

# **Mechanisms for Air Quality Modeling: Development and Applications of the Regional Atmospheric Chemistry Mechanism**

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## **ABSTRACT**

The Regional Atmospheric Chemistry Mechanism (RACM) is a highly revised version of the RADM2 mechanism (RACM; Stockwell et al., 1997). The changes to the inorganic chemistry were relatively minor but there were substantial changes for many organic compounds. These revisions included improvements to the mechanisms for the oxidation of alkanes by HO radical, the ozonolysis of alkenes, the reaction of alkenes with NO<sub>3</sub> radical, peroxy radical reactions, aromatic chemistry and better treatment of the chemistry of isoprene and terpenes.

The RACM mechanism has been applied to evaluate incremental reactivities for the production of ozone from volatile organic compounds and to assess the aerosol particle formation reactivity of nitrogen oxide (NO<sub>x</sub>) emissions (Stockwell et al., 1999a;b). The concept of incremental reactivity was extended to multi-day scenarios. Ethane and acetone are regarded as unreactive compounds but for a five day scenario their reactivity is appreciable. The maximum ozone incremental reactivities (MOIR) of ethane, acetone and dimethoxymethane (a proposed low reactivity replacement solvent) have incremental reactivities that are about equal for a scenario with a duration of six days.

A similar approach was developed to assess the aerosol particle formation reactivity of nitrogen oxide (NO<sub>x</sub>) emissions for wintertime conditions in central California (Stockwell et al., 1999b). Our calculations found that about 33% of emitted NO<sub>x</sub> were converted to particulate nitrate on a molar basis and about 0.6 g of ammonium nitrate is produced for each gram of NO<sub>x</sub> emitted (the mass of NO<sub>x</sub> calculated as NO<sub>2</sub>). This estimate is in reasonable agreement with field measurements.

## **INTRODUCTION**

The gas-phase chemical mechanism is one of the most important components of an atmospheric chemistry model. It is difficult to include all significant chemical reactions in an air quality model because the organic chemistry of the polluted atmosphere is very complicated. There are large numbers of emitted volatile organic compounds (VOC) and each compound's degradation mechanism may include many chemical intermediates and reactions.

The Regional Atmospheric Chemistry Mechanism (RACM; Stockwell et al., 1997) is a compromise between chemical detail and accurate chemical predictions. The RACM is a new version of the Regional Acid Deposition Model mechanism (RADM2; Stockwell et al., 1990). There were relatively minor changes made to the inorganic chemistry but

the mechanisms for many organic compounds were highly revised. The alkane chemistry was revised to decrease the ratio of the yields of aldehydes to ketones. The yield of HO from the reaction of alkenes with ozone was increased. The branching ratios for the reaction of acetyl peroxy radicals with NO and NO<sub>2</sub> were revised and the reactions of organic peroxy radical + NO<sub>3</sub> reactions were added and these changes cause predicted concentrations of peroxyacetyl nitrate (PAN) from RACM to be lower than RADM2. The reactions of unbranched alkenes with NO<sub>3</sub> produce relatively large amounts of nitrates during the nighttime and this is now included. The RACM mechanism has a new condensed mechanism for aromatics, isoprene and terpenes but further improvement will be necessary in view of recent laboratory measurements. The RACM is becoming widely used in Europe, Asia and the United States. It has been accepted as the baseline mechanism for the German Tropospheric Research Program.

The RADM2 and the new RACM mechanisms were tested against the same set of representative environmental chamber experiments used previously to evaluate the RADM2 (Stockwell et al., 1990). An agreement of ±30% in peak ozone concentrations is within the limits imposed by uncertainties in the chamber experimental characteristics including wall loss, wall radical sources, actinic flux and initial conditions. The peak ozone concentrations predicted by the RACM mechanism had a mean normalized deviation of 19% from the chamber experiments while the mean normalized deviation was 13% for the RADM2 mechanism (Stockwell et al., 1997). The RACM and the RADM2 mechanisms predict peak NO<sub>2</sub> concentrations and the timing that the peak occurs very well. The mean normalized deviations of NO<sub>2</sub> peak concentrations from the chamber experiments are both near 10%. The mean normalized deviations of timing of the NO<sub>2</sub> peak concentrations for both mechanisms are near 3%.

The concentrations of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and PAN predicted by the RACM and the RADM2 mechanisms were compared for a set of urban and rural conditions (Stockwell et al., 1997). Although the differences between the two mechanisms for O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are small the differences in predicted PAN concentrations are very significant. The average predicted noontime PAN concentration ratios of RACM to RADM2 were 0.58.

## **MECHANISM APPLICATIONS AND METHODS**

The RACM mechanism has been applied to the calculation of incremental reactivity and the equivalence between NO<sub>x</sub> emissions and ammonium nitrate particle formation. Incremental reactivity, IR, is the change in the peak ozone concentration, Δ[O<sub>3</sub>], divided by an incremental change in the VOC present in the atmosphere, Δ[VOC], (Carter, 1994).

$$IR = \Delta[O_3] / \Delta[VOC]$$

A base scenario of initial VOC concentrations and emissions is defined and a NO<sub>x</sub> emission rate that gives the highest peak ozone concentration for the available VOC is determined. This scenario is known as the maximum ozone incremental reactivity scenario (MOIR). Another scenario with the NO<sub>x</sub> emission rate adjusted to give the greatest possible incremental reactivity for VOC mixture is known as the maximum

incremental reactivity scenario (MIR). The RACM mechanism was modified to include with an explicit chemical mechanism for dimethoxymethane and acetone (Stockwell et al., 1999a). Simulations were made to determine the incremental reactivity of these compounds for single and multiple day scenarios.

The box model with the RACM mechanism was modified to investigate the equivalence between  $\text{NO}_x$  emissions and ammonium nitrate particle formation (Stockwell et al., 1999b). The model included the heterogeneous reaction of  $\text{N}_2\text{O}_5$  with water, deposition loss processes for ozone, NO,  $\text{NO}_2$ , PANs,  $\text{HNO}_3$ , HONO,  $\text{N}_2\text{O}_5$ , organic nitrates,  $\text{SO}_2$ ,  $\text{SO}_4^-$ ,  $\text{H}_2\text{O}_2$  and organic peroxide and the yield of ammonium nitrate particles from nitric acid. The yield of nitric acid was defined to be the fraction of gaseous nitric acid that combines with ammonia to form particulate ammonium nitrate for the conditions of central California. The yields were calculated with the Simulating Composition of Atmospheric Particles at Equilibrium model, version 2 (SCAPE-2) (Kim and Seinfeld, 1993a,b; 1995).

## RESULTS AND CONCLUSIONS

Single day scenarios do not give a complete picture of a VOC's incremental reactivity. Our calculations showed that the incremental reactivity of ethane, acetone and dimethoxymethane increase as the duration of the scenario increases (Stockwell et al., 1999a). The MOIR of dimethoxymethane was greater for scenarios between one and six days but the three compounds reached almost the same MOIR value for the six day time period. The MIRs of ethane, acetone and dimethoxymethane increased as the duration of the scenario increased. Although the MIR of dimethoxymethane was greater than the MIR of ethane for all six scenarios the MIR of acetone increased so that its MIR became greater than the MIR of dimethoxymethane for scenarios lasting longer than 2 days. This result suggests that even unreactive compounds may become relatively reactive over multiple day scenarios. Ozone control strategies that intend to reduce the concentrations of highly reactive VOC by increasing the use of "unreactive VOC" in urban regions might even increase ozone concentrations over the regional scale.

A photochemical box model and an equilibrium ammonium nitrate particulate model were used to investigate the wintertime equivalence between  $\text{NO}_x$  emissions and ammonium nitrate particle formation (Stockwell et al., 1999b). During the wintertime: the total ammonia to nitrate ratio was greater than one; the relative humidity was greater than 70%; and the temperature was less than 292 K in central California. Under these conditions approximately 80% of the nitric acid resulting from  $\text{NO}_x$  emissions was calculated to be in the particulate nitrate phase. It was calculated that  $33 \pm 7\%$  of the moles of emitted  $\text{NO}_x$  are converted to particulate nitrate. This corresponds to a particle equivalent of  $\text{NO}_x$  emissions on the order of  $0.57 \pm 0.13$  g of ammonium nitrate for each gram of  $\text{NO}_x$  emitted (where the mass of  $\text{NO}_x$  emissions was calculated as  $\text{NO}_2$ ). The particle equivalent of  $\text{NO}_x$  emissions was most sensitive to uncertainties in the mixing height which affected the deposition of nitrogenous species. The calculated equivalence between  $\text{NO}_x$  emissions and ammonium nitrate particle formation values were in reasonable agreement with field measurements for central California.

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