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Reactivity of the Nitrate Radical towards Alkynes and some other Molecules

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A time-resolved flow method has been used to obtain absolute rate constants (in units of 10^{16} cm³ molecule⁻¹ s⁻¹) for the reaction of the nitrate radical with acetylene (0.51 ± 0.35), propyne (2.66 ± 0.32), but-1-yne (4.55 ± 0.46), but-2-yne (670 ± 150), pent-1-yne (7.54 ± 0.75), hex-1-yne (16.0 ± 1.9), ethylene (1.85 ± 0.24), isobutene (3400 ± 700) and buta-1,3-diene (2200 ± 600). The possible influences of secondary reactions are considered and it is concluded that only in the cases of but-2-yne and buta-1,3-diene are secondary processes likely to interfere with the calculation of rate constants. For these two species, therefore, the rate constants above must be taken as upper limits, although it is improbable that the values are grossly high. The nitrate radical was generated by the reaction

$$F + HNO_3 \rightarrow HF + NO_3$$
 (1)

and an absolute kinetic method was used. Upper limits of 1×10^{-17} cm³ molecule⁻¹ s⁻¹ were measured for the coefficients of any interactions of NO₃ with SO₂ and O₂. The rate of the reaction

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \tag{2}$$

was measured in the range 2-8 Torr[‡] and good agreement with literature values for the pressure dependence (M = He) was obtained. Comparisons with rate constants for the corresponding reaction rates with OH, $O({}^{3}P)$ and O_{3} were made.

Recent observations on the abundances of alkynes in the atmosphere¹ have stimulated renewed interest in the interactions of these species with atmospherically reactive intermediates such as OH radicals.² We report here for the first time the rate constants for the reactions at 295 ± 2 K of the nitrate radical (NO₃) with acetylene, but-1-yne, but-2-yne, pent-1-yne and hex-1-yne. In addition, rate constants were measured for the reactions of NO₃ with nitrogen dioxide in the three-body process

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \tag{2}$$

and with ethylene, isobutene and buta-1,3-diene. In the case of ethylene, there is a tenfold discrepancy within the literature values. We also give upper limits for any interactions of NO_3 with sulphur dioxide and molecular oxygen.

We attempt to correlate alkyne reactivity with that of ozone, oxygen atoms $O({}^{3}P)$ and OH radicals. A discharge-flow technique was used to provide time resolution and hence absolute rate constants.

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^{‡ 1} Torr = 101 325/760 Pa.

Experimental

Apparatus and Technique

The apparatus used in this work consisted of a low-pressure flow system constructed from an uncoated Pyrex reaction tube, 38 mm i.d. and 102 cm long, containing four reactant injection ports *ca.* 20 cm apart. The reaction tube was connected downstream *via* SVL joints (J. Bibby Ltd) to an absorption chamber for measuring NO₃ concentration. The chamber consisted of a four-pass White cell giving a total pathlength of 35.2 cm. The cell was inserted into the sample beam of a modified Pye spectrophotometer, model SP700A. A spectral scan through the visible region gave the nitrate radical absorption curve with the maximum at 662 ± 2 nm, and this wavelength was used for monitoring [NO₃]. The minimum detectable [NO₃] for a 1:1 signal-to-noise ratio was *ca.* 6×10^{11} molecule cm⁻³. Nitrate radicals were formed in the flow system by the reaction

$$F + HNO_3 \rightarrow HF + NO_3.$$
 (1)

Molecular fluorine diluted with helium (supplied by B.O.C.) was passed through a microwave discharge and into a stream of nitric acid vapour, also in a helium carrier. Partial pressures of all gases used were calculated from flows measured by calibrated ball flowmeters. Linear flow rates were generally *ca*. 3 m s^{-1} and total pressures were 1-10 Torr. Initially, anhydrous HNO₃ was made by distilling a mixture of NaNO₃ and H₂SO₄, but we found later that it was more convenient to bubble helium through a 2:1 reagent-grade H₂SO₄/HNO₃ mixture held at -12 °C by an ethylene glycol slush. Helium diluent was passed through an 'Oxisorb' (Messer Griesheim) trap followed by two molecular sieve traps at room temperature. All reactants were the commercially available materials and were purified by successive trap-to-trap distillations. In each case at least two different samples of the reactant were studied, each having been distilled a different number of times; also included were experiments done using the undistilled reactant. No differences in the results were found between these experiments.

Treatment of Data

In most cases, NO_3 reactions were studied under pseudo-first-order conditions, with the co-reactant in at least tenfold excess over $[NO_3]$. For the fastest reactions, however, the NO_3 and reactant concentrations were sometimes comparable, and the data were then treated assuming second-order kinetics with a 1:1 (NO_3 :reactant) stoicheiometry. Results using both sets of conditions were compared and computer simulation was used to investigate the influence of possible secondary reactions which could affect the stoicheiometry.

First-order Kinetics

We assume that NO_3 is consumed by the reactions

$$NO_3 + X \rightarrow product$$
 (3)

$$NO_3 + wall \rightarrow product$$
 (4)

where $[X] \gg [NO_3]$, and that the addition of the reactant to the gas stream has a negligible effect on the gas velocity. Then

$$\ln ([NO_3]_0 / [NO_3]_l) = k_3 [X]_l / v$$
 (I)

where $[NO_3]_0$ and $[NO_3]_l$ are the concentrations of $[NO_3]_l$ at the detection point in the absence of reactant and when reactant is added at a distance *l* from the detection point;

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v is the linear flow velocity. Losses of NO₃, other than by the gas-phase reaction(s), do not appear in the expression.

Second-order Kinetics

To keep conversions, x, of NO₃ within convenient limits it is necessary to restrict the concentration of the co-reactant. Thus, for those substrates reacting most rapidly with NO₃, the inequality $[X]_0 \gg [NO_3]_0$ cannot be maintained. The second-order integrated rate law is then employed:

$$B = k_3 t = \frac{v}{l([NO_3]_0 - [X]_0)} \ln \frac{[X]_0([NO_3]_0 - x)}{[NO_3]_0([X]_0 - x)}$$
(II)

where $[X]_0$ is the concentration of added reactant at the injection port. We shall show later that $[NO_3]_0$ at the injection point can be adequately approximated by $[NO_3]_0^{obs}$, the concentration of NO₃ at the observation region in the absence of added reactant, because wall losses of NO₃ are sufficiently slow.

A value of 2.23×10^{-17} cm² molecule⁻¹ was used for the absorption cross-section of NO₃ at room temperature and 662 nm, as previously determined in this laboratory,³ and it falls in the range of the most recent determinations.⁴⁻⁶ For the spectrometer bandwidth used in this work the absorption cross-section was corrected by a convolution factor of 0.74 giving $\sigma = 1.65 \times 10^{-17}$ cm² molecule⁻¹. We shall discuss later the sensitivity of our derived rate constants to the absolute value of the cross-section adopted.

The fast titration reaction

$$NO + NO_3 \rightarrow 2NO_2$$
 (5)

can be used to estimate absolute NO_3 concentrations and was used here to confirm roughly the experimental convoluted cross-section employed. We note that the stoicheiometry and validity of the titration technique are highly dependent on the experimental conditions. Previous studies³ in this laboratory have established the procedure and corrections to be used.

Diffusion Effects

The effects of the axial and radial NO₃ concentration gradients were estimated following the treatment of Kaufman.⁷ We calculated the value for the diffusion coefficient of NO₃ in helium of 400 cm² s⁻¹ at 293 K and 1 Torr, using the empirical correlation of Fuller, Schetter and Giddings, as quoted by Reid *et al.*⁸ Axial diffusion of NO₃ could introduce an error into the calculated rate constant. For the reaction with isobutene, this error will be less than $\pm 2\%$, and less than $\pm 1\%$ for the rate constants of the slower reactions, in both cases at a total pressure of 2 Torr. The upper limits for the radial concentration gradients are $\pm 1\%$ at 2 Torr and $\pm 5\%$ at 10 Torr for the reactants studied under pseudo-first-order conditions. Thus we are able to conclude that the assumption of plug flow can be applied without significant error.

Results and Discussion

Direct measurements of the NO₃ decay along the reaction tube cannot be made in the absence of reactant because the position at which the NO₃ is created is fixed. However, an indirect estimate of the rate constant, k_w , for the loss of NO₃ on the wall can be obtained by titration experiments using nitric oxide to remove the NO₃. Nitric oxide was injected into the flow tube using the port closest to the region where the NO₃ was

generated, and also through the port nearest to the observation region where the NO_3 concentration was monitored.

The difference between the concentration of NO₃ in the absorption cell, when the same amount of NO is added first in the further port and then in the nearer, is related to k_w by the approximate expression

$$k_{\rm w} = (v/\Delta l)(\Delta[\rm NO_3]/[\rm NO]) \tag{III}$$

subject to Δ [NO₃] being small and the distance between the nearer jet and the observation region being much less than the distance between the injection ports, Δl . In these experiments, no change in the NO₃ concentration could be measured. As pointed out earlier, concentrations of F₂, HNO₃ and NO must be chosen carefully to minimize the effects of interfering reactions. Of course, in the case described here, where no change in titrant concentration is observed, any small errors in the assumed stoicheiometry only affect the limit of the wall loss rate. For the conditions chosen, the reaction with NO will go to 95% completion within 1.5 cm of the injection point.

In our apparatus, the estimated minimum detectable value of $\Delta[NO_3]$ is 6×10^{11} molecule cm⁻³, which for our experimental conditions corresponds to $k_w < 0.1 \text{ s}^{-1}$. Thus the fraction of the collisions with the wall leading to removal of NO₃ is less than 5×10^{-5} . This result for the upper limit of k_w substantiates our earlier statement that $[NO_3]_0$ can be taken as $[NO_3]_0^{\text{obs}}$, in the absence of reactant. There remains the problem that the wall removal efficiencies may alter when reactant is added to the system, as a result, for example, of adsorption of the reactant itself or of the products of reaction. However, in the course of numerical modelling of the reaction kinetics, to be described later, we have established that even a tenfold increase in k_w (to 1 s^{-1}) would have no discernible effect on the derived second-order rate coefficients.

We used reaction (2) to validate our experimental technique. The reaction is strongly pressure dependent below *ca.* 50 Torr, and we measured rate constants in the range 1-8 Torr. The ratio of the initial concentrations $[NO_2]_0/[NO_3]_0$ used in these experiments varied from 0.5 to 4.3, so that the reaction kinetics are in the second-order regime. Our results are plotted in fig. 1, together with those of Smith *et al.*⁹ The excellent agreement of the two sets of data lends confidence to our methods of measurement and data handling. There is no significant effect on the calculated rate constants resulting from changes of a factor of 9 in the ratio $[NO_2]_0/[NO_3]_0$.

For the reactants acetylene, ethylene, propyne, but-1-yne, pent-1-yne and hex-1-yne, rates were small enough that the reactant could be used in sufficient excess to ensure pseudo-first-order conditions. Pseudo-first-order rate constants can, in principle, be extracted from the slopes of $\ln[NO_3]$ against time plots, and $[NO_3]$ does not need to be known absolutely. However, it rapidly became clear that the logarithmic plots cease to be linear for large conversions of NO_3 . We therefore employed only that portion of the graph which did not deviate from linearity within experimental error. We shall show later that the departures from linearity are probably the result of secondary reactions and that numerical integration of the rate equations including such processes allows us to simulate adequately the observed behaviour even at high conversions. In the event, it turns out that the approach using initial slopes gives results the same, within experimental error, as those obtained by computer fitting; we adopt the values obtained from linear regions on the grounds of simplicity and directness. Plots of the pseudo-first-order constants against reactant concentration (see fig. 2) were linear, but sometimes gave small positive intercepts (typically ca. $0.4 \, \text{s}^{-1}$). Experiments repeated on separate occasions with the same reactants gave identical slopes, but different intercepts (often zero), thus suggesting that the effect can be attributed to a surface interaction.

In the cases of but-2-yne, isobutene and buta-1,3-diene it was not possible to work under pseudo-first-order conditions because reaction rates are too fast at suitable reactant concentrations. The appropriate second-order analysis was therefore carried out [see



Fig. 1. Plot of second-order rate constant as a function of pressure for the reaction of NO₃ with NO₂ in a helium diluent at 296 ± 2 K. \bullet , Data from ref. (9). Error limits are $\pm 2\sigma$. \bigcirc , This work (individual experimental points).



Fig. 2. Plot of pseudo-first-order rate constants against partial pressure of reactant for acetylene
 (○), propyne (▲), but-1-yne (□), ethylene (●), pent-1-yne (♦) and hex-1-yne (■).

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	Bracouro	[NO ₃] ₀	$[\mathbf{X}]_{0}$	
run no.	pressure /Torr	$/10^{13}$ molecule cm ⁻³		- k ^a
		isobutene		
12	2.02	2.86	2.59	3630
13	2.01	2.77	3.34	2840
14	2.01	2.57	1.59	2970
16	2.09	3.02	2.17	3830
6	5.00	2.67	2.30	3410
7	5.01	2.61	3.14	3800
9	5.00	2.52	1.72	3100
10	5.00	2.33	2.49	3260
11	5.03	2.30	2.72	3340
				3400 ± 700
		but-2-yne		
31	1.95	4.98	8.04	683
9	2.03	5.06	11.2	787
24	2.95	4.46	6.35	585
5	3.99	4.11	3.89	655
6	3.99	3.99	11.9	582
26	4.09	3.59	8.39	682
16	4.09	4.86	5.61	663
30	5.90	4.08	7.10	774
15	6.05	4.54	6.45	749
8	6.10	4.09	11.5	718
29	7.95	4.20	23.4	631
7	8.10	3.93	12.4	560
27	10.1	3.02	21.0	609
				670 ± 150
		buta-1,3-dier	ne	
18	2.02	3.35	3.47	1950
19	2.06	3.33	6.54	1600
20	2.02	3.26	1.87	2050
21	2.02	3.26	4.18	2030
17	2.00	3.29	1.26	1920
25	2.02	3.70	3.40	2140
26	2.00	2.84	3.11	1960
23	4.01	3.04	1.77	2240
24	4.01	3.09	3.76	2160
22	4.03	3.07	1.89	2610
12	4.08	3.69	1.46	2240
13	4.16	3.82	4.05	2620
14	4.18	4.28	7.71	1960
15	4.18	4.28	2.21	2720
16	4.17	4.11	4.83	2820
				2200 ± 700

Table 1. Second-order kinetics

^{*a*} Units are 10^{-16} cm³ molecule⁻¹ s⁻¹.



Fig. 3. Second-order plots of

$$B = \frac{1}{[NO_3]_0 - [X]_0} \ln \frac{[X]_0 - [NO_3]}{[NO_3]_0 - [X]}$$

against distance along the flow tube between the reactant injector and the observation point. (\bigcirc) NO₃+i-C₄H₈, [NO₃]₀ = 2.61 × 10¹³ molecule cm⁻³, [i - C₄H₈]₀ = 3.14 × 10¹³ molecule cm⁻³, P = 5.0 Torr, $k_3 = 3.8 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, flow velocity = 2.80 m s⁻¹. (\triangle) NO₃+1,3-C₄H₆, [NO₃]₀ = 4.28 × 10¹³ molecule cm⁻³, [1,3-C₄H₆]₀ = 7.71 × 10¹³ molecule cm⁻³, P = 4.2 Torr, $k_3 = 2.0 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, flow velocity = 3.15 m s⁻¹. (\square) NO₃+2-C₄H₆. [NO₃]₀ = 4.98 × 10¹³ molecule cm⁻³, [2-C₄H₆]₀ = 8.12 × 10¹³ molecule cm⁻³, P = 1.95 Torr, $k_3 = 6.8 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, flow velocity = 2.80 m s⁻¹.

eqn (II)] and the results, with appropriate experimental conditions, are listed in table 1. Fig. 3 shows some typical results analysed in this way. The same remarks about departures from linearity apply to these second-order data as for the first-order case, and the method used to extract rate constants was also the same. The reason for the curvature will be discussed shortly. Experiments performed using differing ratios of starting concentrations of NO₃ and co-reactant yielded indistinguishable rate constants.

The rate constants obtained with the organic reactants are given in table 2, together with the upper limits for the interactions with SO_2 and O_2 . The error limits given in table 2 for the rate constants of the reactions of NO₃ with C_2H_2 , C_2H_4 , C_3H_4 and $1-C_6H_{10}$ correspond to twice the standard deviations of the slopes of the straight lines shown in fig. 2. In the case of $1-C_4H_6$ and $1-C_5H_8$, the error limits are taken as $\pm 10\%$ because the standard deviations of the slopes are less than 5% (4.4 and 4.1%, respectively). For the reactions of isobutene, but-2-yne and buta-1,3-diene the rate constant for each single experiment, listed in table 1, is the slope of a line of the type shown in

	$k_{295}/10^{-16} \mathrm{cm}^3 \mathrm{molec}$		
reactant	lit. values (ref.)	this work ^a	total pressure range /Torr
acetylene	$< 0.23 (20) < 0.39^{b}$	0.51 ± 0.35	1-10
propyne	$0.94 \pm 0.44 (20) \\ 1.58 \pm 0.74^{b}$	2.66 ± 0.32	2-7
but-1-yne	_	4.55 ± 0.46	2-5
but-2-yne	_	$670 \pm 150^{\circ}$ $(520 \pm 120)^{d}$	2-10
pent-1-yne		7.54 ± 0.75	1-2
hex-1-yne		16.0 ± 1.9	2
SO ₂	$<4(23); \approx 7 \times 10^{-5} (24)$	< 0.1	2-4
O ₂	_	< 0.1	1.7-5
ethylene	1.1 (18, 10, 19) 10.9 (25)	1.85 ± 0.24	2-5
isobutene	3100 (18, 10, 19) 5200; ^b 3300 (11)	3400 ± 700	2-5
buta-1,3-diene	960 (17, 10) 1600 ^b	$2200 \pm 600^{\circ}$ 1780 ± 500^{d}	2-4

Table 2. Rate constants for the reactions of NO₃ at 295 ± 2 K

^{*a*} Error limits $\pm 2\sigma$. ^{*b*} Recalculated using our values for the rate constant for the reaction of NO₃ with C₂H₄. ^{*c*} 1:1 stoicheiometry (upper limit). ^{*d*} Estimated lower limit.

fig. 3; these plots sometimes exhibited curvature, and in such cases the initial slope was used. The values of k given in table 2 are the means of these rate constants and the error limits are twice the standard deviations of the means. As stated earlier, the second-order rate constants evaluated using eqn (II) depend on the value of the absorption cross-section. In order to estimate the effect on k of varying σ we recalculate the rate constants for the maximum and minimum values of $[X]_0/[NO_3]_0$, taking the absorption cross-section as $\sigma \pm 0.1\sigma$. The largest error appears for isobutene; when [isobutene]_0/[NO_3]_0 = 0.6, variation of +10% or -10% in σ produces changes of -15% or +33%, respectively, in k. The changes in k for a ±10% change in σ are generally $ca. \pm 2\%$ for the majority of reactants and experimental conditions studied.

Several different methods of generating NO₃ have been reported in the literature.¹⁰ The advantage of the $F+HNO_3$ method is that it yields absolute rate constants, *i.e.* there is no dependence for the calculation of the rate coefficient on any other rate or equilibrium constant. It is important to establish whether the apparent rate constants are sensitive to the conditions obtaining in the production of NO₃. The NO₃ absorption signal itself depends on the flows of F_2 and HNO₃, but for a fixed [HNO₃] it possesses a fairly broad plateau as a function of [F₂], (see, for example, fig. 4). This result is understood in the simplest terms as the result of the reactions

$$F + HNO_3 \rightarrow HF + NO_3$$
 (1)

$$F + NO_3 \rightarrow \text{ products.}$$
 (6)

So long as HNO₃ is in large excess, F is consumed predominantly in reaction (1), and reaction (6) does not proceed significantly. Excess F, however, leads to depletion of NO₃. The situation is complicated by the fact that the products of reaction (6) are in reality FO and NO₂,

$$F + NO_3 \rightarrow FO + NO_2$$
 (7)



Fig. 4. (a) Effect of F_2 partial pressure on measured rate constants for reaction with buta-1,3-diene (\bigcirc) and ethylene (\bigcirc); total pressure 5 Torr. Rate constants normalized to those obtained at the lowest partial pressure of fluorine. (b) Effect of F_2 partial pressure on NO₃ partial pressure at a total pressure of 4 Torr (\triangle).

so that the processes

$$FO+FO \rightarrow F+F+O_2$$
 (8)

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$
 (2)

tend to maintain [F] at the expense of catalytic destruction of NO₃. When organic reactant is present, further reactions of F and even F_2 can be envisaged that might lead to additional destruction of NO₃. Such removal of NO₃ appears to occur. Some data obtained for reaction with buta-1,3-diene and with ethylene are presented in the top part of fig. 4. For the more slowly reacting ethylene, where interference is more likely, there is clear evidence for an increase in the apparent rate constant as $[F_2]$ increases, and especially as $[F_2]$ passes the level beyond which $[NO_3]$ decreases (see lower portion of fig. 4). All experimental measurements of the rate constants were therefore performed with the $[F_2]/[HNO_3]$ ratios low enough to ensure that $[NO_3]$ was well short of the maximum on the curve.

Secondary Reactions and Overall Stoicheiometry

Because relatively large concentrations of NO₃ (up to 5×10^{13} molecule cm⁻³) and significant fractional conversions had to be employed in this work, the possibility of interference by secondary reactions arises. Indeed, such interference is implicit in the curvature sometimes observed in the first- or second-order plots used to extract rate constants, and in the consequent use of initial slopes. Curvature argues, of course, that although secondary reactions are occurring, they are not fast enough to yield an integral increase in the stoicheiometric factor. Ideally, one would wish to avoid potential errors resulting from uncharacterized secondary processes. Given, however, the limitations of the particular experimental technique, we now present arguments to assess the validity of using the initial slopes. These arguments take several directions. First, we consider

the possible products of the initial interaction between NO_3 and alkenes or alkynes. Secondly, we demonstrate that numerical modelling of the experimental data over the full range of contact times is consistent with the mechanisms and rate coefficients suggested. Thirdly, we discuss the effect of added molecular oxygen on possible secondary radical reactions.

We consider first reactions with the alkenes, which were used in our work to confirm the validity of the experimental technique. Ravishankara and Mauldin¹¹ give kinetic evidence that the reaction of NO₃ with *trans*-but-2-ene proceeds with 1:1 stoicheiometry under the experimental conditions that they used. Following this line of reasoning, they quote a rate constant for the reaction of NO₃ with isobutene that is in excellent agreement (see table 2) with the value that we derive by our initial-slope method.

Experimental data¹² provide information about the nature of the initial adduct between NO₃ and alkenes, and its subsequent fate. Addition of NO₃ to the unsaturated bond is followed by intramolecular decomposition of the adduct, producing NO₂ and an organic radical that will further rearrange rapidly to the epoxy derivative or its corresponding carbonyl isomer. Secondary reactions of NO₂ at least must thus be included in the reaction mechanism, to produce a sequence of the form:

$$NO_3 + X \rightarrow NO_2 + Z$$
 (9)

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M.$$
⁽²⁾

We have performed numerical integrations of the differential rate equations describing the scheme (to which was added the wall loss of NO₃) in order to see whether our data could be satisfactorily explained. The rate constant for reaction (2) appropriate to the pressure employed (and assuming M = He, since partial pressures of added reactants were always less than 10% of the total pressure) was taken from Smith *et al.*⁹ Good fits to the full experimental concentration – time measurements were obtained with this scheme, and inclusion of any reaction faster than reaction (2) led to a markedly poorer fit. Furthermore, the expected pressure dependence of reaction (2) is followed, suggesting that the secondary reaction in the simple alkene systems does, indeed, involve only NO₂. We return at the end of this section to the special case of buta-1,3-diene. Additional indirect evidence that there are no unsuspected fast secondary processes with alkene reactants comes from the measurements of NO₃ absorption cross-sections by Sander.⁴ Partial removal of NO₃ by titration with 2,3-dimethylbut-2-ene proceeds with the same stoicheiometry as for titration with NO, where one NO₃ is removed for each NO added.

We turn now to possible secondary processes in the reaction of NO_3 with alkynes. The adduct from the initial interaction is likely to rearrange ultimately to NO_2 and a ketene.^{13,14} In that case, consideration must be given to secondary consumption of NO₃ by the ketene as well as by NO_2 . No rate data appear to exist for such reactions, but comparison of the reactivities of $O({}^{3}P)$ and NO₃ towards alkenes¹⁵ and acetaldehyde¹⁰ suggests a rate constant for NO₃+CH₂CO between 50 and 200 times slower than that for O(³P)+CH₂CO, or ca. 10^{-14} cm³ molecule⁻¹ s⁻¹. This value is relatively small compared with the rate constants of the NO2 interaction at the pressures used [pseudosecond-order rate constants $(5-12) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹]. In fact, those experimental runs in which the relationship between [NO₃] and contact time deviates from the simple linear first- or second-order rate law can again be adequately explained by the two-reaction scheme of processes (9) and (2). Fig. 5 shows some results for (a)first-order and (b) second-order experiments in which the appropriate functions of [NO₃] do not bear the expected linear relationship to time. In the case of the first-order reaction, it is seen that the modelled lines match well the experimental points, with no concessions made about the rate constants used. We used our upper limit of k_w (0.1 s⁻¹) to obtain the solid line; however, the behaviour with k_w set to 1 s^{-1} is very similar



Fig. 5. (a) Numerical model of the reaction between NO₃ and propyne, (pseudo-first-order conditions). Plot of ln [NO₃] against time. \bigcirc , Experimental points; (----) $k_w = 0.1 \text{ s}^{-1}$, (---) $k_w = 1.0 \text{ s}^{-1}$. (b) Numerical model of the reaction between NO₃ and but-2-yne, (second-order conditions). The solid line is for the case where reaction (2) is included in the kinetic model ($k_3 = 6.5 \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹) and the dashed line for the case where it is omitted ($k_3 = 7.7 \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹). The dashed line also represents the initial slope and its continuation, used here to calculate the experimental rate constant. Experimental points (\bigcirc).

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(dashed line), suggesting that a wall activity enhanced in the presence of organic reactant will not invalidate our results. There remains, of course, the possibility of k_w being a function of [X] over the range of concentrations employed, and thus of contributing an apparent concentration-dependent effect that would be added to the true rate constants for the homogeneous processes. For the second-order reactions the situation is less clear-cut. As illustrated in fig. 5(b), the behaviour modelled with the inclusion of the NO₃ + NO₂ reaction fits the experimental data well for a value of k_3 ca. 20% lower than that obtained from the initial slope. The values of the rate constants given in table 1, and in table 2 for isobutene, buta-1,3-diene and but-2-yne, are therefore probably too high. However, deriving the lower rate constants by numerical modelling demands certainty about the reaction mechanism, and since other problems arise, as we shall show shortly, it seems preferable to quote the unadjusted results.

The discussion of the preceding paragraphs is intended to show that the curvature of the kinetic plots can be adequately explained in terms of expected secondary reactions, and that taking initial slopes gives a good representation of the rate of the primary process, regardless of the detailed nature of the secondary steps. The remaining danger is that there are additional secondary reactions participating at a rate great enough that the intermediates are essentially at steady-state concentrations, so that the reactions do not contribute to the curvature of the kinetic plots. Any such reaction would have to proceed with a rate constant in excess of ca. 10^{-12} cm³ molecule⁻¹ s⁻¹, and would therefore probably have to involve a radical process for which there is neither kinetic nor mechanistic evidence. In order to assess the possible interference of hypothetical product radicals in the removal of NO_3 , experiments with acetylene and propyne were performed in which the reactant mixtures contained up to 50% of O_2 and in which $[O_2]/[NO_3]$ was always greater than 10, and sometimes as high as 100. Plots of ln $[NO_3]$ against l were identical in the presence or absence of O_2 for up to 70% conversion of NO_3 . This result strongly suggests that radical reactions are unimportant, and in the absence of further evidence, we propose that our rate coefficients be taken to refer to the primary interaction alone. An additional complication, of a different kind, arises in the reactions that must be treated by second-order kinetics (the reactions with isobutene, buta-1,3-diene and but-2-yne). The appearance of secondary reactions here not only constitutes an additional correction term for loss of NO₃, but also affects how the effective loss of the co-reactant is to be treated. With isobutene, the problem is unlikely to arise, the arguments advanced earlier indicating that the possible reactions of any products are unlikely to compete with the primary process. However, in the reaction of buta-1,3-diene with NO_3 , the product of the initial reaction is likely to be olefinic, and might react with NO₃ at a rate comparable with that of the parent diene, and itself produce NO₂ that would consume further NO₃. Rate constants in the range $(1-2) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ would be reasonable. Similar remarks apply to the reaction with but-2-yne, because the first product may be $(CH_3)_2C=CO$, a species proposed in the rearrangement of the expected intermediate epoxide.¹⁴ Comparisons of the kind outlined earlier suggest that a rate constant for the reaction of this ketene with NO₃ might be as high as 3×10^{-13} cm³ molecule⁻¹ s⁻¹. If such secondary reactions did occur, the entries in tables 1 and 2 for buta-1,3-diene and but-2-yne would be too high for this reason as well as because of the consumption of NO_3 by NO_2 . In fact, the detailed dependence of $[NO_3]$ on time is not consistent with secondary reactions possessing rate constants as large as suggested. To obtain a reasonable match between the experimental data and the results of numerical integrations, rate constants of ca. 1×10^{-15} cm³ molecule⁻¹ s⁻¹, two orders of magnitude smaller than those suggested, have to be employed, with a consequent small (<20%) effect on the derived value of the rate constant for the primary reaction. Larger rate constants than those thought to be reasonable for secondary reactions would permit generation of concentration-time curves of the correct shape, but there is no evidence for such values. The conclusion

that the first product of the reaction of NO₃ with the diene does not consume a second NO₃ radical is analogous to that reached by Cvetanovic¹⁶ for the reaction of O atoms with buta-1,3-diene. Although the rate constants quoted in tables 1 and 2 for isobutene, buta-1,3-diene, and but-2-yne must be upper limits, we suggest that these limits are almost certainly less than 30%, and probably less than 20%, too high. The main entries in table 2 for isobutene, buta-1,3-diene and but-2-yne are therefore the upper limits, while we have presented in parentheses the lower limits that we think are compatible with the data.

Comparisons

Where possible, comparisons with the literature have been made and are shown in table 2. It will be seen that the published data of Atkinson et al.¹⁷ for butadiene, obtained by observing decay of the diene, are lower than both our upper limit and our expected lower limit. The rate constants determined by the Riverside group depend on the value for the equilibrium constant connecting reaction (2) and its reverse, reaction (-2). The values given in table 2, ref. (18), (19) and (17) for ethylene, isobutene and buta-1,3-diene, respectively, correspond to $K_{eq} = 3.35 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ and are 1.8 times larger than in the original publications. A comprehensive discussion of this point is given by Finlayson-Pitts and Pitts,¹⁰ but it is evident that the modification brings the value for buta-1,3-diene closer to ours. Very recently,²⁰ Atkinson *et al.* have reported rate constants for the reactions of NO_3 with acetylene and propyne. As with these workers' results for the reaction with isobutene and butadiene, the rate constants are obtained relative to that for the reaction with ethylene. We show in table 2 the rate constants derived from the data of Atkinson and co-workers¹⁷⁻²⁰ on the basis of our $k(NO_3 + C_2H_4)$. The upper limit for $k(NO_3 + C_3H_2)$ falls within our measured range and that for the reaction with buta-1,3-diene approaches ours. For the reaction with propyne, the value of Atkinson *et al.*²⁰ still falls short of ours by a factor of between 1.5 and 2.0. It is tempting to speculate that the remaining difference between our value and that of Atkinson et al. is a consequence of the stoicheiometry of the interaction; however, as we have shown earlier, we have no evidence in support of this idea and, indeed, the detailed kinetic behaviour argues against it.

The agreement between the absolute rate constant reported for the reaction of NO₃ with isobutene is very good, as can be seen from table 2: the value for this rate constant is thus established with some certainty. This agreement emphasizes the tenfold discrepancy in the literature values for $k(NO_3 + \text{ethylene})$ that has been noted previously.¹⁸ Although our value for the ethylene reaction is not exactly the same as that of Atkinson and co-workers, ^{18,19} who used a relative method, our value confirms the lower value, the average of our result and that of Atkinson and co-workers being $1.5 \times 10^{-16} \text{ cm}^3$ molecule⁻¹ s⁻¹.

Rate data for the reactions of NO₃ with some of the same alkenes that we studied have been obtained recently by mass spectrometry (R. N. Schindler, personal communication). Both [NO₃] and hydrocarbon concentration could be followed, and the results give added support to our determinations and interpretation of stoicheiometry. Thus for isobutene and buta-1,3-diene, the mass-spectrometrically determined rate constants were, in units of 10^{-16} cm³ molecule⁻¹ s⁻¹, 3400 and 2100, comparing well with our values (table 2) of 3400 and 2200.

Correlations

Our data afford the first opportunity of comparing the rate constants for the reactions between NO_3 and alkynes with those for other systems. A convenient way of displaying the data is to plot logarithms of the rate constants for the reactions with NO_3 against



Fig. 6. Plot of log $k(NO_3)$ against log $k(O^3P)$ and log k(OH) for reactions with alkenes and alkynes. Data from ref. (2), (15), (21), (26) and table 2. 1, Acetylene; 2, ethylene; 3, propene; 4, but-1-ene; 5, buta-1,3-diene; 6, but-2-ene; 7, isobutene; 8, but-2-yne; 9, but-1-yne; 10, propyne; 11, pent-1-yne; 12, hex-1-yne.

logarithms of the rate constants for the reactions with other species; such plots are the kinetic analogues of linear free-energy relationships.

Atkinson's compilation²¹ shows that rate constants for the reactions of OH with alkenes correlate well with those for $O({}^{3}P)$ + alkene reactions, less well with those for NO_3 + alkene reactions and poorly with those for O_3 + alkene reactions, thus emphasizing the difference in mechanism. Far fewer data are available for alkyne reactions, but we have compared rate constants for the NO₃ reactions with alkenes and alkynes with those for the corresponding $O({}^{3}P)$ and OH reactions in fig. 6. The plots for alkynes are reasonably linear for both comparisons. For the alkynes there are insufficient data for the reactions of $O({}^{3}P)$ to permit further evaluation. There is obviously a good correlation between the reactivity of the alkynes towards OH and NO₃, although it appears that but-2-yne is relatively more reactive in its interaction with NO₃. We think it unlikely that it is the acetylene result which is anomalously high (i.e. that the data were affected by a small quantity of reactive impurity) because four different samples of acetylene were used, involving increasing numbers of trap-to-trap distillations. It is interesting to note that but-2-ene reacts more rapidly with NO₃ than does but-1-ene, but in the case of but-2-yne and but-1-yne, the ratio of rate constants is even greater. All these reactions presumably occur by simple addition because, as has been pointed out,¹⁰ the strong C-H bond (*ca.* 550 kJ mol⁻¹) makes abstraction unlikely.

A plot to compare the reactivity of NO_3 with that of O_3 is shown in fig. 7. Ozone attacks alkenes to form a five-membered ring, and the rate constants show virtually no correlation with those for the NO_3 reactions. In the case of the alkynes, ozone reacts very slowly and the rate constants are not much influenced by the chemical nature of the alkyne. However, the rate constants for the reaction with NO_3 show considerable variation with chain length.

In an attempt to display all our rate data, we have plotted logarithmically the rate constants obtained by us and others for the reactions of NO_3 with alkenes and alkynes as a function of ionization potential. Fig. 8 shows that all the data for a particular series of reactants lie on a smooth curve, but that an approach to a linear correlation can be envisaged more easily for the alkenes.



Fig. 7. Plot of log $k(NO_3)$ against log $k(O_3)$ for reactions with alkenes and alkynes. Identification numbers for compounds listed in caption for fig. 6. Data from ref. (27) and table 2.



Fig. 8. Plot of log k(NO₃) against ionization potentials for alkenes and alkynes. (●) alkynes, (○) alkenes, (●) buta-1,3-diene, (- -) alkenes, (−−) alkynes. Identification numbers for compounds listed in caption for fig. 6. Data from ref. (28) and (29) and table 2.

It is clear from our work that the atmospheric reactions of alkynes with NO₃ during the day cannot normally be significant compared with the much faster rates of the corresponding reactions with OH. At night, however, [OH] drops from a typical value of 5×10^6 molecule cm⁻³ in the polluted troposphere²² to less than 2×10^5 molecule cm⁻³. [NO₃] can rise from less than 6×10^7 molecule cm⁻³ during the day to 1.1×10^{10} molecule cm⁻³ in an urban polluted atmosphere at night.¹⁰ Alkyne lifetimes may then be determined by their reactions with NO₃.

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