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Kinetics and Chemiluminescence in the Reaction of N Atoms with O_2 and O_3

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Room-temperature rate constants for the reactions

$$N+O_2 \rightarrow NO+O \qquad (1)$$

$$N+O_3 \rightarrow NO+O_2 \qquad (2)$$

have been measured using the discharge flow chemiluminescence technique. Values obtained are

$$k_1 = (8.8 \pm 0.4) \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_2 = (1.0 \pm 0.2) \times 10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

Visible and near-i.r. emissions were observed on adding O_2 or O_3 to a flow of N atoms, but neither reaction (1) nor reaction (2) appears to be the source of the chemiluminescence. Further experiments were conducted to elucidate the excitation mechanisms. Chemiluminescence from electronically excited NO and O_2 was observed and mechanisms for the formation of these species are proposed.

Two reactions of atomic nitrogen

$$N+O_2 \rightarrow NO+O \qquad (1)$$

$$N+O_3 \rightarrow NO+O_2 \qquad (2)$$

are potentially important sources of NO in the upper atmosphere;[1] consequently, many kinetic studies of reaction (1) have been made[2-6] and its rate constant (at least at room temperature) is well established. The kinetics of reaction (2), however, have only been investigated by three groups of workers.[7-9] Room-temperature measurements alone have been made, and the results are shown in table 1. There are clearly considerable discrepancies between the measured rate constants. The currently accepted view[10] follows that of Stief *et al.*,[9] who were only able to measure an upper limit for k_2. Stief suggested that the much higher values for k_2 reported by other workers were a result of H-atom impurities in their systems.

The main study of chemiluminescence in these reaction systems was performed by Garvin and Broida.[11] They looked at the emission spectrum of O_3 added to a stream of N atoms. A number of emitting species were observed in the visible and near-i.r. ($\lambda \leqslant 900$ nm) regions. However, chemiluminescence was only observed if traces of H atoms were present.

The initial aim of this work was to study chemiluminescence in reactions (1) and (2). While investigating emission from these systems, work was undertaken to measure k_1 and k_2.

Experimental

Materials

Helium, nitrogen and oxygen were supplied by BOC and were further purified. Helium and nitrogen were passed through an 'Oxisorb' cartridge (Messer-Griesheim) to remove

Table 1. Determinations of k_2

workers	k_2/cm^3 molecule^{-1} s^{-1}
Chen and Taylor[7]	1.67×10^{-14}
Phillips and Schiff[8]	5.70×10^{-13}
Stief *et al.*[9]	$\leqslant5\times10^{-16}$
this work	1.0×10^{-16}

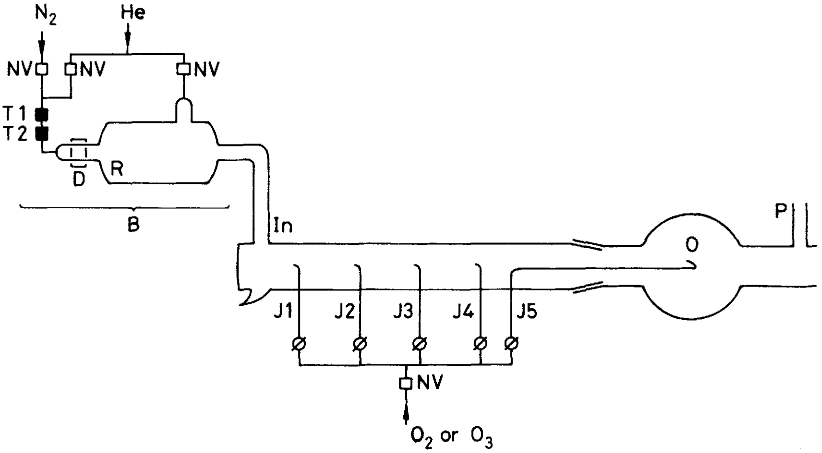

Fig. 1. Schematic diagram of the apparatus. B, discharge bypass; D, discharge cavity; In, atom inlet to flow tube; J1–J5, fixed injectors; NV, needle valve; O, observation region; P, pressure port; T1, molecular-sieve trap; T2, glass-wool trap.

oxygen and water vapour, a P_2O_5 drying tower and a molecular-sieve trap cooled to 195 K. Oxygen was dried by passing through a P_2O_5 column and a molecular-sieve trap cooled to 195 K.

Nitric oxide was supplied by BOC at a stated purity of 99.5%. The gas was further purified by trap-to-trap distillation to remove NO_2 and N_2O_3. Ozone was prepared by passing oxygen through a silent electric discharge (Argentox model GLX10 ozoniser). The product was adsorbed onto silica gel at 195 K. After excess oxygen had been pumped off, ozone (*ca.* 80%) was desorbed into a storage bulb (5 dm^3) suitably protected against explosion. The ozone purity was determined by measuring its optical absorption at $\lambda = 254$ nm.

Apparatus

Fig. 1 shows a schematic diagram of the apparatus used in this work. It consisted of a conventional discharge flow system combined with a system for detection of chemiluminescence. The flow tube was built from borosilicate glass of 3 cm diameter and was *ca.* 60 cm long. Time resolution was achieved by injecting reactants through one of the five fixed injectors. The observation region was a glass sphere of 9 cm diameter. The sphere was wrapped in aluminium foil to enhance light collection efficiency.

Nitrogen atoms were produced by passing N_2 in an He carrier through a microwave discharge. In order to minimize impurities formed in the discharge, only *ca.* 5% of the He carrier was passed through it. The remaining 95% was added to the flow downstream in the recombination volume, which consisted of a 20 cm long glass tube of 5.5 cm diameter. In a further effort to exclude impurities from the apparatus, all gases entering the discharge were first passed through traps of molecular sieve and glass wool, cooled to 77 K, on the low-pressure side of the metering needle valves.

Gas flow rates were measured using capillary flow meters. For N_2, He and O_2 the backing pressure was kept constant at 1 atm† by means of a di-n-butyl phthalate bubbler, while for NO and O_3 pressures were measured by electronic spoon gauges built in this laboratory.[12] The flow tube pressure was measured using an oil manometer. Absolute concentrations of N atoms were determined by using the N+NO titration reaction.

Detection Systems

A number of detection methods were used in this work. For visible emission studies and the kinetics of reaction (1) an S20 photomultiplier (EMI model 9558B) was used in conjuction with a monochromator (Applied Photophysics, $f/3.4$; Czerny Turner configuration). For the determination of k_2 the photomultiplier was used with a Wratten filter no. 8 to cut out interfering emission from NO. In both of these arrangements, a small piezo-electric chopper was used to modulate the signal, which was then processed by a Brookdeal 9501D lock-in amplifier before being displayed on a strip chart recorder.

For work in the near-infrared region ($800 \leqslant \lambda/\text{nm} \leqslant 1600$) an intrinsic germanium detector built by McLaren and Wayne[13] was used with one of two optical arrangements. The detector was used either with a monochromator followed by signal processing as described above, or with a Fourier transform instrument. The F.t. machine was developed in this laboratory by Biggs *et al.*[14] and resulted in considerable improvements in the signal-to-noise ratio and the resolution when compared to the monochromator.

Absolute concentrations of $O_2(^1\Delta_g)$ were determined by comparing the $O_2(^1\Delta_g)$ emission intensity at 1.27 μm with that of the O+NO chemiluminescence intensity at that wavelength. From the known Einstein A coefficient for O_2 $(^1\Delta_g)$ and the known emission rate constant for the chemiluminescence in the O+NO reaction, concentrations of $O_2(^1\Delta_g)$ could be measured. The method is well known and has recently been described by Choo and Leu.[15]

Basis of the Method

k_1 and k_2 were determined by measuring the decrease in N-atom concentration as a function of time in the presence of excess reagent (O_2 or O_3). Typically, initial N-atom concentrations would be between 5×10^{13} and 5×10^{14} molecule cm^{-3}, whereas reagent concentrations would be as high as 3×10^{16} molecule cm^{-3}. Because the rate of N-atom loss is pseudo-first-order under these conditions, it is only necessary to measure relative concentrations of N. Measurement of relative N-atom concentrations was achieved by monitoring the emission resulting from the recombination of N atoms. The emission is of the first positive band system of N_2 and extends from $\lambda = 500$ nm into the infrared. The intensity of the emission is proportional to the square of the concentration of N atoms.[16] Thus, the square root of the intensity can be used as a relative measure of the concentration of N atoms.

Results

Kinetic Experiments

$N+O_2$

On addition of O_2 to a stream of N atoms, reaction (1) is followed by the very fast reaction

$$N+NO \rightarrow N_2+O; \qquad k_3 = 3.4 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.^{10} \qquad (3)$$

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† 1 atm = 101 325 Pa.

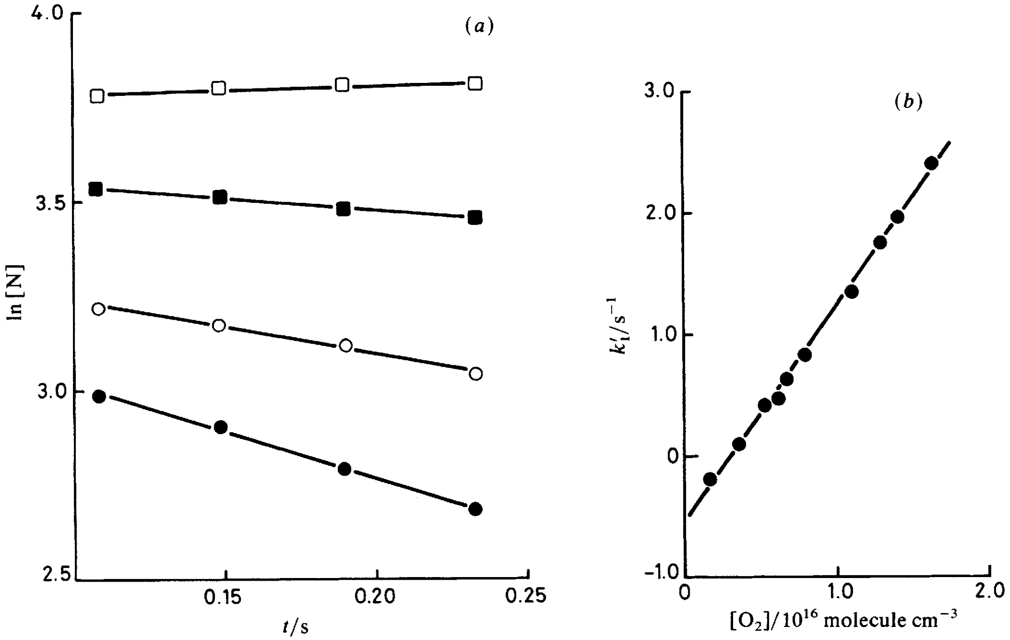


Fig. 2. (*a*) Atomic nitrogen concentration as a function of time for the reaction $N+O_2$. □, $[O_2]=1.60\times10^{15}$ molecule cm^{-3}; ■, $[O_2]=6.82\times10^{15}$ molecule cm^{-3}; ○, $[O_2]=1.10\times10^{16}$ molecule cm^{-3}; ●, $[O_2]=1.64\times10^{16}$ molecule cm^{-3}. (*b*) Pseudo-first-order rate constant (k_1') *vs.* $[O_2]$ in the reaction of N with O_2.

As a result, the rate of loss of N atoms is twice that expected from reaction (1) alone. A plot of ln [N] as a function of time is shown in fig. 2(*a*). The slope, k_1', is given by

$$k_1'=2k_1[O_2]+\Delta k_w$$

where Δk_w is the change in the N-atom wall-loss rate constant on addition of oxygen. Plotting k_1' as a function of $[O_2]$ gives a straight line of gradient $2k_1$. Fig. 2(*b*) shows such a plot. From the slope we obtain

$$k_1=(8.8\pm0.4)\times10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

The latest NASA recommendation[10] for k_1 is

$$k_1=(8.90\pm2.0)\times10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

(quoted error ≈1 standard deviation).

The value for k_1 obtained in our work is in excellent agreement with this recommendation.

$N+O_3$

Adopting the same approach used for the reaction with O_2, we can obtain a value for k_2; however, the ozone used always has some oxygen present. Consequently, the rate of loss of N atoms is a result of contributions from both reactions (1) and (2). Plots of ln [N] as a function of time therefore give pseudo-first-order rate constants, k_2'

$$k_2'=2[(1-p)k_1+pk_2][O_3]+\Delta k_w$$

where p is the fractional purity of the ozone. A plot of k_2' as a function of $[O_3]$ is shown

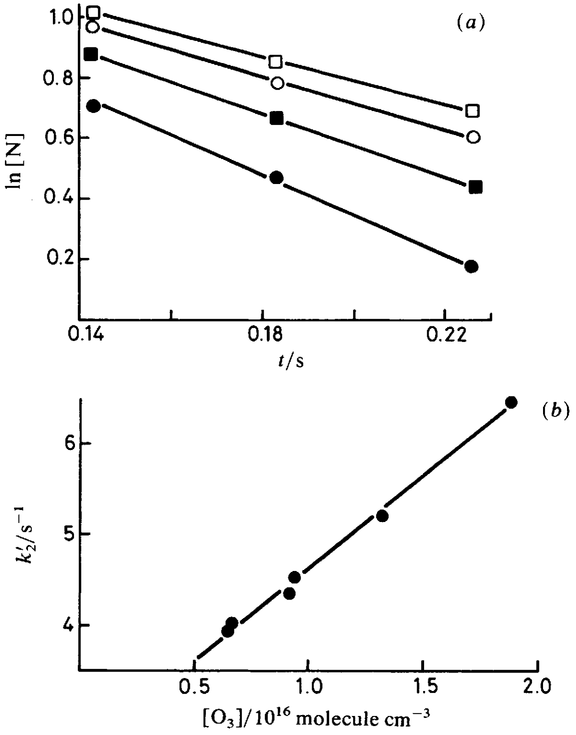


Fig. 3. (*a*) Atomic nitrogen concentration *vs.* time for the reaction $N+O_3$. Ozone purity 85%. □, $[O_3]=6.50\times10^{15}$ molecule cm^{-3}; ○, $[O_3]=9.30\times10^{15}$ molecule cm^{-3}; ■, $[O_3]=1.32\times10^{16}$ molecule cm^{-3}; ●, $[O_3]=1.89\times10^{16}$ molecule cm^{-3}. (*b*) Pseudo-first-order rate constant (k_2') *vs.* $[O_3]$ in the reaction of N with O_3.

in fig. 3. From the value of the slope k_2 is easily calculated and the value obtained is

$$k_2=(1.0\pm0.2)\times10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

This value for k_2 is consistent with the upper limit determined by Stief *et al.*[9]

The Effect of Impurities

Table 1 shows that the previously published values or limits for k_2 are not self-consistent. Stief *et al.*[9] suggested that the high values of k_2 measured by Chen and Taylor[7] and by Phillips and Schiff[8] could be due to the loss of N atoms in a catalytic cycle, initiated by H-atom impurities formed in the discharge, the reactions being

$$H+O_3 \rightarrow OH+O_2;\ k_4=2.9\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ {}^{10} \tag{4}$$

and

$$N+OH \rightarrow NO+H;\ k_5=4.2\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.{}^{17} \tag{5}$$

However, although this cyclic process would make a contribution to the loss of N, it can only affect our derived value of k_2 if the loss efficiency increases with increasing $[O_3]$. Removal of OH by the (Pyrex) flow-tube walls constitutes the main chain-breaking step. At low $[O_3]$, the catalytic cycle would be effective in removing N only at short contact times and would make a negligible contribution to the measured loss of N atoms.

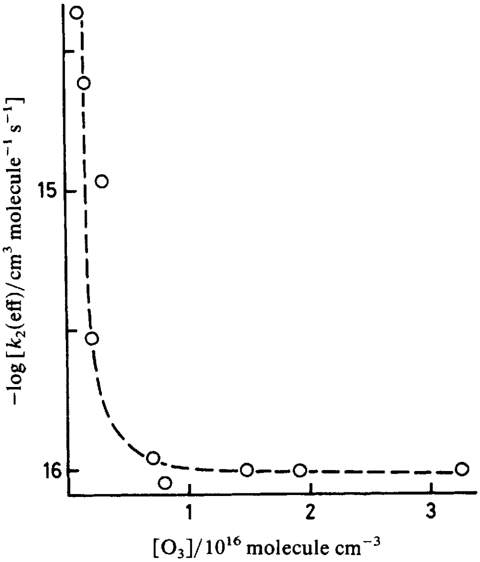


Fig. 4. Plot of −log [k_2(eff)] *vs.* [O_3].

At higher [O_3], the cylic processes

$$OH + O_3 \rightarrow HO_2 + O_2;\ k_6 = 6.8 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ {}^{10} \tag{6}$$

$$N + HO_2 \rightarrow NO + OH;\ k_7 = 2.2 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ {}^{17} \tag{7}$$

provide a mechanism for retaining 'odd' hydrogen (H, OH, HO_2), because HO_2 is lost at the walls much more slowly than OH,[18] as well as providing an additional loss of N in reaction (7). While reaction (6) is in competition with heterogeneous loss of OH, the rate of consumption of N in reactions (5) and (7) will be [O_3]-dependent. If, on the other hand, reaction (6) completely dominates over wall loss of OH, then [O_3] affects only the partitioning of odd hydrogen between the radical species. Given the comparable rate coefficients for reactions (5) and (7), further increases in [O_3] will have a weak influence on the impurity-mediated catalytic loss of N at the same time that the direct consumption of N by O_3 in reaction (2) increasingly swamps any other losses.

According to this reasoning, we expect higher values of k_2 to be measured at low ozone concentrations than we do at higher concentrations. In this work, effective values of k_2, k_2 (eff), were measured for different concentrations of ozone. Fig. 4 shows a plot of $-\log_{10}[k_2(\text{eff})]$ *vs.* [O_3]. For high concentrations of ozone ([O_3] $\geq 5 \times 10^{15}$ molecule cm^{-3}), k_2(eff) is independent of [O_3]. It is in this concentration range that the measured loss rate of N atoms reflects solely the reaction of N atoms with O_3.

Similar effects to those described in the previous paragraphs are observed when measuring k_1, but they are not so serious. The reaction corresponding to reaction (4) in the N + O_2 system is

$$H + O_2 + M \rightarrow HO_2 + M;\ k_8 = 5.5 \times 10^{-32}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}.\ {}^{10} \tag{8}$$

At the pressures used in this work (*ca.* 5 Torr†), k_8 [M] is *ca.* 10^4 times smaller than the rate coefficient for reaction (4).[10] Nevertheless, if precautions were not taken to remove water from the system, non-linear decay plots were recorded, and these would

† 1 Torr = 101 325/760 Pa.

result in anomalously high values of k_1 if they were assumed to be linear. The increased rate of loss of N atoms can be explained qualitatively by the scheme

$$H+O_2+M \rightarrow HO_2+M \qquad (8)$$

$$N+HO_2 \rightarrow NO+OH \qquad (7)$$

$$N+OH \rightarrow NO+H. \qquad (5)$$

The important points about this sequence of reactions are that N atoms are removed by the presence of H atoms and that H atoms are regenerated. Non-linearity in pseudo-first-order plots can occur because for low extents of reaction there is an acceleration of rate with time as more H atoms are converted to HO_2 and OH.

Errors

Errors quoted for the values of k_1 and k_2 are 95% confidence limits and reflect the precision of the measured data. As well as these statistical errors, there are also systematic errors caused by the errors in calibration of, for example, capillary flow meters. These systematic errors are estimated at *ca.* 15%.

Studies of Chemiluminescence

Fig. 5 shows the spectra of the visible (*a*) and near-i.r. (*b*) emissions from the reaction of N atoms with O_2. Very similar spectra were obtained from the reaction of N atoms with O_3. The strongest emission comes from vibrational overtone transitions of OH. That these bands are observed is corroborative evidence that H atoms are the cause of the unusual kinetic measurements described above. It would appear that, in the reaction of N atoms with O_2, O atoms produced by reactions (1) and (3) react with O_2 to give O_3, which then reacts with H to give vibrationally excited OH:

$$H+O_3 \rightarrow OH(v\leqslant 9)+O_2. \qquad (4a)$$

However, we also have some evidence that the reaction

$$N+HO_2 \rightarrow NO+OH(v\leqslant 10) \qquad (7a)$$

may be a source of vibrationally excited OH, and work is now being undertaken to explore further this possibility.

What is clear is that because of the short lifetime of the species, the reaction generating vibrationally excited OH must occur in the observation region: *i.e.* H atoms (or 'odd' H) must be regenerated down the length of the flow tube.

The peak at $\lambda = 1223$ nm is attributed to the $NO(C\,^2\Pi \rightarrow A\,^2\Sigma^+)$ transition and the emission at $\lambda = 1268$ nm is due to the $O_2(a\,^1\Delta_g \rightarrow X\,^3\Sigma_g^-)$ transition. In the visible spectrum, emission is seen from the first positive system of N_2 and from the β bands $(B\,^2\Pi \rightarrow X\,^2\Pi)$ of NO.

It is well known[19] that NO $(B\,^2\Pi)$ and $NO(C\,^2\Pi)$ are formed in the combination of N atoms with O atoms:

$$N+O(+M) \rightarrow NO(B\,^2\Pi, C\,^2\Pi)(+M). \qquad (9)$$

This reaction seems the most plausible mechanism for the formation of excited NO in both the $N+O_2$ and $N+O_3$ reactions. Reactions such as (1), (2) and (5) are not energetically capable of populating the *C* state of NO. For the $N+O_2$ system, computer simulations were run using the simple kinetic scheme shown in table 2. It was possible to match measured relative intensities of emission as a function of time and $[O_2]$ quite well using this computer model (see fig. 6).

The mechanism for the formation of $O_2(a\,^1\Delta_g)$ is not clear. However, when trying to measure concentrations of $O_2(a\,^1\Delta_g)$ as a function of time or of $[O_2]$ it was found

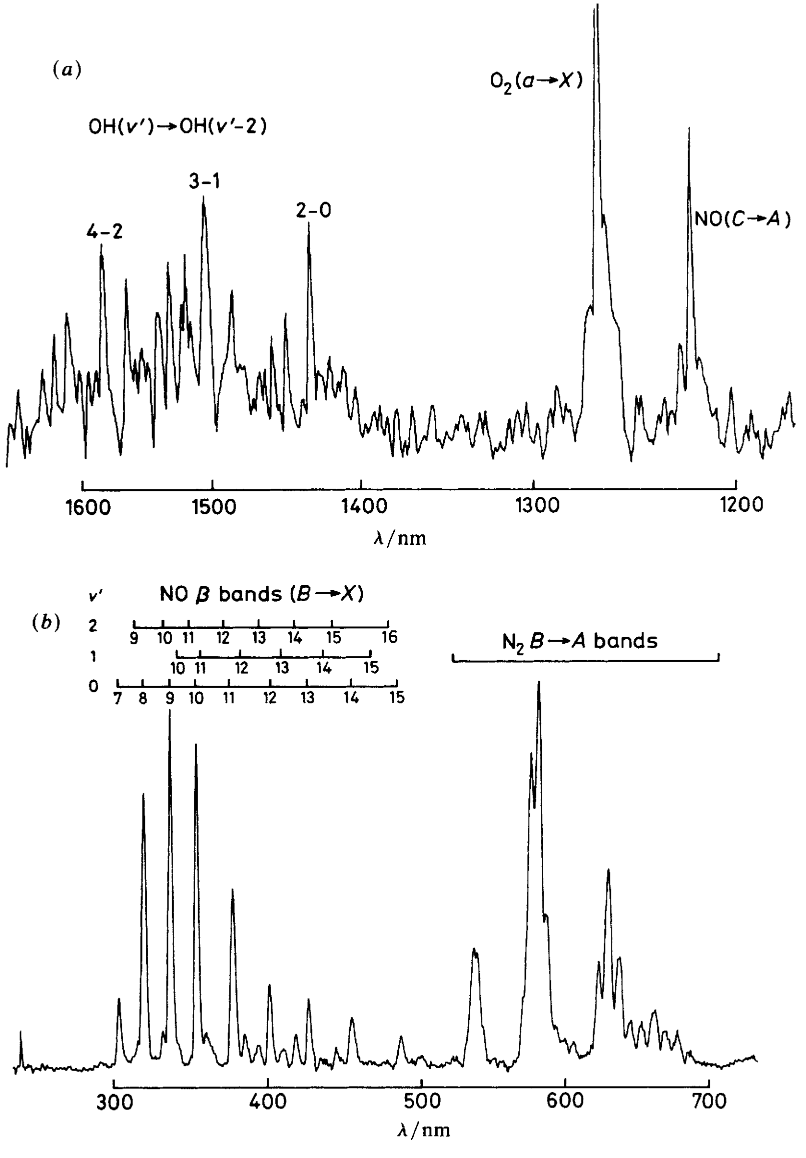


Fig. 5. Chemiluminescence from the $N+O_2$ system. (*a*) Near-infrared region, (*b*) visible region.

that experiments were difficult to repeat from day to day. Further, when efforts were made to eliminate H atoms, $O_2(a\,^1\Delta_g)$ disappeared completely. It therefore seems that $O_2(a\,^1\Delta_g)$ is generated by a mechanism involving H atoms.

In the reaction of N atoms with O_2 two possible mechanisms are:

mechanism (1*a*):

$$H+O_2+M \rightarrow HO_2+M \qquad (8)$$

$$H+HO_2 \rightarrow H_2+O_2(a\,^1\Delta_g) \qquad (10)$$

mechanism (1*b*):

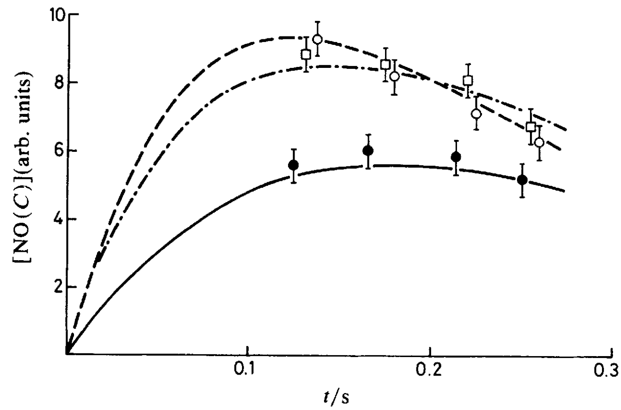
$$H+O_2+M \rightarrow HO_2^*+M \qquad (8a)$$

$$HO_2^*+O_2 \rightarrow O_2(a\,^1\Delta_g)+HO_2. \qquad (11)$$

Table 2. Kinetic scheme for modelling of NO($C\ ^2\Pi$) in the reaction of N atoms with O_2

reaction	rate constant[a]	ref.
$N+O_2 \rightarrow NO+O$	8.8×10^{-17}	this work
$N+NO \rightarrow N_2+O$	3.4×10^{-11}	10
$N+O \rightarrow NO(C)$	1.5×10^{-17}	19
$N \rightarrow$ wall	1.7	this work
$O \rightarrow$ wall	2.9	this work
$NO(C) \rightarrow NO+h\nu$	5.8×10^{7}	19

[a] Units for bimolecular reactions are cm^3 molecule^{-1} s^{-1}, and for unimolecular reactions they are s^{-1}.



$[N]_0$[a]	$[O_2]$[b]	experiment	computer simulation
3.70	5.7	●	(———)
3.70	11.7	□	(— - —)
3.53	15.6	○	(— —)

[a] Units are 10^{14} molecule cm^{-3}. [b] Units are 10^{15} molecule cm^{-3}.

Fig. 6. NO($C \rightarrow A$) emission as a function of time. Comparison of computer simulations with experiment.

Mechanism (1*a*) is that proposed by Washida *et al.*[20] to interpret their experiments on the $H+O_2$ system. It is difficult to explain the results of this study in terms of mechanism (1*a*). Washida *et al.* suggested that 5% of reaction (10*a*)

$$H+HO_2 \rightarrow H_2+O_2 \qquad (10a)$$

would result in $O_2(a\ ^1\Delta_g)$. As there are a number of other loss processes for H atoms in this system (wall loss, and indirectly by reactions of OH) not more than a small fraction of H atoms could actually lead to $O_2(a\ ^1\Delta_g)$ formation. In fact, concentrations of $O_2(a\ ^1\Delta_g)$ can be as high as 5×10^{12} molecule cm^{-3}, whereas Clyne and Nip[21] suggest that $[H]=10^{12}$ molecule cm^{-3} might be expected in this type of system.

Mechanism (1*b*) has the advantage that no odd H is lost in forming $O_2(a\ ^1\Delta_g)$. The reverse of reaction (11) has been investigated by Podolske and Johnston.[22] A statisticalmechanical argument suggests that the forward reaction would have a rate constant

$$k_{11} = 1.2 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Computer models of the system using this value of k_{11} show that mechanism (1*b*) can give the concentrations of O_2 ($a\ ^1\Delta_g$) observed. However, by altering the unknowns, it is possible to get concentrations of $O_2(a\ ^1\Delta_g)$ ranging over several orders of magnitude. Trying to fit the experimental data using computer simulation did not seem to be a fruitful course to take, especially bearing in mind the variability in the intensity of emission from $O_2(a\ ^1\Delta_g)$ under supposedly constant conditions.

A third possibility is that a branch of reaction (7) leads to $O_2(a\ ^1\Delta_g)$:

$$N + HO_2 \rightarrow NH + O_2(a\ ^1\Delta_g). \tag{7b}$$

Reaction (7) is very fast ($k_7 = 2.2 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ [17]) and presumably proceeds adiabatically. Consideration of the energetics of reaction and the symmetry correlation for a planar transition state suggest that if the products were O_2 and NH, then the O_2 could be formed in either the $^1\Delta_g$ or the $^3\Sigma_g^-$ state. When Brune *et al.*[17] studied this reaction, they were unable to detect NH, but as they had no method for determining absolute concentrations, they were unable to estimate an upper limit for the fraction of reaction (7) that led to NH. However, on the basis of computer simulations of their system, they concluded that the major branch of reaction (7) is that leading to NO and OH.

In the $N + O_3$ system, $O_2(a\ ^1\Delta_g)$ was not observed when particular care was taken to reduce H-atom impurities, as described in the Experimental section. It is concluded that H atoms play a part in generating $O_2(a\ ^1\Delta_g)$. Two possible mechamisms that could explain the formation of $O_2(a\ ^1\Delta_g)$ are:

mechanism (2*a*)

$$H + O_3 \rightarrow OH + O_2(a\ ^1\Delta_g) \tag{4b}$$

mechanism (2*b*):

$$H + O_3 \rightarrow OH(v \leqslant 9) + O_2 \tag{4a}$$

$$OH(v \geqslant 3) + O_2 \rightarrow OH + O_2(a\ ^1\Delta_g). \tag{12}$$

Washida *et al.*[23] have attempted to observe formation of $O_2(a\ ^1\Delta_g)$ in reaction (4). They concluded that the fraction of reaction (4) leading to $O_2(a\ ^1\Delta_g)$ is less than 0.001. Mechanism (2*b*) is analogous with the mechanism favoured in the $N + O_2$ system. Evidence for this mechanism comes from previous work in this laboratory,[24] in which emission at $\lambda = 1270$ nm was observed in the reaction of H atoms with O_3. On addition of O_2, the intensity of emission was enhanced, and extrapolation of the results to $[O_2] = 0$ suggested that emission was only observed if some O_2 was present; *i.e.* $H + O_3$ was not the source of emission. Formation of $O_2(a\ ^1\Delta_g)$ in reaction (12) would be consistent with these observations, although they are slightly complicated as the emission in the earlier work was believed to be at least in part due to $HO_2(A\ ^2A', \nu_3 = 1 \rightarrow X\ ^2A'', \nu_3 = 0)$. Mechanism (2*b*) thus seems the more likely route to $O_2(a\ ^1\Delta_g)$.

Conclusions

Kinetic Experiments

A rate constant has been measured for the reaction of N atoms with O_2. The measured value agrees well with the latest NASA recommendation.[10]

The rate constant for the reaction $N + O_3$ has also been measured. The value obtained disagrees with early studies,[7,8] but is encompassed by the upper limit given by Stief *et al.*[9] High values of k_2 were often measured. Following a proposal of Stief *et al.*, this discrepancy was attributed to the catalytic destruction of N atoms in the presence of H-atom impurities.

Chemiluminescence Experiments

Emission in the visible and near-i.r. regions shows that $NO(B\ ^2\Pi, C\ ^2\Pi)$, $O_2(a\ ^1\Delta_g)$ and vibrationally excited OH are formed in the reaction of N atoms with O_2 and with O_3.

Vibrationally excited OH is believed to be populated in the reaction of H atoms with O_3, itself a product of secondary reactions. That emission is observed downstream of the mixing region shows that H atoms are regenerated down the flow tube. This observation lends support to the suggestion that traces of H atoms can markedly affect the measured value of k_2.

It is proposed that $NO(B\ ^2\Pi)$ and $NO(C\ ^2\Pi)$ are formed by combination of N with O atoms. Both these excited states have been observed previously in the combination reaction. Computer simulations of the system using the combination as the source of $NO(C\ ^2\Pi)$ are in good agreement with experiment.

Formation of excited O_2 is observed only in the presence of H atoms. In the reaction of N with O_2, it is proposed that reaction of H atoms with O_2 leads to excited HO_2, which can then transfer energy to O_2. In the reaction of N with O_3 an analogous mechanism is suggested with vibrationally excited OH transferring energy to O_2.

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