

Figure 10. Pressure dependences of volume changes: A, for ΔV_c^{\ddagger} ; B, for ΔV_m ; C, for ΔV_i . Values calculated with equations used in extrapolating kinetic parameters to p = 0 (Figure 8) are shown.

that k_2 becomes greater on increasing the pressure. It is possible, therefore, to expect that $k_2 \gg k_3$ at sufficiently high pressures if we assume that k_3 decreases with pressure, i.e., $\Delta V_3^{\dagger} > 0$. In addition, we can expect that $\Delta V_c^{\dagger}(p) = 0$ at certain pressure p^* where $k_2 \Delta V_3^{\ddagger} = -k_3 \Delta V_2^{\ddagger, 20}$ Then it is obvious that V_{max} exhibits maximum at $p = p^*$. Thus, the experimental result for V_{max} (Table I) and that for ΔV_c^{\ddagger} (Figure 10A) can be qualitatively explained. It must be noted that the above-mentioned explanation is equivalent to stating that the rate-determining step has shifted from ES \rightarrow EF + G (low pressure) to EF \rightarrow E + F (high pressure). In addition, it must be noted here that the explanation

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is quite similar to that reported by Morild²⁰ for a complex enzymic reaction in a homogeneous solution. This strongly supports the consideration that kinetics of heterogeneous enzymic reactions can be treated by extending the formalisms proposed for homogeneous enzymic reactions.

At low pressures where $k_3 \gg k_2$, we can write that $K_{\rm m} = k_{-1}/k_{+1}$ as mentioned previously. However, at high pressures where k_2 $\gg k_3$, this is no longer valid; instead, we have to consider the $K_{\rm m}$ = $[(k_{-1} + k_2)/k_{+1}](k_3/k_2)$. Thus, the discussion on the pressure dependence of K_m needs some simplifications. For instance, in the case of $k_{\pm 1} \gg k_2$, we can write that $K_m = (k_{-1}/k_{\pm 1})(k_3/k_2)$ and hence $\Delta \tilde{V}_m = \Delta V_m \pm \Delta V_3^{\dagger} - \Delta V_2^{\dagger}$, where $\Delta \tilde{V}_m$ is defined by $-RT(\partial \ln K_{\rm m}/\partial p)$ and $\Delta V_{\rm m}$ is the intrinsic volume change of the dissociation of the Michaelis complex, i.e., $\Delta V_{\rm m} = -RT[\partial \ln$ $(k_{-1}/k_{+1})/\partial p$]. According to the experimental results, $\Delta \tilde{V}_{\rm m}$ (= $\Delta V_{\rm m}$) > 0 at p = 0 while $\Delta \tilde{V}_{\rm m} < 0$ at high pressure. In addition, we have to consider that $\Delta V_2^{\dagger} < 0$ and $\Delta V_3^{\dagger} > 0$. Consequently, $\Delta V_{\rm m}$ should have negative values at pressures higher than 49-98 MPa where $K_{\rm m}$ exhibits a minimum. The fact that $\Delta V_{\rm m} > 0$ at low pressures indicates that the Michaelis complex has a volume larger than the initial state. It is thus possible to expect that the Michaelis complex would have a looser structure with a larger compressibility than the initial state at low pressures. The large compressibility of the Michaelis complex would result in a smaller volume of this complex than the initial state and hence negative values of $\Delta V_{\rm m}$ at sufficiently high pressures. This explanation is plausible but not conclusive because there exists an alternative case where $k_2 \gg k_{-1}$.

In the case where $k_2 \gg k_{-1}$, we obtain the following relations: $K_{\rm m} = k_3/k_{+1}$ and $\Delta \tilde{V}_{\rm m} = \Delta V_3^{\dagger} - \Delta V_1^{\dagger}$. At high pressures, we have, in addition, $\Delta \tilde{V}_{\rm m} < 0$ and $\Delta V_3^{\dagger} > 0$. Thus, we obtain $\Delta V_1^{\dagger} > \Delta V_3^{\dagger}$ > 0. In this case, therefore, we have to consider that the transition state (SE[‡]) for the formation of the Michaelis complex (SE) has a larger and looser structure than the initial state S + E. Unfortunately, however, we have no experimental data to support this view.

Finally, we discuss about the behavior of K_i . The fact that the K_i value tends to increase at 49–98 MPa suggests that the releasing of glucose (G) from the enzyme-glucose complex (E-G) is facilitated at high pressures. Considering a simple structural analogy between EG and ES (E-G-F), we may expect that the releasing of G from ES would also be facilitated at high pressures and this could result in an increase of the rate constant k_2 , as actually observed.

Discharge Flow Kinetic Study of NO_3 Reactions with Free Radicals: The Reaction of NO_3 with Cl

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The discharge flow technique was used to perform a direct measurement of the rate constant for the reaction NO₃ + Cl \rightarrow ClO + NO₂ (1) under pseudo-first-order conditions with NO₃ in excess. NO₃ was produced via the reaction F + HNO₃ \rightarrow HF + NO₃ (2) for which the rate constant was also determined: $k_2 = (2.7 \pm 0.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K. Absolute titration of NO₃ was done using NO and 2,3-dimethyl-2-butene as the titrants. The titration experiments with NO were simulated, and the analysis of potential errors resulting from the secondary chemistry indicated that NO is a precise titrant of NO₃ in discharge flow studies. In the kinetic investigation of reaction 1, the obtained value of k_1 at 298 K was $k_1 = (2.6 \pm 0.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

Introduction

 NO_3 radicals, formed in the atmosphere via the reaction NO_2 + $O_3 \rightarrow NO_3 + O_2$, are rapidly destroyed by photolysis during the day. But at nighttime, they react with NO_2 to produce the temporary reservoir N_2O_5 . The absolute rate constant for the recombination reaction $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$ has been extensively measured.¹⁻⁴ It is also known that, during the night,

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NO3 radicals can oxidize many organic species (see, e.g., ref 5 and references therein). In order to assess the importance of these oxidation processes in the atmosphere as well as in laboratory photochemical studies, it is necessary to provide precise kinetic data about reactions of NO3 with other free radicals involved in such processses. Very few kinetic studies of these reactions have been performed. Kinetic information on the reaction $NO_3 + O$ \rightarrow NO₂ + O₂ was obtained from the computer simulation of modulation experiments on the N_2O_5 - O_3 system.⁶ Recently, the reaction between NO₃ and HO₂ was suggested as a sink for NO₃ in the spectroscopic study of the NO₃ + H_2CO reaction.⁷ The NO₃ reactions with OH and HO₂ were also recently observed in the photolysis of HNO₃ at 254 nm.⁸

The kinetics of the reactions between NO₃ radicals and Cl atoms has been studied in two laboratories using the modulated photolysis of Cl₂-ClONO₂ mixtures^{4,9} where the reaction

$$Cl + NO_3 \rightarrow ClO + NO_2$$
 (1)

was identified as a secondary reaction. k_1 was derived from the NO3 kinetics which were measured by means of time-resolved absorption at 662 nm. These indirect experiments led to values for k_1 at 298 K ranging from $(7.6 \pm 1.1) \times 10^{-11.9}$ to (2.7 ± 1.0) $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.4}$

The direct kinetic measurements previously published are relative to the reactions of NO_3 with NO_2 ,^{1,3} NO,^{10,11} and organic compounds,^{5,12} obtained by either the flash photolysis^{1,5,11} or discharge flow^{3,10,12} method. In each of these studies, the pseudo-first-order conditions were used with the stable reactant in excess over NO₃, the kinetics being monitored by either laserinduced fluorescence or visible absorption of NO₃.

In the present study, the discharge flow technique was also used to measure the absolute rate constant of reaction 1, but NO₃ radicals were in excess over Cl atoms. For such a measurement, a precise titration of NO₃ was necessary. That was performed under the same conditions as for the measurements^{13,14} of the absolute cross sections of NO₃. In the recent study of Sander,¹⁴ $\sigma(NO_3)$ was found to be lower in the discharge flow experiment than in the flash photolysis one. Since an accurate value of $\sigma(NO_3)$ must be known, especially for atmospheric measurements, potential sources of experimental errors have been analyzed.^{13,14} In the present work, the possible errors in the discharge flow method have been also quantified by simulating the NO₃ titration experiments. The simulation appeared to be sensitive to the value of the rate constant k_2 for the reaction 2 which was used as the NO_3 source:

$$F + HNO_3 \rightarrow HF + NO_3$$
 (2)

Since k_2 has not been determined so far, independent experiments were also performed to measure k_2 .

Experimental Section

The discharge flow reactor used was coupled to an EPR spectrometer and a quadrupole mass spectrometer. This system

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has been detailed previously,¹⁵ and only the aspects relevant to the present work will be described.

The conventional flow tube was constructed with 2.4-cm-i.d. quartz and had a total length of about 80 cm. The Pyrex movable axial tube had a 0.9-cm o.d. and a 0.7-cm i.d. All the surfaces of the apparatus, including the inner and outer walls of this movable injector, were coated with halocarbon wax to reduce the heterogeneous loss of active species (F, Cl, NO_3). The various reactants of the two studied reactions were produced and flowed into the reactor as follows.

For the reaction

$$F + HNO_3 \rightarrow HF + NO_3$$
 (2)

a microwave discharge in CF₄ diluted in helium produced F atoms in a side-arm tube connected to the main reactor at about 60 cm upstream of the EPR cavity. HNO3, diluted in helium, was added through the central injector. CF_4 was preferred to F_2 as a precursor of F atoms since possible complications due to F₂ reactions could not occur.

For the reaction

$$Cl + NO_3 \rightarrow ClO + NO_2$$
 (1)

F atoms, produced as above, reacted with excess HNO₃ which was introduced 7 cm downstream of the microwave cavity. A distance of 15 cm was provided for the NO_3 production through reaction 2 to be completed before NO3 entered the main flow tube. This source for NO₃ was preferred to the thermal decomposition of N₂O₅ since higher concentrations (up to 4×10^{13} molecules cm⁻³) could be produced in the reactor. Cl atoms were produced in a second microwave discharge fixed to the central injector where Cl₂, diluted in helium, was dissociated. NO₃ was titrated before and after each kinetic run, all flows being kept constant.

For the NO₃ titration experiments, two titrants were used as proposed previously by Sander:¹⁴ nitric oxide and 2,3-dimethyl-2-butene. This last molecule, (CH₃)₂C=C(CH₃)₂ (called C_6H_{12} in the present text), is known to react rapidly with NO₃ since the rate constant of this reaction is¹⁶ 6.1 \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. This value is comparable to the rate constant of the other titration reaction NO + NO₃ recently measured^{10,11} for which the recommended value¹⁷ is 3.0×10^{-11} cm³ molecule⁻¹ s⁻¹. NO or C_6H_{12} was introduced through other side inlets into the main tube.

All gas flows in the reactor were measured with mass flowmeters, the stock mixtures being contained in 10-L bulbs. Gaseous HNO_3 and C_6H_{12} were stored at maximum pressures of 40 and 100 Torr, respectively, at room temperature. These molecules could be analyzed by means of the mass spectrometer, the sampling cone being located 20 cm downstream of the EPR cavity. All the other relevant species (F, Cl, and NO) were detected from their specific EPR lines and calibrated as described by Westenberg.18

Since reactions 1 and 2 were expected to be fast, high linear flow velocities were achieved in the reactor by using a 250 m³ h^{-1} roots pump. The total pressure measurements were made with a Baratron (MKS) at 5 cm upstream of the EPR cavity. Correction using Poiseuille's law was done to obtain the mean pressure at the center of the reaction zone. The maximum value for this correction was 0.05 Torr. The apparent rate constants observed for k_1 and k_2 were also corrected for the axial diffusion of Cl and F atoms, respectively. The magnitude of this last correction was always lower than 5%.

The helium carrier gas (>99.9995%) was passed through a nitrogen liquid trap before entering the discharge tube. Matheson Gas Products NO (>99.0%) and Cl_2 (>99.9%) and CF_4 (L'Air

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Figure 1. Plot of the pseudo-first-order rate constant as a function of HNO₃ concentration at 298 K for the reaction $F + HNO_3 \rightarrow HF + NO_3$ (2).

Liquide, >99.9%) were used as supplied. C_6H_{12} (Merck, >97%) was further purified by pumping before storage in the 10-L bulb. HNO₃ was prepared by distilling a mixture of NaNO₃ and concentrated H₂SO₄, and the resulting gaseous HNO₃ was passed through a H₂SO₄ bubbler and collected at 77 K. Then, before each experiment, HNO₃ was evaporated and diluted in helium in a blackened bulb at room temperature.

Results and Discussion

Production Reaction of NO₃: $F + HNO_3 \rightarrow HF + NO_3$ (2). First, the absence of any important heterogeneous loss of F atoms was verified by introducing through the axial injector Cl₂, which rapidly converted F into Cl atoms via the reaction F + Cl₂. The observation of a constant EPR signal for Cl when the injector was moved indicated a negligible loss of F atoms along the coated reactor walls. Then, the pseudo-first-order kinetics of reaction 2 was observed by introducing an excess of HNO₃ over F through the central injector. Thirteen experiments were carried out at 298 K and over the following ranges of experimental parameters: flow velocity, 3300-3400 cm s⁻¹; total pressure, 0.45-0.48 Torr; [HNO₃], (0.40-3.25) × 10¹³ molecules cm⁻³; and [F], (0.60-4.70) × 10¹² atoms cm⁻³, with initial ratios [HNO₃]/[F] ranging from 5 to 13.

Figure 1 is a plot of the pseudo-first-order rate constant, ranging from 136 to 912 s⁻¹, vs HNO₃ concentration. For the lowest ratios [HNO₃]/[F], a correction with a magnitude lower than 10% was included in these values. Finally, the linear least-squares fit to these data gave, from the slope of the straight line obtained, k_2 = $(2.7 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The error is twice the standard deviation. The value of the zero intercept, -11 ± 22 s⁻¹, confirms the negligible heterogeneous loss of F atoms within the experimental uncertainties. The good linearity observed also shows that secondary chemistry does not alter the present measurement. In fact, the secondary reaction

$$F + NO_3 \rightarrow FO + NO_2$$
 (3)

was observed to be very fast by Ravishankara and Wine,¹³ who used reaction 2 as a source of NO₃. They proposed a lower limit of 5×10^{-11} cm³ molecule⁻¹ s⁻¹ for the rate constant k_3 at room temperature. In the simulation of a similar NO₃ source, Sander¹⁴ considered a value of 7×10^{-11} cm³ molecule⁻¹ s⁻¹ for k_3 . Such a high value for k_3 could have led to an overestimation of k_2 in our kinetic measurements. Consequently, a simulation using this latter value of k_3 was done in order to correct each value obtained for the pseudo-first-order rate constant of reaction 2. Plotting these corrected values as a function of [HNO₃] led to $k_2 = (2.4 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. That clearly indicated that the present measurement of k_2 was not significantly influenced by the value of k_3 . Furthermore, in another experiment, NO was

TABLE I: Mechanism and Rate Constants for the Formation of NO_3 and Its Titration with NO

	$k(298 \text{ K}), 10^{-11}$		
reaction	cm ³ molecule ⁻¹ s ⁻¹	note	
$(2) F + HNO_3 \rightarrow HF + NO_3$	2.7	this work	
(3) $F + NO_3 \rightarrow FO + NO_2$	1-7	see text	
(4) $FO + NO \rightarrow F + NO_2$	2.6	ref 19	
(5a) FO + FO \rightarrow 2F + O ₂	1.5	ref 17	
(6) $NO_3 + NO \rightarrow 2NO_2$	3.0	ref 17	

added into the reactor in order to scavenge NO₃ radicals formed in reaction 2. The concentration of F atoms was found to be insensitive to this addition. In that case, simulation showed that the value of k_3 would be in fact lower than 7×10^{-11} cm³ molecule⁻¹ s⁻¹. Nevertheless, it is preferable to include in the error on k_2 an additional uncertainty (of around 10%) resulting from the possible occurrence of the secondary reaction 3. Finally, the value given for k_2 is, at 298 K

 $k_2 = (2.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

This is the first determination of k_2 . This value is high, as expected, and is about 3 times higher than that considered by Sander¹⁴ in the simulation of his NO₃ source (see below).

Titration of NO_3 . Before the kinetics where NO_3 is used in excess over the other reactant is studied, an absolute titration of NO_3 must be done. This is achieved, in discharge flow systems, by using NO or C_6H_{12} (2,3-dimethyl-2-butene, see Experimental Section). In a previous study,¹⁴ C_6H_{12} appeared to be more appropriate since, when NO is used, complication can result from the chemistry following the formation of NO_3 :

$$F + HNO_3 \rightarrow HF + NO_3$$
 (2)

$$F + NO_3 \rightarrow FO + NO_2$$
 (3)

$$FO + NO \rightarrow F + NO_2$$
 (4)

FO radicals, formed in reaction 3, can rapidly react with NO, and F atoms, produced in reaction 4, can regenerate NO_3 radicals by reaction with excess HNO₃. Thus, titration with NO can lead to overestimating the NO₃ concentration which is present in the kinetic study.

In our experiments, a quantitative comparison was done between the two titration reactions. First, NO3 radicals were produced in the side-arm discharge tube and under the following conditions: [F], $(1.0-4.0) \times 10^{13}$ atoms cm⁻³; [HNO₃], $(0.58-8.65) \times 10^{14}$ molecules cm⁻³; flow velocity, 1700-2300 cm s⁻¹; and total pressure, 0.99–1.13 Torr. Then, the two titrants NO and C_6H_{12} were successively introduced through the central injector at the same concentration. The NO consumption was measured by EPR and the C_6H_{12} one at the parent peak (m/e 84) of the mass spectrum. When the injector was moved, the observed consumption of both reactants did not change, indicating that no loss of NO₃ occurred in the reactor. Since the recombination reaction $NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$ was not significant at the NO_3 concentrations used ($k \simeq 2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K^6), the heterogeneous loss of NO₃ could be considered to be negligible: $k_{\text{wall}}(\text{NO}_3) < 5 \text{ s}^{-1}$.

Considering that no secondary reaction occurred when C_6H_{12} was used, the observed consumption of C_6H_{12} was taken as the actual value of NO₃ concentration in the flow tube ($[NO_3]_{C_6H_{12}}$). The observed consumption of NO was generally found very close to this value, but in some cases, it was found higher due to the possible regeneration of NO₃ as mentioned earlier. In order to validate the NO₃ titration with NO, a computer simulation was done to calculate the NO₃ concentration obtained in this case. The value obtained, $[NO_3]_{NO}$, was further compared to $[NO_3]_{C_6H_{12}}$.

The rate constants used in this simulation are given in Table I. Since the initial concentrations of F atoms were not known accurately, the calculation of $[NO_3]_{NO}$ was done in several steps: in the absence of the titrant NO, the NO₃ concentration was first calculated, for a typical reaction time of 10 ms and using the experimental value of HNO₃ concentration, as a function of F concentrations ranging from 0 to 4×10^{13} molecules cm⁻³. Then,

TABLE II: Titration of NO₃ with NO: Comparison of the Experimental and Simulated Data

		$k_2 = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1 a}$		$k_2 = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
$k_{5a}{}^{c}$	[F] ^d	[NO ₃] _{sim} ^e	Δ [NO] _{exptl} ^e	% error	[NO ₃] _{sim} ^e	Δ [NO] _{exptl} ^e	% error
0	1.00	0.935	1.00	6	0.975	1.00	2.5
1.5	1.00	0.94	0.99	5	0.98	1.00	2
0	3.00	2.495	3.00	20	2.785	3.00	8
1.5	3.00	2.63	2.80	6	2.83	2.94	4
0	6.00	4.30	6.00	39	5.20	6.00	15
1.5	6.00	4.78	5.03	5	5.46	5.65	3

^{*a*} Used in ref 14. ^{*b*} Measured in this work. ^{*c*} In units of 10^{-11} cm³ molecule⁻¹ s⁻¹; used in ref 14. ^{*d*} In units of 10^{13} molecules cm⁻³. ^{*e*} In units of 10^{13} molecules s⁻¹; see text.



Figure 2. Comparison of the titration of NO₃ with NO and C_6H_{12} (2,3-dimethyl-2-butene).

NO was added after 10 ms, and for each calculated value of NO_3 concentration (i.e., for each F concentration), a second simulation was done using the experimental value of NO concentration. The NO consumption was thus calculated as a function of F concentration; this consumption was always completed within less than 5 ms. Finally, from the experimental value of the NO consumption, a last simulation allowed for the determination of $[NO_3]_{NO}$.

Eleven independent experiments were performed. The results are shown in Figure 2 where the calculated values of $[NO_3]_{NO}$ are plotted as a function of $[NO_3]_{C_6H_{12}}$. Since the rate constant of reaction of F with NO₃ (reaction 3) is not known, $[NO_3]_{NO}$ was calculated for values of k_3 ranging from 1×10^{-11} to 7×10^{-11} cm³ molecule⁻¹ s⁻¹. The plot of Figure 2 was obtained for $k_3 =$ 1×10^{-11} cm³ molecule⁻¹ s⁻¹, which gave the least-squares fit, with 1% error:

$$[NO_3]_{NO} = (1.01 \pm 0.05)[NO_3]_{C_6H_{12}}$$

It was always found that the difference between this calculated value of $[NO_3]_{NO}$ and the observed value of the NO consumption ranged from 10% to 0% for HNO₃ concentrations ranging from 0.58×10^{14} to 8.65×10^{14} molecules cm⁻³, respectively. In fact, HNO₃ concentrations were generally taken high enough (i.e., >3 $\times 10^{14}$ molecules cm⁻³) to make reaction 3 negligible. When the value of 7×10^{-11} cm³ molecule⁻¹ s⁻¹ was used for k_3 , the above difference ranged from 25% to 5% for the same range of HNO₃ concentrations. This indicated that, for this value of k_3 , a significant amount of FO would be formed in reaction 3 which then reacted with NO through reaction 4. Consequently, for this higher value of k_3 , the calculated values of $[NO_3]_{NO}$ were found to be lower than in the first calculation, and a plot similar to that given in Figure 2 led to

$$[NO_3]_{NO} = (0.96 \pm 0.05)[NO_3]_{C_6H_{12}}$$

Finally, provided that HNO₃ concentrations used in the NO₃ source are high enough, reaction 3 can be kept slow enough (even for $k_3 = 7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) to make NO₃ regeneration insignificant in the NO titration experiments.

As indicated in the study of Sander,¹⁴ another uncertainty factor in the simulation of the NO_3 source is the rate constant and product branching ratio for the reaction

$$FO + FO \rightarrow 2F + O_2$$
 (5a)

$$\rightarrow$$
 F₂ + O₂ (5b)

In the above simulation (see Table I) k_{5b} was neglected although it is not possible to assess that channel 5a is unique,²⁰ and the recommended value¹⁸ for $k_{5a} = 1.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ was used, which was the average of the data of two previous studies.^{20,21} If channel 5a took place in the NO₃ source region, upstream from the NO titration region, F atoms produced in this channel could reproduce NO₃ radicals by reaction 2. This effect was already estimated in two sets of simulation done in ref 14. We have also performed computer simulations using the same conditions for F atoms concentration $(1 \times 10^{13}, 3 \times 10^{13}, \text{and } 6 \times 10^{13} \text{ molecules})$ cm⁻³) and for the same reaction time (30 ms) corresponding to each reaction zone in the flow tube (NO3 source region and NO3 titration region). An initial concentration of 1×10^{15} molecules cm⁻³ was used for HNO₃ and the value 7×10^{-11} cm³ molecule⁻¹ s^{-1} for k_3 . Under these conditions, we calculated the effect of the new value obtained in the present work for k_2 : 2.7 × 10⁻¹¹ instead of 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹ as used in ref 14. The results are shown in Table II. In the extreme case where reaction 5a was neglected $(k_{5a} = 0)$, the overestimation of NO₃ concentration, taken as the difference between the NO consumption (Δ [NO]_{exptl}) and the value of NO3 concentration obtained from the simulation ([NO₃]_{sim}), ranged from 6% to 39% for $k_2 = 1.0 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹. But, for the new value of 2.7×10^{-11} cm³ molecule⁻¹ s^{-1} , this range was reduced to 2.5–15%. For the other set of simulations using the recommended value $k_{5a} = 1.5 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹, the influence of k_2 was less important, the maximum error in the titration with NO being 4%.

Finally, from the experimental and simulated results discussed above, it can be concluded that if (i) HNO₃ concentration is high enough in the NO₃ source (i.e., >3 × 10¹⁴ molecules cm⁻³) to make reaction 3 negligible and (ii) the rate constant of reaction 5a is in the order of magnitude of its recommended value (1.5×10^{-11} cm³ molecule⁻¹ s⁻¹), then the NO₃ titration using NO is in good agreement with the titration using C₆H₁₂. The maximum overestimation of NO₃ concentration when NO is used is only about 4% as a consequence of uncertainty in the kinetic data of secondary reactions.

Consequently, NO can be used as a titrant of NO₃ instead of C_6H_{12} , which appears to be necessary in some cases. For example, in the NO₃ source presently used, NO₃ concentrations higher than 4×10^{13} molecules cm⁻³ could not be easily obtained when CF₄ was used as a precursor of F atoms. And, in a subsequent kinetic study of NO₃ reactions which needed these higher concentrations, that could be achieved by replacing CF₄ by F₂ diluted in helium. But, when C_6H_{12} was used to titrate NO₃, a fast reaction was observed between F₂ and C_6H_{12} . Therefore, since F₂ was not totally dissociated in the microwave discharge, the NO₃ titration with C_6H_{12} could overestimate the NO₃ concentration. In such

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Figure 3. Plot of the pseudo-first-order rate constant as a function of NO₃ concentration at 298 K for the reaction $Cl + NO_3 \rightarrow ClO + NO_2$ (1).

experiments, NO was preferred to C_6H_{12} as a titrant.

Although uncertainties in the NO₃ concentration are also the main source of error in the measurements of $\sigma(NO_3)$ using the discharge flow method,^{13,14,22} a very good agreement was observed: at 662 nm and 298 K, $\sigma(NO_3)$ was found to be 1.78 ± 0.23,¹³ 1.83 ± 0.27 ,¹⁴ and 1.90 ± 0.22^{22} in 10^{-17} cm² molecule⁻¹ units. These values were also in excellent agreement with other recent measurements using other methods (see, for example, the extensive discussion by Burrows et al.⁴). However, a higher value of (2.28 \pm 0.34) \times 10⁻¹⁷ cm² molecule⁻¹ was measured in the flash photolysis experiments by Sander,14 who used both methods and preferred this higher value, although the uncertainty limits overlap. Since the present work concludes that the flow tube experiments yield a good precision in the NO₃ titration, the above discrepancy of about 30% in the values of $\sigma(NO_3)$ is unlikely due to a systematic error in flow studies using NO₃ titration by NO^{13,14,22} or C_6H_{12} .¹³

Reaction of NO_3 with Cl. The kinetic study of the reaction

$$Cl + NO_3 \rightarrow ClO + NO_2$$
 (1)

was performed using an excess of NO₃ over Cl. NO₃ was titrated, as described above. Fourteen experiments were carried out at 298 K under the following experimental conditions: flow velocity, $5000-5200 \text{ cm s}^{-1}$; total pressure, 0.7-0.8 Torr; [NO₃], $(0.26-2.14) \times 10^{13}$ molecule cm⁻³; and [Cl], $(0.5-5.0) \times 10^{12}$ atoms cm⁻³. A high excess of HNO₃ over F atoms was used to optimize the NO₃ production in the side-arm tube of the reactor. It was verified, in the absence of NO₃, that wall loss of Cl atoms was negligible, by moving the central discharge tube where Cl atoms were produced; the observed heterogeneous rate constant was $k_w(Cl) \le$ 4 s^{-1} . For the runs using the lowest [NO₃]/[Cl] ratios, a correction no larger than 15% was used to take into account the deviation from the pseudo-first-order conditions. The pseudo-first-order rate constants, measured as a function of [NO₃], are plotted in

TABLE III: Rate Constant at 298 K for the Reaction $Cl + NO_3 \rightarrow ClO + NO_2$ (1)

technique	ref
modulated photolysis	9
modulated photolysis	4
modulated photolysis	23
discharge flow	this work
	technique modulated photolysis modulated photolysis modulated photolysis discharge flow

Figure 3. The slope of the least-squares straight line yields the following value for k_1 at 298 K (the error is twice the standard deviation):

$$k_1 = (2.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The intercept, which represents $k_w(Cl)$, is $38 \pm 30 \text{ s}^{-1}$. Given the magnitude of the error, this value of $k_w(Cl)$ is in good agreement with the measured one. No complication may arise from the secondary reaction $ClO + NO_3 \rightarrow \text{products}$, since its rate constant was found to be about 2 orders of magnitude lower than k_1 .⁹

The value of k_1 obtained in this work is compared to previous results summarized in Table III. Our measurement is the first direct determination since, in the other studies,^{49,23} k_1 was derived from the analysis of the decay of NO₃ (measured from its absorption at 662 nm) in the modulated photolysis of Cl₂-ClONO₂ mixtures. The first value⁹ was recently remeasured in the same system,²³ the new value still being about twice higher than our value. There is a very good agreement between our value of k_1 and the value obtained by Burrows et al.⁴ This lower value makes reaction 1 less important as the secondary step of the reaction

$$Cl + ClNO_3 \rightarrow Cl_2 + NO_3$$
 (7)

which is an alternative source of NO₃ radicals in laboratory studies. When this source is used, the assumption of a stoichiometric conversion of ClNO₃ into NO₃ may deviate from unity if reaction 1 is fast. For example, under the conditions of the $\sigma(NO_3)$ measurements by Sander¹⁴ using reaction 7 as a source of NO₃, i.e., $[NO_3] = 2 \times 10^{13}$ molecules cm⁻³, simulations show that the deviation in the stoichiometry decreases from 9% to 3% when k_1 is varied from 7.6 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹¹⁰ to the present value of 2.6 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

Conclusion

The present work provides new kinetic data for the reaction $F + HNO_3 \rightarrow HF + NO_3$, which is known to be a very convenient source for laboratory studies of NO₃ radicals. That allows for a better characterization of the NO₃ source and for a more accurate titration of NO₃ in discharge flow systems using either NO or 2,3-dimethyl-2-butene as a titrant. A double discharge flow reactor has been used to perform the direct kinetic study of a radical-radical reaction involving NO₃. Although the fast reaction between Cl and NO₃ may have no impact on atmospheric chemistry, it may not be the case for other similar reactions which are now under study and which are relevant to the nighttime behavior of HO_x radicals.

Registry No. NO₃, 12033-49-7; Cl, 22537-15-1; HNO₃, 7697-37-2; F, 14762-94-8; NO, 10102-43-9; 2,3-dimethyl-2-butene, 563-79-1.

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