Experimental and Theoretical Study of the OH-Initiated Photo-oxidation of Formamide

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ABSTRACT: The kinetics of OH radical reaction with formamide was studied by the relative rate method employing proton transfer reaction—mass spectrometry detection at the European Photochemical Reactor in Valencia, Spain. The rate coefficient was determined to be $(4.5 \pm 0.4) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at $309 \pm 3$ K and $1013 \pm 1$ hPa. Isocyanic acid was observed as the sole product. The experimental results are supported by quantum chemical calculations and kinetic simulations using a master equation model. The calculated rate coefficient is independent of pressure at tropospheric conditions and can be accurately described by an Arrhenius expression having negative activation energy. The reaction is predicted to proceed exclusively via C–H abstraction.

1. INTRODUCTION

Formamide is a high production volume chemical (HPV) with an annual global production of several hundred thousand tons; the compound is used in the plastics and polymers industry as a solvent, plasticizer, or as a substance associated with a blowing agent used in the creation of foam. A comprehensive screening information data set initial assessment report (SIAR) is available from the Organization for Economic Cooperation and Development website. The 2007 SIAR concludes that with respect to human health the chemical is currently of low priority for further work. Although formamide possesses properties indicating a hazard for human health (genotoxicity, carcinogenicity, toxicity to reproduction, and developmental toxicity), exposure to humans is anticipated to be low and adequate risk management measures are in place. With respect to environment the SIAR states that formamide is currently of low priority for further work: “the chemical has a low hazard profile”.

Recently, formamide has been detected in the outgas of consumer products and the European Chemicals Agency (ECHA) has now placed formamide on the list of “Substances of Very High Concern”.

To the best of our knowledge, there are no reports on natural formamide emission to the atmosphere. Formamide has been identified as a primary product in methylvamine photo-oxidation with a yield of around 12%,4 and as a minor secondary product in the subsequent atmospheric degradation of methanimine, the major photo-oxidation product from methylvamine.5 Formamide has also been identified as a major product in 2-aminoethanol (MEA) gas phase photo-oxidation,6,7 and as a degradation product of aqueous MEA used for CO$_2$ capture at the postcombustion carbon capture facility at Technology Centre Mongstad.8 Large-scale implementation of MEA containing solvents in CCS facilities may therefore result in a significant perturbation of local atmospheric formamide content.

The Henrys Law constant ($K_{b}$) of formamide has not been measured, but standard estimation methods, as implemented in the EPI suite,9 places $K_{b}$ in the region between $1.5 \times 10^{-8}$ and $1.4 \times 10^{-9}$ atm m$^3$ mol$^{-1}$ at 298 K. Formamide is therefore predicted to partition to droplets in clouds and fog, but with a vapor pressure of around 9 Pa at 298 K the compound is otherwise not expected to partition to particles in the atmosphere.

Amides react fast with OH, Cl, and NO$_3$ radicals, but slowly with O$_3$.11 Reported OH rate coefficients fall in the range $(0.04 \pm 2) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$,11–17 Borduas et al.17 recently presented $k_{\text{NHCHO-OH}} = (4.4 \pm 0.5) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from relative rate experiments at 298 K. The amide Cl rate coefficients are about an order of magnitude larger than the corresponding OH values, whereas the scarce NO$_3$ rate coefficients are in the order of $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Alkyl amides show no absorption in the actinic region,18 and the main atmospheric sinks of formamide are therefore expected to be reactions with OH and NO$_3$ radicals resulting in a typical atmospheric lifetime of 2–3 days.11

Barnes et al. reported isocyanic acid as the sole product in formamide photo-oxidation.11 This was confirmed in the ADA-project,19 and more recently by Borduas et al.17 who also presented results from a theoretical study of the OH radical reactions of several amides besides formamide.

Supporting Information

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