International Journal of Mass Spectrometry 207 (2001) 205–215

Gas phase reactions of negative ions with $ClONO_2$

C. Amelynck[a,*], C. Stépien[b], N. Schoon[a], V. Catoire[b], D. Labonnette[b], E. Arijs[a], G. Poulet[b]

[a]Belgian Institute for Space Aeronomy, B-1180 Brussels, Belgium
[b] Laboratoire de Physique et Chimie de l'Environnement, UMR 6115 CNRS - Université d'Orléans, F-45071 Orléans Cedex 2, France

Received 4 December 2000; accepted 15 January 2001

Abstract

The reactions of the halide anions (F^-, Cl^-, Br^-, and I^-), NO_2^-, SF_6^-, CO_3^- and CO_4^- with $ClONO_2$ have been studied at room temperature in a flowing afterglow apparatus. All these reactions are found to proceed at the collision limit and the experimental data are compared with literature values. The reaction of I^- with $ClONO_2$ was studied at stratospheric pressures and temperatures in view of its use as a possible precursor ion for the measurement of stratospheric N_2O_5+$ClONO_2$ mixing ratio height profiles by chemical ionization mass spectrometry. No pressure or temperature dependence of the rate constant has been observed. In order to correct the observed rate constants for HNO_3 impurities, the reaction rate constants of F^-, Br^-, and NO_2^- with HNO_3 have also been determined. In addition, the apparent second-order clustering rate constant of NO_3^- with $ClONO_2$ in Ar/N_2 and Ar/He mixtures has been measured. (Int J Mass Spectrom 207 (2001) 205–215) © 2001 Elsevier Science B.V.

Keywords: Ion/molecule reactions; Chemical ionization; Flowing afterglow; Chlorine nitrate; Nitric acid

1. Introduction

Chlorine nitrate is an important molecule in stratospheric chemistry since it acts as a reservoir of both reactive nitrogen and reactive chlorine, which are responsible for the catalytic destruction of ozone. Under polar stratospheric conditions, $ClONO_2$ can be efficiently converted into reactive chlorine species (HOCl, Cl_2) through heterogeneous chemical reactions on polar stratospheric cloud particles leading to the ozone hole formation [1].

Most negative ion chemistry studies involving $ClONO_2$ are related to atmospheric chemistry. Experimental [2–5] and theoretical [5,6] studies have considered the possible role of ion mechanisms in the gas phase reaction $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$. Other studies have aimed at elucidating reaction schemes for the in situ detection of $ClONO_2$ by chemical ionization mass spectrometry [7–9].

With the aim of simultaneously measuring various trace gases, a balloon-borne chemical ionization mass spectrometer containing a flow tube and several ion sources has been built by our group and flown in the stratosphere [10]. One of these ion sources is producing I^- (and I_3^-) ions. Of all NO_y species present in the stratosphere, only N_2O_5 and $ClONO_2$ are known to react with I^- to a reasonable extent to produce NO_3^-. Consequently a total N_2O_5 + $ClONO_2$ concentration height profile can in principle be obtained from the

---

*Corresponding author. E-mail: Crist.Amelynck@bira-iasb.oma.be

1387-3806/01/$20.00 © 2001 Elsevier Science B.V. All rights reserved
PII S1387-3806(01)00373-6

ratio $[NO_3^-]/[I^-]$ measured with the mass spectrometer, provided the rate constants of the ion/molecule reactions are known and the ion residence time in the flow tube is experimentally determined. Mixing ratios versus altitude as inferred from the I^- ion source, however, turned out to be overestimated by about a factor of 3 compared to the expected N_2O_5 and $ClONO_2$ profiles obtained by other techniques [11,12].

This discrepancy may be due to an incomplete understanding of the ion chemistry in the chemical ionization mass spectrometry (CIMS) apparatus using the iodide source ions. Therefore, a detailed kinetic study of the ion/molecule reactions involved has to be undertaken. An important issue in this respect is the study of $I^- + ClONO_2$ at stratospheric conditions, which is reported in this article.

Only a limited number of negative ion/molecule reactions with $ClONO_2$ have been reported in the literature so far. Having at our disposal a reliable optical method for the measurement of the $ClONO_2$ concentrations in the flow tube, reactions of some other anions (F^-, Br^-, Cl^-, SF_6^-, NO_2^-, CO_3^-, and CO_4^-) with $ClONO_2$ have been studied at room temperature as well.

2. Experiment

Three flowing afterglow instruments have been used in this study. One of them is located at the Laboratoire de Physique et Chimie de l'Environnement (LPCE) and will hereafter be referred to as FA/LPCE. The other two are located at the Belgian Institute for Space Aeronomy (BISA) and will be denoted as FA/BISA-I and FA/BISA-II. These instruments have all been described in previous publications [13–15] and therefore only details relevant to the present study will be given hereafter.

The reaction of I^- with $ClONO_2$ has been studied at pressures ranging from 2.2 to 13.3 mbar and at four temperatures (232 ± 5 , 271 ± 5 , 298 ± 1, and 323 ± 5 K) in the FA/LPCE apparatus. Nitrogen was used as buffer gas at flow rates ranging from 2 to 30 STP L min^{-1} (STP = standard temperature and pressure, i.e. 273.16 K and 1013.25 mbar, respectively). The iodide ions were produced in a discharge ion source, described further on, which was located at 108.2 cm from the mass spectrometer inlet. The $ClONO_2$ reactant gas was introduced into the 3.5 cm i.d. stainless steel flow tube reactor through a finger inlet located 24.4 cm upstream the ion source.

The FA/BISA-I instrument has a flow tube diameter of 6.5 cm and pressures as high as 20 mbar can be attained through differential pumping of the detection chamber. Since using $ClONO_2$ requires passivation of the surfaces of the gas inlet lines and of the flow tube walls in order to avoid HNO_3 formation by heterogeneous reactions (i.e. $ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$), the FA/BISA-I instrument was only used in this work to study ion/molecule reactions with $ClONO_2$. Ion/molecule reactions with HNO_3 were studied in the FA/BISA-II instrument. This instrument has a flow tube diameter of only 3.5 cm. Since the detection chamber of this instrument is not differentially pumped, the flow tube pressure is limited to 2 mbar.

In the FA/BISA-I instrument, He was used as carrier gas at a typical flow rate of 4.5 STP L min^{-1}. Measurements were performed at three different flow tube pressures (0.67, 0.93, and 1.33 mbar) which were obtained by throttling the valve between the flow tube reactor and the Roots blower. Two electrically insulated ring shaped reactant gas inlets were used to introduce $ClONO_2$ into the reactor. These inlets were located at a distance of 43.4 and 77.8 cm from the mass spectrometer inlet. The six holes in the rings through which $ClONO_2$ entered the flow tube were directed in the opposite direction of the buffer gas flow to obtain efficient homogenization of the reactant gas. The instrument was equipped with two discharge ion sources, which were located at a distance of 86 cm (DIS-A) and 123 cm (DIS-B) from the mass spectrometer inlet.

In the FA/BISA-II instrument, the HNO_3 glass finger inlet and the discharge ion source were located at a distance of 38.3 and 112.3 cm, respectively, from the mass spectrometer inlet. Nitrogen was used as carrier gas at typical flow rates of 2–3 STP L min^{-1} and the measurements were performed at flow tube pressures ranging from 0.80 to 1.33 mbar.

In all three instruments, the reactant ions (apart from CO_3^-, CO_4^-, and NO_2^-) were produced by attachment of electrons to electronegative gases which were added to the afterglow of an external high voltage Ar discharge ion source. The Ar flow through the discharge ion source ranged between 200 and 600 STP cm^3 min^{-1}. Small flows (of the order 10^{-3} STP cm^3 min^{-1}) of NF_3, CH_2Br_2, CCl_4, CH_3I, and SF_6 were used for the production of F^-, Br^-, Cl^-, I^-, and SF_6^-, respectively. These gases were obtained commercially (Air Products) as 1000 ppm mixtures in Ar and were used without further purification.

NO_2^- ions were formed by charge transfer of SF_6^- to NO_2 which proceeds with a rate constant of 1.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1} [8]. SF_6^- ions were produced in the afterglow of the Ar discharge ion source and NO_2 (a 1000 ppm mixture in N_2) was added upstream in sufficient amounts for the reaction of SF_6^- with NO_2 to be completed in the region upstream the reactant gas inlets.

The CO_3^- and CO_4^- ions were produced either by flowing a mixture of O_2 (600 STP cm^3 min^{-1}) and CO_2 (20 STP cm^3 min^{-1}) through the discharge ion source or by establishing a discharge in a mixture of Ar and O_2 and adding CO_2 to the discharge afterglow. To quench Ar metastables leaving the discharge ion source, a 14 STP cm^3 min^{-1} N_2 flow was added to the main flow.

Pure HNO_3 was obtained by vacuum distillation of a liquid mixture of HNO_3 (65% aqueous solution) and H_2SO_4 in a volume ratio of 1 to 3, and stored in a glass reservoir at 213 K. It was diluted with Ar in a stainless steel dilution chamber and flown through an absorption cell prior to entering the flow tube reactor. Optical absorption measurements of HNO_3 were carried out at a wavelength of 186 nm, for which the absorption cross section is 1.58×10^{-17} cm^2 $molecule^{-1}$ [16]. The optical setup has also been described in detail previously [14].

$ClONO_2$ was synthesized at LPCE from the reaction of Cl_2O with N_2O_5 by the method of Schmeisser [17]. The latter two gases were prepared according to the method of Cady [18] and Davidson et al. [19], respectively. $ClONO_2$ was stored in the dark at 190 K in a glass reservoir equipped with Teflon-coated bellow valves. During the experiment, the reservoir was kept at 208 K and He was added to the reservoir up to a pressure of about 1 bar. To perform kinetic studies, controlled amounts of the He/$ClONO_2$ mixture were introduced into the absorption cell through a mass flow meter located between the $ClONO_2$ reservoir and the cell. By adding a pure He flow, the total flow through the absorption cell was kept at a constant value (100 STP cm^3 min^{-1}). A needle valve between the absorption cell and the reactant gas inlet allowed for changing the pressure in the cell (which typically ranged between 150 and 300 mbar). In the course of a rate constant measurement the pressure in the absorption cell was kept constant. The $ClONO_2$ concentration in the cell was obtained by optical absorption measurements at a wavelength of 216 nm, for which the absorption cross section is 3.45×10^{-18} cm^2 $molecule^{-1}$ [20]. The optical set-up was similar to the one used for HNO_3 measurements, but the diameter of the absorption cell was reduced to 8 mm to obtain a much smaller residence time of $ClONO_2$ in the cell.

Despite the passivation of the surfaces and the reduction of the residence time in the absorption cell, the formation of HNO_3 could not be completely avoided. The ratio of HNO_3 to $ClONO_2$ concentrations in the flow tube was always between 3% and 5% and was measured by chemical ionization mass spectrometry using CF_3O^- precursor ions. In the FA/BISA-I apparatus, CF_3O^- ions are produced by adding a small flow of CF_3OOCF_3 to the afterglow of the Ar discharge ion source located at 86 cm from the mass spectrometer inlet. $ClONO_2$ is then introduced at a distance of 43.4 cm to separate the reaction zone from the ion relaxation zone. Both HNO_3 and $ClONO_2$ react with CF_3O^- ions producing $FHNO_3^-$ (92%–95% yield) [9,21] and $FClNO_3^-$ (97%–100% yield) [9,22], respectively, and NO_3^- in a minor channel:

$$CF_3O^- + HNO_3 \rightarrow FHNO_3^- + CF_2O \quad (1a)$$

$$\rightarrow NO_3^- + CF_3OH \quad (1b)$$

$$CF_3O^- + ClONO_2 \rightarrow FClNO_3^- + CF_2O \quad (2a)$$

$$\rightarrow NO_3^- + \text{products} \quad (2b)$$

The rate constants k_1 and k_2 for reactions (1) and (2) as determined in the present apparatuses were found to be $(2.3 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} [21] and $(1.2 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} [22], respectively, and are in perfect agreement with literature values [9]. When adding small $ClONO_2$ flows to the flow tube reactor in order to have a low conversion of CF_3O^- ions and practically no secondary reaction products, the $[HNO_3]/[ClONO_2]$ ratio is approximated by:

$$\frac{[HNO_3]}{[ClONO_2]} = \frac{k_2 \times P_1}{k_1 \times P_2} \tag{3}$$

where P_1 and P_2 are the concentrations of the reaction products of reactions (1) and (2), respectively.

For an ion X^- reacting both with $ClONO_2$ and HNO_3 (with rate constants k_a and k_b, respectively), the rate constant k_a for the reaction with $ClONO_2$ is obtained from

$$k_a = k_{\text{obs}} - k_b \times \frac{[HNO_3]}{[ClONO_2]} \tag{4}$$

where k_{obs} is the experimental rate constant which is obtained from the linear increase of $-\ln([X^-]/[X_0^-])$ versus $[ClONO_2]\tau$, where $[X_0^-]$ is the concentration of the reactant ion without addition of reactant gas and τ is the reaction time. Correction is not required for the rate constant of I^- with $ClONO_2$ because no reaction was observed between I^- and HNO_3 [23],

In all instruments the reaction time was obtained experimentally by disturbing the ion swarm and simultaneously recording the arrival of this disturbance on the ion detector. Disturbance of the ion swarm was realized by putting a negative pulse of 100 μs on the electrically insulated reactant gas inlets for the FA/BISA-I instrument or by pulsing a grid in the vicinity of the reactant gas inlet for the other two instruments.

3. Results and discussion

In Secs. 3.1–3.3, the product ions and reaction mechanisms of the individual ion/molecule reactions that were studied will be discussed. Sec. 3.4 deals with the rate constant measurements.

3.1. Reactions with HNO_3

Because of the presence of some nitric acid impurity (3%–5%) in the $ClONO_2$ reactant gas flow, the observed rate constants for the ion/molecule reactions with HNO_3 had to be corrected using formula (4). Of all halides, the reaction of F^- with HNO_3 had not been studied before and was therefore investigated in this work. Previous measurements performed in our and in other laboratories have shown that most exothermic bimolecular negative ion/molecule reactions with HNO_3 proceed at the collision limit. Since the reported rate constants of Br^- [24] and NO_2^- [23] seem to make an exception to this rule, the rate constants of these ions with HNO_3 have also been measured.

In the study of Br^- with HNO_3, both a proton transfer channel producing NO_3^- and an association channel producing $BrHNO_3^-$ have been observed, in agreement with the previous study of Davidson et al. [24]. The branching ratios of the proton transfer and the association channel at 1.06 mbar in N_2 were 86% and 14%, respectively, in our experiments.

In the study of F^- with HNO_3, NO_3^- appeared to be the major product ion. Because of the presence of $FHNO_3^-$ in the product ion spectrum, with $[FHNO_3^-]/[NO_3^-] \approx 0.20$ at low HNO_3 concentrations (at a flow tube pressure of 0.8 mbar), the possibility of a three-body channel for the reaction of F^- with HNO_3 could not be ruled out. However, since during the measurements SF_6 was introduced upstream the ion source in order to trap remaining electrons leaving the ion source, most of the $FHNO_3^-$ observed originated from the reaction of SF_6^- with HNO_3, which proceeds at the collision limit and which has a branching ratio of 92% for fluoride transfer [8]. It should be noted that the $[SF_6^-]/[F^-]$ ratio was around 0.20 at zero HNO_3 concentration in the flow tube.

NO_3^- was found to be the only primary product ion of the reaction of NO_2^- with HNO_3. Apart from NO_2^- (88% of all primary ions), the spectrum without addition of HNO_3 also contained Cl^- (7%), SF_5^- (4%)

and two small peaks at 66 and 93 u (both <1%). The appearance of Cl^- was due to a contamination of the ion source. However, since the electron affinity of Cl (3.6 eV) is much larger than that of NO_2 (2.3 eV), electron transfer from Cl^- to NO_2 did not take place and therefore did not hamper the rate constant measurement of NO_2^- with HNO_3. SF_5^- is a minor product of electron attachment to SF_6 and its reaction with NO_2 to produce NO_2^- and SF_5 is endothermic by 143 kJ mol^{-1} [25] and will therefore not disturb the rate constant measurement of NO_2^- with nitric acid as well.

3.2. Reactions of halide anions with $ClONO_2$

The reactions of Cl^-, Br^-, and I^- with $ClONO_2$ resulted in the formation of NO_3^- ions, which accounted for more than 98% of the product ions appearing in the mass spectrum when adding small flows of $ClONO_2$ to avoid secondary reactions. The other 2% were identified as Cl^- (only in the case of Br^- and $I^- + ClONO_2$), $ClONO_2^-$ and NO_2^-. Upon further addition of $ClONO_2$, the secondary reaction products $NO_3ClONO_2^-$ and $NO_3HNO_3^-$ appeared. From the evolution of all ions versus $ClONO_2$ concentration, it was clear that $NO_3ClONO_2^-$ is the association product of NO_3^- with $ClONO_2$:

$$NO_3^- + ClONO_2 + M \rightarrow NO_3ClONO_2^- + M \quad (5)$$

The formation of the $NO_3HNO_3^-$ ion resulted from the reactions of NO_3^- and $NO_3ClONO_2^-$ with HNO_3:

$$NO_3^- + HNO_3 + M \rightarrow NO_3HNO_3^- + M \quad (6)$$

$$NO_3ClONO_2^- + HNO_3 \rightarrow NO_3HNO_3^- + ClONO_2 \quad (7)$$

When studying the reaction of F^- with $ClONO_2$, NO_3^- was again the major product ion species (88%) appearing in the mass spectra with additional contribution, in this case, of ClO^- (10%) and Cl^- (2%).

In the case of F^-, Br^-, and $I^- + ClONO_2$, the sum of the intensities of the NO_3^-, $NO_3ClONO_2^-$ and $NO_3HNO_3^-$ product ions exceeded the intensity of the precursor halide without $ClONO_2$ addition to the reactor. A similar behavior, previously reported by Wincel et al. [4] for the study of $Cl^-(H_2O)_n$ with $ClONO_2$, was attributed to the presence of thermal electrons in the flowing afterglow. According to Van Doren et al. [26], these electrons attach very rapidly to $ClONO_2$ resulting mainly in NO_2^- (~50%), NO_3^- (~30%) and ClO^- (~20%). Beside these ions, Van Doren et al. also observed small amounts of Cl^- and $ClONO_2^-$ in their mass spectra. Since ClO^- was not observed in our mass spectra of Cl^-, Br^-, and I^- with $ClONO_2$, and because the $[NO_2^-]/[NO_3^-]$ ratio at small $ClONO_2$ concentrations was lower than 0.5%, the excess of product ions in the present experiment can hardly be attributed to thermal electrons in the reaction zone. Since the excess of product ions cannot be explained, the branching ratios of the two major product ion channels in the reaction of F^- with $ClONO_2$ should be considered as indicative. The Cl^- ion which appeared in the product ion spectra may result from the reaction of excited species formed in the ion source with $ClONO_2$ since its intensity increased fivefold when stopping the 14 STP cm^3 min^{-1} N_2 flow which served to quench Ar metastable atoms. The presence of N_2, however, had no effect on the NO_3^- and ClO^- ion signals, indicating again that these ions are both reaction products of F^- with $ClONO_2$. The occurrence of ClO^- as a product ion is not surprising since

$$F^- + ClONO_2 \rightarrow ClO^- + FNO_2 \quad (8)$$

was found to be slightly exothermic by 1.2 kJ mol^{-1} [25].

3.3. Reactions of SF_6^-, NO_2^-, CO_3^- and CO_4^- with $ClONO_2$

The reaction products of SF_6^- with $ClONO_2$ were found to be $FClNO_3^-$, $ClONO_2^-$, SF_5^- and $SF_5NO_3^-$. Their abundances at 0.67 mbar were 83%, 15%, 1%, and 1%, respectively. This is in good agreement with the results of Huey et al. who reported 80%, 17%, 1%, and 2%, respectively, [8]. The abundance of $FClNO_3^-$ slightly decreased with pressure in favor of SF_5^-. The contribution of the latter ion became 2.5% at 1.33 mbar.

Table 1
Rate constants for the ion/molecule reactions with HNO_3; k_{exp} are the experimental values and k_{SC} are the collision limits obtained using the formula of Su and Chesnavich [27]; the global error on the experimental rate constants obtained in this work is 30% and the precision, defined here as twice the standard deviation, equals 15%

	k_{exp}[a]		
Reaction	This work	Literature	k_{SC}[a]
$F^- + HNO_3 \rightarrow NO_3^- + HF$	**3.4 (−9)**[b]		3.0 (−9)
$Cl^- + HNO_3 \rightarrow NO_3^- + HCl$		1.6 (−9)[c] 2.8 (−9)[d] **3.1 (−9)**[e]	2.4 (−9)
$Br^- + HNO_3 \rightarrow NO_3^- + HBr$ $\rightarrow NO_3^- HBr$	**5.3 (−10)**	7.0 (−10)[f]	1.9 (−9)
$I^- + HNO_3 \rightarrow$ products		<5 (−11)[c]	1.8 (−9)
$CO_3^- + HNO_3 \rightarrow$ products		0.8 (−9)[c] **1.3 (−9)**[g] 1.2 (−9)[h]	2.1 (−9)
$CO_4^- + HNO_3 \rightarrow$ products		2.0 (−9)[g]	1.9 (−9)
$SF_6^- + HNO_3 \rightarrow NO_3^- HF + SF_5$ $\rightarrow SF_5^- + HF + NO_3$ $\rightarrow SF_5NO_3^- +$ products $\rightarrow NO_3^- +$ products		**2.0 (−9)**[i]	1.7 (−9)
$NO_2^- + HNO_3 \rightarrow NO_3^- + HNO_2$	**2.6 (−9)**	1.6 (−9)[c]	2.2 (−9)

[a] The rate constants are expressed in units of cm^3 $molecule^{-1}$ s^{-1}; 1.6 (−9) means 1.6×10^{-9}.

[b] The values in bold have been used to correct the rate constants for reaction with $ClONO_2$ (rate constant k_b in formula II).

[c] See [23].

[d] See [31].

[e] See [14].

[f] See [24].

[g] See [32].

[h] See [13].

[i] See [8].

The reaction of NO_2^- with $ClONO_2$ was carried out at higher pressures (2.7, 4, and 5.3 mbar) to slow down the ion velocity in the flow tube to make sure that the reaction of SF_6^- with NO_2 went to completion before the NO_2^- product ions reached the reaction zone. NO_3^- and $ClONO_2^-$ were observed as reaction products with respective abundances at 2 mbar of 94% and 6%. We did not observe $NO_2ClONO_2^-$ which was observed as a minor reaction product (<1%) of $NO_2^- + ClONO_2$ at 0.57 mbar in He by Van Doren et al. [3].

When studying the reactions of CO_3^- and CO_4^- with $ClONO_2$, the $[CO_4^-]/[CO_3^-]$ ratio could be varied from 3% to 40% by changing the CO_2 flow which was added to the afterglow of the Ar+O_2 discharge ion source. The major product ion of the reaction of CO_3^- with $ClONO_2$ was clearly NO_3^- (>98%). There was also a small contribution of $ClONO_2^-$ (<2%) which could be attributed to the reaction of CO_4^- since the abundance of $ClONO_2^-$ increased with increasing initial $[CO_4^-]/[CO_3^-]$ ratio. From an analysis of the evolution of the source and product ions as a function of $ClONO_2$ concentration, we were able to derive that both NO_3^- and $ClONO_2^-$ are product ions of the reaction of CO_4^- with $ClONO_2$ with a branching ratio for $ClONO_2^-$ formation of about 50%.

3.4. Rate constants

3.4.1. Rate constants for the reactions with HNO_3

The rate constants for the ion/molecule reactions with HNO_3 which have been measured in this work are listed in Table 1, together with the available literature data for the reactions studied and for those which are required to correct the rate constants of the reactions with $ClONO_2$, due to the presence of HNO_3 impurities. The collision rate constants calculated using the method of Su and Chesnavich based on trajectory calculations [27] are also given in Table 1. For this calculation, a value of 4.5×10^{-30} m^3 was used for the polarizability of HNO_3 [8] and a value of 2.17 D for its dipole moment [28].

For the rate constant of F^- with HNO_3, a pressure-independent value of $(3.4 \pm 1.0) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} was inferred, which is in good agreement with the collision rate constant of 3.0×10^{-9} cm^3 molecule^{-1} s^{-1} as calculated using the method of Su and Chesnavich.

The rate constant of Br^- with nitric acid was found to be $(5.3 \pm 1.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and showed no significant pressure dependence. This value is about 25% lower than the value previously obtained by Davidson et al. [24], which is $(7.0 \pm 2.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, but in agreement with the latter considering the experimental errors.

The rate constant of NO_2^- with HNO_3 was measured to be $(2.6 \pm 0.8) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} and was pressure independent. This value is about 1.6 times higher than the value previously reported by Fehsenfeld et al. [23]. From the exponential decay of the Cl^- impurity ion, a rate constant of 2.8×10^{-9} cm^3 molecule^{-1} s^{-1} was obtained for the rate constant of Cl^- with HNO_3 (average of only two measurements), which is in good agreement with previously reported values [14,31]. Further, the ratio of the rate constants of Cl^- and NO_2^- with HNO_3 as derived from our results is found to be 1.1 and is identical to what is expected if both reactions occur at the collision limit.

Taking into account the errors on the pressure and mass flow measurements, the error on the absorption measurements and on the experimentally determined reaction time, the global accuracy of the rate constants of the ion/molecule reactions with HNO_3 as determined in this work is estimated to be 30%. The precision of the measurements, defined here as twice the standard deviation, is typically 15% (or less for NO_2^-).

3.4.2. Rate constants for the reactions with $ClONO_2$

The rate constants of the ion/molecule reactions obtained in this work are shown in Table 2, together with previous literature values. The global error on the rate constants is also 30% and the precision ranges from 10% to 15%. Also shown in Table 2 are the collision rate constants as calculated using the theory of Su and Chesnavich [27]. To calculate the collision rate constants, a value of 0.77 D was taken into account for the dipole moment of $ClONO_2$ [28] and a value of 8.61×10^{-30} m^3 was used for its polarizability [5].

In Fig. 1, the rate constant of I^- with $ClONO_2$ is shown versus flow tube pressures as obtained using the FA/LPCE and the FA/BISA-I apparatus. From Table 2, it can be noticed that the rate constant exhibits a very slight negative temperature dependence resulting in a value at 223 K which is around 15% higher than the room temperature value.

Apart from the bimolecular reactions listed in Table 2, the apparent second-order clustering rate constant of reaction (5), $NO_3^- + ClONO_2 + M \rightarrow NO_3ClONO_2^- + M$, has also been measured. This resulted in a value for k_3 of $(2.2 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This value was obtained from the decrease of the NO_3^- product ion as a function of $ClONO_2$ (at high $ClONO_2$ concentrations) during the studies of the reactions of Br^- and NO_2^- with $ClONO_2$. Measurements were performed at 2.7 and 4 mbar in a buffer gas mixture of 12% Ar in N_2, and at 4 and 5.3 mbar in a mixture of 10% Ar in He. Since Ar was required for an efficient operation of the ion source producing Br^- and NO_2^- ions, the presence of Ar in the buffer gas flow could not be avoided.

To correct for the presence of HNO_3 a value of 2.6×10^{-10} cm^3 molecule^{-1} s^{-1} was taken into account for the apparent second-order rate constant of reaction (6). This value corresponds to the high-pressure limit obtained by Viggiano et al. [29] in He. No pressure dependence was noticed, in the pressure range used, for the observed apparent second-order rate constant of reaction (5), meaning that the high-pressure limit was already obtained at 2.7 mbar. Van Doren et al. [3] reported a room temperature value of 3.0×10^{-11} cm^3 molecule^{-1} s^{-1} for k_3 at 0.57 mbar in a He buffer gas. Although our value of k_3 is much higher, the two values are not necessarily in contradiction given the difference in pressure and the fact

Table 2
Rate constants for the ion/molecule reactions with $ClONO_2$; k_{exp} are the experimental values and k_{SC} are the collision limits obtained using the formula of Su and Chesnavich [27]; the global error on the experimental rate constants obtained in this work is 30% and the precision, defined here as twice the standard deviation, equals 10%–15%

	k_{exp} [a]				
Reaction	This work		Literature	k_{SC} [a]	
$F^- + ClONO_2 \rightarrow NO_3^- + ClF$	2.2 (−9)			2.0 (−9)	
$\rightarrow ClO^- + FNO_2$					
$Cl^- + ClONO_2 \rightarrow NO_3^- + Cl_2$	1.5 (−9)		1.16 (−9)[b] 9.2 (−10)[c]	1.6 (−9)	
$Br^- + ClONO_2 \rightarrow NO_3^- + BrCl$	1.3 (−9)			1.2 (−9)	
$I^- + ClONO_2 \rightarrow NO_3^- +$ products	1.3 (−9)	223 K	1.1 (−9)[d]	1.1 (−9)	223 K
	1.2 (−9)	271 K		1.1 (−9)	271 K
	1.1 (−9)	298 K		1.1 (−9)	298 K
	1.1 (−9)	323 K		1.1 (−9)	323 K
$CO_3^- + ClONO_2 \rightarrow NO_3^- +$ products	1.4 (−9)		2.1 (−9)[e]	1.3 (−9)	
$CO_4^- + ClONO_2 \rightarrow NO_3^- +$ products	1.4 (−9)			1.2 (−9)	
$\rightarrow ClONO_2^- +$ products					
$SF_6^- + ClONO_2 \rightarrow NO_3^-ClF + SF_5$	1.1 (−9)		1.1 (−9)[d]	1.0 (−9)	
$\rightarrow ClONO_2^- + SF_6$					
$\rightarrow SF_5NO_3^- + ClF$					
$\rightarrow SF_5^- +$ products					
$NO_2^- + ClONO_2 \rightarrow NO_3^- + ClONO$	1.5 (−9)		1.5 (−9)[f] 1.3 (−9)[f,g] 1.0 (−9)[b]	1.4 (−9)	
$\rightarrow ClONO_2^- + NO_2$					

[a] The rate constants are expressed in units of cm^3 $molecule^{-1}$ s^{-1}.
[b] See [4].
[c] See [5].
[d] See [8].
[e] See [7].
[f] See [3].
[g] Taking into account the value for the rate constant of $NO_2^- + HNO_3$ obtained in this work.

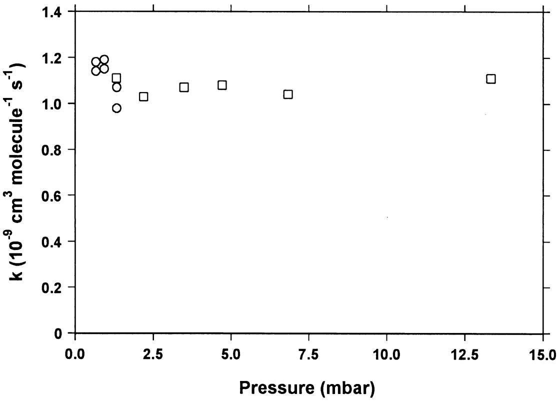

Fig. 1. Rate constant of I^- with $ClONO_2$ vs. flow tube pressure. The squares represent data obtained with the FA/LPCE instrument. The circles represent data obtained with the FA/BISA-I instrument.

that stabilization in He is 2–3 times less efficient than in Ar and N_2.

From Table 2 and Fig. 2 it is clear that all the reaction rate constants of anions with $ClONO_2$, which are reported in this work, follow the same trend versus ion mass as the collision rate constant k_{SC} calculated with the formula of Su and Chesnavich. In the case of $ClONO_2$ and at room temperature, k_{SC} is a factor of 1.17 larger than the Langevin rate constant k_L. In order to show that the studied ion/molecule reactions proceed at the collision limit, it is therefore even more illustrative to plot the experimental rate constants k_{exp} as a function of the inverse square of the reduced mass of the ion/molecule system as shown in Fig. 3. The linear relationship between k_{exp} and the inverse square of the reduced mass is in agreement with the Langevin formula [30]:

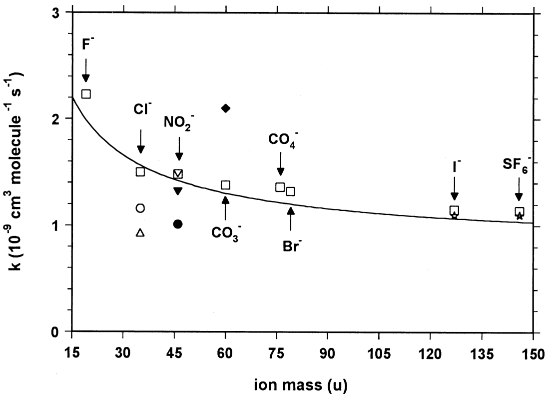

Fig. 2. Experimental reaction rate constants of negative ions with $ClONO_2$ vs. ion mass. Open symbols: measurements at room temperature; closed symbols: measurements at low temperature. Open squares: present results; open stars: Huey et al. [8]; open triangles up: Haas et al. [5]; open circles: Wincel et al. [4]; closed circles: Wincel et al. [4] (170 and 200 K); open triangles down: Van Doren et al. [3]; closed triangles down: Van Doren et al. [3] (corrected taking into account our rate constant value for $NO_2^- + ClONO_2$); closed diamonds: Viggiano et al. [7] (232 K). The line represents the collision rate constant as calculated using the parameterized theory of Su and Chesnavich.

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}} \tag{9}$$

where q denotes the charge of the ion, α is the polarizability and μ is the reduced mass of the ion/molecule system.

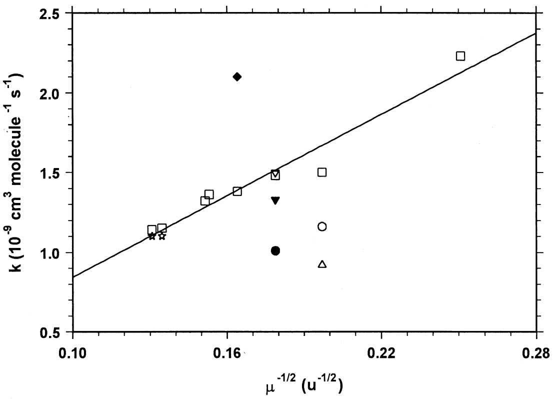

Fig. 3. Plot showing the linear dependence of our experimentally determined rate constants (open squares) versus the inverse square of the reduced mass (see text). Also shown are literature data with the same symbols as in Fig. 2.

The difference between the experimentally determined rate constants and the linear fit through these data is less than 5%, except for the rate constant of $Cl^- + ClONO_2$ (10% deviation).

In general, there is a good agreement between our values and the values previously reported in the literature, given the global uncertainty of 30%–40% on all measurements. The rate constant of $CO_3^- + ClONO_2$ as obtained by Viggiano et al. [7] is about 50% higher than our value. Viggiano et al. carried out their measurements at 232 K. However, this cannot explain the difference since the collision rate constant k_{SC} should not decrease by more than 5% from 232 to 298 K. The rate constants of Cl^- with $ClONO_2$ as measured by Haas et al. [5] and Wincel et al. [4] and of NO_2^- with $ClONO_2$ as obtained by Wincel et al. [4] are also somewhat low with respect to our values. Van Doren et al. reported a rate constant of 1.5×10^{-9} cm^3 molecule^{-1} s^{-1} for the reaction of $NO_2^- + ClONO_2$ [3]. This value was obtained by correcting the observed rate constant for the presence of HNO_3 using formula (3) from [3]. By taking into account our value for the rate constant of $NO_2^- + HNO_3$ which is 1.6 times larger than the one Van Doren et al. used in their calculation, a value of 1.3×10^{-9} cm^3 molecule^{-1} s^{-1} is obtained for the rate constant of NO_2^- with $ClONO_2$.

There is a perfect agreement between our rate constants for I^- and $SF_6^- + ClONO_2$ and the ones reported by Huey et al. [8].

4. Conclusion

The double objective of this study was to extend the kinetic database for ion/molecule reactions with $ClONO_2$ and to understand the application of some of them for the detection of atmospheric species by the CIMS technique.

Eight bimolecular negative ion/molecule reactions with $ClONO_2$ have been studied, of which three (F^-, Br^-, and $CO_4^- + ClONO_2$) being reported for the first time. By considering the linear trend of the experimentally obtained rate constants as a function of the inverse square of the reduced mass, it appears that all reactions (apart perhaps from the reaction of Cl^- with $ClONO_2$) proceed at the collision limit. In order to correct the rate constants for HNO_3 impurities in the $ClONO_2$ flow, three ion/molecule reactions with HNO_3 (Br^-, NO_2^-, and $F^- + HNO_3$) have been studied of which the reaction of F^- with HNO_3, as far as we know, has been reported for the first time.

As mentioned in Sec. 1, the total stratospheric $N_2O_5 + ClONO_2$ mixing ratios that were inferred from the data obtained with a balloon-borne chemical ionization mass spectrometer were too high (by a factor of 3) when taking into account the literature values for the rate constants of I^- with $ClONO_2$ and N_2O_5.

In order to find out the reason for this discrepancy, we found it worthwhile to revisit the ion/molecule chemistry involved under more realistic conditions of pressure and temperature. An important reaction in this respect, which is reported in this paper, is the reaction of I^- with $ClONO_2$. It has been found that the rate constant of this reaction is constant over the pressure and temperature range investigated here. Therefore, the present results show that the discrepancy cannot be explained by a pressure or temperature dependence for the rate constant of the $I^- + ClONO_2$ reaction. The analysis of the flight data obtained with the I^- ion source shows that, apart from NO_3^- ions (the product ions of I^- with N_2O_5 and $ClONO_2$), product ions of reactions of I^- with other stratospheric constituents (e.g. O_3) also appear in the mass spectra. These product ions (e.g. IO_3^-) may undergo secondary reactions with stratospheric HNO_3 (which is more abundant than N_2O_5 and $ClONO_2$ below 30 km altitude), also resulting in NO_3^- ions [33]. This additional NO_3^- producing channel might partially explain the above discrepancy. Laboratory studies are going on in order to quantify the effect of these interfering reactions on the derivation of total $ClONO_2 + N_2O_5$ mixing ratios from the flight data.

Acknowledgements

The authors would like to thank the Commission of the European Communities (contract ENV4-CT95-0042) as well as the “Conseil Régional du Centre” (F) for financial support.

References

[1] Scientific Assesment of Ozone Depletion, WMO Report No. 44, 1998.
[2] J.M. Van Doren, A.A. Viggiano, R.A. Morris, J. Am. Chem. Soc. 116 (1994) 6957.
[3] J.M. Van Doren, A.A. Viggiano, R.A. Morris, T.M. Miller, J. Chem. Phys. 103 (1995) 10806.
[4] H. Wincel, E. Mereand, A.W. Castleman Jr., J. Phys. Chem. A 101 (1997) 8248.
[5] B.-M. Haas, K.C. Crellin, K.T. Kuwata, M. Okumura, J. Phys. Chem. 98 (1994) 6740.
[6] A.M. Mebel, K. Morokuma, J. Phys. Chem. 100 (1996) 2985.
[7] A.A. Viggiano, R.A. Morris, J.M. Van Doren, J. Geophys. Chem. 99 (1994) 8221.
[8] L.G. Huey, D.R. Hanson, C.J. Howard, J. Phys. Chem. 99 (1995) 5001.
[9] L.G. Huey, P.W. Villalta, E.J. Dunlea, D.R. Hanson, C.J. Howard, J. Phys. Chem. 100 (1996) 190.
[10] C. Amelynck, E. Arijs, E. Neefs, D. Nevejans, W. Vanderpoorten, A. Barassin, C. Guimbaud, D. Labonnette, H.-P. Fink, E. Kopp, H. Reinhard, in Proceedings of the 13th ESA Symposium on European Rocket and Balloon Programmes and Related research, Öland, Sweden, 26–29 May 1997, ESA SP-397 (September 1997), pp. 193–196.
[11] B. Sen, G.C. Toon, G.B. Osterman, J.-F. Blavier, J.J. Margitan, R.J. Salawitch, G.K. Yue, J. Geophys. Res. 103 (1998) 3771.
[12] R. Zander, E. Mahieu, M.R. Gunson, M.C. Abrams, A.Y. Chang, M. Abbas, C. Aellig, A. Engel, A. Goldman, F.W. Irion, N. Kämpfer, H. A. Michelsen, M.J. Newchurch, C.P. Rinsland, R.J. Salawitch, G.P. Stiller, G.C. Toon, Geophys. Res. Lett. 23 (1996) 2357.
[13] C. Guimbaud, D. Labonnette, V. Catoire, R. Thomas, Int. J. Mass Spectrom. Ion Processes 178 (1998) 161.
[14] C. Amelynck, E. Arijs, N. Schoon, A.-M. Van Bavel, Int. J. Mass Spectrom. Ion Processes 181 (1998) 113.
[15] C. Amelynck, A.-M. Van Bavel, N. Schoon, E. Arijs, Int. J. Mass Spectrom. 202 (2000) 207.
[16] J. Burkholder, R.K. Talukdar, A.R. Ravishankara, S. Solomon, J. Geophys. Res. 98 (1993) 22937.
[17] M. Schmeisser, Inorg. Syn. 9 (1967) 127.
[18] G.H. Cady, Inorg. Syn. 5 (1957) 156.
[19] J.A. Davidson, A.A. Viggiano, C.J. Howard, I. Dotan, F.C. Fehsenfeld, D.L. Albritton, E.E. Ferguson, J. Chem. Phys. 68 (1978) 2085.
[20] J.B. Burkholder, R.K. Talukdar, A.R. Ravishankara, Geophys. Res. Lett. 21 (1994) 585.
[21] C. Amelynck, N. Schoon, E. Arijs, Int. J. Mass Spectrom. 203 (2000) 165.
[22] C. Stépien, V. Catoire, C. Amelynck, D. Labonnette, N. Schoon, G. Poulet and E. Arijs, unpublished results.

[23] F.C. Fehsenfeld, C.J. Howard, A.L. Schmeltekopf, J. Chem. Phys. 63 (1975) 2835.
[24] J.A. Davidson, F.C. Fehsenfeld, C.J. Howard, Int. J. Chem. Kinet. 9 (1977) 17.
[25] By taking into account the heats of formation of the reactantsand products as reported in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, W.G. Mallard, P.J. Linstrom (Eds.),National Institute of Standards and Technology, Gaithersburg MD, 2000 (http://webbook.nist-.gov).
[26] J.M. Van Doren, J. McClellan, T.M. Miller, J.F. Paulson, A.A. Viggiano, J. Chem. Phys. 105 (1996) 104.
[27] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[28] CRC Handbook of Chemistry and Physics, D.R. Lide (Ed.), CRC Press, Boca Raton, FL, 1999.
[29] A.A. Viggiano, F. Dale, J.F. Paulson, J. Geophys. Res. 90 (1985) 7977.
[30] T. Su, M. T. Bowers, in Gas Phase Ion Chemistry, Vol. 1, M. T. Bowers (Ed.), Academic, new York, 1979, Chapter 3.
[31] L.G. Huey, Int. J. Mass Spectrom. Ion Processes 153 (1996) 145.
[32] O. Möhler, F. Arnold, J. Atmos. Chem. 13 (1991) 33.
[33] R.S. MacTaylor, J.J. Gilligan, A.W. Castleman Jr., Int. J. Mass Spectrom. 179/180 (1998) 327.