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Evaluation of the UNC toluene-SOA mechanism with respect to other chamber studies and key model parameters

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Abstract

In a companion paper by Hu et al. [2007. A kinetic mechanism for predicting secondary organic aerosol formation from toluene oxidation in the presence of NO_x and natural sunlight. Atmospheric Environment, doi:10.1016/j.atmosenv.2007.04.025], a kinetic mechanism was developed from data generated in the University of North Carolina's (UNC) 270 m^3 dual outdoor aerosol smog chamber, to predict secondary organic aerosol (SOA) formation from toluene oxidation in the atmosphere. In this paper, experimental data sets from European Photoreactor (EUPHORE), smog chambers at the California Institute of Technology (Caltech), and the UNC 300 m^3 dual-outdoor gas phase chamber were used to evaluate the toluene mechanism. The model simulates SOA formation for the 'low-NO_x' and 'mid-NO_x' experiments from EUPHORE chambers reasonably well, but over-predicts SOA mass concentrations for the 'high-NO_x' run. The model well simulates the SOA mass concentrations observed from the Caltech chambers. Experiments with the three key toluene products, 1,4-butenedial, 4-oxo-2-pentenal and *o*-cresol in the presence of oxides of nitrogen (NO_x) are also simulated by the developed mechanism. The model well predicts the NO_x time–concentration profiles and the decay of these two carbonyls, but underestimates ozone (O_3) formation for 4-oxo-2-pentenal. It well simulates SOA formation from 1,4-butenedial but overestimates (possibly due to experimental problems) the measured aerosol mass concentrations from 4-oxo-2-pentenal. The model underestimates SOA production from *o*-cresol, mostly due to its under-prediction of *o*-cresol decay. The effects of varying temperature, relative humidity, glyoxal uptake, organic nitrate yields, and background seed aerosol concentrations, were also investigated.

Keywords: Toluene; Kinetic mechanism; Aerosol modelling; Secondary organic aerosol (SOA)

1. Introduction

A number of kinetic models for predicting ozone (O_3) and secondary organic aerosol (SOA) formation from the photo-oxidation of aromatic hydrocarbons have been developed over the past 5 years. Stroud et al. (2004) used the Master Chemical Mechanism version 3.0 (MCMv3.0) and implemented more than 20 partitioning species that participated in SOA accumulation. They observed that nitro-aromatics and multifunctional organic nitrates are the most significant contributors to SOA. Griffin et al. (2002) and Pun et al. (2002) developed a gas phase mechanism and shunted both terpene and aromatic SOA accumulations into 10 surrogate species. Johnson and Jenkin et al. modified the master

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mechanism (Master Chemical Mechanism Version 3.1 (MCMv3.1) (Bloss et al., 2005)) to include aerosol phase reactions of aldehydes and hydroperoxides (Johnson et al., 2004). With a different scaling factor applied to aerosol mass concentrations observed in each experiment, they were able to model toluene SOA formation in the 195 m^3 European Photoreactor (EUPHORE) in the presence of natural sunlight and oxides of nitrogen (NO_x). To fit the toluene decay, an artificial source of OH was added and "tuned" to each experiment. Although many advances have been made, all of the above mechanisms do not address the recent discovery of particle phase reactions that may lead to very significant SOA formation from aromatic systems (Jang and Kamens, 2001; Kalberer et al., 2004).

Most recently, a kinetics mechanism developed at the University of North Carolina was designed to include particle phase oligomerization reactions (Hu et al., 2007). It also employs an alkyl peroxy radical reaction with gas phase toluene (Broyles and Carpenter, 2005) to remove toluene after OH has peaked in the system. Very good to reasonable simulations of NO_x, O_3 and particle time–concentration behaviours were observed for eight different experiments in the University of North Carolina's (UNC) 270 m^3 dual outdoor aerosol smog chambers, operated under natural sunlight. The most important particle phase compounds are glyoxal oligomers (GLYPOLY), ketene oligomers (SEED1) from the photolysis of the toluene OH reaction product, 2-methyl-2, 4-hexadienedial, organic nitrates (RONO2), acylperoxy nitrates (RCO-OONO2), methyl nitro-phenol analogues, C7 organic peroxides, and for the low concentration experiments, unsaturated hydroxyl nitro-acids. A glossary of terms is given in details in a companion paper (Hu et al., 2007). The distribution of products depends on different initial conditions. The starting conditions, depending on the experiment, had toluene that ranged from 0.1 to 1.0 ppmV and NO_x that ranged from 0.09 to 0.45 ppm. The maximum O_3 concentration ranged from 0.21 to 0.95 ppm. In this paper, the model's ability to simulate toluene SOA data reported by other investigators will be described and model sensitivity to different parameters will be discussed.

2. Discussion

2.1. Model simulations of toluene experimental data from the EUPHORE outdoor chamber system

Three toluene experiments were carried out in the 195 m^3 EUPHORE chamber A (Johnson et al., 2004; Bloss et al., 2005) and were simulated with the UNC toluene mechanism. These experiments were conducted on 24 September 2001, 25 September 2001 and 27 September 2001, and experimental conditions are listed in Table 1. The initial concentration ratio of toluene to NO ranged from 1.21 to 10.9 and temperatures ranged from 298 to 304 K. Aerosol mass concentrations were calculated from reported scanning mobility particle sizer (SMPS) aerosol volume concentrations by assuming a particle density of 1.4 $g\,cm^{-3}$(Bahreini et al., 2005). The mean particle diameter was 130 nm,

Table 1
Initial conditions of experiments conducted in EUPHORE chambers that are used to evaluate the UNC toluene mechanism

Experiment ID	Initial concentration (ppm)			Temp. (K)	Relative humidity (%)
	$[Tol]_0$[a]	$[NO]_0$	$[Tol]_0/[NO]_0$		
'low-NO_x' 092401	0.514	0.047	10.9	298–303	0
'mid-NO_x' 092701	0.496	0.122	4.07	298–303	0
'high-NO_x' 092501	0.512	0.422	1.21	298–304	0
1,4-Butenedial	$[Bud]_0$[a]	$[NO]_0$	$[Bud]_0/[NO]_0$		
	0.681	0.082	8.30	NA[b]	NA[b]
4-Oxo-2-pentenal	$[Oxo]_0$[a]	$[NO]_0$	$[Oxo]_0/[NO]_0$		
	0.302	0.186	1.62	NA[b]	NA[b]
o-Cresol	[*o*-cresol]$_0$	$[NO]_0$	[*o*-cresol]$_0$/$[NO]_0$		
	0.298	0.024	12.42	NA[b]	NA[b]

[a] Tol, Bud and Oxo stand for toluene, 1,4-butenedial and 4-oxo-2-pentenal, respectively.

[b] No temperature and relative humidity data were available for 1,4-butenedial, 4-oxo-2-pentenal and *o*-cresol. Model simulations were run at 298–303 K and 10% relative humidity.