



## 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.

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### 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

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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<sub>x</sub> 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-Climatology-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 received 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 received 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.

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