an unlimited number of equations, even the ratio of molar absorptivities can be obtained for species with overlapping absorption spectra. The reliability of the data obtained by this approach is confirmed in each case by simulation and direct comparison of the experimental and calculated decay curves.

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Absorption Spectrum of NO_3 and Kinetics of the Reactions of NO_3 with NO_2, Cl, and Several Stable Atmospheric Species at 298 K

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The absorption spectrum of NO_3 has been measured between 615 and 670 nm in the photolysis of Cl_2–$ClONO_2$–N_2 and F_2–HNO_3–N_2 mixtures. The absorption cross section was found to be $(1.19 \pm 0.36) \times 10^{-17}$ cm^2 molecule^{-1} at 622.3 nm, and this leads to a value of $(1.85 \pm 0.56) \times 10^{-17}$ cm^2 molecule^{-1} at 662 nm in good agreement with most recent studies. The rate coefficient for the reaction $NO_3 + NO_2 \rightarrow N_2O_5$ was measured to be $(4.8 \pm 0.3) \times 10^{-13}$ and $(5.8 \pm 0.8) \times 10^{-13}$ cm^3 molecule^{-1} at total pressures of 24 and 40 torr of N_2, respectively. A rate coefficient for the reaction between Cl and NO_3 was derived from the NO_3 behavior in the photolysis of Cl_2 and $ClONO_2$ mixtures and its value at 298 K is $(2.7 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. In addition, upper limits were determined for the rates of reaction of NO_3 with SO_2, CO, CH_4, H_2O_2, and CS_2.

Introduction

The appreciation of the important role played by the oxides of nitrogen in atmospheric chemistry has led to many detailed studies of the elementary reactions involving NO_x.[1,2] Although the NO_3 radical was not considered important in these early studies, it is now also thought to exert a considerable influence on the NO_x balance of the atmosphere, and the recent detection of NO_3 at night in both the troposphere[3,4] and stratosphere[5] necessitates a better understanding of the elementary processes which determine the atmospheric fate of NO_3.

NO_3 builds up at night in the atmosphere, where it is formed by the reaction of NO_2 with O_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (1)$$

The relative concentrations of the oxides of nitrogen are regulated by the equilibrium between NO_2, NO_3, and N_2O_5, which is normally set up rapidly under atmospheric conditions:

$$NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M \qquad (2)$$

The establishment of this equilibrium does not lead to overall loss of NO_x. However, it has been pointed out that reactions of NO_3 with stable atmospheric molecules could be a considerable sink for NO_x,[6] and due to the relatively high NO_3 concentrations encountered at night, these reactions need not be particularly fast. Recent measurements of NO_3 in the nighttime troposphere do support the view that NO_3 is scavenged, even in relatively unpolluted air.[7] Work by Niki's group in the 1970s showed that NO_3 reacts reasonably quickly with, for example, unsaturated hydrocarbons, but these reactions cannot account for the observed scavenging.[8] Recent publications from the Riverside group have shown that NO_3 is very reactive toward a wide range of naturally emitted hydrocarbons, particularly monoterpenes.[9] The goals of the present study, therefore, were to investigate the known reaction of NO_3, with NO_2, and to attempt to identify further reactions which might constitute a nighttime sink for NO_x in the atmosphere. Due to the discrepancies in the literature between different measurements of the magnitude of the absorption cross section of NO_3, it was necessary first to measure this parameter.

NO_3 absorbs light between 670 and 400 nm in a banded absorption first observed by Jones and Wulf[10] and later studied at higher resolution by Ramsey.[11] Below 630 nm the absorption leads to dissociation and the atmospheric lifetime of NO_3 during daylight is consequently of the order of seconds. The two strongest features in the spectrum at 662 and 623 nm have been assigned as the 0–0 band and the 1–0 band of the v_1 symmetric stretch, respectively. The 0–0 band at 662 nm has been used to monitor NO_3 both in the laboratory and in the atmosphere.

At the outset of this work several studies of the NO_3 spectrum had been published[12-15] and, although agreement existed on the positions of the absorption features, estimates of the absolute magnitude of the cross section varied by up to a factor of two. The studies of Graham and Johnston[13] and Mitchell et al.[15] do not rely on a calculation of the NO_3 concentration to determine its absorption cross section and agree well on the integrated strength of the 0–0 band. However, the maximum absorption cross section derived by the latter group is lower by about 40%. Other studies relied on calculating the equilibrium concentration of NO_3 in a flowing NO_x mixture. Marinelli et al.[14] undertook the most detailed investigation of the band positions and line shapes of NO_3, but the maximum absorption cross section at 662 nm and the total integrated intensity of the 0–0 band are both about 12% lower

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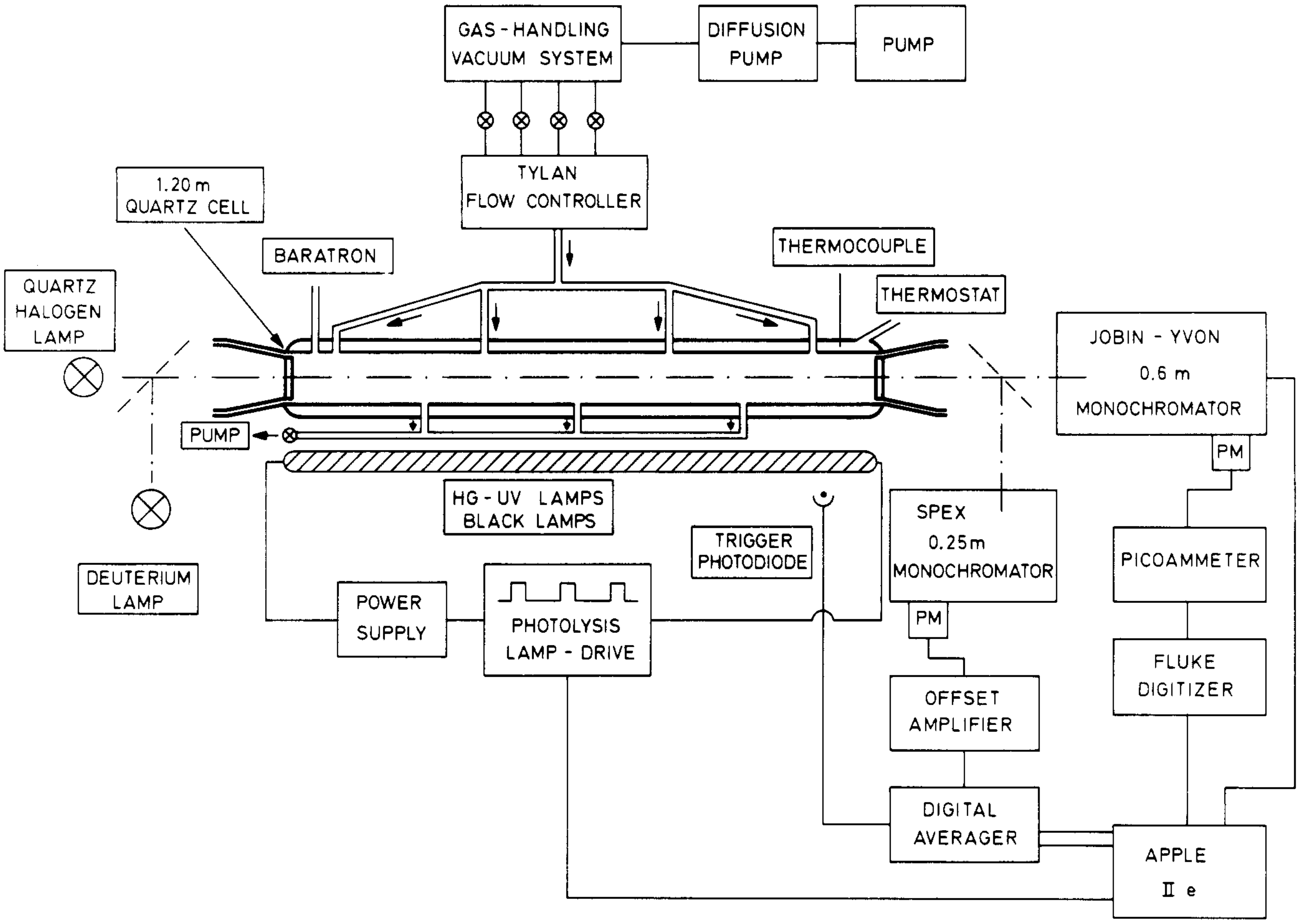

Figure 1. Schematic of the apparatus used for modulated photolysis studies of NO_3.

than the values derived by Graham and Johnston. On the other hand, in their determination of the yields of O and NO from NO_3 photolysis, Magnotta and Johnston[16] derived cross sections 30–40% larger than those of Graham and Johnston.

Recently two further absolute measurements of the NO_3 absorption spectrum have been published. Ravishankara and Wine[17] generated NO_3 in a discharge-flow tube and monitored the absorption with a tunable dye laser. Cox et al.[18] generated NO_3 by modulated photolysis and recorded the entire spectrum of NO_3 simultaneously using an optical multichannel analyzer. However, these two later studies differ by at least 10% over the whole range. It therefore seemed worthwhile to investigate the NO_3 spectrum once more, paying particular attention to the regions showing discrepancies.

Prior to the start of this work the only direct study of the reaction between NO_2 and NO_3 was that of Fowles et al.,[19] who derived values for k_2 and k_{-2} from measurement of the average NO_3 concentration along the length of a flow tube. In the meantime three other groups have also studied this reaction. Kircher et al.,[20] in an extensive study of reaction 2 between 20 and 700 torr, produced NO_3 in the presence of excess NO_2 by the flash photolysis of Cl_2–$ClONO_2$ mixtures. Ravishankara and co-workers[21] used a discharge-flow tube to generate NO_3 by the reaction of F atoms with HNO_3 and measured the rate coefficient for reaction 2 in the low-pressure region (0.5–8 torr). Finally, Croce de Cobos et al.[22] investigated reaction 2 by laser flash photolysis between 2 and 200 atm, using O + NO_2 as a high-pressure source of NO_3.

During our experiments to measure the NO_3 absorption cross section it was realized that a reaction between Cl atoms and NO_3 occurred. Cox et al.[18] reported a value for the rate of reaction between Cl and NO_3, obtained in a study of the photolysis of Cl_2–$ClONO_2$ mixtures, and a preliminary report from our laboratory has also been published.[23]

We report here the investigation of some NO_3 reactions using a novel oblong-waveform-modulated photolysis apparatus suitable for measuring the growth and decay of NO_3 concentration on time scales between milliseconds and tens of seconds. The visible spectrum of NO_3 has been remeasured and the rate of reaction between NO_2 and NO_3 studied directly by using different sources of NO_3. In addition, experiments were carried out to determine the rate of reaction of Cl with NO_3, and to see if any significant reaction occurred between NO_3 and the atmospheric species CH_4, CO, SO_2, CS_2, and H_2O_2.

Experimental Section

NO_3 was generated by the blacklamp photolysis (310–400 nm) of Cl_2–$ClONO_2$–N_2 or F_2–HNO_3–N_2 mixtures.

$$Cl_2 + h\nu \rightarrow Cl + Cl \quad (3)$$

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3 \quad (4)$$

$$F_2 + h\nu \rightarrow F + F \quad (5)$$

$$F + HNO_3 \rightarrow HF + NO_3 \quad (6)$$

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TABLE I: Absorption Cross Sections Used for the Measurement of Reactants

gas	wavelength, nm	absorption cross section, cm^2 molecule^{-1}	ref
Cl_2	310	1.8×10^{-19}	26
$ClONO_2$	220	3.4×10^{-18}	26
F_2	350	7.5×10^{-21}	27, this work
	330	1.4×10^{-20}	
HNO_3	205	2.9×10^{-18}	26
NO_2	350	4.4×10^{-19}	28
	400	6.0×10^{-19}	
H_2O_2	330	1.2×10^{-21}	26
N_2O_5	220	2.2×10^{-18}	26

The apparatus used here is shown schematically in Figure 1 and described in detail elsewhere.[24] It is essentially a development of the molecular modulation apparatus of Johnston et al.,[25] but with the advantage that the modulated absorptions are observed in real time. The reactor consists of a quartz cell of length 148 cm whose quartz end windows are inset, yielding an optical path length of 114 cm. The photolysis cell is coated internally with Teflon to minimize any wall reactions. The vessel has four gas inlets on one side of the vessel and three outlets on the opposite side. The outlets are sited midway between the inlets to ensure thorough mixing. The residence time, t_{res}, of species in the cell is given by

$$t_{res} = V/F$$

where V is the volume of the cell and F is the bulk flow rate of gas through the vessel, as measured and maintained by calibrated mass flow meters. In these experiments t_{res} was varied between 3 and 8 s.

The photolysis cell was surrounded by up to six blacklamps (310–400 nm), powered by a 20-kHz signal of up to 1-kV amplitude. This operational procedure leads to an increased lifetime for the photolysis lamps and better switching reproducibility. The lamps could be switched at photolysis frequencies between 2.5 kHz and 0.02 Hz and the ratio of time on to time off could be varied from 0.1 to 9.

Two light sources were used for optical measurements, a D_2 lamp for measurements in the UV and a tungsten halogen lamp for the visible. The collimated beam of light passed once through the cell and, after dispersion by a 0.3-m monochromator (Spex Minimate), was detected by a photomultiplier (Hamamatsu, R106UH). A helium neon laser was used to check the absolute calibration and the effective resolution of the monochromator at 630 nm, and a Pen-Ray low-pressure mercury lamp between 250 and 400 nm. The current from the photomultiplier was converted to a voltage and then offset by an equal and opposite constant d.c. voltage V_0. The residual signal, Δv, was then sent to a 1024-channel 9-bit signal avenger (E.G.&G. Model 4203). A photodiode (rise time less than 1 μs) positioned next to the photolysis lamps provided a trigger pulse for the averager to synchronize the start of the sweep with the lamps. The optical density, O.D., for small signals is given by

$$\text{O.D.} = \Delta v / V_0$$

The signal in the averager and the voltage V_0 were sent after an experiment to an Apple IIe minicomputer where the data could be mathematically manipulated.[24] Relatively small absorptions could be measured in this way, and a noise level corresponding to an optical density of 5×10^{-6} was achieved in about 20 min of averaging.

For NO_3 measurements a resolution of 1 nm was used and a 580-nm cutoff filter was placed in front of the monochromator to reduce scattered light at shorter wavelength. A 610-nm filter placed between the tungsten halogen lamp and the photolysis cell minimized photolysis of NO_3 by the analyzing beam. The concentrations of the species listed in Table I were determined optically by use of 5-nm resolution. The wavelengths used and the values of the appropriate absorption cross sections (from ref 26–28) are also given in Table I.

$ClONO_2$ was prepared by reacting freshly prepared Cl_2O with N_2O_5 between 195 and 250 K:[29]

$$Cl_2O + N_2O_5 \rightarrow 2ClONO_2 \qquad (7)$$

Cl_2O was generated by flowing Cl_2 through a column containing HgO:[30]

$$2Cl_2 + (n + 1)HgO \rightarrow Cl_2O + HgCl_2{\cdot}nHgO \qquad (8)$$

N_2O_5 was prepared by flowing a mixture of NO and O_3 repeatedly between two traps held at 195 K.[31] The $ClONO_2$ was purified by trap-to-trap distillation between three traps held at 77, 153, and 195 K. N_2 and dilute mixtures of NO_2 (1%), Cl_2 (1%), and F_2 (5%) in N_2 were used as purchased from Linde. A flow of HNO_3 in N_2 was produced by passing a stream of N_2 through white nitric acid held at 270 K. This flow was subsequently passed through a P_2O_5 drying column.

Static mixtures of $ClONO_2$ did decay when left standing in the reaction vessel. This process may be both homogeneous and heterogeneous. However, as the effective rate coefficient for $ClONO_2$ decomposition was observed to be less than 3×10^{-5} s^{-1}, it was of negligible significance in the flowing mixtures used in the experiments, other than that it may have been the source of the small amounts of NO_2 present in the $ClONO_2$.

Results

Photolysis Rates of Reactant Species. As explained in the next section, the photolysis rates of Cl_2 and F_2 are used to determine the absolute NO_3 absorption cross section. It is therefore necessary to determine their values. The photolysis rate of Cl_2, k_3, was measured in the photolysis of static Cl_2–H_2–O_2 mixtures. The Cl_2 decays via the reactions

$$Cl_2 + h\nu\ (310\text{–}400\ \text{nm}) \rightarrow Cl + Cl \qquad (3)$$

$$Cl + H_2 \rightarrow H + HCl \qquad (9)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (10)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (11)$$

The decay of Cl_2 in the system is given by

$$d \ln [Cl_2]/dt = -k_3$$

The Cl_2–N_2–H_2–O_2 mixtures were varied in the following ranges (molecules cm^{-3}): Cl_2, (6–30) × 10^{14}; H_2, (2–8) × 10^{18}; O_2, (2–8) × 10^{18}. Absorption at 310 nm was used to monitor Cl_2, and analysis of the logarithmic Cl_2 decays yielded $k_3 = (1.35 \pm 0.2) \times 10^{-3}$ s^{-1} per blacklamp.

The photolysis rate of F_2 was measured in an analogous way from the photolysis of F_2–H_2–O_2 mixtures.

$$F_2 + h\nu\ (310\text{–}400\ \text{nm}) \rightarrow F + F \qquad (5)$$

$$F + H_2 \rightarrow H + HF \qquad (12)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (10)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (11)$$

The F_2 concentration was monitored at 330 nm. However, the product H_2O_2 also absorbs at this wavelength, $\sigma(F_2)_{330}/\sigma(H_2O_2)_{330} = 12$, and consequently at long photolysis times the product absorption must be taken into account. A typical photolysis

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TABLE II: Determination of the Absolute NO_3 Absorption Cross Section at 622.3 nm in the Photolysis of Cl_2–$ClONO_2$–N_2 Mixtures at Total Pressures of 24 torr of N_2, and in the Photolysis of F_2–HNO_3–N_2 Mixtures at Total Pressures of 40 torr

$[Cl_2]^a$	$[ClONO_2]^a$	$[F_2]^a$	$[HNO_3]^a$	lamps	$(d(OD)/dt)_0$, $s^{-1} \times 10^3$	σ, $cm^2 \times 10^{17}$
12	1.6			3	16	1.44
14	1.5			1	4.5	1.05
14	1.5			1	3.7	0.96
6.8	3.6			2	4.5	1.07
6.8	2.2			2	6.0	1.43
7.5	2.2			3	8.9	1.3
2.2	6.8			2	1.3	1.0
		122	6.4	4	10.7	1.45
		122	6.4	2	4.0	1.14
		120	6.4	4	7.4	1.02
		100	6.4	4	6.3	1.01
		120	6.4	2	6.8	1.3
		78	6.4	2	3.0	1.22
		63	6.4	2	2.7	1.23
		85	6.4	2	3.0	1.14
		86	6.4	2	3.3	1.25
						mean 1.19 ± 0.17

[a] $\times 10^{-14}$ molecules cm^{-3}.

mixture contained F_2 (1.7×10^{17} molecules cm^{-3}), H_2 (9.0×10^{18} molecules cm^{-3}), and O_2 (9.0×10^{18} molecules cm^{-3}). The initial slopes of the logarithmic decays of F_2 yielded $k_5 = (7.4 \pm 1.3) \times 10^{-5}\ s^{-1}$ per lamp. This is in good agreement with a value of $k_5 = 6.8 \times 10^{-5}\ s^{-1}$ per lamp estimated from the relative overlap of the lamp intensity distribution with the Cl_2 and F_2 absorption spectra between 310 and 400 nm.

The photolysis rate of NO_2 was measured by monitoring the decay of pure NO_2 at 400 nm during photolysis

$$NO_2 + h\nu\ (310\text{–}400\ \text{nm}) \rightarrow NO + O \qquad (13)$$

$$O + NO_2 \rightarrow NO + O_2 \qquad (14a)$$

$$O + NO_2 + M \rightarrow NO_3 + M \qquad (14b)$$

If up to a few torr of pure NO_2 are used, the NO_2 decay is given by the expression:

$$d \ln [NO_2]/dt = -2k_{13}$$

and this yielded a value of $k_{13} = (3.3 \pm 1.0) \times 10^{-3}\ s^{-1}$ per lamp.

$ClONO_2$ also absorbs in the 310–400-nm region but its photolysis was observed to be slow, with a rate coefficient of less than $2 \times 10^{-4}\ s^{-1}$ per lamp. Under the conditions used in these experiments this represented a negligible loss of $ClONO_2$ and a negligible production of NO_3 or Cl, the expected products of the photolysis.[26]

The Visible Spectrum of NO_3. Absorption attributable to NO_3 was observed in three different chemical systems: in the photolysis of Cl_2–$ClONO_2$ mixtures and F_2–NHO_3 mixtures, and in flowing mixtures of N_2O_5 in N_2.

The relative absorption spectrum was first obtained in the photolysis of a flowing mixture of Cl_2 (7×10^{14} molecules cm^{-3}), and $ClONO_2$ (3.3×10^{14} molecules cm^{-3}) in 20 torr of N_2. Steady-state NO_3 absorptions between 615 and 670 nm were recorded at intervals of 0.5 nm by using a resolution of 1 nm. Four sets of experiments were carried out, covering the above range twice and particularly comparing the relative heights of the maxima at 622.3 and 662.0 nm. The relative NO_3 spectrum obtained from this photolytic source of NO_3 was checked by switching a flow of N_2O_5 (typically 4×10^{14} molecules cm^{-3}) in and out of the cell, and recording the optical density due to NO_3 as a function of wavelength. During these experiments, the concentration of N_2O_5 was less than 1×10^{15} molecule cm^{-3} and that of NO_2 less than 1×10^{13} molecule cm^{-3}, and therefore absorption due to N_2O_5 or NO_2 in this spectral region was negligible compared with that of NO_3.

The cross section of NO_3 was determined at 622.3 nm from the rate of production of NO_3 in the photolysis of Cl_2–$ClONO_2$–N_2 and F_2–HNO_3–N_2 mixtures. Cl_2–$ClONO_2$–N_2 mixtures were chosen to be similar to those used in the determination of the relative absorption spectrum of NO_3. In both systems the dominant loss process for the NO_3 was flow out of the cell, since the reaction of NO_3 with itself is very slow ($k_{15} = 2.0 \times 10^{-16}$ molecules cm^{-3}).[13]

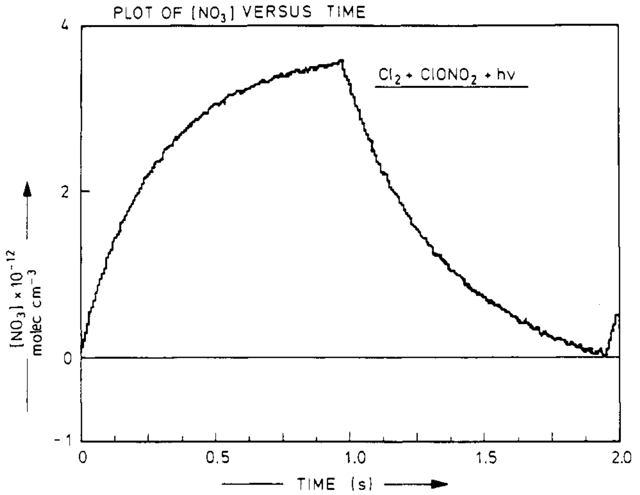

Figure 2. Trace of NO_3 modulation at 622.3 nm from photolysis of a Cl_2–$ClONO_2$–N_2 mixture: Cl_2, 1.7×10^{15} molecules cm^{-3}; $ClONO_2$, 1.6×10^{14} molecules cm^{-3}; total pressure, 25 torr of N_2. Photolysis period 2.0 s, using three blacklamps. Average of 578 sweeps.

$$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2 \qquad (15)$$

Both the rise to steady state and the decay of the NO_3 were observed to be first order. Figure 2 shows an example of a modulated NO_3 absorption at 662.3 nm produced from the Cl_2–$ClONO_2$ source. The absorption cross section of NO_3 is related to the initial rate of increase of OD, $(d(OD)/dt)_0$, by the relationship

$$\sigma = (d(OD)/dt)_0/(2lk_p[X_2])$$

where l is the optical path length and $2k_p[X_2]$ is the rate of production of Cl, $2k_3[Cl_2]$, or F, $2k_5[F_2]$ in the two sources.

The values of σ obtained from the two sources are listed in Table II. The two systems are in reasonable agreement, and the data can be combined to give a mean value of $\sigma(NO_3)_{622.3} = (1.19 \pm 0.17) \times 10^{-17}\ cm^2\ molecule^{-1}$ at 298 K at a pressures of 24 or 40 torr of N_2. The error in the cross section represents one standard deviation from the mean value. When account is taken of the measurement of the Cl_2 concentration and photolysis rate, we estimate the overall maximum error to be ±30% (2 standard deviations). In experiments in which the two peaks (622.3 and 662 nm) were measured relative to one other, the ratio of their intensities was found to be 1.55 ± 0.1. The complete spectrum,

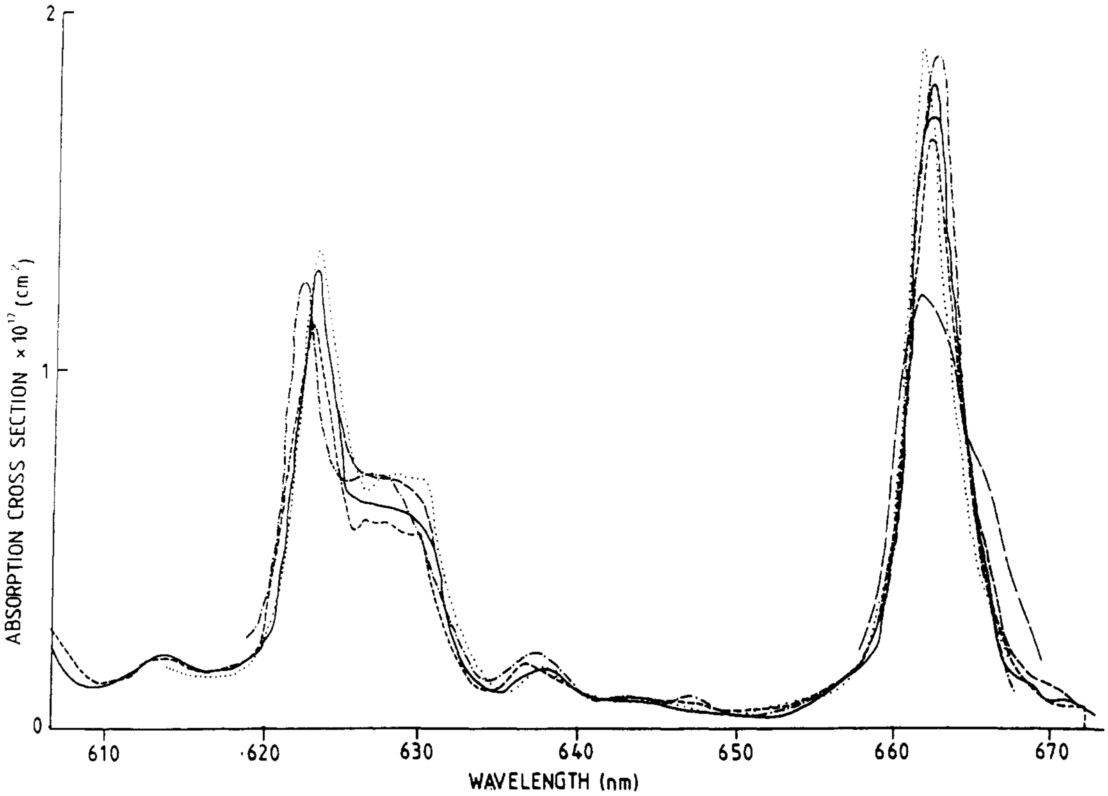

Figure 3. Comparison of NO_3 spectra between 610 and 670 nm: (····) Marinelli;[14] (----) Cox;[18] (––––) Graham;[13] (——) Mitchell;[15] (—) Ravishankara;[17] (-···) this work. Spectrum from ref 14 scaled to a maximum value of 1.9×10^{-17} cm^2 molecule^{-1} (see text). Spectrum from ref 15 only between 657 and 670 nm to indicate trend (points taken from ref 14).

TABLE III: Scheme of Chemical Reactions in the Photolysis of Cl_2–$ClONO_2$–N_2 Mixtures

reaction	rate coeff	units	ref
(3) $Cl_2 + h\nu \rightarrow Cl + Cl$	1.35×10^{-3}	*a*	see text
(4) $Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1.12×10^{-11}	*b*	26
(15) $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	2.0×10^{-16}	*b*	13
(16) $Cl + NO_3 \rightarrow ClO + NO_2$	2.7×10^{-11}	*b*	see text
(2) $NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M$	2.2×10^{-11}	*c*	13
(17a) $ClO + NO_3 \rightarrow ClOO + NO_2$	2.3×10^{-13}	*b*	33
(17b) $ClO + NO_3 \rightarrow OClO + NO_2$	1.7×10^{-13}	*b*	33
(18) $OClO + h\nu \rightarrow ClO + O$	$k_{18} = 20k_3$	*a*	est
(19) $Cl + OClO \rightarrow 2ClO$	5.9×10^{-11}	*b*	26
(20) $Cl + O_2 + M \rightleftharpoons ClOO + M$	2.0×10^{-20}	*c*	26
(21) $ClO + NO_2 + M \rightarrow ClNO_3 + M$	1.7×10^{-31}	*d*	26
(22) $O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	*b*	13
(23) $O + ClONO_2 \rightarrow$ products	2.0×10^{-13}	*b*	26
(24) $O + Cl_2 \rightarrow ClO + Cl$	5.0×10^{-14}	*b*	26
(25) flow terms			
NO_3 = flow out	$k_{25} = 1/t_{res} = 0.2$	*a*	see text
Cl_2 = flow out	k_{25}	*a*	
$ClONO_2$ = flow out	k_{25}	*a*	
NO_2 = flow out	k_{25}	*a*	
flow in = Cl_2	$k_{25}[Cl_2]_0$	*e*	
flow in = $ClONO_2$	$k_{25}[ClONO_2]_0$	*e*	
flow in = NO_2	$k_{25}[NO_2]_0$	*e*	

[a] s^{-1}. [b] cm^3 molecule^{-1} s^{-1}. [c] cm^3 molecule^{-1}. [d] cm^6 molecule^{-2} s^{-1}. [e] molecule cm^{-3} s^{-1}.

scaled to the above value at 662.3 nm, is shown in Figure 3, and compared with other published spectra.

Reactions of Cl and F with NO_3. In the photolysis of Cl_2–$ClONO_2$ mixtures, as the ratio of $[Cl_2]/[ClONO_2]$ increased, the measured steady-state concentration of NO_3 deviated from a linear dependence on the number of photolysis lamps. The most plausible explanation of this effect is a rapid reaction of NO_3 with Cl forming ClO which can itself react further with NO_3:

$$Cl + NO_3 \rightarrow ClO + NO_2 \qquad \Delta H = -57 \text{ kJ mol}^{-1} \quad (16)$$

$$ClO + NO_3 \rightarrow ClOO + NO_2 \qquad \Delta H = -51 \text{ kJ mol}^{-1} \quad (17a)$$

$$\rightarrow OClO + NO_2 \qquad \Delta H = -43 \text{ kJ mol}^{-1} \quad (17b)$$

(The enthalpies of formation were taken from ref 32.)

The reactions in Table III describe the system. Cox et al. have pointed out that the sequence of reactions 16, 17a, and 20 leads to an overall loss of NO_3 but does not deplete Cl.[18] If we assume that these three reactions and transport out of the cell are dominant, the free radicals Cl, ClO, NO_2, and NO_3 reach steady values given by

$$d[Cl]/dt = 0 = 2nk_3[Cl_2] - k_4[Cl]_{ss}[ClONO_2] - k_{16}[Cl]_{ss}[NO_3]_{ss} + k_{17a}[ClO]_{ss}[NO_3]_{ss}$$

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(32) Baulch, D. L.; Cox, R. A.; Crutzen, P. J.; Hampson, R. F.; Kerr, J. A.; Troe, J.; Watson, R. T. *J. Phys. Chem. Ref. Data* **1982**, *11*, 327.

$$d[ClO]/dt = 0 = k_{16}[Cl]_{ss}[NO_3]_{ss} - k_{17}[ClO]_{ss}[NO_3]_{ss} - k_{25}[ClO]_{ss}$$

$$d[NO_2]/dt = 0 = k_{25}[NO_2]_0 + k_{16}[Cl]_{ss}[NO_3]_{ss} + k_{17}[ClO]_{ss}[NO_3]_{ss} + k_{-2}[N_2O_5] - k_2[NO_2]_{ss}[NO_3]_{ss} - k_{25}[NO_2]_{ss}$$

$$d[NO_3]/dt = 0 = k_4[Cl]_{ss}[ClONO_2] + k_{-2}[N_2O_5] - k_{16}[Cl]_{ss}[NO_3]_{ss} - k_{17}[ClO]_{ss}[NO_3]_{ss} - k_{25}[NO_3]_{ss} - k_2[NO_2]_{ss}[NO_3]_{ss}$$

where n is the number of photolysis lamps, $[X]_0$ represents the concentration of species X prior to photolysis, and $[X]_{ss}$ that at steady state. Provided the concentration of NO_3 is greater than those of the other minor species, the above equations simplify to

$$n[Cl_2]_0/[NO_3]_{ss} = 4nk_{16}[Cl_2]_0/k_4[ClONO_2]_{ss} + k_{25}/2k_3$$

Experiments were performed in which the ratio $[Cl_2]_0/[ClONO_2]_0$ was varied and the steady-state NO_3 concentration was measured. The data obtained are shown in Figure 4. The plot yields an intercept value $k_{25}/2k_3 = 95 \pm 45$, which is in fair agreement with the ratio of the measured value of the Cl_2 photolysis rate and $1/t_{res}$, which has a value of 80 for these experiments. The slope of the plot yields a value for $4k_{16}/k_4$ of 9.5 ± 3.0. From the literature value[26] for $k_4 = (1.12 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{16} = (2.7 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This estimate agrees with the most recent value from Cox et al. of $(4.2 \pm 2.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [33] within the large experimental error. One reason the analogous plot by Cox et al. (Figure 2, ref 18) led to a higher value for k_{16} (7.5×10^{-11} cm^3 molecule^{-1} s^{-1}) may be that ClO, which was assumed to be produced and removed only via reactions 16 and 17, was regenerated from the buildup of secondary products such as OClO in their static mixtures (reactions 18 and 19 in Table III). In our flowing system this should not be a problem. If the OClO were only removed from the reaction vessel by flow out then the value obtained for k_{16} would be underestimated by a maximum of 25%.

The NO_3 steady state achieved in the photolysis of F_2–HNO_3 mixtures also deviated from a linear dependence on the number of photolysis lamps as the $[F_2]/[HNO_3]$ ratio was increased, and by analogy with the Cl_2–$ClONO_2$ system this indicates that the exothermic reactions 26 and 27 of F and FO with NO_3 may be rapid enough to compete for F atoms with reaction 6:

$$F + HNO_3 \rightarrow HF + NO_3 \quad \Delta H = -146 \text{ kJ mol}^{-1} \quad (6)$$

$$F + NO_3 \rightarrow FO + NO_2 \quad \Delta H = -8 \text{ kJ mol}^{-1} \quad (26)$$

$$FO + NO_3 \rightarrow FO_2 + NO_2 \quad \Delta H = -97 \text{ kJ mol}^{-1} \quad (27)$$

Unfortunately due to the low photolysis rate of F_2 the ratio $[F_2]/[HNO_3]$ could not be increased sufficiently to obtain a sensitive measurement of the ratio of k_{26}/k_6 from the changes in NO_3 steady state. An upper limit for the ratio $k_{26}/k_6 \leq 20$ may be inferred from the NO_3 steady states.

Reaction of NO_2 with NO_3. The reaction of NO_2 with NO_3 was studied at total N_2 pressures of 24 and 40 torr at 298 K, using two different photolytic sources of NO_3.

At 24 torr, NO_3 was produced by the photolysis of flowing Cl_2–$ClONO_2$–NO_2 mixtures. It was found that the addition of approximately 1×10^{14} molecule cm^{-3} of NO_2 reduced the NO_3 concentration by about a factor of 100 compared with that used to determine the absorption spectrum.

The rise to steady state and the decay of NO_3 were analyzed and both were found to be logarithmic and to have the same decay constant, within experimental error. The NO_3 decay is given by

$$d \ln [NO_3]/dt = -k_2[NO_2]_{ss}$$

where the NO_2 is depleted to a steady-state value given to a first approximation by

$$[NO_2]_{ss} = [NO_2]_0(1 - 2k_3[Cl_2]_0/k_{25}[NO_2]_0)$$

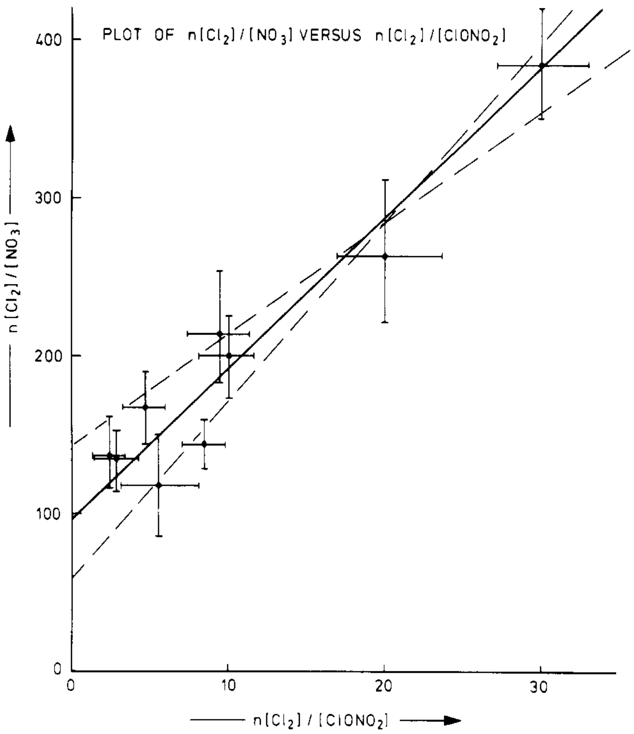

Figure 4. Determination of rate coefficient of the reaction NO_3 + Cl. Plot of $n[Cl_2]/[NO_3]$ vs. $n[Cl_2]/[ClONO_2]$.

TABLE IV: Rate Coefficients for the Reaction of NO_2 with NO_3 at 24 and 40 torr of N_2 and 298 K

N_2, torr	$[NO_2]$, molecules cm^{-3} × 10^{-12}	decay constant, s^{-1}	k_2, cm^3 molecule^{-1} s^{-1} × 10^{13}
24	7	3.1	4.4
24	23	11.5	4.9
24	23	11.6	4.9
22	93	48.3	5.0
40	45	29	6.4
40	50	33	6.6
40	86	44	6.2
40	93	57	5.0
40	135	68	5.0

In the presence of excess NO_2, $k_2[NO_2] \gg k_{16}[Cl]$. Consequently, reactions 16 and 17 can be ignored. However, NO_3 can be removed by NO, produced from the photolysis of NO_2.

$$NO_2 + h\nu \rightarrow NO + O \quad (13)$$

$$O + NO_2 \rightarrow NO + O_2 \quad (14)$$

$$NO + NO_3 \rightarrow NO_2 + NO_2 \quad (28)$$

The maximum NO concentration possible would occur when the only loss processes are reaction 28 and flow out 25, and would be given by

$$[NO]_{max} = 2k_{13}[NO_2]/(k_{25} + k_{28}[NO_3]_{ss})$$

In these experiments the reaction of NO_3 with NO_2 was always at least 10 times greater than with NO, and so no correction to the NO_3 decay is necessary. The values found for k_2 at 298 K and 24 torr of N_2 are listed in Table IV and yield a mean value of $(4.8 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

At 40 torr total pressure the F_2–HNO_3 mixtures were used as a source of NO_3. The decays of NO_3 in the presence of excess NO_2 were again logarithmic. An example is shown in Figure 5, for $[NO_2] = 4 \times 10^{13}$ molecule cm^{-3}. Results of these experiments are also given in Table IV and yield a mean value of $k_2 = (5.8 \pm 0.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 40 torr of N_2.

However, it was observed that the initial rate of production of NO_3 increased with increasing NO_2. The most plausible expla-

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TABLE V: Scheme of Chemical Reactions in the Photolysis of F_2-HNO_3-N_2 and F_2-HNO_3-NO_2-N_2 Mixtures

reaction	rate coeff	units	ref
(5) $F_2 + h\nu \rightarrow F + F$	7.4×10^{-5}	*a*	see text
(6) $F + HNO_3 \rightarrow HF + NO_3$			
(2) $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$	2.2×10^{-11}	*d*	13
(26) $F + NO_3 \rightarrow FO + NO_2$			
(27) $FO + NO_3 \rightarrow FO_2 + NO_2$			
(13) $NO_2 + h\nu \rightarrow NO + O$	3.3×10^{-3}	*a*	see text
(14) $O + NO_2 \rightarrow NO + O_2$	9.0×10^{-12}	*b*	13
(29) $O + F_2 \rightarrow FO + F$			
(30) $NO + F_2 \rightarrow FNO + F$			
(31) $FO + FO \rightarrow 2F + O_2$	1.5×10^{-11}	*b*	26
(32) $FO + NO + M \rightarrow FONO + M$			
(33) $FO + NO \rightarrow F + NO_2$	2.6×10^{-11}	*b*	26
(34) $FO + NO_2 + M \rightarrow FNO_3 + M$	2.6×10^{-31}	*c*	26
(35) $FO + NO_2 \rightarrow FO_2 + NO$			
(25) flow terms			
NO_3 = flow out	$k_{25} = 1/t_{res}$	*a*	see text
F_2 = flow out	k_{25}	*a*	
HNO_3 = flow out	k_{25}	*a*	
NO_2 = flow out	k_{25}	*a*	
flow in = F_2	$k_{25}[F_2]_0$	*e*	
flow in = HNO_3	$k_{25}[HNO_3]_0$	*e*	
flow in = NO_2	$k_{25}[NO_2]_0$	*e*	

[a] s^{-1}. [b] cm^3 molecule^{-1} s^{-1}. [c] cm^6 molecule^{-2} s^{-1}. [d] cm^3 molecule^{-1}. [e] molecule cm^{-3} s^{-1}.

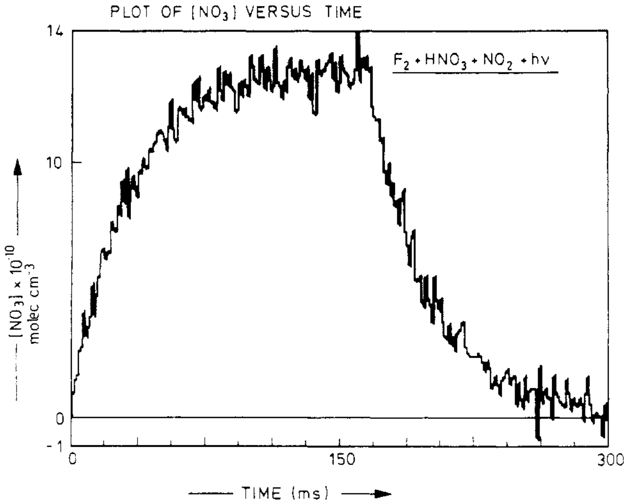

Figure 5. NO_3 modulation at 622.3 nm from photolysis of a F_2-HNO_3-NO_2-N_2 mixture: F_2, 1.1×10^{16} molecules cm^{-3}); HNO_3, 4×10^{-14} molecules cm^{-3}); NO_2, 5.6×10^{13} molecules cm^{-3}; total pressure, 40 torr of N_2. Photolysis period 320 ms, using two blacklamps. Average of 11064 sweeps. NO_3 decay constant 30 ± 2 s^{-1}.

nation of this effect is that following the photolysis of NO_2 the products O and/or NO react with F_2 to generate F.

$$O + F_2 \rightarrow FO + F \qquad \Delta H = -60.8 \text{ kJ mol}^{-1} \qquad (29)$$

$$NO + F_2 \rightarrow FNO + F \qquad \Delta H = -75.5 \text{ kJ mol}^{-1} \qquad (30)$$

Further reactions which could follow are (see also Table V)

$$FO + NO_3 \rightarrow FO_2 + NO_2 \qquad (27)$$

$$FO + FO \rightarrow 2F + O_2 \qquad (31)$$

$$FO + NO + M \rightarrow FONO + M \qquad \Delta H = -132 \text{ kJ mol}^{-1} \qquad (32)$$

$$FO + NO \rightarrow F + NO_2 \qquad (33)$$

$$FO + NO_2 + M \rightarrow FNO_3 + M \qquad (34)$$

$$FO + NO_2 \rightarrow FO_2 + NO \qquad \Delta H = -1.7 \text{ kJ mol}^{-1} \qquad (35)$$

Assuming that the initial rate of increase of NO_3 is given by

$$(d[NO_3]/dt)_0 = 2nk_5[F_2] + ank_{13}[NO_2]_{ss}$$

where *a* is the number of NO_3 molecules produced per NO_2 photolyzed, then rearranging yields the equation:

$$(d[NO_3]/dt)_0/(n[F_2]) = 2k_5 + ak_{13}[NO_2]_{ss}/[F_2]$$

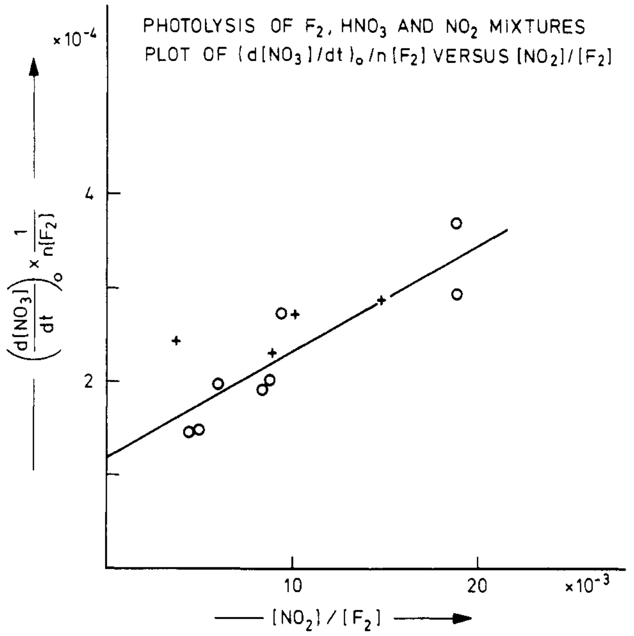

Figure 6. Plot showing dependence of rate of formation of NO_3 on NO_2 concentration (see text for details of axes).

A plot of $(d[NO_3]/dt)_0/(n[F_2])$ vs. $[NO_2]_{ss}/[F_2]$ is presented in Figure 6. The slope of the plot has a value of $(10 \pm 3.0) \times 10^{-3}$ s^{-1}, but the scatter in the data indicates that this quantity is not well defined. Substituting the measured value for the rate of NO_2 photolysis yields a value for $a = 3.2 \pm 1.0$, which implies that an extra production of NO_3 does exist.

Reactions of NO_3 with SO_2, CO, CH_4, CS_2, and H_2O_2. Experiments were also carried out to see whether the kinetic behavior of NO_3 was modified in the presence of a large excess of several other stable atmospheric constituents.

$$SO_2 + NO_3 \rightarrow SO_3 + NO_2 \qquad \Delta H = -137 \text{ kJ mol}^{-1} \qquad (36)$$

$$CO + NO_3 \rightarrow CO_2 + NO_2 \qquad \Delta H = -321 \text{ kJ mol}^{-1} \qquad (37)$$

$$CH_4 + NO_3 \rightarrow CH_3 + HNO_3 \qquad \Delta H = 14 \text{ kJ mol}^{-1} \qquad (38)$$

$$H_2O_2 + NO_3 \rightarrow HO_2 + HNO_3 \qquad \Delta H = -58 \text{ kJ mol}^{-1} \qquad (39)$$

$$CS_2 + NO_3 \rightarrow \text{products} \qquad (40)$$

In none of the experiments could an additional loss process greater

TABLE VI: NO_3 Absorption Cross Section at 662, 623, and 627 nm and the Integrated Absorption in the 0–0 Band between 654 and 670 nm

ref	cross section, 10^{-17} cm^2 molecule^{-1} 662	623	627	ratio 662/623	662/627	$10^{15}I$, cm molecule^{-1}
Johnston and Graham[a]	1.48	0.97	0.57	1.52	2.61	1.83
Graham and Johnston[b]	1.71	1.21	0.70	1.41	2.46	1.99
0.25-nm resolution[c]	1.86				2.65	
Mitchell et al.[d]	1.21	0.92	0.76	1.32	1.59	2.06
Marinelli et al.[e]	1.61	1.11	0.60	1.45	2.73	1.77
scaled[f]	1.90					2.02
Ravishankara and Wine[g]	1.78	1.28	0.63	1.39	2.84	1.88
Cox et al.[h]	1.64	1.11	0.58	1.48	2.83	1.85
this work	1.85	1.19	0.68	1.55	2.73	1.82

[a] Reference 12. Absolute magnitude recalculated in ref 14. [b] Reference 13. Published values in ref 13, 1-nm resolution. [c] Cross section obtained with limiting resolution (0.25 nm), as reported in ref 14 and 16. [d] Reference 15. [e] Reference 14. Reported values. [f] Reference 14. Scaled to give same integrated absorption as ref 13 and 15. [g] Reference 17. [h] Reference 18.

than 0.5 s^{-1} be observed. Upper limits of 4×10^{-16} cm^3 molecule^{-1} s^{-1} can be estimated for the rate coefficients k_{36}, k_{37}, k_{38}, and k_{40}, and 2×10^{-15} cm^3 molecule^{-1} s^{-1} for k_{39}. Previously Daubendiek and Calvert had estimated $k_{36} = 7 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} from a study of mixtures of N_2O_5 and SO_2.[34]

It should be noted that formation of an equilibrium, between NO_3 and SO_2, CO, CH_4, H_2O_2, or CS_2, which does not lead to appreciable loss of NO_3 on our time scale cannot be ruled out for the above reactions.

Discussion

The spectrum of NO_3 obtained in this study is shown in Figure 3 together with other published spectra. The spectrum from Marinelli et al.[14] has been scaled to the same integrated intensity as that of Graham and Johnston,[13] as suggested by Marinelli. Only a part of the published spectrum of Mitchell et al.[15] is shown, around the sharp peak at 662 nm. It is evident that good agreement exists on the shape of the visible NO_3 absorption. The planar form of NO_3 suggested by Walsh[35] led Ramsey[11] to predict a short progression in the v_1 symmetric stretching mode. Mitchell et al. assigned the peaks at 662, 623, and 598 nm to this sequence.

The absorption cross sections obtained by the various groups at the maximum 662 nm together with the integrated absorption under the 0–0 band between 654 and 670 nm are listed in Table VI for purposes of comparison. It can be seen that the values obtained here lie close to the values of Graham and Johnston (at 0.25-nm resolution as given in ref 14 and 16), but are slightly larger than those of Ravishankara and Wine.[17] However, this agreement should be treated a little cautiously, since at our spectrometer resolution (nominally 1 nm) the 0–0 band peak absorption of NO_3 is not fully resolved and is expected to be 7 to 10% lower than the fully resolved peak. One other potential source of error in this measurement of the 0–0 band absorption is the reproducibility of the wavelength setting on the grating. The monitoring wavelength 622.3 nm is not precisely at the absorption maximum and is therefore very sensitive to irreproducibilities in the grating setting. In his reevaluation of the Cl_2–$ClONO_2$ system, Cox also found a maximum cross section around 1.8×10^{-17} cm^2 molecule^{-1} (R. A. Cox, personal communication). None of the authors quotes an error of less than about 20%.

As discussed by Marinelli et al., the lower values of Mitchell et al. are probably caused by degraded resolution in the spectrometer. It is interesting to note that the peak cross sections given by Marinelli et al. appear to show a strong dependence on ozone concentration, and extrapolate back to a value of 1.86×10^{-17} cm^2 molecule^{-1}, in good agreement with that found by us and by Graham and Johnston. The exact reason for this systematic error is not clear, a slow reaction between NO_3 and ozone being one possibility, but it does lend credence to the "scaling" of the cross section which Marinelli proposed.

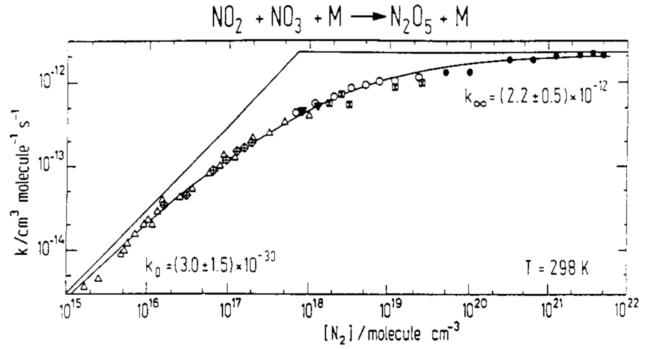

Figure 7. Dependence of rate coefficient of the reaction $NO_2 + NO_3$ on total pressure. Graph adapted from ref 22, along with low- and high-pressure limits: △, Connell;[36] ⊠, Viggiano;[37] ○, Kircher;[20] ●, Croce de Cobos;[22] ◆, Smith;[21] ▼, this work. Data from Connell and Johnston and from Viggiano et al. derived by combining rate coefficients for reverse reaction with equilibrium constants from Graham and Johnston (ref 13).

In Magnotta's determination of the quantum yield for NO_3 photolysis, it was found that yields in excess of unity were obtained when the NO_3 light absorption was calculated by using the absorption cross sections of Graham and Johnston. Magnotta proposed that Graham's cross sections should be increased by a factor of around 1.5. In view of the present agreement on the magnitude of the cross section, it seems more likely that the error was due to heating by the resonance lamp, one of the possible causes listed by Magnotta.[16] This would have led to increased dissociation of N_2O_5, and thus to a larger than calculated yield of product. It would therefore seem sensible to scale at all wavelengths the total quantum yield (for channels producing O + NO_2 or O_2 + NO), such that at 580 nm the value is 1.0.

The value obtained here for the rate of reaction between NO_3 and Cl atoms (2.7×10^{-11} cm^3 molecule^{-1} s^{-1}) is in reasonable agreement with the value of 7.6×10^{-11} cm^3 molecule^{-1} s^{-1} recently published by Cox et al.[18] and in good agreement with the results of their latter, more extended study of the Cl_2–$ClONO_2$ system.[33] This study utilized least-squares computer fitting of both NO_3 and ClO modulations and yielded a rate coefficient $k_{16} = (4.2 \pm 2.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. However, both groups have used the same method (modulated photolysis of Cl_2–$ClONO_2$ mixtures), and it is therefore recommended that a different method be used to confirm the rapid rate of reaction 16. It must be said that the atmospheric importance of a fast reaction between NO_3 and Cl is probably minimal, unless there exists an unidentified nighttime source of Cl in the atmosphere.

The reaction between NO_3 and NO_2 has now been studied by a variety of methods and the agreement for the pressure dependence of the reaction at 298 K between the different techniques is remarkable as shown in Figure 7. The data on the thermal decay of N_2O_5 from Connell and Johnston[36] and Viggiano et al.[37] have been converted to rate coefficients for the association by dividing by the equilibrium constant determined by Graham and Johnston.[13] Kircher et al.[20] have discussed the discrepancy between the earlier study by Fowles et al.[19] and the later determinations shown here.

Both the rate constant for reaction between NO_3 and NO_2 and the equilibrium constant K_2 have been subjected to recent study.[38-40] Kircher et al. conclude that the discrepancy between

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the measured atmospheric lifetime of NO$_3$[3,4,7] and that expected from the sequence of reactions 1 and 2 is not due to errors in the previous measurements of these parameters, and that the NO$_3$ is certainly scavenged. Neither does it seem that the scavenging is due to reaction with any of the other molecules studied here. Platt et al.[3] estimate that a rate coefficient of the order of 1×10^{-15} cm^3 molecule^{-1} s^{-1} with CO would be required to reduce the NO$_3$ lifetime to that observed. The upper limits observed for the reaction of NO$_3$ with CO, H$_2$O$_2$, and SO$_2$ are two slow for these reactions to explain the atmospheric scavenging of NO$_3$ and are also in accord with preliminary data reported by Noxon[4,7] and Calvert.[34]

In conclusion we report here a study of the NO$_3$ spectrum and a direct study of some reactions of NO$_3$ using a new modulated photolysis apparatus designed to measure small optical density changes from 200 to 700 nm. F$_2$ has been used as a photolytic source of free radicals and the resuls obtained confirm the anticipated high reactivity of NO$_3$ with other free radicals.

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Registry No. SO$_2$, 7446-09-5; CO, 630-08-0; CH$_4$, 74-82-8; H$_2$O$_2$, 7722-84-1; CS$_2$, 75-15-0; NO$_2$, 10102-44-0; NO$_3$, 12033-49-7; N$_2$O$_5$, 10102-03-1; Cl$_2$, 7782-50-5.

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Theoretical Analysis of Radical Addition Reactions: On the Anomalous Behavior of CH$_3$ toward Fluoro-Substituted Olefins

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Although radicals usually attack the less substituted site of olefins, CH$_3$ adds to the more substituted end of CF$_2$=CFH. A theoretical study of this anomalous reaction as well as the addition of CH$_3$ to CH$_2$=CHF, which conforms to the normal orientation rule, has been done by means of UHF 3-21G calculations. In contrast with semiempirical results (MNDO), the ab initio calculations are found to account correctly for the experimental facts. The energy barriers have been analyzed by means of the energy partitioning proposed by Morokuma. From these results and a comparison with available data on fluoro-substituted ethanes the origin of the anomalous regioselectivity in the reaction of CH$_3$ with CF$_2$=CFH is rationalized.

Simple as they seem to be, radical addition reactions have provided a seemingly endless series of surprising results.[1] Among them, those concerning the regioselectivity of the reaction are still not well understood. Several effects are apparently in competition along the reaction, and the final result is difficult to predict. Thus Tedder[1c] and Giese[1f] have independently proposed sets of five different rules to predict the outcome of these reactions. The picture remaining after these works, summarizing more than 20 years of experimental effort, is that bond strength, polarity, and steric effects compete in a rather complex way. It is not surprising that a simple rule could not be formulated. In passing, let us note that a similar situation has been found in the case of intramolecular addition reactions.[1e] There, in addition, the entropic effects can also play a substantial role.

Although many theoretical studies on these reactions have been reported[2-35] the regioselectivity problem has not been frequently faced by theoreticians.[29-35] Using a three-center three-electron valence bond approach Salem and co-workers[30] pointed out the importance of the relative electronegativity of the reaction partners in determining the orientation ratio of the reaction. More recently,[32,33] application of the Morokuma energy decomposition analysis[36] to this problem led to the suggestion[32] that the deformation energy of the reactants to attain the transition-state structure (DEF) is a good index for the regioselectivity. Nevertheless the generality of this proposal cannot be considered conclusive as will be discussed later. Moreover, since the DEF term can only be obtained after determination of the transition-

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