Reactions of CF₃O⁻ core ions with ClONO₂ and H₂O

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The reactions of CF_3O^- , CF_3OHF^- and $CF_3OH_2O^-$ with $CIONO_2$ have been studied in the temperature range 225–325 K. The reactions of CF_3O^- and $CF_3OH_2O^-$ with $CIONO_2$ proceed at the collision rate whereas the reaction of CF_3OHF^- with $CIONO_2$ is slower. No significant temperature dependence of the rate constant has been found for each reaction. The mechanistic study has shown that the reaction of CF_3O^- with $CIONO_2$ proceeds by fluoride transfer and the product of the reaction between $CF_3OH_2O^-$ and $CIONO_2$ is the cluster ion $CF_3OCIONO_2^-$. The equilibrium reaction of CF_3O^- with H_2O has been also studied between 262 and 295 K. Values of -63.2 ± 6.7 kJ mol⁻¹ and -114.6 ± 23.9 J mol⁻¹ K⁻¹ were derived for the standard reaction enthalpy and entropy, respectively.

Introduction

Chlorine nitrate (ClONO₂) is an important species in controlling stratospheric ozone destruction by acting as a temporary reservoir for active chlorine. $ClONO_2$ is formed during nighttime *via* the reaction of nitrogen dioxide (NO₂) and chlorine monoxide (ClO) and is photolysed during daytime.¹ In the presence of polar stratospheric clouds, heterogeneous chemistry converts the major inactive forms of chlorine (ClONO₂, HCl) into active ones leading to the polar ozone loss.^{2,3}

Chemical ionization mass spectrometry (CIMS) is currently used as an in situ method to measure concentrations of atmospheric trace gases.⁴⁻⁹ In the CIMS method, specific reactant ions are injected into a flow tube coupled to a mass spectrometer where they react with trace constituents to form specific product ions.¹⁰ In a joint project of the "Belgian Institute for Space Aeronomy" (BISA), the "Laboratoire de Physique et Chimie de l'Environnement" (LPCE), and the "Physikalisches Institut of the University of Bern" (PIUB), a new balloonborne CIMS apparatus has been developed. Its goal was the simultaneous measurement of stratospheric HCl, HNO3, $ClONO_2$ and N_2O_5 concentrations by using several ion sources. Recently, the instrument has been equipped with an ion source generating CF_3O^- since this ion appeared to be a good candidate for the detection of stratospheric HCl, HNO₃ and $ClONO_2$. In the laboratory, the CF_3O^- ion has been shown to react with HCl, HNO₃ and ClONO₂, mainly by fluoride transfer at room temperature and low pressure, leading to the specific ions FHCl⁻, FHNO₃⁻ and FClONO₂⁻, respectively.¹¹

In addition to CF_3O^- ions, unexpectedly abundant amounts of CF_3OHF^- and $CF_3OH_2O^-$ source ions were observed in the flow reactor during two recent balloon flights (June 1997 and June 1999).¹² The presence of other ions, CF_3OHCl^- , $CF_3OHNO_3^-$ and $CF_3OCIONO_2^-$, in the flight spectra, led to the assumptions that CF_3OHF^- and $CF_3OH_2O^-$ react with HCl, HNO₃ and CIONO₂, respectively, by ligand switching. These assumptions required experimental evidence from laboratory studies. The reactions of CF_3O^- core ions with HCl and HNO₃ have been previously studied.^{13,14} In the present paper, the study of the reactions of CF_3O^- , CF_3OHF^- and $CF_3OH_2O^-$ with ClONO₂ has been undertaken under conditions close to those of the stratosphere, *i.e.* in the temperature range 225–325 K and pressure range 0.4–16 Torr. The equilibrium reaction of CF_3O^- with H₂O, previously studied by Amelynck *et al.* at room temperature,¹³ has been also investigated in the temperature range 262–295 K in order to estimate the equilibrium constant at stratospheric temperature, which is needed for the interpretation of the CIMS flight mass spectra.

Experimental

Experiments were performed in two flowing-afterglow apparatuses located at LPCE and at BISA. Both instruments have been described in detail elsewhere¹³⁻¹⁵ and are only briefly presented here.

At LPCE, the ion-molecule reactions were studied in a 3.5 cm id stainless steel flow tube. The flow of the carrier gas (N₂, purity >99.9999%) was in the range 1.5-30 STP L min⁻¹ (STP = 273 K, 760 Torr), resulting in flow tube pressures between 0.8 and 16 Torr. The ions were sampled through three differentially pumped chambers and introduced into the quadrupole mass analyzer, where they were selected according to mass-to-charge ratio and subsequently detected by a secondary electron multiplier (SEM).

The reaction of CF_3O^- with $CIONO_2$ was studied at 225, 274, 295 and 325 K; the reactions of $CF_3OH_2O^-$ and CF_3OHF^- with $CIONO_2$ were studied at 225 and 295 K, and the reaction of CF_3O^- with H_2O was studied at 262, 276, 285 and 295 K. To obtain a temperature of 325 K, the outer walls of the tube were resistively heated. The studies at 262, 274 and 276 K were performed by cooling the tube with cold accumulator bags, and at 225 K by wrapping the tube with CO_2 pellets in the pressure range 1.0–1.7 Torr. All gases were flowed through a precooling zone of 60 cm, so that the temperature was measured by a Pt resistance probe located at the center of the flow tube. The CF_3O^- ions were produced in a Published on 13 August 2001. Downloaded by Brown University on 22/10/2014 13:16:02.

high-pressure ion source by dissociative attachment of electrons to CF₃OOCF₃, as described by Amelynck et al.^{13,14} Electrons were produced by a 500 V discharge in an argon flow (purity >99.9999%, 150 STP cm³ min⁻¹). A small flow (2 STP cm³ min⁻¹) of a CF₃OOCF₃ mixture (2500 ppm in Ar) was added downstream of the discharge zone. The $CF_2O^$ ions were introduced into the flow tube through a capillary tube (6 mm id) located 108.6 cm upstream of the ion analysis zone. Above 273 K, only CF₃O⁻ and CF₃OHF⁻ ions were observed in the mass spectra, with CF_3O^- as the major ion. The presence of CF₃OHF⁻ was attributed to the reaction of CF_3O^- with trace impurities in the $CF_3OOCF_3 + Ar$ mixture. The ratio of CF₃OHF⁻ to CF₃O⁻ ion count rates in the mass spectra increased with the flow tube pressure and ranged from 0.3 to 10% between 0.8 and 16 Torr. At 225 K, $CF_3OH_2O^-$ and $CF_3O(H_2O)_2^-$ were formed from the reaction between CF_3O^- and H_2O , which is much faster at 225 K than at room temperature (see below). The presence of H_2O was attributed to the presence of impurities in the buffer gas $(H_2O < 0.5 \text{ ppm})$, to desorption of water from the flow tube walls or/and to possible leaks at low temperature (due to contraction of the Teflon ring used as a seal between the ion source and the reactor). This enabled a study of the reaction of CF₃OH₂O⁻ with ClONO₂ at low temperature.

The neutral reactant ClONO2 was introduced by a finger inlet located 46 cm upstream of the ion source in order to get a homogeneous mixture of ClONO₂ and the carrier gas before introduction of the reactant ion. Thus, the distance between the ion source and the analysis zone (108.6 cm) was taken as the reaction distance. Electron attachment to ClONO₂ has been previously studied by Van Doren et al.,16 who found that this process led to the production of NO_2^- (~50%), NO_3^- (~30%), and CIO^- (~20%) with a rate constant of $(1.1 \pm 0.5) \times 10^{-7}$ cm³ molecule⁻¹ s⁻¹. During the study of the reaction of CF₃O⁻ with CIONO₂, the NO₂⁻ and CIO⁻ ions were never observed, showing that the presence of electrons in the flow tube was negligible. The ion residence time in the flow tube was typically 18 ms. The latter was measured by pulsing a biased grid and by synchronously recording the arrival time of the ion swarm on the SEM detector.¹ The ClONO₂ concentration range in the flow tube was typically $(0.2-2.0) \times 10^{11}$ molecule cm⁻³

ClONO₂ was synthesized at LPCE, using the method of Schmeisser¹⁸ based on the reaction of Cl₂O with N₂O₅. Cl₂O and N₂O₅ were synthesized by the methods of Cady¹⁹ and Davidson,²⁰ respectively. During each step of the synthesis, special care was taken to minimize water traces and hydrolysis reactions that would produce HOCl and HNO₃. Cl₂O was obtained by condensing Cl₂ on freshly crystallized and dried mercuric oxide (HgO) in excess at 77 K. The trap was slowly warmed up to 233 K. After 3 days at this temperature, Cl₂O was separated from HgO by distillation. N₂O₅ was synthesized by adding a flow of NO (purity >99%) to a flow of O_3 (diluted in O_2) at atmospheric pressure. NO₂ and NO₃, resulting from the oxidation of NO by O3, reacted to form N_2O_5 which was collected in a trap cooled at 195 K. ClONO₂ was synthesized by adding Cl₂O to an excess of N₂O₅ in a 77 K trap. The trap was slowly warmed up to 233 K and the reaction was complete after 3 days. ClONO₂ was purified by trap-to-trap distillations to remove traces of N₂O₅, Cl₂O and Cl₂. ClONO₂ purity was checked by measuring its vapor pressure $P_{\rm vap}$ in the temperature range 186 to 216 K. The plot of $\ln P_{\rm vap} = f(1/T)$ yielded the values of the vaporization enthalpy $\Delta_{vap}H^{\circ} = 29.4 \text{ kJ mol}^{-1}$, and of the vaporization entropy, $\Delta_{vap}S^{\circ} = 155.4 \text{ J mol}^{-1} \text{ K}^{-1}$ in the above temperature range. These values are in very good agreement with literature values: $\Delta_{vap}H^{\circ} = 29.3 \text{ kJ mol}^{-1} \text{ and } \Delta_{vap}S^{\circ} = 153.7 \text{ J mol}^{-1}$ K^{-1} in the temperature range $185-238 K^{21} K^{21}$ and $\Delta_{vap}H^{\circ} =$ 28.8 kJ mol⁻¹ and $\Delta_{vap}S^{\circ} = 152.7$ J mol⁻¹ K⁻¹ in the temperature range 193–299 K.²² This pure ClONO₂ was then

stored in a bubbler at 213 K in the dark and was cooled to 194 K for the experiments.

At BISA, the reactions of CF_2O^- and $CF_2OH_2O^-$ with ClONO₂ were studied in a 6.5 cm id flow tube at room temperature and at pressures ranging from 0.4 to 1 Torr. A flow of He (purity >99.9999%) of 4.5 STP L min⁻¹ was used as a carrier gas and pumped by a Roots blower. ClONO₂ was introduced through two electrically insulated fixed ring inlets located at 43.4 and 77.8 cm from the mass spectrometer inlet. CF_3O^- core ions were produced in the same way as at LPCE. To study the reaction of $CF_3OH_2O^-$ with $ClONO_2$ at room temperature, the $CF_3OH_2O^-$ ions were generated by the three-body reaction of CF_3O^- with residual water in a cooled (195 K) high-pressure section of the flow tube upstream of the reaction zone.^{13,14} A large fraction of the $CF_3OH_2O^-$ ions exiting the cooled high pressure zone dissociated into CF₃O⁻ and H₂O in the section of the flow tube at room temperature. The formation of CF₃OH₂O⁻ at low pressure in this section was negligible, as verified by using a second CF_3O^- ion source located upstream of the reaction zone. The $[CF_3OH_2O^-]/[CF_3O^-]$ ratio at the end of the flow tube was found to be around 5%.

Ions were sampled through an orifice of 0.2 mm diameter in a first chamber pumped by a 1600 L s⁻¹ turbo-molecular pump. They were guided by an octopole from the gas expansion zone, behind the inlet orifice, to the mass filter located in a second, separately pumped, chamber. To minimize collisioninduced dissociation of ions in the gas expansion zone, the difference in bias voltage between the inlet plate and the octopole rods was kept at a value of only 0.5 V. After analysis by a quadrupole mass filter, ions were detected by a SEM.

The determination of the absolute rate constants for the reactions involving ClONO₂ required the measurement of the ClONO₂ concentration in the flow tube. In both apparatuses, this concentration was measured by UV absorption spectrometry in a cell connected to the flow tube. The UV absorption system consisted of a 50 cm long \times 0.7 cm id absorption cell fitted with Suprasil windows and connected to the flow tube by a Teflon tube. A diluted mixture of ClONO₂ and argon (purity >99.9999%) was flowed at 2–15 STP cm³ min⁻¹ with an additional Ar flow to obtain a constant total flow of 100 STP $\rm cm^3 \ min^{-1}$ through the absorption cell before being introduced into the main reactor. In order to check the purity of the chlorine nitrate introduced in the flowing afterglow apparatus, the reaction of SF_6^- with ClONO₂ was used. SF_6^- is known to react with ClONO₂ and with all possible impurities in ClONO₂ with a comparable rate constant.^{23,24} SF_6^- was produced in the same ion source as CF_3O^- , by electron attachment to SF_6 (purity > 99.9%) flowing at 2–5 STP cm³ min⁻¹. ClONO₂⁻ and mainly FClONO₂⁻ were observed as products of the reaction of \tilde{SF}_6^- with \tilde{CIONO}_2 , in agreement with previous studies.^{23,24} However, FHNO₃⁻ produced by the reaction of SF_6^- with HNO₃ was also observed in the mass spectra. This HNO3 was assumed to result from the $ClONO_2$ hydrolysis by the trace water adsorbed on the walls of the tube between the ClONO₂ bubbler and the reactor. This was confirmed by doing experiments in which no FHNO3⁻ was observed when ClONO2 was introduced directly into the flow tube without passing through the UV-absorption cell. The residence time of ClONO₂ in the UV cell was reduced by minimizing its volume and by increasing the total flow in the cell. By heating and passivating the feedlines, the HNO₃ concentration could be significantly decreased, but not totally reduced in the system. Using the rate constants of the reaction of SF_6^- with ClONO₂ and HNO₃²³ and the ratio of the products of these reactions, the [HNO₃]/[ClONO₂] ratio was evaluated to be 2 to 10% in the flow tube.

The ClONO₂ absorption was measured at 216 nm, where the absorption cross section σ is maximum ($\sigma = 3.45 \times 10^{-18}$

 cm^2 molecule⁻¹).²⁵ The concentration of ClONO₂ in the flow tube, was determined using the following equation:

$$[\text{ClONO}_2] = \frac{\ln\left(\frac{I^0}{I}\right)Q_{\text{AC}}P_{\text{FT}}T_{\text{AC}}}{l\sigma Q_{\text{FT}}P_{\text{AC}}T_{\text{FT}}}$$
(I)

where l is the length of the absorption cell (cm), Q is the total standard flow, P the pressure, T the temperature (AC and FT denoting the absorption cell and the flow tube, respectively), and I and I° the measured light intensities with and without ClONO₂ present in the absorption cell, respectively.

The rate constants of the reactions of the ions with $CIONO_2$ were inferred from the slopes of the logarithmic decays of the reactant ion count rates as a function of the product of the $CIONO_2$ concentration and the reaction time, given that $CIONO_2$ was always in large excess with respect to the ions used. Overall uncertainties for the rate constants were estimated to be 30%, including two standard deviations, the uncertainty in the reaction time measurement and the uncertainty in the determination of $CIONO_2$ concentrations.

The reaction of CF_3O^- with H_2O was studied at LPCE. Water vapor was introduced into the flow tube by two finger inlets located 56 and 76 cm upstream of the sampling cone. H₂O concentrations in the flow tube were in the range 1×10^{12} -1 × 10¹⁴ molecule cm⁻³. Three methods were used to introduce controlled flows of H_2O into the reactor. In the first method, a mass flowmeter controlled the flow of mixtures of H_2O vapor and N_2 (purity >99.9999%) prepared in a bulb. The second method consisted in determining the rate of pressure drop in the bulb containing known mixtures of H₂O vapor and nitrogen that were introduced into the flow tube. In the third method, a flow of nitrogen, controlled by a flowmeter, was sent through a bubbler containing distilled water. This bubbler was designed to avoid H₂O droplets being carried by N₂ with H₂O vapor, which would lead to an underestimation of the H₂O concentration in the flow tube. In this method, the flow was assumed to be saturated with water vapor. The three methods agreed within experimental error.

Results and discussion

1. Reaction of CF_3O^- with $CIONO_2$

1.1. Mechanism. At room temperature, the reaction of CF_3O^- with $CIONO_2$ was studied at pressures ranging from 0.4 to 16 Torr. The major product ion observed in the mass spectra was $FCIONO_2^-$, obtained by fluoride transfer, as previously reported by Huey *et al*:¹¹

$$CF_3O^- + CIONO_2 \rightarrow FCIONO_2^- + CF_2O$$
 (1)

 NO_3^- (~5% of the product ions), $FHNO_3^-$ (4–15%) and traces of $CF_3OCIONO_2^-$ (<1%) were also observed. $CF_3OCIONO_2^-$ could not be unambiguously assigned as formed in a minor channel of reaction (1) since CF_3OHF^- , which was also present in the flow tube, may lead to the formation of $CF_3OCIONO_2^-$ by ligand switching. For NO_3^- , Huey *et al.*¹¹ found that this ion was not pro-

For NO₃⁻, Huey *et al.*¹¹ found that this ion was not produced by the reaction of CF₃O⁻ with ClONO₂, but was the main product of the reaction of CF₃O⁻ with N₂O₅. In the present experiments, the temperature of the ClONO₂-containing bubbler was too low to allow for the presence of N₂O₅ in the flow tube. Moreover, the ClONO₂ concentration was determined at three wavelengths (200, 216, 230 nm), for which the ClONO₂ to N₂O₅ cross-section ratios vary from 0.31 to 2.10. At all wavelengths, the same value of ClONO₂ concentration was inferred, indicating that N₂O₅ could only be present at insignificant levels. Another potential source of NO₃⁻ is the reaction of CF₃O⁻ with HNO₃ which leads to NO₃⁻ as a minor product ion (5–8%).^{11,14} However, due to

the low ratio $[HNO_3]/[CIONO_2]$ in the present experiments, the observation of NO_3^- could not be assigned to the presence of HNO_3 in the flow tube. A possible explanation is that NO_3^- is formed by decomposition of $FCIONO_2^-$ in the sampling zone. Changing the electrostatic conditions of the ion guiding elements indeed led to changes in the ratio $[NO_3^-]/[FCIONO_2^-]$, with a minimum ratio of 5% in the LPCE spectra. In the BISA spectra, this ratio was only 3%.

The FHNO₃⁻ ions were the main product ions of the reaction of CF_3O^- with the HNO₃ impurity:^{11,14}

$$CF_3O^- + HNO_3 \rightarrow FHNO_3^- + CF_2O$$
 (2)

As reaction (1) progresses further, secondary product ions, $NO_3CIONO_2^-$, $NO_3HNO_3^-$ and $NO_3(HNO_3)_2^-$, were also observed, as shown in Fig. 1. The mechanism of formation of these ions is discussed hereafter.

First, $NO_3CIONO_2^-$, which was the most abundant of the secondary products, was formed in the reaction of FCIONO₂⁻ with CIONO₂. This suggests that FCIONO₂⁻ has the structure of a FCI·ONO₂⁻ cluster, reacting with CIONO₂ by ligand switching:

$$FCl \cdot ONO_2^- + ClONO_2 \rightarrow NO_3ClONO_2^- + FCl$$
 (3)

This is in agreement with the results reported by Huey *et al.*¹¹ The reaction

$$FHNO_3^- + CIONO_2 \rightarrow NO_3 CIONO_2^- + HF \qquad (4)$$

also occurred as a minor channel for the production of $NO_3CIONO_2^-$, because $FHNO_3^-$ has the structure of a $FH \cdot ONO_2^-$ cluster, allowing switching between HF and $CIONO_2$. This structure was deduced from previous studies^{11,14} which reported that $NO_3HNO_3^-$ was produced in reaction (5):

F

$$FH \cdot ONO_2^- + HNO_3 \rightarrow NO_3 HNO_3^- + HF$$
 (5)



Fig. 1 Example of the ion count rates vs. $[CIONO_2]$ in the study of the reaction $CF_3O^- + CIONO_2$ (\diamond) $[CF_3O^-]$; (\square) $[CF_3OHF^-]$; (\blacktriangle) $[FCIONO_2^-]$; (\blacksquare) $[FHNO_3^-]$; (\diamond) $[NO_3^-]$; (\bullet) $[NO_3^-]$; (\bullet) $[NO_3CIONO_2^-]$; (\times) $[NO_3HNO_3^-]$; (\bigcirc) $[CF_3OCIONO_2^-]$; (\bigtriangleup) $[NO_3(HNO_3)_2^-]$).

Reaction (5) also occurred in the present study as a minor channel for the $NO_3HNO_3^-$ production, in addition to reaction (6) and reaction (7):²⁶

$$FCl \cdot ONO_2^- + HNO_3 \rightarrow NO_3 HNO_3^- + FCl$$
 (6)

$$NO_3CIONO_2^- + HNO_3 \rightarrow NO_3HNO_3^- + CIONO_2$$
 (7)

Finally, the least abundant of the secondary product ions, $NO_3(HNO_3)_2^-$, was produced by the reaction of $NO_3HNO_3^-$ with HNO_3 :

$$NO_3HNO_3^- + HNO_3 + M \rightarrow NO_3(HNO_3)_2^- + M$$
 (8)

In *ab initio* calculations, Mebel and Morokuma²⁷ have determined the structures and energies of the species ClONO₂, HNO₃, NO₃⁻, NO₃ClONO₂⁻ and NO₃HNO₃⁻ using the density functional B3LYP/6-31G(d) approach. Using the same method with the GAUSSIAN 98 program,²⁸ the energies and structures of $FCIONO_2^-$ and $FHNO_3^-$ have been determined and are shown in Fig. 2. In agreement with the experimental results, the structure of the former ion was found to be that of the $FCl \cdot ONO_2^-$ cluster, with atomic charges of -0.28e on FCl and of -0.72e on NO₃, with a geometry of NO₃⁻ similar to that of free NO₃⁻ (1.264 Å),²⁷ with a FCl bond length close to that of the free FCl (1.664 Å) and a ClO bond length much longer than in free ClONO₂ (1.708 Å).²⁷ Similarly, FHNO₃ was found to be a $FH \cdot ONO_2^{-}$ cluster (Fig. 2). These theoretical results confirm the mechanisms presented above. The existence of the cluster ions F^- ·ClONO₂ and F^- ·HONO₂ can thus be excluded and other mechanisms involving these clusters, which lead to the same final products as those observed in the present study, can be rejected. For instance, "attachment-detachment" mechanisms, similar to that of the reaction of $Cl^- \cdot HONO_2$



Fig. 2 Geometries (in Å and degrees) of $\text{FH} \cdot \text{ONO}_2^-$ (a) and $\text{FCl} \cdot \text{ONO}_2^-$ (b) optimized at the B3LYP/6-31G(d) level. Bold numbers are the natural atomic charges (in *e*).

1.2. Kinetics. Since the rate constant for the reaction of CF_3O^- with HNO₃ is twice as large as that with $CIONO_2$ presently determined,14 the presence of HNO3 had to be taken into account to correct the rate constant of CF₃O⁻ with $CIONO_2$. The value of the rate constant k_1 was derived by multiplying the apparent rate constant by the ratio of the count rates of primary product ions resulting from reaction (1), i.e. $FCIONO_2^-$ and NO_3^- , to the count rates of all the product ions, representing a yield of 85 to 96%, obtained at low ClONO₂ concentration. The dependence of the roomtemperature rate constant of the $CF_3O^- + ClONO_2$ reaction on pressure is presented in Fig. 3. There is a slight difference (less than 10%) between the values determined at LPCE and at BISA, but this is not significant with respect to the reported statistical uncertainties (two standard deviations). The average of 35 series of experiments led to $k_1 = (1.2 \pm 0.4) \times 10^{-9} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 295 K, where the quoted uncertainties include estimated systematic errors. This value is in very good agreement with that of Huey et al.,11 who obtained $(1.1 \pm 0.3) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹, and with the collision rate constant $k_{\rm c}$ calculated from the parametrized theory of Su and Chesnavich, 29,30 1.1 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹, using a value of 0.77 D³¹ for the dipole moment μ_D and a value of 6.28 Å³ for the polarizability α of ClONO₂.²⁷ This theory is based on a combined variational transition state theory/ classical trajectory study of thermal energy ion-polar molecule capture collisions. Su and Chesnavich have shown that the ratio of k_c to the Langevin rate constant depends on μ_D , α and the temperature.^{29,30}

Kinetic results have been obtained at three other temperatures, with average values of k_1 of $(1.3 \pm 0.4) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ from 2 series of experiments at 225 K, $(1.2 \pm 0.4) \ 10^{-9}$ cm³ molecule⁻¹ s⁻¹ from 2 series of experiments at 274 K and $(1.1 \pm 0.4) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ from 4 series of experiments at 325 K. Given the reported statistical uncertainties (10%), no significant temperature



Fig. 3 Rate constant of the reaction $CF_3O^- + ClONO_2$ as a function of pressure. Circles and triangles correspond to values obtained at LPCE and at BISA, respectively. Error bars represent two standard deviations.

dependence of the rate constant k_1 can be derived, even if a slight increase seems to be observed as the temperature decreases.

From the measurement of the rate constant k_1 , and using the rate constant value $k_2 (2.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$,¹⁴ the ratio [HNO₃]/[CIONO₂] could be inferred for the low CIONO₂ concentrations:

$$\frac{[\text{HNO}_3]}{[\text{CIONO}_2]} = \frac{k_1 P_2}{k_2 P_1} \tag{II}$$

where P_1 and P_2 are the ion count rates of the products of reaction (1) and (2), respectively. The ratio varied between 2% and 9%, in excellent agreement with that obtained using the reactions of SF₆⁻ with ClONO₂ and HNO₃, as reported in the Experimental section. Additionally, the rate constant of the reaction of FClONO₂⁻ + ClONO₂ has been estimated by analyzing the linear part of the FClONO₂⁻ decay shown in Fig. 1. A lower limit of $(8.2 \pm 0.4) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 1 Torr of He and at room temperature has been found, using the rate constant of the reaction of FClONO₂⁻ with HNO₃ to take into account the presence of HNO₃ in the reactor. The latter rate constant was derived to be 1.8×10^{-9} cm³ molecule⁻¹ s⁻¹ as derived from the theory of Su and Chesnavich^{29,30} using values of 2.17 D for the dipole moment³² and 4.5 Å³ for the polarizability of HNO₃.¹¹

2. Reaction of CF₃OHF⁻ with ClONO₂

The reaction of CF₃OHF⁻ with ClONO₂

$$F_3OHF^- + ClONO_2 \rightarrow products$$
 (9)

led principally to the formation of FCIONO₂⁻. Traces of CF₃OCIONO₂⁻ were also observed, but could not be unambiguously assigned as product of this reaction because of the simultaneous presence of CF₃O⁻ in the flow tube. The FCIONO₂⁻ formation was deduced from the unchanged ratio [FCIONO₂⁻]/[CF₃OCIONO₂⁻] as [CF₃OHF⁻]/[CF₃O⁻] increased from 0.3 to 10%. In order to obtain the rate constant k_9 , the rate constant for reaction (10) had to be considered:

$$CF_3OHF^- + HNO_3 \rightarrow products$$
 (10)

A simple correction was obtained from the expression:

$$k_9 = k_{\text{meas}} - k_{10} [\text{HNO}_3] / [\text{ClONO}_2]$$
(III)

where k_{meas} is the measured rate constant and $k_{10} = 2.1 \times 10^{-9} \text{ cm}^3$ molecule⁻¹ s⁻¹.¹⁴ At room temperature, k_9 was found to be $(0.7 \pm 0.2) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹, obtained from 15 linear plots in the pressure range 1.6–4 Torr N₂. This value is lower than the collision rate constant, 1.0×10^{-9} cm³ molecule⁻¹ s⁻¹, determined from the theory of Su and Chesnavich.^{29,30} At 225 K, a rate constant $k_9 = (0.8 \pm 0.2) \ 10^{-9}$ cm³ molecule⁻¹ s⁻¹ was obtained from 2 series of experiments. No study could be performed at other temperatures, since CF₃OHF⁻ was present at too low concentration. Thus, no firm conclusion could be drawn for the temperature dependence of the rate constant.

3. Reaction of $CF_3OH_2O^-$ with $CIONO_2$

The reaction of $CF_3OH_2O^-$ with $CIONO_2$ was studied at 295 K in 0.4 Torr of He at BISA, and at 225 K in 1.3–1.9 Torr N₂ at LPCE. At room temperature, the ratio $[CF_3OH_2O^-]/[CF_3O^-]$ was around 0.05. At 225 K, this reaction was studied for different $[CF_3OH_2O^-]/[CF_3O^-]$ values: 0.20, 0.31 and 6.10. For the highest $[CF_3OH_2O^-]/[CF_3O^-]$ ratio, $CF_3O(H_2O)_2^-$ ions were also observed. The major ion produced by reaction (11),

$$CF_3OH_2O^- + CIONO_2 \rightarrow CF_3OCIONO_2^- + H_2O$$
 (11)

was $CF_3OCIONO_2^-$, formed by ligand switching. At further extent of the reaction, the secondary reaction of $CF_3OCIONO_2^-$ with $CIONO_2$ occurred, leading to $NO_3CIONO_2^-$:

$$CF_3OCIONO_2^- + CIONO_2 \rightarrow NO_3CIONO_2^- + products$$
(12)

This suggests that CF₃OClONO₂⁻ has the structure of a CF₃OCl·ONO₂⁻ cluster. CF₃OH₂O⁻ also reacted with HNO₃ with a rate constant $k_{13} = 2.1 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹.¹⁴

$$CF_3OH_2O^- + HNO_3 \rightarrow products$$
 (13)

The measured constant rate k_{meas} was corrected by using the formula

$$k_{11} = k_{\text{meas}} - k_{13} [\text{HNO}_3] / [\text{ClONO}_2]$$
 (IV)

The average value of 5 series of experiments yielded a rate constant $k_{11} = (1.2 \pm 0.4) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ at room temperature. This value is close to the calculated collision limit of 1.0×10^{-9} cm³ molecule⁻¹ s⁻¹.^{29,30} At 225 K, a rate constant of $(1.3 \pm 0.4) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ was found. All the rate constants determined in this work are summarized in Table 1.

4. Reaction of CF_3O^- with H_2O

The reaction between CF_3O^- and H_2O has been studied between 262 and 295 K. As described previously, known amounts of water vapor were introduced into the flow tube at 56 and 76 cm from the sampling zone. The decay of $CF_3O^$ ions was found to be independent of the length of the reaction zone (*i.e.* the reaction time), indicating that the equilibrium was reached under the experimental conditions used:

$$CF_3O^- + H_2O \leftrightarrow CF_3OH_2O^-$$
(14)

The equilibrium constant is

$$K = \frac{[CF_{3}OH_{2}O^{-}]}{[CF_{3}O^{-}][H_{2}O]}$$
(V)

Since $CF_3OH_2O^-$ was the only product ion observed, its concentration could be taken as: $[CF_3OH_2O^-] = [CF_3O^-]_0$ $- [CF_3O^-]$ where $[CF_3O^-]_0$ is the concentration of CF_3O^- in the absence of H_2O in the flow tube. Therefore, *K* was expressed as a function of CF_3O^- concentrations and its value could be deduced from the slope of $([CF_3O^-]_0/[CF_3O^-] - 1)$ vs. $[H_2O]$. The determination of the equilibrium constant was thus not sensitive to mass discrimination. The overall uncertainty in the value of *K* was estimated to be 50%, essentially coming from the experimental scatter (two standard deviations) and from the uncertainty in the measurements of H_2O concentrations. At 295 K, the equilibrium constant was measured at pressures ranging from 1.7 to 2.7 Torr. Values of 6.3×10^{-15} , 7.2×10^{-15} and 6.5×10^{-15} cm³ molecule⁻¹ were derived from the first,

Table 1 Summary of the rate constants obtained in this work

Reaction	Temperature/K	$k/10^{-9}$ cm ³ molecule ⁻¹ s ⁻¹
$CF_{2}O^{-} + CIONO_{2}$	225 + 5	1.3 ^a
5 2	274 ± 5	1.2
	295 ± 1	1.2
	325 ± 5	1.1
$CF_{3}OHF^{-} + CIONO_{2}$	225 ± 5	0.8
5 2	295 ± 1	0.7
$CF_{3}OH_{2}O^{-} + CIONO_{2}$	225 ± 5	1.3
5 2 2	295 ± 1	1.2
A True standard deviations load to 100/ some m		

^a Two standard deviations lead to 10% errors.

second and third methods of introduction of H₂O (as described in the Experimental section), respectively. The average value was derived from the linear regression of 120 data, shown in Fig. 4, leading to $K = (6.5 \pm 3.3) \times 10^{-15} \text{ cm}^3$ molecule⁻¹. This value is somewhat higher than the value of $(3.8 + 1.9) \times 10^{-15}$ cm³ molecule⁻¹ determined in a recent study¹³ in the pressure range 0.35–1.2 Torr of He. However, the values overlap within the combined error bars. The standard Gibbs energy of the reaction $CF_3O^- + H_2O$ at 295 K was derived as $\Delta G^{\circ} = -29.4 \pm 1.7 \text{ kJ mol}^{-1}$. The equilibrium constant K was also determined at 262, 276 and 285 K at 1.7 Torr, by using the first method for H₂O determination, with values of $(1.4 \pm 0.7) \times 10^{-13}$, $(4.1 \pm 2.1) \times 10^{-14}$ and $(1.4 \pm 0.7) \times 10^{-14}$ cm³ molecule⁻¹, respectively. Thermochemical data could be deduced from the Van't Hoff plot shown in Fig. 5. The standard reaction enthalpy ΔH° obtained from this plot equals -63.2 ± 6.7 kJ mol⁻¹ and the standard reaction entropy ΔS° equals $-114.6 \pm 23.9 \text{ J mol}^{-1} \text{ K}^{-1}$, neglecting their temperature dependences in the range 262-295 K with respect to the experimental uncertainties. No value of the equilibrium constant could be obtained at lower temperature because CF₃OH₂O⁻ was already present in the flow tube without introduction of water (see Experimental section) and water could be condensed on the introduction inlet of the flow tube.



Fig. 4 Plot of $[CF_3O^-]_0/[CF_3O^-] - 1$ as a function of $[H_2O]$ giving the equilibrium constant for the reaction $CF_3O^- + H_2O \leftrightarrow CF_3OH_2O^-$ at 295 K (see text).



Fig. 5 Van't Hoff plot of the equilibrium constant K for the reaction $CF_3O^- + H_2O \leftrightarrow CF_3OH_2O^-$.

5. Implications for the interpretation of the CIMS measurements

The data obtained for the equilibrium reaction forming $CF_3OH_2O^-$ can be applied to the balloon-borne CIMS flight conditions. At a temperature comparable with that of the highest measurement altitude of the balloon-borne CIMS instrument (31 km, 234 K, 7.5 Torr), a value of the equilibrium constant $K = 4.3 \times 10^{-12}$ cm³ molecule⁻¹ can be extrapolated from the above thermochemical data. Considering a water vapor mixing ratio of 5 ppm at 31 km,³³ the ratio $[CF_3OH_2O^-]/[CF_3O^-]$ is expected to be around 7, which is in disagreement with the ratio of 1 observed in the flight data at this altitude. Several arguments may be invoked to explain this discrepancy. One is that the temperature in the flow tube might be higher than that outside the balloon gondola (which was actually measured) by a few degrees, and would result in a lower $[CF_3OH_2O^-]/[CF_3O^-]$ ratio. Another explanation is the possible decomposition of CF₃OH₂O⁻ and/or CF₃OHF in the sampling zone of the flight instrument, which would lead to an overestimation of the above calculated ratio. Finally, the existence of unexpected or unknown chemistry of the ions produced in the source may also have an impact on the $[CF_3OH_2O^-]/[CF_3O^-]$ ratio.

The rate constants and the product distributions of all reactions determined at 225 K in the present study can also be used to analyze the flight data. A preliminary analysis already shows that the product ions resulting from the reactions of the primary ions (CF₃O⁻, CF₃OH₂O⁻, CF₃OHF⁻) with ClONO₂ are not observed at the expected levels in the flight spectra. For example, using the measured ratio [CF₃OH₂O⁻]/[CF₃O⁻], the signal of FClONO₂⁻, produced in the reactions of CF_3O^- and CF_3OHF^- with $CIONO_2$, is too low in contrast with that of CF₃OClONO₂⁻, produced in the reaction of $CF_3OH_2O^-$ with $CIONO_2$. An overestimation of $[CF_3O^-]$ in the flight reactor, which could be due to the dissociation of $CF_3OH_2O^-$ and/or CF_3OHF^- in the sampling zone, might explain the low level of signal of $FCIONO_2^{-}$ in the flight spectra. However, this overestimation of $[CF_3O^-]$ cannot be quantified at present, partly due to the lack of kinetic data for the reaction of CF_3O^- with HF.

Conclusion

The reaction of CF_3O^- with $ClONO_2$ has been studied over a large range of pressure and temperature in two flowing afterglow apparatuses. No pressure and temperature dependence of the nature of the ions produced (mainly $FCIONO_2^{-}$) has been noticed. No significant temperature dependence has been inferred for the rate constant. The CF₃OH₂O⁻ ion has been observed to react with ClONO₂ with a rate constant close to the collision limit to form the cluster $CF_3OCIONO_2^-$, whereas the reaction between CF_3OHF^- and $ClONO_2$ proceeds at a lower rate with $FClONO_2^-$ being the major product. The rate constants and the product distributions of all these reactions can be used to analyze the flight data obtained with the balloon-borne CIMS instrument using a CF_3O^- ion source. A preliminary analysis shows that the product ions (such as FClONO₂⁻ and CF₃OClONO₂⁻) are not present at the expected concentrations given the rate constants and mechanisms determined in this work. The present laboratory study indicates that this cannot be explained by a change in mechanism between room temperature and low temperature for the reaction $CF_3O^- + ClONO_2$. The study of the equilibrium between CF_3O^- and H_2O also shows a discrepancy between the expected and observed ratios $[CF_3OH_2O^-]/[CF_3O^-]$ at the highest altitude of the balloon flight. A laboratory kinetic study of the formation of CF₃OHF⁻, which is also an abundant ion in the flight

spectra, is clearly required in order to improve the interpretation of the in situ data. In addition, further flight data analysis together with laboratory studies using the flight instrument are needed in order to derive an accurate stratospheric ClONO₂ concentration profile.

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