

# Study of Ion/Molecule Reactions for Detection of Atmospheric Trace Gases by Chemical Ionization Mass Spectrometry: Reactions of $\text{CF}_3\text{O}^-$ and $\text{CF}_3\text{O}^-\text{H}_2\text{O}$ with Atmospheric Acids.

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## Introduction

Since recent laboratory measurements<sup>1</sup> have shown that  $\text{CF}_3\text{O}^-$  is a promising precursor ion for atmospheric trace gas measurements by CIMS (Chemical Ionization Mass Spectrometry), we have incorporated a  $\text{CF}_3\text{O}^-$  ion source in our balloon-borne CIMS instrument<sup>2</sup> for the measurement of stratospheric  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{ClONO}_2$ . At stratospheric conditions, however, rapid hydration of  $\text{CF}_3\text{O}^-$  complicates the reaction schemes to derive trace gas concentrations. The analysis of the flight data required additional laboratory measurements of gas phase reactions of  $\text{CF}_3\text{O}^-$  and  $\text{CF}_3\text{O}^-\text{H}_2\text{O}$  ions with  $\text{HNO}_3$ . The results of this study are presented here.

With the aim of elaborating new reaction schemes for trace gases of tropospheric importance, the reactions of the same ions with formic ( $\text{HCOOH}$ ) and acetic acid ( $\text{CH}_3\text{COOH}$ ) have also been studied and the results are also reported hereafter.

## Experiment

The gas phase ion/molecule reactions were studied at room temperature in a flowing afterglow apparatus. A plate with a central aperture (4 mm diameter) separates the flow tube into a low-pressure reaction zone (0.53-1.33 mb) and a high-pressure zone (20 mb) to which an ion source is connected.  $\text{CF}_3\text{O}^-$  ions are produced by dissociative electron attachment to  $\text{CF}_3\text{OOF}_3\text{C}$ . When cooling the walls of the high-pressure zone at 197 K, hydrated  $\text{CF}_3\text{O}^-$  ions were produced in the high-pressure zone by a three-body reaction with residual water vapour in the helium buffer gas<sup>3</sup>. It was checked experimentally that no further hydration of  $\text{CF}_3\text{O}^-$  takes place in the low-pressure reaction zone.

The nitric acid concentration in the flow tube was determined by UV-absorption measurements at 186 nm in a 50 cm cell through which the  $\text{HNO}_3$ /argon mixture flows in the instrument.

For the study of reactions with formic and acetic acid, dilute mixtures of these substances in nitrogen were prepared manometrically and were introduced into the

reactor by a commercial mass flow meter. The existence of carboxylic acid dimers was taken into account by using the formula of Büttner and Maurer<sup>4</sup>.

## Results

The reactions of bare  $\text{CF}_3\text{O}^-$  with  $\text{HNO}_3$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  were studied at pressures ranging from 0.53 to 1.33 mb. Their rate constants were found to be pressure-independent and are respectively  $(2.3 \pm 0.2) \times 10^{-9}$ ,  $(1.7 \pm 0.2) \times 10^{-9}$  and  $(1.5 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate constant of  $\text{CF}_3\text{O}^-$  with  $\text{HNO}_3$  is in excellent agreement with the value reported by Huey et al<sup>1</sup>. As was also reported by this author, this reaction is observed to proceed through fluoride transfer and proton transfer, resulting in  $\text{NO}_3\text{HF}$  and  $\text{NO}_3^-$  product ions. The proton transfer channel was found to account for 7 to 8 % of the primary product ions. The main reaction mechanism (> 90 %) of  $\text{CF}_3\text{O}^-$  with  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  was fluoride transfer, resulting in  $\text{HCOOHF}^-$  and  $\text{CH}_3\text{COOHF}^-$  product ions.

The reactions of  $\text{CF}_3\text{O}^-\text{H}_2\text{O}$  with  $\text{HNO}_3$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  were studied at 0.53 mb and rate constants of respectively  $(2.1 \pm 0.2) \times 10^{-9}$ ,  $(1.8 \pm 0.2) \times 10^{-9}$  and  $(1.6 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  have been inferred. Apart from a small ligand switching channel (at most 20 %), the reaction of  $\text{CF}_3\text{O}^-\text{H}_2\text{O}$  with  $\text{HNO}_3$  was observed to result in  $\text{NO}_3\text{HF}$  product ions. This is consistent with what is observed in the stratospheric mass spectra<sup>6</sup>. Ligand switching is the major mechanism for the reactions of  $\text{CF}_3\text{O}^-\text{H}_2\text{O}$  with  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$ . Other reaction products such as  $\text{HF}_2^-$  and  $\text{F}(\text{HF})_2^-$  are also emerging in small quantities. However, because of the simultaneous presence of  $\text{CF}_3\text{O}^-$  and  $\text{CF}_3\text{O}^-\text{H}_2\text{O}$  (and also  $\text{CF}_3\text{O}^-\text{HF}$ ,  $\text{CF}_3\text{OF}_2$  and  $\text{F}(\text{CF}_3)\text{OOF}_3\text{C}$  which are present in small concentrations), an unambiguous determination of the product ion distribution of  $\text{CF}_3\text{O}^-\text{H}_2\text{O}$  with  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  is not possible.

The global error on the rate constant measurements is estimated to be 30 %. A more detailed description of the experiments and the results, together with a more extended discussion will be published elsewhere<sup>5</sup>.

## References

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