



TNA User Report

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Project title	The molecular composition of products formed from chlorine oxidation
Name of the accessed chamber	PACS-C3
Number of users in the project	3
Project objectives (max 100 words)	<p>The objective of this project was to identify differences between chlorine-initiated and OH-initiated oxidation of volatile organic compounds (VOCs). We studied the oxidation of toluene, decane and car exhaust emissions. We aim to:</p> <ul style="list-style-type: none"> • Demonstrate and explain differences between the molecular compositions of chlorine and OH oxidation products. • Explore the volatility properties of these oxidation products. • Establish that ClNO₂ can be created in the chamber environment from the reaction of N₂O₅ with chlorine-containing particles. • Use results from these experiments to inform the analysis of field data from an urban background site in Delhi, India.
Description of work (max 100 words):	<p>State-of-the-art instrumentation including a Chemical Ionisation Time-of-Flight High Resolution Mass Spectrometer with a Filter Inlet for Gases and AEROSols (FIGAERO-CIMS), an Extractive ElectroSpray Ionisation Mass Spectrometer (EESI-MS) and a Volatility Tandem Differential Mobility Analyser (VTDMA) were used to examine the products of various reactions between oxidants and precursors in both the gas and particle phase. Toluene, decane or car exhaust emissions were injected into the PACS-C3 chamber alongside the oxidants. A rig of UV lights were used to stimulate photochemical activity, and we measured aerosol properties using a suite of instrumentation. This has provided a comprehensive dataset demonstrating the effects of chlorine oxidation in comparison with OH on VOC oxidation and SOA formation.</p>

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¹ Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

² UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

³ UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Sophie Haslett

Chamber name and location: PACS-C3, PSI, Switzerland

Campaign name and period: Chlorine oxidation campaign 01/04/2019 – 19/04/2019

Text:

The molecular composition of products formed from chlorine oxidation

Introduction and motivation

The chlorine radical can act as a powerful oxidant, reacting with some volatile organic compounds (VOCs) such as toluene at a rate up to an order of magnitude faster than more prevalent oxidants such as the hydroxy radical (OH) and ozone (Baker et al., 2016; Dhulipala et al., 2019). In the atmosphere, natural chlorine concentrations are typically low. Recent measurement campaigns, however, have shown that the concentration of particulate chloride in megacities including Beijing (Le Breton et al., 2018) and Delhi (Gani et al., 2018) can be considerable, with concentrations exceeding $100 \mu\text{g m}^{-3}$ being observed in Delhi during the winter. This particulate chloride is formed from gaseous chlorine compounds in the atmosphere. Under these conditions, chlorine oxidation is likely to become a major oxidation pathway and therefore have a significant impact on the composition of secondary organic aerosols (SOA) formed in the urban haze. Nevertheless, very few controlled chamber experiments have been carried out to assess the chemical products of chlorine oxidation (Wang and Hildebrandt Ruiz, 2018).

Chlorine radicals in the atmosphere can originate from nitryl chloride (ClNO_2), a compound that builds up overnight from N_2O_5 (itself a product of NO_2 and O_3) reacting at the surface of chlorine-containing particles. The ClNO_2 compound breaks apart photolytically at sunrise, which liberates the chlorine radical. Therefore, chlorine oxidation follows a diurnal cycle, with a spike in oxidation activity in the early mornings (e.g. Faxon & Allen 2013, Le Breton et al., 2018).

We carried out a field campaign over the winter of 2018-2019 in Delhi, during which we observed high concentrations of ClNO_2 and other chlorine-containing compounds. A diurnal cycle was observed, with ClNO_2 increasing during the night and decreasing at sunrise. A Time-of-Flight Mass Spectrometer with a Filter Inlet for Gases and AEROSols (FIGAERO-CIMS) and an Extractive ElectroSpray Ionisation Mass Spectrometer (EESI-MS) were used to monitor these precursors and the resulting SOA.

Using the PACS-C3 chamber, we simulated the Delhi atmosphere in a controlled environment to identify differences between chlorine- and OH-initiated oxidation. The same instrumentation was employed during these chamber experiments as were used in the field, with the addition of a Volatility Tandem Differential Mobility Analyser (VTDMA) to analyse particle volatility. The results will help us both to identify the extent to which chlorine drives SOA formation in Delhi during the winter, and improve the general understanding of chlorine oxidation.

Scientific objectives

The scientific objectives of this campaign include:

1. To demonstrate and explain differences in molecular composition between chlorine- and OH-initiated oxidation products.
2. To explore other differences between the two oxidation pathways, including reaction rates and the volatility properties of the products.
3. To establish that ClNO_2 can be created from reacting ammonium chloride (NH_4Cl) particles with N_2O_5 (created from the reaction of NO_2 and O_3) in the chamber environment.
4. To use results from these experiments to inform the analysis of data from our field campaign in Delhi, thereby establishing the extent to which chlorine oxidation controls the composition of the urban Delhi haze.

Reasons for choosing this simulation chamber

The PSI-SCACS is a 9 m³ teflon chamber, suspended in a temperature-controlled enclosure. It was designed to simulate the formation and growth of secondary organic aerosol particles under polluted conditions. The chamber can be connected to a number of different monitoring instruments. Both simple and complex SOA precursors, including combustion engine exhaust, can be injected into the chamber. Previous experiments have shown the chamber to be valuable in monitoring photochemistry based on OH and ozone (Platt et al., 2014; Platt et al., 2017), which will provide valuable reference points for this campaign. The chamber can be operated at a range of temperatures (0-40 °C), relative humidities (0-100%) and light conditions, making it possible to simulate various atmospheric conditions closely. All of these properties make this chamber an ideal choice for these experiments.

Method and experimental setup

We formed ClNO₂ inside the chamber from the reaction between NH₄Cl seed particles and N₂O₅. These were generated, respectively, from nebulising an NH₄Cl solution and from the reaction between N₂ and O₃. The chamber was kept dark for up to an hour to allow ClNO₂ to form. After this, we added VOCs and switched on the UV lights in the chamber, photolysing ClNO₂ to produce chlorine radicals (Cl), which went on to oxidise the VOCs. We investigated three VOC types: toluene, decane and VOCs from car exhaust emissions. For comparison, we investigated OH oxidation by injecting nitrous acid (HONO) and using ammonium sulphate ((NH₄)₂SO₄) seed particles. Aerosol particles and trace gases were sampled directly from the chamber by a suite of instrumentation (see Table 1) including the FIGAERO-CIMS and the VTDMA.

Instrument	Data
FIGAERO CIMS	Molecular composition of gas- and particle-phase compounds
VTDMA	Aerosol volatility
Aerosol Mass Spectrometer	Quantitative bulk aerosol composition (organics, sulphate, nitrate, chloride, ammonium)
Extractive ElectroSpray Ionisation Mass Spectrometer	Molecular composition of particle-phase compounds
Proton-Transfer-Reaction Mass Spectrometer	Composition of VOCs
Ozone monitor	Ozone concentration
NO_x monitor	Concentration of NO and NO ₂
Scanning Mobility Particle Sizer	Aerosol size distribution

Table 1: Instrumentation used to monitor chamber contents.

Data description

Twelve experiments were carried out, with one oxidant and one precursor being used in each case. In some cases, further VOCs or oxidants were introduced near the end of the experiment run. Data from the FIGAERO-CIMS were successfully collected from the second day onwards. The experimental schedule is shown in Table 2.

Date	Oxidant	Precursor	Notes
2019-04-03			<i>Nitrate campaign overrun</i>
2019-04-04			<i>Nitrate campaign overrun</i>
2019-04-05			<i>Testing ClNO₂ generation</i>
2019-04-06			<i>Testing ClNO₂ generation</i>
2019-04-07	Chlorine	Toluene	<i>Also testing ClNO₂ generation</i>

2019-04-08	Chlorine	Toluene	
2019-04-09	Chlorine	Toluene	<i>Car emissions included later in the day</i>
2019-04-10	Chlorine	Car exhaust	
2019-04-11	Chlorine	Car exhaust	
2019-04-12	OH	Car exhaust	<i>Alpha pinene included later in the day</i>
2019-04-13	Chlorine	Toluene	
2019-04-14			<i>Day for testing Cl production</i>
2019-04-15	OH	Toluene	
2019-04-16	Chlorine	Decane	<i>OH added later in the day</i>
2019-04-17	Chlorine	Decane	
2019-04-18	OH	Toluene	
2019-04-19			<i>ClNO₂ generation tested at different relative humidities</i>

Table 2: The experimental schedule.

The duration of this campaign was several days longer than originally planned. This was for a number of reasons: two days were added as a result of the preceding NO₃ oxidation campaign overrunning due to delays in the arrival of our instruments at PSI. Secondly, two test experiment days were added to ensure that we could sufficiently generate enough ClNO₂ for our experiments. We continued work on the campaign during the weekends, which increased the total number of chamber TNA days for this campaign from 11 to 17.

Preliminary results and conclusions

Our method for generating ClNO₂ in the chamber was successful. While the compound is thought to be formed in the atmosphere from interaction between chlorine-containing particles and N₂O₅, this is the first time, to our knowledge, that it has been successfully generated in this way in a laboratory setting. The resulting ClNO₂ behaved as it does in the atmosphere, building up in the dark and then breaking apart photolytically when the UV lights were switched on. Figure 1 shows this process from an experiment on 9th April. The ClNO₂ production starts as soon as the O₃ and NO₂ have been injected into the chamber, creating N₂O₅. The decrease can be seen as soon as the UV lights are turned on.

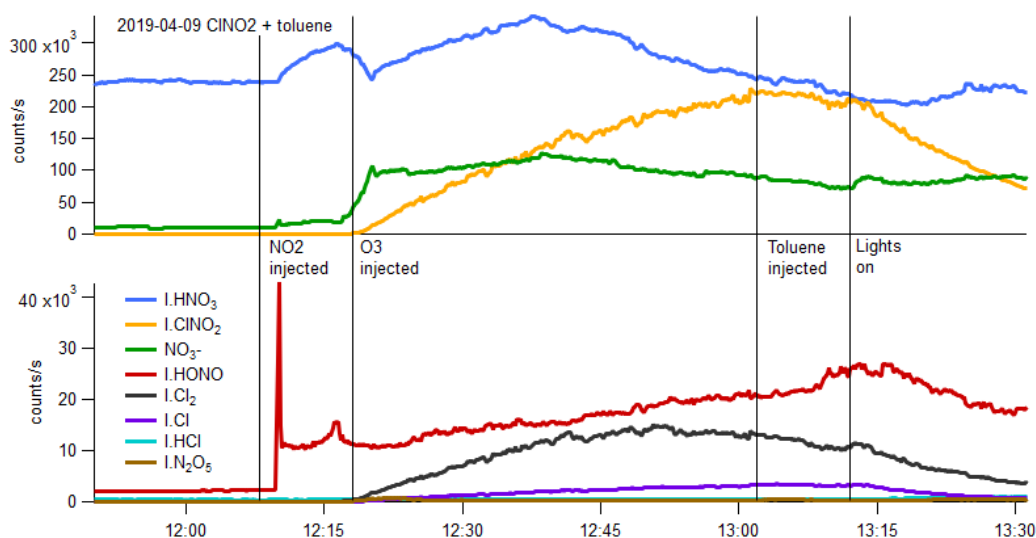


Figure 1: Key gas phase species measured by the FIGAERO-CIMS during the experiment on 9th April. The concentration of ClNO₂ can be seen rising after the injection of ozone, and falling again when the UV lights come on, due to photolysis.

Figure 2 shows the bulk aerosol composition, as measured by the Aerosol Mass Spectrometer (AMS) for the same experiment on 9th April. Here, the organic aerosol concentrations start to increase

dramatically when the lights come on, due to rapid oxidation of the toluene precursor by chlorine radicals.

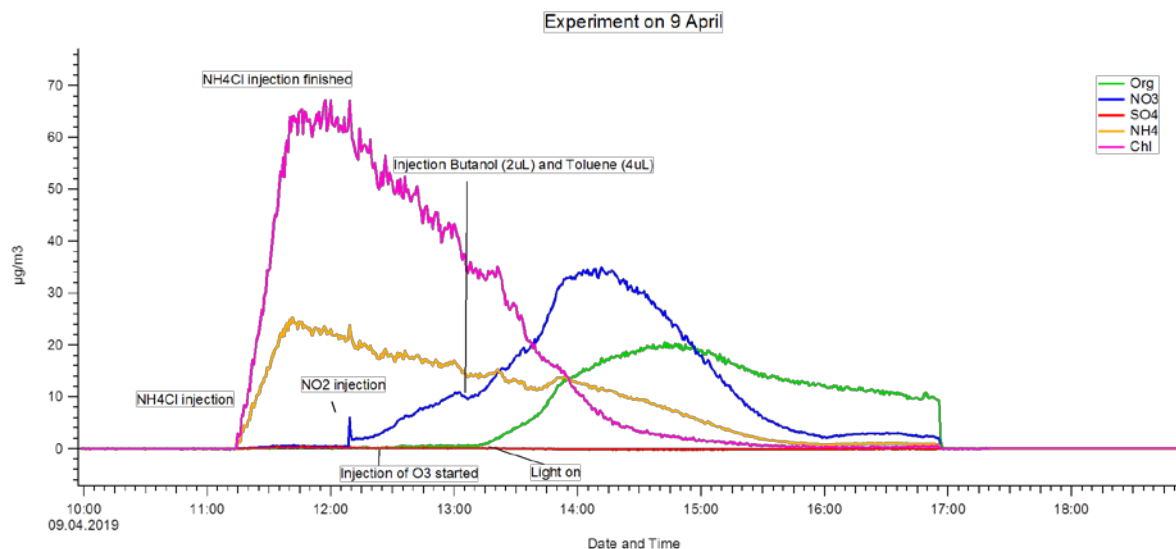


Figure 2: AMS results from the experiment on 9th April. Traces show concentrations of organic aerosol (Org), nitrate (NO₃), sulfate (SO₄), ammonium (NH₄) and chloride (Cl). The chloride and ammonium traces show the presence of the NH₄Cl seed. This decreases as N₂O₅ begins to form. When the chlorine radicals are liberated by the UV lights, there is a steep increase in the concentration of organic aerosol.

Figure 3 shows the mass spectra of SOA formed from car exhaust emissions, from both chlorine- and OH-initiated oxidation. Further analysis will show the similarities and differences between these mass spectra in more detail. Some chlorine-containing products have been identified; for example, C₂ClH₃O₂ is present in the gas phase. This has been observed in previous studies (e.g. Le Breton et al., 2018; Priestley et al., 2018) and was present in winter 2018-2019 during our field campaign in Delhi. This suggests that certain compounds may be identifiable as tracers for chlorine oxidation.

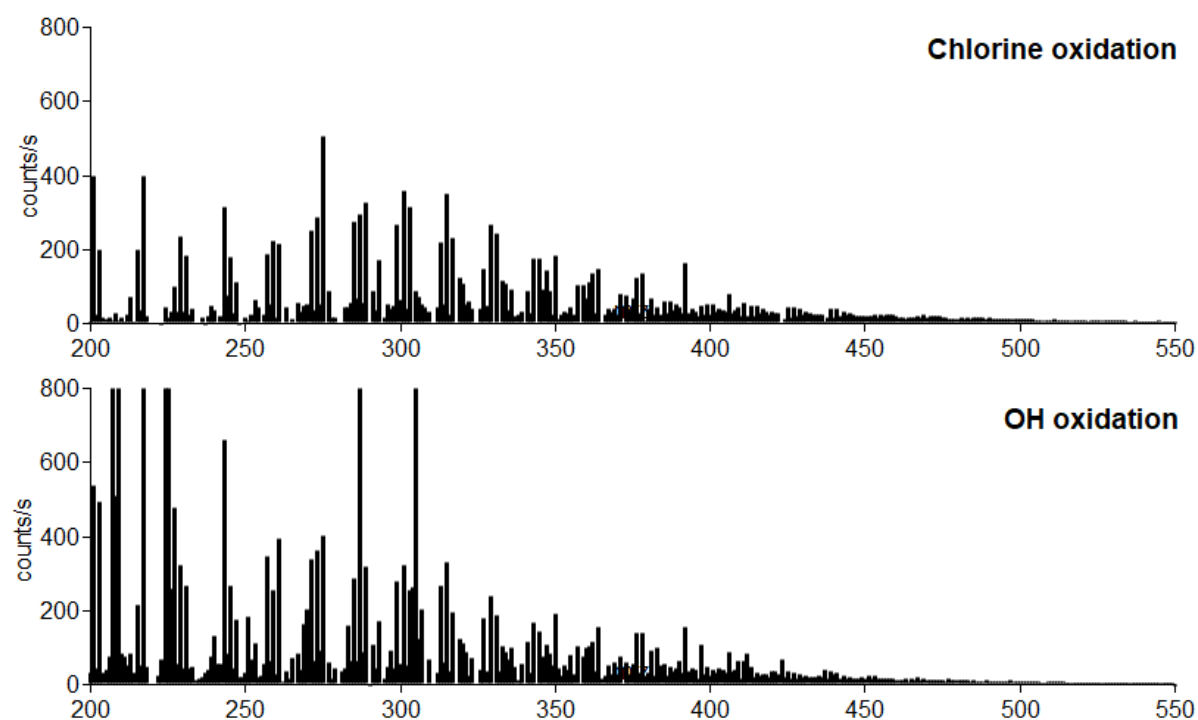


Figure 3: A comparison of the particulate mass spectra produced by chlorine oxidation and OH oxidation, as measured by the FIGAERO-CIMS.

Outcomes and future studies

While the analysis of this dataset is still in progress, early results suggest that it will provide a significant and important insight into the properties of chlorine oxidation products. This study highlights key differences between chlorine oxidation and the more typical OH oxidation pathway, and represents one of the first attempts to study atmospherically-relevant chlorine oxidation in a chamber. Early results from this study will be presented at an international conference (EAC, Gothenburg, in August 2019) and a number of journal publications based on these results are in progress. Furthermore, these results will contribute beneficially towards the interpretation of data from our fieldwork campaign in Delhi.

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