Chemical Mechanism and Reactivity Projects at U.C. Riverside

William P. L. Carter
CE-CERT, University of California, Riverside, CA
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Outline

- Gas-phase chemical mechanism development projects
- Stationary source and coatings reactivity projects
- Experimental and mechanism development project for SOA modeling

Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales

- Objectives: Update the SAPRC mechanism and reactivity scale
- Status: Completed in January, 2008. CARB contract 03-318
- Accomplishments:
  - See RSAC presentation for further discussion
  - SAPRC-99 updated to SAPRC-07
  - New reactivity scales derived
- Work Remaining:
  - Project did not include implementation, condensation, or peer review of the new mechanism

International Conference on Atmospheric Chemical Mechanisms

- Objectives: Co-organize and participate in the first International Conference on Atmospheric Chemical Mechanisms
- Status: Completed in 2007. CARB contract 05-750
- Accomplishments:
  - Conference held in Davis, CA, on December 6-8, 2006
  - Papers and posters given on variety of subjects related to gas-phase and multiphase atmospheric chemistry
  - Gave presentations on the SAPRC-07 mechanism being developed and the UCR environmental chamber database
  - Prepared conference summary presentation and document.
- Ongoing work:
  - These conferences are continuing every 2 years. Participated in second conference Davis in 2008.

Development of a Condensed SAPRC-07 Chemical Mechanism

- Objectives: Developed condensed versions of SAPRC-07 for airshed modeling.
- Status: Completed in 2008 as part of CARB Contract 05-750.
- Accomplishments:
  - Two condensed mechanisms derived from SAPRC-07:
    - CS07A: Same peroxy radical treatment as SAPRC-99. Similar in size to CB05. Suitable for O_3 modeling.
    - CS07B: More detailed peroxy radical treatment, larger but more suitable for adaptation to SOA modeling.
  - Chemical validity of both derived directly from full SAPRC-07 and give essentially the same O_3 predictions.
- Work Remaining:
  - Not yet widely implemented into airshed models.

Implementation of Updated Chemical Mechanisms for Airshed Model Applications

- Objectives:
  - Participate in SAPRC-07 peer review process and address peer review comments
  - Assist CARB in implementing versions of SAPRC-07
  - Work on improving aromatics portion of mechanism
- Status: Ongoing CARB contract 07-730
- Accomplishments:
  - Peer review of SAPRC-07 is complete. Response to reviews prepared. Mechanism revised to correct errors found during review and ongoing projects.
  - Documentation, evaluation and reactivity scales for SAPRC-07 updated to reflect results of review and corrections
  - See presentations at the RSAC meeting

Implementation of Updated Chemical Mechanisms for Airshed Model Applications

(continued)

- Work Remaining - Near Term:
  - Condensed SAPRC-07 (and its documentation) needs to be updated to reflect recent changes to SAPRC-07
  - Files implementing the full and mechanisms need to be updated and made available
  - Assist CARB in implementing SAPRC-07 as needed
- Priorities for additional work need to be determined:
  - Develop and evaluate alternative aromatics mechanisms as originally proposed for CARB contract 07-750
  - Develop and evaluate a version of SAPRC-07 with a lower OH + NO_2 rate constant as recommended in Harley's review
  - Update SAPRC-07 and CS07 with a new base ROG mixture when it becomes available (also recommended by Harley).

Implementation of the SAPRC-07 Mechanism in CMAQ

- Objectives:
  - Develop a version of SAPRC-07 with more explicit species as needed for toxics modeling
  - Assist the EPA in implementing SAPRC-07 in CMAQ
- Status: Ongoing project funded by the U.S. EPA through a contract to the Computer Sciences Corporation
- Accomplishments:
  - A “toxics” version of SAPRC-07 developed with 14 additional species to represent specific compounds of interest to EPA
  - Emissions assignments made for all versions of SAPRC-07 and other mechanisms for use with EPA’s “Speciation Tool”

Implementation of the SAPRC-07 Mechanism in CMAQ

(continued)

- Remaining Work - Near Term:
  - The “Toxics” version needs to be updated to be consistent with the recent changes to SAPRC-07
- Other Remaining Work:
  - Continue to assist the EPA with implementing SAPRC-07
  - Optionally update the mechanism when a new base ROG mixture is available

Reactivity Estimates for Selected Consumer Products Compounds

- Objectives: Reduce uncertainties of ozone impact estimates of selected consumer product compounds of interest to the CARB. Representative amines and d-limonene were chosen for study.
- Status: Completed in February, 2008. CARB Contract 06-408
- Accomplishments - d-Limonene:
  - Results were consistent with the existing mechanism
- Accomplishments - Amines:
  - Chamber experiments conducted with AMP, ethanolamine, isopropyl amine and *t*-butyl amine.
  - Quantitative mechanism evaluation was complicated by the lack of an analysis method for gas-phase amines. Amounts injected had to be treated as adjustable parameters

Reactivity Estimates for Selected Consumer Products Compounds

(continued)

- Accomplishments - Amines (continued):
  - Despite the analysis problems, the data could still be used to develop and evaluate alternative amine mechanisms
  - General methods were derived to estimate amine mechanisms that were consistent with the data obtained
  - The new mechanisms gave much different reactivity values than previously. Tertiary amines such as AMP inhibit O_3
  - Tabulated reactivities may be overestimates because of possible removal of amines by reaction with HNO_3.
- Remaining work needed - Amines:
  - Reliable methods are needed to measure gas-phase amines
  - The importance of removal of amines by HNO_3 under atmospheric conditions needs to be determined.

Investigation of Atmospheric Ozone Impacts of Selected Compounds

- Objectives: Quantify ozone impacts for compounds of interest to various private sector groups
  - Methyl Iodide (for Arysta LifeScience Corporation)
  - Trans 1,3,3,3-tetrafluoropropene (for Honeywell Corporation)
- Status: Arysta contract completed in 2007. Honeywell project recently completed for this compound but ongoing for others.
- Accomplishments:
  - Chamber experiments conducted with the compounds and mechanisms developed that were consistent with these data.
  - Methyl iodide found to inhibit O_3 but enhance PM.
  - Trans 1,3,3,3-tetrafluoropropene is predicted to have a somewhat lower O_3 impact than ethane on a mass basis.

Environmental Chamber Studies of Ozone Impacts of Coatings VOCs

- Objectives:
  - Improve correlation of reactivities measured in chamber experiments to reactivities calculated for the atmosphere
    - Chamber experiments are less sensitive to secondary reactions of oxidized products than atmosphere.
    - This is attributed to lower integrated OH levels. Therefore, objective is to increase this in experiments
  - Reduce uncertainties in reactivity estimates of coatings VOCs of interest to the CARB
- Status: Project is in its initial stages. CARB contract no. 07-339

Environmental Chamber Studies of Ozone Impacts of Coatings VOCs

(continued)

- Accomplishments and Plans to Date:
  - Model simulations indicate following approaches will increase integrated OH levels in chamber experiments:
    - Increase light intensity
    - Increase duration of experiments
    - Add radical initiators (has drawbacks)
  - The light intensity in the UCR EPA chamber will be increased by doubling number of blacklights. Construction should be completed by the end of May.
  - Long duration experiments will require reproducibly adding make-up air during run. A system to do this has been designed and parts have been ordered.

Environmental Chamber Studies of Ozone Impacts of Coatings VOCs

(continued)

- Remaining Work:
  - Once chamber modifications are complete, experiments to test the new methods will be conducted with selected previously studied compounds:
    - n-Butane (well established mechanism) (positive reactivity in both chamber and atmospheric MIR)
    - n-Octane (established mechanism but reactivity of bifunctional products is uncertain) (negative reactivity in chamber but positive atmospheric MIR)
    - Texanol® (important coatings VOC) (zero reactivity in chamber but positive atmospheric MIR)
    - Other compounds(s) to be selected by the CARB

Environmental Chamber Studies of Ozone Impacts of Coatings VOCs

(continued)

- Remaining Work (continued):
  - CARB (with input from RRAC) needs to prioritize additional compounds to study.
  - Previous CARB suggestions include:
    - Synthetic Mineral Spirits: ASTM D235, Type III C-1
      - Studied previously, but would benefit from experiments using higher integrated OH
    - Triethylamine and/or Dimethylethanolamine
      - Not studied previously. Mechanisms uncertain
      - Analytical method development needed
      - Would be useful to study effect of HNO_3

Environmental Chamber Studies of Ozone Impacts of Coatings VOCs

(concluded)

- Remaining Work (continued):
  - Previous CARB suggestions (continued):
    - Ethyl Methyl Ketone Oxime
      - Not studied previously, mechanism uncertain
    - 2-Ethylhexyl Benzoate
      - Not studied previously, mechanism uncertain
      - Experiments would reduce uncertainty of reactivity estimates for other benzoates
    - 1-Nitropropane
      - Not studied previously, mechanism uncertain
      - Reactivity probably quite low (current MIR=0.2). May be a candidate for VOC exemption)

SOA Formation: Chamber Study and Model Development

- Objectives: Develop improved mechanisms to predict secondary organic aerosol (SOA) from aromatics and other compounds.
- Status: Approved by the CARB Research Screening Committee.
- Proposed Overall Approach:
  - This project to be carried out in collaboration with Dr. David Cocker at UCR and Dr. Robert Griffin at Rice University.
  - UCR EPA chamber experiments will be conducted to develop and evaluate models for SOA from aromatics, aromatic products, and selected other VOCs
  - The SAPRC-07 mechanism will be expanded and adapted for SOA modeling based on the results of the experiments.
  - Use the results to develop improved mechanisms for predicting SOA in 3-D airshed models.