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 $\geq C3$ 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 $\geq C3$ 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

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., $\geq$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.
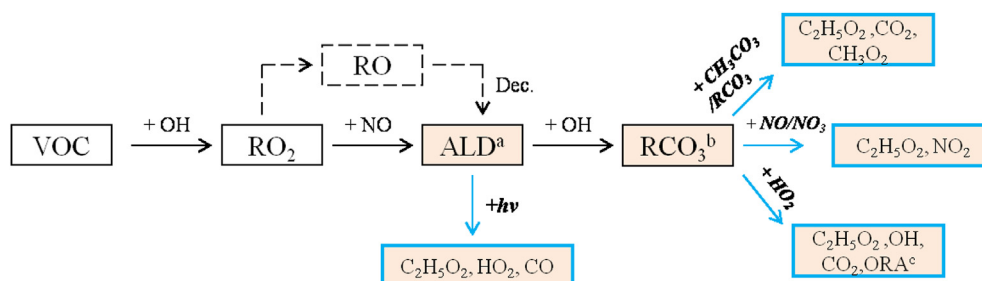

Fig. 1. Representation of the chemistry of the $\geq$C3 higher aldehydes in the RACM2. [a]ALD and [b]RCO_3 are lumped model species, and account for $\geq$C3 aldehyde species and $\geq$C3 acyl peroxy radicals, respectively.
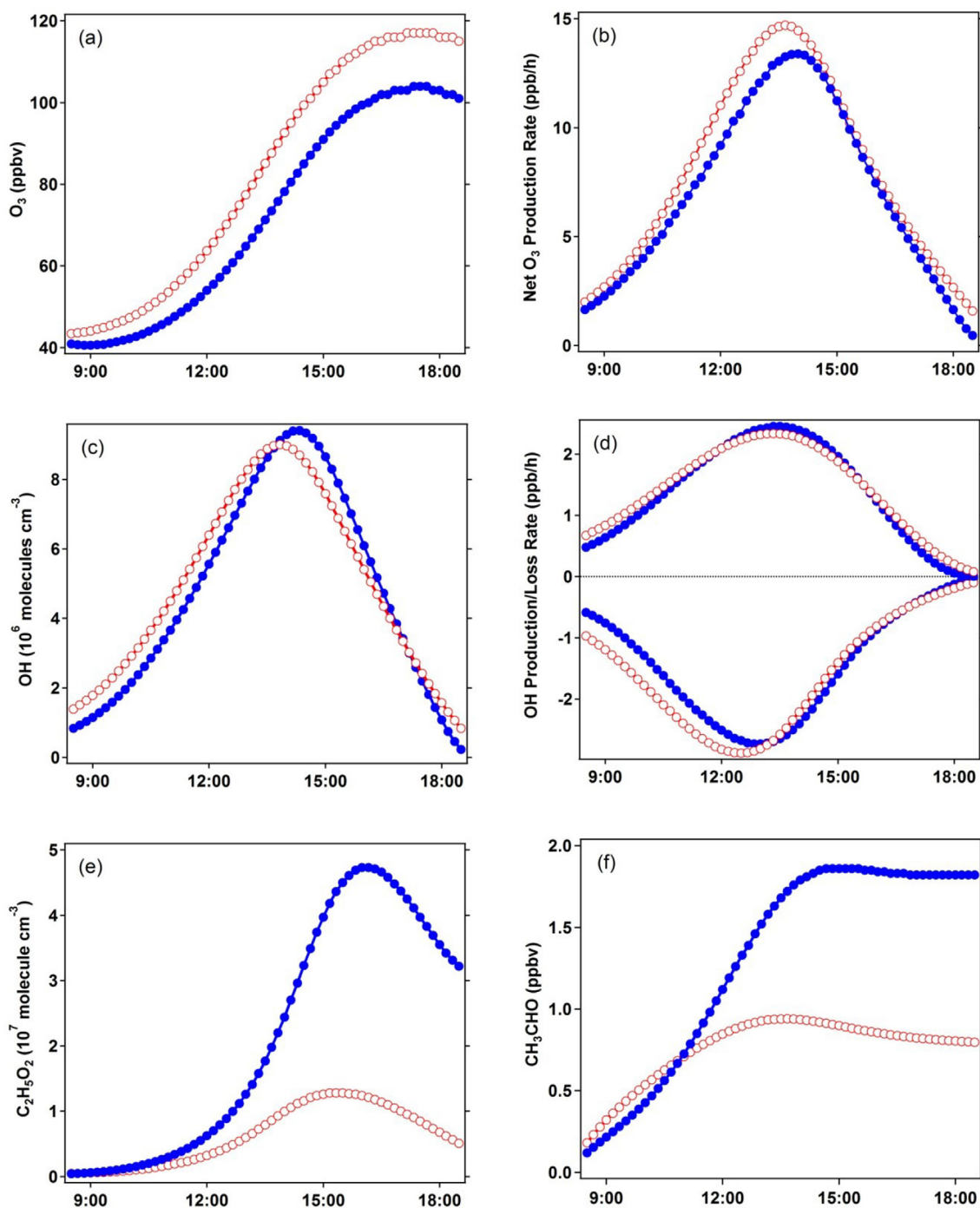
Fig. 2. Comparison of the model-simulated daytime evolution curves of (a) O_3, (b) net O_3 production rate, (c) OH, (d) OH production and destruction rates, (e) $C_2H_5O_2$, and (f) CH_3CHO between RACM2 (blue color) and MCMv3.3.1 (red color). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussions

3.1. Simulation results on O_3 and OH

Fig. 2a shows the model-simulated daytime evolution of ozone concentrations for the two mechanisms. Both RACM and MCM models predicted the significant photochemical ozone production, with daytime O_3 increments (derived from the difference between the maximum and initial concentrations) of 60 and 73 ppbv, respectively. The MCM model tends to produce more O_3 compared to RACM, and the differences are generally within 13%. Fig. 2b shows the fairly good

agreement between the two mechanisms on the calculated net O_3 production rates. The MCM yields slightly higher net O_3 production rates than RACM2 ($< 20\%$) during the morning and early afternoon period (before 13:00 LT), whilst the modeling results in the late afternoon are excellently consistent between each other. The difference in the daytime average net O_3 production rates between both mechanisms was 11%. We also examined the detailed chemical budgets of O_3 formation and losses, and found that the results of both mechanisms were essentially the same (see Figure S2). Overall, the comparison illustrates the fair agreement between MCM and RACM on the simulation of photochemical O_3 formation.

The OH radical is the predominant oxidant in the atmosphere and hence plays a central role in the tropospheric chemistry. It is crucial to evaluate the performance of current chemical mechanisms on the simulation of the OH chemistry. Fig. 2c–d document the simulation results of both RACM2 and MCM v3.3.1 on the ambient OH and its chemical rates. Clearly, both mechanisms agreed well with each other on the OH simulation. They predicted similar variation patterns and concentrations of OH radical, and the difference in the daytime average OH levels was 4.2%. In addition, the model-computed formation and loss rates of OH are also generally consistent between the two mechanisms (see Fig. 2d). The detailed chemical budgets of OH derived from both mechanisms were also essentially the same, as shown in Figure S3. The OH source was dominated by the reaction of HO_2 with NO, and the OH loss was governed by the oxidation of VOCs and CO. It should be noted that the models here were not constrained by observations of some important radical reservoirs, such as HONO and carbonyls, and thus the OH simulation results may be subject to some uncertainties. Nonetheless, the objective of the present study was just to evaluate the performance of both mechanisms via theatrical studies, rather than to reproduce the absolute concentrations of OH radicals.

Ozone formation and radical chemistry are two essential areas of atmospheric chemistry and major targets of current air pollution modeling studies. The above inter-comparison indicates that the RACM2 and MCM models work consistently to simulate the O_3 formation and OH chemistry under typical polluted urban conditions. We also examined the modeling results of HO_2, RO_2, RCO_3 radicals, and PAN (Figure S4). Overall, both mechanisms agreed reasonably well on the simulations of these species. The differences between RACM2 and MCM in the daytime average (maximum) levels of HO_2, RO_2, RCO_3 and PAN were 4.3% (10%), 26% (40%), 14% (28%) and 8.3% (4.4%), respectively. In the following section, we will check the performance of the two chemical mechanisms on the simulation of $C_2H_5O_2$ and CH_3CHO.

3.2. Simulation results on $C_2H_5O_2$ and CH_3CHO

Fig. 2e depicts the diurnal variation curves of $C_2H_5O_2$ radical simulated by the RACM and MCM models. Apparently, the RACM2 produced much higher $C_2H_5O_2$ levels compared to the MCM v3.3.1. For example, RACM2 predicted a maximum $C_2H_5O_2$ concentration in the afternoon of 4.7×10^7 molecules cm^{-3}, which is about 3.7 times higher than the peak value of MCM (1.3×10^7 molecules cm^{-3}). We checked the rate constants of the $C_2H_5O_2 + NO$ reaction in both mechanisms, and found that the value in RACM2 was slightly lower than that in MCM v3.3.1. We performed a "revised RACM2" sensitivity model run with the rate constant adjusted to the MCM value, and the changes in the modeling results were negligible (< 1%; Figure S5). This means that the difference in the kinetic data between the two mechanisms is not the reason for the discrepancy. The simplified lumping treatment of the ≥C3 aldehydes chemistry in the RACM2 should be responsible for its higher simulated levels of $C_2H_5O_2$. As mentioned above, all of the aldehyde species with more than 3 carbon atoms are lumped into one aldehyde species (ALD) in RACM2, and the chemical degradation of ALD produces $C_2H_5O_2$ radicals (Fig. 1). Actually, only propyl aldehyde can undergo photolysis and reactions with NO, HO_2 and RO_2 radicals to yield $C_2H_5O_2$, whilst the other higher aldehydes (i.e. ≥C4 aldehydes) would not produce $C_2H_5O_2$ (i.e., the reactions of C_n aldehyde produce $C_{n-1}H_{2n-3}O_2$ radical). This would explain the much higher $C_2H_5O_2$ simulated by RACM2 compared to the explicit MCM.

Fig. 3 presents the $C_2H_5O_2$ formation rates from individual major source pathways and the comparison between RACM2 and MCM v3.3.1. Both mechanisms predicted similar $C_2H_5O_2$ formation budget. Specifically, the reactions of acyl peroxy radicals (RCO_3; an intermediate of the reaction of ALD with OH) with NO dominated the formation of $C_2H_5O_2$, followed by the reactions of alkyl peroxy radicals with NO, reactions of OH with ethane, and photolysis of ALD. Note that

the ALD and RCO_3 denote the ≥C3 aldehydes and ≥C3 acyl peroxy radicals in the RACM2, but propyl aldehyde and $C_2H_5CO_3$ radical in the MCM v3.3.1. Moreover, the RACM-simulated $C_2H_5O_2$ formation rates from $RCO_3 + NO$ reactions and ALD photolysis were much higher than those from $C_2H_5CO_3 + NO$ reactions and propyl aldehyde photolysis predicted by the MCM model. This further confirms that the higher simulated $C_2H_5O_2$ by the RACM2 should be due to the lumping of other higher aldehydes into the ALD species.

We then examined the modeling results of CH_3CHO, a major product of further reactions of $C_2H_5O_2$ radicals. As expected, Fig. 2f shows the large discrepancy in the model-simulated CH_3CHO levels between the two mechanisms. In general, the RACM2 model gave about 2 times higher CH_3CHO concentrations than the MCM v3.3.1 in the afternoon. The simulated peak concentrations of CH_3CHO were ~1.9 ppbv and ~0.9 ppbv for the RACM2 and MCM v3.3.1, respectively. Fig. 4 shows the comparison of CH_3CHO formation rates from the major source pathways. Both mechanisms showed similar chemical budgets of CH_3CHO production, but the rates calculated by RACM2 were much higher than those of MCM v3.3.1. The reactions of $C_2H_5O_2 + NO$ dominated the CH_3CHO production, with mean contributions of 57% and 71% for MCM and RACM2. The RACM2-simulated CH_3CHO formation rate from the $C_2H_5O_2 + NO$ reaction was on average 2.5 times higher than that of MCM v3.3.1. Therefore, the higher CH_3CHO predicted by RACM2 should be mainly owing to its higher simulated $C_2H_5O_2$ levels.

As discussed above, although RACM2 and MCM generally agreed with each other on the simulations of O_3 formation and HOx chemistry, large discrepancy existed on the prediction of CH_3CHO and $C_2H_5O_2$. The simplification of ≥C3 higher aldehydes chemistry in RACM2 may be responsible for this discrepancy. It would be useful if this potential 'overestimation' of CH_3CHO by RACM2 could be corrected according to the chemical kinetics data and atmospheric conditions. The exact fraction of propyl aldehyde in the total ≥C3 aldehydes (the lumped 'ALD' species) is required to quantify and correct the 'overestimation' for the true $C_2H_5O_2$ radical. However, the fraction of propyl aldehyde to the ALD may vary from place to place and mainly depends on the VOC compositions. It is thus difficult to correct for $C_2H_5O_2$ and CH_3CHO with a uniform equation unless propyl aldehyde is treated as an explicit species in the mechanism. Besides, most of the highly lumped chemical mechanisms move organic carbon into the model species that represents acetaldehyde or a generalized aldehyde. It is not just a RACM2 problem but may be a general problem for the highly aggregated chemical mechanisms. Therefore, we recommend that both RACM2 and MCM should be suitable for the simulations of O_3 and HOx, but their performances for $C_2H_5O_2$ and CH_3CHO are quite different and need further evaluation. Further refinement of the representation of aldehyde chemistry is required for the RACM2 (or any other highly lumped mechanism) to fulfill the explicit simulation of CH_3CHO, and more experiments are urgently needed to directly validate and improve the current atmospheric chemistry mechanisms.

4. Conclusions

We conducted theoretical modeling analyses to compare the performances of RACM2 and MCM on the simulation of O_3, HOx, $C_2H_5O_2$ and CH_3CHO. Under a typical urban pollution condition, both mechanisms predicted reasonably consistent modeling results for O_3 and HOx, but the RACM2 produced significantly higher levels of $C_2H_5O_2$ and CH_3CHO than MCM v3.3.1. The lumping of ≥C3 aldehydes and the simplification of its subsequent chemistry in RACM2 should be responsible for the discrepancy. It is difficult to correct this uncertainty for different atmospheric conditions with a uniform equation, as it highly depends on the VOC compositions and may vary from place to place. We recommend the applicability of RACM2 and MCM to simulate the O_3 formation and HOx chemistry, but their performance on the CH_3CHO simulation need further evaluation. Additional update of the
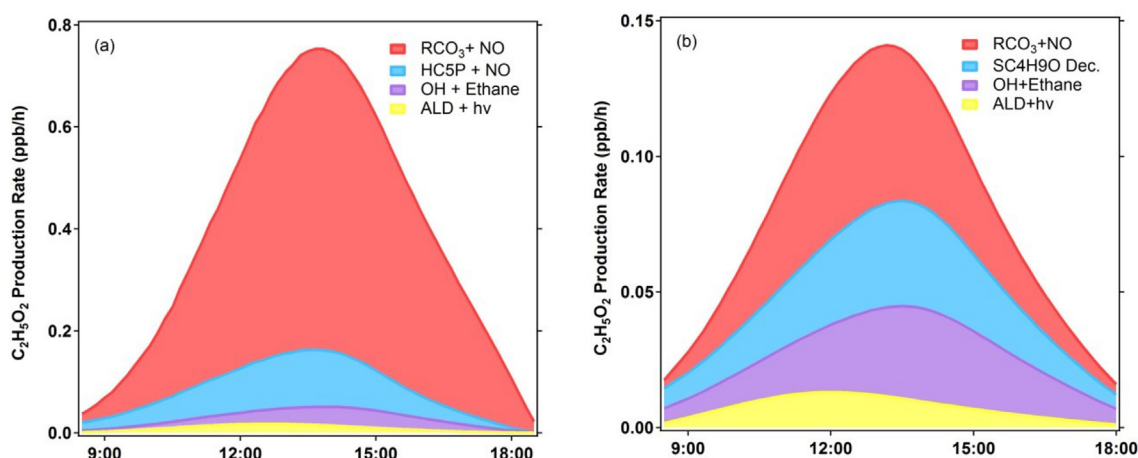
Fig. 3. Model-calculated formation rates of $C_2H_5O_2$ from the major source pathways by (a) RACM2 and (b) MCMv3.3.1 models.
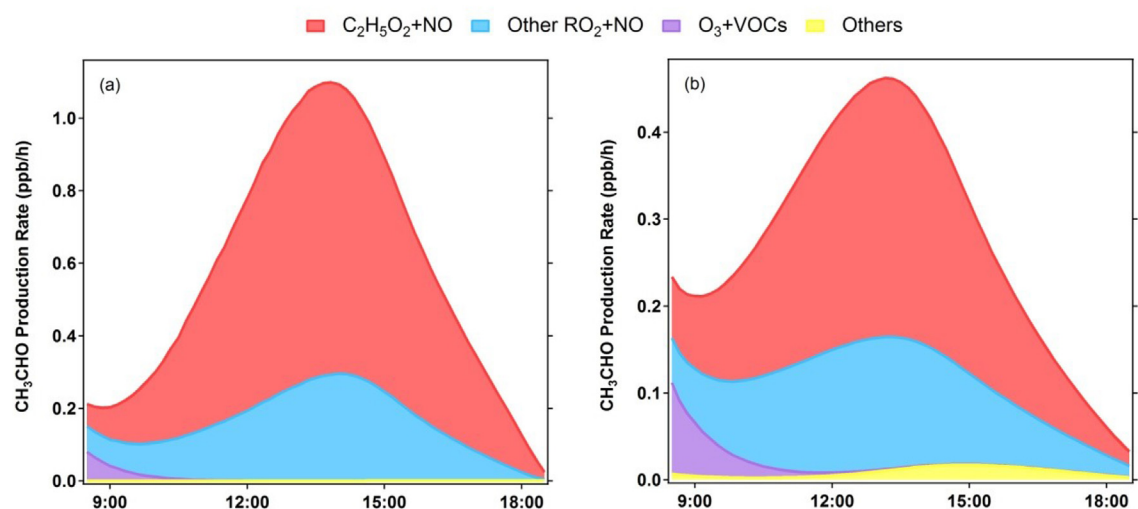

Fig. 4. Model-calculated formation rates of CH_3CHO from the major source pathways by (a) RACM2 and (b) MCMv3.3.1 models.

representation of higher aldehyde chemistry is needed for the RACM2 (or any other highly lumped mechanism) for explicit simulation of atmospheric CH_3CHO. This study is a pure modeling work. Despite the significant difference between the two mechanisms, it is somewhat hard to say which one is correct without validation against experimental data. Chamber experiments are urgently needed to directly validate and further improve these mechanisms.

Acknowledgement

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2018.05.013.

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