

Laser Flash Photolysis photooxidation study of N,N'-Dimethylformamide by Laser Induced Fluorescence and Proton Transfer Mass Spectrometry

Thomas Speak^{1*}, Diogo de Jesus Medeiros¹, Amy Peace¹, Dr. Mark Blitz¹, Prof. Paul Seakins¹

¹ School of Chemistry, University of Leeds. Leeds. UK

* Corresponding author: cm11ths@leeds.ac.uk

Dimethylformamide (DMF, (CH₃)₂NC(O)H) and its degradation products are important atmospheric pollutants. Amides such as DMF are found in biomass burning plumes and as biomass burning increases, the thermal degradation products will become increasingly important. There are already significant emissions of amides from natural sources (animal dung, decomposition) and agricultural emissions including from fertilizers and animal waste. With increased use of amine based Carbon Capture and Storage (CCS), there will be increased amide emissions, due to amides being degradation product of amines in the atmosphere and in CCS systems, and as such amides will become an increasingly significant pollutant.

The impact of DMF emissions is not purely due to its toxicity but also due to the photo oxidation of DMF having several potentially significant products including: imines, nitrosamines, nitramines and particularly methylisocyanate. The significance of these emissions is the potential carcinogenic nature of nitrosamines and nitramines, along with the toxicity of the other products.

There are only a small number of studies on amine and amide atmospheric degradation due to difficulties in studying such compounds. Nitrogen containing compounds in particular amines and amides tend to have low vapour pressures and other delivery issues that make having a well known concentration difficult.

Work by the Leeds group has assigned a room temperature rate coefficient of $(1.65 \pm 0.30) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for reaction with OH. This large rate coefficient means that photooxidation will be a significant removal of DMF versus heterogeneous uptake. The temperature profile of the bimolecular rate coefficients has been evaluated between RT and 500 °C. This work utilized bubbler systems to introduce consistent amounts of amide at high enough concentrations to allow for measurable rate coefficients. Hydrogen peroxide was used as an OH precursor. The concentration of OH was measured by Laser induced fluorescence and the decay of this was used to measure the removal rate by reaction with DMF.

The products of the photooxidation have also been studied via proton transfer reaction mass spectrometry. How the product distribution will be affected by high NO_x environments was evaluated by the addition of NO₂ to the reaction system. This is important as CCS plants are attached to power stations where the atmospheric environment includes high NO_x levels. These experiments confirmed the formation of nitrosamines and nitramines.