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# Heterogeneous Reactions of $(NH_4)_2SO_4$ particles with chlorine reactive species: coated wall flow tube studies

Raluca CIURARU, Nicolas VISEZ, Sylvie GOSSELIN, Denis PETITPREZ

Laboratoire de Physico-Chimie des Processus de Combustion et de l'Atmosphère (PC2A), UMR 8522, Universite de Lille 1, Cité Scientifique - Bâtiment C11, 59655 Villeneuve d'Ascq, France

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## INTRODUCTION

The chlorine atoms could be the most important oxidant in the marine boundary layer at dawn when the OH concentration is small. The chlorine species will be photolyzed at sunrise to generate Cl atoms at concentrations estimated to be on the order of $10^5$ atoms $cm^{-3}$ [(1)]. It can modify the acidity budget (HCl), oxidize various volatile organic compounds (VOCs), contribute to sulphur oxidation in the aqueous phase. It can also participate to ozone destruction or production, depending on the (VOCs) concentrations [(2)].

The sulfates represent the majority compounds of the particles of aerosols, which are produced from the anthropic $SO_2$ emissions.

The presence of ammonium salts in the troposphere has a significant influence upon the atmospheric concentrations of their acid constituents, which can be regenerated during transport. Ammonium sulfate concentration ranges from 2.78 to 23.7 μg $m^{-3}$ in fine particles, and from 0.15 to 1.39 μg $m^{-3}$ in coarse particles [(3)].

In order to better understand the heterogeneous reactivity between these aerosol particles and chlorine reactive species, kinetic studies are in progress in our laboratory.

## EXPERIMENTAL

The heterogeneous uptake of some chlorine reactive species by ammonium sulfate particles has been investigated at room temperature and low pressure. Studies were performed in a laminar coated wall flow tube reactor coupled to a quadrupole mass spectrometer.

Our experimental set-up and techniques to prepare coated surfaces will be detailed. Salt samples of ammonium sulfate are prepared in two different ways: as spray deposited substrates, using a constant output atomizer and as powder substrates.

The measurement of the first order rate constant, *k* is achieved by changing the contact time between the surface and the gas, using a movable injector. From the rate constant, we can determine the uptake coefficient, $\gamma$, which represents the ratio between the number of gas molecules removed by the condensed phase and the number of gas molecules striking the interface per unit time.

Chlorine atoms are produced within a DC microwave discharge in a mixture of molecular chlorine and helium.

## RESULTS

The uptake of Cl atoms on ammonium sulfate particles was found to be fast with an uptake coefficient of $\gamma = (5 \pm 2)\times10^{-4}$. This result is in agreement with the only available data from Martin et al, 1980[(4)].

The secondary product, molecular chlorine, $Cl_2$, was observed, owing to the heterogeneous recombination of halogen atoms on the surface of the particles. Studies below room temperature are now in progress.

These measurements will be also extended to other particles of atmospheric interest such as ammonium bisulfate ($NH_4HSO_4$) and ammonium nitrate ($NH_4NO_3$).

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