O_2 + M$

In view of the atmospheric importance of reaction (1) in the case where $M = N_2$, molecular nitrogen is considered in particular detail in presenting an example of the determination of k_1. The third-order dependence for the removal of Na(3^2S) is clearly established: fig. 6(*b*) gives an example of the overall first-order decay of Na(3^2S) in the presence of O_2 and N_2: fig. 8(*a*) and (*b*) show the linear dependence of k' on p_{O_2} and p_{N_2}, respectively, at $T = 724$ K. To determine k_1, each value of k' in fig. 8(*a*) and (*b*) could be corrected individually for diffusional removal. Alternatively, we may consider the overall data in terms of:

$$k' = k_{diff} + k_1[O_2][N_2] \tag{iii}$$

where the determination of k_{diff} has been described. Hence, a plot of $(k' - k_{diff})/p_{O_2}$ against p_{N_2} yields k_1. The resulting plots for $T = 724$ and 844 K are given in fig. 9(*a*) and (*b*) and yield

$$k_1(M = N_2, T = 724\ K) = (1.1 \pm 0.1) \times 10^{-30}\ cm^6\ molecule^{-2}\ s^{-1} (2\sigma)$$

$$k_1(M = N_2, T = 844\ K) = (1.0 \pm 0.15) \times 10^{-30}\ cm^6\ molecule^{-2}\ s^{-1} (2\sigma).$$

The scatter in these plots primarily arises from the weighting generated by the division of $k' - k_{diff}$ by the necessarily small pressures of O_2 employed. We are unable to detect any significant temperature dependence of k_1 for $M = N_2$ in this range. Kaufman[7] suggests a temperature dependence of the order of T^{-1} to T^{-2}. This latter dependence would only yield $k_1(844\ K)/k_1(724\ K) = 0.7$. The prime immediate conclusion of this work on N_2 is the difference between the result obtained here and the third-order rate data derived from flames by Carabetta and Kaskan[2] where k_1 (flame composition, $T = 1420 - 1600$ K) $= 8.2 \times 10^{-34}$ cm^6 molecule^{-2} s^{-1}. The present result yields a value of k_1 which is approximately three orders of magnitude greater than that expected from extrapolating the flame measurements of Carabetta and Kaskan using, say, a T^{-2} dependence of the rate on temperature. Indeed, we are in accord with an estimate[7] of k_1 derived from

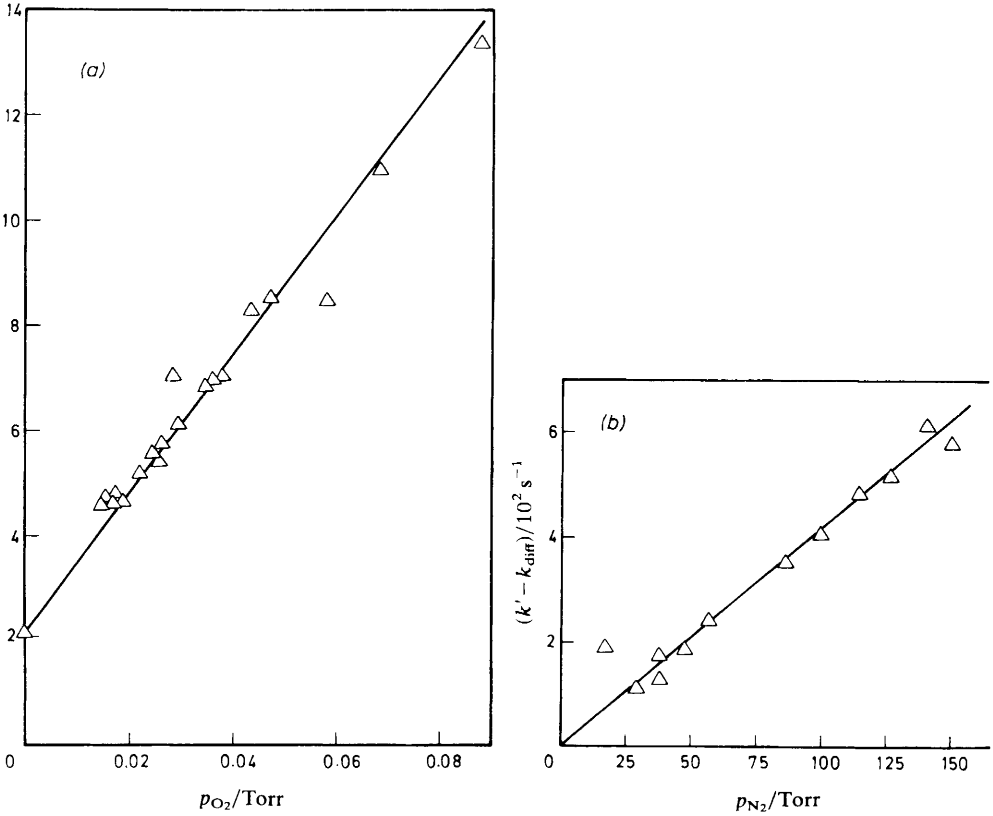

FIG. 8.—(*a*) Variation of the pseudo-first-order rate coefficient (k') for the decay of Na(3^2S) in the presence of O_2 and N_2 (p_{N_2} = 40.2 Torr, T = 724 K). (*b*) Variation of the pseudo first-order rate coefficient ($k' - k_{diff}$) for the decay of Na(3^2S) in the presence of O_2 and N_2 (p_{O_2} = 0.02 Torr, T = 724 K).

the early sodium diffusion flame measurements of Bawn and Evans[34] where $k_1 \approx 10^{-30}$ cm^6 molecule^{-2} s^{-1},[7,34] notwithstanding the suggested complication in the kinetic analysis due to quenching of Na(3^2P) by N_2,[35] nor that Bawn and Evans' experiments were not designed for measurement of k_1. We are in agreement with Kaufman[7] that the value of k_1 resulting from flames[7] is too low for an allowed atom–molcule recombination process. In fact, such a value of k_1 would yield a mean lifetime (τ) for the initially energised NaO_2^* formed on recombination of $\tau \approx 4 \times 10^{-15}$ s which is approximately two orders of magnitude lower than that expected for a diatomic molecule.

The diffusion-corrected first-order rate coefficients for the decay of Na(3^2S) in the presence of O_2 and He showed a clear linear dependence on p_{He}, as indicated, for example, in fig. 10(*a*) for the data at $T = 724$ K. A linear dependence on p_{O_2} at the same temperature is shown in fig. 10(*b*), it clearly being unnecessary to make a correction for the diffusional contribution to the decay of Na(3^2S) for a rate variation at effectively a fixed total pressure. Similar plots were obtained for $T = 844$ K and are not presented here. The values of the third-order rate constants for reaction (1), based on the slopes and conditions of fig. 10(*a*) and the equivalent plot for $T = 844$ K, are $k_1(M = He) = (5.3 \pm 0.2) \times 10^{-31}$ and $(6.7 \pm 0.4) \times 10^{-31}$ cm^6

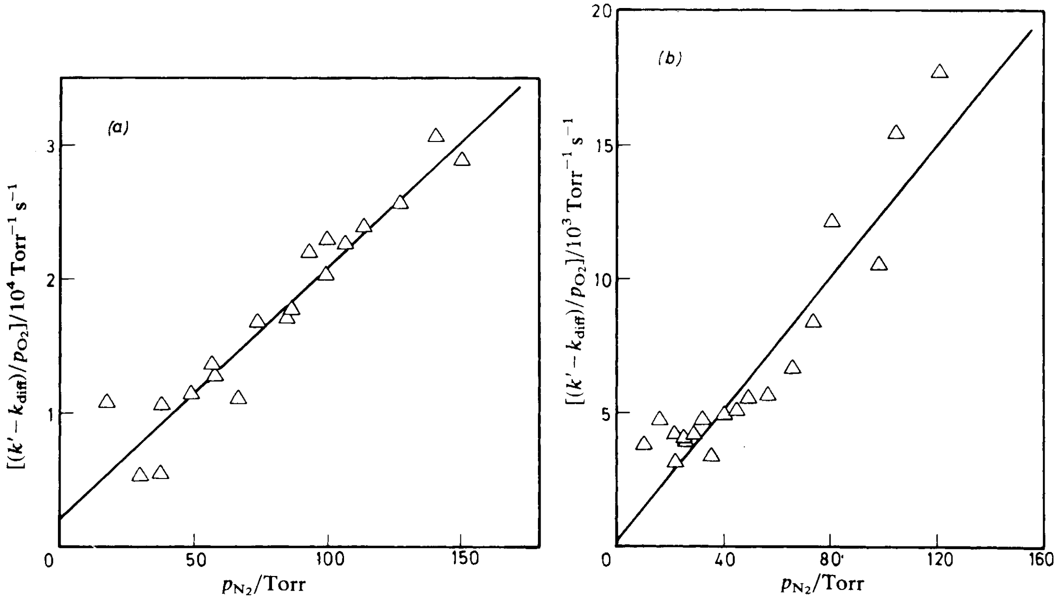

FIG. 9.—(*a*) Plot derived from the variation of the pseudo-first-order rate coefficient (k') for the decay of Na(3^2S) in the presence of O_2 and N_2 indicating overall third-order kinetics for the reaction between Na + O_2 + N_2 (T = 724 K). (*b*) Plot derived from the variation of the pseudo-first-order rate coefficient (k') for the decay of Na(3^2S) in the presence of O_2 and N_2 indicating overall third-order kinetics for the reaction between Na + O_2 + N_2 (T = 844 K).

molecule^{-2} s^{-1} (2σ), respectively. The above data are considered consistent, noting that the principal error arises from the use of low pressures of O_2. No temperature dependence is concluded from these results. The values of k_1(M = He) based on fig. 10(*b*) and the equivalent plot for T = 844 K are $(1.9 \pm 0.2) \times 10^{-30}$ and 9.0×10^{-30} cm^6 molecule^{-2} s^{-1}, respectively. The third-order dependence of reaction (1) on [Na], [O_2] and [He] is established. Any kinetic contribution to the decay of Na(3^2S) apart from reaction (1) and the diffusional contribution will appear in the *intercept* of fig. 10(*a*), for example, but in the *slope* of fig. 10(*b*) for the same temperature. We do not feel that the measurements justify detailed postulation of factors that may account for the effective acceleration of the rate at high [O_2] as, for example, the inclusion in eqn (iii) of a second-order kinetic term of the type $k[O_2]$ would be inconsistent with the thermochemistry [$D_0^0(O_2) = 5.1156$ eV,[36] D(NaO) = 2.6 eV[36,37]]. A bimolecular reaction between Na and O_2 would be characterised by a very large activation energy ($E > 2.5$ eV). Hence, we employ the results from the variation of $k' - k_{diff}$ with p_{He} to yield k_1(M = He, T = 724–844 K) = $(6 \pm 1) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}. The result indicates a rate constant marginally slower than that for M = N_2, as expected for a third-order raction of this type. The results for CO_2 were less consistent. Sensible plots were obtained for the variation of k' with p_{O_2} at the two temperatures [fig. 11(*a*) and (*b*)], yielding from the slopes and the experimental conditions, third-order rate constants with values k_1(M = CO_2, 724 K) = 4×10^{-30} and k_1(M = CO_2, 844 K) = 7×10^{-30} cm^6 molecule^{-2} s^{-1}. However, we have emphasised that bimolecular contributions to the decay of Na(3^2S) other than that due to reaction (1) appear in the slopes of these plots. We were unable to obtain a clear dependence of

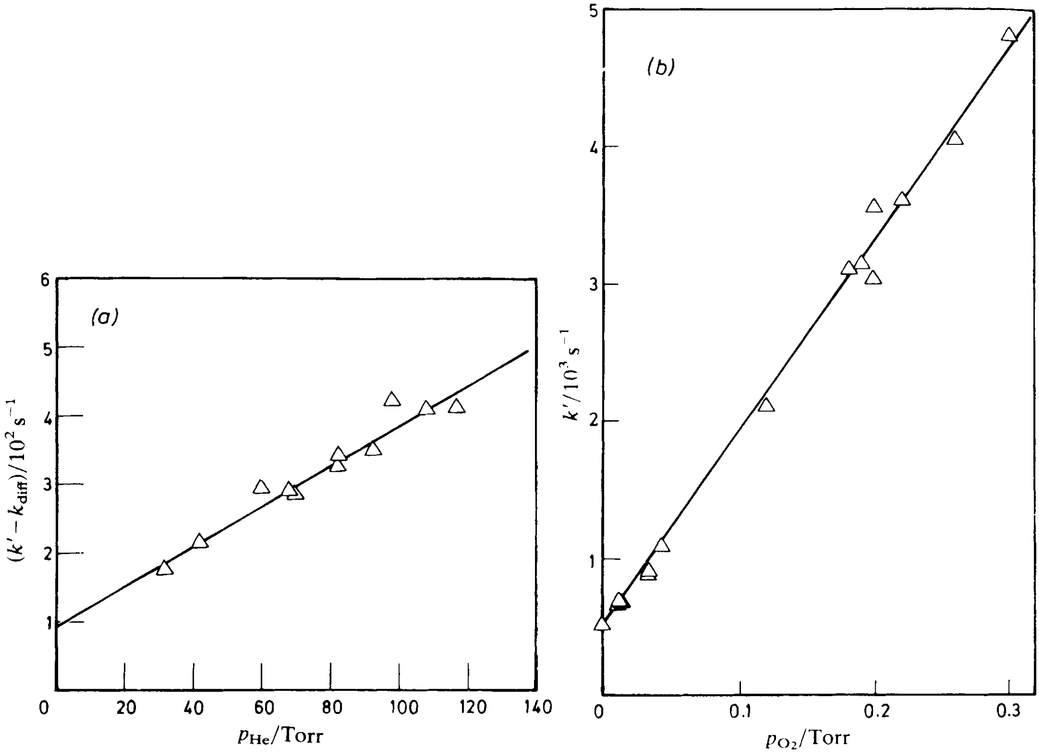

FIG. 10.—(*a*) Variation of the pseudo-first-order rate coefficient $(k' - k_{diff})$ for the decay of Na(3^2S) in the presence of O_2 and He ($p_{O_2} = 30$ mTorr, $T = 724$ K). (*b*) Variation of the pseudo-first-order rate coefficient (k') for the decay of Na(3^2S) in the presence of O_2 and He ($p_{He} = 40.3$ Torr, $T = 724$ K).

$k' - k_{diff}\ p_{CO_2}$ beyond a pressure of *ca.* 30 Torr and there is clearly some complex mechanism operating. From the range $p_{CO_2} = 20 - 30$ Torr, we were able to estimate an average rate constant of $k_1(M = CO_2,\ T = 724\text{–}844\ K) = 2 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} to within a factor of two.

Finally, we may compare the magnitudes of the present results for k_1 with those derived for analogous reactions of Pb (6^3P_0) and Sb ($5^4S_{3/2}$) studied by time-resolved atomic resonance absorption and fluorescence spectroscopy.[15,38-40] In view of the small or negligible temperature dependence, certainly for the reactions investigated here over the limited temperature range of 724–844 K, a comparison with rate data for 300 K is meaningful in terms of magnitudes, which is a prime issue of this paper. The approximate datum value for Bi($6^4S_{3/2}$) [$k_1(M = He) \approx 3 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}][41] is not included in the comparison since third-order kinetics could not be established in the resonance absorption study of Bi($6^4S_{3/2}$) in the presence of O_2 and He,[41] neither could a linear dependence of k' for Bi($6^4S_{3/2}$) on [O_2] be observed.[41] Hence, the comparison here is restricted to the relevant data for Pb(6^3P_0) and Sb($5^4S_{3/2}$) as shown in table 1. The results for Na(3^2S) and Pb(6^3P_0) are very close and the results for Sb($5^4S_{3/2}$) are approximately three times smaller than those for Na(3^2S). All the data in table 1, apart from those describing flame measurements, are consistent with an expected lifetime for an energised triatomic intermediate initially formed on collision of [$\tau_{XO_2}{}^* \approx 10^{-11} - 10^{-10}$ s). Whilst the

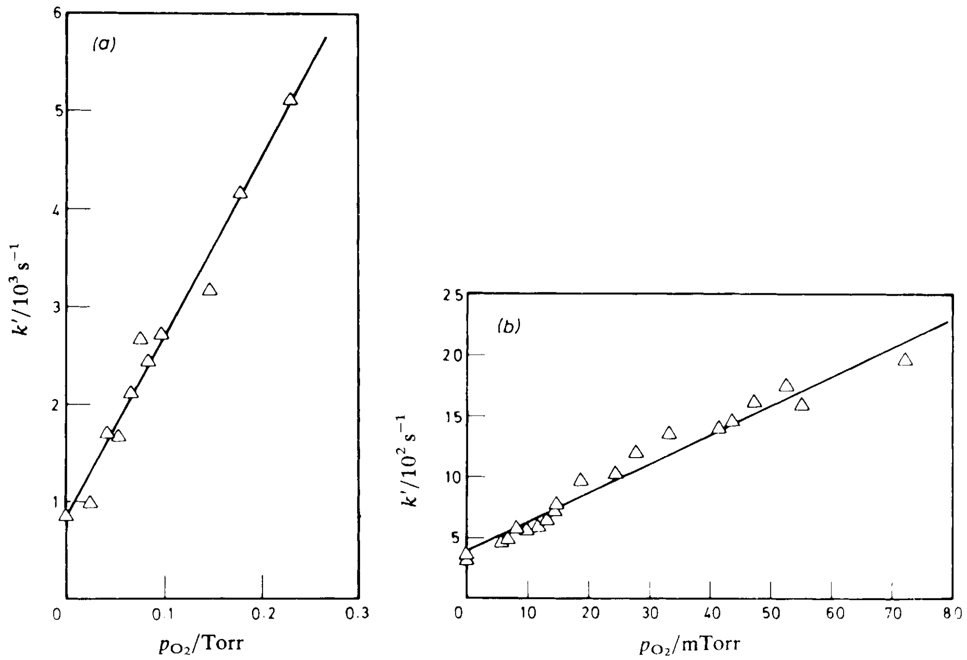

FIG. 11.—(*a*) Variation of the pseudo-first-order rate coefficient (k') for the decay of Na(3^2S) in the presence of O_2 and CO_2 (p_{CO_2} = 26.9 Torr, T = 724 K). (*b*) Variation of the pseudo-first-order rate coefficient (k') for the decay of Na(3^2S) in the presence of O_2 and CO_2 (p_{CO_2} = 26.9 Torr, T = 844 K).

TABLE 1.—COMPARISON OF THIRD-ORDER RATE CONSTANTS ($cm^6\ molecule^{-2}\ s^{-1}$) FOR REACTIONS BETWEEN $X+O_2+M$ (X = Na, Pb, Sb)

X	Na (3^2S)(724–844 K)	Pb (6^3P_0)(300 K)	Sb ($5^4S_{3/2}$)(300 K)
M = He	$(6\pm1)\times10^{-31}$ [a]	$\sim2.0\times10^{-30}$ [c] $\sim2.6\times10^{-30}$ [d]	$(2.2\pm0.2)\times10^{-31}$ [e] $(1.8\pm0.2)\times10^{-31}$ [f]
M = N_2	$(1.0\pm0.2)\times10^{-30}$ [a]	$(1.2\pm0.2)\times10^{-30}$ [c]	$(3.2\pm0.3)\times10^{-31}$ [e]
M = CO_2	2×10^{-30} [a]	$(1.7\pm0.3)\times10^{-30}$ [c] $(2.1\pm0.2)\times10^{-30}$ [d]	
M = flame composition (T = 1420–1600 K)	8.2×10^{-34} [b]		

[a] This work; [b] ref. (2); [c] ref. (15); [d] ref. (38); [e] ref. (39); [f] ref. (40).

kinetic measurements presented here are subject to some limitations, the magnitudes for k_1 and the trend in the values of k_1 for M = He, N_2 and CO_2, the comparison with analogous rate data for other atoms and the magnitudes of the diffusion coefficients resulting from the present investigation are clear. We suggest that the flame measurements on reaction (1) yield values of k_1 which are too low by approximately three orders of magnitude.

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(PAPER 1/976)