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Short communication

Inter-comparison of the Regional Atmospheric Chemistry Mechanism (RACM2) and Master Chemical Mechanism (MCM) on the simulation of acetaldehyde

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ABSTRACT

Acetaldehyde (CH_3CHO) is a key player of atmospheric chemistry, an important air pollutant, and hence a major target of air quality modeling and management. The Regional Atmospheric Chemistry Mechanism (RACM) is a highly lumped gas-phase chemical mechanism that has been widely applied in atmospheric chemistry modeling studies. A significant update of the latest version of RACM (RACM2) is the addition of CH_3CHO as an explicit aldehyde species, facilitating the direct simulation of CH_3CHO. In this study, we compared the performances of RACM2 and Master Chemical Mechanism (MCM; v3.3.1) on the simulation of CH_3CHO. Zero-dimensional chemical box models based on these two independent mechanisms were prescribed to a polluted scenario to simulate the evolution of ozone (O_3), hydroxyl radical (OH), $C_2H_5O_2$ (ETHP) and CH_3CHO, as well as their detailed chemical budgets. Overall, both mechanisms agreed with the simulation of O_3 and OH, but the RACM2 model simulated significantly higher levels of ETHP and CH_3CHO than the MCM model. The difference in the chemical kinetic data in both mechanisms is not the reason for this discrepancy. The oversimplification of the lumped peroxy acyl radicals (RCO_3) and ≥C3 aldehydes chemistry of RACM2 should be responsible for its higher simulated ETHP and CH_3CHO. We caution the use of RACM2 or any other highly aggregated chemical mechanism for the simulation of $C_2H_5O_2$ and CH_3CHO. Better methods are needed to represent the chemistry of peroxy acyl radicals and ≥C3 aldehydes for aggregated chemical mechanisms. More experiments are required to directly validate and further improve the current chemistry mechanisms.

1. Introduction

Chemical transport models (CTMs) have proved their great values in understanding the evolution of atmospheric environment and air quality, and thus support the formulation of air quality management strategies (Stockwell et al., 2012). It couples the existing knowledge of emissions, atmospheric chemistry and physics to simulate the chemical degradation and transport of atmospheric constituents (Jacobson et al., 1996). A principal component of CTMs is the chemical mechanism that compiles the available state of the art kinetic data to represent the complex chemical processes occurring in the atmosphere (e.g., Dodge, 2000). Given the complexity of the real atmospheric chemistry, most mechanisms are developed on a simplification way by lumping many organic species with similar molecular structure or reactivity into one model species (Atkinson et al., 1982; Leone and Seinfeld, 1984; Whitten et al., 1980). Such simplification reduces the request of computational resources, making air quality modeling a reality, but may inevitably introduce additional uncertainties to modeling studies (Dodge, 2000; Jimenez et al., 2003).

The Regional Atmospheric Chemistry Mechanism (RACM) is one of the most widely used lumped atmospheric chemistry mechanisms. It was developed in 1990s on the basis of the Regional Acid Deposition Model version 2 (RADM2) (Stockwell et al., 1990, 1997), and has been recently updated to its second version (RACM2) in 2010s (Goliff et al., 2013). It was designed to simulate the chemical evolution of atmosphere under various tropospheric conditions, from the Earth's surface to the upper troposphere and from clean remote area to polluted regions (Goliff et al., 2013; Stockwell et al., 1997). The RACM2 contains 363 chemical reactions to represent the gas-phase chemistry of 120 model species (Goliff et al., 2013). Owing to its wide applicability and small computational resource request, RACM has been adapted to a variety of atmospheric models, from zero-dimensional chemical box model to three-dimensional chemical transport models, to investigate several essential aspects of tropospheric chemistry, including but not

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limited to, ozone formation (Gross and Stockwell, 2003), peroxy acetyl nitrate (PAN) budget (Fischer et al., 2014), secondary organic aerosol formation (Sarwar et al., 2013), and radical chemistry (Hofzumahaus et al., 2009; Lu et al., 2012). The performance of RACM2 on the simulations of O_3 and NOx has also been tested against field measurement data (Goliff et al., 2013).

Acetaldehyde (CH_3CHO) is a key ingredient in the atmospheric chemistry as an important RO_2 radical reservoir and an O_3 precursor (Cheng et al., 2014). It is also a common air toxin that has detrimental effects on human health, and is hence among the targets of air pollution studies (Yang et al., 2017) In the ambient atmosphere, CH_3CHO is either directly emitted from various natural and anthropogenic primary sources or produced from the photochemical degradation of a number of reactive hydrocarbons (Anderson et al., 1996; Atkinson and Arey, 2003). In the RACM2, CH_3CHO has been added as an explicit aldehyde species in addition to formaldehyde, the only explicit aldehyde in the first version of RACM (Goliff et al., 2013; Stockwell et al., 1997). This progress facilitates the direct simulation of CH_3CHO formation by air quality models. However, the simplification of the chemistry of higher aldehydes in this lumped mechanism may introduce some uncertainty to the explicit CH_3CHO simulation. In RACM2, all the aldehyde compounds with ≥3 carbon atoms are lumped into one model species (referred to as "ALD" in the mechanism). As shown in Fig. 1, the further degradation of ALD, not only photolysis but also the oxidation by OH, ultimately yields an ethyl peroxy radical ($C_2H_5O_2$; referred to as "ETHP" in the mechanism) as a reaction intermediate. This is only true for the propyl aldehyde, but is not the case for the other higher aldehydes (e.g., ≥C4 aldehydes). Such oversimplification of the "ALD" chemistry would probably result in an overestimation of ETHP, a key intermediate of CH_3CHO formation. Consequently, it is of great interest and importance to examine the performance of the RACM2 on the explicit simulation of $C_2H_5O_2$ radical and CH_3CHO.

In the present work, we designed theoretical simulation studies to compare the performances of RACM2 and another widely applied mechanism, namely Master Chemical Mechanism (MCM v3.3.1), on the simulations of $C_2H_5O_2$ and CH_3CHO. MCM is a nearly explicit chemistry mechanism that describes the atmospheric degradation of ~6700 organic species by ~17000 chemical reactions (Jenkin et al., 2003, 2015; Saunders et al., 2003). Both mechanisms are based on the state-of-the-art chemistry knowledge but are compiled with different methods (lumped vs. explicit). We used a zero-dimensional chemical box model that was set up with these two independent chemical mechanisms. The model was initialized with a typical polluted scenario observed in urban Beijing in the summer of 2008. We compared the modeling results of O_3, HOx, $C_2H_5O_2$ and CH_3CHO, as well as their chemical budgets. Overall, both mechanisms agree reasonably well with the simulation of O_3 and HOx, but the RACM2 simulated much stronger production of $C_2H_5O_2$ and CH_3CHO than the MCM v3.3.1. This study elucidates the large difference between RACM2 and MCM in the CH_3CHO simulation, and chamber studies are urgently needed to directly validate and further improve the current atmospheric chemistry mechanisms.

2. Model configuration and observational data

The model used in the present study was the same to the one we have deployed in many previous studies (Xue et al., 2013, 2014a, 2014b, 2015, 2016). It is a zero-dimensional box model built upon detailed atmospheric chemistry mechanisms, and aims at simulating the chemical evolution of atmosphere based on the state of the art chemistry knowledge. Besides, several physical processes such as dry deposition and mixing dilution of atmospheric constituents in the planetary boundary layer were also represented in the model (Xue et al., 2014a). In this study, the chemistry module of this model was switched between RACM2 and MCM v3.3.1 to examine the difference of the modeling results, which was believed to be only due to the difference in the chemistry mechanisms. Detailed description of the model configuration can be found elsewhere (Xue et al., 2014a, 2016).

We selected an urban pollution scenario for model simulations as the abundant photochemical precursors (especially VOCs) have potential to produce more aldehydes (not only CH_3CHO but also higher aldehydes). This facilitates a good comparison between the two sets of models for the simulation of photochemical production of CH_3CHO, the precursors of which are relatively few. The case was the photochemical pollution episode we observed at a suburban site of Beijing on July 22, 2008 (Wang et al., 2010). Figure S1 shows the measured time series of major air pollutants and meteorological parameters during this case, and Table S1 summarizes the observed daytime average concentrations of major VOC species. A glance of these measurement data illustrates elevated levels of photochemical precursors as well as the extensive O_3 production. The measurement techniques, pollution characteristics, and physical and chemical causes of this episode have been described in Wang et al. (2010) and Xue et al. (2014b). In the present study, we just used these observational data to prescribe our models to a typical urban pollution condition, nor simulate the chemical processes for this particular pollution episode.

The models were initialized with the daytime average concentrations of CO, NO, NO_2, SO_2, methane, C_2-C_{10} non-methane hydrocarbons (see Table S1 for the detailed initial conditions for both models; note that we didn't have continuous observations of VOCs in this case), and were constrained by the measured continuous diurnal data of meteorological parameters, e.g., temperature and relative humidity. The photolysis frequencies (J values) of photolytic species were calculated as a function of solar zenith angle within the model with an assumption of clear sky conditions (Saunders et al., 2003). The models simulated the temporal evolution of O_3, HOx, $C_2H_5O_2$ and CH_3CHO, and also computed the detailed chemical budgets of these species (refer Xue et al., 2016 for the chemical budget calculation methods). The models were performed for a 24-h period with 08:00 local time (LT) on 22nd July 2008 as the initial time.

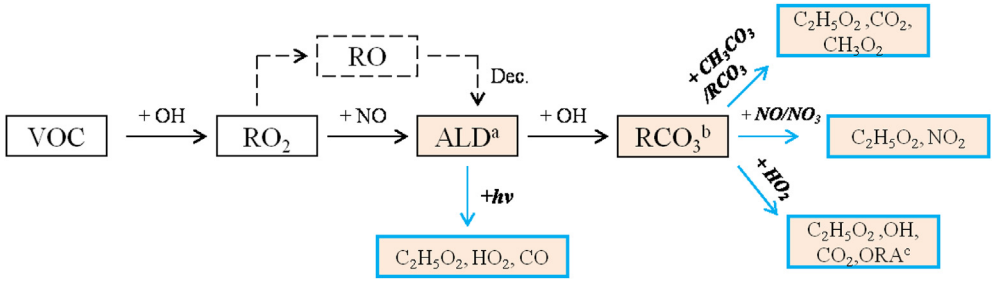

Fig. 1. Representation of the chemistry of the ≥C3 higher aldehydes in the RACM2. [(a)]ALD and [(b)]RCO_3 are lumped model species, and account for ≥C3 aldehyde species and ≥C3 acyl peroxy radicals, respectively.