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Evaluation of detailed mechanism (MCM v3) against smog chamber data of 1,3,5-trimethylbenzene

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Air quality simulation models are used to understand photochemical ozone production and to formulate appropriate and cost-effective control strategies to lower ozone levels. An important component of such air quality simulation models is the chemically mechanistic model which describes the gas-phase reactions leading to ozone and other secondary pollutants. The Master Chemical Mechanism (MCM) has been developed in a near explicit way using available kinetic and mechanistic literature data. Environmental chamber experiments, in which known amounts of smog precursors undergo reactions under controlled conditions can in theory be used to test individual mechanistic schemes. A special challenge in chamber experiments is the occurrence of chamber effects and their influence on the results. Photo-oxidation experiments were carried out in a 27-m3 Teflon chamber at PSI. The chamber was equipped with instruments to measure ozone, NO, NO2, CO, HCHO and H2O2. A proton transfer reaction mass spectrometer was used to follow the precursor concentration and organic oxidation products at a high time resolution. We also operated a wet effluent diffusion denuder - aerosol collector connected to an ion-chromatography mass spectrometer system to capture the inorganic ions and organic acids in the gas and aerosol phase which form in many atmospherically relevant photo-oxidation systems. In a first step experiments were carried out to determine smog chamber dependent reactions. Based on simpler systems like pure air, “NOx only” and CO addition a chamber characteristic auxiliary mechanism was developed. We then investigated the anthropogenically emitted precursor 1,3,5 trimethylbenzene (TMB) and compared the experimental results with the MCM. It was observed that the oxidative capacity of this aromatic system strongly depends on the initial VOC/NOx ratio. At low VOC/NOx ratios the reactivity of TMB towards OH radical reaction is underestimated while it is overestimated at high

VOC/NOx ratios. This coincides with the underestimation/overestimation of ozone at low/high VOC/NOx ratios, respectively. From the large set of oxidized species measured we then investigated possible deficiencies in the mechanism.