A New Mechanism for Regional Atmospheric Chemistry Modelling

A contribution to subproject CMD

W.R. Stockwell[1], F. Kirchner[2], M. Kuhn[1] and S. Seefeld[3]

[1]*Fraunhofer Institute for Atmospheric Environmental Research (IFU), Kreuzeckbahnstr. 19, D-82467 Garmisch-Partenkirchen, Germany*
[2]*Swiss Federal Institute of Technology, DGR, Ecole Polytechnique, Federale de Lausanne, CH-1015 Lausanne, Switzerland*
[3]*Swiss Federal Institute for Environmental Science Technology (EAWAG), ETH Zürich, Switzerland*

Introduction

Chemical mechanisms are used by air quality models to predict the formation of photochemical air pollutants. Therefore the chemical mechanism used by a model is one of its most important components. Unfortunately there are many unknowns in the knowledge of gas-phase atmospheric chemistry. As new information becomes available it must be incorporated into the mechanisms. Therefore the development of mechanisms must be a continuing process. The "Regional Atmospheric Chemistry Mechanism" (RACM) (Stockwell *et al.*, 1997) is a new gas-phase chemical mechanism for the modelling of the troposphere. The RACM mechanism is based upon the earlier Regional Acid Deposition Model, version 2 (RADM2) (Stockwell *et al.*, 1990) mechanism and the more detailed Euro-RADM mechanism (Stockwell and Kley, 1994). The revisions made use of the extensive amount of new laboratory data available, including: Atkinson *et al.* (1997), DeMore *et al.* (1997) and Le Bras (1997). The RACM mechanism can be used to model atmospheric chemistry for conditions that range from the polluted urban boundary layer to the remote global and upper troposphere. The RACM mechanism and a comparison of the RACM mechanism with the RADM2 mechanism is presented.

The RACM mechanism

The RACM mechanism includes 237 reactions. The mechanism includes 17 stable inorganic species, 4 inorganic intermediates, 32 stable organic species and 24 organic intermediates. The RACM mechanism differs from the

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RADM2 and Euro-RADM mechanisms in many significant ways. The ratios of the yield of aldehyde to the yield of ketone from alkanes were reduced. The relatively large production of organic nitrates from alkenes is now included. The aromatic chemistry was revised to reduce the yield of cresol and the reactions of HO, NO_3 and O_3 with unsaturated dicarbonyl species and unsaturated peroxynitrate were added. A new degradation scheme for biogenically emitted compounds, isoprene, α-pinene and *d*-limonene, is included in RACM. The new isoprene mechanism includes the formation of methacrolein and MPAN, isoprene ozonolysis and hydroperoxide production, and the formation of organic nitrates from the reaction of isoprene with NO_3. The methyl vinyl ketone formed from isoprene is treated as a terminal alkene. In comparison with isoprene there is relatively little available information for α-pinene and *d*-limonene. For these terpenes many of the reactions of their products were assumed to be analogous to known reactions for lower alkenes. Revisions were made to the rate constants for the formation and decomposition reactions of peroxyacetyl nitrate (PAN) and for the reaction of acetyl peroxy radical with NO. The rate constants for organic peroxy radicals, peroxy radical reactions and the reactions of organic peroxy radicals with nitrate radicals were added. These revisions to the PAN and acetyl peroxy radical chemistry lead to significant changes in simulated PAN concentrations under many atmospheric conditions.

Comparison of the RACM and RADM2 mechanisms

The concentrations of several important chemical species, O_3, H_2O_2, H_2SO_4, HNO_3 and PAN calculated by using the two mechanisms were compared for 18 scenarios. Two days were simulated for summer time conditions beginning and ending at 06:00 hours, local time. The initial conditions and the organic mixtures used for this comparison were typical of urban and rural regions at the Earth's surface and they are given in detail in Stockwell *et al.* (1997). The simulation conditions that were typical of rural air had initial NO_x concentrations that ranged from 0.5 to 5 ppb and total non-methane organic compound (NMOC) concentrations that ranged from 10 to 100 ppbC. For urban conditions the initial NO_x concentrations ranged from 10 to 100 ppb and the initial NMOC concentrations ranged from 100 to 1000 ppbC. The photolysis rate parameters were calculated for 40° latitude. The original and updated photolysis rate parameters were used for the RADM2 and the RACM mechanisms respectively. For these simulations no emissions, dilution or deposition were included but these simulations ended before the concentrations of NO_x and reactive organic compounds were reduced to unrealistically low values. The results of these simulations (Stockwell *et al.*, 1997) are shown in Fig. 1 and Table 1.

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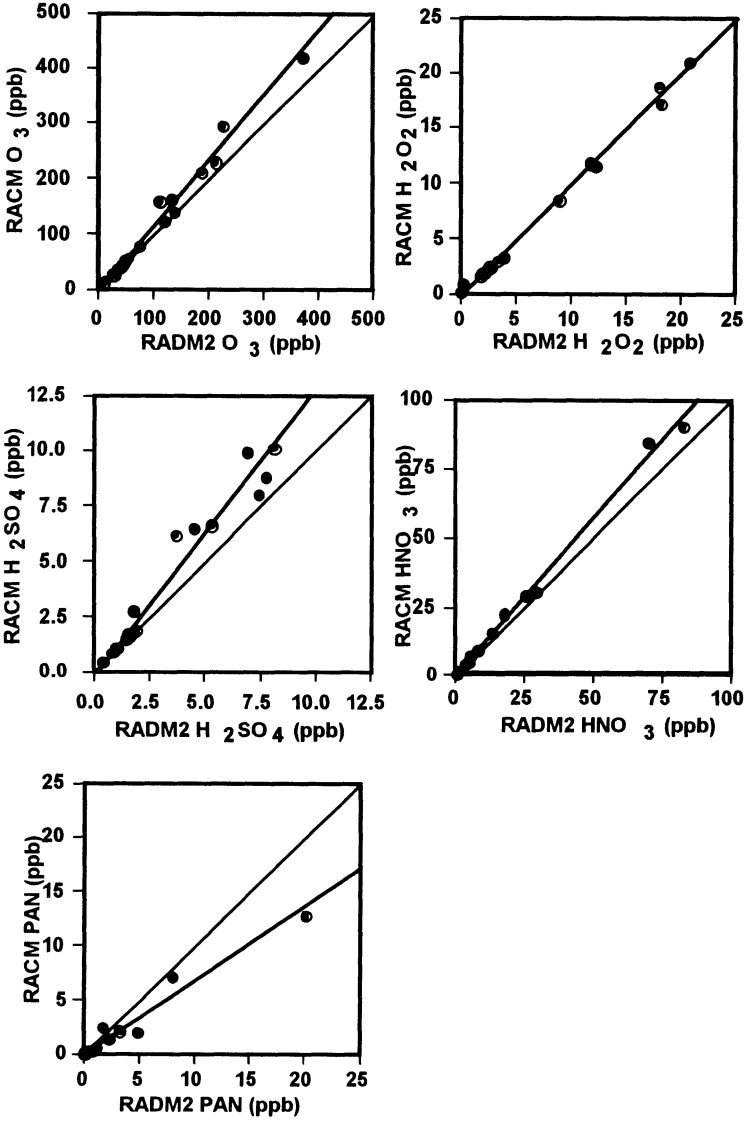

Fig. 1: The maximum concentrations of O_3 H_2O_2, H_2SO_4, and HNO_3 and the PAN concentrations at noon on the second day for the RACM and RADM2 mechanisms for 18 different scenarios. The thick line is the best fit line and the thin line is the 1–1 line of perfect agreement.

Table 1: Correlations between the RACM and RADM2 mechanisms for calculated maximum concentrations of O_3 H_2O_2, H_2SO_4, and HNO_3 and the PAN concentrations at noon on the second day for the 18 scenarios.

Species	Slope	Intercept (ppb)	Variance (r^2)
O_3	1.168	–4.619	0.983
H_2O_2	1.004	–0.274	0.996
H_2SO_4	1.243	0.009	0.957
HNO_3	1.141	–0.015	0.996
PAN	0.661	0.040	0.966

The RACM mechanism predicts higher maximum O_3 concentrations than the RADM2 for 11 of the 18 scenarios simulated. The O_3 concentration differences are greatest for the scenarios with the greatest concentrations of alkenes and aromatics. The mechanisms give calculated H_2O_2 concentrations that are almost equal but the RACM mechanism calculated greater H_2SO_4 concentrations. This suggests that while the integrated HO_2 concentrations are about the same, the integrated HO concentrations are greater for the RACM mechanism. The differences in H_2SO_4 between the RACM and RADM2 mechanisms are greatest for the urban scenarios and these differences are greater for those scenarios with the higher initial NMOC/NO_x ratios. Slightly higher HNO_3 concentrations are calculated with the RACM mechanism than with the RADM2. The differences in HNO_3 concentrations are due to differences in the calculated HO concentrations, changes in PAN chemistry and changes in the night-time NO_3 – RO_2 chemistry. The RACM mechanism yields significantly less PAN than RADM2 and these results are in agreement with our previous results (Kirchner and Stockwell, 1996; 1997). The loss rate of the ACO_3 radical is greater in the RACM mechanism due to revisions to the rate constant for the reaction with NO and the addition of the reaction of ACO_3 with NO_3. This shows the importance of the revisions to the NO_3 and peroxy radical chemistry (Stockwell *et al.*, 1997).

Conclusions

The RACM mechanism predicts somewhat higher concentrations of O_3, H_2SO_4 and HNO_3 than the RADM2, they both predict almost the same H_2O_2 concentrations and the RACM mechanism predicts significantly lower concentrations of PAN. We strongly recommend the RACM mechanism for use in regional atmospheric chemistry models over the RADM2 because the RACM chemistry is based upon more significantly reliable data than RADM2.

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