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International Journal of Mass Spectrometry 181 (1998) 113–121

International Journal of Mass Spectrometry

Gas phase reactions of HNO_3 with Cl^-, Cl^-H_2O, and Cl^-HCl, of Cl_2 with Cl^-H_2O and Cl^-HCl, and of HCl with Cl^-H_2O

C. Amelynck*, E. Arijs, N. Schoon, A.-M. Van Bavel

Belgian Institute for Space Aeronomy, Ringlaan 3, B-1180 Brussels, Belgium

Received 29 June 1998; accepted 30 August 1998

Abstract

This paper reports on the gas phase reactions of HNO_3 with Cl^-, Cl^-H_2O, and Cl^-HCl, of Cl_2 with Cl^-H_2O and Cl^-HCl, and of HCl with Cl^-H_2O. Rate constants and product ions have been determined at room temperature and at low pressures (0.7–1.7 mb) by means of a flow tube reactor coupled to a quadrupole mass spectrometer. Apart from $Cl^-HCl + Cl_2$, all reactions proceed at the collision rate. The reaction mechanism for all reactions, except for $Cl^- + HNO_3$, seems to be ligand switching. The implication of the results on a chemical ionisation method for the in situ derivation of stratospheric nitric acid concentrations is discussed. (Int J Mass Spectrom 181 (1998) 113–121) © 1998 Elsevier Science B.V.

Keywords: Ion-molecule reactions; Rate constant measurements; Flowing afterglow

1. Introduction

Recently a balloon borne chemical ionisation mass spectrometry (CIMS) instrument has been developed within the project MACSIMS (Measurement of Atmospheric Constituents by Selective Ion Mass Spectrometry). [MACSIMS is a cooperation between the Belgian Institute for Space Aeronomy (B), the Physikalisches Institut of the University of Berne (CH), and the Laboratoire de Physique et Chimie de l'Environnement of the CNRS in Orléans (F).] The purpose of this project is the development of a chemical ionisation method for the simultaneous in situ measurement of several stratospheric trace gas concentrations (HNO_3, $ClONO_2$, N_2O_5, HCl) through the use of a balloon borne instrument equipped with selective ion sources [1–3]. The CIMS method [4] consists in the production of specific source ions that are injected in a flow tube and carried towards the mass spectrometer by a stratospheric air flow sustained by a small turbine. During transport these ions react selectively with stratospheric trace gases leading to specific product ions. From the mass spectra, the reaction time of the ions (measured in situ) and the rate constants of the involved ion molecule reactions, the concentration of the reactant neutrals can, in principle, be inferred.

One of the reaction schemes for the derivation of HNO_3 concentrations used in the MACSIMS instrument is based upon the reaction of Cl_3^- with HNO_3:

$$Cl_3^- + HNO_3 \rightarrow NO_3^-HCl + Cl_2 \quad (1)$$

and the subsequent loss of the product ion NO_3^-HCl by reaction with HNO_3:

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* Corresponding author. E-mail: crist.amelynck@oma.be

PII S1387-3806(98)14163-5

$$NO_3^-HCl + HNO_3 \rightarrow NO_3^-HNO_3 + HCl \qquad (2)$$

These reactions have been studied in our laboratory [5] in a relative way by using as a reference the reaction of Cl^- with HNO_3:

$$Cl^- + HNO_3 \rightarrow NO_3^- + HCl \qquad (3)$$

Reaction (3) was first studied by Fehsenfeld et al. [6] who obtained a rate constant k_3 of 1.6×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. Recently, however, a new value for k_3 was measured by Huey et al. [7]. This value differs from the previous one by a factor 1.75. Because the accuracy of the stratospheric HNO_3 mixing ratios obtained with the CIMS instrument largely depends on k_3, we decided to perform a third, independent measurement of the rate constant of Cl^- with HNO_3.

In order to apply the abovementioned reaction scheme in the stratosphere, our CIMS instrument was equipped with a chlorine discharge ion source producing mainly Cl^- and Cl_3^- ions. The ratio of Cl_3^- to Cl^- ion concentrations at the exit of the ion source strongly depends on the pressure and the Cl_2 concentration in the ion source. An ideal reaction scheme for CIMS applications requires the absence of source ion formation outside the ion source. In our configuration, however, the reaction scheme is thought to be influenced by a possible conversion of Cl^- to Cl_3^- ions in the flow tube.

Two mechanisms might be responsible for this conversion:

(i) Because Cl_2 is used as parent gas of the source ions, its concentration in the flow reactor is non-negligible. Part of the Cl^- ions leaving the ion source may therefore undergo a three-body association reaction with Cl_2. Babcock and Streit [8] studied this reaction at low pressures in helium and obtained a rate constant of 9×10^{-30} cm^6 $molecule^{-2}$ s^{-1}.

(ii) Because the stratospheric water vapour concentration is of the order of a few ppm, chloride ions are assumed to undergo three-body association with H_2O molecules to form Cl^-H_2O ions. As will be pointed out in Sec. 3, these ions rapidly react with Cl_2 to form Cl_3^- ions.

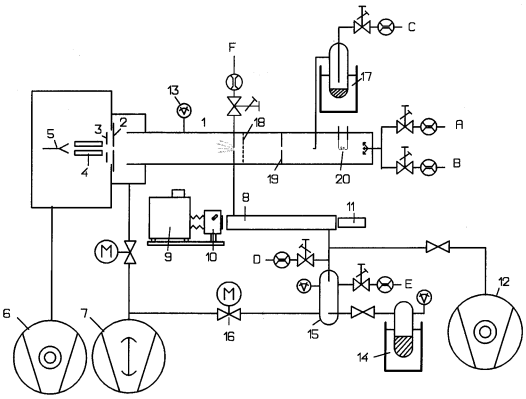

Fig. 1. Schematic representation of the flowing afterglow laboratory apparatus: (1) flow tube; (2) ion inlet plate; (3) electrostatic lens system; (4) quadrupole mass filter; (5) channeltron electron multiplier; (6) turbomolecular pump; (7) rootspump; (8) absorption cell; (9) deuterium lamp housing; (10) grating monochromator; (11) photomultiplier; (12) turbomolecular pump; (13) pressure sensor; (14) nitric acid reservoir; (15) nitric acid dilution chamber; (16) electronically controlled valve; (17) water reservoir; (18) grid; (19) membrane; (20) filament; (A) ion parent gas inlet; (B) main flow inlet; (C) Ar + water vapor inlet; (D) and (E) Ar inlet.

Apart from Cl^- and Cl_3^-, which were the most abundant source ions, we also observed the Cl^- core ions Cl^-H_2O and Cl^-HCl in the in situ mass spectra with the MACSIMS instrument. In order to have a better understanding of the ion chemistry in the flow reactor of the stratospheric experiment when using the chlorine discharge ion source, we also studied the reactions of Cl^-H_2O with HCl, Cl_2, and HNO_3 and of Cl^-HCl with Cl_2 and HNO_3. The results of these studies and the implications on the reaction scheme for the derivation of stratospheric HNO_3 concentrations with the balloon borne CIMS apparatus will be discussed.

2. Experiment

The ion molecule reactions were studied in a flowing afterglow apparatus at room temperature. The instrument has been described in more detail in earlier publications [5,9] and is shown schematically in Fig. 1. It consists of a 4 cm inner diameter stainless steel flow tube ion molecule reactor coupled to a quadrupole mass spectrometer. Ions are convectively transported to the mass spectrometer inlet by means of an Ar buffer gas flow created by a 250 m^3 h^{-1} roots pump. After being sampled into the mass spectrometer through a 0.3 mm diameter orifice, the ions are analysed by a quadrupole mass filter and detected by a Channeltron electron multiplier working in the pulse mode. By using a 2000 L s^{-1} turbopump an appropriate vacuum ($<5 \times 10^{-5}$ mb) is maintained in the mass spectrometer section at the operating flow tube pressures (0.7–1.7 mb). Neutral reactants are introduced into the flow tube downstream from the ion source at a distance of 38.3 cm from the inlet orifice. The reaction time of the ions is measured by pulsing a grid, located just upstream from the neutral reactant gas inlet, and synchronously recording the ion swarm arrival time on the detector by means of a multichannel scaler. Rate constant measurements were performed by measuring the ion signal at the mass spectrometer inlet as a function of the neutral reactant gas concentration in the flow tube reactor.

Although the basic features of the apparatus remained unchanged, some important modifications were made with respect to the former configuration. When studying ion molecule reactions with nitric acid previously, we only performed relative rate constant measurements by using the reaction of Cl^- (as a reference ion) with nitric acid. The absolute accuracy of the measured rate constants is therefore limited by the accuracy of the rate constant k_3 of this reference reaction. In view of the large difference between the two reported values of k_3 [6,7] and to perform absolute rate constant measurements, a determination of the nitric acid concentration in the flow tube is required. To do so, a spectroscopic method was chosen that has been successfully applied in the past for the measurements of several reactant gas concentrations in a flowing afterglow apparatus [10].

A diluted HNO_3 + Ar flow, produced in a dilution chamber [5], is sent along with a small Ar flow (typically 1.66×10^{-1} STP cm^3 s^{-1}) through the absorption cell before entering the flow tube at a distance of 38.3 cm from the mass spectrometer inlet. The cell has a length L of 50 cm and an internal diameter of 2.5 cm and is sealed with Suprasil windows to transmit light at a wavelength of 186 nm. This light is produced by a deuterium lamp of 30 W and wavelength-selected by means of an Ebert–Fastie grating monochromator. It is detected at the other end of the absorption cell by means of a solar blind photomultiplier that is sensitive in the spectral domain of 115–320 nm. From the decrease of the light beam intensity I_λ due to absorption by nitric acid molecules, one can derive the nitric acid concentration in the absorption cell ($[HNO_3]_{ac}$) by using the Beer–Lambert law:

$$[HNO_3]_{ac} = \frac{-\ln(I_\lambda/I_{\lambda,0})}{\sigma_\lambda L} \tag{4}$$

where I_λ and $I_{\lambda,0}$ are, respectively, the light intensity with and without addition of HNO_3 in the absorption cell and σ_λ is the absorption cross section of HNO_3 for light at wavelength λ. For $\lambda = 186$ nm a value of 1.58×10^{-17} cm^2 $molecule^{-1}$ was used for σ_λ [11].

After calibrating the wavelength setting of the monochromator with a mercury line spectrum, the entire absorption system was validated by measuring the absorption cross section of dichlorodifluoromethane (CF_2Cl_2) versus wavelength within the range 185–195 nm. Within this region our results corresponded to literature data [12] within five percent.

The nitric acid used in our experiments was purified by vacuum distillation from a mixture of commercially obtained HNO_3 (90% aqueous solution) and H_2SO_4 (100% pure) with a volume mixing ratio of 3:2. Pure HNO_3 was trapped in a glass reservoir in a cold ethanol bath (−54 °C) where it was stored in the dark.

A capacitance manometer was mounted halfway along the absorption cell in order to measure the pressure in the absorption cell. Because of the conservation of particle flux, the HNO_3 concentration in the flow tube can be derived from the total gas flows through the flow tube (Q_{ft}) and the absorption cell (Q_{ac}), the pressures in the flow tube (P_{ft}) and the absorption cell (P_{ac}), and the HNO_3 concentration in the absorption cell by the following formula [10]:

$$[HNO_3]_{ft} = [HNO_3]_{ac} \frac{P_{ft} Q_{ac}}{P_{ac} Q_{ft}} \tag{5}$$

The other neutral reactants, HCl and Cl_2, were obtained commercially as diluted gas mixtures in Ar (1000 ppm). They were introduced axially into the flow tube by mass flow controllers at the same distance from the mass spectrometer inlet as the HNO_3 inlet. Introduction of HCl in the flow tube required passivation of the stainless steel gas line. This was done by flushing the gas line with a 2.3 STP $cm^3\ s^{-1}$ Ar + HCl flow for about an hour. Furthermore, stability of the HCl flow was enhanced by heating the gas line to ≈100 °C.

A second modification of our instrument consisted in the use of a "poorman's" ion source (PMIS) for the production of Cl^-H_2O and Cl^-HCl ions. This type of ion source was introduced by Fahey et al. for the production of $O_2^-(H_2O)_n$ (n = 0–4) ions [13]. The ion source is separated from the flow tube by a thin stainless steel membrane with a central opening of 4 mm in diameter. Because the entire carrier gas flow is constrained to flow through the ion source the ratio of ion source pressure to flow tube pressure is about 20 at a typical pressure of 1.33 mb in the flow tube. As a consequence, the average gas flow velocity in the ion source is lower with respect to the one in the flow tube by the same factor. The ion source contains a heated emission-controlled thoriated iridium filament biased at −50 V. Emission currents between −80 and −500 μA were used. Cl^- ions are produced by dissociative attachment of the emitted electrons to CCl_4 that is added upstream. Downstream the filament hydration of Cl^- ions takes place by adding water vapour to the ion source. Because of the elevated pressure and the low flow velocity in the ion source (i.e. relatively high residence times), only small water vapour concentrations are needed in the ion source to obtain appropriate Cl^-H_2O count rates. Because the corresponding water vapour concentration in the flow tube is lower by a factor 20, no further hydration is thought to occur in the reaction region. This was checked experimentally by inserting the same amount of H_2O vapour in the flow tube reactor after taking away the membrane.

Apart from Cl^-H_2O, Cl^-HCl ions were always formed in the ion source by a yet unknown mechanism. When studying the reaction of Cl^- with HNO_3 the membrane was not used and the filament was installed off axis to avoid the detection by the Channeltron electron multiplier of light emitted in the neighbourhood of the filament.

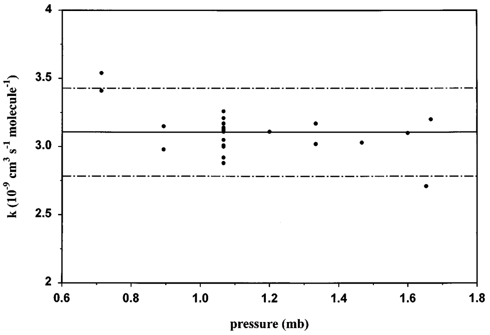

Fig. 2. Rate constant of Cl^- + HNO_3 (k_6) vs. flow tube pressure. The full line corresponds to the average value. The dash–dotted lines correspond to a deviation of 2 × σ from the average value.

3. Results

3.1. Reactions with HNO_3

Rate constant measurements of the reaction

$$Cl^- + HNO_3 \rightarrow NO_3^- + HCl \qquad (6)$$

were performed at different flow tube pressures ranging from 0.7 to 1.65 mb. Cl^- ions were produced by using a filament operated at flow tube pressures (i.e. no membrane present). The results are presented in Fig. 2. No explicit pressure dependence was observed and an average rate constant of $(3.1 \pm 0.5) \times 10^{-9}$ $cm^3\ molecule^{-1}\ s^{-1}$ was obtained. From the mass spectra it is clear that NO_3^- is the only product ion in the pressure range covered by our experiments.

To study the reactions of the cluster ions Cl^-H_2O and Cl^-HCl with HNO_3 the "poorman's" ion source was used to produce the reactant ions. A neat spectrum obtained by adding CCl_4 and H_2O to the PMIS is shown in Fig. 3(a). Apart from Cl^- (35 and 37 amu), Cl^-H_2O (53 and 55 amu), and Cl^-HCl (71, 73, and 75 u), small contributions of NO_3^- (62 amu) and NO_3^-HCl (98 and 100 u) are present due to residual HNO_3 evaporating from the walls of the ion source

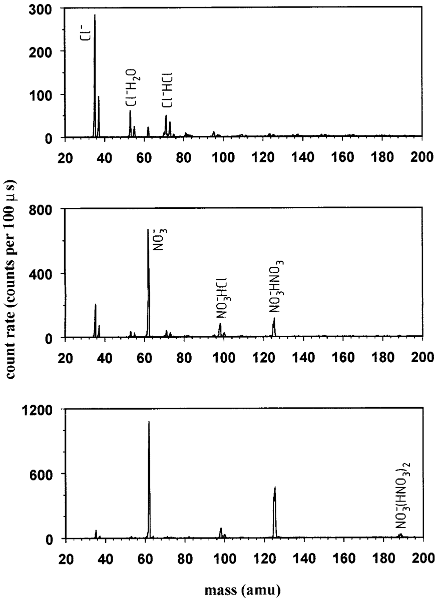

Fig. 3. Evolution of the involved ion species with increasing HNO_3 concentration in the flow tube reactor. The total carrier gas flow is 38 STP cm^3 $molecule^{-1}$ s^{-1}, corresponding to a flow tube pressure of 1.38 mb. Pressure in and Ar flow through the absorption cell are respectively 3.73 mb and 0.17 STP cm^3 $molecule^{-1}$ s^{-1}. The reaction time is 8.18 ms. In the upper spectrum no HNO_3 is added to the system. The HNO_3 concentrations in the flow tube corresponding to the middle and lower spectra are respectively 2.8×10^{10} and 6.9×10^{10} molecules cm^{-3}.

compartment or from the flow tube. After introducing HNO_3 in the flow tube, Cl^-, Cl^-H_2O, and Cl^-HCl concentrations decrease whereas NO_3^-, NO_3^-HCl, and $NO_3^-HNO_3$ concentrations increase, as can be noticed in Fig. 3(b). Because NO_3^- is the only product ion of Cl^- with HNO_3, NO_3^-HCl must be the product ion of Cl^-H_2O and Cl^-HCl with HNO_3:

$$Cl^-H_2O + HNO_3 \rightarrow NO_3^-HCl + H_2O \tag{7}$$

$$Cl^-HCl + HNO_3 \rightarrow NO_3^-HCl + HCl \tag{8}$$

Upon further addition of HNO_3 to the flow tube [Fig. 3(c)], NO_3^-HCl decreases in favour of $NO_3^-HNO_3$ by reaction (2) and $NO_3^-(HNO_3)_2$ starts forming by the termolecular reaction:

$$NO_3^-HNO_3 + HNO_3 + M \rightarrow NO_3^-(HNO_3)_2 + M \tag{9}$$

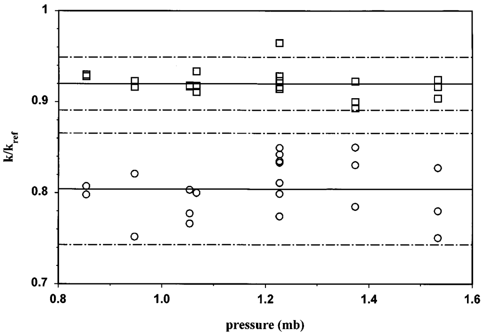

Fig. 4. k_7/k_6 (□) and k_8/k_6 (O) vs. flow tube pressure. The full lines correspond to the average values. The dash–dotted lines correspond to a deviation of $2 \times \sigma$ from the average values.

Absolute rate constant measurements of HNO_3 with Cl^-, Cl^-H_2O, and Cl^-HCl, generated in the PMIS, show an increase of the rate constants with flow tube pressure for all three ion species. However, the rate constant ratios k_7/k_6 and k_8/k_6, presented in Fig. 4, show no pressure dependence, indicating that the rate constant increase could possibly be attributed to gas flow dynamics. Because the entire buffer gas flow is constrained to leave the ion source through a hole of 4 mm diameter, a certain distance is required for the flow to become fully developed. The higher the carrier gas flow, the longer this distance will be which could explain why absolute rate constant measurements with HNO_3 are disturbed at higher pressures (i.e. at higher carrier gas flows). This hypothesis is corroborated by the fact that the rate constant of Cl^- with HNO_3 at low pressures (<1.1 mb) coincides with the pressure-independent value obtained without membrane over a larger pressure range. The values we obtained for k_7/k_6 and k_8/k_6 are respectively 0.92 ± 0.03 and 0.80 ± 0.06. The uncertainty on the rate constant ratios corresponds to the statistical error at the 95% confidence level.

3.2. Reaction of Cl^-H_2O with HCl

Rate constant measurements were performed at four different pressures (0.88, 1.11, 1.33, and 1.47 mb) and are shown in Fig. 5. This resulted in an average value of 1.3×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. The precision (statistical error at the 95% confidence

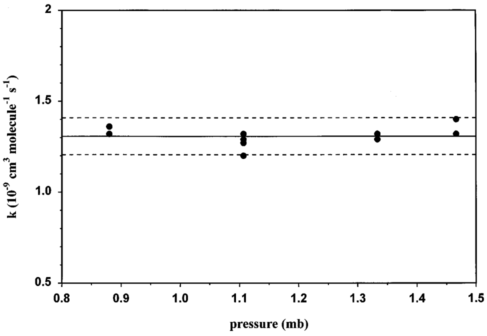

Fig. 5. Rate constant of $Cl^- H_2O + HCl$ vs. flow tube pressure. The full line corresponds to the average value. The dash–dotted lines correspond to a deviation of 2 × σ from the average value.

level) and the accuracy of the measurement are respectively 8% and 15%. The latter mainly resulted from the error on the reaction time and the individual errors on the instrumental parameters.

By using the value 2.58×10^{-30} m^3 for the polarisability and 3.6×10^{-30} C · m for the electric dipole moment of HCl [14], a collision rate constant of 1.4×10^{-9} cm^3 $molecule^{-1}$ s^{-1} is obtained for the reaction of Cl^-H_2O with HCl by using the formula of Su and Chesnavich [15] which is based on trajectory calculations. From the good agreement between this value and our experimental results, we can conclude that the reaction essentially proceeds at the collision frequency.

The variation of the three source ion species as a function of HCl concentration in the flow tube is shown in Fig. 6. Because Cl^-HCl is the only product ion that was observed in the mass spectra, the reaction mechanism is thought to be ligand switching:

$$Cl^-H_2O + HCl \rightarrow Cl^-HCl + H_2O \tag{10}$$

3.3. Reaction of Cl^-H_2O and Cl^-HCl with Cl_2

Spectra without and with addition of Cl_2 (1.5×10^{11} molecules cm^{-3}) to the flow tube are shown in Fig. 7. From these spectra it is clear that Cl^-H_2O and Cl^-HCl concentrations decrease upon addition of Cl_2 and that Cl_3^- appears as a product ion, indicating that the reaction mechanism of Cl^-H_2O and Cl^-HCl with Cl_2 is also ligand switching:

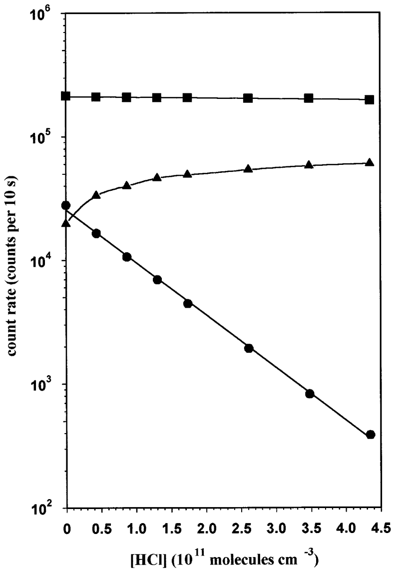

Fig. 6. Evolution of the concentration of the involved ion species as a function of HCl concentration in the flow tube reactor. (squares: Cl^-, circles: Cl^-H_2O; triangles: Cl^-HCl).

$$Cl^-H_2O + Cl_2 \rightarrow Cl_3^- + H_2O \tag{11}$$

$$Cl^-HCl + Cl_2 \rightarrow Cl_3^- + HCl \tag{12}$$

Rate constant measurements were again performed at four different pressures (0.86, 1.12, 1.25, and 1.47 mb), showing no explicit pressure dependence.

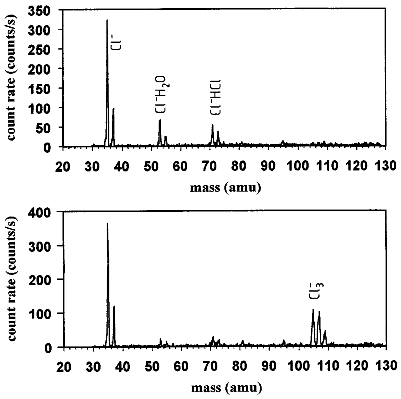

Fig. 7. Upper figure: source ion spectrum obtained with the PMIS, indicating the simultaneous presence of Cl^-, $Cl^- H_2O$, and $Cl^- \cdot HCl$ ions in the flow tube. Lower figure: spectrum after addition of 1.7×10^{-4} STP cm^3 $molecule^{-1}$ s^{-1} Cl_2 to the flow tube reactor.

An average value of 1.09×10^{-9} and 5.3×10^{-10} cm^3 molecule^{-1} s^{-1} was obtained for the rate constant of Cl^-H_2O and Cl^-HCl with Cl_2, respectively. The total measurement error, mainly determined by the accuracy of the Cl_2 concentration in the Ar + Cl_2 mixture (20%) and by the error on the reaction time (10%), is about 25%.

The decrease of $[Cl^-HCl]$ with increasing Cl_2 concentration in the flow tube, however, should not a priori be attributed to the reaction of this ion with Cl_2. Because the production mechanism of Cl^-HCl in the ion source is not understood, we considered the possibility of HCl production in the ion source and consequently the presence of HCl in the reaction zone of the flow tube. Depending on the HCl concentration in the flow tube, this could be a major source of error for the rate constant measurement of Cl^-HCl with Cl_2. Suppose Cl^-HCl is partly produced in the flow tube by reaction of Cl^-H_2O with HCl that is made in the ion source. Even if no reaction occurs between Cl^-HCl and Cl_2, a decrease of $[Cl^-HCl]$ would be observed upon addition of Cl_2 to the flow tube because the precursor ion Cl^-H_2O reacts with Cl_2.

Therefore, special attention was given to the reaction of Cl^-HCl with Cl_2. From the ratio $R = [Cl^-H_2O]_0/[Cl^-HCl]_0$ obtained with the mass spectrometer without addition of Cl_2 to the flow tube, the residence time τ_{ft} of the ions between the ion source and the mass spectrometer inlet and the rate constant k_{10} of Cl^-H_2O with HCl, an upper limit $[HCl]_{max}$ for the HCl concentration is obtained by assuming that all Cl^-HCl is formed by reaction (10):

$$[HCl]_{max} = \frac{1}{k_{10} \times \tau_{ft}} \ln(1 + R) \tag{13}$$

By taking into account this upper limit for the HCl concentration, the "worst case" initial Cl^-H_2O and Cl^-HCl concentrations, $[Cl^-H_2O]_i$ and $[Cl^-HCl]_i$, at the reactant gas inlet without Cl_2 addition are given by:

$$[Cl^-HCl]_i = [Cl^-HCl]_0[1 - \exp(k_{10}[HCl]_{max}\tau_r] \tag{14}$$

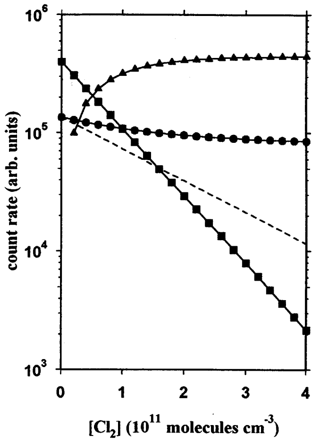

Fig. 8. Evolution of $[Cl^-H_2O]$ (□), $[Cl^-HCl]$ (O), and $[Cl_3^-]$ (Δ) resulting from the model vs. Cl_2 concentration in the flow tube in a realistic situation (by assuming Cl^-HCl is not reacting with Cl_2). The dotted line corresponds to the decrease of $[Cl^- \cdot HCl]$ that was observed experimentally (normalised with respect to the Cl^-HCl concentration resulting from the model at zero Cl_2 concentration). The flow tube pressure is 0.87 mb and the ratio *R* equals 0.34.

$$[Cl^-H_2O]_i = [Cl^-H_2O]_0 \exp(k_{10}[HCl]_{max}\tau_r) \tag{15}$$

In these expressions τ_r is the residence time of the ions between the reactant gas inlet and the mass spectrometer inlet. By taking $[Cl^-H_2O]_i$ and $[Cl^-HCl]_i$ as initial values and by assuming that Cl^-HCl does not react with Cl_2 (i.e. by putting k_{12} to zero) we then calculated $[Cl^-H_2O]$, $[Cl^-HCl]$, and $[Cl_3^-]$ at the end of the reaction zone at different Cl_2 concentrations from the solution of the set of differential equations describing the time evolution of $[Cl^-H_2O]$, $[Cl^-HCl]$, and $[Cl_3^-]$ by taking into account reactions (10), (11), and (12).

A typical result of these calculations corresponding to real working conditions is shown in Fig. 8. From this figure, which shows the theoretical as well as the experimentally observed decrease of $[Cl^-HCl]$, it is clear that the observed decrease can never be attributed to a decrease of $[Cl^-H_2O]$ alone.

From the solution of the same set of differential equations, it was found by trial and error that a value of 4.3×10^{-10} cm^3 molecule^{-1} s^{-1} for k_{12} had to be taken into account for the calculated and the observed $[Cl^-HCl]$ to coincide at the upper limit HCl concentration in the flow tube. This means that the real k_{12} is at most 20% lower than the experimentally derived value.

4. Discussion and implications for HNO_3 derivation by the CIMS method

The contribution of this work to the atmospheric CIMS method for nitric acid derivation is twofold. First, the good agreement between our pressure independent value for k_6 and the one obtained by Huey [7] enhances the accuracy of the nitric acid concentrations as inferred by CIMS. Second, this study improved our insight into the ion molecule chemistry inside the flow tube reactor when using chlorine ions (Cl^- and Cl_3^-) as source ions in the CIMS method [3].

Of the reactions reported in this work, only $Cl^- + HNO_3$ ([7,6]) and $Cl^-H_2O + Cl_2$ (more precisely $Cl^-D_2O + Cl_2$ [16,17]) have been studied before and allow for comparison with literature data. From our results, it is clear that the reactions of Cl^-, Cl^-H_2O, and Cl^-HCl with nitric acid proceed at essentially the collision rate, as was already noticed by Huey for the reaction of Cl^- with HNO_3. The rate constant we obtained for this reaction agrees within 10% with the one reported by Huey [7].

Our rate constant of Cl^-H_2O with Cl_2 agrees well with the value obtained by Wincel et al. (9.2×10^{-10} cm^3 molecule^{-1} s^{-1}) and with the Langevin collision limit (9.05×10^{-10} cm^3 molecule^{-1} s^{-1}), indicating that this reaction also proceeds at the collision rate. This high value explains why, at high ion parent gas (Cl_2) concentrations in the flow tube ($\approx 2 \times 10^{12}$ molecules cm^{-3}) as was the case in the balloon flight of our CIMS instrument of November 1995 from León (Spain) [3], almost no Cl^-H_2O is present in the mass spectra. Because the reaction of Cl^-H_2O with HCl also proceeds in a fast way, Cl^-H_2O produced by hydration of Cl^- source ions could well be the precursor of Cl^-HCl ions in the MACSIMS instrument through reaction with stratospheric HCl.

By using a chlorine discharge ion source in the MACSIMS instrument, stratospheric nitric acid concentrations could be inferred by using two different methods, as explained in a companion paper [3]. A first method was based on a reaction scheme containing Eqs. (1) and (2). However, because part of the Cl_3^- is produced in this reaction zone by hydration of Cl^- source ions followed by reaction (11) and by three-body reaction of Cl^- with Cl_2, the HNO_3 concentration derived with this method should be considered as a lower limit. In a second derivation method all Cl^- core ions are grouped as the source ion family S^- and all NO_3^- core ions are considered as the product ion family P^-. The HNO_3 concentration was obtained by considering an overall conversion of S^- to P^- ions with a rate constant equal to the one of Cl_3^- with HNO_3 ($0.82 \times k_3$), this ion being the most abundant one of the S^- family.

This study revealed that, apart from Cl^-HCl that is only present in the in situ mass spectra in small amounts, the rate constant of the other Cl^- core ions (Cl^-H_2O and more important Cl^-) exceeds the one of Cl_3^- with HNO_3. Therefore, the nitric acid concentration derived with this method should be considered as an upper limit. Because of the small differences between the rate constants of all Cl^- core ions with HNO_3 the inaccuracy of the global rate constant can affect the derived HNO_3 concentrations by no more than 20%.

Acknowledgements

The authors are grateful to the Commission of the European Communities (contract nos. EV5V-CT92-0062 and ENV4-CT95-0042) and the FKFO/MI (Fonds voor Kollektief Fundamenteel Onderzoek-Ministerieel Initiatief) for partly financing this work. One of us (C.A.) was supported by the Belgische Staat, Diensten van de Eerste Minister, Federale Diensten voor Wetenschappelijke, Technische en Culturele Aangelegenheden.

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