MECHANISTIC STUDY OF THE ATMOSPHERIC PHOTOOXIDATION OF TRIMETHYLBENZENE IN THE SMOG CHAMBER

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Mixtures of 1,3,5-trimethylbenzene, propene, NO and NO_2 have been irradiated in our smog chamber. The temporal development of these precursors and many of the formed gaseous oxidation products have been measured and compared with model simulations based on the Master chemical mechanism. The fast reaction progress in the beginning of the experiment lets us assume that there is an additional OH radical source probably due to wall production of HONO. Higher production rates of photooxidants in the model despite lower reactivity point to some mechanistic deficiencies of the model.

1 INTRODUCTION

It is well documented that the oxidation of aromatics in the troposphere plays an important role in the generation of ozone (O_3) and secondary organic aerosols (SOA) [1]. In our smog chamber, experi-ments with 1,3,5-trimethylbenzene (TMB) were carried out showing the generation of SOA and the formation of oligomers within the particles upon ageing [2]. To understand the particle generation and their chemical composition gas phase chemistry needs to be understood. We operate several instruments at our smog chamber to monitor a large suite of different gas phase species. The results of these measurements are compared with a detailed description of the gas phase chemistry. This mechanism was extracted from the Master Chemical Mechanism Version 3 (MCM v3) which aims to reflect the most detailed current knowledge on hydrocarbon oxidation provided by kinetic and mechanistic studies [3].

2 EXPERIMENTAL

Experiments using irradiations of 600 ppb TMB, 150 ppb NO, 150 ppb NO_2, 300 ppb propene and 50% relative humidity were conducted in the smog chamber. Ozone is measured by UV-absorption (Environics S300), CO by UV-vacuum fluorescence (AeroLaser AL 5002), and NO via gas-phase chemiluminescence detection (Monitor Labs 9841A). A proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria) is used to monitor the parent HC and its oxygenated oxidation products. The measurement method is based on proton transfer reactions that cause a soft ionization with only little fragmentation, and a subsequent detection of the product ions in a quadrupole mass spectrometer.

3 RESULTS

The temporal evolution of some precursors and oxidation product species after irradiation of the initial mixture is shown in Figure 1a. The precursors TMB, measured as mass m/z 121 with PTR-MS, and NO decrease in the course of the reaction while ozone, CO and methylglyoxal (m/z 73) increase with time. Methylglyoxal starts to increase from the beginning of the experiment since it is directly formed in the first oxidation step of the TMB oxidation by OH radicals. In contrast, CO is formed by further oxidation of such primary oxidation products and increases therefore much later.

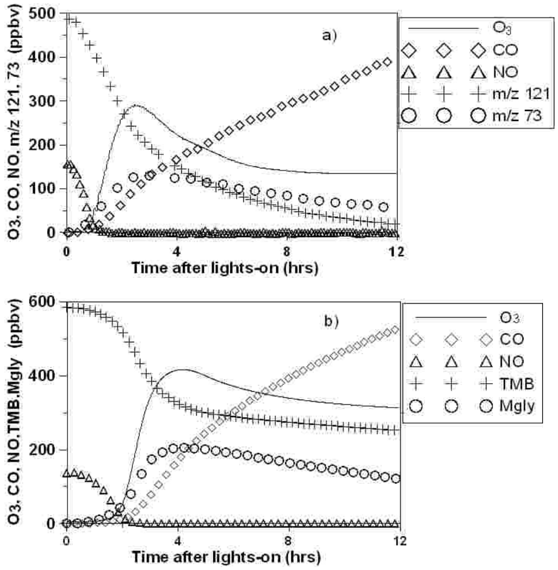

Fig. 1: Measured mixing ratios of gas phase species in smog chamber (a) and temporal development of these species simulated with the MCM (b).

The corresponding model simulations are shown in Fig. 1b. Obviously, the modelled degradation of TMB is slower in the beginning than the observed one. It is known from other chambers that HONO may be formed at the chamber walls leading to a higher concentration of OH radicals. Despite of this, the model simulates higher ozone and CO levels after a few hours, while TMB decreases at a slower rate. This points to deficiencies in the TMB degradation mechanism. Firstly, we now have to characterize our chamber with respect to its HONO formation rate at the walls and can then compare the observed and simulated formation of various intermediate species to find the causes of the discrepancies.

4 ACKNOWLEDGEMENT

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5 REFERENCES

[1] J.H. Seinfeld, S.N. Pandis, *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*, Wiley, New York (1998).

[2] M. Kalberer et al., Science **303**, 1659 (2004).

[3] http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html