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**Sensitivity of Atmospheric Models to
Rate Terms within Complex Chemical
Mechanisms**

Executive Summary

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COORDINATING RESEARCH COUNCIL, INC.

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Sensitivity of Atmospheric Models to Rate Terms within Complex Chemical Mechanisms

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EXECUTIVE SUMMARY

Photochemical grid models (PGM's) are used to develop emission control strategies for ozone (O₃) and particulate matter (PM), and a key component of such models is the gas-phase chemical mechanism. Despite several decades of work, there are still important uncertainties in the chemistry, due in part to the large number of volatile organic compounds (VOC's) in emissions and the difficulty of replicating atmospheric conditions in the laboratory. The Coordinating Research Council has sponsored a series of reviews by J. G. Calvert et al. to evaluate our understanding of atmospheric gas-phase chemistry.

The objectives of this project were (1) to improve tools for analyzing how predictions of PGM's depend upon chemical mechanisms and their uncertainties, (2) identify important mechanistic uncertainties in chemical mechanisms of regulatory importance, and (3) use published data to determine whether uncertainties can be narrowed or new data are needed.

In the project, we used the Comprehensive Air Quality Model with Extensions (CAMx) and added a new capability to the model to calculate sensitivities to rate terms in the chemical mechanism. Taking the reaction $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$ as an example, the rate term for loss of OH is $k c_{\text{OH}} c_{\text{NO}_2}$, where k is the rate constant and c_{OH} and c_{NO_2} are the concentrations of OH and NO₂, respectively. This rate term is part of the differential equation defining the time evolution of OH in the model. We defined the sensitivities to the rate terms such that the sum of these sensitivities equals the sensitivity to the rate constant. I.e., the sensitivities to the rate terms decompose the sensitivity to the rate constant into separate contributions representing the sensitivity to the loss of each reactant and gain of each product.

The sensitivity to rate terms was implemented by extending the decoupled direct method (DDM) for sensitivity analysis already used within CAMx to calculate sensitivities to initial and boundary concentrations, emissions, and rate constants. We checked that the sensitivity to rate terms was implemented correctly in CAMx by comparing sensitivities obtained by the DDM to sensitivities obtained by manually varying the rate terms (brute-force method). We also checked that the sum of the sensitivities to rate terms equaled the sensitivity to the rate constant as obtained by the DDM. The new capability to calculate sensitivities to rate terms will be released in CAMx version 6.2.

Two CAMx applications were used in the project, a simplified configuration, termed the box model, and the full three-dimensional (3-D) model. The box model simulated the chemical reactions of initial concentrations of VOC's and nitrogen oxides (NO_x) in a single grid cell over 24 hours, but the model did not include transport into the cell, deposition, or continuous emissions. We simulated four scenarios with the box model: two VOC mixtures representing urban and rural areas; two VOC concentrations for each mixture giving initial VOC/NO_x of 5 and

10 ppbC/ppb. The 3-D model was run for the period of July 2008 using the same meteorological inputs, emissions, and boundary concentrations previously used in the 2008 base case simulation for CRC Project A-76-1. A 36-km domain covered the continental U.S. with a nested 12-km domain for the eastern U.S.

Using first-order sensitivities from the box model, we screened rate terms in the Carbon Bond 2005 (CB05) and Carbon Bond 6 (CB6) chemical mechanisms for the importance of rate terms in affecting the concentrations of O₃, formaldehyde (FORM) and HOx (HO + HO₂). The screening covered the rate terms for the products of oxidation of ethene (ETH), terminal olefins (OLE), internal olefins (IOLE), mono-alkyl aromatics (TOL), poly-alkyl aromatics (XYL), isoprene (ISOP), and mono-terpenes (TERP), the terms for NO_x removal by organic nitrate formation, the terms for NO_x re-formation from nitrates, and the terms for the reactants and product of the OH + NO₂ → HNO₃ reaction. The sensitivities to the formation of certain products of ISOP oxidation and to the loss of the reactants in the OH + NO₂ → HNO₃ reaction are the largest in magnitude for multiple box-model scenarios and for both the CB05 and CB6 mechanisms. Consequently, we focused simulations with the 3-D model on the oxidation of ISOP and the OH + NO₂ → HNO₃ reaction.

To determine whether the box-model results provided representative rankings of the sensitivities, sensitivities were calculated with the 3-D model for products of ISOP oxidation in the CB05 mechanism. The 3-D results were analyzed to determine sensitivities of maximum daily average 8-hour (MDA8) O₃ averaged over sites in EPA's Interagency Monitoring of Protected Visual Environments (IMPROVE) network and over sites in the Chemical Speciation Network (CSN). The IMPROVE sites are primarily in rural areas and the CSN sites in urban/suburban areas. The O₃ sensitivities for the ISOP products at the IMPROVE sites are highly correlated (correlation coefficient = 0.95) with the box-model sensitivities for the rural scenario with VOC/NO_x = 10. Also, the HOx sensitivities at the IMPROVE and CSN sites are highly correlated (coefficients = 0.84-0.97) with the box-model sensitivities for the rural and urban scenarios, respectively. Other comparisons of 3-D and box-model results for O₃ and FORM have correlation coefficients in the range 0.30-0.82. Overall, the product formation sensitivities from the box-model identify the most and least important products in reasonable agreement with the 3-D model.

As indicated in the most recent review by Calvert et al. (2014), there have been numerous studies of ISOP oxidation in recent years, and consequently our knowledge of this oxidation mechanism has been evolving at a rapid pace. An updated version of the CB6 mechanism, CB6 revision 2 (CB6r2) was recently completed (under other funding), and CB6r2 incorporates the information on ISOP chemistry reviewed by Calvert et al. (2014). For additional work with the 3-D model, we chose the CB6r2 mechanism rather than the CB6 mechanism to include the

latest understanding of the ISOP oxidation. We calculated product formation sensitivities for oxidation of ISOP by OH, which is the dominant route for oxidation of ISOP. The MDA8 O₃ sensitivities at the IMPROVE and CSN sites are largest in magnitude for the products NO₂, organic nitrates (INTR), HO₂, and methacrolein/methyl vinyl ketone (ISPD) and smallest for the peroxy radical operator (RO₂), methylperoxy radical (MEO₂), OH, and acetic acid (AACD).

In calculating the sensitivities to the rate terms for the reactants and products in a reaction, there is an implicit assumption that the terms are independent. This simplifying assumption is reasonable for the purpose of screening a large number of products of VOC oxidation to determine which have a significant impact on O₃ formation. However, the formation of a product is generally coupled to the loss of some fraction of one or more reactants. Consequently, a more refined approach is to define *net* product formation sensitivities that take into account both the formation of the product and the loss of reactants. Net product formation sensitivities provide an improved ranking and give the net effect on O₃ formation (increase or decrease). The disadvantage of net product formation sensitivities is that they require examining each reaction in detail to assign reactants to products and thus require more effort to calculate.

Thus, to understand the ISOP results in more detail, we also calculated net product formation sensitivities. In the 3-D simulation, the 4 products having the largest and smallest magnitude sensitivities of MDA8 O₃ are the same whether product formation or net product formation sensitivities are used for the ranking at the IMPROVE and CSN sites. However, the *net* formation sensitivity for NO₂ is significantly smaller than the NO₂ formation sensitivity because the positive sensitivity to NO₂ formation is offset by the negative sensitivity to NO loss in the reaction. Also, the sensitivities for several products including INTR and ISPD show some sign reversals when switching from product formation to net product formation sensitivities.

The 3-D model results showed that loss of NO₂ in the OH + NO₂ → HNO₃ reaction is more important than loss of OH over most of the eastern U.S. modeling domain, except for small areas near Chicago, Detroit and New York where the relative importance of the two loss terms becomes comparable. This suggests that much of the O₃ formation in the simulation is NO_x limited. Using a more recent rate constant for this reaction had little impact on O₃ concentrations or sensitivities.

Our conclusions are:

1. Formation of products from the oxidation of ISOP and loss of NO₂ and OH in the OH + NO₂ → HNO₃ reaction have the largest impact on O₃, FORM and HO_x concentrations. Surprisingly, products from the oxidation of ISOP are important in urban as well as rural areas, based on our results.

2. Product formation sensitivities provide a useful, approximate ranking of the importance of products from oxidation of VOC's. Net product formation sensitivities provide an improved ranking and give the net effect on O₃ formation (increase or decrease).
3. Some oxidation products of the VOC's studied in this project have very little effect on O₃, FORM, and HOx concentrations and could be omitted from specific reactions. However, these products have roles elsewhere in the chemistry and likely could not be excluded entirely from the chemical mechanisms. An exception is formic acid (FACD), which could possibly be excluded without affecting O₃ predictions.
4. A recent update to the OH + NO₂ rate constant has little effect on model predictions.

Two recommendations are:

1. Any new experimental results on ISOP chemistry should be incorporated into the chemical mechanisms used in air quality models and the impact of the updates determined. Given the current understanding of ISOP emissions and chemistry, it is very important to have a correct representation of ISOP oxidation for both urban and rural areas.
2. Calculating net product formation sensitivities for VOC's other than ISOP would improve our understanding of oxidation of these VOC's. For this purpose, some additional modifications to CAMx would be useful and allow easier calculation of the net sensitivities.

The results of this study are documented in a journal article that has been submitted to a peer review publication. Once the article has been accepted and published, a link to the paper will be posted on the CRC website.