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Kinetic Study of the Na + O_2 + He Reaction in the Temperature Range 392–777 K

Chris Vinckier,* An Dumoulin and Stephan De Jaegere
Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

A kinetic study of the reaction $Na + O_2 + He \xrightarrow{k_2} NaO_2 + He$ has been carried out in a fast-flow reactor in the temperature and pressure ranges of, respectively, 392–777 K and 4–14 Torr.† Sodium atoms are generated either by thermal evaporation of sodium metal or by the technique of microwave-induced plasma afterglow atomization. Atomic absorption spectroscopy is used as the detection technique for atomic sodium. A fit of k_2 to the expression $A(T/300)^n$ yields $k_2 = (8.6 \pm 0.7) \times 10^{-31}\ (T/300)^{-1.04\pm0.16}$ cm^6 molecule^{-2} s^{-1}. This rate expression will be compared with kinetic data derived for the above reaction on the basis of time-resolved flash photolysis and excimer laser photolysis measurements. Using the Troe formalism, values of k_2 are calculated in the temperature range 200–2000 K and the importance of the reaction in the burnt-gas region of oxygen-rich flames is discussed.

The relevance of sodium metal atom reactions has been limited for a long time to the interpretation of flame characteristics. In particular, the addition of sodium-containing compounds had a direct application in the sodium line-reversal method for the determination of flame temperatures.[1] Also, the chemiluminescence of alkali-metal atoms has been used as a diagnostic tool for monitoring radical concentrations.[2] In addition, the burnt-gas region of hydrogen–oxygen flames was the only medium for the derivation of kinetic parameters of alkali-metal atom reactions, and especially of Na(^{2}S) atoms.[3–6] Renewed interest has been generated in the combination reaction

$$Na + O_2 + M \rightarrow NaO_2 + M \qquad (1)$$

in view of its importance in the upper atmosphere, where it is considered as a major sink for atomic sodium.[7] Also, the product molecule NaO_2 remains a topic for theoretical calculations, and its structure and bond energy are still under investigation.[8–10]

It has been recognized, however, that the kinetic constants derived from flame data are either incorrect or largely underestimated.[11,12] This is mainly due to a lack of reliable concentration data of a number of flame components and the rather complex reaction mechanism, involving many consecutive and competitive reactions. A large step forwards was the introduction of a simple reaction system in which sodium atoms were generated by pulsed irradiation of NaI vapour.[12–15] The decay of the sodium atoms produced by chemical reaction is then followed by time-resolved atomic resonance absorption. With another technique sodium atoms are produced by thermal evaporation of the sodium metal in a fast-flow reactor.[11] Here the sodium atom decay is monitored as a function of the reaction distance by the laser-induced fluorescence detection technique. With nitrogen acting as a third body a recent evaluation[16] showed the low-pressure limit $k_1(N_2) = (2.4 \pm 0.5) \times 10^{-30}\ (T/300)^{-1.2\pm0.5}$ cm^6 molecule^{-2} s^{-1}, which is the average between the value of $(2.9 \pm 0.7) \times 10^{-30}\ (T/300)^{-1.3\pm0.04}$ cm^6 molecule^{-2} s^{-1} derived by Plane *et al.*[15] and $(1.9 \pm 0.4) \times 10^{-30}\ (T/300)^{1.1\pm0.5}$ cm^6 molecule^{-2} s^{-1} determined by Silver *et al.*[11] Only a few kinetic data are available with other third-body gases such as CO_2,[13] He[11,13] and Ar.[11] On the basis of sodium profile modelling in H_2–O_2–N_2 flames an expression for $k_1 = 1.8 \times 10^{-28}\ T^{-1}$ has been derived[5] in the temperature range 1650–2400 K.

In this work the combination reaction of sodium atoms with molecular oxygen has been investigated in the carrier gas helium:

$$Na + O_2 + He \rightarrow NaO_2 + He \qquad (2)$$

and a temperature and pressure range of, respectively, 392–777 K and 4–14 Torr have been covered. At low temperature thermal evaporation of sodium metal was used as a sodium atom source while at higher temperatures the method of plasma afterglow atomization was employed. The latter system is based on the rapid conversion of a sodium halide in a microwave-induced plasma (MIP) afterglow, containing hydrogen atoms: $NaX + H \rightarrow Na(g) + HX$.[17] Under well defined conditions this atomization process offers an attractive and new source of metal atoms in the gas phase. The derived values for k_2 are compared with the few literature data and the Troe formalism[18,19] is applied to extrapolate k_2 in the temperature range 200–2000 K.

Experimental

Technique

Details of the experimental set-up have been given in an earlier publication[17] and so the essential characteristics will be summarized briefly. The Na + O_2 reaction was investigated in a quartz fast-flow reactor with an internal diameter d of 5.7 cm and a length of 1 m. The flow velocity v was 320 ± 10 cm s^{-1} at 295 K and a reactor oven enabled the whole reactor assembly to be heated to $T_g = 800$ K. The detection of sodium atoms was carried out at 588.9 nm by atomic absorption spectroscopy (AAS). At 500 K the detection limit was 1.1×10^9 atom cm^{-3}, corresponding to a mole fraction of 1.14×10^{-8} at 6 Torr total pressure. Below 550 K the thermal evaporation of sodium metal was used as a source of sodium atoms in the gas phase. Good mixing was achieved when the mixing time was larger than the characteristic diffusion time for a sodium atom to travel a distance r from the centre of the reactor to the reactor wall. This criterion was fulfilled when the dimensionless parameter[20] $vr/2D_{Na,He} < 20$. At a total pressure P of 5 Torr, an average temperature T_g of 500 K and with a diffusion coefficient $D_{Na,He} = 185$ cm^2 s^{-1},[21] this parameter becomes equal to 4.9. Most of the experiments were carried out at this pressure.

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† 1 Torr = 101 325/760 Pa.

At higher temperatures the initial sodium absorbances became too high and the linear relationship between the sodium absorbance A_{Na} and the sodium concentration $[Na_g]$ was lost.[22] Under these circumstances, however, the plasma afterglow atomization[17] offers an attractive alternative source for sodium atoms. A relatively volatile sodium salt such as NaBr(s) or NaCl(s) was thermally evaporated at a temperature T_s and the gaseous molecules were mixed with hydrogen atoms from a microwave-induced plasma. Through the rapid conversion reaction $NaX(g) + H \rightarrow Na(g) + HX$ a flow of sodium atoms in the concentration range $(1\text{–}30) \times 10^9$ atom cm^{-3} could be maintained. Downstream known amounts of molecular oxygen were added through a movable inlet, and the decay of Na(g) atoms was followed as a fraction of the axial distance, z. Pseudo-first-order plots were made using the statistical package SAS[23] available at the University Computing Center. The reported uncertainties on the calculated rate constant are standard deviations.

Procedure

The procedure for deriving kinetic data from flow-tube experiments has been described in detail in the literature,[22,24] and the same mathematical formalism will be used as in our previous work on the gas-phase reaction of copper atoms with molecular oxygen.[25] When the decay of Na atoms is due to both a chemical reaction with O_2 and diffusion to the reactor wall, the natural logarithm of the measured absorbance A_{Na} can be expressed as[22,24,25]

$$\ln A_{Na} = -\left(\frac{k_2[O_2][He]}{\eta} + \frac{7.34 D_{Na,He}}{2r^2}\right)t + B \qquad (I)$$

where k_2 is the third-order rate constant of reaction (2), η is a correction factor which varies between 1 for complete plug-flow conditions and 1.6 when the wall sticking coefficient γ for sodium on the quartz wall is larger than 10^{-2}, and t is equal to the reaction time z/v. The term B is an integration constant and is equal to $\ln A_{Na}$ at $t = 0$.

The value of k_2 can now be determined by two methods. In the first method $\ln A_{Na}$ is followed as a function of the added amount O_2 at constant reaction time. The slope a_1 of this graph allows us to calculate k_2:

$$k_2 = -\eta a_1/[He]t \qquad (II)$$

In the second method $\ln A_{Na}$ is followed as a function of the reaction time. The slope a_2 of this graph is given by

$$a_2 = -\left(\frac{k_2[O_2][He]}{\eta} + \frac{7.34 D_{Na,He}}{2r^2}\right) \qquad (III)$$

A plot of a_2 as a function of $[O_2]$ allows us to calculate k_2 from its slope a_3:

$$k_2 = \eta a_3/[He] \qquad (IV)$$

while the intercept I immediately yields the diffusion coefficient of Na atoms in helium from the relation

$$D_{Na,He} = 2r^2 I/7.34 \qquad (V)$$

It is clear that both methods should yield values for the rate constants which lie within each others error range.

Results

Evaporation of the Sodium Metal

In a first series of experiments $\ln A_{Na}$ was followed as a function of $[O_2]$ at a reaction temperature T_g of 450 K and a pressure of 5 Torr (Fig. 1). Straight lines were obtained for the various reaction times between 12.2 and 24.5 ms. Applying eqn. (II) the rate constants k_2 can be calculated from the slopes from the lines at the various reaction times with the value for η set equal to 1.6 (Table 1). One sees that the reaction time has no systematic influence on k_2, for which an average value of $(6.1 \pm 0.6) \times 10^{-31}$ cm^6 $molecule^{-2}$ s^{-1} is found.

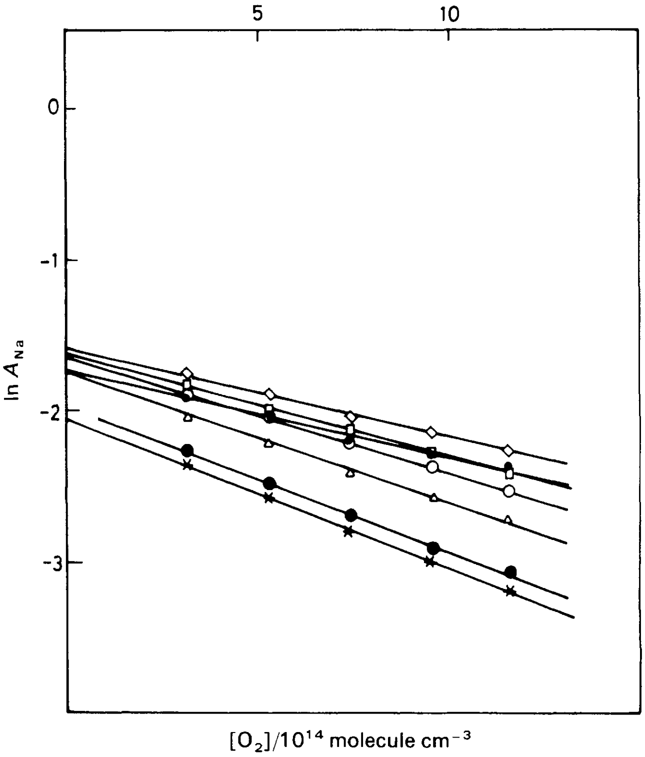

Fig. 1 Logarithm of the Na absorbance A_{Na} as a function of added oxygen at various reaction times. Experimental conditions: reactor pressure $P = 5$ Torr; temperature $T_g = 450$ K; Na source, Na metal evaporation at $T_s = 487$ K; reaction times: ◇, 12.3; □, 14.3; ○, 16.3; •, 18.3; △, 20.4; ●, 22.4 and ✱, 24.5 ms

When the same experimental results are used to make plots of $\ln A_{Na}$ as a function of the reaction time t, reasonably straight lines are obtained for the various oxygen concentrations, as expected from the results shown in Table 1. The slopes a_2 of these lines are now plotted *vs.* $[O_2]$ (Fig. 2). Using eqn. (IV) the value of k_2 can be calculated from $a_3 = (4.2 \pm 0.40) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. With $\eta = 1.6$, one obtains $k_2 = (6.3 \pm 0.6) \times 10^{-31}$ cm^6 $molecule^{-2}$ s^{-1}, which is in good agreement with the value of $(6.1 \pm 0.6) \times 10^{-31}$ cm^6 $molecule^{-2}$ s^{-1} derived with the first method. From the intercept I, which is equal to 57 ± 2.8 s^{-1}, the diffusion coefficient $D_{Na,He}$ at 450 K and 5 Torr can be calculated using eqn. (V): $D_{Na,He} = 126.1 \pm 6.2$ cm^2 s^{-1} or 630 ± 31 cm^2 Torr s^{-1}. With the expression given in the literature[21] for

Table 1 Values of k_2 calculated from the sodium decay as a function of added oxygen[a]

t/ms	$k_2/10^{-31}$ cm^6 $molecule^{-2}$ s^{-1}
12.2	7.1 ± 0.3
14.3	5.2 ± 0.4
16.3	6.3 ± 0.3
18.3	6.1 ± 0.1
20.4	6.1 ± 0.2
22.4	6.3 ± 0.2
24.5	5.9 ± 0.2
	$k_2^{av} = 6.1 \pm 0.6$

[a] Temperature T_g and pressure P were respectively, 450 K and 5 Torr. The Na source was Na metal evaporation.

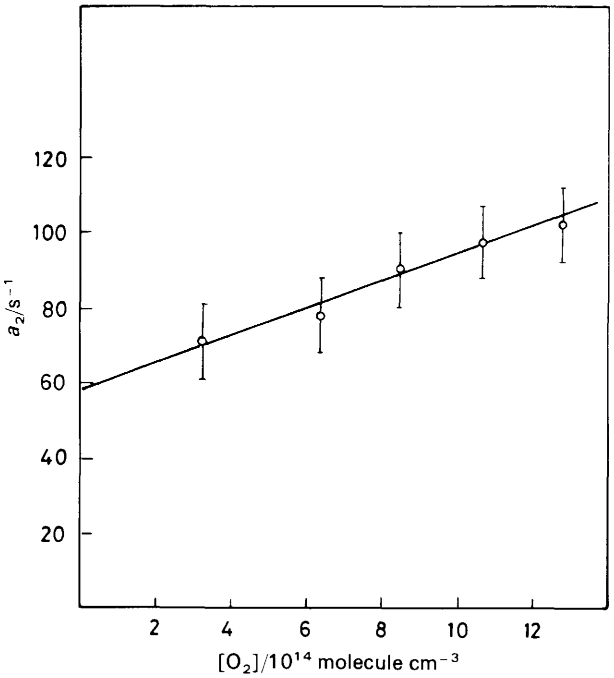

Fig. 2 Pseudo-first-order rate constant a_2 [eqn. (III)] plotted *vs.* added oxygen. Same experimental condition as in Fig. 1

$D_{Na,He} = (385 \pm 40)\ (T/300)^{1.72 \pm 0.18}$ cm^2 Torr s^{-1}, and which was derived for the 211–424 K temperature range, one finds $D_{Na,He}$ at 450 K to be equal to 770^{+148}_{-138} cm^2 Torr s^{-1}. Although our value for $D_{Na,He}$ may only be seen as a first approximation, it lies within the error limits calculated from the above expression. This result clearly shows that, in addition to chemical reaction with O_2, wall loss of the sodium atoms is important and that the sticking coefficient γ must be of the order of unity. Under these circumstances plug-follow conditions are not realized, and the use of $\eta = 1.6$ in eqn. (I)–(IV) is warranted.

By means of an additional heating element, the temperature of the sodium metal can be increased and so the evaporation is enhanced. By varying the temperature between 529 and 542 K, the initial sodium atom concentration goes from 8.2×10^9 to 9.0×10^{10} atom cm^{-3}. From the decay of ln A_{Na} as a function of $[O_2]$, the rate constant k_2 could be derived at 417 K. It was found that the initial Na atom concentration has no noticeable effect on k_2, the average value of which is $(6.6 \pm 0.6) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} at 417 K.

We also have determined the values for k_2 at 4 and 10 Torr and at a temperature T_g of 517 K. This time the temperature of the sodium pellet had to be kept at $T_s = 515$ K, which is nearly the reaction temperature. From the pseudo-first-order decay of the sodium concentration as a function of time, the values of a_2 could be calculated and are plotted *vs.* $[O_2]$ in Fig. 3. From the slopes a_3 of both lines the values for k_2 can be calculated and are equal to $(5.2 \pm 0.2) \times 10^{-31}$ and $(5.0 \pm 0.4) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} at, respectively, 4 and 10 Torr, which proves that in this region k_2 is independent of the pressure. This is expected in view of the findings of Silver *et al.*,[11] which indicate that with a maximum helium concentration of 2×10^{17} atom cm^{-3} the rate constant k_2 reaches its low pressure limit within 10%.

Plasma Afterglow Atomization

As mentioned above, the MIP afterglow atomization was used as a Na atom source at temperatures higher than 700 K. The sodium thermal evaporation source cannot be used here, since the atomic sodium fluxes at 700 K would lead to absorbances much higher than 1. In a first series of experiments the decay of Na atoms was followed as a function of added oxygen at various reaction times. The experimental conditions were as follows: the reactor pressure was 5 Torr, the amount of hydrogen added to the microwave-induced plasma was 0.2 mTorr, the microwave power was 100 W and the temperature T_g was 733 K, with T_s of NaBr equal to 772 K. The pseudo-first-order plots are shown in Fig. 4. The rate constant k_2 can now be derived by applying eqn. (II) to the slopes a_1 of the straight lines. We have now taken the value for η in eqn. (II) equal to 1.3, and the systematic uncertainty is estimated to be *ca.* 10%, as discussed extensively by Fontijn and Felder.[22,26] Indeed, since most of the lines have more or less the same intercept, the initial Na atom concentration is only a slight function of the reaction time and thus of the axial distance z. Under these conditions the Na atom loss to the reactor wall will be controlled by γ instead of by diffusion, as will be shown later. The values of k_2 obtained are given in Table 2.

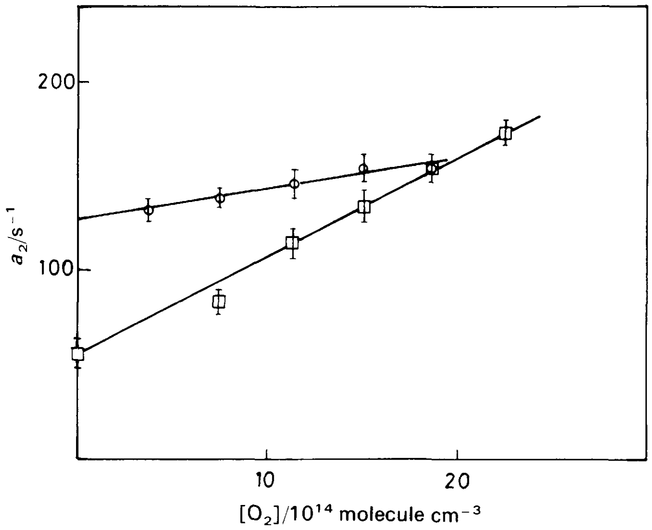

Fig. 3 Pseudo-first-order rate constant a_2 [eqn. (III)] plotted *vs.* added oxygen. Experimental conditions: temperature $T_g = 517$ K; reactor pressure: ○, 4; and □, 10 Torr; Na source, Na metal evaporation at $T_s = 515$ K

One clearly sees that the reaction time has no effect on k_2, the average value of which is given by $k_2^{av} = (3.4 \pm 0.35) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} at $T_g = 733$ K. The same experimental data are further used to plot ln A_{Na} as a function of reaction time. The slopes a_2 of these lines plotted *vs.* $[O_2]$ are shown in Fig. 5. A linear regression through the weighted points yields an intercept of 23.1 ± 23.4 s^{-1} and a slope of $1.5 \pm 0.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The reason for the rather poor quality of this plot must be attributed to the relatively small timescale between 8.8 and 13.8 ms over which the decay of Na atoms was followed. This leads to uncertainties of *ca.* 25% on the pseudo-first-order decay constants a_2. However, these uncertainties have their major impact on the intercept I of the line in Fig. 5 and not so much on the slope. Although the value of I carries an error margin of 100% and is thus not suited for the calculation of the sticking coefficient γ of Na atoms on quartz, it offers sufficient evidence that the Na atom loss is certainly not diffusion-controlled. Using the mathematical expression for $D_{Na,He}$ mentioned earlier in this paper, $D_{Na,He}$ at 5 Torr and 733 K can be calculated and is equal to 358 cm^2 s^{-1}. This would lead to a diffusion pseudo-first-order decay constant of $7.34\ D_{Na,He}/2r^2 = 161$ s^{-1}, which is much larger than observed. In view of the uncertainty on the magnitude of the

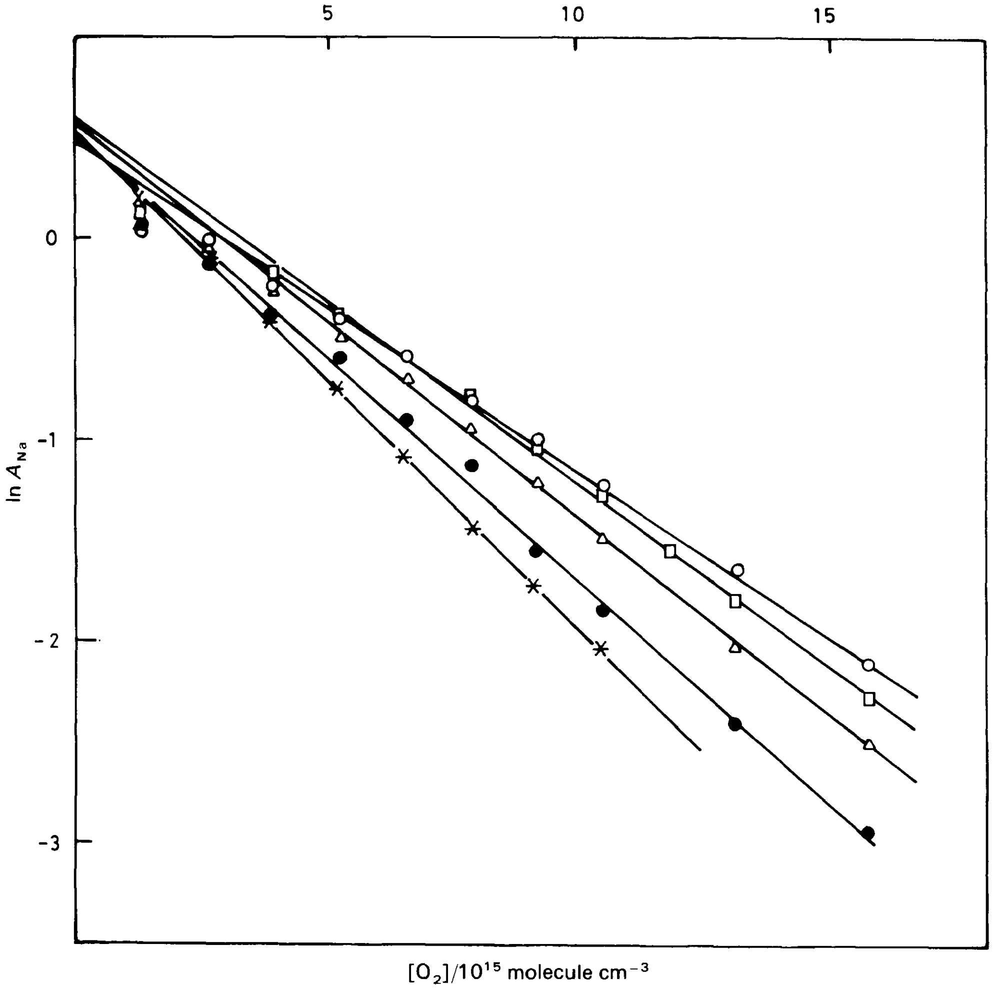

Fig. 4 Logarithm of the Na absorbance A_{Na} as a function of added oxygen at various reaction times. Experimental conditions: reactor pressure $P = 5$ Torr; temperature $T_g = 733$ K; Na source, MIP afterglow atomization of NaBr at $T_s = 772$ K; reaction times: ○, 8.8; □, 10.1; △, 11.3; ●, 12.6 and ✱, 13.9 ms

wall losses, the value of $\eta = 1.3$ will be used as a correction factor in eqn. (IV) for the derivation of k_2 at temperatures above 700 K. From the slope a_2 of the line from Fig. 5, one obtains $k_2 = (2.9 \pm 0.3) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}. This value is about 20% lower than k_2 calculated from the data given in Table 2. We suggest the use of the average value $k_2^{av} = (3.2 \pm 0.3) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} at 733 K.

In order to check whether the initial Na atom concentration has an effect on k_2, the hydrogen content of the microwave plasma was varied between 1.2 and 9.1×10^{12} molecule cm^{-3}. The experimental conditions were as follows: the reactor pressure $P = 6$ Torr, the gas temperature T_g was 777 K and the temperature of the NaBr pellet was $T_s = 818$ K. It was found that a variation of the initial Na atom concentration by a factor of 5 between 2.1×10^9 and 11×10^9 atom cm^{-3} has no effect on the rate constant, the average value of which was $k_2^{av} = (2.2 \pm 0.3) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}. Interference of other plasma afterglow products such as H_2 and HBr with the kinetics of the Na + O_2 reaction did not

Table 2 Values of k_2 calculated from the Na atom decay as a function of added oxygen[a]

t/ms	$k_2/10^{-31}$ cm^6 molecule^{-2} s^{-1}
8.9	3.5 ± 0.35
10.1	3.5 ± 0.35
11.3	3.4 ± 0.35
12.6	3.4 ± 0.35
13.8	3.4 ± 0.35
	$k_2^{av} = 3.4 \pm 0.35$

[a] The reactor pressure P and temperature T_g were, respectively, 5 Torr and 733 K. The Na source was MIP afterglow atomization of NaBr.

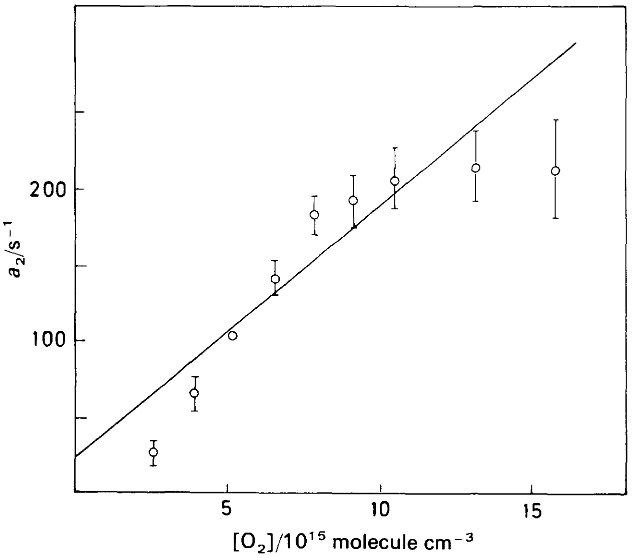

Fig. 5 Pseudo-first-order rate constant a_2 [eqn. (III)] plotted *vs.* added oxygen. Same experimental conditions as in Fig. 4

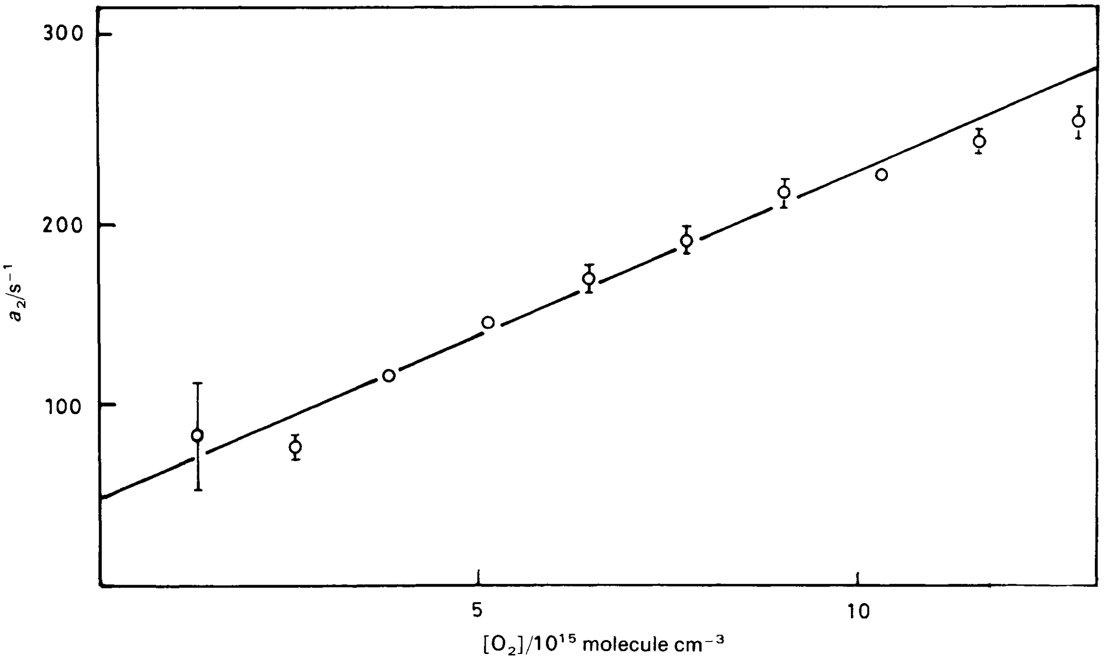

Fig. 6 Pseudo-first-order rate constant a_2 [eqn. (III)] plotted *vs.* added oxygen. Experimental conditions: reactor pressure P = 5 Torr; temperature T_g = 746 K; Na source, MIP afterglow atomization of NaCl at T_s = 788 K

seem to be a problem. This was confirmed in a separate experiment in which NaBr(s) was replaced by NaCl(s). The experimental conditions were as follows: the reactor pressure was 5 Torr, 0.1 mTorr H_2 was added to the MIP afterglow, and the reactor temperature T_g was 746 K. In order to achieve a sufficiently high Na atom concentration, the solid NaCl(s) had to be brought to 788 K by means of the sample heater. The pseudo-first-order rate constant a_2 is plotted *vs.* $[O_2]$ in Fig. 6. From the slope the value of k_2 was found to be $(3.4 \times 0.6) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}, which lies in the range of values derived in the NaBr + H system. This confirms again that the nature of the anion X of the metal compound MeX used as metal source in the plasma afterglow atomization technique is not critical for the derivation of reaction rate parameters.[25]

Finally, the effect of helium pressure on the value of k_2 has been verified. The MIP afterglow contained 0.2 mTorr hydrogen and the reaction temperature T_g was 759 K. The results are shown in Table 3. One sees that the rate constants at 5 and 6.5 Torr tend to be somewhat higher than in the 8–14 Torr range. This will be taken into account by a standard deviation of 27% on the average value of $k_2 = (3.2 \pm 0.8) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}.

Temperature Dependence of the Na + O_2 + He Reaction

The values of k_2 determined in this work in the temperature range 392–777 K are listed in Table 4 and compared with other literature data in Fig. 7. Assuming the formalism for this third-order rate constant $k_2(T) = A(T/300)^n$, a weighted non-linear regression on our data gives the expression $k_2 = (8.6 \pm 0.7) \times 10^{-31}\ (T/300)^{-1.04 \pm 0.16}$ cm^6 molecule^{-2} s^{-1}. When compared with the expression $k_2 = (1.4 \pm 0.3) \times 10^{-30}\ (T/300)^{-0.9 \pm 0.5}$ cm^6 molecule^{-2} s^{-1} derived by Silver *et al.*,[11] one sees that the exponent n of the temperature factor is similar and close to -1, but our A factor is about 40% lower. There is no direct explanation for this discrepancy, especially since the fast-flow reactor technique was used by both groups.

Table 3 Determination of k_2 at various pressures[a]

P/Torr	$k_2/10^{-31}$ cm^6 molecule^{-2} s^{-1}
5	3.9 ± 0.8
6.5	4.5 ± 0.7
8	3.1 ± 0.6
10	2.4 ± 0.3
12	2.5 ± 0.3
14	2.7 ± 0.3
	k_2^{av} = 3.2 ± 0.8

[a] The reaction temperature T_g was 759 K. The Na source was MIP afterglow atomization of NaBr.

Table 4 Values of k_2 at various temperatures

T/K	$k_2/10^{-31}$ cm^6 molecule^{-2} s^{-1}	P/Torr	metal atom source[a]
392	6.0 ± 0.2	5	me
417	6.6 ± 0.6	5	me
431	5.8 ± 0.6	5	me
450	6.2 ± 0.6	5	me
517	5.1 ± 0.1	4–10	me
717	2.6 ± 0.6	5	pa
733	3.2 ± 0.3	5	pa
746	3.4 ± 0.6	5	pa
759	3.2 ± 0.8	5–14	pa
777	2.2 ± 0.3	6	pa

[a] me, metal evaporation; pa, MIP afterglow atomization.

It is interesting to compare the value of k_2 with the kinetic data derived for the Na + O_2 reaction with N_2 acting as a third body. The combined results of Plane *et al.*[15] and Fontijn *et al.*[27] cover a wide temperature range from 233 to 1513 K and are also shown in Fig. 7. One can calculate from these experimental data that the third-body efficiency of nitrogen in the temperature interval between 250 and 800 K is a factor of 3.2 ± 0.4 higher than that of helium.

In order to extrapolate the values of k_2 in the temperature range 200–2000 K use is made of the so-called Troe formalism as described in the literature.[18,19] Since this type of calculation and selection of the input parameters has already been extensively discussed in the literature for the reaction Na + O_2 + N_2,[12,15] it will not be repeated here. Only the slightly different Lennard-Jones parameters $\sigma_{NaO_2/He}$ = 3.95 Å

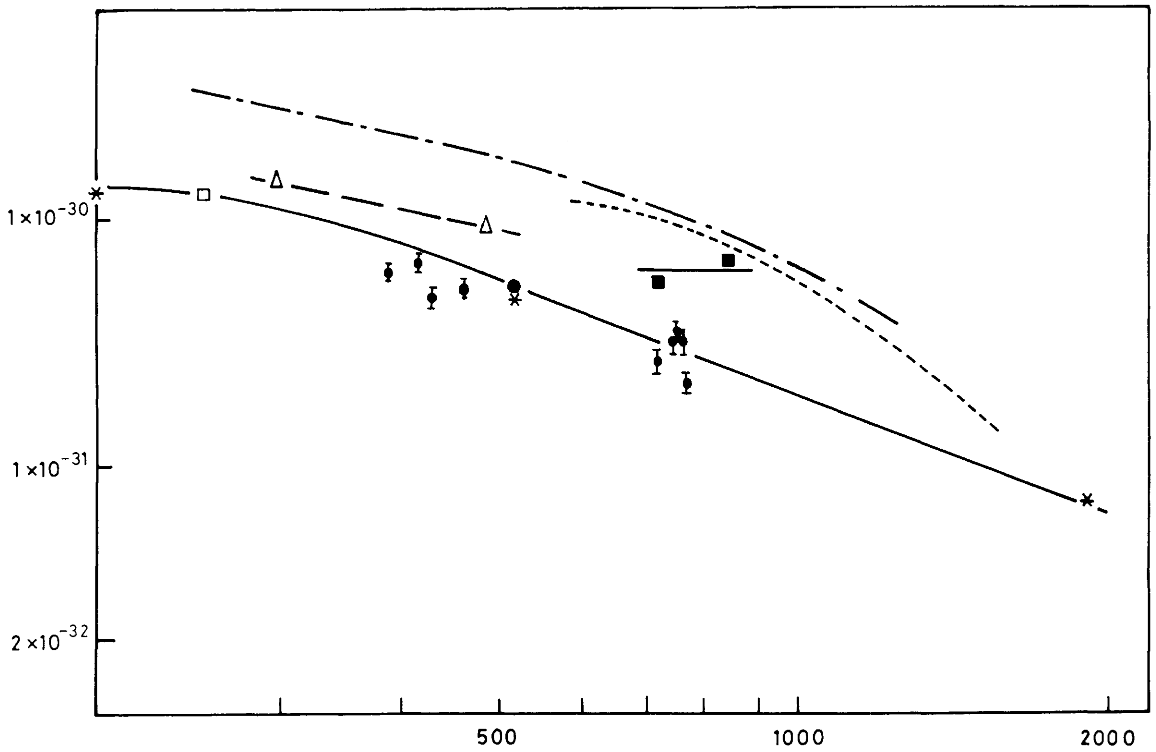

Fig. 7 Logarithm of the rate constant k_2 *vs.* the logarithm of the temperature: □, Plane *et al.*;[15] △, Silver *et al.*;[11] ■, Husain *et al.*;[12] ⧳, our data; ✱, k_2 calculated with the Troe formalism. The kinetic data for the reaction Na + O_2 + N_2 are also shown: (– · – · –) Plane *et al.*;[15] (· · · ·) Fontijn *et al.*[27]

and $\varepsilon/k_{NaO_2/He}$ = 150.4 K will now be used, since the collision partner for the NaO_2 complex is now helium instead of nitrogen.

The results of the calculation are summarized in Table 5. If we take 733 K as the reference temperature in our temperature interval one sees that the collision efficiency β_c is equal to 0.10 and the average energy $-\langle\Delta E\rangle$ transferred by a collision between NaO_2 and He is 1.06 kJ. Compared to the value of $-\langle\Delta E\rangle = 3.15$ kJ when nitrogen acts as a third body, it is of course logical that helium is a less effective species for collisional quenching than nitrogen. In addition the values of β_c and $-\langle\Delta E\rangle$ for the Na + O_2 + He reaction are close to $\beta = 0.12$ and $-\langle\Delta E\rangle = 1087$ kJ derived by Husain *et al.*[28] for the similar reaction Na + OH + He at 653 K.

In order to extrapolate k_2 in the range 200–2000 K a fit was made of the $-\langle\Delta E\rangle$ values as a function of temperature, resulting in the relation $-\langle\Delta E\rangle \sim T^{0.47}$. This relation allowed us to estimate $-\langle\Delta E\rangle$ (and thus also β_c) values at 200, 250 and 2000 K. The results are also shown in Table 5, and the solid line passing through the asterisks in Fig. 7 shows the best fit through these calculated values. The extrapolation to lower temperatures shows an excellent agreement with the value of k_2 determined at 250 K by the technique of pulsed photolysis of a sodium salt followed by time-resolved laser-induced fluorescence detection.[15] This single measurement yields $k_2 = (1.2 \pm 0.2) \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}, compared to the value 1.19×10^{-30} cm^6 molecule^{-2} s^{-1} obtained from the Troe extrapolation. It should be mentioned here that the above calculations are performed with the value $E_0 = 170$ kJ mol^{-1} for the threshold energy of NaO_2, as was determined in oxygen-rich flames.[29] Changing this value to 202 kJ mol^{-1} as suggested by Plane *et al.*[10,15] has a negligible effect of < 10% on the extrapolated rate constants.

Even with a threshold energy $E_0 > 230$ kJ mol^{-1} the effect

Table 5 Extrapolation from 200 to 2000 K using the Troe formalism[a]

T/K	$k_2^{exp}/10^{-31}$ cm^6 molecule^{-2} s^{-1}		$k_2^{sc}/10^{-30}$ cm^6 molecule^{-2} s^{-1}		β_c		$-\langle\Delta E\rangle$/J
200	13.2[b]	←	8.31	←	0.16[b]	←	514[b]
250	11.9[b]	←	7.48	←	0.16[b]	←	571[b]
							↑
392	6.0		4.92		0.12		617
431	5.8		4.54		0.13		754
517	5.1		3.98		0.13		912
733	3.2		2.96		0.10		1063
759	3.3		2.94		0.11		1111
777	2.2		2.92		0.08		725
							↓
2000	0.61[b]	←	1.06	←	0.058[b]	←	1517[b]

[a] k_2^{sc} is the strong-collision rate constant, β_c is the collision efficiency for energy transfer and $-\langle\Delta E\rangle$ is the average amount of energy transferred per collision. [b] Calculated values using the extrapolation $-\langle\Delta E\rangle \sim T^{0.47}$.

on the temperature dependence of k_2 is minor. With $E_0 \approx 240$ kJ mol^{-1}, as suggested by Steinberg *et al.*,[30] the calculated values of k_2 are 25% higher at the utmost. This can of course be expected, since the exponential terms E_0/RT in the unimolecular decomposition rate constant and the equilibrium constant cancel out.

Finally, it is worthwhile to investigate the possible role of the $Na + O_2 + M$ reaction in the burnt-gas zone, especially of hydrogen–oxygen–nitrogen flames. With a value of k_1 equal to 8.2×10^{-34} cm^6 $molecule^{-1}$ s^{-1}, as derived from flame studies,[31] the recombination reaction of Na atoms with oxygen could only play a minor role in the overall sodium chemistry. This should of course change in view of the much larger values of k_1 and even k_2. This can best be illustrated for a number of oxygen-rich or -lean H_2–O_2–N_2 flames listed by Hynes *et al.*[5] and where Na atom profiles have been taken in the downstream zone between 0.25 and 4 ms. One may assume that the third-body efficiency of M is at least equal to that of helium atoms in order to estimate the upper limit of the lifetime of Na atoms. With the rate constant $k_2 = 6.2 \times 10^{-32}$ cm^6 $molecule^{-2}$ s^{-1} at 2000 K and the lowest O_2 concentration of 5.1×10^{16} molecule cm^{-3}, the pseudo-first-order destruction constant k'_2 becomes equal to $k_2[M][O_2] = 1.42 \times 10^4$ s^{-1}, and thus the average lifetime of the Na atoms is at the utmost 7×10^{-5} s. On the other hand, the lifetime of NaO_2 can be calculated from the equilibrium constant of reaction (2): $K_c = 8.37 \times 10^{-20}$ cm^3 $molecule^{-1}$ at 2000 K. Using $\beta_c = 0.058$ from Table 5 one arrives at a dissociation rate constant $k_{-2} = 4.3 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, yielding a pseudo-first-order destruction constant for NaO_2 of $k_{-2}[M] = 1.9 \times 10^6$ s^{-1} or a lifetime of 0.52 μs. From the above results it is evident that the average chemical lifetime of the Na atoms and NaO_2 molecules is orders-of-magnitude lower than the residence time in the burnt-gas zone, which is of the order of milliseconds. This allows us to conclude that even with helium acting as a third body, the reaction $Na + O_2 + He \rightleftharpoons NaO_2 + He$ will be balanced, and thus *a fortiori* this will also be the case in flames with N_2, H_2O *etc.* as third-body partners. This finding corroborates the very important role of NaO_2 as reported by Hynes *et al.*[5] in the complex mechanisms governing sodium chemistry in oxygen-rich H_2–O_2–N_2 flames.

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