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This paper describes the identification of a reaction between atomic oxygen, $O(^{3}P)$, and the nitrate radical, NO₃, and the measurement of the kinetics of the process at room temperature. A discharge-flow technique was used, and atomic oxygen concentrations were determined by resonance fluorescence. The rate coefficient obtained was $(1.7 \pm 0.6) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. This value is compared with recently measured rate constants for the reactions of other atoms and radicals with NO₃. The possibility is discussed of the reaction between O and NO₃ occurring in the stratosphere.

Although the nitrate radical, NO_3 , is relatively unreactive towards closed-shell species, it has recently become apparent that the radical is much more reactive towards atoms and other radicals. Kinetic studies have been performed on the reactions of NO_3 with H,¹ OH,^{1,2} HO₂,^{2,3} Cl⁴⁻⁷ and ClO.⁶ The rate constant for the fastest of these reactions (with H) is of the same order of magnitude as the gas-kinetic collision frequency factor. In order to understand further the factors determining the reactivity of the NO₃ radical towards other open-shell species, we have now studied the reaction with atomic oxygen, and we describe the results in the present paper. The kinetic data permit an interesting comparison between the reactions of O with NO₂ and with NO₃.

Quite apart from the fundamental kinetic interest that attaches to radical (or atom)radical reactions, the nitrate radical is proving to be of particular importance in atmospheric chemical transformations, both in the troposphere and in the stratosphere. NO₃ is an intermediate in atmospheric chemical cycles involving ozone and the oxides of nitrogen, being formed by the reaction between NO₂ and ozone, and being removed mainly by photodissociation during the day. The radical is thus a temporary reservoir for NO_x, and a detailed knowledge of its reactivity is essential for a full interpretation of the factors that control stratospheric ozone concentrations,^{8,9} and of the response of atmospheric ozone to anthropogenic disturbance. At night, NO₃ may be the most important oxidant, especially in the troposphere, and the products of its reactions can yield toxic compounds as well as contributing to the acidification of rainwater.¹

The experiments described in this paper were carried out using a discharge-flow technique. Atomic resonance fluorescence was used to detect O. NO_3 was generated by the reaction between F and HNO_3 , and its concentration was determined by multipass optical absorption in the visible region. Consumption of O and of NO_3 were observed, and it is assumed that reaction proceeds *via* oxygen-atom transfer:

$$O + NO_3 \rightarrow O_2 + NO_2. \tag{1}$$

The reaction is relatively rapid, being rather faster than the comparable reaction of O with NO_2 :

$$O + NO_2 \rightarrow O_2 + NO.$$
 (2)

Although reaction (1) has been invoked previously¹⁰ in interpreting a complex photochemical system, we believe that our experiments represent the first direct determination of the kinetics of the process.

Experimental

Apparatus and Procedure

A glass flow apparatus, provided with a sliding injector, was employed for the experiments. Two observation ports were provided; at the first port, atomic resonance fluorescence could be excited and detected, while at the second, $[NO_3]$ could be monitored by optical absorption at $\lambda = 662$ nm. A detailed description of the apparatus has been published previously.¹ In most experiments, oxygen atoms were produced by passing a microwave discharge through a flow of oxygen in helium, and added to the main carrier gas flow (helium) through an upstream sidearm. Nitrate radicals were produced by the reaction of atomic F (generated by a microwave discharge passed through F_2/He mixtures) with anhydrous HNO₃, following the standard procedure adopted in this laboratory.¹¹ The NO₃ radicals joined the main flow through a sliding injector that terminated in a spray nozzle to ensure good mixing. All walls of the reaction system in contact with the NO₃ radicals or with O atoms were coated with halogenocarbon wax (Halocarbon Corp., series 15-00). Typical flow velocities were 1400 cm s⁻¹, and experiments were conducted at total pressures of 2.1 and 3.7 mmHg.[†]

Nitrate Radical Concentrations

Optical absorption at $\lambda = 662$ nm was used to measure [NO₃]. A dual-beam spectrometer was used in conjunction with a White-type cell (optical path = 156 cm). The absorption cross-section for NO₃ in this system was found to be 1.9×10^{-17} cm⁻² from *in situ* titrations,¹¹ a value that is consistent with the peak absorption cross-section at $\lambda = 662$ nm convoluted with the transmission characteristics of the filter employed.¹ The absolute sensitivity for [NO₃] was *ca.* 10^{11} molecule cm⁻³ for a signal-to-noise ratio of unity, and an integration time of 10 s.

Atomic Oxygen Concentrations

Concentrations of O(³P) were monitored by resonance fluorescence using the unresolved triplet transition $(3s)^3S_{1-}(2p^4)^3P_{2,1,0}$ (corresponding to $\lambda = 130.2$, 130.5, and 130.6 nm). The excitation lamp was of the normal microwave discharge type, electrodeless. Fluorescent radiation was measured with a solar-blind photomultiplier (CsI photocathode, EMR model 542G-08-18) mounted at right angles to the exciting radiation beam. Conventional pulse-counting electronics with ratemeter facilities were used for signal processing. Both the lamp and the detector optical paths were suitably collimated.

The gas in which the microwave discharge was struck was always supplied as a slow flow to the lamp, at a pressure of *ca.* 1 mmHg. Some exploratory experiments were performed with a gas mixture consisting of 5% O₂ in He, and with a polished LiF window separating the lamp from the main flow system. However, spectral analysis (0.3 m spectrometer, McPherson model 218) of the radiation from such a lamp indicated that impurity emission of the Ly- α line from atomic hydrogen at $\lambda = 121.6$ nm dominated over the radiation of the oxygen resonance lines, especially when the window was new. Significant intensities of Ly- α radiation must be avoided if the detection system is to respond solely to O, and not to H atoms that may be present adventitiously in the reacting gases. Windows of LiF, CaF₂, and MgF₂ (all BDH Crystran Products) were tested with a variety of gas mixtures. The most satisfactory combination was an MgF₂ window with nominally 'pure', and dried, Ar as the discharge gas. Exposure of the MgF₂ window to the discharge rapidly reduced its transmission at the Ly- α wavelength

without significantly affecting the behaviour at $\lambda \approx 130$ nm, so that the intensity of H resonance radiation could be kept to 10% that of the O resonance lines.

Initial absolute calibrations of the sensitivity of the system towards atomic oxygen employed a modification of the 'titration' reaction between O and NO_2 ,

$$O + NO_2 \rightarrow O_2 + NO$$
 (3)

which is normally used to equate losses of [O] with the absolute $[NO_2]$ added to the system. With the concentrations and contact times used in our experiments, reaction (3) does not proceed even near to completion. However, by appropriate mathematical manipulation, it is still possible to extract the initial absolute value of [O] from the decrease that arises on addition of known $[NO_2]$. A full description of the procedure will appear elsewhere.¹² The calibration experiments demonstrated that, for the concentrations of atomic oxygen employed in this work, $[O] < 2 \times 10^{12}$ molecule cm⁻³, the measured resonance fluoresence signal is linearly proportional to [O]. The limiting sensitivity in our apparatus was *ca*. 5×10^{10} molecule cm⁻³ for a signal-to-noise ratio of unity and a 10 s integration time.

As will be explained later, absolute atomic oxygen concentrations were subsequently determined in each individual kinetic run by measuring the decay of NO_3 in what was essentially an internal calibration procedure.

Materials

Argon (BOC) for use in the discharge lamp was dried by passing over phosphorus pentoxide at roughly atmospheric pressure, and then through molecular sieve (5A). All other materials were from the same sources, and handled in the same way, as described previously.¹

Results and Discussion

Occurrence of Reaction

Addition of NO₃ to a flow of carrier gas containing O led to a diminution in [O]. Similarly, the presence of O caused a decrease in [NO₃] in the flow gases, thus pointing to the existence of a true chemical reaction between O and NO₃. Interferences from the molecular precursors of O and NO₃ were tested for by investigating the various combinations of excitation of the two microwave discharges that produce F (used to generate NO₃) and O. These experiments showed clearly that, with all precursor species present, O atoms were not consumed without the F discharge excited, and NO₃ was not consumed without the O discharge excited. In particular, NO₃ does not react significantly with O₂, as we have demonstrated previously,¹³ the upper limit for the rate constant for a hypothetical interaction being 1×10^{-17} cm³ molecule⁻¹ s⁻¹. It is conceivable that F atoms themselves might consume O, but a large excess of [HNO₃] over [F] was used, so that no free F survives to the injector nozzle. Furthermore, depletions of O were unaffected by employing differing ratios of [HNO₃] to [F], but retaining the same [NO₃]. The only reasonable products of a reaction between O and NO₃ are O₂ and NO₂:

$$O + NO_3 \rightarrow O_2 + NO_2. \tag{1}$$

Wall Reactions

In the absence of O, $[NO_3]$ showed no variation with the position of the sliding injector. Thus, not only are gas-phase reactions with the molecular species unimportant, but wall losses are also negligible. This result is in accordance with our earlier determinations¹³ made in a similar reaction system, where the first order rate constant for wall loss was $<0.1 \text{ s}^{-1}$.

	n		[O] _{NO3=0}	$[NO_3]_{O=0}$		1
run	/mmHg	$/\mathrm{cm}~\mathrm{s}^{-1}$	/10 ¹² mole	ecule cm ⁻³	k'/s^{-1}	$/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
\mathbf{A}^{a}	2.2	1291	1.9	3.21	65.5 ± 7.4	(2.5)
\mathbf{B}^{a}	2.2	1291	1.7	4.11	89.0 ± 6.1	(2.3)
C ^a	2.1	1320	3.5	2.85	70.6 ± 4.9	(2.7)
F	2.1	1357	1.70	3.71	65.1 ± 2.2	1.83 ± 0.10
G	2.1	1357	0.81	3.78	61.0 ± 3.4	1.67 ± 0.09
Н	2.1	1357	0.45	4.18	69.0 ± 3.7	1.64 ± 0.07
I	2.1	1357	0.39	2.34	33.2 ± 1.8	1.43 ± 0.07
Μ	2.1	1355	0.85	3.56	63.5 ± 2.0	1.88 ± 0.06
Ν	3.7	1405	0.98	4.07	52.5 ± 2.1	1.30 ± 0.07
Р	3.7	1405	1.47	5.43	87.5 ± 3.3	1.62 ± 0.06
Q	3.7	1405	0.69	5.08	73.0 ± 3.2	1.48 ± 0.04
R	3.7	1404	0.93	4.76	86.7 ± 4.2	1.84 ± 0.07
S	3.7	1404	0.80	2.08	36.8 ± 3.2	1.89 ± 0.15
Т	3.7	1404	0.77	3.44	57.6 ± 3.7	1.68 ± 0.10

Table 1. Experimental conditions for $O + NO_3$, and derived values of k' and k_1

^a These runs were performed using an LiF lamp window, and are not included in the calculation of k_1 . Error limits are 95% confidence limits.

Possible wall losses of atomic oxygen were investigated in two ways. First, in the calibrations for absolute [O], NO_2 was injected at different points in the flow tube. No significant change in [O] could be detected. Secondly, in a separate series of experiments, oxygen atoms were produced inside the sliding injector, and added to the main flow to give contact times between 1.5 and 28 ms. Again, there was no evidence for loss of O. The absence of wall removal of O is entirely consistent with the known recombination efficiencies of O on glass surfaces.^{14,15}

Kinetic Experiments

The appropriate flows of O_2 , F_2 , HNO₃, and the diluent and main flows of He were established in the flow tube. For each position of the sliding injector, a measurement was made of $[NO_3]_{O=0}$ with the F discharge alone excited, and of $[O]_{NO_3=0}$ with the O discharge alone excited. Both discharges were then excited to yield concentrations of NO_3 and O after reaction for the contact time determined by the injector position.

The first five columns of table 1 show the experimental conditions employed in the 14 runs that were completed. The values of both $[NO_3]_{O=0}$ and of $[O]_{NO_3=0}$ are averages for all injector positions used in a given run (*ca.* 10). There is obviously scatter in these values, even though there is no discernible trend with contact time.

The data were analysed in two ways. In the first method, simple pseudo-first order decay of atomic oxygen, with no secondary reaction, is assumed, while in the second, the experimental data were fitted by a numerical model of a more complete reaction mechanism. Three of the runs (A, B, C) employed a lamp for excitation of resonance fluorescence whose emission was severely contaminated by Ly- α radiation (see Experimental section), and the main flow, rather than a small fraction of it, passed through the microwave discharge intended to produce O atoms. Although the data from these runs were analysed, the results were not incorporated into the final mean rate coefficient because of the danger that they partially reflect the reactivity of H, rather than only that of O, towards NO₃.



Fig. 1. Time-dependent loss of O in the presence of NO₃ plotted as a first-order process. $(a) \square$, run P; $(b) \oplus$, run M; $(c) \blacksquare$, run N; $(d) \bigcirc$, run I. Experimental conditions for the individual runs are specified in table 1.

Fig. 1 shows plots of $\ln ([O]_{NO_3=0}/[O])$ as a function of time in four representative cases of differing initial [NO₃]. Such plots were generally apparently good straight lines, even though there is measurable consumption of NO₃. A pseudo-first order rate coefficient, k', was derived from the slopes for each experimental run, and the values are displayed in column 6 of table 1. The pseudo-first order rate constant, k', is a linear function of $[NO_3]_{O=0}$ with zero intercept, as shown in fig. 2. There is no apparent effect on changing the total pressure from 2.1 to 3.7 mmHg. The slope of fig. 2 yields a first estimate of the rate constant for reaction (1), k_1 , at room temperature of 1.7×10^{-11} cm³ molecule⁻¹ s⁻¹.

The excess of NO₃ over O is not large enough to ensure pure first order kinetics, so that the rate constant simply derived by using values of $[NO_3]_{O=0}$ is likely to be somewhat too small. In addition, since NO₂ is presumed to be the product of reaction (1), some secondary reaction of O with NO₂ in the fast reaction (2) is inevitable. We therefore numerically integrated the kinetic equations for the most important reactions that control the loss of O and NO₃ in our system, and fitted the experimental data by varying the rate constant k_1 . The reactions, together with their rate constants, used in the analysis were:

$$O + NO_3 \rightarrow O_2 + NO_2$$
(1)
 k_1 : fitting parameter

$$O + NO_2 \rightarrow O_2 + NO$$

$$k_2 = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [ref. (16)]}$$
(2)

$$NO + NO_3 \rightarrow NO_2 + NO_2$$
 (3)

$$k_3 = 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [ref. (16)]}$$

NO₃ + NO₂ + M → N₂O₅ + M (4)

$$k_4 = 5.6, 8.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for $P = 2.1, 3.7 \text{ mmHg}$ [ref. (17)].

Fig. 3, curve (a), shows the fit of the experimental points to the modelled decay of [O] for the four runs shown as examples in fig. 1. The best fit to the decay curve was



Fig. 2. Pseudo-first-order rate constants for the loss of O in the reaction with NO₃ plotted as a function of initial concentration of NO₃. \bigcirc , P = 2.1 mmHg; \bigcirc , P = 3.7 mmHg.



Fig. 3. Decay of O in the presence of NO₃ shown as a direct function of time. (a) \Box , run P; (b) **\blacksquare**, run N; (c) \bullet , run M; (d) \bigcirc , run I. Experimental conditions for the individual runs are specified in table 1. The curves are obtained by numerical integration of the rate equations for reactions (1)-(4), as described in the text, using the values for k_1 shown in the last column of the appropriate entries in table 1.



Fig. 4. Time dependence of [O] and [NO₃] in run F, where $[NO_3]_{O=0}/[O]_{NO_3=0} = 2.18$ (see table 1). Experimental points: \bullet , $[NO_3]$; O, [O]. Modelled curves: (a) $[NO_3]$ and (b) [O] for $[O]_{NO_3=0} = 1.7 \times 10^{12}$ molecule cm⁻³; $k_1 = 1.83 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; (c) and (d) $[NO_3]$ for $[O]_{NO_3=0} = 1.4$ and 2.1×10^{12} molecules⁻³; $k_1 = 1.83 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; (e), (f) $[NO_3]$ and (g), (h) [O] for $[O]_{NO_3=0} = 0.85$ and 3.4×10^{12} molecule cm⁻³; $k_1 = 1.83 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; (j) $[NO_3]$ and (g), (h) [O] for $[O]_{NO_3=0} = 1.7 \times 10^{12}$ molecule cm⁻³; $k_1 = 2.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; (j) $[NO_3]$ + $[NO_2]$ for $[O]_{NO_3=0} = 1.7 \times 10^{12}$ molecule cm⁻³; $k_1 = 1.83 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

obtained by a least-squares minimization of the differences between experimental and calculated [O]. The values of k_1 obtained are shown as the last column in table 1, the errors being 95% confidence limits.

One potential source of error is the absolute calibration for [O], since the reaction is not truly first order. As we described in our experimental section, an initial calibration factor was obtained by a variant of the standard procedure in which O is titrated by NO_2 . However, since the intensity of the lamp used to excite resonance fluorescence can change from run to run from a variety of causes, we felt it expedient to use the decay of $[NO_3]$ itself in each individual run to obtain the absolute value of [O]. The variation of $[NO_3]$ with time in one run (run F) is shown as the solid circles in fig. 4; the open circles show the decay of [O]. Both concentrations are normalized to the values at t = 0. This run is chosen because it is the one with the smallest excess of NO₃ over O, and thus the one in which the influence of calibration errors would be most severe. Curves (a) and (b) show the modelled depletions of $[NO_3]$ and [O] for the values of $[O]_{NO_1=0}$ and k_1 obtained by fitting to the experimental data. The scatter in the [NO₃] measurements might permit $[O]_{NO_3=0}$ values up to 20% lower or higher than the 'best' value, as indicated by fig. 4 (c) and (d). In fact, even though the decay of [NO₃] in this run is as much as 40%, the influence of the calibration factor is small. Curves (e) and (f) show the effect of $[O]_{NO_3=0}$ values two times smaller, (e), and two times larger, (f), than those estimated to be present. Curves (g) and (h) show the corresponding predicted decays of the normalised atomic oxygen concentrations. At least for contact times less than 10 ms, the change in calculated decay is comparable with the experimental scatter even for a range of $[O]_{NO_3=0}$ far outside that permitted by the [NO₃] measurements. This small influence of the absolute value of $[O]_{NO_3=0}$ is, of course, consistent with the near-linearity of logarithmic plots such as fig. 1. The

mutual influence of k_1 and the calibration for $[O]_{NO_3=0}$ can be determined by obtaining the best fit for the [O] decay for a value of $[O]_{NO_3=0}$ twice that believed to be present. In run F, the 'best' k_1 is increased from 1.73×10^{-11} only to 2.00×10^{-11} cm³ molecule⁻¹ s⁻¹, and the calculated decay curve is almost indistinguishable from curve (b). However, curves (a), (c) and (d) for the decay of NO₃ are virtually unaffected by the small change in k_1 [curve (a) becomes curve (i), for example]. It follows, then, that the assumed larger value of $[O]_{NO_3=0}$ makes little difference to the calculated value of k_1 (which the experiments are designed to obtain), but the measured decays of $[NO_3]$ are still incompatible with the assumption. Fitting of the decay of NO₃ is therefore not particularly critical in determining k_1 .

The mean value of k_1 in the last column of table 1 is $(1.66 \pm 0.34) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (random error quoted as two standard deviations). Systematic errors are estimated to add an additional 15% uncertainty, so that we may quote

$$k_1 = (1.7 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

It may be shown that diffusion effects do not interfere in our system with the determination of rate constants of this magnitude, a conclusion consistent with the lack of influence of total pressure on the rate of reaction.

Kinetic modelling is seen to give a value of k_1 almost identical with that obtained by the simple first-order analysis. The small effect of decay of NO₃ and of secondary loss of O turns out to be a consequence of the chemical changes in the reaction system, and of the absolute magnitude of k_1 . Reaction (1) converts NO₃ to NO₂; both oxides of nitrogen show the same order of magnitude of reactivity towards O. Curve (j) of fig. 4 demonstrates that the sum ([NO₃]+[NO₂]) remains almost invariant with time, so that pseudo-first-order kinetics are observed.

Potential Interference by Atomic Hydrogen

As pointed out in our Experimental section, efforts were made to employ a resonanceexcitation source that was, as far as possible, free from contamination from emission not due to atomic oxygen. However, H-atom impurities are hard to eliminate entirely, either in the excitation sources or in the reactant gases. As the reaction of H with NO₃ is so rapid (with a rate constant¹ of 1.1×10^{-10} cm³ molecule⁻¹ s⁻¹), a danger exists that some of the measured decay refers to H, rather than O, loss. We decided, therefore, to check the operation of our reaction and detection systems by investigating reaction (2) between O and NO₂, for which the rate constant is well known [the most recent recommendation¹⁶ is $(9.7 \pm 1.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹]. Since atomic hydrogen reacts with NO₂ even more rapidly¹⁸ (rate constant 1.3×10^{-10} cm³ molecule⁻¹ s⁻¹) than with NO₃, any contribution of H to the measured resonance fluorescence signal will become evident by an anomalously high measured rate constant for reaction (2). Experiments were performed using the same lamp (Ar discharge, with MgF₂ window) and bypass source of reactant O as were used in the main runs with NO₃. Determinations in seven runs gave $k_2 = (9.7 \pm 2.6) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, a value the same as the recommended value. It seems unlikely, therefore, that there is interference from detection of atomic hydrogen in the measurement of k_2 , or, by implication, in the measurement of k_1 either.

A separate potential interference from H lies not in the detection of H, but in H produced as an impurity along with the O-atom reactant that could itself influence the decay of O. A mechanism for such loss exists, since the pair of reactions

$$H + NO_3 \rightarrow OH + NO_2$$

$$k_5 = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [ref. (1)]}$$
(5)

$$O + OH \rightarrow O_2 + H$$

$$k_2 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ [ref. (16)]}$$
(6)

	alastronia	$k/10^{-11}$ cm ³ molecule ⁻¹ s ^{-1 a} oxide of nitrogen		
reactant	degeneracy	NO ₂	NO ₃	
Н	2	13 ^{<i>b</i>}	11 ^c	
ОН	4	t	2.0°	
Cl	4	t	2.1^{d}	
0	9	0.97 ^e	1.7′	

 Table 2. Rate constants at room temperature for some reactions of atoms and radicals with oxides of nitrogen

"'t' indicates that the reaction is termolecular. ^b Ref. (18). ^c Ref.

(1). ^d Ref. (7). ^e Ref. (16). ^f This work.

are both fast and catalytically recycle H. Model calculations indicate that if [H] reached 0.1 [O] in the flow tube, a value that we consider to be unrealistically large, then the value of k_1 derived from our data would have to be reduced by between 3 and 6%, depending on the exact experimental conditions of the individual run.

Conclusions

We present here evidence for a reaction between O and NO₃, and obtain a rate constant for the interaction at room temperature of $k_1 = (1.7 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Our work seems to be the first direct investigation of reaction (1). A decade ago, Graham and Johnston¹⁰ invoked the reaction in their modulation studies of NO₃. The decrease in NO₃ modulation amplitude on substituting O₂ for the N₂ carrier gas was ascribed to the scavenging of O by O_2 and consequent suppression of reaction (1). Computer of the complex reaction mechanism suggested $k_1 =$ simulation that $(1.0\pm0.4)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹, although Graham and Johnston add the caveat that the value is highly dependent on the other kinetic parameters measured in their study. In the event, the indirect estimate is remarkably close to our own new and direct determination, the values overlapping within the error limits.

The reaction affords another clear example of a process in which NO_3 exhibits high reactivity. It was observed previously¹ that other rapid reactions of NO_3 with atoms or radicals involve oxygen atom transfer from the NO_3 radical, and reaction (1) appears to fall into this category as well.

Table 2 shows rate constants at room temperature for some reactions of NO₂ and NO₃. The results of Graham and Johnston¹⁰ imply little dependence of the rate of reaction (1), between O and NO₃, on temperature, while the reactions of H with NO₂ and NO₃ are too rapid^{1,18} at room temperature to accommodate a significant activation energy. Similarly, all the other bimolecular reactions for which data are shown in the table are thought to have near-zero activation energies.¹⁶ Thus the entries in the table closely reflect intrinsic reactivities as embodied in the Arrhenius pre-exponential factors. The rate constant for reaction (1) with NO₃ is greater than that for reaction (2) with NO₂ by a factor of $1.7/0.97 \approx 1.8$. The enhanced reactivity of NO₃ compared with NO₂ might result from a steric effect related to the availability of the extra oxygen atom in NO₃, although steric effects are often small for radical-radical reactions. However, the same behaviour is not evident in the reaction of H atoms with the two oxides of nitrogen, where NO₂ is, if anything, very slightly more reactive than NO₃. Possibly the availability of an energized collision complex corresponding to nitric acid, HONO₂, accounts for the behaviour in the reaction of H with NO₃.

There is a striking contrast between the reactivity of H and that of O towards both NO_2 and NO_3 . The probability of reaction may be affected by the degeneracy of the reactants. Smith¹⁹ has pointed out that the probability of reaction cannot be greater than the ratio of the number of bound to the number of unbound surfaces. If reactants pass over to products on a *single* potential-energy surface, then the probability of reaction could be inversely proportional to the degeneracy of the system. Included in table 2 are the total (spin × orbital) degeneracies of the free co-reactants. The general trend in reactivity with NO_3 (and, where the bimolecular reactions exist, with NO_2) does, indeed, decrease with increasing degeneracy.

Atmospheric Chemistry

The nitrate radical is rapidly photodissociated in the troposphere and the stratosphere during the day. Measurements of atmospheric [NO₃] are, indeed, confined to the night [see, for example, ref. (8) and (9)]. Models^{20,21} and measurements⁸ show that [NO₃] increases after sunset as the reaction between NO_2 and O_3 produces the radical, and that the concentration drops sharply after dawn. Since atomic oxygen concentrations in the stratosphere are relatively high during the day, it is instructive to see whether reaction (1) can supplement the photolytic loss of NO_3 . It is currently assumed that the quantum yield for photolysis of NO_3 is unity throughout the visible absorption region.¹⁶ On that basis, the absorption flux indicates²² that the first-order rate for photolysis is roughly $2 \times 10^{-1} \text{ s}^{-1}$. At an altitude of 40 km, [O] can reach^{23,24} 10^9 molecule cm⁻³. With our rate constant for reaction (1) of $1.7 \times$ 10^{-11} cm³ molecule⁻¹ s⁻¹, the first-order rate constant for the reaction thus approaches 2×10^{-2} s⁻¹, or ca. 10% of the photolysis rate. The reaction could, therefore, make a minor, but significant, contribution to the destruction of NO₃. That conclusion does not argue for any major change in the interpretation of daytime stratospheric chemistry, since NO₃ already plays so small a role during the hours of sunlight.

The situation at night is less clear. Atomic oxygen concentrations in the stratosphere drop sharply at night as the atomic source in this atmospheric region, ozone photolysis, is cut off.^{20,21} However, Norton and Noxon⁹ have noted that observed stratospheric concentrations of NO₃ are often smaller than those calculated and have concluded that there is some hitherto unknown scavenging process that removes NO₃. Reaction (1) between O and NO₃ might conceivably be of importance just after sunset at altitudes high enough for there to be a time lag between the cessation of O₃ photolysis and the recombination of virtually all O with O₂. However, the lifetime of O against recombination does not reach 1 h until the atmospheric molecular concentration is below *ca*. 1.5×10^{15} molecule cm⁻³ (corresponding to an altitude of more than 60 km), while Norton and Noxon conclude that the scavenger of NO₃ must be continuously created in stratospheric air at high altitude, and presumably at altitudes corresponding to the peak NO₃ concentrations (35-40 km). On the basis of this evidence, therefore, it seems improbable that the reaction of atomic oxygen in reaction (1) is the night-time scavenging process.

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