Bifunctional metal-pyridonate complexes as acceptorless dehydrogenation catalysts

Highlights
- Reaction of air pollutants on sea salt particles yields new chemical pathways.
- Chlorine activation oxidises volatile organic compounds and reduces the lifetime of the climate-forcing gas methane.
- Impacts for atmospheric composition and air quality, health and climate, especially in an island nation like the UK.

Overview
Natural and manmade processes emit huge quantities of gases. Were it not for oxidation chemistry occurring in the atmosphere, such emissions would build up to harmful concentrations. The emitted gases and their oxidation products affect atmospheric composition, air quality, environmental and public health, and influence climate. [1]

The removal of most trace gases from the atmosphere is initiated by molecules reacting with OH radicals, NO₃ radicals, or with ozone [e.g. 2]. Recently however, chlorine atoms (Cl) have been recognised as another important oxidant [3,4,5]. Chlorine atoms are extremely reactive: this means that even small levels of atomic chlorine can enhance atmospheric oxidation rates, and thereby also promote formation of tropospheric ozone and other secondary air pollutants.

Chlorine is activated in a two step process. This starts with the night-time reaction of N₂O₅ with chloride from particles of sea salt:

\[ \text{N}_2\text{O}_5 + \text{NaCl} \rightarrow \text{ClNO}_2 + \text{NaNO}_3 \]

Photolysis of ClNO₂ the next morning produces Cl atoms:

\[ \text{ClNO}_2 + \text{light} \rightarrow \text{Cl} + \text{NO}_2 \]

Note how the first step involves the reaction of a natural component of the atmosphere (sea salt aerosol) with N₂O₅, a species derived from primarily manmade emissions of nitrogen oxides (NOx).

Early studies conducted in the USA focussed on coastal regions, the assumption being that ClNO₂ production would be limited by the availability of sea salt. However, later studies observed ClNO₂ at inland locations 1000 km or more...
from the sea [3,4]. Our group has observed CINO₂ at two UK coastal sites and on almost every night when we made measurements in Leicester in central England [5,6]. Thus CINO₂ is widespread in the UK too. However its effects are not well understood. Since we inhabit a (somewhat) polluted island, CINO₂ chemistry could be especially important for the United Kingdom.

Methodology

Detection of CINO₂ at ambient concentrations requires a highly sensitive analytical technique: this project uses Chemical Ionisation Mass Spectrometry (CIMS). We have successfully deployed a CIMS instrument to measure CINO₂ and molecular chlorine (Cl₂) from the Leicester University campus and at two clean(ish) UK coastal sites. These existing field data necessarily represent “snapshots” in time – in contrast, the aim of this CENTA project is to produce a long-term CIMS data series for Leicester in order to capture the full seasonal cycle in chlorine chemistry. We also want to deploy the instrument in a coastal UK city (e.g. Plymouth) to compare and contrast CINO₂ production with that in Leicester in the centre of the country. Atmospheric chemistry models will be used to identify the ambient conditions under which CINO₂ is most likely to form, and to model the effects of chlorine chemistry on downstream atmospheric processes.

Further Reading


Funding

This research project is one of a number of projects in the Department. It is in competition for funding with one or more of these projects. Usually the project which receives the best applicant will be awarded the funding.

Home/EU Applicants

This project is eligible for a fully funded Graduate Teaching Assistant studentship which includes:

- A full UK/EU fee waiver for 4 years
- A stipend/salary package
International Applicants
This project does not have any funding for international students.

Application Instructions

The online application and supporting documents are due by Thursday 25th April 2019.

Any applications submitted after the deadline will not be accepted for the studentship scheme.

References should arrive no later than Monday 29th April 2019.

Applicants are advised to apply well in advance of the deadline, so that we can let you know if anything is missing from your application.

Required Materials

1. Online application form
2. Two academic references
3. Transcripts
4. Degree certificate/s (if awarded)
5. Curriculum Vitae
6. English language qualification (if English is not your first language)

Applications which are not complete by the deadline will not be considered for the studentship scheme. It is the responsibility of the applicant to ensure the application form and documents are received by the relevant deadlines.

All applications must be submitted online, along with the supporting documents as per the instructions on the website.

Please ensure that all email addresses, for yourself and your referees, are correct on the application form.