Evaluation of the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2)

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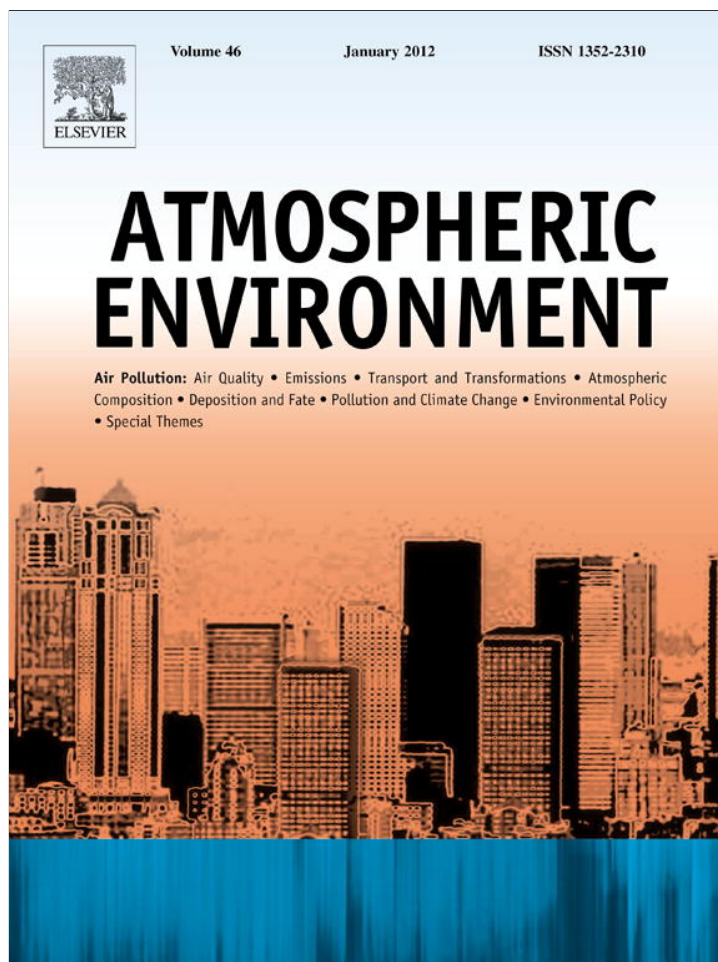**138** PUBLICATIONS **4,451** CITATIONS

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The regional atmospheric chemistry mechanism, version 2

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HIGHLIGHTS

► The RACM2 mechanism includes updated reactions, rate constants and product yields.
► It has been tested against environmental chamber data.
► The aromatic chemistry was expanded to include a greater number of species.
► The reaction mechanism for isoprene was expanded.

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ABSTRACT

The Regional Atmospheric Chemistry Mechanism (RACM) is a gas-phase chemical mechanism that is widely used for the modeling of regional atmospheric chemistry. Much new data has been published since the original RACM was completed (Stockwell et al., 1997). The RACM mechanism was updated to create the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2). Like the RACM1 mechanism, the RACM2 mechanism is designed to simulate remote to polluted conditions from the Earth's surface through the upper troposphere. The RACM2 mechanism includes updated reaction schemes, rate constants and product yields. It has been tested against environmental chamber data and compared with previous RACM scenario simulations. The aromatic chemistry was expanded to include a greater number of species with highly revised reaction schemes. The reaction mechanism for isoprene was expanded to include a more explicit treatment of methyl vinyl ketone. Alcohols were speciated to more accurately reflect peroxy–peroxy reactions in the remote atmosphere. Acetone was speciated due to its importance in the upper troposphere.

1. Introduction

Atmospheric chemistry models are used for research and the development of public policy for air quality. Representative tropospheric models include the Community Multi-scale Air Quality Model, CMAQ, ((Byun et al., 1998); the Weather Research and Forecasting Model with Chemistry, WRF/Chem (Grell et al., 2005); and the GEOS-CHEM (Bey et al., 2001)). These models are used to make numerical estimates of the formation and loss of air pollutants such as ozone, particulate matter, acid deposition, toxic air pollutants and mercury. These applications require chemical mechanisms that include nitrogen oxides, reactive organics and sulfur containing compounds. The development of chemical mechanisms is difficult because there is an extremely high number

of organic compounds present (Fuentes et al., 2000; Stockwell et al., 2012). A comprehensive mechanism consisting of explicit chemical reactions for every known compound under the wide-range of tropospheric and stratospheric conditions for all levels of the Earth's atmosphere would consist of millions of chemical species and reactions (Szopa et al., 2005). There are insufficient computer resources to simulate a mechanism this large except in a box model because Eulerian models require that for every prognostic species a differential equation at each grid point must be numerically solved.

The first widely used chemical mechanisms for air quality modeling were first developed for the simulation of highly polluted urban areas such as Los Angeles. The early versions of the Carbon Bond mechanism (Whitten et al., 1980), Atkinson et al. (1982) and Leone and Seinfeld (1984) are significant examples. These mechanisms were used to simulate atmospheres with very high NO_x concentrations and this allowed many simplifications including the over-simplification of peroxy–radical–peroxy–radical reactions that lead to the formation of hydrogen peroxide and organic peroxide.

During the early 1980s acid deposition became a concern of international proportions and several regional air quality models were developed (Chang et al., 1987; Venkatram et al., 1988). This required the development of chemical mechanisms that could be used to simulate a much wider range of pollutant concentrations. Regional mechanisms were required to simulate pollutant concentrations that ranged from background continental to highly polluted urban conditions. The first mechanisms of this series, the Regional Acid Deposition Model mechanism (RADM, Stockwell, 1986) and the Regional Acid Deposition Model mechanism, version 2 (RADM2, Stockwell et al., 1990) were developed to meet this need. They had much more detailed chemistry for the gas-phase formation of atmospheric acids and the formation of hydrogen peroxide and organic peroxides that were important for the simulation of the aqueous-phase oxidation of sulfur dioxide. The RADM2 mechanism was incorporated into models such as the Regional Acid Deposition Model (Chang et al., 1987), the Community Multi-scale Air Quality Model (CMAQ; O'Neill and Lamb, 2005), 3-dimensional Meteorology-Climate-Chemistry Model (MCCM; Grell et al., 2000) and the Weather Research and Forecasting Model (WRF; Grell et al., 2005). The RADM2 model and its mechanism have had a major impact on subsequent research; the RADM2 model has receive an average of 17.73 citations per year in the Web of Science for a total of 461 citations from the time it was published and the RADM2 mechanism has receive an average of 17.70 citations per year for a total of 407 citations since it was published to date.

Because of the wide-use of the RADM2 mechanism and the availability of new laboratory data the mechanism was updated to create the Regional Atmospheric Chemistry Mechanism (RACM, Stockwell et al., 1997). One important source of new data for development of the RACM2 was European tropospheric chemical research programs (Geiger et al., 2002). The RACM has been widely used with an average of 22.75 citations per year in the Web of Science for a total of 364 citations as of January 2011. The purpose of the development of the new Regional Atmospheric Chemistry Mechanism, version 2 (RACM2) is to provide a new mechanism with condensed atmospheric chemistry that can be used for 3-D air quality modeling. The new RACM2 has been implemented in a beta-test version of CMAQ and its performance is under evaluation by the U.S. Environmental Protection Agency (EPA).

For practical modeling applications the chemical mechanism must be sufficiently condensed for its host model to run efficiently while being faithful to the known chemistry and with sufficient detail for its purpose. Simplification of the organic chemistry is made by aggregating large numbers of compounds with similar structure, reactivity and products into a limited number of grouped model species. Available mechanisms vary widely in the numbers of chemical species and reactions (Henderson et al., 2011) and their intended atmospheric domain and application. Mechanisms are simplified by limiting them to a specific atmospheric domain: stratosphere, troposphere, remote air, polluted urban air, etc. The chemical mechanisms that are widely used in CMAQ and WRF include the SAPRC07 (Carter, 2010), the Carbon Bond V mechanism of Yarwood et al. (2005), the Regional Atmospheric Chemistry Mechanism (RACM1; Stockwell et al., 1997) and their predecessors. These mechanisms along with the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2, presented here) are used to simulate the atmosphere from the Earth's surface to the upper troposphere for conditions that range from highly polluted to remote.

The RACM2 mechanism includes 17 stable inorganic species, 4 inorganic intermediates, 55 stable organic species (3 of these are primarily of biogenic origin) and 43 organic intermediates (see Table S1 in Supplementary material). The RACM2 mechanism includes 363 reactions (see Table S2 in Supplementary material). It

is a highly revised version of the RACM1 mechanism that incorporates new data from the laboratory studies and reviews that have appeared since the RACM1 mechanism was published. These revisions are described in this paper.

Among the more significant revisions incorporated in RACM2 are changes to the chemistry of ketones, aromatics and biogenically emitted compounds. More explicit treatments of acetaldehyde and acetone as separate model species are included in RACM2. Aromatic compounds are highly reactive in the production of ozone and aerosol precursors and the chemistry of these compounds has been a major research focus (Calvert et al., 2002). This research has guided the revisions to RACM2 aromatic chemistry so that the RACM2 chemistry has been modified to incorporate more primary aromatic species and a more realistic representation of their products.

Revisions to the inorganic chemistry and organic chemistry are discussed first in this paper. There were new organic species added to the RACM2 mechanism and therefore the aggregation scheme for organic species was modified. The organic chemistry section includes a description of the revisions to the chemical mechanisms for alkanes, alkenes, biologically emitted compounds, aromatic species and oxygenated compounds. Any mechanism needs to be tested and data from environmental chamber experiments were used. Although there are acknowledged limitations to environmental chamber experiments, testing against this data remains the most important way to compare the chemistry simulated by mechanisms with measurements in the absence of meteorological effects. Finally it is important for the community to know how the revised chemistry in RACM2 impacts its forecasts. The results of an inter-comparison between RACM1 and RACM2 are presented in the final section for an ambient case, and for more diverse "real world" cases in the Supplementary information.

2. Inorganic chemistry

The inorganic chemistry portion of RACM2 contains 46 reactions (including 9 photolysis reactions). The rate constants for the inorganic reactions previously included in RACM1 were updated using the review data from Sander et al. (2011) and IUPAC (2010). The quantum yields for the photolysis reaction of ozone to produce $O(^1D)$ were modified according to Matsumi et al. (2002). The quantum yields for the photolysis of nitric acid and hydrogen peroxide were revised to be equal to unity for RACM2.

The products of the reaction of HO_2 with nitrate radical, NO_3, were modified to be consistent with Le Bras (1997). The yields for this reaction, although uncertain, are based on the average branching ratios from two discharge flow studies reported in Le Bras (1997). One was performed by Le Bras using EPR detection and the second was performed Schindler using MS/RF detection.

The homogeneous reaction of dinitrogen pentoxide, N_2O_5, with water was added using the recommended rate constant of IUPAC (2010). HNO_3 formation from $HO_2 + NO$ (Butkovskaya et al., 2007) was also added.

3. Revision of the organic reactions of RACM2

3.1. Revision of the organic species aggregation scheme

The RACM2 approach for aggregating organic compounds into the model species is derived from the methods developed for the Regional Acid Deposition Model chemical mechanism and RACM1 (Middleton et al., 1990; Stockwell et al., 1990, 1997). The magnitude of a compound's emission rate, typical concentration, similarity in reaction mechanism and its reactivity were all significant considerations and the overall approach for RACM2 is the same as RACM1.

RACM1 consisted of 32 stable organic species and 24 organic intermediates. However, improved knowledge of the organic decomposition mechanisms makes a significant increase in the number of model organic species very desirable. Another reason for increasing the number of model organic species is to allow RACM2 to be more effective in the simulation of organic aerosol precursors. Finally the highly improved computational resources available today make it more practical to use a larger mechanism in a detailed Eulerian atmospheric chemistry model. RACM2 consists of 54 stable organic species and 42 organic intermediates.

New model organic species added to the RACM2 mechanism include acetylene, benzene, m-xylene, p-xylene, o-xylene, species to represent a more detailed treatment of aromatic products, acetaldehyde, a higher molecular weight aldehyde, methanol, ethanol, higher molecular weight alcohols, ethylene glycol, acetone, methyl vinyl ketone and methacrolein.

In RACM1 acetylene was aggregated with the group HC3 that represents alkanes with low reactivity with HO. However, the latest reviews (IUPAC, 2010; Sander et al., 2011) show that the rate constant for the reaction of acetylene with HO is dependent upon pressure. The new species for acetylene, ACE, was added to allow for this pressure dependence.

Benzene is another chemical with a relatively low rate constant for its reaction with HO that was added to the RACM2 mechanism (Calvert et al., 2002). Benzene had been aggregated with toluene with an aggregation factor of 0.293 in RACM1 because its degradation rate in the atmosphere was assumed to be too slow to be an important source of ozone or aerosol on a regional level. Although this assignment was consistent with benzene's initial reactivity with HO, this resulted in a poor representation of benzene's secondary products and poor carbon mass balance. The more explicit benzene species in RACM2 improves the representation of its carbon mass and reactivity. It also has the advantage that benzene can be simulated for air toxics modeling.

RACM1 included only one model species to represent the three isomers of xylene but there are differences in their chemistry (Calvert et al., 2002). In addition, many routine measurements of the xylenes provide the concentrations of o-xylene and the total concentration of the mixture of m-xylene and p-xylene because m-xylene and p-xylene co-elute in many gas-chromatography systems. The xylene species are speciated with o-xylene represented by XYO and the m- and p-xylenes isomers represented by the XYM and XYP, respectively in RACM2. Disaggregating the isomers from the xylene mixture allows more direct comparisons of RACM2 simulations with field measurements, as well as allowing for their differing rates of reactivity.

Calvert et al. (2002) provides information regarding the decomposition mechanism for benzene, toluene, xylene and other aromatic products. Additional model species were added to more accurately represent the reactivity of the products of aromatics in the RACM2 mechanism as described in Calvert et al. (2002). The number of species representing the reaction products of toluene and the xylenes oxidation was increased similarly.

The decomposition of alkanes and many other compounds produces aldehydes and ketones (Atkinson and Arey, 2003). RACM1 represented the aldehyde products as formaldehyde, HCHO, and aldehyde species modeled as acetaldehyde. This somewhat premature formation of acetaldehyde underestimates the length of many organic degradation pathways and therefore contributes to problems with peroxy acetyl nitrate and HCHO formation. Aldehydes containing three or more carbon atoms are treated as the species ALD which is treated as propionaldehyde. The species ALD, a higher molecular weight PAN analogue (PPN) and a new explicit species for acetaldehyde were added to RACM2 to partially correct this problem in RACM2.

A single species was used similarly to represent ketones that were modeled as a mixture of acetone and methyl ethyl ketone in RACM1. Singh et al. (1995) and Jaeglé et al. (1997) showed that acetone plays a very important role in the upper troposphere. Acetone was disaggregated from the generalized RACM1 ketone, and is represented as separate species in RACM2. The addition of an explicit acetone species improves the RACM2's treatment of upper tropospheric chemistry and it also allows it to be better tracked in emissions inventories. In RACM2 the KET is treated as diethyl ketone.
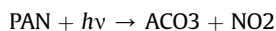
Ethylene glycol was added to the RACM2 mechanism because it is produced by the oxidation of ethene in a relatively clean atmosphere with low NO_x. Another reason for treating ethylene glycol as separate species is that it reacts as fast as a species with eight carbon atoms, but it has only two carbon atoms. In order to maintain correct reactivity of products for the ETEP + MO2 reaction ETEG would of necessity be replaced by the mechanism species HC8. However, the inclusion of HC8 would significantly alter the carbon balance of the reaction in an undesirable manner. (With ETEG the products of this reaction total 3.15 carbons, whereas the substitution of HC8 would cause a total carbon of 4.65). The alcohols methanol and ethanol are now explicit in the RACM2 mechanism, along with a species for higher molecular weight alcohols in order to more accurately represent these products that are produced in cleaner atmospheres.

Methyl vinyl ketone, produced by the oxidation of isoprene, was aggregated with terminal alkenes in the RACM1. The RACM2 isoprene scheme as been expanded to include the explicit production of both methyl vinyl ketone and methacrolein. This change not only improves RACM2 but it will aid in future mechanism development for the simulation of organic aerosol. The products of methacrolein lead to formation of secondary organic aerosol while the products of methyl vinyl ketone do not (Kroll et al., 2006).
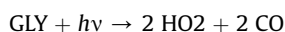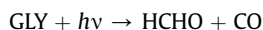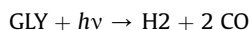
3.2. Organic photolysis reactions

In the first version of RACM, there were 23 photolysis reactions; in RACM2 there are 33. The new photolytic species are: acetaldehyde (ACD), acetone (ACT), unsaturated aldehydes (UALD), methyl ethyl ketone (MEK), methyl vinyl ketone (MVK), one additional dicarbonyl (DCB2), benzaldehyde (BALD), peroxyacetylnitrate (PAN) (two photolysis channels) and an additional photolysis channel for glyoxal (GLY).

The two photolysis channels PAN are:

$$PAN + h\nu \rightarrow ACO3 + NO2$$

$$PAN + h\nu \rightarrow MO2 + CO2 + NO3$$

The first channel may lead to the reformation of PAN, but the second channel leads to the destruction of PAN. This second photolysis channel gains importance in the upper troposphere where PAN may be transported over long distances due to lower temperatures.

The photolysis channels and values for ketone (KET) are modeled after diethyl ketone. The glyoxal photolysis reactions (Sander et al., 2011) incorporated in RACM2 are:

$$GLY + h\nu \rightarrow H2 + 2\ CO$$

$$GLY + h\nu \rightarrow HCHO + CO$$

$$GLY + h\nu \rightarrow 2\ HO2 + 2\ CO$$

The cross section and quantum yields for the photolysis of acetaldehyde, ACD, were taken from Sander et al. (2011), however, only the first reaction of the recommendation was used. For ALD, the recommendation of Heicklen et al. (1986) was used for the quantum yields of propionaldehyde because Sander et al. (2011) does not make a recommendation. The cross sections and quantum yields for UALD were based upon on crotonaldehyde (Magneron et al., 2002). The Sander et al. (2011) recommendations for cross sections and quantum yields were used for acetone and methyl vinyl ketone photolysis. For the photolysis of MEK and KET, cross section data was taken from Yujing and Mellouki (2000); and quantum yield data from Raber and Moortgat (1996). Quantum yield and cross section data for BALD were taken from SAPRC07 (Carter, 2010), with products from Zhu and Cronin (2000). Quantum yield and cross section data for ONIT were taken from Talukdar et al. (1997). Data for all other photolysis reactions are taken from the Sander et al. (2011) recommendation.

3.3. Alkanes

Reaction with HO is the only significant reaction for alkanes in the troposphere. The reaction of alkanes with HO forms alkyl radicals which immediately react with O_2 to form peroxy radicals. The peroxy radicals react with NO in polluted conditions to convert the NO to NO_2 although a fraction (that increases with the molecular weight of the peroxy radical) yields organic nitrates (Atkinson and Arey, 2003). Under cleaner, more remote these peroxy radicals react with HO_2, CH_3O_2 (MO2) and CH_3CO_3 (ACO3) to form a variety of products. The CH_3CO_3 peroxy radicals may also react with NO_3 during the nighttime hours.

In RACM1 and RACM2, methane and ethane are explicit, while HC3 represents mainly propane and a few, similar, lower reactive compounds. The higher molecular weight alkanes are represented by HC5 and HC8 (the number following the HC is a rough approximation of the average number of carbon atoms aggregated in the group). The chemistry for HC5 and HC8 in RACM2 has been improved by removing alcohols and acetylene from the aggregation scheme for these species. When determining the rate constants for the alkane species, the respective rate constants and product yields have been updated with the most recent literature data and then weighted according to their emissions as was done for the RACM1 mechanism. The RACM2 alkane degradation scheme has been enhanced by the increased speciation of the secondary oxygenated products (including acetaldehyde, higher aldehydes, acetone, higher ketones and alcohols).

In RACM1, alcohols and other compounds were aggregated with n-butane in the HC3 species. Alcohols react with HO to promptly produce HO_2, glyoxal, formaldehyde, etc. In RACM2 there is no prompt formation of radicals other than an organic peroxy radical or photoreactive products (such as glyoxal or formaldehyde) from the hydroxyl–alkane reaction because alcohols are no longer aggregated into this species. The reaction in RACM2 is given in Table S2b, Reaction R073 in the Supplemental information. However, in both mechanisms, the HC3P species (peroxy radical formed in the reaction of HC3 with HO) may react with NO, HO2, MO2, ACO3 or NO3.

3.4. Alkenes

Alkenes may react with HO, ozone, and NO_3, but they do not photolyze in sunlight in the troposphere (Atkinson and Arey, 2003). In the case of HO, addition to the double bond is followed by addition of O_2 at the radical site to produce a peroxy radical. These peroxy radicals react with the same species as the alkane-peroxy radicals although there are important differences in the products.

Reactions of alkenes with NO_3 are analogous to those with HO, with the alkene-NO_3 adduct either forming organic nitrates in the presence of NO, or decomposing to form aldehydes and ketones. When ozone reacts with alkenes, the ozone molecule adds to the double bond to form a primary ozonide which decomposes rapidly to form aldehydes and excited Criegee biradicals. The excited biradical may either be stabilized by collisions, or decompose to form radicals and occasionally including hydroxyl (Finlayson-Pitts and Pitts, 1999). This is significant source of HO during the nighttime. RACM1 and RACM2 both include model species for ethene (ETE), alkenes with the double bond at the end or terminal position of the molecule (OLT) and alkenes with the double bond elsewhere in the molecule (OLI).

The reactions of ethene with hydroxyl radical and ozone were updated in RACM2. RACM1 represented the HO rate constant as an Arrhenius expression while RACM2 uses a Troe expression following the recommendation of Sander et al. (Sander et al., 2011). This update allows for a more accurate representation of this reaction in the upper troposphere, where temperatures and pressures are low. Another important modification in RACM2 to the ethene mechanism was to include ethylene glycol as a model species. The peroxy radical produced from the reaction of HO with ethene may react with the methyl peroxy radical (CH_3O_2) to form ethylene glycol under low NO_x conditions.

Alkenes grouped into OLT and OLI have different rate constants and product yields for their reactions with HO, ozone, and NO_3. For example, in RACM2 the reaction of OLI with ozone has HO yield of 0.63, while for the reaction of OLT with ozone has an HO yield of 0.40. Propene is represented by OLT in both RACM1 and RACM2 and propene emissions are the bulk (>50%) of the total OLT emissions although OLT aggregates 19 terminal olefins in the U.S. inventory. The resulting update to the RACM2 makes a significant difference to the yields of HO from OLT. In RACM2 another modification to the products of OLT and OLI is to include the MOH, EOH and ROH species as the products of the model reactions OLIP + MO2 and OLTP + MO2. The more explicit alcohol species will be more important in remote atmospheres with low NO_x levels.

3.5. Carbonyls

Aldehydes, ketones and other compounds with a carbonyl group react through photolysis as discussed above. Aldehydes also react with HO and NO_3 which most readily abstract the hydrogen attached the carbonyl group (Atkinson and Arey, 2003). Ketones react, more slowly, with HO through the abstraction of a hydrogen atom. Unsaturated compounds with a carbonyl group react at the site of the double bond with HO, NO_3 and O_3 as alkenes.

The rate constant for the reaction of acetaldehyde with the HO radical was taken from the IUPAC (2010) recommendation. For the reaction of acetaldehyde with NO_3 the recommendations of Sander et al. (2011) were used. When acetaldehyde was added explicitly to RACM2, ALD referred to aldehydes C3 and higher. This necessitated the addition of RCO3 to the mechanism so that C3 and higher aldehydes did not form ACO3 and to maintain carbon balance. However, RCO3 reacts with NO2 for form peroxypropionyl nitrate (PPN), not PAN, so PPN was added to the mechanism as well.

The reaction of UALD with HO is based upon crotonaldehyde, with the rate constant taken from Magneron et al. (2002). For the reaction of UALD with O_3 the rate constant was taken as the average of Grosjean and Grosjean (1998) and Sato et al. (2004). For the reaction of UALD with NO_3 the rate constant is taken from Salgado et al. (2008).

The recommendation of IUPAC (2010) was used for the reaction of HO with acetone. For the reaction of methyl vinyl ketone reaction

with HO, the recommendation of Atkinson and Arey (2003) was used.

3.6. Aromatic chemistry

A separate reaction mechanism for benzene was added to the RACM2 mechanism. The degradation scheme for benzene in RACM2 was based upon the Master Chemical Mechanism (MCM v3.1; (Bloss et al., 2005)). The reaction of HO with benzene yields a short-lived intermediate with a yield of 64.8%. The intermediate reacts with molecular oxygen to abstract a hydrogen atom to produce HO_2 and phenol (C_6H_5OH). Phenol is included as the model species PHEN in addition to the cresol (CSL) that is produced from the other aromatics in RACM2 because phenol reacts with HO more slowly than cresol. However because the subsequent degradation mechanism products of phenol and cresol are very similar their products are the same in RACM2 as in RACM1. The short-lived intermediate also reacts a significant fraction of the time to break the aromatic ring to produce unsaturated aldehydes, as represented by DCBs.

The reaction of hydroxyl radical with benzene also produces an aromatic peroxy radical (BENP) with a yield of 35.2%. One chief difference between the MCM and the RACM2 mechanisms is the treatment of the peroxy radical reactions. The MCM has a single generalized organic peroxy radical species (RO2) that react with peroxy radicals to represent their parent history. For example:

BZBIPERO2 + RO2 → BZBIPERO

In contrast RACM2 does not contain a generalized organic peroxy radical rather it contains peroxy radicals that correspond to each parent model organic species. The RACM2 approach allows more explicit treatment of the reaction products then would be possible with a generalized organic radical operator. A problem with this approach is that the mechanism could contain a very large number of organic peroxy radical cross-reactions. The approach adopted for the RADM/RACM series of mechanisms (Stockwell et al., 1990, 1997) has been to include only the organic peroxy–radical reactions involving HO_2, NO_3, methyl peroxy radical (MO2), acetyl peroxy radical (ACO3) and higher saturated acyl peroxy radicals (RCO3) with all other organic peroxy radicals. For the vast majority of atmospheric conditions the radicals HO_2, NO_3, MO_2, ACO3 and RCO3 have the greatest concentrations and the remaining organic peroxy radical − organic peroxy–radical cross-reactions are not significant (Stockwell et al., 1995; Kirchner and Stockwell, 1996, 1997).

The toluene and xylenes mechanisms were completely reconstructed based upon Calvert et al. (2002), with new products included to more accurately reflect their degradation in the atmosphere, such as the inclusion of benzaldehyde. The product yields were optimized using the University of California Riverside Evacuable Chamber (EC) data as described in Section 4 of this manuscript.

3.7. Isoprene

The oxidation scheme for isoprene (2-methyl-1,3-butadiene) has been updated for RACM2 based on the scheme published by Geiger et al. (2003) and GEOS-Chem version 8-02-04. This scheme has been improved upon by adding methyl vinyl ketone (MVK) explicitly to RACM2. (In the RACM1, MVK was aggregated into the methacrolein (MACR) species.) The new isoprene scheme contains the new species detailed in Geiger et al. (2003) (i.e., ISON, ISHP). The new scheme was tested against chamber data and field data, as described in Section 4.

Hydroxyl radicals may add to the 1- or 4- position to form an allylic hydroxyalkyl radical (Atkinson and Arey, 2003). This radical then reacts with O_2 to form the corresponding peroxy radical. In the presence of NO, these peroxy radicals can form hydroxynitrates or hydroxyalkoxy radicals and NO_2. In the case of isoprene, hydroxynitrates are formed with a yield of 12% (Sprengnether et al., 2002), while the 1,2-hydroxyalkoxy radicals decompose to form formaldehyde and either methacrolein (MACR) or methyl vinyl ketone (MVK). For RACM2 MACR and MVK are the major products formed, along with formaldehyde, glyoxal and HO_2, with the MACR/MVK yields from Sprengnether et al. (2002).

The reaction of ozone with isoprene is like other alkenes, it reacts by addition to the double bond and the resulting ozonide rapidly decomposes. The major products of this reaction are MACR, MVK, HCHO, formic acid and hydroxyl radicals. Minor products include CO, HO_2 and the methyl peroxy radical.

Isoprene may also react with the nitrate radical (NO_3), an important reaction pathway during the night. The reaction proceeds by the addition of NO_3 to the double bond to form an unstable adduct. This adduct immediately reacts with O_2 to form a peroxy radical, which can then react with NO under polluted conditions and under low NO_x conditions with HO_2 and RO_2 radicals to form multifunctional nitrates. A recent paper (Perring et al., 2009) reported a 65 ± 12% yield for organic nitrates, a combined yield of 10% (upper limit) for MACR and MVK, HCHO a yield of 11% and the remaining carbon balance attributed to nitro-oxy carbonyls. Because the combined yield for MACR and MVK is an upper limit in the Perring et al. study, the yield of 3.5% for both MVK and MACR from Kwok et al. (1996) was used.

3.8. α-Pinene

The RACM2 species API represents α-pinene and other cyclic terpenes with one double bond. Because α-pinene emissions dominate the group of compounds aggregated into, the α-pinene literature values are used for the API species in RACM2. The rate constant for the reaction of α-pinene with HO has been updated according to the IUPAC (2010) recommendation, with the products according to Atkinson and Arey (2003). The reaction rate and products of α-pinene with ozone and α-pinene with nitrate radical were also taken from Atkinson and Arey (2003).

3.9. Limonene

LIM represents D-limonene and other cyclic diene-terpenes. The reaction rate constant for the reaction of D-limonene with HO has been updated according to Gill and Hites (2002), with products from Atkinson and Arey (2003). For the reaction of D-limonene with O_3 the reaction rate constant and products are taken from Atkinson and Arey (2003). For the reaction of D-limonene with NO_3, the rate constant is taken from Atkinson and Arey (2003), with products from Spittler et al. (2006). Spittler et al. found no evidence of NO_3 reaction with the exocyclic double bond and therefore no formaldehyde formation. Rather, the NO_3 attack is selective to the cyclic double bond, forming ring opening products such as endolim.

3.10. New reactions for alcohols and organic acids

Alcohols are represented by methanol (MOH) and ethanol (EOH) and a higher molecular weight alcohol species (ROH). The rate constant for the reactions of methanol and ethanol with HO and were taken from IUPAC (2010). The reaction of the higher molecular weight alcohol species was based on 2-propanol and its rate constant was also taken from IUPAC (2010).

The reaction for formic acid (ORA1) with HO was added to RACM2, its rate constant from Singleton et al. (1988). For the reaction of acetic acid with HO a new organic intermediate species, ORAP, was added to RACM2. The products of ORAP with NO conform to a branching ratio of 64% acidic hydrogen abstraction and 36% H abstraction from the CH_3 group (Butkovskaya et al., 2004; De Smedt et al., 2005).

4. Comparison of RACM1 and RACM2 mechanisms against environmental chamber experiments

Testing of atmospheric chemical mechanisms against environmental reaction chamber data is a necessary element of the mechanisms development process. This testing allows significant errors to be found. In addition, the comparison of the RACM1 and RACM2 chemical mechanisms against environmental reaction chamber data benchmarks some of the differences between them. Twenty of the environmental chamber runs presented here are the same as used previously to test RADM2 and RACM1 (Stockwell et al., 1990, 1997). These twenty chamber runs were performed using the Evacuable Chamber (EC) of the Statewide Air Pollution Research Center (SAPRC) of the University of California, Riverside (Carter et al., 1995). These experiments represent a sample of runs that reflect a wide-range of atmospheric chemistry and their simulation has been found to mirror the results of more comprehensive testing (Carter and Lurmann, 1989). Additional benzene chamber data collected during the EXACT campaign were obtained from Dr. Michael Pilling (personal communication, 2008).

Environmental reaction chambers suffer from wall effects and difficulties in matching the actinic flux in the chamber with the outdoor actinic flux. Experimentalists use inert materials and cleaning procedures to minimize wall effects. However, walls may still be a significant source and sink of the trace gases and particles as well as serving as a reaction sites for heterogeneous chemistry (Killus and Whitten, 1990). Therefore, when modeling smog chamber experiments, it is always necessary to take these effects into account by appending a chamber model to the chemical mechanism being evaluated. There are three major ways wall effects can interact with experimental photochemistry: (1) the introduction of free radicals, e.g., through HONO production, (2) trace NO_x species can allow the formation of O_3 and PAN and serves as a radical sink, and (3) the off-gassing of organic compounds that may convert hydroxyl radicals (HO) to HO_2. The actinic flux data and an auxiliary mechanism that characterized wall reactions were the same as previously used to evaluate RACM1 (Stockwell et al., 1997). In the case of the EXACT data, the auxiliary mechanism developed by Bloss et al. (2005) was used. The auxiliary mechanism for the EXACT campaign was developed using ethene chamber data for the MCM. The ethene degradation scheme is well understood, and so the RACM2 scheme and MCM scheme for ethylene are quite similar, and so the auxiliary scheme may be used for both mechanisms.

Table 1 summarizes the measured and calculated ozone values for the modeled EC and EXACT experiments. The average percent difference between RACM2 predictions and measured peak ozone concentrations for the EC experiments is 5.2%, while the percent difference for RACM1 is 14.5%. For the benzene experiments conducted for the EXACT campaign, RACM2 under-predicted the peak ozone by 26.7% for the low NO_x experiment and over-predicted the peak ozone by 12.1% for the high NO_x experiment. Meanwhile, RACM1 over-predicted the peak ozone by 37.4% and 119% for the low and high NO_x experiments, respectively.

Fig. 1a illustrates the measured versus modeled maximum ozone concentrations for the modeled experiments. For ozone the slopes of the lines for RACM2 and RACM1 are 0.926 and 0.712, respectively, showing the RACM2 is in better agreement with chamber measurements than RACM1. Both RACM1 and RACM2 overestimate the maximum ozone for the lower mixing ratios and underestimate it for the higher mixing ratios.

Table 2 shows the measured and calculated peak NO_2 values for the EC and EXACT experiments. The RACM2 predictions differ from the measured NO_2 concentrations in the EC chamber an average of 6.6%, while the percent difference for RACM1 is 9.2%. With regard to the EXACT benzene chamber data, while the RACM1 predictions for the peak NO_2 concentration is closer to the measured value, the

Table 1
Comparison of RACM2 and RACM1 with SAPRC and EXACT ozone data.

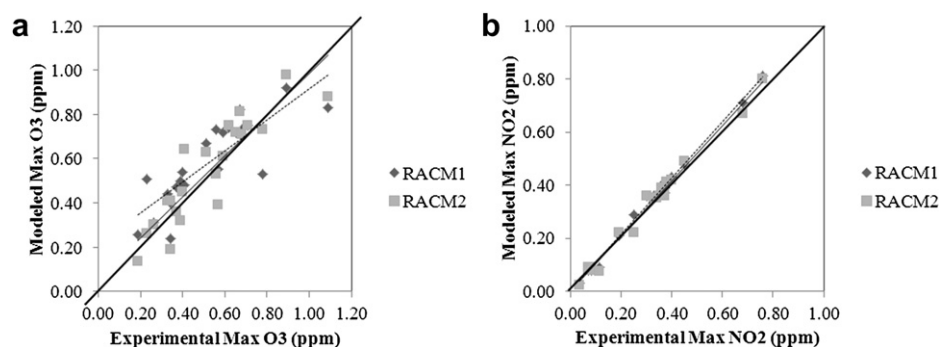|	Principal organic compounds	VOC/NO_x ratio	O3 expt (ppm)	RACM2	% Difference	RACM1	% Difference
SAPRC expt							
142	Ethene	4.2	0.78	0.73	−7.1	0.53	−32.1
143	Ethene	8.1	1.09	0.88	−19.5	0.83	−23.9
178	*n*-Butane	80.1	0.37	0.36	−2.5	0.47	27.0
216	Propene	3.1	0.56	0.53	−5.6	0.73	30.4
231	Mixture	27.9	0.62	0.75	20.7	0.74	19.1
232	Mixture	19.8	0.34	0.19	−42.7	0.40	17.6
233	Mixture	96.8	0.33	0.41	25.9	0.44	35.1
237	Mixture	22.5	0.65	0.72	11.4	0.72	10.9
238	Mixture	11.0	0.67	0.81	21.2	0.82	22.7
241	Mixture	11.1	0.41	0.64	57.7	0.48	18.3
242	Mixture	25.9	0.68	0.71	5.0	0.73	7.7
243	Mixture	19.8	0.71	0.75	5.9	0.75	5.3
245	Mixture	13.0	0.89	0.98	10.1	0.92	3.4
246	Mixture	17.6	0.57	0.39	−30.8	0.55	−3.5
254	Acetaldehyde	8.4	0.26	0.30	14.4	0.31	18.1
305	*n*-Butane	175.7	0.40	0.45	11.8	0.54	35.0
331	Toluene + *n*-butane	47.4	0.51	0.63	23.1	0.67	31.4
340	Toluene	9.2	0.34	0.41	20.8	0.24	−28.8
344	m-Xylene	5.6	0.59	0.61	2.7	0.72	22.0
345	m-Xylene	13.3	0.39	0.32	−18.9	0.50	28.2
EXACT expt							
080702	Benzene	42	0.187	0.137	−26.7	0.257	37.4
090702	Benzene	5.6	0.231	0.259	12.1	0.505	119

Fig. 1. Comparison of model predictions to chamber measurements listed in Tables 1 and 2 for RACM1 (open diamonds) and RACM2 (solid squares) for ozone (plot A) and NO$_2$ (plot B), respectively. The dark gray and light gray lines are best-fit lines for the correlation between RACM1 and RACM2 simulations, respectively, and chamber measurements. The dark black line in both plots is the 1–1 line of perfect agreement between experiment and model.

RACM2 time for the peak concentration is closer to the observed time of the peak.

Fig. 1b shows the measured versus modeled nitrogen dioxide concentrations. The agreement between the experiments and the mechanisms is good for both RACM1 and RACM2. The slopes of the lines for RACM2 and RACM1 are 1.004 and 1.057, respectively, showing the RACM2 is in better agreement with the chamber measurements than RACM1. Both RACM1 and RACM2 overestimate the maximum NO$_2$ for the most of the experiments.

4.1. Comparison of RACM2 and RACM1 for individual species

The RACM1 and RACM2 simulated ozone mixing ratios produced from ethene were very similar. RACM1 and RACM2 performed similarly for the EC n-butane experiments (EC178 and EC305). In each case, RACM2 predicts slightly less ozone concentrations than RACM1. To simulate propene the model species OLT, the species with the double bond in the terminal position, was used in both mechanisms. The most significant difference between the OLT degradation schemes in RACM1 and RACM2 is the amount of

HO produced. RACM2 predicts HO concentrations two orders of magnitude less than RACM1. For the acetaldehyde simulation, EC254, RACM1 and RACM2 predict ozone concentrations to within 5% of one another during the entire simulation.

There are significant differences in the RACM1 and RACM2 simulations for benzene. In comparison with the EXACT campaign data RACM1 over-predicts ozone production for both high and low NO$_x$ cases. The problem with aggregating benzene with toluene is that toluene degradation products have higher ozone formation potentials than those produced from benzene degradation (e.g., glyoxal from benzene versus methyl glyoxal from toluene), and ring-retaining product yields for benzene are much higher (53%) than for toluene (<20%). In addition, the RACM1 mechanism predicts peak formaldehyde concentrations to be 50% higher than RACM2 for the benzene-low NO$_x$ experiment, and 29% higher for the benzene-high NO$_x$ experiment.

There were two EC chamber experiments which had toluene as a principal component: EC331 (toluene and n-butane) and EC340 (toluene only). Fig. 2 illustrates the comparison of RACM1 and RACM2 predictions for ozone concentrations to chamber

Table 2
Comparison of RACM2 and RACM1 NO$_2$ peak values with chamber data (EC and EXACT).

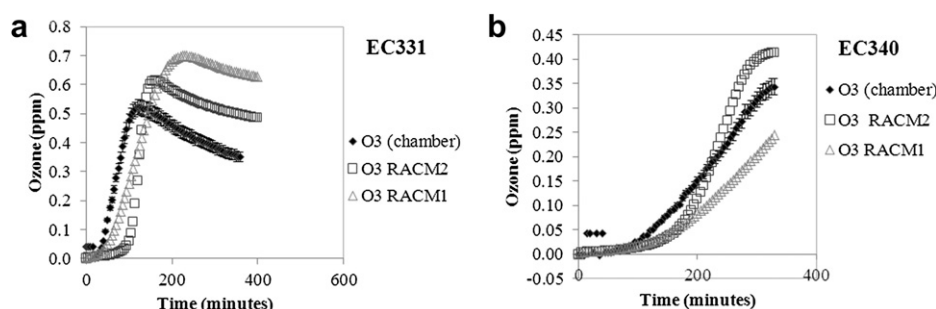|	Principal organic compounds	VOC/NO$_x$ ratio	NO$_2$ expt (ppm)	RACM2	% Difference	RACM1	% Difference
SAPRC expt							
142	Ethene	4.2	0.30	0.36	19.4	0.36	18.8
143	Ethene	8.1	0.38	0.41	10.2	0.41	9.2
178	n-Butane	80.1	0.07	0.09	35.5	0.08	21.8
216	Propene	3.1	0.37	0.37	1.8	0.39	6.2
231	Mixture	27.9	0.36	0.39	6.6	0.40	9.6
232	Mixture	19.8	0.34	0.35	1.2	0.36	4.7
233	Mixture	96.8	0.08	0.09	12.0	0.09	15.5
237	Mixture	22.5	0.37	0.38	1.7	0.39	4.2
238	Mixture	11.0	0.68	0.67	−0.3	0.71	5.1
241	Mixture	11.1	0.35	0.36	2.5	0.36	3.9
242	Mixture	25.9	0.40	0.42	4.9	0.43	6.8
243	Mixture	19.8	0.40	0.42	5.5	0.42	5.7
245	Mixture	13.0	0.76	0.80	4.9	0.81	6.4
246	Mixture	17.6	0.37	0.36	−4.1	0.37	−0.9
254	Acetaldehyde	8.4	0.07	0.08	9.0	0.09	25.6
305	n-Butane	175.7	0.08	0.08	2.4	0.08	0.2
331	Toluene + n-butane	47.4	0.33	0.35	6.3	0.36	7.8
340	Toluene	9.2	0.25	0.22	−11.9	0.29	16.0
344	m-Xylene	5.6	0.45	0.49	9.0	0.48	6.7
345	m-Xylene	13.3	0.19	0.22	15.6	0.21	10.5
EXACT expt							
080702	Benzene	42	0.035	0.024	−31.4	0.031	−11.4
090702	Benzene	5.6	0.112	0.074	−33.9	0.090	−19.6

Fig. 2. Comparison of ozone concentrations for (a) EC331 (toluene and *n*-butane) and (b) EC340 (toluene only) to RACM1 and RACM2 predictions.
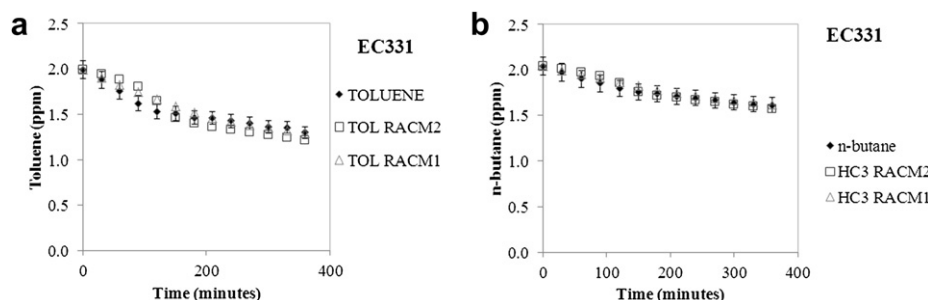

Fig. 3. Comparisons of (a) toluene and (b) *n*-butane concentrations for the EC331 chamber experiment for RACM1 and RACM2.

observations for EC331 and EC340. In the case of EC331, RACM2 comes closer to predicting the maximum ozone concentration as well as the time of the ozone peak concentration than RACM1. In the case of EC340, RACM2 over-predicts the peak ozone concentration by 20.8%, while RACM2 under-predicts peak ozone by 28.8%. For EC331, both mechanisms predict the decay of toluene and *n*-butane within 10% (Fig. 3), indicating the mechanisms predict levels of hydroxyl radicals adequately. For EC340, RACM1 slightly over-predicts toluene concentrations (Fig. 4), while RACM2 slightly under-predicts toluene concentrations. Fig. 5 shows product formation for EC340, both measured and predicted. For cresol and PAN, RACM2 comes closer to measured concentrations than RACM1. RACM2 also predicts benzaldehyde formation reasonably well, while RACM1 does not represent this compound as a separate species.

EC344 and EC345 are chamber experiments with m-xylene as the principle component. Each run had the same amount of m-xylene injected (0.48 ppm), while EC344 had an initial NO_x concentration of 0.75 ppm and EC345 had 0.3 ppm of NO_x. Fig. 6 shows the comparison of measured and predicted ozone concentrations for EC344 and EC345. RACM2 more closely matches the timing and value of the peak ozone concentration for these chamber experiments. Fig. 7 illustrates the comparison of
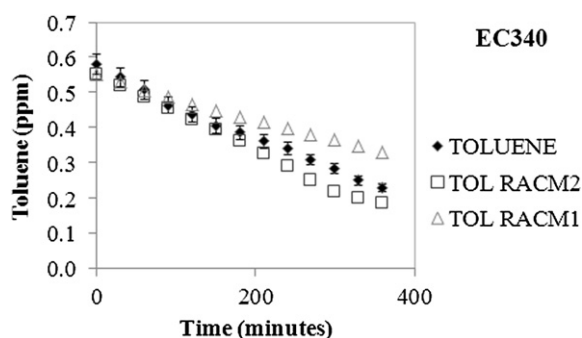

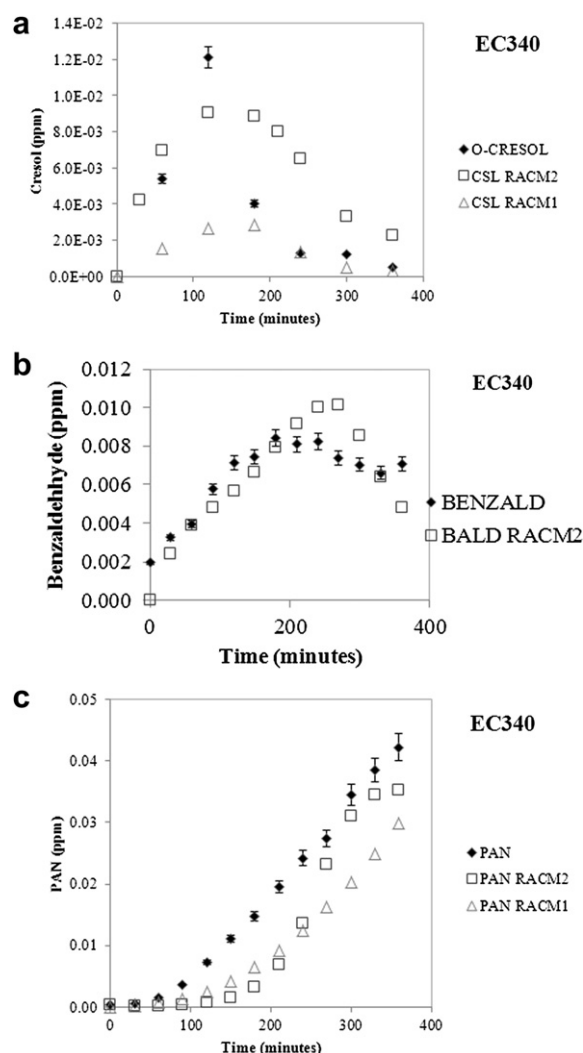**Fig. 4.** Toluene concentrations (measured and modeled) for EC340.

Fig. 5. Comparison of measured products formed in EC340 to RACM1 and RACM2 predictions: (a) cresol, (b) benzaldehyde and (c) PAN.
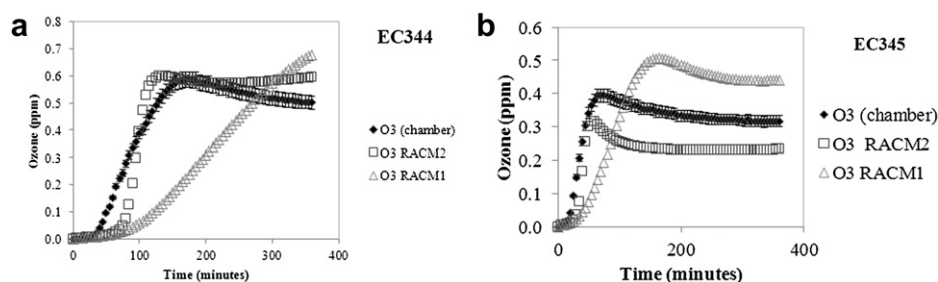
Fig. 6. Comparison of ozone concentrations for (a) EC344 (m-xylene) and (b) EC345 (m-xylene) to RACM1 and RACM2 predictions.
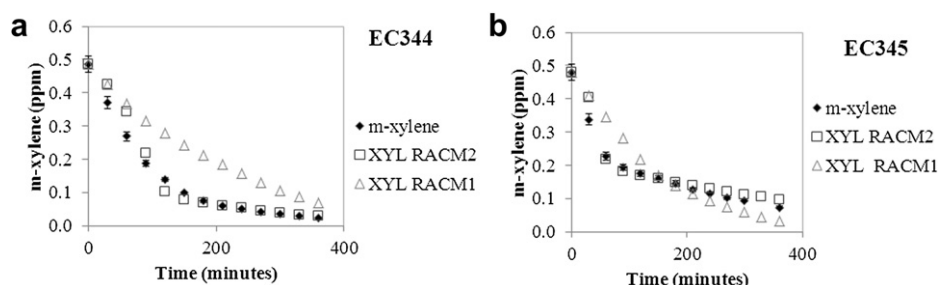

Fig. 7. M-xylene concentrations (measured and modeled) for (a) EC344 and (b) EC345.

measured and modeled m-xylene decay during the EC344 and EC345 experiment. RACM2 is in better agreement with measured m-xylene values than RACM1, indicating that hydroxyl concentrations are better simulated in RACM2 than RACM1 (since m-xylene does not react with ozone).

5. Comparison of RACM1 and RACM2 mechanisms for an "ambient" case

The RACM1 and RACM2 mechanisms were each employed by a box model (SBOX:Seefeld, 1997) to simulate ambient field data collected during the Clark County Regional Ozone and Precursor Study (CCROPS) (Goliff, 2006). Data from July 15, 2005 at the JD

Smith site were used for initial conditions in the model, and model output were compared to observed data for ozone, NO, NO_2. Here model output for PAN, HCHO and HNO_3 for each mechanism are also compared, although these were not measured as part of the field campaign.

In the case of ozone, RACM2 overestimated the peak concentration of ozone by 40% (Fig. 8) and was an hour earlier than observed. The likely reason for this is because RACM2 underestimated NO concentrations (Fig. 9), and so less NO was available to titrate the ozone in the simulation. RACM1 overestimated the peak concentration of ozone by 50% with the peak 2 h earlier than observed (Fig. 8). For NO, RACM1 predicted concentrations 62% lower than observed, while RACM2 predictions were 45% lower
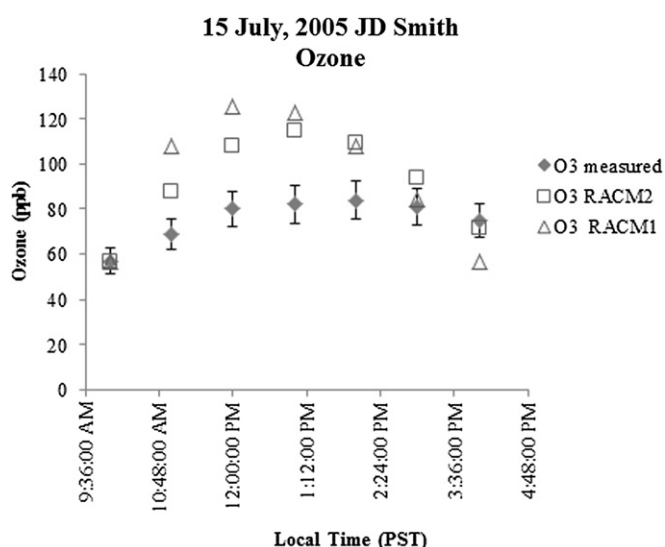

Fig. 8. Comparison of ozone concentrations for JD Smith site on July 15, 2012. Observed values are dark gray diamonds, RACM1 predictions are gray triangles, RACM2 predictions are light gray squares.
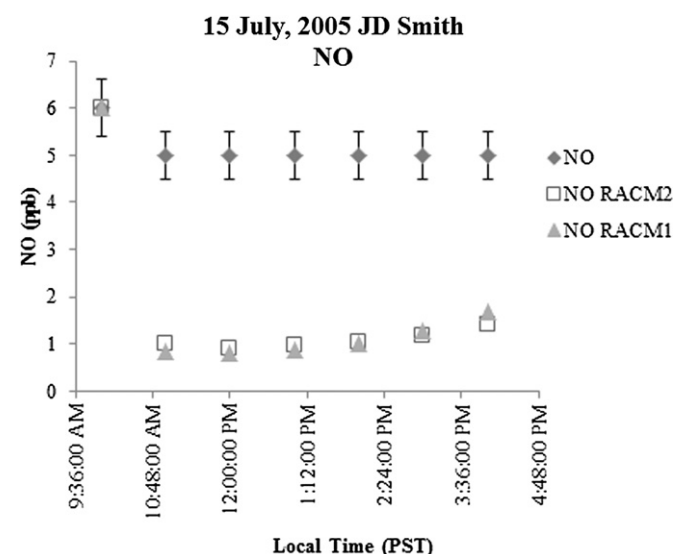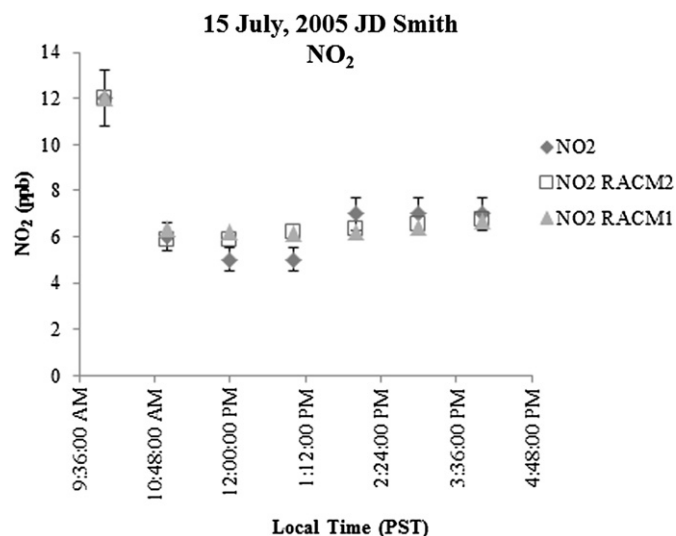

Fig. 9. Comparison of NO concentrations for JD Smith site on July 15, 2012. Observed values are dark gray diamonds, RACM1 predictions are gray triangles, RACM2 predictions are light gray squares.

Fig. 10. Comparison of NO$_2$ concentrations for JD Smith site on July 15, 2012. Observed values are dark gray diamonds, RACM1 predictions are gray triangles, RACM2 predictions are light gray squares.

Fig. 12. Comparison of HCHO concentrations for JD Smith site on July 15, 2012. RACM1 predictions are light gray squares, RACM2 predictions are dark gray diamonds.

than observed (Fig. 9). Both mechanisms were able to simulate NO$_2$ concentrations (Fig. 10).

Model output for HNO$_3$ for RACM1 and RACM2 differed by 20% at the peak concentrations, with RACM2 making less HNO$_3$ (Fig. 11). RACM1 also predicted higher HCHO concentrations than RACM2 in the beginning of the simulation, and slightly lower HCHO during the second half of the simulation (Fig. 12). In the case of PAN (Fig. 13), RACM1 predicts higher concentrations in the first half of the simulation and lower concentrations later in the simulation.

6. Conclusions and future work

The RACM2 chemical mechanism is intended to be used in atmospheric chemistry models that are used to simulate tropospheric chemistry ranging from remote continental to highly polluted urban regional. It can simulate ozone formation, acid
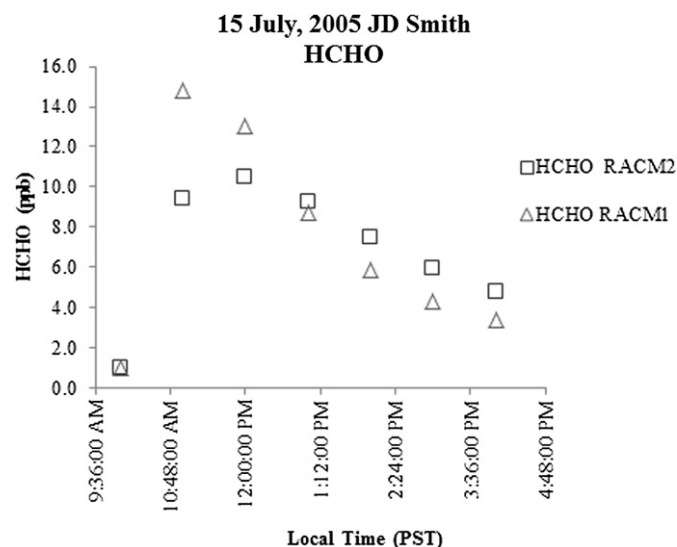
deposition and aerosol precursor formation. The RACM2 mechanism is an aggregated chemical mechanism with grouped model species which includes 17 stable inorganic species, 4 inorganic intermediates, 55 stable organic species (3 of these are primarily of biogenic origin) and 43 organic intermediates in 363 reactions. Although RACM2 is more complex than RACM1 it remains well within an acceptable range for use within a comprehensive Eulerian atmospheric chemistry model.

Photolysis reactions were updated for the inorganic and organic species. The updates to the inorganic chemistry were not dramatic although the potentially revolutionary reaction of photo-excited nitrogen dioxide with water vapor to produce HONO was considered and rejected. Several organic species were added to the RACM2 mechanism that were disaggregated from RACM1. Acetaldehyde and acetone were added to lengthen the decomposition chains of organic compounds. The addition of an explicit model species for acetone makes the RACM2 better for simulating the
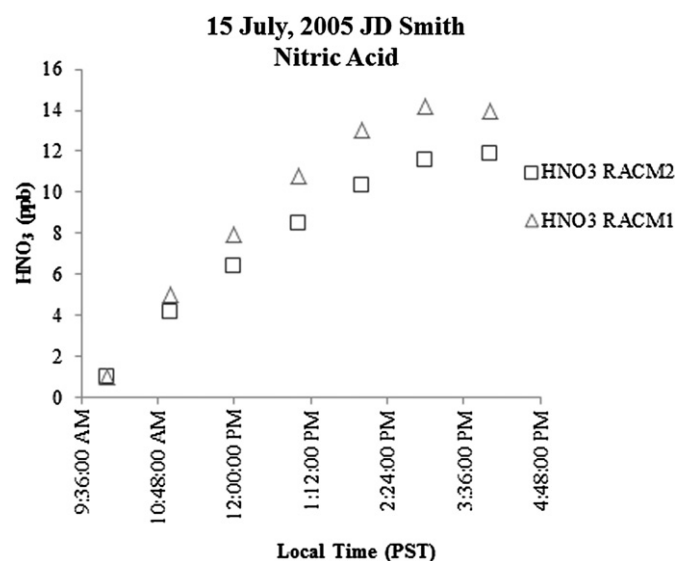

Fig. 11. Comparison of HNO$_3$ concentrations for JD Smith site on July 15, 2012. RACM1 predictions are light gray squares, RACM2 predictions are dark gray diamonds.
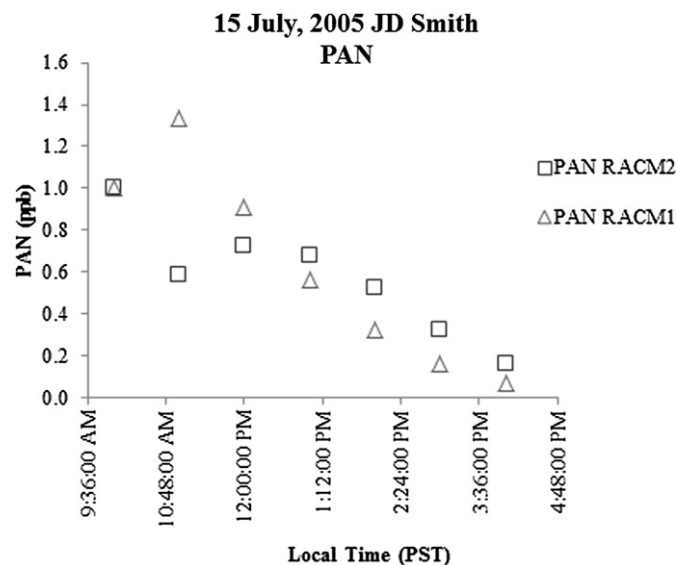

Fig. 13. Comparison of PAN concentrations for JD Smith site on July 15, 2012. RACM1 predictions are light gray squares, RACM2 predictions are dark gray diamonds.

upper atmosphere. There was a very significant revision to the aromatic scheme in RACM2; benzene, toluene, the individual isomers of m-, p- and o-xylene are now included in place of only toluene and a mixture of the three xylene isomers in RACM1. The production of alcohols is important in rural regions and these are represented by methanol, ethanol and a higher molecular weight alcohol species in RACM2. The mechanism for isoprene was updated and improved by including the explicit production of both methyl vinyl ketone and methacrolein. The mechanisms for α-pinene and ᴅ-limonene were also revised.

RACM2 was tested against twenty of the environmental chamber runs and compared to RACM1 predictions for the same experiments. The RACM2 simulations of the peak ozone and NO_2 concentrations were closer to the experiments than RACM1. A comparison of the two mechanisms in an ambient case showed RACM2 predicted more realistic ozone concentrations than RACM1. A comparison of the RACM1 and RACM2 mechanisms for "Real Atmosphere" cases showed that the RACM2 mechanism forecasts less ozone than RACM1 for most of the initial conditions simulated and that this trend to simulate lower predictions becomes greater at the higher ozone mixing ratios (see Supplementary information).

Future research needs include studies of the chemistry of aromatic and biogenically emitted species. A major limitation of atmospheric chemical mechanisms is due to the fact that the bulk of the laboratory data comes from room temperature experiments while there is significant temperature variation in the atmosphere. The temperature dependences of the inorganic rate constants require improvements that can only be addressed by making measurements over a greater temperature range.

Acknowledgments

Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2012.11.038.

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