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Gas phase reactions of CF_3O^- and $CF_3O^- \cdot H_2O$ and their relevance to the detection of stratospheric HCl

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Abstract

The reactions of CF_3O^-, $CF_3O^- \cdot H_2O$ and $CF_3O^- \cdot HF$ with HCl and of CF_3O^- with H_2O have been studied at room temperature in a flowing afterglow instrument. All reactions with HCl proceed at the gas kinetic rate. The reaction of CF_3O^- with HCl proceeds by fluoride transfer, whereas $CF_3O^- \cdot H_2O$ and $CF_3O^- \cdot HF$ react with HCl by ligand switching. The Gibbs free energy change of the reaction of CF_3O^- with H_2O has been determined at room temperature as well as the collisional dissociation rate constant of $CF_3O^- \cdot H_2O$ ions. (Int J Mass Spectrom 202 (2000) 207–216) © 2000 Elsevier Science B.V.

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1. Introduction

To enhance our understanding of the physicochemical processes causing polar as well as midlatitude ozone changes and to monitor the status of the Earth's atmosphere, frequent and accurate measurements of stratospheric and tropospheric trace gases are required. Although ground-based and satellite-borne remote sensing instruments currently can provide long-term data sets of trace gas concentrations with global or extended coverage, in situ measurements with balloon or airplane-borne instruments are still valuable to measure local phenomena and are necessary for the validation of satellite instruments.

A promising technique for in situ measurements of atmospheric trace gas concentrations is chemical ionization mass spectrometry (CIMS). This technique, which is based on very selective ion-molecule reactions taking place in a flow tube reactor connected to an ion mass spectrometer, has been successfully applied for measurements of several trace gases in the troposphere and stratosphere [1–7]. Recently, a promising new reaction scheme for the CIMS detection of HCl, HNO_3, $ClONO_2$, and other atmospheric trace gases has been proposed by Huey et al. [8]. This scheme is based on the reactions of CF_3O^- ions with these gases, which proceed by fluoride transfer, resulting in the formation of very specific product ions.

To determine simultaneously the concentrations of stratospheric HNO_3, HCl, and $ClONO_2$, an ion source producing CF_3O^- was installed in our balloon-borne CIMS instrument [9]. Although this ion source generated mainly bare CF_3O^- ions, mass spectra re-

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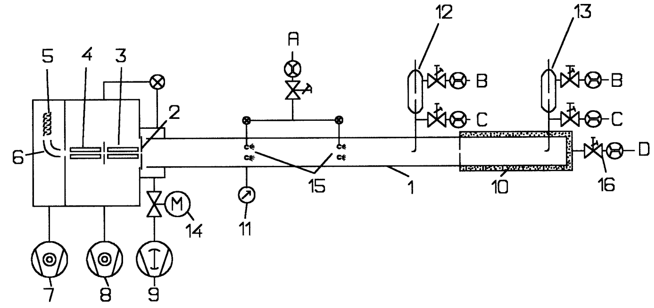

Fig. 1. Schematic representation of the apparatus. (A) reactant gas inlet; (B) Ar inlet; (C) Ar + CF_3OOCF_3 inlet; (D) buffer gas inlet; (1) flow tube; (2) polarizable inlet plate; (3) octopole; (4) quadrupole mass filter; (5) secondary electron multiplier; (6) deflecting lenses; (7) and (8) turbomolecular pumps; (9) rootspump; (10) flow tube high-pressure section (can be cooled with CO_2 pellets); (11) pressure sensor; (12) discharge ion source; (13) idem; (14) throttle valve; (15) ring-shaped reactant gas inlets; (16) mass flow meter.

corded during two recent balloon flights (June 1997 and June 1999) revealed the presence of $CF_3O^- \cdot H_2O$ ions that were at least as abundant as the CF_3O^- source ions. Next to CF_3O^- and $CF_3O^- \cdot H_2O$, $CF_3O^- \cdot HF$ ions were also present in the mass spectra. The contribution of the latter ions to the source ion family was ~10% when the balloon was at ceiling altitude (31 km) and gradually increased during descent to ~30% at an altitude of 19 km. The occurrence of the $CF_3O^- \cdot H_2O$ ion was rather unexpected in view of the low water vapor mixing ratio in the stratosphere (4 to 5 ppmv) and the small rate constant reported by Huey et al. [8] for the reaction of CF_3O^- with H_2O. The presence of $CF_3O^- \cdot HCl$, $CF_3O^- \cdot HNO_3$ and $CF_3O^-.ClONO_2$ in the flight spectra led to the assumption that $CF_3O^- \cdot H_2O$ and $CF_3O^- \cdot HF$ react with the trace gases of interest by ligand exchange. In this case, knowledge of the rate constants of these reactions is required for the derivation of stratospheric HNO_3, HCl and $ClONO_2$ concentrations from CIMS measurements. Therefore, we started a study of the appropriate ion-molecule chemistry in our laboratory flowing afterglow apparatus. In this article, we report the results of the study of the reactions of CF_3O^-, $CF_3O^- \cdot H_2O$ and $CF_3O^- \cdot HF$ with HCl. Additionally, we investigated the collisional dissociation of the $CF_3O^- \cdot H_2O$ ion and the equilibrium constant of the $CF_3O^-/CF_3O^- \cdot H_2O$ system.

2. Experiment

The reactions were studied at room temperature in a new stainless steel flowing afterglow apparatus, which is shown schematically in Fig. 1. The flow tube has a diameter of 6.5 cm and a total length of 160 cm. Reactant gases can be introduced at two fixed, electrically insulated ring-shaped stainless steel inlet ports with a ring diameter of 3/8 of the flow tube diameter and situated at a distance of 43.4 and 77.8 cm from the mass spectrometer inlet. To obtain an efficient homogenization, the reactant gas is introduced through six holes in the ring inlet, pointing against the buffer gas flow. The ions are produced in a high-pressure ion source, which will be described hereafter, and are carried along the flow tube by an inert buffer gas flow maintained by a 2000 $m^3 h^{-1}$ Roots blower. They are sampled downstream the flow tube through a small orifice in the center of an insulated stainless steel disk that separates the flow tube and the ion detection chamber. To allow experiments at pressures comparable to those in the stratosphere, the detection chamber is pumped differentially. The first compartment, pumped by a 1500 L s^{-1} turbomolecular pump, contains an octopole (working in the rf-only mode) to guide the ions from the gas expansion zone behind the orifice to the second compartment. To minimize cluster break-up in the gas expansion zone, the octopole rods are put at a bias potential that is only 0.5 V higher than the voltage on the interface plate, which is biased at +5 V.

In the second compartment, which is additionally pumped by a 56 L s^{-1} turbomolecular pump, the ions are separated according to their mass-to-charge ratio by a quadrupole mass filter and subsequently detected by an electron multiplier that is mounted off axis. To optimize ion transmission, an additional lens is mounted between the two compartments. To measure the reaction time, a short disturbance (200 μs duration) of the continuous ion flow was produced by pulsing the electrically insulated reactant gas inlet and synchronously recording the arrival of this disturbance at the detector by the use of a multichannel scaler. The ratio of the plasma velocity to the buffer gas velocity was found to be in good agreement with the one expected from theory [10].

The CF_3O^- ions were produced in a high-pressure ion source, which consists of a dc high-voltage argon discharge coupled to a small flow tube. Electrons produced in the discharge are transported into the small flow tube by the argon flow sent through the discharge. In the small tube downstream the discharge, a flow of an argon + CF_3OOCF_3 mixture is added to the main argon flow and CF_3O^- ions are produced by dissociative attachment of electrons to CF_3OOCF_3 molecules. The ion source is coupled to the main flow tube by a small stainless steel tube of 2-mm inner diameter. The ions are convectively transported to the main flow tube by the argon flow, which has a typical value of 10 STP $cm^3\ s^{-1}$ (STP:= Standard Temperature and Pressure: 273.16 K, 1013.25 mb). In our experimental configuration, an argon discharge was used to have a sufficiently high electron production. Attempts to use helium resulted in a much lower ion intensity for this kind of ion source.

The attachment of electrons to CF_3OOCF_3 has recently been studied in a flowing afterglow–Langmuir probe apparatus by Morris et al. [11] and was found to proceed rapidly with a rate constant of $9.2 \times 10^{-9}\ cm^3\ s^{-1}$. As a consequence, only a small CF_3OOCF_3 flow was required to obtain high CF_3O^- count rates. Typically, $\sim 2 \times 10^{-2}$ STP $cm^3\ s^-$ of a 2500 ppmv gas mixture of CF_3OOCF_3 in argon was used.

For the production of $CF_3O^- \cdot H_2O$ ions, a copper plate containing a central hole of 4-mm diameter was inserted into the flow tube to create a high-pressure region for reactant ion production. The plate was located at a distance of 108 cm from the mass spectrometer inlet. The entire buffer gas flow was constrained to flow through this hole. As a result, the pressure in the ion production region was ~30 times larger than the one in the reaction zone at a typical buffer gas flow of 85 STP $cm^3\ s^{-1}$ and a typical reaction zone pressure of 0.67 mb. The CF_3O^- ions produced in the discharge afterglow source were injected into the high-pressure region of the flow tube at a distance of 21 cm upstream the copper plate. The presence of this plate resulted in a decrease of the primary ion signal by a factor of 100, compared to the situation without the plate. This signal, however, was still high enough to perform the kinetic studies reported here.

When cooling the outer walls of the high-pressure region of the flow tube with solid CO_2 pellets (195 K), $CF_3O^- \cdot H_2O$ ions were formed through the reaction of CF_3O^- ions with residual H_2O in the buffer gas (<1 ppmv), which is favored by low temperatures. After ~1 h, the ratio $[CF_3O^- \cdot H_2O]/[CF_3O^-]$ was stabilized to ~10%. To perform accurate reaction rate constant measurements of $CF_3O^- \cdot H_2O$ with HCl, it is important that the $CF_3O^- \cdot H_2O$ formation is essentially restricted to the cooled high-pressure region. This was verified by using a second, identical discharge afterglow CF_3O^- ion source, mounted 22 cm downstream of the copper plate, which injected bare CF_3O^- ions into the low-pressure region. When operating this second ion source, a ratio of only 0.2% was obtained for $[CF_3O^- \cdot H_2O]/[CF_3O^-]$, proving that almost all $CF_3O^- \cdot H_2O$, observed when using the first ion source, is indeed formed in the cooled high-pressure region.

Apart from $CF_3O^- \cdot H_2O$, also $CF_3O^- \cdot HF$ was produced in the high-pressure region, probably by reaction of CF_3O^- with trace impurities in the CF_3OOCF_3 + argon mixture. The $[CF_3O^- \cdot HF]$/

$[CF_3O^-]$ ratio could be varied from .01 to .1 by changing the CF_3OOCF_3 flow in the ion source.

To keep the complete reaction zone of the flow tube at room temperature, the carrier gas leaving the high-pressure ion source should be warmed up as fast as possible. Temperature measurements showed that the best result was obtained when using helium as carrier gas. On the other hand, the use of pure helium as buffer gas was excluded because, as explained before, argon was needed to sustain the gas discharge, which is the upstream part of the CF_3O^- ion source. As a result, the measurements were carried out in a mixture of argon (12%) and helium (88%).

The reactant HCl gas was introduced in the flow tube in controlled amounts by a mass flow controller from a mixture containing 1000 ± 50 ppmv HCl in argon. When studying the hydration of CF_3O^-, two methods were applied to introduce controlled flows of water vapor into the flow tube. In a first method (M1), the H_2O flow was measured by determining the rate of change of pressure in a calibrated volume containing a mixture of H_2O and N_2. In a second method (M2), a stable N_2 flow was sent over a reservoir containing liquid H_2O (purified by vacuum distillation). The resulting gas mixture of N_2 and H_2O was subsequently sent through a mass flow meter before being introduced into the flow tube. By taking into account the appropriate gas correction factor for the $N_2 + H_2O$ mixture [12], the H_2O flow was obtained by subtraction of the pure N_2 flow from the mixed flow. Furthermore, the H_2O concentration in the flow tube was also obtained from the pressure increase in the flow tube upon addition of pure water vapor.

Rate constants k for the ion/molecule reactions are calculated from the primary ion signals $[X^-]$ at different HCl concentrations in the flow tube by using the formula:

$$-1\mathrm{n}\left(\frac{[X^-]}{[X_0^-]}\right) = k \times \tau \times [HCl] \tag{1}$$

where $[X_0{}^-]$ is the primary ion signal without addition of HCl to the reaction zone and τ is the measured value for the ion residence time.

3. Results

3.1 Reaction of CF_3O^- with HCl

Rate constant measurements of the reaction of CF_3O^- (85 u) with HCl have been performed at pressures ranging from 0.5 to 1.7 mb. The only reaction product observed is $(HFCl)^-$ (55 and 57 u), confirming that the reaction mechanism is fluoride transfer as was already reported by Huey et al. [8]. The structure of this ion is probably $Cl^-{\cdot}HF$. Because $F^- + HCl \rightarrow Cl^- + HF$ is an exothermic reaction ($\Delta H = -159.4$ kJ mol^{-1}) proceeding at the collision rate [13], the reverse bimolecular reaction is not expected to take place and the structure of $(HFCl)^-$ most probably will be an HF molecule associated to a chloride anion.

$$CF_3O^- + HC1 \rightarrow C1^-{\cdot}HF + CF_2O \tag{2}$$

No explicit pressure dependence was observed for k_2 and a value of $1.4 \times 10^{-9} cm^3$ molecule^{-1} s^{-1} was obtained with an estimated uncertainty of 30%. This is exactly the same value as the one Huey et al. obtained for this reaction in a helium buffer gas at 0.53 mb.

Upon further addition of HCl, the $Cl^-{\cdot}HF$ ion signal decreases and $Cl^-{\cdot}HCl$ (71, 73, and 75 u) appears in the spectra, indicating that $Cl^-{\cdot}HF$ reacts with HCl by ligand exchange to $Cl^-{\cdot}HCl$.

$$C1^-{\cdot}HF + HC1 \rightarrow C1^-{\cdot}HC1 + HF \tag{3}$$

This reaction was recently investigated by Lovejoy and Wilson [14], who obtained a rate constant of 7×10^{-10} cm^3 molecule $^{-1}$ s^{-1}. Apart from $Cl^-{\cdot}HCl$, $Cl^-{\cdot}HF{\cdot}HCl$ (91, 93, and 95 u) also appears when increasing the concentration of HCl. This suggests that the $Cl^-{\cdot}HF$ ion also partly reacts with HCl by three-body association, resulting in $Cl^-{\cdot}HF{\cdot}HCl$.

$$C1^-{\cdot}HF + HC1 + M \rightarrow C1^-{\cdot}HF{\cdot}HC1 + M \tag{4}$$

3.2. Reaction of CF_3O^- with H_2O

Our experimental configuration enabled us to estimate the backward rate constant of the reaction:

$$CF_3O^- + H_2O + M \rightleftarrows CF_3O^-\cdot H_2O + M \qquad (5)$$

As described in the Experiment section, the use of a second CF_3O^- ion source enabled us to conclude that no further hydration of CF_3O^- occurs in the low-pressure reaction zone. Therefore, only collisional dissociation of $CF_3O^-\cdot H_2O$ is supposed to occur in this region.

In our experimental conditions, the concentration of $CF_3O^-\cdot H_2O$ at the mass spectrometer inlet is well approximated by the following formula [15]:

$$[CF_3O^-\cdot H_2O]_i = [CF_3O^-\cdot H_2O]_o \times \exp\left(\frac{\lambda_1^2 DL}{a^2 v_p}\right) \times \exp\left(\frac{k_{5r}[M]L}{v_p}\right) \qquad (6)$$

where D is the diffusion constant of $CF_3O^-\cdot H_2O$ in the Ar + He buffer gas mixture, a is the flow tube radius, v_p is the plasma velocity, L is the distance between the high-pressure source region and the mass spectrometer inlet, $[M]$ is the buffer gas density, and λ_1 equals 2.405. The subscripts i and o in this formula refer to the $CF_3O^-\cdot H_2O$ concentrations at the mass spectrometer inlet and at the end of the cooled high-pressure source region, respectively. The first exponential in Eq. (6) represents the attenuation of the ion signal by diffusion, whereas the second exponential expresses the loss by dissociation. It is assumed that single mode diffusion is quickly obtained after the ions are leaving the high-pressure source.

The procedure to determine k_{5r} was as follows. While keeping the total buffer gas flow constant, the pressure in the flow tube was varied (from 0.47 to 1.60 mb) by throttling the valve between the flow tube and the Roots blower. This had no effect on the pressure upstream the copper plate (which is determined by the conductance of the hole in the plate), and therefore ion source production was not affected. Because at constant buffer gas flow, the ion residence time between the copper plate and the mass spectrometer inlet is proportional to the flow tube pressure, and because the diffusion coefficient is inversely proportional to the flow tube pressure, the exponential diffusion loss factor is expected to be independent of pressure.

As a result, the $CF_3O^-\cdot H_2O$ ion signal as a function of the buffer gas density can be expressed by the following relationship:

$$-1n\left(\frac{[CF_3O^-\cdot H_2O]_M}{[CF_3O^-\cdot H_2O]_{ref}}\right) = C \times k_{5r} \times ([M]^2 - [M_{ref}]^2) \qquad (7)$$

$$C = \frac{7.32 \times 10^{-20} \times a^2 \times L}{Q} \qquad (8)$$

where Q is the buffer gas flow (in STP cm^3 s^{-1}).

In Fig. 2, a typical variation of $-1n([CF_3O^-\cdot H_2O]_M/[CF_3O^-\cdot H_2O]_{ref})$" with $([M]^2 - [M_{ref}]^2)$ is shown. From a series of 10 measurements, a value of (1.05 ± 0.20) × 10^{-14} cm^3 s^{-1} $molecule^{-1}$ was obtained for k_{5r}.

In determining k_{5r}, the following assumptions were made: (a) single mode diffusion of the $CF_3O^-\cdot H_2O$ ions is quickly obtained after they leave the ion source; (b) the buffer gas is at room temperature (this is not the case in the vicinity of the ion source exit, but local heating of the flow tube wall reduced the length of this low temperature zone, as was verified experimentally using a thermocouple); and (c) k_{5r} is pressure independent. An upper limit for k_{5r} of 1.6 × 10^{-14} cm^3 s^{-1} $molecule^{-1}$ is also obtained from the experimental data, if we assume that conversion of CF_3O^- to $CF_3O^-\cdot H_2O$ is complete in the cooled high-pressure region, and that, in absence of any neutral reactant gas in the reaction zone, all CF_3O^- ions at the end of the flow tube are the result of dissociation of $CF_3O^-\cdot H_2O$ ions in the low-pressure section. Because the collisional dissociation of $CF_3O^-\cdot H_2O$ ions at room temperature is found to proceed rather rapidly, room temperature measurements of the forward rate constant of $CF_3O^- + H_2O$ will be disturbed by this reaction even at low pres-

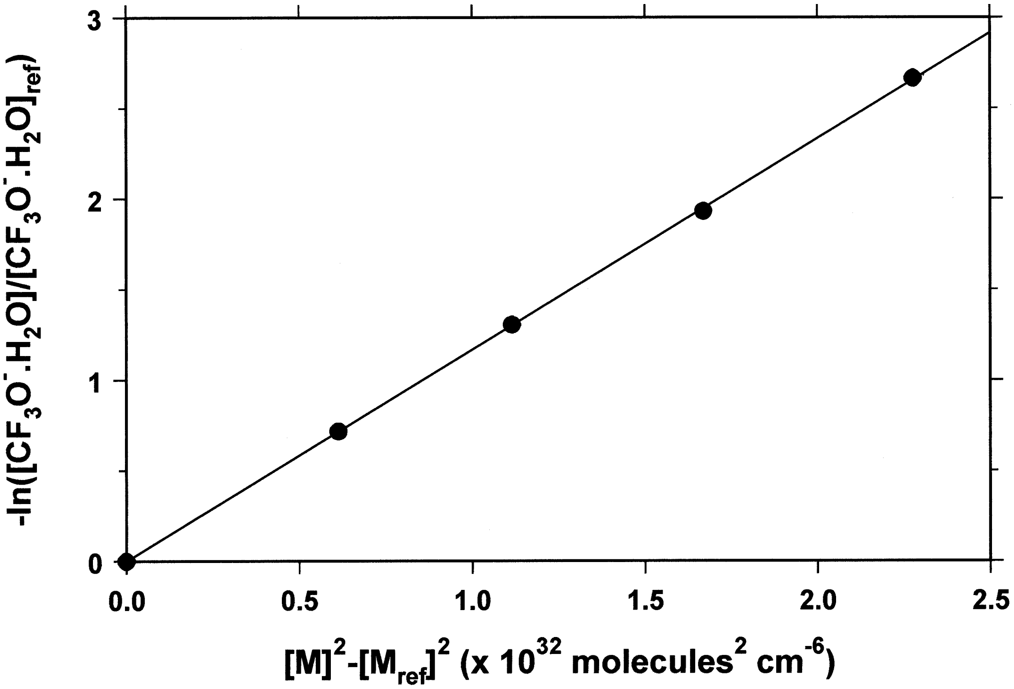

Fig. 2. Typical plot to determine the dissociation rate constant k_{5r} of $CF_3O^-{\cdot}H_2O$ in our experimental configuration. The product of the slope of this line and the value of C (Eq. 8) equals k_{5r}.

sures. Moreover, the decay of CF_3O^- ions as a function of H_2O vapor concentration in the flow tube was found to be independent of the length of the reaction zone at pressures above 0.8 mb, indicating that equilibrium was already established.

Thus, by introducing controlled amounts of H_2O vapor at the different reactant gas inlets and at different flow tube pressures, the equilibrium constant $K_{eq,5}$ of reaction (5) could be obtained from the simple formula:

$$K_{eq,5}(cm^3 molecule^{-1}) = \frac{[CF_3O^- \cdot H_2O]}{[CF_3O^-][H_2O]} \qquad (9)$$

Experiments were performed in a He + Ar buffer gas using three different methods to determine the H_2O concentration in the flow tube (see Experiment section). The value for $K_{eq,5}$ was found to be independent of flow tube pressure (from 0.4 to 1.7 mb), H_2O concentration (from 1.5×10^{12} molecules cm^{-3} to 7×10^{14} molecules cm^{-3}), and of reaction inlet port (at more than 0.8 mb for the smallest reaction distance), as expected for an equilibrium constant. When determining the H_2O concentration from the pressure increase in the flow tube, an average value for $K_{eq,5}$ of 3.2×10^{-15} cm^3 $molecule^{-1}$ is obtained, whereas for the two other methods of $[H_2O]$ determination, an average value of 4.4×10^{-15} cm^3 $molecule^{-1}$ was found. As can be noticed in Fig. 3, the values obtained with the different methods are in good agreement with each other within the experimental error. On average, the value for $K_{eq,5}$ is 3.8×10^{-15} cm^3 $molecule^{-1}$ with a total estimated measurement error of 50%.

From this number and the experimentally obtained value for k_{5r}, a forward rate constant k_{5f} of reaction (5) of $(4.0 \pm 2.8) \times 10^{-29}$ cm^6 s^{-1} $molecule^{-2}$ can be calculated. By varying the voltages of the ion lenses and the octopole, the $[CF_3O^-{\cdot}H_2O]/[CF_3O^-]$ ratio remained constant, suggesting that the measurement of $K_{eq,5}$ was not affected by additional break-up of $CF_3O^-{\cdot}H_2O$ during sampling.

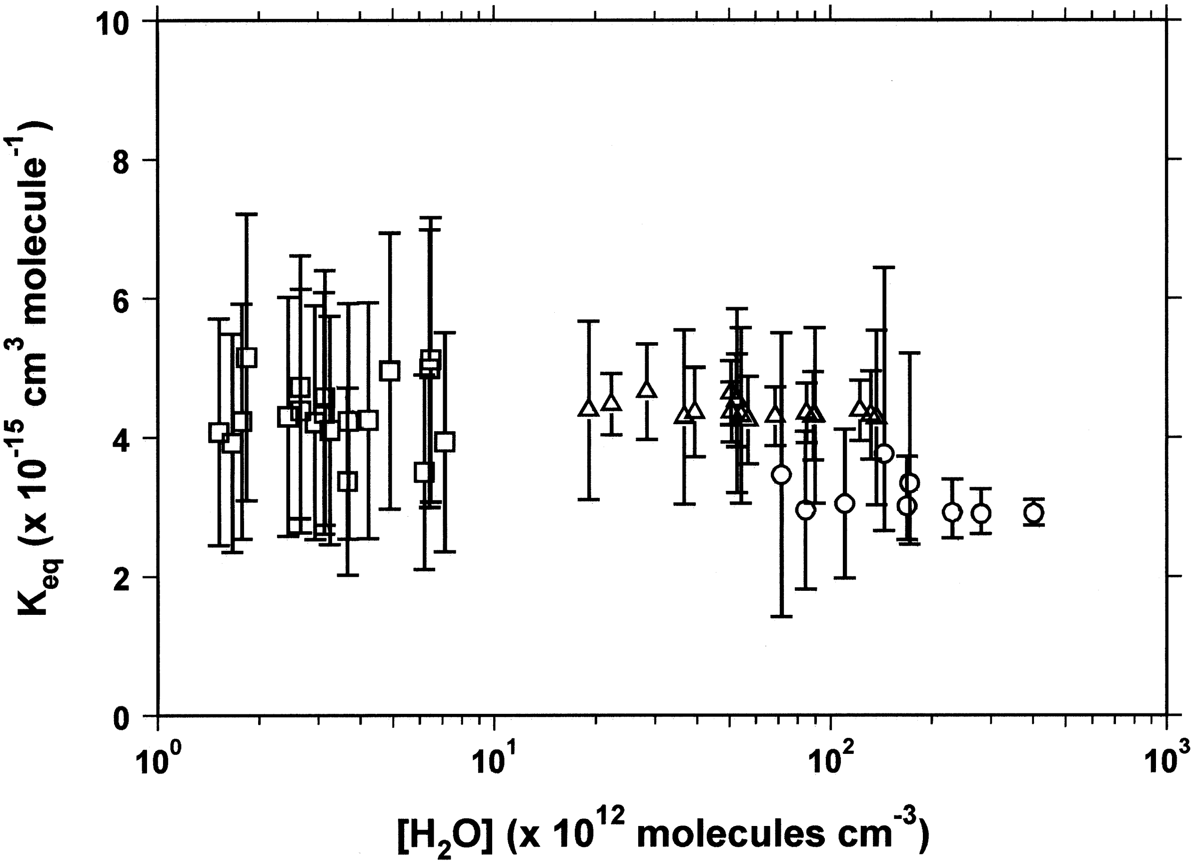

Fig. 3. Equilibrium constant of the system $CF_3O^- + H_2O + M \leftrightarrow CF_3O^- \cdot H_2O + M$, obtained with different methods. Circles: [H_2O] calculated from pressure increase in the flow tube; squares: [H_2O] obtained with method M1; triangles: [H_2O] obtained with method M2.

3.3 Reaction of CF_3O^-·H_2O and CF_3O^-·HF with HCl

Rate constant measurements of CF_3O^-·H_2O and CF_3O^-·HF were performed in the pressure range 0.5–0.6 mb. Because the water vapor mixing ratio in the flow tube is expected to be smaller than 1 ppmv (residual water concentration in the buffer gas containers as specified by the manufacturer), no hydration of CF_3O^- should occur when taking into account the value of k_{5f} obtained above. A small CF_3O^-·H_2O signal (0.2% of the CF_3O^- count rate), however, appears in the mass spectra when using the ion source that injects CF_3O^- ions directly into the low-pressure region. This might be attributed to either contamination of this ion source or to the fact that formation of CF_3O^-·H_2O is favored by low temperatures and that the buffer gas in the flow tube near the ion inlet might not yet be at room temperature. Because this CF_3O^-·H_2O signal is about 50 times smaller than the CF_3O^-·H_2O signal obtained by using the cooled high-pressure ion source, it is not expected to affect our measurements.

A value of $(1.4 \pm 0.1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} and $(1.3 \pm 0.1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} was obtained for the rate constant of HCl with CF_3O^-·H_2O and CF_3O^-·HF, respectively. The global accuracy of these rate constants is also 30%.

The major reaction mechanism for both reactions is ligand switching, resulting in CF_3O^-·HCl ions.

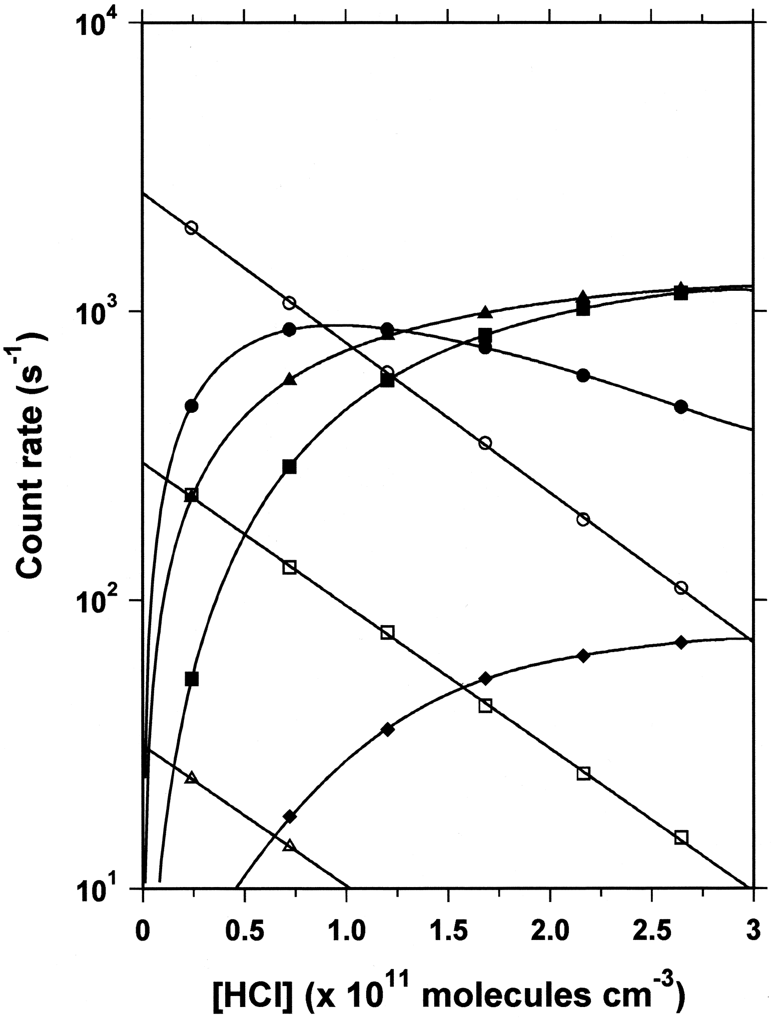

Fig. 4. Evolution of the concentration of the involved ion species as a function of the HCl concentration in the flow tube reactor. Open circles: CF_3O^-; open squares: $CF_3O^- \cdot H_2O$; open triangles: $CF_3O^- \cdot HF$; full circles: $Cl^- \cdot HF$; full squares: $Cl^- \cdot HCl$; full triangles: $CF_3O^- \cdot HCl$; full diamonds: $Cl^- \cdot HF \cdot HCl$.

$$CF_3O^- \cdot H_2O + HC1 \rightarrow CF_3O^- \cdot HC1 + H_2O \quad (10)$$

$$CF_3O^- \cdot HF + HC1 \rightarrow CF_3O^- \cdot HC1 + HF \quad (11)$$

In Fig. 4, the evolution of source and product ions versus HCl concentration in the flow tube is shown under conditions where the CF_3OOCF_3 flow through the ion source was kept to a minimum to avoid $CF_3O^- \cdot HF$ formation as much as possible. The pressure in the reaction zone and the buffer gas flow are, respectively, 0.52 mb and 85 STP cm^3 s^{-1}. The reaction length is 77.75 cm and the measured reaction time is 8.3 ms.

If there would be no break-up of $CF_3O^- \cdot H_2O$ in the flow tube, the gain in $[CF_3O^- \cdot HCl]$ should compensate for the loss in $[CF_3O^- \cdot H_2O]$. However, as is observed in Fig. 4, $[CF_3O^- \cdot HCl]$ at HCl concentrations $>2 \times 10^{11}$ molecules cm^{-3} is about four times higher than $[CF_3O^- \cdot H_2O]$ at zero HCl concentration in the flow tube. This supports the assumption that $CF_3O^- \cdot H_2O$ ions leaving the ion source are very efficiently broken up to CF_3O^- ions in the reaction zone.

4. Discussion

The results of our measurements point out that CF_3O^-, $CF_3O^-{\cdot}H_2O$ and $CF_3O^-{\cdot}HF$ all react with HCl with a rate constant that is close to the collision rate constant as calculated with the parameterized formula of Su and Chesnavich based on trajectory calculations [16]. Using the value $2.58 \times 10^{-30} m^3$ for the polarizability and 3.6×10^{-30} C.m for the electric dipole moment of HCl [17], a value of $1.3 \times 10^{-9} cm^3$ molecule^{-1} s^{-1}, is calculated for the rate constant of all three ion species with HCl.

As already mentioned in the Introduction, CF_3O^-, $CF_3O^-{\cdot}H_2O$, and $CF_3O^-{\cdot}HF$ are the major precursor ions in our balloon-borne stratospheric CIMS experiment when using a CF_3O^- ion source. Whether the latter two ion species are either formed from CF_3O^- in the ion source or in the flow tube itself (i.e., the reaction zone) is not important for deriving trace gas concentrations if all three ions react with this trace gas with approximately the same rate constant. Because this is the case for HCl, no substantial error is made if HCl concentrations are inferred by lumping together all source ions into one family S^- ($[S^-] = [CF_3O^-] + [CF_3O^-{\cdot}H_2O] + [CF_3O^-{\cdot}HF]$) and all product ions into another family P^- ($[P^-] = [Cl^-{\cdot}HF] + [CF_3O^-{\cdot}HCl]$) and by assuming that the conversion of S^- into P^- proceeds with a rate constant that is the average of the rate constants of CF_3O^-, $CF_3O^-{\cdot}H_2O$, and $CF_3O^-{\cdot}HF$ with HCl.

From the measurements of k_{5r} and $K_{eq,5}$, we were able to calculate a value for the forward rate constant of $CF_3O^- + H_2O$ of 4×10^{-29} cm^6 molecule^{-2} s^{-1}, which corresponds to a pseudo–second-order rate constant of 1.7×10^{-12} cm^3 molecule^{-1} s^{-1} at 1 mb. This value is in disagreement with the pseudo–second-order rate constant value of 3×10^{-14} cm^3 molecule^{-1} s^{-1} as reported by Huey et al. [8] over the pressure range 13–33 mb in N_2. However, because in the laboratory the reaction of CF_3O^- with H_2O was found to equilibrate rapidly, the pseudo–second-order rate constant reported by Huey et al. is more likely to be a measure of the equilibrium constant $K_{eq,5}$ divided by the reaction time. Taking into account our value for $K_{eq,5}$ it can easily be shown that at equilibrium conditions and at H_2O concentrations below 2×10^{13} molecules cm^{-3}, the semilogarithmic decay plot of $[CF_3O^-]$ with $[H_2O]$ is a straight line, the slope of which is $K_{eq,5}$ instead of the product of $k_{5,f}$ and the reaction time.

Taking into account that the value of the reaction time in the experiments of Huey was of the order of 100–200 ms [18], an equilibrium constant $K_{eq,5}$ of $3–6 \times 10^{-15}$ cm^3 molecule^{-1} is derived using the value of the pseudo–second-order forward rate constant reported by this author. This inferred value of $K_{eq,5}$ is in good agreement with our result, given the uncertainty of a factor 2 on the value of k_{5r} reported by Huey.

At the highest measurement altitude of our balloon-borne CIMS instrument (31 km, 234 K, 13.5 mb), CF_3O^- and $CF_3O^-{\cdot}H_2O$ are by far the most abundant ions in the mass spectrum, and the observed $[CF_3O^-{\cdot}H_2O]/[CF_3O^-]$ ratio is 1. The time constant of the $CF_3O^-/CF_3O^-{\cdot}H_2O$ system to reach equilibrium is given by $(k_{5f} \times [M] \times [H_2O] + k_{5r} \times [M])^{-1}$, with [M] the number density of stratospheric air. An upper limit τ_u for this time constant is given by $(k_{4f} \times [M] \times [H_2O])^{-1}$. If we assume a T^{-3} dependence of k_{5f} and take into account a typical increase of a factor of 3 for k_{5f} due to the difference in buffer gas (air instead of helium), a value of 7×10^{-11} cm^3 molecule^{-1} s^{-1} can be calculated for the stratospheric flight conditions. Using a water vapor mixing ratio of 5 ppmv at 31 km altitude [19] and the appropriate number for [M] at this altitude, a value of 8 ms is found for τ_u. Because this is about three to four times smaller than the residence time of the ions in the flow tube, the system is expected to be in equilibrium, and a value for $K_{eq,5}$ of 6.1×10^{-13} cm^3 molecule^{-1} is obtained at 234 K from the $[CF_3O^-{\cdot}H_2O]/[CF_3O^-]$ ratio observed in flight.

The corresponding ΔG^0 value at 234 K is calculated to be -33.0 kJ mol^{-1}. The ΔG^0 at 295 K as calculated from our room temperature measurements of the equilibrium constant is -28.3 kJ mol^{-1}. These two ΔG^0 values yield a value for ΔH^0 and ΔS^0 of reaction (5) of, respectively, -51.0 kJ mol^{-1} and -76.9 J mol^{-1} K^{-1}. The latter value is in good agreement with typical reaction entropy changes for the gas-phase hydration of polyatomic negative ions [20].

By taking into account this value for the binding energy of CF_3O^- to H_2O (-51.0 kJ mol^{-1}), the two most recent values for the formation enthalpy of CF_3O^- (-969.0 ± 11.7 kJ mol^{-1} [20] and -1067 ± 9.6 kJ mol^{-1} [22]) and the accurately determined formation enthalpies of CF_2O [23], $Cl^-\cdot HF$ [24] and HCl [23], it is found that the reaction

$$CF_3O^-\cdot H_2O + HC1 \rightarrow C1^-\cdot HF + CF_2O + H_2O \tag{12}$$

is also exothermic.

With the abovementioned values, an enthalpy change of reaction (12) is found ranging from -118.6 kJ mol^{-1} (using $\Delta H_f(CF_3O^-)$ from reference [21]) to -20.58 kJ mol^{-1} (using $\Delta H_f(CF_3O^-)$ from reference [22]).

Because $CF_3O^-\cdot H_2O$ dissociates in the reaction zone to CF_3O^- and H_2O and because $Cl^-\cdot HF$ is also the reaction product of CF_3O^- with HCl, it was not possible to verify whether the reaction of $CF_3O^-\cdot H_2O$ with HCl partly proceeds through this pathway or not. Preliminary laboratory studies of the reactions of CF_3O^-, $CF_3O^-\cdot H_2O$, and $CF_3O^-\cdot HF$ + HCl at low temperatures and high pressures, however, indicate that $Cl^-\cdot HF$ can only be a minor product ion under these conditions.

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References

[1] F. Arnold, S. Spreng, Geophys. Res. Lett. 21 (1994) 1255.
[2] T. Reiner, O. Möhler, F. Arnold, J. Geophys. Res. 104 (1999) 13,943.
[3] K.H. Wohlfrom, T. Hauler, F. Arnold, H. Singh, Geophys. Res. Lett. 26 (1999) 2849.
[4] A.A. Viggiano, Mass Spectrom. Rev. 12 (1993) 115.
[5] D.J. Tanner, A. Jefferson, F.L. Eisele, J. Geophys. Res. 102 (1997) 6415.
[6] L.G. Huey, E.R. Lovejoy, Int. J. Mass Spectrom. Ion Processes 155 (1996) 133.
[7] L.G. Huey, E.J. Dunlea, E.R. Lovejoy, D.R. Hanson, F.C. Fehsenfeld, C.J. Howard, J. Geophys. Res. 103 (1998) 3355.
[8] L.G. Huey, P.W. Villalta, E.J. Dunlea, D.R. Hanson, C.J. Howard, J. Phys. Chem. 100 (1996) 190.
[9] E. Arijs, A. Barassin, E. Kopp, C. Amelynck, V. Catoire, H.P. Fink, C. Guimbaud, U. Jenzer, D. Labonette, W. Luithardt, E. Neefs, D. Nevejans, N. Schoon, A.-M. Van Bavel, Int. J. Mass. Spectrom. 181 (1998) 99.
[10] E.E. Ferguson, F.C. Fehsenfeld, A.L. Schmeltekopf, Adv. At. Mol. Phys. 5 (1969) 1.
[11] R.A. Morris, T.M. Miller, J.F. Paulson, A.A. Viggiano, M.T. Feldmann, R.A. King, H.F. Schaefer III, J. Chem. Phys. 110 (1999) 8436.
[12] MKS Instruments France, private communication.
[13] J.C. Weisshaar, T.S. Zwier, S.R. Leone, J. Chem. Phys. 75 (1981) 4873.
[14] E.R. Lovejoy, R.R. Wilson, J. Phys. Chem. A 102 (1998) 2309.
[15] N.G. Adams, M.J. Church, D. Smith, J. Phys. D. 8 (1975) 1409.
[16] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[17] E.W. McDaniel, E.A. Mason, The Mobility and Diffusion of Ions in Gases, Wiley-Interscience, New York, 1988.
[18] L. Gregory Huey, personal communication.
[19] M.M. Abbas, H.A. Michelsen, M.R. Gunson, M.C. Abrams, M.J. Newchurch, R.J. Salawitch, A.Y. Chang, A. Goldman, F.W. Irion, G.L. Manney, E.J. Moyer, R. Nagaraju, C.P. Rinsland, G.P. Stiller, R. Zander, Geophys. Res. Lett. 23 (1996) 2401.
[20] R.G. Keesee, A.W. Castleman Jr., J. Phys. Chem. Ref. Data, 15 (1986) 1011.
[21] R.W. Taft, I.J. Koppel, R.D. Topsom, F. Anvia, J. Am. Chem. Soc. 112 (1990) 2047.
[22] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 105 (1983) 2944.
[23] M.W. Chase Jr., NIST-JANAF Thermochemical Tables, fourth ed., J. Phys. Chem. Ref. Data, Monograph 9, 1998, pp. 1–1951.
[24] J.W. Larson, J.W., T.B. McMahon, J. Am. Chem. Soc. 106 (1984) 517.