Reactions of NO₃ and N₂O₅ with Molecular Species of Possible Atmospheric Interest

C. A. Cantrell,* J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert

National Center for Atmospheric Research,[†] Boulder, Colorado 80307 (Received: January 23, 1987; In Final Form: June 22, 1987)

The nitrate radical (NO₃) has been shown to play an important role in nighttime tropospheric chemistry, particularly in polluted atmospheres. In order to understand more fully the role of NO₃ in loss processes for various atmospheric species, a number of laboratory kinetic studies have been undertaken. Reported here are rate constant upper limits for the reaction of NO₃ and N₂O₅ with HCl, ClNO, H₂S, NH₃, N₂O, CH₃CN, and CH₄. Chemical reaction was observed in several of these systems (HCl, ClNO, H₂S, and NH₃), but possible heterogeneous (wall-catalyzed) reactions cannot be excluded. Possible mechanisms are presented for those cases where reaction occurred. In addition, studies of the reactions $HCl + NO_2$, H_2S + NO₂, and Cl + HNO₃ are also reported. The upper limits reported here rule out the reactions of NO₃ or N₂O₅ in the gas phase as important removal processes for these species, but it is possible that the reaction of HCl with N_2O_5 catalyzed by aerosol surfaces may play an important role in linking the chemistry of the stratospheric odd nitrogen and odd chlorine cycles.

Introduction

The potential for important influences due to the nitrate radical (NO₃) in tropospheric chemistry has been recognized and has resulted in laboratory kinetic studies of this species with numerous organic compounds.¹ These reactions have the potential to be responsible for nighttime generation of free radicals and free radical precursors (for example, peroxyacetyl nitrate), and contribute significantly to acid generation in urban polluted atmospheres.² There also have been studies of the reaction of NO_3 with some free radicals and inorganic molecules.^{3,4} These reactions also could have a profound influence on our understanding of atmospheric chemistry. Reported here are investigations of the rate constants for the reactions of NO₃ (and/or N_2O_5) with HCl, ClNO, H₂S, NH₃, and N₂O, as well as the organic species CH₃CN and CH₄. These rate constants are presented as upper limits. In the course of these studies, the reactions $NO_2 + HCl$ and $NO_2 + H_2S$ also were examined.

Experimental Section

The techniques used in the study of NO_3 reactions in this laboratory have been presented elsewhere.^{2,5} Therefore, only a brief description will be given here. All studies were performed in a 450-L Pyrex cell at room temperature (6-m total length, 0.17-cm⁻¹ surface to volume ratio). It is equipped with a set of modified White optics (5.31-m base path, 32 passes, 170-m total optical path length). Equilibrium amounts of NO₃ were generated by the addition of N_2O_5 to calibrated volumes which were then swept into the cell with N_2 from liquid nitrogen boil-off. The N_2O_5 was synthesized by the technique of Davidson et al.,⁶ modified in the following ways in order to provide for more efficient conversion of NO to N_2O_5 . The usual two traps between which the oxides of nitrogen were transferred were replaced by a four-trap arrangement. In the initial stages of oxidation of NO, the resultant products can be fairly easily trapped at dry ice/ethanol temperature. However, once N_2O_5 is formed, the trapping process becomes more difficult, because N_2O_5 is a solid at temperatures below 30 °C. This problem was overcome with tandem traps; the first of a normal design and the second trap partially filled with glass beads. The other modification to the synthesis was the removal of the 1-L reaction volume between traps, because in the present case all the ozone was consumed very early after the evaporation of the $N_x O_v$ mixture.

In some cases ozone was added to the cell to reduce the ratio of NO_2 to NO_3 in the experiments. Ozone was generated by corona discharge of UHP O₂ (Linde; 99.995%). In other cases excess NO2 was added to increase the NO2 to NO3 ratio. Nitrogen dioxide was synthesized from pure NO and UHP O_2 (Linde). The gas under study for a particular experiment was then added to the cell, and the total pressure was brought to 760 Torr with nitrogen. The concentrations of reactants and products were determined by long path absorption Fourier transform infrared spectroscopy using a BOMEM DA3.01 FT spectrometer. Spectra were collected with a resolution of 0.125 cm⁻¹ and typically 100-500 interferometer scans. Typical reactant concentrations were in the range from 10¹³ to 10¹⁷ molecules cm⁻³. Standard mixtures of reactants and products were made by adding pressures (measured with an estimated accuracy of 0.1% by using MKS Baratron pressure transducers) of pure substances to calibrated volumes, which were then subsequently added to the cell with a flow of N_2 . Gases were purchased from Linde in lecture bottle size cylinders at the highest purity available (typically 99.0-99.99%). For our conditions the concentration of NO₃ could not be determined spectroscopically in the infrared and thus was calculated from the concentrations of NO₂ and N₂O₅ and the equilibrium constant based on the data of Graham and Johnston.⁷

Rate constant upper limits were determined by one of two methods. (1) The rate of decay of the concentration of a particular reactant (X) was measured as a function of $[X][NO_3]$, or $[X][N_2O_5]$, where the time rate of change of [X] versus the above products is a straight line with slope k_X :

$$NO_3 + X \rightarrow products$$
 (1)

$$d[X]/dt = -k_X[X][NO_3]$$
 (a)

(2) When little or no reaction could be seen, then a lower concentration limit for an expected product was determined, and that information was converted into an upper limit rate constant. In the first case the value of the upper limit is determined primarily by uncertainty in the concentration determination of X and the maximum amount that can be put into the cell and quantitatively measured. In the second case the value is determined primarily by base-line noise and usually results in smaller upper limit rate constants. Both of these techniques will yield larger upper limits in the cases where wall catalysis of the reactions are important.

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 TABLE I: Calculated Enthalpy Changes of Reactions That Could

 Possibly Occur in the Chemical Systems Studied Here^a

reaction	$\Delta H_{\rm rxn}$, kcal mol ⁻¹
$\begin{array}{l} HCl + 2NO_2 \rightarrow NOCl + HNO_3 \\ HCl + N_2O_4 \rightarrow NOCl + HNO_3 \\ HCl + NO_3 \rightarrow Cl + HNO_3 \\ Cl + NO_2 + M \rightarrow NO_2Cl + M \\ HCl + N_2O_5 \rightarrow NO_2Cl + HNO_3 \end{array}$	-13.4 -0.2 1.3 -33.9 -9.8
$NOC1 + NO_3 \rightarrow NO_2C1 + NO_2$ $NOC1 + N_2O_5 \rightarrow NO_2C1 + 2NO_2$	-19.2 3.6
$\begin{array}{l} H_2S + 3NO_2 \rightarrow SO_2 + H_2O + 3NO\\ H_2S + NO_2 \rightarrow HS + HONO\\ H_2S + 2NO_2 \rightarrow HSO + HONO + NO\\ H_2S + NO_2 \rightarrow H_2SO + NO\\ H_2S + NO_3 \rightarrow HNO_3 + HS\\ H_2S + N_2O_5 \rightarrow HNO_3 + HSNO_2\\ H_2S + N_2O_5 \rightarrow H_2SO + 2NO_2 \end{array}$	-82.9 13.1 -8.3 2.5 -10.2 2.0
$\begin{array}{l} \mathrm{NH_3} + \mathrm{NO_3} \rightarrow \mathrm{HNO_3} + \mathrm{NH_2} \\ \mathrm{NH_3} + \mathrm{N_2O_5} \rightarrow \mathrm{HNO_3} + \mathrm{N_2O} + \mathrm{H_2O} \\ \mathrm{NH_2} + \mathrm{NO_2} \rightarrow (\mathrm{NH_2NO_2}) \rightarrow \mathrm{N_2O} + \mathrm{H_2O} \\ \mathrm{NH_3} + \mathrm{NO_3} \rightarrow \mathrm{NH_2OH} + \mathrm{NO_2} \end{array}$	5.5 -62.3 -90.3 -5.0
$\begin{array}{l} N_{2}O + NO_{3} \rightarrow NO_{2} + 2NO \\ N_{2}O + N_{2}O_{5} \rightarrow 2NO_{2} + 2NO \\ N_{2}O + NO_{3} \rightarrow N_{2} + NO_{2} + O_{2} \\ N_{2}O + N_{2}O_{5} \rightarrow N_{2} + 2NO_{2} + O_{2} \end{array}$	13.9 36.7 -29.3 -6.5
$\begin{array}{l} CH_4 + NO_3 \rightarrow CH_3 + HNO_3 \\ CH_4 + N_2O_5 \rightarrow CH_3 + HNO_3 + NO_2 \\ CH_4 + N_2O_5 \rightarrow CH_3ONO + HNO_3 \\ CH_4 + N_2O_5 \rightarrow CH_3NO_2 + HNO_3 \end{array}$	3.0 25.8 -28.6 -31.2
$\begin{array}{l} CH_3CN + NO_3 \rightarrow CH_2CN + HNO_3\\ CH_3CN + N_2O_5 \rightarrow CH_2CN + HNO_3 + NO_2\\ CH_3CN + NO_3 \rightarrow CH_3NO_2 + NCO\\ CH_3CN + N_2O_5 \rightarrow CH_3NO_2 + NO_2 + NCO\\ CH_3CN + N_2O_5 \rightarrow CH_3NO_2 + N_2O + CO_2\\ \end{array}$	~ 0 ~ 23 -21 2 -114

^aHeats of formation used to calculate these heats of reaction are from ref 20 or 21, except for HSO, H_2SO , and HSOH, which are from ref 22.

In all these studies upper limits for rate constants are quoted for $NO_3 + X$ and $N_2O_5 + X$.

Discussion

Table I shows reactions that could possibly occur in the systems under study as well as estimates of the enthalpy change for each reaction. In some cases the reactions indicate overall processes, while others show elementary reactions. The listing of a reaction does not imply that it occurs as a homogeneous gas-phase reaction. The results of upper limits for rate constants for the reactions of this study are shown in Table II. The details of each chemical system studied are described below.

HCl. A moderately fast reaction in the N_2O_5 system with HCl was observed in early experiments, and a preliminary result for the reaction of NO₃ with HCl has been reported.⁸ A more detailed examination of this system showed the reaction to be either

$$HCl + NO_3 \rightarrow Cl + HNO_3$$
 (2)

$$HCl + N_2O_5 \rightarrow ClNO_2 + HNO_3$$
(3)

The chlorine atoms formed in (2) can react with NO₂ in a three-body reaction to form nitrosyl chloride (ClNO₂). It was determined in experiments with the cell surface altered that most of the reaction observed in the system was due to a heterogeneous reaction on the walls of the glass vessel. Apparent rate constants for reaction with NO₃ as high as 2×10^{-14} cm³ molecule⁻¹ s⁻¹ were observed. The highest rates were measured after experiments were

TABLE II: Bimolecular Rate Constant Upper Limits for Reactions of NO₃ and N_2O_5 with Several Molecular Species from the Present Study

reactant	$k(X + NO_3)$	$k(\mathbf{X} + \mathbf{N}_2\mathbf{O}_5)$	R or NR ^a
HCl	$<7 \times 10^{-18}$	<2 × 10 ⁻¹⁹	R
NOCl	<1 × 10 ⁻¹⁴	$<9 \times 10^{-18}$	R
H_2S	<2 × 10 ⁻¹⁴	$<3 \times 10^{-18}$	R
NH3	$<6 \times 10^{-16}$	<2 × 10 ⁻¹⁹	R
N ₂ O	$<2 \times 10^{-17}$	<1 × 10 ⁻¹⁹	NR
CH ₃ CN	$<3 \times 10^{-19}$	$< 6 \times 10^{-23}$	NR
CH₄	$<4 \times 10^{-21}$	$<2 \times 10^{-23}$	NR

^aSymbol indicates that the upper limit shown is based on a reaction occurring (R) or based on no reaction occurring (NR).

performed in the cell in which SO₂ was oxidized in an ozoneethylene mixture, resulting in the deposition of H₂SO₄ on the reaction chamber walls. The reaction in this case appeared to be reaction with N₂O₅ rather than NO₃. (In principle, one can ascertain whether reaction is with N₂O₅ or NO₃ by addition of NO₂, which shifts the equilibrium and reduces the concentration of NO₃.) When the cell was taken apart and physically cleaned, the rate slowed to a level resulting in the upper limits quoted here ($<7 \times 10^{-18}$ and $<2 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹ for reaction with NO₃ and N₂O₅, respectively). The reaction still appeared to be between HCl and N₂O₅ as evidenced by no change in the observed rate with the addition of NO₂ at the beginning of an experiment.

The consistency of the upper limit for reaction 2 can be checked because an upper limit rate constant for the reverse reaction has been determined⁹ and the equilibrium constant can be calculated from thermodynamic data. The upper limit quoted here should be smaller than $(k_{-2}K_{eq})$. If an upper limit of k_{-2} of 1.7×10^{-14} cm⁻³ molecule⁻¹ s⁻¹ and an equilibrium constant of 4.26×10^{-2} are used, then k_2 should be smaller than 7.2×10^{-16} cm³ molecule⁻¹ s^{-1} . As a check on this, experiments were performed in which the chlorine atoms were allowed to react competitively with CH₄ and HNO₃, in order to estimate an upper limit for k_{-2} . Molecular chlorine $(7.4 \times 10^{15} \text{ molecules cm}^{-3})$ was photolyzed with fluorescent black lights in a mixture of CH_4 (7.0 × 10¹⁴), HNO₃ (1.6×10^{14}) , NO (1.8×10^{14}) , all in molecules per cubic centimeter), and 1 atm of N_2 . After 45 min of photolysis, 79% of the methane had reacted, while greater than 95% of the HNO₃ remained. Using a rate constant for the $CH_4 + Cl$ reaction⁹ of 1 \times 10⁻¹³ cm³ molecule⁻¹ s⁻¹, this leads to $k_{-2}/k_{(CH_4+Cl)} \leq (ln$ $(0.95)/(\ln 0.22) = 0.033$ and an upper limit for k_{-2} of 3.3×10^{-15} cm³ molecule⁻¹ s⁻¹, about a factor of 5 slower than currently accepted values. This means that k_2 must be less than 1.4×10^{-16} cm³ molecule⁻¹ s⁻¹. Finally, the upper limit quoted here for k_2 can be used to calculate an upper limit for k_{-2} : 1.6×10^{-16} cm³ molecule⁻¹ s⁻¹, approximately 2 orders of magnitude slower than the value proposed by the NASA panel,⁹ and suggests that the extrapolated result of Poulet et al.¹⁰ of 2×10^{-17} cm³ molecule⁻¹ s^{-1} for k_{-2} may be correct. Our present determination ensures that reaction -2 is of no importance in the removal of stratospheric HNO₃.

In the study of reactions of NO_3 with various species in the presence of N_2O_5 , the concentration of NO_3 can be reduced by the addition of NO_2 , as discussed above. The rate of reaction for HCl in the N_2O_5 system was so fast in the presence of sulfuric acid that NO_2 was typically added to the mixture in an attempt to slow the overall rate of HCl consumption, because in early experiments the assumption was that HCl was reacting with NO_3 . In these cases ClNO was also observed to increase with time. It was found in separate experiments that there is a slow reaction between NO_2 and HCl, with stoichiometry and products as shown:

$$HCl + 2NO_2 \rightarrow ClNO + HNO_3 \tag{4}$$

The third-order rate constant for reaction 4 was measured to be 2×10^{-35} cm⁶ molecule⁻² s⁻¹. This reaction could also be viewed

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as a reaction between HCl and N_2O_4 :

$$HCl + N_2O_4 \rightarrow ClNO + HNO_3$$
 (5)

This results in a bimolecular rate constant for reaction 5 of $6 \times$ 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹. We cannot judge from our experiments whether the observed loss of HCl results from a gas-phase reaction or a wall reaction. Reactions between HCl and NO₂ have been observed by other workers,^{11,12} with the stoichiometry

$$4\text{HCl} + 2\text{NO}_2 \rightarrow 2\text{ClNO} + \text{Cl}_2 + 2\text{H}_2\text{O}$$
 (6)

Of course we could not observe Cl_2 by infrared absorption, but we noticed formation of H₂O in the early stages of these experiments; its concentration came up to a low level, corresponding to less than to 5% of the initial HCl, and remained constant throughout the remainder of the experiment. This suggests that H_2O and Cl_2 are formed from secondary processes in this system. The reaction between NO₂ and HCl is far too slow to be of importance to atmospheric chemistry.

The reaction of ClNO in the N_2O_5 system was also examined. CINO was oxidized to $CINO_2$ in this case:

$$CINO + NO_3 \rightarrow CINO_2 + NO_2$$
 (7)

This reaction is analogous to the reaction of NO with NO₃, which has a rate constant of about 3×10^{-11} cm³ molecule⁻¹ s^{-1,13,14}

$$NO + NO_3 \rightarrow 2NO_2$$
 (8)

Reaction 7 has been studied previously¹⁵ by Johnston and Leighton and appears to offer an explanation as to why the reaction of nitrosyl chloride in an ozone-containing system has shown wide variability.

$$CINO + O_3 \rightarrow CINO_2 + O_2 \tag{9}$$

The production of ozone by corona discharge is known to produce odd nitrogen if molecular nitrogen is present in the oxygen being discharged. Thus some NO_3 and N_2O_5 would be formed, and the nitrosyl chloride loss would be due to reaction 7 rather than (9). Johnston and Leighton found reaction 9 to be very slow when the contaminants were removed from the ozone and in separate experiments found the rate constant for (7) to be about 1×10^{-16} cm³ molecule⁻¹ s⁻¹. This value is about 100 times slower than our upper limit and may indicate that this reaction is also susceptable to heterogeneous catalysis. It is interesting that the value in Table II for reaction 7 ($<1 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹) is very close to the room temperature rate constant for the reaction of NO with O_3 . The result expressed as reaction between ClNO and N_2O_5 gives a rate constant of 9×10^{-18} cm³ molecule⁻¹ s⁻¹.

In the reactions of HCl with NO_2 or in the N_2O_5 system, mass balance (within 10%) was always seen for H, N and Cl, even when the cell wall was contaminated with H₂SO₄, indicating the catalytic nature of a sulfuric acid coated surface in these reactions. In the N_2O_5 system, the stoichiometry observed was one N_2O_5 per HCl lost with the formation of one molecule of ClNO₂ and one HNO₃. Likewise it could be viewed as a loss of one NO₃ and one NO₂ per HCl. The results for these reactions remove them from importance in the chemistry of the stratosphere as gas-phase reactions. It is possible that the HCl + N_2O_5 reaction could be important on stratospheric aerosols, much the same way the reaction of HCl with ClONO₂ could be. The results for the NO₃ + HCl reaction also places constraints on the upper limit for the reverse reaction.

 H_2S . The reactions of H_2S with NO₂ and in the N₂O₅ system were studied in great detail. The reaction of H_2S with NO₂ showed very unusual stoichiometry:

$$H_2S + 3NO_2 \rightarrow SO_2 + H_2O + 3NO$$
(10)

This reaction, like the reaction of NO₂ with HCl, proved to be very slow ($k < 6 \times 10^{-20}$ cm³ molecule⁻¹ s⁻¹) and possibly heterogeneous in nature. This system also resulted in the formation

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(12) Harris, L.; Siegel, B. M. J. Am. Chem. Soc. 1941, 63, 2520.
(13) Sander, S. P.; Kircher, C. C. Chem. Phys. Lett. 1986, 126, 149.
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of nitrous acid (HONO) in some experiments. Usually the concentration of HONO was less than 10% that of NO, but seems to indicate at least two channels for reduction of NO_2 , or possibly that HONO is an intermediate in the overall process. The nature of the technique used (FTIR) to measure the loss of reactants and buildup of products does not allow us to be able to unequivocally determine what the overall mechanism or the initial reaction is in this system, because transient species cannot be observed, but some speculation can be made, based on results of computer simulations of possible reactions in this system. There have been previous reports of a reaction similar to this one, between CH₃SH and NO₂.¹⁶ Balla and Heicklen observed a bimolecular reaction with a rate constant of about 2×10^{-22} cm³ molecule⁻¹ s⁻¹ at room temperature, and they interpreted their temperature-dependent data in terms of two pathways. A four-center reaction would explain the formation of CH₃SNO (plus HO) in their system, while oxygen atom transfer would result in formation of $CH_3S(O)H$ and NO. In the case of H_2S , oxygen atom transfer from NO_2 (reaction 11) seems more plausible than the four-center reaction analogous to the CH₃SH case (reaction 12):

$$H_2S + NO_2 \rightarrow H_2SO + NO \tag{11}$$

$$H_2S + NO_2 \rightarrow HSNO + HO$$
 (12)

The species formed from (11) can isomerize:

$$H_2SO + M \rightarrow HSOH + M$$
 (13)

It is conceivable then that this species could react with another NO₂:

$$HSOH + NO_2 \rightarrow HOS(O)H + NO$$
(14)

$$HSOH + NO_2 \rightarrow HSO + HONO$$
 (15)

This could explain the formation of nitrous acid we see in this system, depending on the relative rates of (14) and (15). Another isomerization could then take place:

$$HSO + M \rightarrow SOH + M \tag{16}$$

The third NO₂ could then be consumed either by reaction with the product of (14) or (16):

$$HOS(O)H + NO_2 \rightarrow H_2SO_3 + NO$$
(17)

$$SOH + NO_2 \rightarrow HONO + SO$$
 (18)

Reaction 18 is then followed by reaction with another NO₂:

$$SO + NO_2 \rightarrow SO_2 + NO$$
 (19)

The product of reaction 17 is hydrated sulfur dioxide, which could then dissociate to the observed products, SO_2 and H_2O :

$$H_2SO_3 + M \rightarrow SO_2 + H_2O + M$$
(20)

The sequence of reactions 11, 13, 14, 17, and 20 is consistent with the stoichiometry that was observed for SO₂, H₂O, and NO. The sequence 11, 13, 15, 16, 18, and 19 could explain the observed minor channel that results in HONO formation $(k_{15} \ll k_{14})$. Our results suggest that the oxidation of H₂S by NO₂ may be important under some unique situations of high NO₂ concentrations in the presence of H_2S but in general is probably not important in the atmosphere and may not occur at all as a homogeneous gas-phase reaction.

Conversion of H_2S to SO_2 in the N_2O_5 system was also observed. with upper limit rate constants of 2×10^{-14} cm³ molecule⁻¹ s⁻¹ for reaction with NO₃ and 3×10^{-18} cm³ molecule⁻¹ s⁻¹ for reaction with N_2O_5 . A value previously reported for the upper limit for the reaction of H₂S with NO₃ is 3×10^{-14} cm³ molecule⁻¹ s⁻¹,¹⁷ a value very close to that reported here. In this system, the stoichiometry is not well-defined because if NO is generated as in the H_2S-NO_2 reaction, it reacts rapidly with NO_3 :

$$NO + NO_3 \rightarrow 2NO_2$$
 (8)

^{1986, 90, 2491.} (15) Johnston, H. S.; Leighton, F., Jr. J. Am. Chem. Soc. 1953, 75, 3612.

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Also if H_2O is formed, it could react with N_2O_5 on the reactor walls:

$$N_2O_5 + H_2O + wall \rightarrow 2HNO_3$$
 (21)

In this system we observed formation of nitric acid, sulfur dioxide, and nitrogen dioxide. This is compatible with the speculation that the oxidation of H_2S in the N_2O_5 system is similar to that which occurs in the H₂S-NO₂ system with perhaps somewhat different chemistry of initialization and the inclusion of (8) and (21). We speculate one of two possible processes in the oxidation of H₂S in this system. One begins with hydrogen abstraction by NO₃:

$$H_2S + NO_3 \rightarrow HS + HNO_3$$
 (22)

Thus instead of formation of H₂O, HNO₃ is produced directly. This mechanism is analogous to the reaction NO₃ with aldehydes:

$$RCHO + NO_3 \rightarrow RCO + HNO_3$$
 (23)

The HS radical formed in (22) is then oxidized by NO_2 :

$$HS + NO_2 \rightarrow HSO + NO$$
 (24)

(A 1)

$$HSO + NO_2 \rightarrow HSO_2 + NO$$
 (25)

The HSO₂ species could react with NO₃:

$$HSO_2 + NO_3 \rightarrow HNO_3 + SO_2$$
 (26)

The mechanism of reactions 22, 24, 25, 26, and 8 results in the following overall process, which is consistent with our observations:

$$H_2S + 4NO_3 \rightarrow 2HNO_3 + SO_2 + 2NO_2 \qquad (27)$$

It is possible that the reaction of NO₃ with methyl sulfides proceeds via adduct formation:

$$CH_3SR + NO_3 \rightarrow CH_3S(ONO_2)R$$
 (28)

The adduct would presumably then decay by loss of NO₂:

$$CH_3S(ONO_2)R \rightarrow CH_3S(O)R + NO_2$$
 (29)

The hypothesis of formation of an adduct between organic sulfides and NO₃ is consistent with the observation of negative temperature dependencies in these systems. In the H_2S case, this is also possible:

$$H_2S + NO_3 \rightarrow HS(ONO_2)H$$
 (30)

$$HS(ONO_2)H \rightarrow H_2SO + NO_2$$
(31)

The H₂SO species could then react as shown for the NO₂ + H₂S case, resulting in H₂O and SO₂ formation (reactions 13, 14, 17, and 20), followed by reactions 8 and 21. This results in the overall process

$$H_2S + 3NO_3 + N_2O_5 \rightarrow 2HNO_3 + SO_2 + 3NO_2 \quad (32)$$

It is unknown what the heterogeneous component is in this system. Studies were done on H₂S both with and without H₂SO₄ contamination in the cell, and very little difference was seen. This does not rule out the possible catalytic effect of glass walls in this reaction analogous to the $N_2O_5 + H_2O$ reaction. In fact, the reaction of NO₃ has been studied in a fast flow system¹⁸ with a resulting room temperature bimolecular rate constant of about 6×10^{-16} cm³ molecule⁻¹ s⁻¹, much slower than the upper limit reported here. This indicates that this system may be susceptible to catalysis by surfaces much like reaction 21.

 NH_3 . A reaction of NH₃ in the NO₃/N₂O₅ system was observed, resulting in the upper limit quoted in Table II (<6 \times 10⁻¹⁶ and $<2 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹ for reaction with NO₃ and N_2O_5 , respectively). The overall reaction is thought to be

$$NH_3 + NO_3 + NO_2 \rightarrow HNO_3 + N_2O + H_2O \quad (33)$$

Nitric acid was not observed since NH₄NO₃ formation is favored for our conditions:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$
 (34)

The concentration of NH₃ was sometimes observed to continue decreasing in experiments where N_2O no longer increased. This suggests possible clustering of NH₃ on the ammonium nitrate formed in (34). A possible mechanism for this system follows, with the initial step being hydrogen abstraction by NO₃:

$$NH_3 + NO_3 \rightarrow NH_2 + HNO_3$$
 (35)

The species NH₂ is known to react rapidly with a variety of molecules including NO₂:

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \tag{36}$$

The fate of NH_2 in the atmosphere is pivotal in determining whether NH_3 is a source or a sink of odd nitrogen (NO_x). Thus the above reaction sequence could possibly be an important sink for odd nitrogen. As in the other systems, this could be viewed as a reaction directly with N_2O_5 :

$$NH_3 + N_2O_5 \rightarrow N_2O + H_2O + HNO_3$$
(37)

We cannot rule out the possibility of other mechanisms in this reaction such as oxygen atom transfer:

$$NH_3 + NO_3 \rightarrow NH_3O + NO_2$$
(38)

The NH₃O species can isomerize to hydroxylamine:

$$NH_3O + M \rightarrow NH_2OH + M$$
 (39)

The hydroxylamine formed in (39) could then react with another NO₃:

$$NH_2OH + NO_3 \rightarrow H_2O + NO_2 + HNO$$
 (40)

The reactive HNO species can react with another HNO:

$$HNO + HNO \rightarrow N_2O + H_2O$$
(41)

HNO can also react with molecular oxygen:

$$HNO + O_2 \rightarrow HO_2 + NO$$
 (42)

This generation of odd hydrogen radicals and NO is a complication in attempting to determine the role of reaction 33 in this system because of the possibility of HO formation and NH₃ loss through reaction with it. This results in an overestimate of the reaction rate coefficient for (33).

 N_2O . The fact that nitrous oxide was observed as a product in the N_2O_5 -NH₃ system led to the study of N_2O in the N_2O_5 system. It was postulated that reactions could take place such as

$$N_2O + NO_3 \rightarrow N_2 + NO_2 + O_2 \tag{43}$$

This reaction is neither a net source nor sink of NO_x . Reactions that do produce NO and NO₂ appear to be too endothermic to occur significantly at tropospheric temperatures:

$$N_2O + NO_3 \rightarrow NO_2 + 2NO \tag{44}$$

Reactions that are a NO_x sink and are exothermic but require complex atom rearrangements are unlikely to occur at a significant rate in the atmosphere:

$$N_2O + N_2O_5 \rightarrow 2N_2 + 3O_2$$
 (45)

No loss of N_2O was seen in this system, and hence we derived the upper limits shown in Table II ($< 2 \times 10^{-17}$ and $< 1 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹ for reaction with NO_3 and N_2O_5 , respectively).

 CH_3CN . The acetonitrile species is of interest in the atmosphere because of the remarkable difference in mixing ratios in the troposphere and stratosphere. Measurements imply a very large sink for CH₃CN that cannot be accounted for by reaction with hydroxyl radicals. Heterogeneous processes have been postulated, because of the reasonably high aqueous solubility of CH₃CN. It was felt that the nitrate radical would also be a good candidate for providing the additional tropospheric loss necessary to explain the measurements. In these experiments, reactant loss and possible product increase were monitored. It was anticipated that NO₃ might react by hydrogen abstraction:

$$CH_3CN + NO_3 \rightarrow CH_2CN + HNO_3$$
 (46)

⁽¹⁸⁾ Dlugokencky, E. J.; Howard, C. J. Presented at the Fall Meeting of American Geophysical Union, San Francisco, CA, December 1986.

As shown in Table I, formation of nitromethane is energetically feasible. The heat of formation of methyl nitrite (CH₃ONO) is about the same as nitromethane and is thus also feasible. None of the products expected from any these schemes were observed to increase, and within the uncertainty of the measurement, acetonitrile did not decrease in the N₂O₅ system. As before, upper limits are shown for the reaction with NO₃ (<3 × 10⁻¹⁹) and with N₂O₅ (<6 × 10⁻²³ cm³ molecule⁻¹ s⁻¹).

 CH_4 . A great deal of research has been aimed at understanding the global budget of CH_4 . Because of the importance of methane as a trace greenhouse gas, and its important role in several atmospheric cycles, it is critical to know its sources and sinks. It is currently assumed that the most important loss process for CH_4 is its reaction with hydroxyl radicals, accompanied by minor losses in the stratosphere due to reaction with $O(^{1}D)$ and Cl. Methane has a relatively long lifetime in the troposphere because the rate coefficient for $CH_4 + HO$ is small and because average hydroxyl concentrations are low. A reaction between CH_4 and NO_3 of about 10^{-16} cm³ molecule⁻¹ s⁻¹ could account for perhaps 10% of the tropospheric loss of methane. As shown in Table I, the reaction of methane with NO_3 to form HNO_3 by hydrogen abstraction is somewhat endothermic:

$$CH_4 + NO_3 \rightarrow CH_3 + HNO_3$$
 (47)

The channel for reaction with N₂O₅ to form CH₃ radicals is very endothermic. The upper limits for these reactions ($<4 \times 10^{-21}$ and $<2 \times 10^{-23}$ cm³ molecule⁻¹ s⁻¹ for reaction with NO₃ and N₂O₅, respectively) are based on absence of CO and CO₂ formation in this system in which a large amount of CH₄ was employed (about 2 Torr in the cell); methyl radicals formed in (44) are expected to eventually form CO and/or CO₂. In other experiments with lesser amounts of CH₄, an upper limit for reaction with NO₃ based on CH₄ loss of about 1 × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹ was determined. Other groups have measured upper limit rate constants for reaction (46)^{1,19} of 4 × 10⁻¹⁶ and 2 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹, respectively. These upper limits are sufficiently small to make NO_3 an unimportant sink for atmospheric CH_4 , as well as an unimportant source of atmospheric nitric acid.

Conclusions

The reactions of the nitrate radical have been examined in a variety of systems. The susceptibility for heterogeneous N_2O_5 reactions in the case of HCl and possibly H_2S has been demonstrated, and thus kinetic data are reported as upper limits for gas-phase reaction. None of the reaction systems reported here are expected to be important in the chemistry of the troposphere or stratosphere as homogeneous gas-phase reactions, but the heterogeneous nature of the HCl + N_2O_5 reaction as catalyzed by H_2SO_4 may deserve further study as participant in the nighttime stratospheric chlorine and nitrogen cycles.

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Registry No. NO₃, 12033-49-7; N₂O₅, 10102-03-1; HCl, 7647-01-0; ClNO, 2696-92-6; H₂S, 7783-06-4; NH₃, 7664-41-7; N₂O, 10024-97-2; CH₃CN, 75-05-8; CH₄, 74-82-8; NO₂, 10102-44-0; Cl, 22537-15-1; HNO₃, 7697-37-2.

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