

Final Report**UPDATES TO THE CARBON BOND 4
PHOTOCHEMICAL MECHANISM**

Prepared for

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1. INTRODUCTION

This project developed an updated version of the Carbon Bond 4 (CB4) chemical mechanism to be used by LADCO and the Midwest RPO for ozone and particulate matter (PM) modeling. The goal was to provide LADCO and the MRPO with a single, consistent chemical mechanism for use in upcoming ozone and PM state implementation plan (SIP) development activities. The new mechanism is called the CB4 with extended inorganic reactions (CB4xi) and will be released in CAMx version 4.20 as chemical mechanism number 4 (M4).

The CB4xi mechanism was developed after reviewing several other versions of the CB4 including the original published version (Gery et al., 1989), CAMx mechanisms 3 and 4 (ENVIRON, 2004), versions of CB4 used in EPA's REMSAD model (EPA, 2004), CB2002 (Jeffries, Voicu, and Sexton, 2002) and CBM-Z (Zaveri and Peters, 1999). The CB4xi is the mechanism 4 version of CB4 from CAMx with 17 additional inorganic chemistry reactions. The added reactions are unimportant for smog chamber conditions (high NO_x levels, 1-day experiments, room temperature and pressure) but potentially important for regional and annual modeling conditions (lower NO_x levels, multi-day simulations, low temperatures and pressures).

Background

The MRPO and LADCO use the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2004) for ozone and particulate matter (PM) modeling. CAMx includes several different chemical mechanisms and most modelers use one of the following three mechanism choices:

Mechanism 3 – The original 1989 CB4 mechanism with updated PAN chemistry, radical reactions and isoprene reactions as used for the Ozone Transport Assessment Group (OTAG) modeling.

Mechanism 4 – Mechanism 3 with updates for PM modeling such as production of secondary organic aerosols (SOA) and updated rate constants for several key reactions (OH with SO₂, NO₂, CO and CH₄) that are pressure dependant.

Mechanism 5 – The SAPRC99 mechanism with a fixed number of chemical reactions (212), chemical species, and reaction parameters. This is called the fixed parameter version of SAPRC99 developed by Dr. William Carter for EPA's CMAQ model.

The development history of the CB4 mechanism is reviewed in Section 2 of this report. CB4 was originally developed for urban/regional ozone modeling, but now is being used for PM/visibility modeling with continental scale domains and annual databases. Annual PM modeling introduces a wider range of ambient conditions than regional ozone modeling, such as:

- Lower temperatures and pressures when modeling the upper troposphere and even the lower stratosphere.
- More pristine atmospheric conditions in remote marine and continental environments.

In developing chemical mechanisms for REMSAD, Dr. Whitten has found that the inorganic reactions in CB4 should be expanded to appropriately represent annual modeling conditions. Since these expansions do not alter the performance of the mechanism for smog chamber conditions they can be considered independent of mechanism chamber evaluations. Extra inorganic reactions for the CB4 mechanism are discussed in Section 3 of this report.

Project Goals and Benefits

LADCO/MRPO has used mechanism 3 for ozone modeling and mechanism 4 for PM/visibility modeling. It would be preferable to use a single mechanism for both ozone and PM modeling. The goal of this project was to implement an updated CB4 in CAMx that is suitable for both ozone and PM modeling and reflects updated science. The benefits will be improved science in the LADCO/MRPO modeling and simplified model application by eliminating the use of two different chemical mechanisms.

2. VERSIONS OF THE CARBON BOND MECHANISM

EPA sponsored the development of the Carbon Bond mechanism version IV (CB4) in the late 1980's for use in urban and regional photochemical modeling and Gery et al., (1989), published the mechanism. The regional models of the late 1980's that utilized CB4 (i.e., EPA's Regional Oxidant Model and Systems Applications' Regional Transport Model, version III) were more limited than current regional models (e.g., formulated for the planetary boundary layer and not the upper troposphere) and the original CB4 was more appropriate for urban than regional scale modeling.

EPA was a reluctant to update the CB4 mechanism in the early 1990s. A technical concern was that updating the mechanism without repeating the evaluation against smog chamber data could upset the overall balance of the mechanism. A policy concern was that updating the mechanism could change photochemical model results that underpinned existing regulatory decisions (e.g., SIPs). Nevertheless, there were three main updates to the CB4 mechanism in the early and mid 1990s. This culminated with the version of CB4 used for the Ozone Transport Assessment Group (OTAG) modeling.

The UAM-IV Version of CB4

The EPA's Urban Airshed Model (UAM-IV; Morris and Myers, 1990) had the first widely used version of the CB4 mechanism. Changes from the Gery et al. (1989) mechanism were the inclusion of explicit chemistry for methanol and ethanol and an update to the PAN chemistry. The explicit alcohol chemistry was included to improve accuracy in modeling the impacts of these compounds as fuel additives. Adding explicit methanol and ethanol chemistry had little or no impact on the smog chamber evaluation.

Dodge (1991) updated the PAN chemistry for CB4 because the Gery et al. (1989) mechanism had an incorrect temperature dependence for PAN formation (Tuazon, Carter and Atkinson, 1991). Changing the temperature dependence of PAN formation could potentially upset the chamber evaluation, however the change implemented by Dodge (1991) mainly affected cold conditions and so did not upset the chamber evaluation for conditions relevant to ozone episodes.

The OTAG Version of CB4

The next update to the CB4 mechanism to see widespread use occurred when the Ozone Transport Assessment Group (OTAG) commenced modeling in 1996. Two updates were made to better represent regional scale oxidant formation in the eastern US where high isoprene levels occur and rural areas have relatively low NO_x concentrations.

Yarwood updated the radical-radical termination reactions (among HO₂ and RO₂ radicals) to better represent oxidant formation under conditions of low NO_x (Yarwood and Burton, 1994). This change would have little or no impact on the smog chamber evaluation because smog chambers operate with moderate to high NO_x concentrations.

Whitten updated the isoprene chemistry in the CB4 (Whitten et al., 1996) to reflect newer scientific data on the products and mechanisms of isoprene oxidation (Carter and Atkinson, 1996). The updated isoprene mechanism is a translation from SAPRC to CB4 species of Carter's condensed "1-product" isoprene mechanism (Carter, 1996). The single lumped isoprene reaction product is called "isoprod" (ISPD) and represents methyl vinyl ketone, methacrolein and other compounds. Comparisons between the original and updated isoprene mechanisms in CB4 showed that both mechanisms performed similarly under smog chamber conditions but differently under regional modeling conditions (Whitten et al., 1996).

The OTAG version of CB4 is implemented in CAMx as mechanism 3. CAMx mechanism 2 has the radical-radical termination update, but not the isoprene update, so running mechanisms 2 and 3 provides a comparison of the original and updated isoprene chemistries. Since the updated isoprene chemistry is now widely accepted mechanism 2 will be retired from CAMx at some point.

CBM-Z – Pacific Northwest National Laboratory

The Pacific Northwest National Laboratory (PNNL) has developed a mechanism based on the Carbon Bond approach called CBM-Z (Zaveri and Peters, 1999). Changes in CBM-Z were intended to update the mechanism from the published Gery et al., (1989) version and improve performance for regional scale modeling, and include:

- Revised inorganic chemistry.
- Explicit treatment of the lesser reactive alkanes - methane and ethane.
- Revised parameterizations of the reactive paraffin, olefin, and aromatic reactions.
- Inclusion of alkyl and acyl peroxy radical interactions and their reactions with the NO₃ radical.
- Inclusion of organic nitrates and hydroperoxides.
- Isoprene chemistry based on the condensed one-product mechanism of Carter (1996).

The CBM-Z and CB4 were evaluated against smog chamber data from the TVA chamber and showing improved performance for CBM-Z on these chamber experiments. Sensitivity tests showed larger differences between CBM-Z and CB4 for regional modeling conditions than for urban or smog chamber conditions. One factor that contributed to differences under regional conditions (Zaveri and Peters, 1999) was the inclusion in CBM-Z of reactions for organic nitrates that slowly recycle nitrogen from an inactive form (nitrates) to an active form (NO_x).

CB2002 – University of North Carolina

In late 1990s, the Jeffries research group at UNC started to update CB4 and re-evaluate the mechanism against smog chamber data. UNC's approach was to retain the overall structure of CB4 but update rate constants and some product yields based on recent data. The first mechanism produced by UNC was called CB99. Unfortunately, the CB99 work was completed just as a critical rate constant (OH + NO₂) was changed. UNC repeated the work with the new OH + NO₂ rate constant and developed CB2002, which supercedes CB99 (Jeffries, Voicu, and Sexton, 2002). The changes between CB2002 and CB4 are discussed below. The CB2002 was evaluated against UNC smog chamber data as described in detail in Jeffries, Voicu, and Sexton (2002).

Micro-CB4

Whitten (1999) has developed a condensed version of the CB4 mechanism called micro CB4 (mCB4) for EPA's REMSAD model (ICF Kaiser, 2002). A summary of the changes from CB4 to mCB4 is provided in EPA's technical support documents for the Clean Air Interstate Rule (EPA, 2004). The inorganic and radical parts of mCB4 are reported to be identical to CB4 except that three new reactions are added that may be important for regional scale and annual applications where wide ranges of temperature and pressure are encountered. The extra inorganic reactions are OH + H₂, OH + NO₃ and HO₂ + NO₃.

The organic parts of mCB4 are much condensed from CB4. A single primary species (VOC) represents the average anthropogenic VOC emissions compared to eight emitted VOCs in CB4. Two primary species (ISOP and TERP) represent biogenic emissions of isoprene and terpenes compared to two in CB4. A single species (CARB) represents carbonyls in mCB4 compared to four in CB4.

Other Versions of CB4

Whitten developed an update to the CB4 for ICF Kaiser called CB5 that is implemented in UAM-V (ICF Kaiser, 2004). Important updates in CB5 are the inclusion of an internal olefin species IOLE and a higher aldehyde species ALDX (Ligocki and Whitten, 1992). Internal olefins have 4 or more carbon atoms with the double bond not located at the end of the carbon chain. The IOLE modification improves the ability of the mechanism to simulate these highly reactive compounds. The higher aldehyde, ALDX, is based on propionaldehyde and makes the ALD2 species more explicitly acetaldehyde. The ALDX modification is useful for modeling air toxics and improves the performance of the mechanism at low VOC/NO_x ratios (Ligocki and Whitten, 1992). The inorganic reactions in CB5 are the same as the original CB4 (Gery et. al., 1989).

Tanaka et al. (2003) developed an extension to the CB4 mechanism with chlorine chemistry to evaluate the potential impact of reactive chlorine emissions (Cl₂, HOCl) on tropospheric ozone formation. The Tanaka et al. chlorine mechanism is shown in Table 2-1 as implemented for CAMx mechanism 1 (reactions 1-96 in CAMx mechanism 1 are the same as mechanism 3, listed below). Table 2-2 identifies the species in the chlorine mechanism.

Table 2-1. Reactions and rate constants for the CB4/chlorine mechanism.

| Reaction Number | Reactants | Products | k_{298}^1 (ppm ⁻ⁿ min ⁻¹) |
|------------------|-----------|--|---|
| 97 | CL2 | 2 CL | Photolysis |
| 98 | HOCL | OH + CL | Photolysis |
| 99 | CL + O3 | CLO + O2 | 1.779E+04 |
| 100 | CLO + NO | CL + NO2 | 2.449E+04 |
| 101 | CLO + HO2 | HOCL + O2 | 7.314E+03 |
| 102 | CL + PAR | HCL + 0.87 XO2 + 0.13 XO2N + 0.11 RCHO + 0.76 ROR - 0.11 PAR | 9.383E+04 |
| 103 | CL + OLE | FMCL + RCHO + 2 XO2 + HO2 - PAR | 8.400E+05 |
| 104 ² | CL | HCL + XO2 + FORM + HO2 | 2.816E+02 |
| 105 | CL + ETH | FORM + 2 XO2 + FMCL + HO2 | 1.502E+05 |
| 106 | CL + ISOP | 0.15 HCL + XO2 + HO2 + 0.28 ICL1 | 6.642E+05 |
| 107 | OH + ICL1 | ICL2 | 2.804E+04 |

| Reaction Number | Reactants | Products | k_{298}^1 ($\text{ppm}^{-n} \text{min}^{-1}$) |
|-----------------|-----------|----------------------|--|
| 108 | CL + BUTA | XO2 + HO2 + 0.7 BCL1 | 6.199E+05 |
| 109 | OH + BCL1 | BCL2 | 5.314E+04 |
| 110 | CLO + CLO | 0.3 CL2 + 1.4 CL | 2.410E+01 |

Table 2-2. Species added for the CB4/chlorine mechanism.

| Species Name | Description |
|--------------|---|
| CL2 | Molecular chlorine |
| HOCL | Hypochlorous acid |
| CL | Chlorine atom |
| CLO | Chlorine monoxide |
| ICL1 | Unique product of CL + isoprene reaction |
| ICL2 | Reaction product of ICL1 |
| BUTA | 1,3-Butadiene |
| BCL1 | Unique product of CL + 1,3-butadiene reaction |
| BCL2 | Reaction product of BCL1 |

Whitten and Yarwood are currently developing an updated mechanism for the EPA called CB4+. The updates in CB4+ include:

- Updated inorganic and explicit organic reactions based on IUPAC (2004).
- Extended inorganic reaction set developed for this project.
- NO_x recycling reactions developed for this project.
- Explicit methane and ethane.
- Explicit methylperoxy radical and hydroperoxides.
- Internal olefin species IOLE (Ligocki and Whitten, 1992).
- Higher aldehyde species ALDX (Ligocki and Whitten, 1992).
- Explicit terpene species
- Updated chlorine chemistry based on Tanaka et al (2003).
- Explicit reactions for several air-toxics.

The CB4+ mechanism will be completed in 2005.

CB4 MECHANISMS IN CAM_x

CAM_x includes four different chemical mechanisms (ENVIRON 2004). The two most commonly used versions of the CB4 mechanism in CAM_x are:

- Mechanism 3 – The OTAG version of CB4 discussed above.
- Mechanism 4 – Mechanism 3 with updates for PM modeling.

The OTAG version of the CB4 mechanism was discussed above and a mechanism listing is shown in Table 2-3. The species names used in Table 2-3 are identified in Table 2-4.

The gas-phase chemistry for Mechanism 4 is based on Mechanism 3 with the following extensions:

- 1) A biogenic olefin species (OLE2) is added to represent terpenes. To use the OLE2 species, prepare your biogenic emissions the same way as for Mechanism 3 but rename the CB4 OLE emissions (representing terpenes) to OLE2.
- 2) Five condensable organic gas species (CG1- CG5) are added as secondary organic aerosol (SOA) precursors. CG1-CG3 and CG5 are formed from anthropogenic VOCs and CG4 is formed from terpenes (OLE2). There are no gas phase reactions for CG1-CG5.
- 3) Ammonia is added as a gas species because it is a precursor for inorganic aerosol. There are no gas phase reactions for ammonia.
- 4) Hydrogen chloride (HCl) is added as a product of acidified sea salt aerosol. There are no gas phase reactions for HCl.
- 5) Rate expressions for gas-phase reactions 26, 36, 51 and 82 (Table 2-3) are updated to explicitly include the pressure dependence of the rate constant.
- 6) The rate for reaction 83 is set to zero. This reaction was used in the UAM to represent heterogeneous SO₂ to sulfate conversion but now should be set to zero because aqueous chemistry is explicitly represented when mechanism 4 is used.
- 7) The rate for reaction 18 ($\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HO}_3$) is reduced to a value that is consistent with just the known gas-phase processes (Mentel, Bleilebens and Wahner, 1996). There is evidence for a heterogeneous pathway to this reaction, but there continues to be considerable uncertainty in how to model the heterogeneous pathway.

Pressure Dependant Rate Constants

Update 5 listed above added explicit pressure dependence for 4 reactions. Gas-phase reactions can be pressure dependant if they require a collision with some other molecule to provide or take away energy. The identity of the other molecule is not chemically important and so it is referred to in reaction equations as "M." Because M is often the third reactant it also may be called a "third body."

An example of a pressure dependant three body reaction is $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$. M appears as both a reactant and product because it is chemically unchanged by the reaction. In the troposphere M will essentially always be N₂ or O₂. The role of M is to take away energy released by forming a new bond. If this energy is not removed from the newly formed molecule, the bond may rupture, undoing the reaction. Higher pressure therefore increases the rate of this reaction by increasing the frequency of collisions that stabilize the product.

Under some pressure conditions, some reactions are completely dependent upon the participation of a third body (M) to enable the reaction. In this case M may be explicitly included as a reactant with a corresponding rate constant. In other cases the reaction may proceed without participation from a third body, but third body collisions do facilitate the reaction. These reactions are described as being in the falloff region because their pressure dependence is "falling off" to zero. The rate constants for falloff reactions are best described using parameterized expressions that include the pressure: therefore M does not appear as a reactant. The most widely used parameterization for falloff reaction rates was developed by Troe (1977) and is presented in both JPL (2003) and IUPAC (2004).

Pressure dependence was included for four reactions in CAMx mechanism 4, the reactions of OH with NO₂, SO₂, CH₄ and CO. Pressure dependence was included for NO₂ and SO₂ because these reactions form PM in plumes from major sources that may be aloft at lower pressure. Pressure dependence was included for CH₄ and CO because their OH reactions have strong pressure dependence and they become increasingly important oxidant precursors at high altitude, where non-methane hydrocarbons are scarce.

Accounting for the pressure dependence in the OH + NO₂ reaction in CAMx mechanism 4 required some care because this rate constant was re-evaluated in the late 1990s. Using the pressure dependant rate expressions from the latest evaluations (JPL, 2003 or IUPAC, 2004) would lower the rate for the OH + NO₂ under smog chamber conditions and unbalance the CB4 mechanism. This problem was avoided in CAMx by using the pressure dependant expression recommended by JPL in 1994 which gives essentially the same rate constant for the OH + NO₂ reaction as CB4 under smog chamber conditions.

Table 2-3. Reactions and rate constants for the OTAG version of the CB4 mechanism (CAMx Mechanism 3).

| Reaction Number | Reactants | Products | k_{298}^1 (ppm ⁻ⁿ min ⁻¹) |
|-----------------|-----------------|-----------------------------|---|
| 1 | NO2 | NO + O | Photolysis |
| 2 | O | O3 | 4.323E+06 |
| 3 | O3 + NO | NO2 | 2.664E+01 |
| 4 | O + NO2 | NO | 1.375E+04 |
| 5 | O + NO2 | NO3 | 2.309E+03 |
| 6 | O + NO | NO2 | 2.438E+03 |
| 7 | NO2 + O3 | NO3 | 4.731E-02 |
| 8 | O3 | O | Photolysis |
| 9 | O3 | O1D | Photolysis |
| 10 | O1D | O | 4.250E+10 |
| 11 | O1D + H2O | 2 OH | 3.260E+05 |
| 12 | O3 + OH | HO2 | 1.000E+02 |
| 13 | O3 + HO2 | OH | 2.999E+00 |
| 14 | NO3 | 0.89 NO2 + 0.89 O + 0.11 NO | Photolysis |
| 15 | NO3 + NO | 2 NO2 | 4.417E+04 |
| 16 | NO3 + NO2 | NO + NO2 | 5.901E-01 |
| 17 | NO3 + NO2 | N2O5 | 1.853E+03 |
| 18 | N2O5 + H2O | 2 HNO3 | 1.900E-06 |
| 19 | N2O5 | NO3 + NO2 | 2.776E+00 |
| 20 | NO + NO | 2 NO2 | 1.539E-04 |
| 21 | NO + NO2 + H2O | 2 HONO | 1.600E-11 |
| 22 | NO + OH | HONO | 9.799E+03 |
| 23 | HONO | NO + OH | Photolysis |
| 24 | OH + HONO | NO2 | 9.770E+03 |
| 25 | HONO + HONO | NO + NO2 | 1.500E-05 |
| 26 | NO2 + OH | HNO3 | 1.682E+04 |
| 27 | OH + HNO3 | NO3 | 2.179E+02 |
| 28 | HO2 + NO | OH + NO2 | 1.227E+04 |
| 29 | HO2 + NO2 | PNA | 0.000E+00 |
| 30 | PNA | HO2 + NO2 | 0.000E+00 |
| 31 | OH + PNA | NO2 | 0.000E+00 |
| 32 | HO2 + HO2 | H2O2 | 4.144E+03 |
| 33 | HO2 + HO2 + H2O | H2O2 | 2.181E-01 |
| 34 | H2O2 | 2 OH | Photolysis |
| 35 | OH + H2O2 | HO2 | 2.520E+03 |
| 36 | OH + CO | HO2 | 3.220E+02 |
| 37 | FORM + OH | HO2 + CO | 1.500E+04 |
| 38 | FORM | 2 HO2 + CO | Photolysis |
| 39 | FORM | CO | Photolysis |
| 40 | FORM + O | OH + HO2 + CO | 2.370E+02 |
| 41 | FORM + NO3 | HNO3 + HO2 + CO | 9.300E-01 |
| 42 | ALD2 + O | C2O3 + OH | 6.360E+02 |

| Reaction Number | Reactants | Products | k_{298}^1 (ppm ⁻ⁿ min ⁻¹) |
|-----------------|-------------|--|---|
| 43 | ALD2 + OH | C2O3 | 2.400E+04 |
| 44 | ALD2 + NO3 | C2O3 + HNO3 | 3.700E+00 |
| 45 | ALD2 | FORM + 2 HO2 + CO + XO2 | Photolysis |
| 46 | C2O3 + NO | FORM + NO2 + HO2 + XO2 | 2.820E+04 |
| 47 | C2O3 + NO2 | PAN | 1.370E+04 |
| 48 | PAN | C2O3 + NO2 | 2.540E-02 |
| 49 | C2O3 + C2O3 | 2 FORM + 2 XO2 + 2 HO2 | 3.700E+03 |
| 50 | C2O3 + HO2 | 0.79 FORM + 0.79 XO2 + 0.79 HO2 + 0.79 OH | 9.600E+03 |
| 51 ² | OH | FORM + XO2 + HO2 | 2.100E+01 |
| 52 | PAR + OH | 0.87 XO2 + 0.13 XO2N + 0.11 HO2 + 0.11 ALD2 - 0.11 PAR + 0.76 ROR | 1.203E+03 |
| 53 | ROR | 0.96 XO2 + 1.1 ALD2 + 0.94 HO2 - 2.1 PAR + 0.04 XO2N | 1.371E+05 |
| 54 | ROR | HO2 | 9.545E+04 |
| 55 | ROR + NO2 | NTR | 2.200E+04 |
| 56 | O + OLE | 0.63 ALD2 + 0.38 HO2 + 0.28 XO2 + 0.3 CO + 0.2 FORM + 0.02 XO2N + 0.22 PAR + 0.2 OH | 5.920E+03 |
| 57 | OH + OLE | FORM + ALD2 - PAR + XO2 + HO2 | 4.200E+04 |
| 58 | O3 + OLE | 0.5 ALD2 + 0.74 FORM + 0.22 XO2 + 0.1 OH + 0.33 CO + 0.44 HO2 - PAR | 1.800E-02 |
| 59 | NO3 + OLE | 0.91 XO2 + FORM + 0.09 XO2N + ALD2 + NO2 - PAR | 1.135E+01 |
| 60 | O + ETH | FORM + 1.7 HO2 + CO + 0.7 XO2 + 0.3 OH | 1.080E+03 |
| 61 | OH + ETH | XO2 + 1.56 FORM + 0.22 ALD2 + HO2 | 1.192E+04 |
| 62 | O3 + ETH | FORM + 0.42 CO + 0.12 HO2 | 2.700E-03 |
| 63 | TOL + OH | 0.44 HO2 + 0.08 XO2 + 0.36 CRES + 0.56 TO2 | 9.150E+03 |
| 64 | TO2 + NO | 0.9 NO2 + 0.9 HO2 + 0.9 OPEN + 0.1 NTR | 1.200E+04 |
| 65 | TO2 | CRES + HO2 | 2.500E+02 |
| 66 | OH + CRES | 0.4 CRO + 0.6 XO2 + 0.6 HO2 + 0.3 OPEN | 6.100E+04 |
| 67 | CRES + NO3 | CRO + HNO3 | 3.250E+04 |
| 68 | CRO + NO2 | NTR | 2.000E+04 |
| 69 | OPEN | C2O3 + HO2 + CO | Photolysis |
| 70 | OPEN + OH | XO2 + 2 CO + 2 HO2 + C2O3 + FORM | 4.400E+04 |
| 71 | OPEN + O3 | 0.03 ALD2 + 0.62 C2O3 + 0.7 FORM + 0.03 XO2 + 0.69 CO + 0.08 OH + 0.76 HO2 + 0.2 MGLY | 1.500E-02 |
| 72 | OH + XYL | 0.7 HO2 + 0.5 XO2 + 0.2 CRES + 0.8 MGLY + 1.1 PAR + 0.3 TO2 | 3.620E+04 |
| 73 | OH + MGLY | XO2 + C2O3 | 2.600E+04 |
| 74 | MGLY | C2O3 + HO2 + CO | Photolysis |
| 75 | O + ISOP | 0.75 ISPD + 0.5 FORM + 0.25 XO2 + 0.25 HO2 + 0.25 C2O3 + 0.25 PAR | 5.320E+04 |
| 76 | OH + ISOP | 0.912 ISPD + 0.629 FORM + 0.991 XO2 + 0.912 HO2 + 0.088 XO2N | 1.476E+05 |
| 77 | O3 + ISOP | 0.65 ISPD + 0.6 FORM + 0.2 XO2 + 0.066 HO2 + 0.266 OH + 0.2 C2O3 + 0.15 ALD2 + 0.35 PAR + 0.066 CO | 1.900E-02 |
| 78 | NO3 + ISOP | 0.2 ISPD + 0.8 NTR + XO2 + 0.8 HO2 + 0.2 NO2 + 0.8 ALD2 + 2.4 PAR | 9.960E+02 |
| 79 | XO2 + NO | NO2 | 1.200E+04 |
| 80 | XO2 + XO2 | | 2.000E+03 |
| 81 | XO2N + NO | NTR | 1.200E+04 |
| 82 | SO2 + OH | SULF + HO2 | 1.110E+03 |
| 83 | SO2 | SULF | 8.167E-05 |
| 84 | MEOH + OH | FORM + HO2 | 1.600E+03 |
| 85 | ETOH + OH | HO2 + ALD2 | 4.300E+03 |
| 86 | XO2 + HO2 | | 8.900E+03 |
| 87 | XO2N + HO2 | | 8.900E+03 |
| 88 | XO2N + XO2N | | 2.000E+03 |
| 89 | XO2 + XO2N | | 4.000E+03 |
| 90 | OH + HO2 | | 1.626E+05 |
| 91 | CRO | | 2.778E-04 |
| 92 | OH + ISPD | 1.565 PAR + 0.167 FORM + 0.713 XO2 + 0.503 HO2 + 0.334 CO + 0.168 MGLY + 0.273 ALD2 + 0.498 C2O3 | 4.967E+04 |
| 93 | O3 + ISPD | 0.114 C2O3 + 0.15 FORM + 0.85 MGLY + 0.154 HO2 + 0.268 OH + 0.064 XO2 + 0.02 ALD2 + 0.36 PAR + 0.225 CO | 1.050E-02 |
| 94 | NO3 + ISPD | 0.357 ALD2 + 0.282 FORM + 1.282 PAR + 0.925 HO2 + 0.643 CO + 0.85 NTR + 0.075 C2O3 + 0.075 XO2 + 0.15 HNO3 | 1.478E+00 |
| 95 | ISPD | 0.333 CO + 0.067 ALD2 + 0.9 FORM + 0.832 PAR + 1.033 HO2 + 0.7 XO2 + 0.967 C2O3 | Photolysis |
| 96 | NO2 + ISOP | 0.2 ISPD + 0.8 NTR + XO2 + 0.8 HO2 + 0.2 NO + 0.8 ALD2 + 2.4 PAR | 2.200E-04 |

Notes:

- ¹ Rate constants are shown for 298 K and 1 atmosphere in units of ppm and minutes. See the CAMx chemistry parameters file (Section 5) for the temperature and pressure dependencies.
- ² Reaction 51 implicitly includes 1.85 ppm of methane in the rate constant.

Table 2-4. Species names for the CB4 mechanism.

| Species Name | Description |
|--------------|--|
| NO2 | Nitrogen dioxide |
| NO | Nitric oxide |
| O | Oxygen atom in the O ³ (P) electronic state |
| O3 | Ozone |
| NO3 | Nitrate radical |
| O1D | Oxygen atom in the O ¹ (D) electronic state |
| OH | Hydroxyl radical |
| HO2 | Hydroperoxy radical |
| N2O5 | Dinitrogen pentoxide |
| HNO3 | Nitric acid |
| HONO | Nitrous acid |
| PNA | Peroxynitric acid (HNO ₄) |
| H2O2 | Hydrogen peroxide |
| CO | Carbon monoxide |
| FORM | Formaldehyde |
| ALD2 | Higher aldehyde (based on acetaldehyde) |
| C2O3 | Acylperoxy radical (based on acetylperoxy) |
| XO2 | NO to NO2 conversion from alkylperoxy (RO ₂) radical |
| PAN | Peroxyacetyl nitrate (based on peroxyacetyl nitrate) |
| PAR | Paraffin carbon bond (C-C) |
| XO2N | NO to organic nitrate conversion from alkylperoxy (RO ₂) radical |
| ROR | Secondary alkoxy radical |
| NTR | Organic nitrate (RNO ₃) |
| OLE | Olefin carbon bond (C=C) |
| ETH | Ethene |
| TOL | Toluene and other monoalkyl aromatics |
| CRES | Cresol and higher molecular weight phenols |
| TO2 | Toluene-hydroxyl radical adduct |
| OPEN | Aromatic ring opening product |
| CRO | Methylphenoxy radical |
| MGLY | Methylglyoxal and other aromatic products |
| XYL | Xylene and other polyalkyl aromatics |
| ISOP | Isoprene |
| ISPD | Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.) |
| SO2 | Sulfur dioxide |
| SULF | Sulfuric acid (gaseous) |
| MEOH | Methanol |
| ETOH | Ethanol |

IMPLEMENTING THE CB2002 MECHANISM IN CAMx

The CB2002 mechanism was implemented in CAM for this project. An ASCII listing of the mechanism provided by the mechanism developers was reformatted to the input format for the CAMx chemical mechanism compiler. The mechanism compiler was used to develop FORTRAN subroutines that implement the mechanism for the CAMx chemistry solvers. A listing of the CB2002 mechanism implemented in CAMx is shown in Table 2-5.

Thermal rate constants are provided to CAMx as an input file. The CB2002 was developed with rate constants in molecular units (molecules cm⁻³) rather than ppm. CAMx has previously read rate constants only in mixing ratio (ppm) units. For this project, CAMx was modified to read rate constants either in ppm or molecular units. CAMx automatically determines what units are being used from the orders of magnitude of the rate constants. All of the rate constants in a chemistry parameters file must be in the same units (do not mix ppm and molecular units). A listing of the CB2002 rate constants in CAMx format is shown in Table 2-6.

Photolysis rates are provided to CAMx via input files. The rates file provides a lookup table for key reactions as a function of several ambient conditions (see the User's Guide for details). These are called primary photolysis reactions. The rates of the primary photolysis reactions are calculated using a radiative transfer model (TUV) as a preprocessor. Other photolysis reactions may be set as ratios to a primary photolysis reaction in the chemistry parameters input file. These are called secondary photolysis reactions. The secondary/primary photolysis rate ratios for CB2002 are shown in Table 2-7.

The CB2002 mechanism developers used specific light absorption spectra and quantum yield data for several photolysis reactions. These data were obtained from the CB2002 developers in electronic format and added to the TUV model. This enables TUV to calculate primary photolysis rates specifically for the CB2002 mechanism.

Table 2-5. Reactions and rate constants for the CB2002 mechanism (Jeffries, Voicu and Sexton, 2002).

| Reaction Number | Reactants | Products | k_{298} ¹ (ppm ⁻ⁿ min ⁻¹) |
|-----------------|------------------|----------------|---|
| 1 | NO2 | NO + O | photolysis |
| 2 | O + O2 + M | O3 + M | 2.22E-05 |
| 3 | O3 + NO | NO2 + O2 | 2.89E+01 |
| 4 | O + NO2 | NO + O2 | 1.51E+04 |
| 5 | O + NO2 | NO3 + O2 | 2.33E+03 |
| 6 | O + NO | NO2 | 2.46E+03 |
| 7 | NO + NO + O2 | 2.0*NO2 | 7.11E-10 |
| 8 | O3 + NO2 | NO3 + O2 | 4.77E-02 |
| 9 | NO3 | NO + O2 | photolysis |
| 10 | NO3 | NO2 + O | photolysis |
| 11 | NO3 + NO | 2.0*NO2 | 3.92E+04 |
| 12 | NO3 + NO2 | NO + NO2 + O2 | 9.69E-01 |
| 13 | NO3 + NO2 | N2O5 | 1.74E+03 |
| 14 | N2O5 | NO3 + NO2 | 2.26E+00 |
| 15 | N2O5 + H2O | 2.0*HNO3 | 3.69E-07 |
| 16 | N2O5 + H2O + H2O | 2.0*HNO3 + H2O | 6.55E-11 |
| 17 | NO3 + OH | NO2 + HO2 | 3.25E+04 |
| 18 | NO3 + HO2 | HNO3 + O2 | 1.36E+03 |
| 19 | NO3 + NO3 | 2.0*NO2 + O2 | 3.38E-01 |
| 20 | O3 | O + O2 | photolysis |
| 21 | O3 | O1D + O2 | photolysis |
| 22 | O1D + O2 | O + O2 | 5.98E+04 |
| 23 | O1D + N2 | O + N2 | 3.85E+04 |
| 24 | O1D + H2O | 2.0*OH | 3.25E+05 |
| 25 | O3 + OH | HO2 + O2 | 1.16E+02 |
| 26 | O3 + HO2 | OH + 2.0*O2 | 3.02E+00 |
| 27 | O3 + O | 2.0*O2 | 1.18E+01 |
| 28 | NO + NO2 + H2O | 2.0*HONO | 1.60E-11 |
| 29 | HONO + HONO | NO + NO2 + H2O | 1.48E-05 |
| 30 | OH + NO | HONO | 1.09E+04 |
| 31 | HONO | OH + NO | photolysis |
| 32 | HONO | HO2 + NO2 | photolysis |
| 33 | OH + HONO | NO2 + H2O | 7.18E+03 |
| 34 | HO2 + NO | OH + NO2 | 1.20E+04 |
| 35 | HO2 + NO2 | PNA | 2.05E+03 |
| 36 | PNA | HO2 + NO2 | 5.17E+00 |
| 37 | OH + PNA | NO2 + H2O + O2 | 6.87E+03 |
| 38 | OH + NO2 | HNO3 | 1.57E+04 |
| 39 | OH + HNO3 | NO3 + H2O | 2.17E+02 |
| 40 | HO2 + HO2 | H2O2 + O2 | 4.29E+03 |

| Reaction Number | Reactants | Products | k_{298}^1 (ppm ⁻ⁿ min ⁻¹) |
|-----------------|--------------------|---|--|
| 41 | HO2 + HO2 + H2O | H2O2 + O2 + H2O | 2.38E-01 |
| 42 | H2O2 | 2.0*OH | photolysis |
| 43 | OH + H2O2 | HO2 + H2O | 2.50E+03 |
| 44 | OH + HO2 | O2 + H2O | 1.64E+05 |
| 45 | OH + CO | HO2 + CO2 | 3.55E+02 |
| 46 | OH + CH4 | XO2 + FORM + HO2 | 9.37E+00 |
| 47 | FORM | 2.0*HO2 + CO | photolysis |
| 48 | FORM | CO + H2 | photolysis |
| 49 | FORM + O | OH + HO2 + CO | 2.34E+02 |
| 50 | FORM + OH | HO2 + CO | 1.36E+04 |
| 51 | FORM + NO3 | HNO3 + HO2 + CO | 8.49E-01 |
| 52 | ALD2 | XO2 + 2.0*HO2 + CO + FORM | photolysis |
| 53 | ALD2 + O | C2O3 + OH | 6.63E+02 |
| 54 | ALD2 + OH | C2O3 + H2O | 2.05E+04 |
| 55 | ALD2 + NO3 | C2O3 + HNO3 | 4.03E+00 |
| 56 | C2O3 + NO | NO2 + XO2 + FORM + HO2 | 2.62E+04 |
| 57 | C2O3 + NO2 | PAN | 1.55E+04 |
| 58 | PAN | C2O3 + NO2 | 2.76E-02 |
| 59 | C2O3 + HO2 | 0.25*O3 | 2.08E+04 |
| 60 | C2O3 + C2O3 | 2.0*XO2 + 2.0*FORM + 2.0*HO2 | 2.45E+04 |
| 61 | OH + PAR | 0.87*XO2 + 0.13*XO2N + 0.11*HO2 + 0.11*ALD2 + 0.76*ROR + -0.11*PAR | 1.20E+03 |
| 62 | ROR | 1.1*ALD2 + 0.96*XO2 + 0.94*HO2 + -2.1*PAR + 0.04*XO2N + 0.02*ROR | 1.32E+05 |
| 63 | ROR | HO2 | 9.60E+04 |
| 64 | ROR + NO2 | RNO3 | 2.22E+04 |
| 65 | O + ETH | 0.49*FORM + 0.60*XO2 + 0.95*CO + 1.55*HO2 + 0.35*OH | 1.08E+03 |
| 66 | OH + ETH | XO2 + 1.56*FORM + HO2 + 0.22*ALD2 | 1.25E+04 |
| 67 | O3 + ETH | 1.03*FORM + 0.325*CO + 0.08*HO2 + 0.02*H2O2 + 0.08*OH | 2.34E-03 |
| 68 | O + OLE | 0.519*ALD2 + 0.147*HO2 + 0.097*XO2 + 0.102*CO + 0.051*FORM + 0.005*XO2N + 0.809*PAR + 0.051*OH | 1.63E+04 |
| 69 | OH + OLE | FORM + ALD2 + XO2 + HO2 + -1.0*PAR | 6.52E+04 |
| 70 | O3 + OLE | 0.150*HO2 + 0.085*OH + 0.130*CO + 0.485*FORM + 0.210*ALD2 + 0.044*XO2 + 0.001*XO2N + 0.966*PAR | 1.66E-02 |
| 71 | NO3 + OLE | 0.7*XO2 + NO2 + FORM + ALD2 + 0.3*XO2N + -1.0*PAR | 2.44E+02 |
| 72 | O + ISOP | 0.25*HO2 + 0.25*XO2 + 0.75*ISPD + 0.50*FORM + 0.25*PAR + 0.25*C2O3 | 5.32E+04 |
| 73 | OH + ISOP | 0.991*XO2 + 0.629*FORM + 0.912*HO2 + 0.088*XO2N + 0.912*ISPD | 1.47E+05 |
| 74 | O3 + ISOP | 0.60*FORM + 0.15*ALD2 + 0.35*PAR + 0.066*CO + 0.066*HO2 + 0.266*OH + 0.20*C2O3 + 0.20*XO2 + 0.65*ISPD | 1.90E-02 |
| 75 | NO3 + ISOP | XO2 + 0.65*ISPD + 0.80*RNO3 + 0.80*HO2 + 0.20*NO2 + 0.80*ALD2 + 2.4*PAR | 9.95E+02 |
| 76 | NO2 + ISOP | 0.80*ALD2 + 2.4*PAR + 0.80*RNO3 + XO2 + 0.80*HO2 + 0.20*ISPD + 0.20*NO | 2.22E-04 |
| 77 | ISPD + OH | 1.565*PAR + 0.167*FORM + 0.713*XO2 + 0.503*HO2 + 0.334*CO + 0.168*MGLY + 0.273*ALD2 + 0.498*C2O3 | 4.96E+04 |
| 78 | ISPD + O3 | 0.114*C2O3 + 0.15*FORM + 0.85*MGLY + 0.154*HO2 + 0.268*OH + 0.064*XO2 + 0.02*ALD2 + 0.36*PAR + 0.225*CO | 1.05E-02 |
| 79 | ISPD + NO3 | 0.357*ALD2 + 0.282*FORM + 1.282*PAR + 0.925*HO2 + 0.643*CO + 0.85*RNO3 + 0.075*C2O3 + 0.075*XO2 + 0.075*HNO3 | 1.48E+00 |
| 80 | ISPD | 0.333*CO + 0.067*ALD2 + 0.90*FORM + 0.832*PAR + 1.033*HO2 + 0.70*XO2 + 0.967*C2O3 | photolysis |
| 81 | OH + TOL | 0.08*XO2 + 0.44*HO2 + 0.36*CRES + 0.56*TO2 | 8.75E+03 |
| 82 | TO2 + NO | 0.90*NO2 + 0.9*HO2 + 0.9*OPEN + 0.1*RNO3 | 1.20E+04 |
| 83 | TO2 | CRES + HO2 | 2.52E+02 |
| 84 | OH + CRES | 0.40*CRO + 0.60*XO2 + 0.6*HO2 + 0.30*OPEN | 6.06E+04 |
| 85 | NO3 + CRES | CRO + HNO3 | 3.25E+04 |
| 86 | CRO + NO2 | RNO3 | 2.07E+04 |
| 87 | OPEN | C2O3 + HO2 + CO | photolysis |
| 88 | OPEN + OH | XO2 + 2.0*CO + 2.0*HO2 + C2O3 + FORM | 4.43E+04 |
| 89 | OPEN + O3 | 0.03*ALD2 + 0.62*C2O3 + 0.70*FORM + 0.03*XO2 + 0.69*CO + 0.08*OH + 0.76*HO2 + 0.2*MGLY | 1.49E-02 |
| 90 | OH + XYL | 0.70*HO2 + 0.10*XO2 + 1.10*PAR + 0.20*CRES + 0.30*TO2 + 0.80*MGLY | 3.71E+04 |
| 91 | MGLY | C2O3 + HO2 + CO | photolysis |
| 92 | OH + MGLY | XO2 + C2O3 | 2.51E+04 |
| 93 | XO2 + NO | NO2 | 1.13E+04 |
| 94 | XO2N + NO | RNO3 | 1.13E+04 |

| Reaction Number | Reactants | Products | k_{298}^1 (ppm ⁻ⁿ min ⁻¹) |
|-----------------|----------------|----------|---|
| 95 | XO2 + XO2 | | 6.99E+02 |
| 96 | XO2 + HO2 | | 8.22E+03 |
| 97 | XO2N + HO2 | | 8.22E+03 |
| 98 | XO2N + XO2N | | 6.99E+02 |
| 99 | XO2 + XO2N | | 1.40E+03 |

Notes:

¹ Rate constants are shown for 298 K and 1 atmosphere in units of ppm and minutes.

Table 2-6. Reactions rate constant parameters for the CB2002 mechanism (Jeffries, Voicu and Sexton, 2002) in CAMx format and molecular units (seconds and molecules cm⁻³).

| Rxn | Type | Order | Parameters (1 to 12 parameters, depending upon Type) | | | | | | | | | |
|-----|------|-------|--|--|--|--|--|--|--|--|--|--|
| 1 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 2 | 3 | 3 | 6.0000E-34 0.0000E+00 -2.4000E+00 3.0000E+02 | | | | | | | | | |
| 3 | 3 | 2 | 3.0000E-12 -1.5000E+03 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 4 | 3 | 2 | 5.6000E-12 1.8000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 5 | 4 | 2 | 9.0000E-32 0.0000E+00 -2.0000E+00 3.0000E+02 2.2000E-11 0.0000E+00 0.0000E+00 3.0000E+02 6.0000E-01 1.0000E+00 | | | | | | | | | |
| 6 | 4 | 2 | 9.0000E-32 0.0000E+00 -1.5000E+00 3.0000E+02 3.0000E-11 0.0000E+00 0.0000E+00 3.0000E+02 6.0000E-01 1.0000E+00 | | | | | | | | | |
| 7 | 3 | 3 | 3.3000E-39 5.3000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 8 | 3 | 2 | 1.2000E-13 -2.4500E+03 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 9 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 10 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 11 | 3 | 2 | 1.5000E-11 1.7000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 12 | 3 | 2 | 4.5000E-14 -1.2600E+03 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 13 | 4 | 2 | 2.0000E-30 0.0000E+00 -4.4000E+00 3.0000E+02 1.4000E-12 0.0000E+00 -7.0000E-01 3.0000E+02 6.0000E-01 1.0000E+00 | | | | | | | | | |
| 14 | 5 | 1 | 13. 3.0000E-27 1.0991E+04 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 15 | 1 | 2 | 2.50E-22 | | | | | | | | | |
| 16 | 1 | 3 | 1.80E-39 | | | | | | | | | |
| 17 | 1 | 2 | 2.20E-11 | | | | | | | | | |
| 18 | 1 | 2 | 9.20E-13 | | | | | | | | | |
| 19 | 3 | 2 | 8.5000E-13 -2.4500E+03 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 20 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 21 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 22 | 3 | 2 | 3.2000E-11 7.0000E+01 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 23 | 3 | 2 | 1.8000E-11 1.1000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 24 | 1 | 2 | 2.20E-10 | | | | | | | | | |
| 25 | 3 | 2 | 1.5000E-12 -8.8000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 26 | 3 | 2 | 2.0000E-14 -6.8000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 27 | 3 | 2 | 8.0000E-12 -2.0580E+03 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 28 | 1 | 3 | 4.40E-40 | | | | | | | | | |
| 29 | 1 | 2 | 1.00E-20 | | | | | | | | | |
| 30 | 4 | 2 | 7.0000E-31 0.0000E+00 -2.6000E+00 3.0000E+02 3.6000E-11 0.0000E+00 -1.0000E-01 3.0000E+02 6.0000E-01 1.0000E+00 | | | | | | | | | |
| 31 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 32 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 33 | 3 | 2 | 1.8000E-11 -3.9000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 34 | 3 | 2 | 3.5000E-12 2.5000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 35 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 36 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 37 | 1 | 1 | 0.00E+00 | | | | | | | | | |
| 38 | 4 | 2 | 3.0000E-30 0.0000E+00 -3.0000E+00 3.0000E+02 3.6000E-11 0.0000E+00 0.0000E+00 3.0000E+02 4.0000E-01 1.0000E+00 | | | | | | | | | |
| 39 | 6 | 2 | 7.2000E-15 7.8500E+02 0.0000E+00 3.0000E+02 4.1000E-16 1.4400E+03 0.0000E+00 3.0000E+02 1.9000E-33 7.2500E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 40 | 7 | 2 | 2.2000E-13 6.0000E+02 0.0000E+00 3.0000E+02 4.6778E-20 9.8000E+02 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 41 | 7 | 3 | 3.0800E-34 2.8000E+03 0.0000E+00 3.0000E+02 6.5489E-41 3.1800E+03 0.0000E+00 3.0000E+02 | | | | | | | | | |
| 42 | 1 | 1 | 0.00E+00 | | | | | | | | | |

| Rxn | Type | Order | Parameters (1 to 12 parameters, depending upon Type) | | | | | | | | | | | | | | | | | |
|-----|------|-------|--|-------------|-------------|------------|------------|------------|-------------|------------|--|--|--|--|--|--|--|--|--|--|
| 43 | 3 | 2 | 2.9000E-12 | -1.6000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 44 | 3 | 2 | 4.8000E-11 | 2.5000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 45 | 7 | 2 | 1.5000E-13 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | 9.0000E-20 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | |
| 46 | 3 | 2 | 2.4500E-12 | -1.7750E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 47 | 1 | 1 | 0.00E+00 | | | | | | | | | | | | | | | | | |
| 48 | 1 | 1 | 0.00E+00 | | | | | | | | | | | | | | | | | |
| 49 | 3 | 2 | 3.4000E-11 | -1.6000E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 50 | 3 | 2 | 8.6000E-12 | 2.0000E+01 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 51 | 3 | 2 | 2.0000E-12 | -2.4300E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 52 | 1 | 1 | 0.00E+00 | | | | | | | | | | | | | | | | | |
| 53 | 3 | 2 | 1.8000E-11 | -1.1000E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 54 | 3 | 2 | 5.6000E-12 | 2.7000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 55 | 3 | 2 | 1.4000E-12 | -1.8600E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 56 | 3 | 2 | 5.3000E-12 | 3.6000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 57 | 4 | 2 | 2.7000E-28 | 0.0000E+00 | -7.1000E+00 | 3.0000E+02 | 1.2000E-11 | 0.0000E+00 | -9.0000E-01 | 3.0000E+02 | | | | | | | | | | |
| 58 | 5 | 1 | 57. | 9.0000E-29 | 1.4000E+04 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | |
| 59 | 3 | 2 | 4.3000E-13 | 1.0400E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 60 | 3 | 2 | 2.8000E-12 | 5.3000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 61 | 1 | 2 | 8.14E-13 | | | | | | | | | | | | | | | | | |
| 62 | 3 | 1 | 1.0000E+15 | -8.0000E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 63 | 1 | 1 | 1.60E+03 | | | | | | | | | | | | | | | | | |
| 64 | 1 | 2 | 1.50E-11 | | | | | | | | | | | | | | | | | |
| 65 | 3 | 2 | 1.0400E-11 | -7.9200E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 66 | 4 | 2 | 7.0000E-29 | 0.0000E+00 | -3.1000E+00 | 3.0000E+02 | 9.0000E-12 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | |
| 67 | 3 | 2 | 9.1000E-15 | -2.5800E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 68 | 3 | 2 | 3.4500E-11 | -3.4000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 69 | 3 | 2 | 8.8700E-12 | 4.7800E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 70 | 3 | 2 | 3.1600E-15 | -1.6800E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 71 | 3 | 2 | 1.7400E-13 | -1.5000E+01 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 72 | 1 | 2 | 3.60E-11 | | | | | | | | | | | | | | | | | |
| 73 | 3 | 2 | 2.5400E-11 | 4.0760E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 74 | 3 | 2 | 7.8600E-15 | -1.9120E+03 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 75 | 3 | 2 | 3.0300E-12 | -4.4800E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 76 | 1 | 2 | 1.50E-19 | | | | | | | | | | | | | | | | | |
| 77 | 1 | 2 | 3.36E-11 | | | | | | | | | | | | | | | | | |
| 78 | 1 | 2 | 7.11E-18 | | | | | | | | | | | | | | | | | |
| 79 | 1 | 2 | 1.00E-15 | | | | | | | | | | | | | | | | | |
| 80 | 1 | 1 | 0.00E+00 | | | | | | | | | | | | | | | | | |
| 81 | 3 | 2 | 1.8000E-12 | 3.5500E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 82 | 1 | 2 | 8.10E-12 | | | | | | | | | | | | | | | | | |
| 83 | 1 | 1 | 4.20E+00 | | | | | | | | | | | | | | | | | |
| 84 | 1 | 2 | 4.10E-11 | | | | | | | | | | | | | | | | | |
| 85 | 1 | 2 | 2.20E-11 | | | | | | | | | | | | | | | | | |
| 86 | 1 | 2 | 1.40E-11 | | | | | | | | | | | | | | | | | |
| 87 | 1 | 1 | 0.00E+00 | | | | | | | | | | | | | | | | | |
| 88 | 1 | 2 | 3.00E-11 | | | | | | | | | | | | | | | | | |
| 89 | 3 | 2 | 5.4000E-17 | -5.0000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 90 | 3 | 2 | 1.7000E-11 | 1.1600E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 91 | 1 | 1 | 0.00E+00 | | | | | | | | | | | | | | | | | |
| 92 | 1 | 2 | 1.70E-11 | | | | | | | | | | | | | | | | | |
| 93 | 3 | 2 | 3.0000E-12 | 2.8000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 94 | 5 | 2 | 93. | 1.0000E+00 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | |
| 95 | 3 | 2 | 2.5000E-13 | 1.9000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 96 | 3 | 2 | 3.8000E-13 | 8.0000E+02 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | | |
| 97 | 5 | 2 | 96. | 1.0000E+00 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | |
| 98 | 5 | 2 | 95. | 1.0000E+00 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | |
| 99 | 5 | 2 | 95. | 2.0000E+00 | 0.0000E+00 | 0.0000E+00 | 3.0000E+02 | | | | | | | | | | | | | |

Notes:

Reaction types and data input formats are defined in the CAMx User's Guide (ENVIRON, 2004).

Table 2-7. Secondary/primary photolysis rate ratios for CB2002.

| Secondary Photolysis Reaction | Primary Reference Reaction | Secondary/Primary Ratio |
|-------------------------------|----------------------------|-------------------------|
| 9 | 1 | 2.55 |
| 10 | 1 | 28.6 |
| 20 | 1 | 0.066 |
| 31 | 1 | 0.190 |
| 32 | 80 | 88.7 |
| 42 | 48 | 0.143 |
| 87 | 47 | 6.0 |
| 91 | 47 | 6.0 |

COMPARISON OF CB2002 AND CB4 RATE CONSTANTS

The rate constants for CB2002 were compared to CB4 as a quality assurance step and to understand differences. The comparison was complicated because reactions are ordered differently and in different units: ppm and minutes for CB4, molecules cm^{-3} and seconds for CB2002. The reaction orders were matched up and the rate constants compared at three different temperatures and pressures, as shown in Table 2-8. This Table shows:

- The CB2002 reaction number (from Table 2-6).
- The CB4 reaction number (from Table 2-3).
- The reactants, to quickly identify each reaction.
- The CB2002 rate constants in units of ppm and minutes at:
 - 298 K and 1013 mbar
 - 273 K and 1013 mbar
 - 298 K and 491 mbar.
- The percent changes in CB2002 reaction rates from CB4 = $100 \times (\text{CB2002}-\text{CB4})/\text{CB4}$.
- A brief comment on reasons for non-trivial differences, or for no comparison being made.

A summary of the main differences between CB2002 and CB4 follows.

- CB2002 updated rate constants for many inorganic reactions including pressure dependencies for some reactions.
- New inorganic reactions for
 - NO_3 with OH, HO_2 and NO_3
 - $\text{O}_3 + \text{O}(^3\text{P})$
- New HONO photolysis reaction to $\text{NO}_2 + \text{H}$
 - IUPAC (2004) recommends setting this reaction to zero
- Different rate expression for the $\text{N}_2\text{O}_5 + \text{water}$
 - $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ same as CAMx mechanism 4
 - $\text{N}_2\text{O}_5 + \text{H}_2\text{O} + \text{H}_2\text{O}$ (i.e., water dimers) included (Wahner et al., 1998).
- Reduced rate constants for radical-radical termination reactions (i.e., XO_2 and HO_2)
- New reaction rates for all olefins: ETH, OLE and ISOP.
- New reaction products for ETH and OLE.

Table 2-8. Comparison of rate constants between CB2002 and the OTAG version of the CB4 mechanism (CAMx Mechanism 3).

| Reaction Number | | Reactants | CB2002 (ppm ⁻¹ min ⁻¹) | | | Change from CB4 ¹ | | | Comment ² |
|-----------------|------|------------------|---|----------|----------|------------------------------|---------|--------|--|
| CB2002 | CB4 | | 298 K | 273 K | 298 K | 298 K | 273 K | 298 K | |
| | | | 1013 mB | 1013 mB | 491 mB | 1013 mB | 1013 mB | 491 mB | |
| 1 | 1 | NO2 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 2 | 2 | O3P + O2 + M | 2.22E-05 | 2.99E-05 | 5.21E-06 | 7% | -8% | -88% | P-dep |
| 3 | 3 | O3 + NO | 2.89E+01 | 1.99E+01 | 1.40E+01 | 8% | 4% | 8% | |
| 4 | 4 | O3P + NO2 | 1.51E+04 | 1.75E+04 | 7.34E+03 | 10% | 16% | 10% | New data |
| 5 | 5 | O3P + NO2 | 2.33E+03 | 2.91E+03 | 6.15E+02 | 1% | -6% | -45% | P-dep |
| 6 | 6 | O3P + NO | 2.46E+03 | 2.99E+03 | 6.35E+02 | 1% | -7% | -46% | P-dep |
| 7 | 20 | NO + NO + O2 | 7.11E-10 | 9.13E-10 | 1.67E-10 | -3% | -3% | -77% | P-dep |
| 8 | 7 | O3 + NO2 | 4.77E-02 | 2.45E-02 | 2.31E-02 | 1% | 1% | 1% | |
| 9 | 14 | NO3 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 10 | 14 | NO3 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 11 | 15 | NO3 + NO | 3.92E+04 | 4.51E+04 | 1.90E+04 | -11% | -13% | -11% | |
| 12 | 16 | NO3 + NO2 | 9.69E-01 | 7.18E-01 | 4.70E-01 | 64% | 63% | 64% | New data |
| 13 | 17 | NO3 + NO2 | 1.74E+03 | 2.07E+03 | 7.79E+02 | -6% | -5% | -13% | New data |
| 14 | 19 | N2O5 | 2.26E+00 | 9.19E-02 | 1.01E+00 | -18% | -6% | -64% | New data |
| 15 | 18 | N2O5 + H2O | 3.69E-07 | 4.03E-07 | 1.79E-07 | -81% | -81% | -81% | New data |
| 16 | #N/A | N2O5 + H2O + H2O | 6.55E-11 | 7.15E-11 | 1.54E-11 | | | | New reaction |
| 17 | #N/A | NO3 + OH | 3.25E+04 | 3.55E+04 | 1.58E+04 | | | | New reaction |
| 18 | #N/A | NO3 + HO2 | 1.36E+03 | 1.48E+03 | 6.59E+02 | | | | New reaction |
| 19 | #N/A | NO3 + NO3 | 3.38E-01 | 1.74E-01 | 1.64E-01 | | | | New reaction |
| 20 | 8 | O3 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 21 | 9 | O3 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 22 | 10 | O1D + O2 | 5.98E+04 | 6.67E+04 | 2.90E+04 | -79% | -81% | -90% | These two reactions compare well to O1D + M in CB4 |
| 23 | 10 | O1D + N2 | 3.85E+04 | 4.34E+04 | 1.86E+04 | 0% | 0% | 0% | |
| 24 | 11 | O1D + H2O | 3.25E+05 | 3.55E+05 | 1.58E+05 | 0% | 0% | 0% | |
| 25 | 12 | O3 + OH | 1.16E+02 | 9.63E+01 | 5.60E+01 | 16% | 18% | 16% | New data |
| 26 | 13 | O3 + HO2 | 3.02E+00 | 2.67E+00 | 1.46E+00 | 1% | -2% | 1% | |
| 27 | #N/A | O3 + O3P | 1.18E+01 | 6.87E+00 | 5.74E+00 | | | | New reaction |
| 28 | 21 | NO + NO2 + H2O | 1.60E-11 | 1.75E-11 | 3.76E-12 | 0% | -8% | 0% | |
| 29 | 25 | HONO + HONO | 1.48E-05 | 1.61E-05 | 7.16E-06 | -2% | -2% | -2% | |
| 30 | 22 | OH + NO | 1.09E+04 | 1.36E+04 | 3.41E+03 | 12% | -1% | -28% | New data |
| 31 | 23 | HONO | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 32 | #N/A | HONO | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | New reaction |
| 33 | 24 | OH + HONO | 7.18E+03 | 6.96E+03 | 3.48E+03 | -26% | -35% | -26% | New data |
| 34 | 28 | HO2 + NO | 1.20E+04 | 1.41E+04 | 5.80E+03 | -3% | -2% | -3% | |
| 35 | 29 | HO2 + NO2 | 2.05E+03 | 2.74E+03 | 6.79E+02 | 1% | -1% | -31% | P-dep |
| 36 | 30 | PNA | 5.17E+00 | 2.42E-01 | 1.71E+00 | 1% | 6% | -67% | P-dep |
| 37 | 31 | OH + PNA | 6.87E+03 | 8.43E+03 | 3.33E+03 | 1% | 1% | 1% | |
| 38 | 26 | OH + NO2 | 1.57E+04 | 1.96E+04 | 5.19E+03 | -7% | -14% | -36% | New data and P-dep |
| 39 | 27 | OH + HNO3 | 2.17E+02 | 3.21E+02 | 1.03E+02 | 0% | -1% | -3% | |
| 40 | 32 | HO2 + HO2 | 4.29E+03 | 5.93E+03 | 1.61E+03 | 3% | -8% | -20% | New data |
| 41 | 33 | HO2 + HO2 + H2O | 2.38E-01 | 6.46E-01 | 4.34E-02 | 9% | -58% | -16% | New data |
| 42 | 34 | H2O2 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 43 | 35 | OH + H2O2 | 2.50E+03 | 2.60E+03 | 1.21E+03 | -1% | 0% | -1% | |
| 44 | 90 | OH + HO2 | 1.64E+05 | 1.93E+05 | 7.95E+04 | 1% | 1% | 1% | |
| 45 | 36 | OH + CO | 3.55E+02 | 3.87E+02 | 1.39E+02 | 10% | 10% | -11% | New data |
| 46 | 51 | OH + CH4 | 9.37E+00 | 5.93E+00 | 4.54E+00 | -22% | -16% | -82% | Explicit CH4, new data |
| 47 | 38 | FORM | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 48 | 39 | FORM | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 49 | 40 | FORM + O3P | 2.34E+02 | 1.56E+02 | 1.13E+02 | -1% | -3% | -1% | |
| 50 | 37 | FORM + OH | 1.36E+04 | 1.49E+04 | 6.59E+03 | -9% | -9% | -9% | |
| 51 | 41 | FORM + NO3 | 8.49E-01 | 4.39E-01 | 4.12E-01 | -9% | -57% | -9% | New data |
| 52 | 45 | ALD2 | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |

| Reaction Number | | Reactants | CB2002 (ppm ⁻¹ min ⁻¹) | | | Change from CB4 ¹ | | | Comment ² |
|-----------------|-----|-------------|---|----------|----------|------------------------------|---------|--------|----------------------|
| CB2002 | CB4 | | 298 K | 273 K | 298 K | 298 K | 273 K | 298 K | |
| | | | 1013 mB | 1013 mB | 491 mB | 1013 mB | 1013 mB | 491 mB | |
| 53 | 42 | ALD2 + O3P | 6.63E+02 | 5.16E+02 | 3.21E+02 | 4% | 1% | 4% | |
| 54 | 43 | ALD2 + OH | 2.05E+04 | 2.43E+04 | 9.92E+03 | -15% | -14% | -15% | New data |
| 55 | 44 | ALD2 + NO3 | 4.03E+00 | 2.48E+00 | 1.95E+00 | 9% | -39% | 9% | New data |
| 56 | 46 | C2O3 + NO | 2.62E+04 | 3.20E+04 | 1.27E+04 | -7% | 10% | -7% | |
| 57 | 47 | C2O3 + NO2 | 1.55E+04 | 1.87E+04 | 7.25E+03 | 13% | 11% | 9% | |
| 58 | 48 | PAN | 2.76E-02 | 4.50E-04 | 1.29E-02 | 9% | 12% | -49% | P-dep |
| 59 | 50 | C2O3 + HO2 | 2.08E+04 | 3.13E+04 | 1.01E+04 | 117% | 199% | 117% | New data |
| 60 | 49 | C2O3 + C2O3 | 2.45E+04 | 3.15E+04 | 1.19E+04 | 562% | 679% | 562% | New data |
| 61 | 52 | OH + PAR | 1.20E+03 | 1.31E+03 | 5.83E+02 | 0% | 0% | 0% | |
| 62 | 53 | ROR | 1.32E+05 | 1.23E+04 | 1.32E+05 | -4% | 5% | -4% | |
| 63 | 54 | ROR | 9.60E+04 | 1.05E+05 | 9.60E+04 | 1% | 10% | 1% | |
| 64 | 55 | ROR + NO2 | 2.22E+04 | 2.42E+04 | 1.07E+04 | 1% | 1% | 1% | |
| 65 | 60 | O3P + ETH | 1.08E+03 | 9.22E+02 | 5.22E+02 | 0% | 0% | 0% | |
| 66 | 61 | OH + ETH | 1.25E+04 | 1.37E+04 | 5.93E+03 | 5% | -7% | 3% | |
| 67 | 62 | O3 + ETH | 2.34E-03 | 1.15E-03 | 1.13E-03 | -13% | -12% | -13% | New data |
| 68 | 56 | O3P + OLE | 1.63E+04 | 1.60E+04 | 7.89E+03 | 175% | 174% | 175% | New data |
| 69 | 57 | OH + OLE | 6.52E+04 | 8.24E+04 | 3.16E+04 | 55% | 54% | 55% | New data |
| 70 | 58 | O3 + OLE | 1.66E-02 | 1.08E-02 | 8.06E-03 | -8% | 5% | -8% | |
| 71 | 59 | NO3 + OLE | 2.44E+02 | 2.66E+02 | 1.18E+02 | 2053% | 2044% | 2053% | New data |
| 72 | 75 | O3P + ISOP | 5.32E+04 | 5.80E+04 | 2.58E+04 | 0% | 0% | 0% | |
| 73 | 76 | OH + ISOP | 1.47E+05 | 1.82E+05 | 7.14E+04 | 0% | 13% | 0% | New data |
| 74 | 77 | O3 + ISOP | 1.90E-02 | 1.15E-02 | 9.20E-03 | 0% | -44% | 0% | New data |
| 75 | 78 | NO3 + ISOP | 9.95E+02 | 9.47E+02 | 4.82E+02 | 0% | -13% | 0% | New data |
| 76 | 96 | NO2 + ISOP | 2.22E-04 | 2.42E-04 | 1.07E-04 | 1% | 1% | 1% | |
| 77 | 92 | ISPD + OH | 4.96E+04 | 5.42E+04 | 2.41E+04 | 0% | 0% | 0% | |
| 78 | 93 | ISPD + O3 | 1.05E-02 | 1.15E-02 | 5.09E-03 | 0% | 0% | 0% | |
| 79 | 94 | ISPD + NO3 | 1.48E+00 | 1.61E+00 | 7.16E-01 | 0% | 0% | 0% | |
| 80 | 95 | ISPD | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 81 | 63 | OH + TOL | 8.75E+03 | 1.07E+04 | 4.24E+03 | -4% | -3% | -4% | |
| 82 | 64 | TO2 + NO | 1.20E+04 | 1.31E+04 | 5.80E+03 | 0% | 0% | 0% | |
| 83 | 65 | TO2 | 2.52E+02 | 2.75E+02 | 2.52E+02 | 1% | 10% | 1% | |
| 84 | 66 | OH + CRES | 6.06E+04 | 6.61E+04 | 2.94E+04 | -1% | -1% | -1% | |
| 85 | 67 | NO3 + CRES | 3.25E+04 | 3.55E+04 | 1.58E+04 | 0% | 0% | 0% | |
| 86 | 68 | CRO + NO2 | 2.07E+04 | 2.26E+04 | 1.00E+04 | 3% | 3% | 3% | |
| 87 | 69 | OPEN | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 88 | 70 | OPEN + OH | 4.43E+04 | 4.84E+04 | 2.15E+04 | 1% | 1% | 1% | |
| 89 | 71 | OPEN + O3 | 1.49E-02 | 1.39E-02 | 7.22E-03 | -1% | -1% | -1% | |
| 90 | 72 | OH + XYL | 3.71E+04 | 4.19E+04 | 1.80E+04 | 2% | 2% | 2% | |
| 91 | 74 | MGLY | 0.00E+00 | 0.00E+00 | 0.00E+00 | | | | Photolysis |
| 92 | 73 | OH + MGLY | 2.51E+04 | 2.74E+04 | 1.22E+04 | -3% | -3% | -3% | |
| 93 | 79 | XO2 + NO | 1.13E+04 | 1.35E+04 | 5.50E+03 | -6% | 3% | -5% | |
| 94 | 81 | XO2N + NO | 1.13E+04 | 1.35E+04 | 5.50E+03 | -6% | 3% | -5% | |
| 95 | 80 | XO2 + XO2 | 6.99E+02 | 8.09E+02 | 3.39E+02 | -65% | -75% | -65% | New data |
| 96 | 86 | XO2 + HO2 | 8.22E+03 | 1.15E+04 | 3.99E+03 | -8% | -21% | -8% | New data |
| 97 | 87 | XO2N + HO2 | 8.22E+03 | 1.15E+04 | 3.99E+03 | -8% | -21% | -8% | New data |
| 98 | 88 | XO2N + XO2N | 6.99E+02 | 8.09E+02 | 3.39E+02 | -65% | -75% | -65% | New data |
| 99 | 89 | XO2 + XO2N | 1.40E+03 | 1.62E+03 | 6.77E+02 | -65% | -75% | -65% | New data |

Notes:

1. Percent change in CB2002 reaction rate from CB4 = 100 x (CB2002-CB4)/CB4
2. Comments on reason for change, or no change calculated.

Photolysis: no rate given or change calculated for photolysis reactions

New reaction: no change calculated for a new reaction in CB2002

New data: rate constant updated in CB2002 based on newer data

P-dep: main effect of rate constant update is explicit representation of pressure dependence.

Explicit CH4: CB2002 has CH4 as an explicit species whereas CB4 incorporates CH4 in the rate constant.

RATE CONSTANT FOR OH + NO₂

One of the motivations for developing CB2002 was that the OH + NO₂ reaction rate constant was revised in the late 1990s. The OH + NO₂ reaction is a major sink for both radicals and NO_x under urban conditions and is so important that a chemical mechanism such as CB4 must be recalibrated against smog chamber data if this rate constant is changed.

The OH + NO₂ reaction rates for CB2002 (Jeffries, Voicu and Sexton, 2002), CB4 mechanism 3 (Gery et al., 1989) CB4 mechanism 4 (JPL, 1994) and SAPRC99 (Carter, 2000) are compared in Table 2-9. Both the NASA (JPL, 2003) and IUPAC (IUPAC, 2004) kinetic data review panels recommend values that are essentially identical to the CB2002 values (Troe, 2001). Comparing the values for 298 K and 1013 mbar is most relevant to smog chamber data and urban ozone formation. For this condition, the OH + NO₂ reaction rate is about 15% low in SAPRC99 and 7% high in CB4 (both M3 and M4). For the low-pressure condition (491 mbar) CB4 (M3) is high because Gery et al. (1989) did not explicitly account for pressure dependence. The pressure dependence in CB4 (M4) is much improved by using the JPL (1994) expression. The SAPRC 99 OH + NO₂ reaction rate is 18% too low for the low-pressure condition.

Table 2-9. Comparison of OH + NO₂ reaction rate constants in CB2002, CB4 and SAPRC99.

| Temperature (K) | 298 | 273 | 298 | Difference from CB2002 |
|-----------------|----------|----------|----------|---------------------------|
| Pressure (mbar) | 1013 | 1013 | 491 | |
| CB2002 | 1.57E+04 | 1.96E+04 | 5.19E+03 | |
| CB4 (M3) | 1.68E+04 | 2.29E+04 | 8.15E+03 | +7% to +36% |
| CB4 (M4) | 1.70E+04 | 2.22E+04 | 5.94E+03 | +7% to +13% |
| SAPRC99 | 1.33E+04 | 1.80E+04 | 4.77E+03 | -9% to -18% |

Notes:

- CB2002 used as the reference because it has currently accepted values from Troe (2001) that are consistent with JPL (2003) and IUPAC (2004).
- CB4 (M3) values from Gery et al., (1999).
- CB4 (M4) values from JPL (1994).
- SAPRC99 values from Carter (2000)

3. EXTENDED INORGANIC REACTION SET FOR CB4

Condensed reaction mechanisms for photochemical modeling, such as the CB4 (Gery et al., 1989) and SAPRC99 (Carter, 2000), require an inorganic reaction set that describes all relevant aspects of tropospheric chemistry with a moderate number of reactions. The relevant aspects of tropospheric chemistry have expanded in recent years as models are applied for particulate matter (PM), air toxics and mercury in addition to ozone. Regional modeling domains also have expanded both horizontally and vertically to encompass pristine parts of the troposphere such as the upper troposphere and oceans.

OVERVIEW OF REACTIONS ADDED

This project reviewed the inorganic reaction set in the CB4 and other mechanisms to identify reactions that should be added. Seventeen reactions were added to CAMx mechanism 4 (M4) as shown in Table 3-1. Since these reactions mostly involve the inorganic reaction set this modification is referred to as extended inorganic chemistry (CB4xi). M4 was selected as the basis for modification because it is most appropriate for regional PM, mercury and toxics modeling as well as ozone. The extended inorganic reactions are summarized briefly here and discussed in more detail below.

- Reactions of molecular hydrogen (101 and 102). Hydrogen is somewhat important to odd-hydrogen (OH and HO₂) for very dry conditions in the upper troposphere. Including hydrogen allows the air quality impacts of hydrogen as an alternative fuel to be evaluated. Currently, hydrogen is included in CAMx with a constant atmospheric concentration of 0.6 ppm (Novelli et al, 1999).
- Odd-oxygen reactions (103 to 107) that may be important for pristine conditions such as the upper troposphere. Including these reactions provides a more complete description of hydroxyl radical (OH) chemistry in the upper troposphere to improve modeling for persistent air toxics and mercury.
- Additional NO₃ radical reactions (108 to 112) to improve nighttime chemistry. NO₃ radical is the main driver for atmospheric chemistry at night and including additional NO₃ removal reactions improves the calculation of nighttime destruction rates for several types of reactive hydrocarbons (e.g., aldehydes, olefins) and for NO_x (via NO₃ and N₂O₅ reactions).
- NO_x recycling reactions (113 to 117) to improve the representation of the fate of NO_x over multi-day timescales. These are all photolysis reactions that occur quite slowly in the troposphere. Reactions 113, 115 and 117 are only important for very cold conditions such as the upper troposphere. Reactions 114 and 116, photolysis of nitric acid and organic nitrates, are important to regional ozone and oxidant chemistry in the lower troposphere (Zaveri and Peters, 1999). The “NO_x recycling reactions” slowly recycle nitrogen from an inactive form (NO_z) to an active form (NO_x).

Table 3-1. Reactions added in the CB4xi mechanism and whether they are included in other condensed chemical mechanisms.

| Number | Reaction | Included in CB2002 | Included in CBM-Z | Included in mCB4 | Included in SAPRC99 |
|--------|---|--------------------|-------------------|------------------|---------------------|
| 101 | O1D + H2 = OH + HO2 | | | | |
| 102 | OH + H2 = HO2 | | | Yes | Yes |
| 103 | OH + O = HO2 | | | | |
| 104 | OH + OH = O | | | | |
| 105 | OH + OH = H2O2 | | | | |
| 106 | HO2 + O = OH | | | | |
| 107 | H2O2 + O = OH + HO2 | | | | |
| 108 | NO3 + O = NO2 | | | | |
| 109 | NO3 + OH = HO2 + NO2 | Yes | | Yes | Yes |
| 110 | NO3 + HO2 = HNO3 | Yes | Yes | Yes | Yes |
| 111 | NO3 + O3 = NO2 | | | | |
| 112 | NO3 + NO3 = 2 NO2 | Yes | Yes | | Yes |
| 113 | PAN = C2O3 + NO2 | | | | |
| 114 | HNO3 = OH + NO2 | | Yes | | Yes |
| 115 | N2O5 = NO2 + NO3 | | | | |
| 116 | NTR = NO2 + XO2 | | Yes | | Yes |
| 117 | PNA = 0.61 HO2 + 0.61 NO + 0.39 OH + 0.39 NO2 | | Yes | | Yes |

CB2002 from Jeffries, Voicu and Sexton (2002)

CMB-Z from Zaveri and Peters (1999)

mCB4 from EPA (2004)

SAPRC99 from Carter (2000)

Table 3-2. Rate constants for reactions added in the CB4xi mechanism.

| Reaction Number | k_{298} (ppm ⁻¹ min ⁻¹) | Temperature Effect E/R (K) | Reference |
|-----------------|--|----------------------------|-----------------|
| 101 | 162600 | | JPL (2003) |
| 102 | 9.89 | 2000 | JPL (2003) |
| 103 | 48640 | -120 | JPL (2003) |
| 104 | 41200 | | JPL (2003) |
| 105 | 9298 | Fall off expression | JPL (2003) |
| 106 | 86750 | -200 | JPL (2003) |
| 107 | 2.5 | 2000 | JPL (2003) |
| 108 | 14780 | | JPL (2003) |
| 109 | 32500 | | JPL (2003) |
| 110 | 5200 | | JPL (2003) |
| 111 | 0.015 | | JPL (2003) |
| 112 | 0.34 | 2450 | JPL (2003) |
| 113 | 0.0014 x JHCHOr | | Jacobson (1999) |
| 114 | 0.025 x JHCHOr | | Jacobson (1999) |
| 115 | 0.006 x JNO2 | | Jacobson (1999) |
| 116 | 0.1 x JHCHOr | | Jacobson (1999) |
| 117 | 0.00063 x JNO2 | | Jacobson (1999) |

Table 3-3. Rate constants for thermal reactions added in the CB4xi mechanism at three temperature/pressure conditions.

| Temperature (K) | 298 | 273 | 298 |
|-----------------|--|------------|------------|
| Pressure (mbar) | 1013 | 1013 | 491 |
| Reaction | Rate constant (ppm ⁻¹ min ⁻¹) | | |
| 101 | 1.6258E+05 | 1.7747E+05 | 7.8802E+04 |
| 102 | 9.8900E+00 | 5.8389E+00 | 4.7937E+00 |
| 103 | 4.8640E+04 | 5.5089E+04 | 2.3576E+04 |
| 104 | 4.1200E+04 | 4.4973E+04 | 1.9970E+04 |
| 105 | 9.2981E+03 | 1.0627E+04 | 2.9912E+03 |
| 106 | 8.6750E+04 | 1.0070E+05 | 4.2048E+04 |
| 107 | 2.5000E+00 | 1.4760E+00 | 1.2117E+00 |
| 108 | 1.4780E+04 | 1.6133E+04 | 7.1639E+03 |
| 109 | 3.2500E+04 | 3.5476E+04 | 1.5753E+04 |
| 110 | 5.2000E+03 | 5.6762E+03 | 2.5204E+03 |
| 111 | 1.5000E-02 | 1.6374E-02 | 7.2705E-03 |
| 112 | 3.4000E-01 | 1.7481E-01 | 1.6480E-01 |

ANALYSIS OF REACTIONS ADDED

Liang and Jacobson (2000) compared the organic part of the CB4 of Gery et al., (1989) against a 4,000-reaction “master mechanism” (Derwent et al., 1998). Liang and Jacobson used the same inorganic reaction set (Jacobson, 1999) with both the CB4 and the master mechanism. The additional inorganic reaction set developed for CB4xi was based mainly on the work of Liang and Jacobson. Each new reaction was evaluated individually either analytically or using a box model as discussed below.

(101) O¹D + H₂ = OH + HO₂

This reaction provides a radical source via ozone photolysis (i.e., O(¹D) production) and the hydrogen molecule analogous to the O(¹D) reaction with water that has always been included in CB4. Novelli et al. (1999) report that hydrogen typically is found in the troposphere at a concentration of ~0.6 ppm. This concentration coupled with the relative rate constants for H₂ and H₂O reaction with O(¹D) implies that this reaction would only be important as a pathway for O¹D when water concentrations drop below about 0.3 ppm. Since water is always well above this value in the lower troposphere (typical concentrations are many thousands of ppm) this pathway is not important except at elevations approaching the top of the troposphere where very cold temperatures reduce water concentrations to near zero.

(102) OH + H₂ = HO₂ + H₂O

The ozone reaction with OH in the standard CB4 reaction set provides one competitive test of the importance of this reaction. Using 0.6 ppm as the typical concentration for hydrogen and the rate constants the “competitive” concentration for ozone would be about 60 ppb. That is, for ozone concentrations below 60 ppb the pathway with H₂ would be more important. Because ozone is often less than 60 ppb in many parts of the troposphere this reaction should be included in CB4xi.

Another competitive test of the importance of this reaction is the reaction of OH with CH₄. The lower tropospheric rate constants for OH reaction with H₂ and CH₄ are similar but the typical

tropospheric concentrations are about 0.6 ppm and 1.75 ppm, respectively. Therefore, H₂ is typically about one third of the importance of CH₄.

(103) OH + O = HO₂

This reaction competes with the reaction of OH with ozone. The ratio of the rate constants (about 500:1) for OH reaction with O atoms and ozone implies that for this reaction to be competitive the ozone concentration needs to be below 500 times the O atom concentration. Since O atoms react rapidly with molecular oxygen to form ozone, ozone will always be formed when O is present. During daylight hours a well known pseudo-photostationary state exists between O atoms, ozone, nitric oxide, and nitrogen dioxide (reactions 1-3 of the CB4 shown in Table 2-1). This relationship shows that the ratio of ozone to O atoms is approximately equal to $k_2/(k_3[\text{NO}])$. Assuming a maximum value of [NO] of 1 ppm, the minimum O₃/O ratio would be about 160,000:1. Since this is very much greater than 500 this reaction is generally unimportant in the lower troposphere.

This reaction is more important in the upper troposphere because the pseudo-steady state relationship between ozone and oxygen atoms changes dramatically as the altitude increases. This stems mainly from the major sink reaction for oxygen atoms being the three-body reaction with O₂ and M. Since the pressure at the top of the troposphere is about a tenth of that at the surface this sink reaction is about two orders of magnitude slower, which results in much lower ozone to oxygen atom ratio. This reaction is included for modeling upper tropospheric conditions.

(104) OH + OH = O + H₂O

Assuming a maximum OH concentration of 10⁻⁶ ppm and that production of O atoms results in ozone production (due to reaction 2 in CB4), the rate constant for reaction 104 implies a maximum ozone production rate of 0.004 ppb over a period of 24 hours. This is too slow to be of significance for tropospheric ozone. This reaction may have some influence by limiting OH concentrations in the upper troposphere where OH sinks are weak and is included to be consistent with Jacobson (1999).

(105) OH + OH = H₂O₂

As for reaction 104, assuming a maximum OH concentration of 10⁻⁶ ppm implies that 24-hour production of H₂O₂ would be 0.01 ppb. This rate of H₂O₂ production is much lower than from the HO₂ + HO₂ reactions in the original CB4. Note that HO₂ and OH concentrations tend to increase and decrease together, because of inter-conversion reactions, so H₂O₂ production will always be dominated by self-reaction of HO₂ rather than OH. This reaction is included to complement reaction 104 and to be consistent with Jacobson (1999).

(106) HO₂ + O = OH

Similar to reaction 103 between OH and O atoms, this reaction competes against the reaction of HO₂ with ozone in the original CB4. In this case, the O atom reaction (106) is faster than the OH reaction (103) such that the competitive point is reached when the ozone to O atom ratio falls below 28,000:1. Nevertheless, the lower limit ozone to O ratio of ~160,000:1 in the lower troposphere estimated above is still above the range for this reaction to become of much

importance in the lower troposphere. This reaction is included for modeling upper tropospheric conditions.

(107) $O + H_2O_2 = OH + O_2$

As with other O atom reactions, reaction 107 would not be important at night because there are essentially no O atom sources at night. During the day this reaction is similar to O atom reactions with aldehydes in converting O atoms to odd hydrogen radicals (OH and HO₂). Aldehydes and H₂O₂ are secondary products and frequently occur together. Based on rate constant ratios, reaction 107 would become competitive when the ratio of aldehydes to H₂O₂ falls below about 50:1. In polluted atmospheres, where the presence of NO inhibits H₂O₂ production and there are significant aldehyde emissions, this ratio is likely to exceed 50:1. For aged air masses the ratio of aldehydes to H₂O₂ may fall below 50:1. The reaction of O atoms with H₂O₂ should be included for aged air conditions but it is unlikely to be very important either as a source of odd hydrogen or a removal mechanism for H₂O₂.

(108) $NO_3 + O = NO_2$

This reaction is potentially important only during the day because O atoms are present only during daylight. This reaction will not be an important daytime sink for O atoms compared to reaction with molecular oxygen. The main daytime sinks for NO₃ are photolysis and reactions with NO and NO₂. A high O atom concentration would be 10⁻⁹ ppm. Using this concentration and corresponding rate constant ratios, the competing levels of NO and NO₂ would need to be below 10⁻⁶ ppm and 10⁻⁵ ppm, respectively. Therefore, this reaction is not important even during daylight.

(109) $OH + NO_3 = HO_2 + NO_2$

At night, NO₃ concentrations could be as high as 1 ppb. Assuming this concentration, NO₃ would be an important sink for OH when other species fall below the following levels: typical VOCs below 100 ppbC; NO₂ below 2 ppb; CO below 100 ppb; ozone below 300 ppb. It is unlikely that all of these competing partners for OH would be below the stated levels under conditions where NO₃ could be as high as 1 ppb. However, this analysis suggests that this reaction could be somewhat important as a sink for OH at night under some conditions.

(110) $HO_2 + NO_3 = HNO_3$

As for the discussion above for the reaction of OH with NO₃ (109), NO₃ could be as high as 1 ppb at night. Assuming this concentration, NO₃ would be an important sink for HO₂ when other species fall below the following levels: ozone below 2 ppm; NO₂ below 2 ppb, NO below 0.5 ppb, and HO₂ itself below about 1 ppb. Hence, this reaction could be important as a sink reaction for HO₂ at night.

(111) $NO_3 + O_3 = NO_2$

At night, NO₃ concentrations could be as high as 1 ppb. Assuming this concentration, NO₃ would be an important sink for O₃ when other species fall below the following levels: NO₂ below 0.3 ppb; NO below 0.6 ppt. It would be rare for NO₃ concentrations to be higher than NO₂ concentrations and so it may be rare for this reaction to be important.

(112) $\text{NO}_3 + \text{NO}_3 = 2 \text{NO}_2$

The importance of this reaction increases as the square of the NO_3 concentration. Zaveri and Peters (1999) included this reaction but Jacobson (1999) did not include this reaction. On close inspection the rate constant for this reaction is so slow compared to other limiting pathways for NO_3 that it appears unlikely that this reaction would be important. For example, even if NO_3 were as high as 1 ppm, this reaction would only compete against the reaction of NO_3 with NO_2 (in the original CB4) when NO_2 levels were less than 0.2 ppb.

(113) $\text{PAN} + h\nu = \text{C}_2\text{O}_3 + \text{NO}_2$

This photolysis reaction is included because thermal decomposition of PAN is strongly temperature dependent. The photolytic and thermal decomposition reactions give the same products. Low temperatures in the upper troposphere or in cold climates will shut down the thermal decomposition of PAN allowing this relatively slow photolysis reaction to become important. This reaction may be important for modeling that includes the upper troposphere and for annual (wintertime) modeling.

(114) $\text{HNO}_3 + h\nu = \text{OH} + \text{NO}_2$

This reaction is included because it slowly recycles nitrogen from an inactive form of NO_z (i.e., HNO_3) to an active form of NO_x (i.e., NO_2). The slow production of NO_x from NO_z may be important to oxidant production on regional scales for rural/remote areas that have relatively low NO_x emissions but are impacted by NO_z transport from more polluted areas. The reaction of OH radical with HNO_3 , included in the original CB4, also converts NO_z to NO_x . The conversion of HNO_3 back to NO_x by photolysis and OH reaction will have a small impact on HNO_3 concentrations because the dominant removal processes for nitric acid will be deposition and conversion to particulate matter.

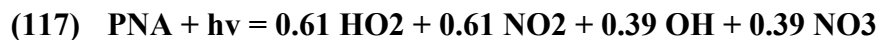
(115) $\text{N}_2\text{O}_5 + h\nu = \text{NO}_2 + \text{NO}_3$

According to Jacobson (1999), this photolysis reaction occurs at a rate as high as 0.003 per minute in the lower troposphere. It competes with the thermal reaction (in the original CB4) at the warm surface, which has a typical rate constant of about 2.8 per minute. Hence, at the surface the thermal reaction is far more important and this photolysis can only become important (like the PAN and HNO_3 photolysis reactions) at high altitude where the thermal reaction slows while the photolysis is even faster.

(116) $\text{NTR} + h\nu = \text{NO}_2 + \text{HO}_2 + \text{ACET} - \text{PAR}$

According to Jacobson (1999), this photolysis reaction (taking ethyl nitrate as a surrogate) occurs at a rate as high as 0.0001 per minute in the lower troposphere and about 3 times faster near the tropopause. This reaction is included because it slowly recycles nitrogen from an inactive form of NO_z (i.e., NTR) to an active form of NO_x (i.e., NO_2). The slow production of NO_x from NO_z may be important to oxidant production on regional scales for rural/remote areas that have relatively low NO_x emissions but are impacted by NO_z transport from more polluted areas. There are no other chemical reactions of NTR to compete against this reaction, so reaction 116 will compete against removal of NTR by deposition. The organic products of this reaction are

not easily defined in the CB4, but this is not particularly important because the main impacts will be due to the production of NO₂. Zaveri and Peters (1999) included this reaction and noted its importance for regional conditions.



According to Jacobson (1999), this photolysis reaction occurs at a rate as high as 0.00033 per minute in the lower troposphere and about 3 times faster near the tropopause. Unlike the PAN and N₂O₅ photolysis reactions discussed above, this reaction gives some (i.e. 39 percent) different products than its thermal counterpart. Similar to PAN and N₂O₅, the main reason to include this photolysis reaction is for high altitude cases where thermal PNA decomposition is slow. Also this reaction could be somewhat more important during extremely cold winter conditions with bright sunlight. The rates of PNA photolysis and thermal decomposition become comparable at about 235 K, which is a possible, but rare, winter temperature.

4. MODELING COMPARISONS

Two new chemical mechanisms were implemented in a special version of CAMx for testing by LADCO/MRPO:

- The CB2002 mechanism (Jeffries, Voicu, and Sexton, 2002), discussed in Chapter 2.
- The CAMx mechanism 4 with extra inorganic reactions (CB4xi), discussed in Chapter 3.

The impacts of the CB2002 and CB4xi mechanism updates were evaluated using three LADCO/MRPO modeling databases. Kirk Baker of LADCO performed the model runs and provided results for analysis and inclusion in this report.

The CB2002 was implemented for modeling ozone but not particulate matter (PM) because CB2002 did not include yields of secondary organic aerosol. Running CB2002 required using a special version of CAMx with a CB2002 chemistry parameters file and CB2002 photolysis rates calculated with a special version of the TUV pre-processor. No emissions file changes were required to run CB2002.

The CB4xi was implemented for modeling both ozone and PM, i.e., as an update to mechanism 4 (M4). Running CB4xi required using a special version of CAMx with a CB4xi chemistry parameters file. No emissions file changes were required to run CB4xi.

OZONE COMPARISON

Ozone comparisons were performed for the LADCO/MRPO June 2001 episode with Base I emission inventories. Daily maximum 8-hour ozone predictions for June 20-24, 2001 are shown in Figures 4-1 to 4-5. Each Figure compares isopleth plots of:

- Observed maximum 8-hr ozone (EPA's air-now display of interpolated observations).
- Predicted maximum 8-hr ozone CB4 (M4).
- Predicted maximum 8-hr ozone CB2002.
- Predicted maximum 8-hr ozone CB4xi.

The color scales were chosen to match EPA's air-now plots.

Compared to CB4, the CB2002 predicts lower ozone regionally on all days:

- The area above 65 ppb (yellow) is slightly smaller.
- The area above 85 ppb (orange) is much smaller.
- Predicted 8-hour peaks are 8 ppb to 9 ppb lower, depending upon the day.
- Lower ozone with CB2002 leads to poorer agreement with the observed ozone levels.

One sensitivity test (sensitivity to OH + NO₂ reaction rate) was performed to investigate why ozone levels were different between CB2002 and CB4, as discussed below. The sensitivity test failed to find a simple explanation of the ozone differences between CB2002 and CB4.

Compared to CB4, the CB4xi predicts higher ozone regionally on all days:

- The area above 65 ppb (yellow) is slightly greater.
- The area above 85 ppb (orange) is greater.
- Predicted 8-hour peaks are 3 ppb to 4 ppb higher, depending upon the day.
- Higher ozone with CB4xi leads to better agreement with the observed ozone levels.

The higher regional ozone with CB4xi than CB4 is due to the NO_x recycling reactions included in CB4xi. These reactions are the photolysis of organic nitrates and nitric acid, discussed in Section 3, that are included in other mechanisms such as SAPRC99 (Carter, 2000) and CBM-Z (Zaveri and Peters, 1999). The effect of these NO_x recycling reactions partially explains why SAPRC99 tends to predict higher regional ozone than CB4. Zaveri and Peters (1999) also concluded that including photolysis of organic nitrates would increase regional ozone predictions.

CB2002 Sensitivity to OH + NO₂ Reaction Rate

One potentially important difference between CB2002 and CB4 (M4) is the rate constant for the OH + NO₂ reaction. As discussed in Section 2 and shown in Table 2-7, the OH + NO₂ reaction rate in CB4 (M4) is about 10% faster than in CB2002. A sensitivity test was conducted in which the CB2002 OH + NO₂ reaction rate (Troe, 2001) was replaced by the CB4 (M4) reaction rate from JPL (1994).

Increasing the OH + NO₂ reaction rate in CB2002 by ~10% had relatively little impact on the daily maximum 8-hour ozone levels compared to the differences between CB2002 and CB4 (M4). Comparisons are shown in Figure 4-6 for June 22 and June 24, 2001. The area with peak 8-hour ozone above 65 ppb is almost identical in the two cases. The peak 8-hour ozone values were decreased slightly (2 to 3 ppb) by increasing the OH + NO₂ reaction rate. Conclusions from this sensitivity test are as follows:

- Changing the OH + NO₂ reaction rate in CB2002 to be the same as CB4 (M4) widened rather than narrowed the ozone differences between CB2002 and CB4 (M4).
- Updating the OH + NO₂ reaction rate in CB2002 is not the main reason for different ozone predictions between CB2002 and CB4 (M4).
- Other rate constant differences between the two mechanisms were described in Section 3. The rate constant differences between CB2002 and CB4 are sufficiently great in number that a systematic sensitivity analysis would be needed to determine how mechanism changes lead to ozone differences.

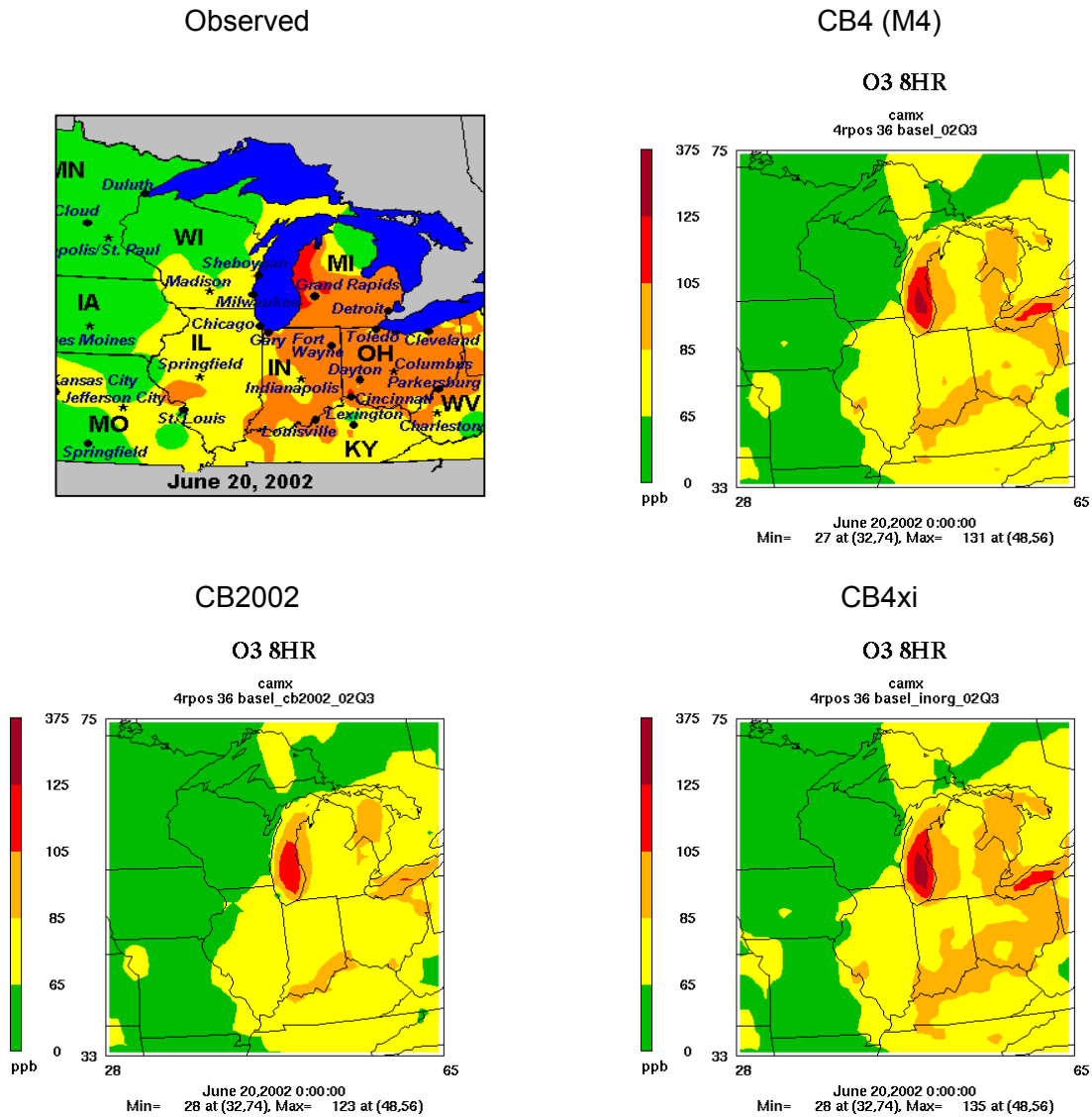


Figure 4-1. Comparison of daily maximum 8-hour ozone with different versions of the Carbon Bond mechanism for June 20, 2002.

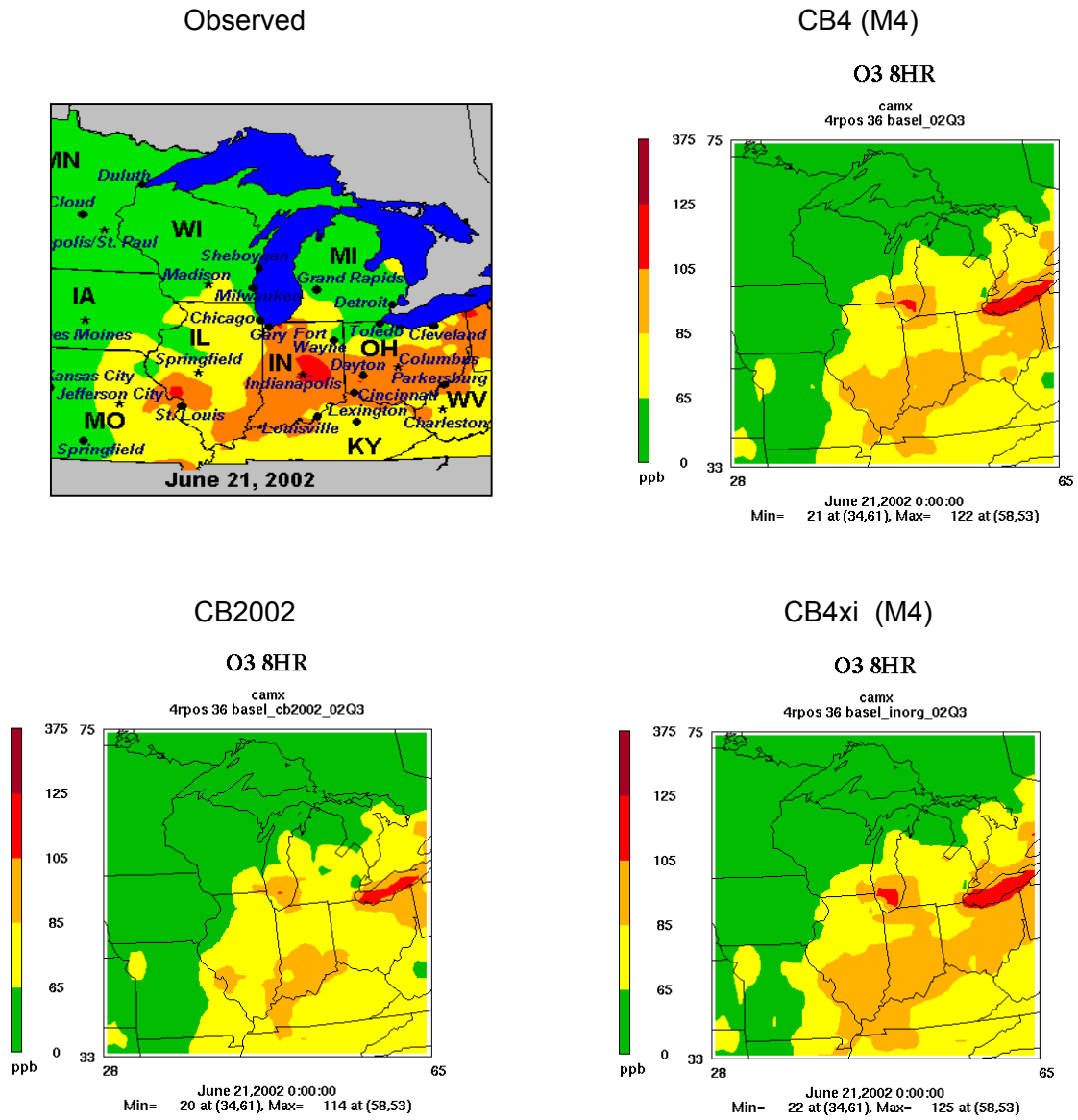


Figure 4-2. Comparison of daily maximum 8-hour ozone with different versions of the Carbon Bond mechanism for June 21, 2002.

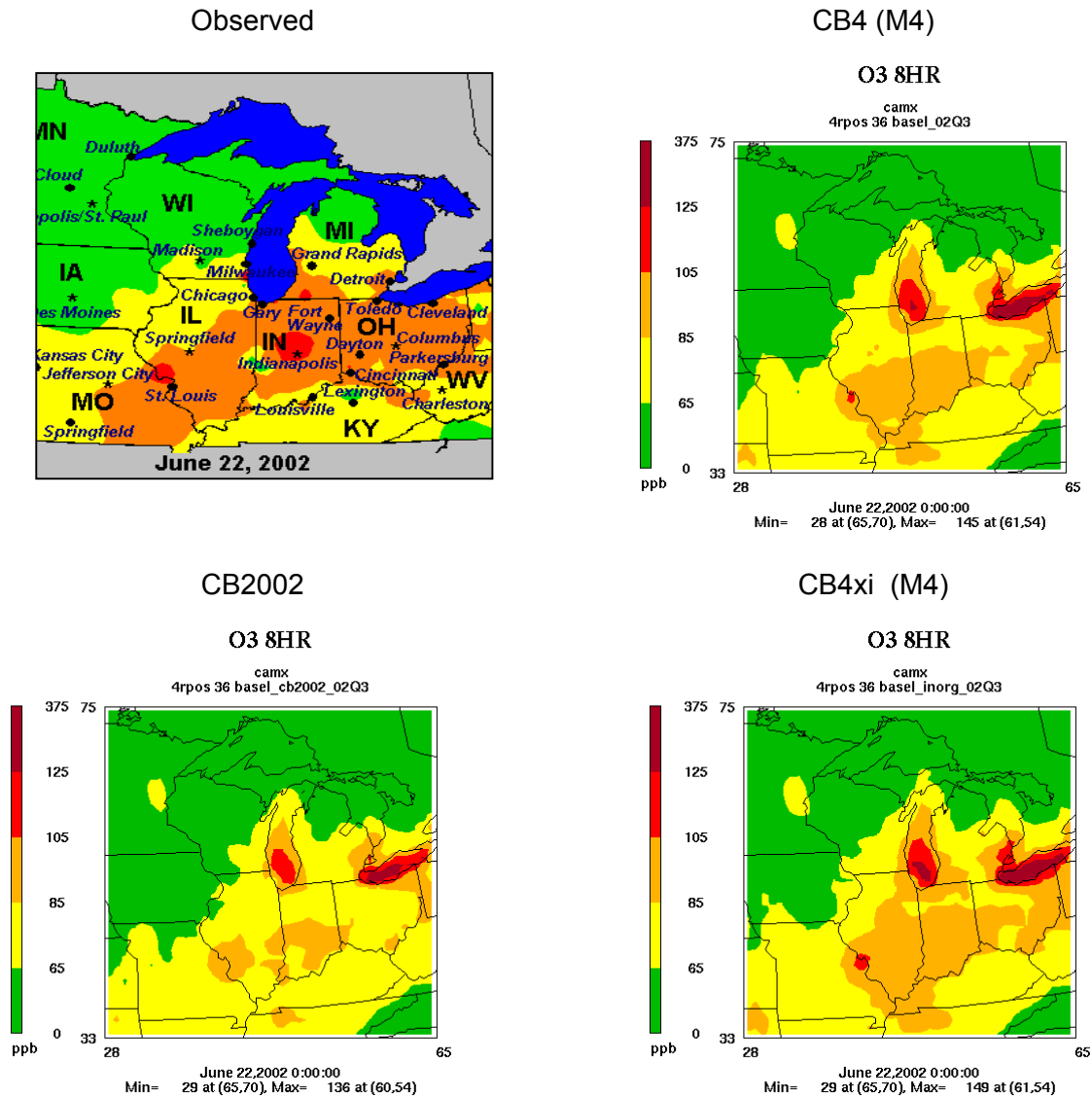


Figure 4-3. Comparison of daily maximum 8-hour ozone with different versions of the Carbon Bond mechanism for June 22, 2002.

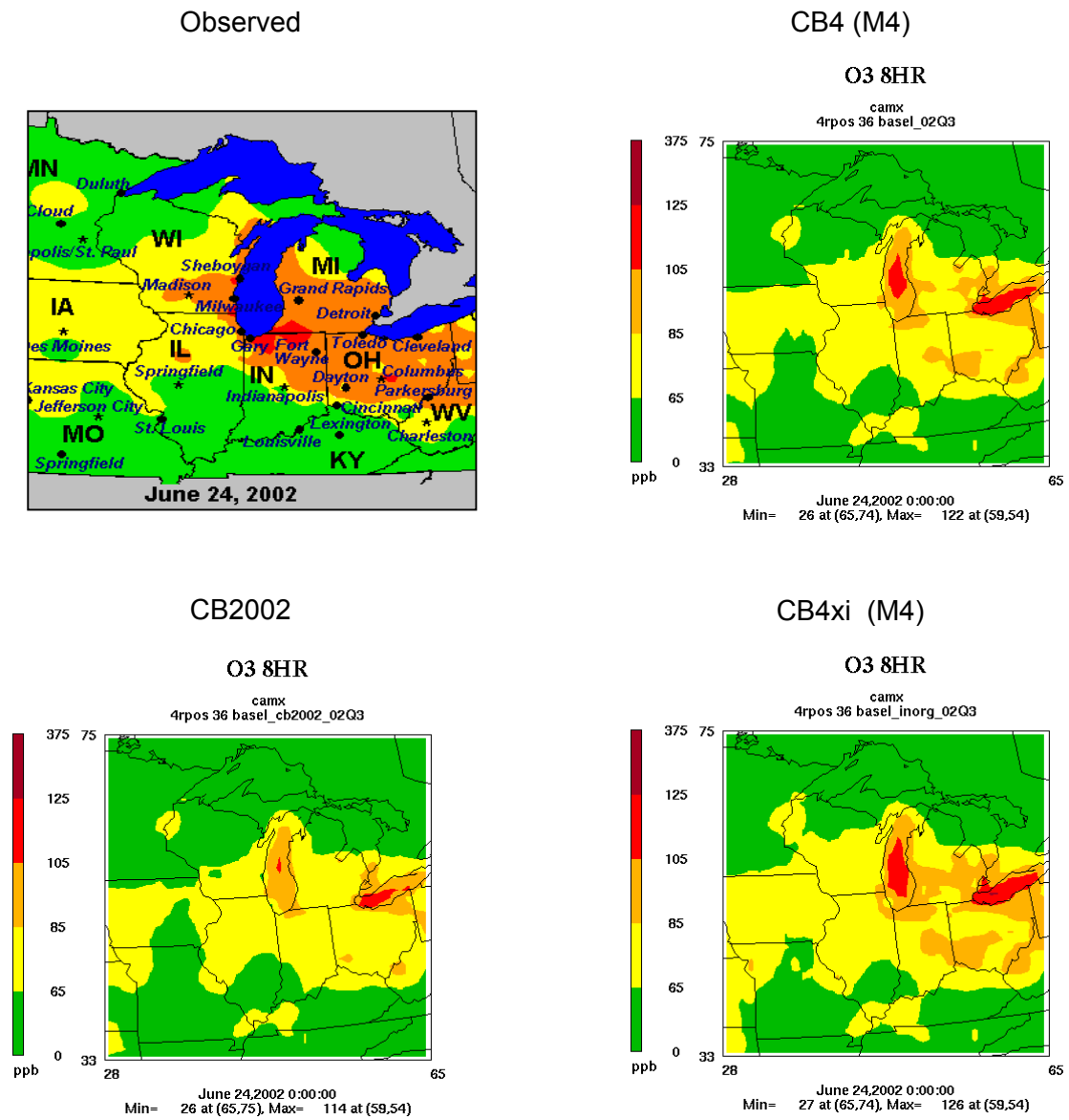


Figure 4-5. Comparison of daily maximum 8-hour ozone with different versions of the Carbon Bond mechanism for June 24, 2002.

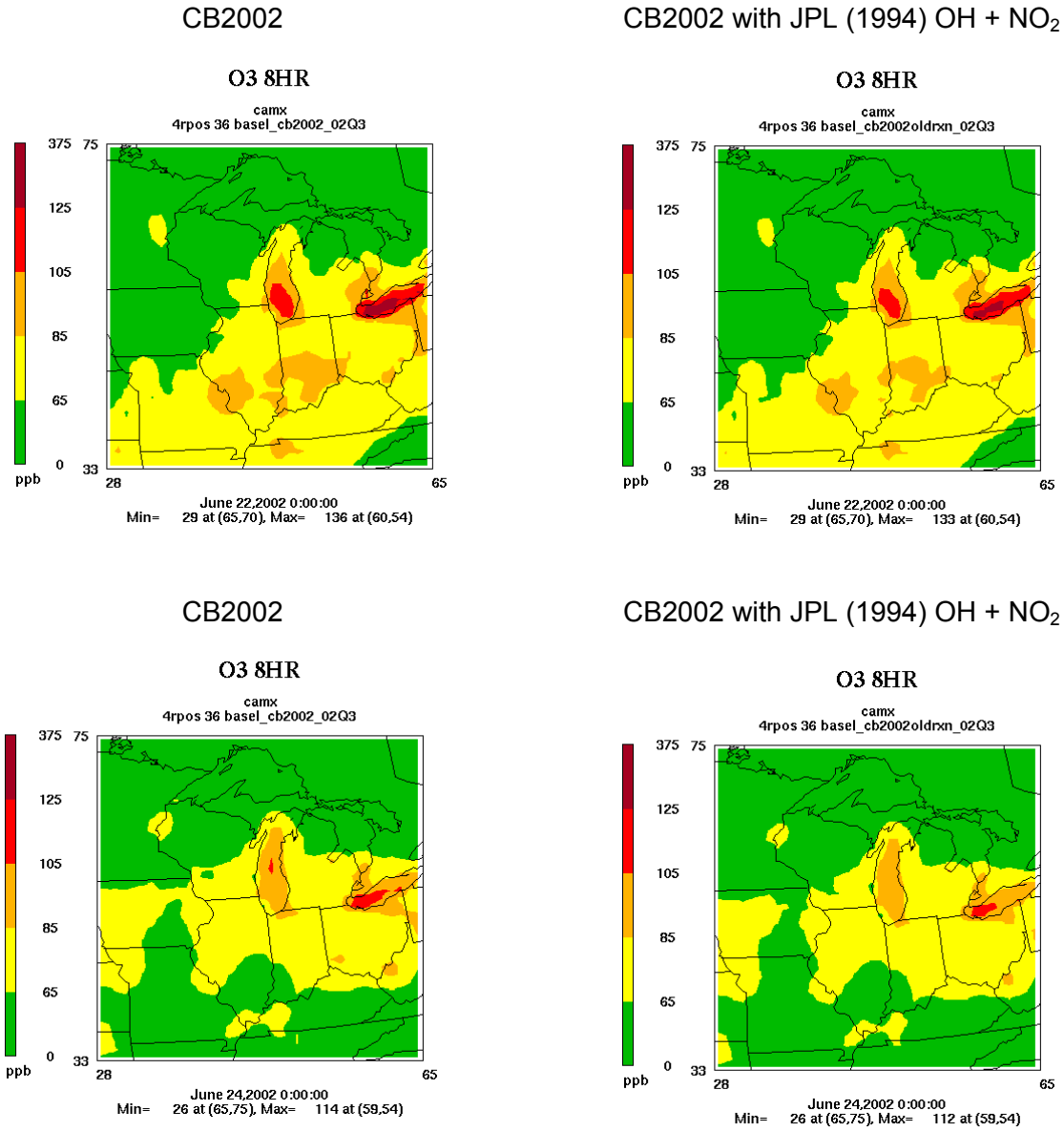


Figure 4-6. Sensitivity of daily maximum 8-hour ozone to OH + NO₂ rate constant in CB2002.

COMPARISON FOR PM SPECIES

PM comparisons were performed between CB4 (M4) and CB4xi for the LADCO/MRPO July 2002 and February 2002 modeling periods with Base I emission inventories. CB2002 was not included in these comparisons because it was not implemented for PM modeling. The 24-hr average model predictions for PM species at all monitoring sites are compared in Figures 4-7 (July, 2002) and 4-8 (February, 2002).

Adding extra inorganic reactions in CB4xi resulted in small difference in 24-hr average predictions for all PM species. The changes are summarized below for each PM species:

- The extra inorganic reactions resulted in slightly higher PM nitrate and sulfate in summer. This is consistent with slightly higher oxidant levels slightly accelerating the oxidation of NO_x and SO₂.
- Adding the NO_x recycling reactions that convert a small amount of nitric acid back to NO_x did not reduce PM nitrate. This is because only a small amount of nitric acid is recycled and the change in oxidant levels is the dominant effect.
- PM ammonium increased slightly along with the PM sulfate and nitrate increases
- Changes in PM sulfate/nitrate/ammonium were smaller in winter than summer because oxidant production is much less active in winter. In winter, oxidant levels are determined mainly by tropospheric background (i.e., CAMx boundary conditions) rather than photochemistry within CAMx.
- There were no changes for soil and EC because they are inert primary PM species.
- There were small decreases in OC that are attributed to differences in secondary organic aerosol (SOA). The chemical reaction updates did not alter any reactions that produce SOA so differences must be due to differences in the oxidants that trigger SOA formation, possibly small spatial and/or temporal shifts.

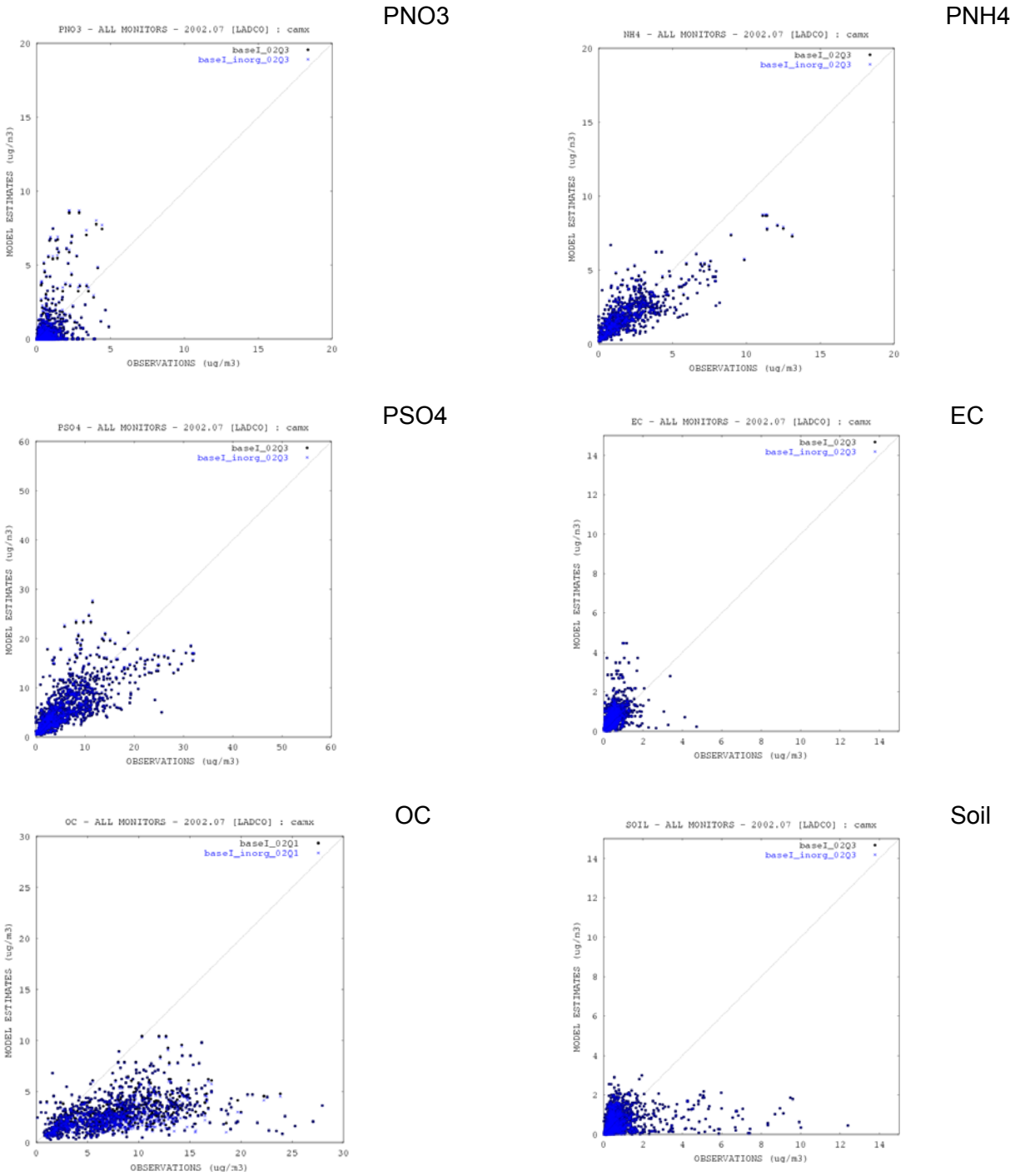


Figure 4-7. Comparison of model performance for PM species with CB4 (M4) (black circle) and CB4xi (blue cross) for July, 2002.

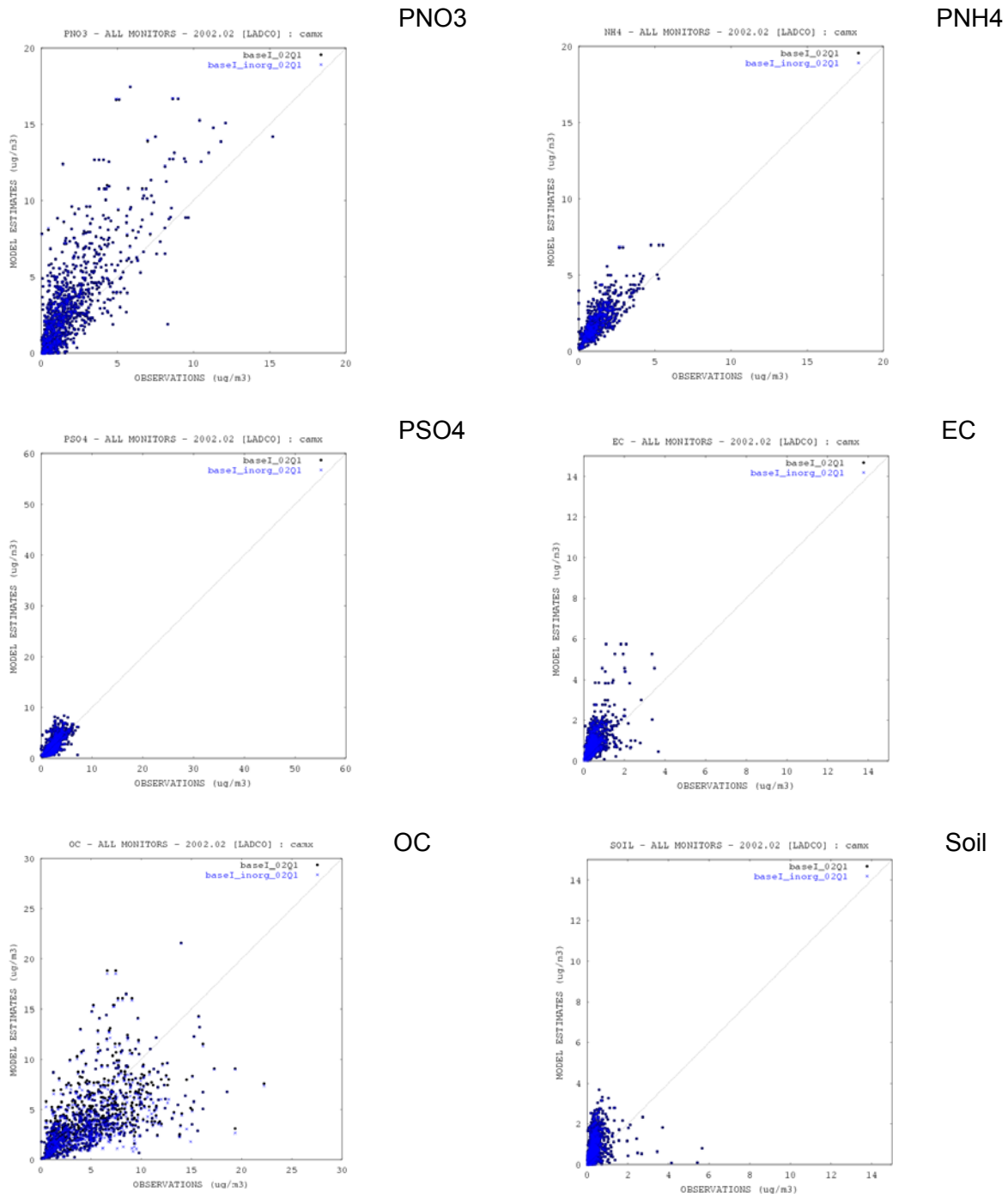


Figure 4-8. Comparison of model performance for PM species with CB4 (M4) (black circle) and CB4xi (blue cross) for February, 2002.

5. CONCLUSIONS

Two new chemical mechanisms were implemented in CAMx and tested for this study:

- The CB2002 mechanism (Jeffries, Voicu, and Sexton, 2002), discussed in Chapter 2.
- The CAMx mechanism 4 with 17 extra inorganic reactions (CB4xi), discussed in Chapter 3.

The CB4xi mechanism improved model performance for ozone and did not significantly change model performance for PM species. The new inorganic reactions included in CB4xi improve the science in the mechanism without creating inconsistency with the evaluation of the CB4 against smog chamber data. These extra inorganic reactions are appropriate for inclusion in any condensed chemical mechanism being used for annual PAM and/or ozone modeling. The CB4xi is recommended for use in all future LADCO/MRPO modeling for both ozone and PM/visibility issues.

CHANGES IN CB4xi

Table 5-1. Reactions added in the CB4xi mechanism and whether they are included in other condensed chemical mechanisms.

| Number | Reaction | Included in CB2002 | Included in CBM-Z | Included in mCB4 | Included in SAPRC99 |
|--------|---|--------------------|-------------------|------------------|---------------------|
| 101 | $O1D + H2 = OH + HO2$ | | | | |
| 102 | $OH + H2 = HO2$ | | | Yes | Yes |
| 103 | $OH + O = HO2$ | | | | |
| 104 | $OH + OH = O$ | | | | |
| 105 | $OH + OH = H2O2$ | | | | |
| 106 | $HO2 + O = OH$ | | | | |
| 107 | $H2O2 + O = OH + HO2$ | | | | |
| 108 | $NO3 + O = NO2$ | | | | |
| 109 | $NO3 + OH = HO2 + NO2$ | Yes | | Yes | Yes |
| 110 | $NO3 + HO2 = HNO3$ | Yes | Yes | Yes | Yes |
| 111 | $NO3 + O3 = NO2$ | | | | |
| 112 | $NO3 + NO3 = 2 NO2$ | Yes | Yes | | Yes |
| 113 | $PAN = C2O3 + NO2$ | | | | |
| 114 | $HNO3 = OH + NO2$ | | Yes | | Yes |
| 115 | $N2O5 = NO2 + NO3$ | | | | |
| 116 | $NTR = NO2 + XO2$ | | Yes | | Yes |
| 117 | $PNA = 0.61 HO2 + 0.61 NO + 0.39 OH + 0.39 NO2$ | | Yes | | Yes |

CB2002 from Jeffries, Voicu and Sexton (2002)

CMB-Z from Zaveri and Peters (1999)

mCB4 from EPA (2004)

SAPRC99 from Carter (2000)

This project reviewed the inorganic reaction set in the CB4 and other mechanisms to identify reactions that should be added for regional/annual modeling conditions. Seventeen reactions were added to CAMx mechanism 4 (M4) as shown in Table 5-1. Since these reactions mostly involve the inorganic reaction set this modification is referred to as extended inorganic chemistry (CB4xi). CAMx M4 was selected as the basis for modification because it is most appropriate for regional PM, mercury and toxics modeling as well as ozone. The extended inorganic reactions are summarized as follows:

- Reactions of molecular hydrogen (101 and 102). Hydrogen is somewhat important to odd-hydrogen (OH and HO₂) for very dry conditions in the upper troposphere. Including hydrogen allows the air quality impacts of hydrogen as an alternative fuel to be evaluated. Currently, hydrogen is included in CAMx with a constant atmospheric concentration of 0.6 ppm (Novelli et al, 1999).
- Odd-oxygen reactions (103 to 107) that may be important for pristine conditions such as the upper troposphere. Including these reactions provides a more complete description of hydroxyl radical (OH) chemistry in the upper troposphere to improve modeling for persistent air toxics and mercury.
- Additional NO₃ radical reactions (108 to 112) to improve nighttime chemistry. NO₃ radical is the main driver for atmospheric chemistry at night and including additional NO₃ removal reactions improves the calculation of nighttime destruction rates for several types of reactive hydrocarbons (e.g., aldehydes, olefins) and for NO_x (via NO₃ and N₂O₅ reactions).
- NO_x recycling reactions (113 to 117) to improve the representation of the fate of NO_x over multi-day timescales. These are all photolysis reactions that occur quite slowly in the troposphere. Reactions 113, 115 and 117 are only important for very cold conditions such as the upper troposphere where corresponding thermal decomposition reactions are slow. Reactions 114 and 116, photolysis of nitric acid and organic nitrates, are important to regional ozone and oxidant chemistry in the lower troposphere (Zaveri and Peters, 1999). These “NO_x recycling reactions” slowly recycle nitrogen from an inactive form (NO_z) to an active form (NO_x).

CHANGES IN CB2002

The CB2002 mechanism was compared to the OTAG version of the CB4 (i.e., CAMx M3) to document the changes. The main differences are:

- CB2002 updated the rate constants for many inorganic reactions. This was a major focus of the CB2002 work (Jeffries, Voicu, and Sexton, 2002).
 - The OH + NO₂ reaction rate is updated.
- New inorganic reactions were included for
 - NO₃ with OH, HO₂ and NO₃
 - O₃ + O(³P)
- New HONO photolysis reaction to NO₂ + H

- Different rate expressions for the $N_2O_5 + \text{water}$
 - $N_2O_5 + H_2O$ reaction rate the same as CAMx mechanism 4
 - $N_2O_5 + H_2O + H_2O$ reaction included (Wahner et al., 1998).
- Lower rate constants for radical-radical termination reactions (i.e., XO_2 and HO_2)
- New reaction rates for olefins: ETH, OLE and ISOP.
- New reaction products for ETH and OLE.

The number of differences shows that CB2002 is a substantial update to the carbon bond mechanism. A sensitivity test showed that ozone differences between CB2002 and CB4 are attributable to more than just updating the $OH + NO_2$ reaction rate.

RATE CONSTANT FOR $OH + NO_2$

One of the motivations for developing CB2002 was that the $OH + NO_2$ reaction rate constant was revised in the late 1990s. The $OH + NO_2$ reaction is a major sink for both radicals and NO_x under urban conditions and is so important that a chemical mechanism such as CB4 must be recalibrated against smog chamber data if this rate constant is changed.

The $OH + NO_2$ reaction rates are compared in Table 2-7 for:

- CB2002 (Jeffries, Voicu and Sexton, 2002).
- CB4 mechanism 3 (Gery et al., 1989).
- CB4 mechanism 4 (JPL, 1994).
- SAPRC99 (Carter, 2000).

CB2002 has the most current values (Troe, 2001). Comparing the values for 298 K and 1013 mbar is most relevant to smog chamber data and urban ozone formation. For this condition, the $OH + NO_2$ reaction rate is about 15% low in SAPRC99 and 7% high in CB4 (both M3 and M4). For the low-pressure condition (491 mbar) CB4 (M3) is high because Gery et al. (1989) did not explicitly account for pressure dependence. The pressure dependence in CB4 (M4) is much improved by using the JPL (1994) expression. The SAPRC 99 is $OH + NO_2$ reaction rate 18% too low for the low-pressure condition.

Table 5-2. Comparison of $OH + NO_2$ reaction rate constants in CB2002, CB4 and SAPRC99.

| Temperature (K) | 298 | 273 | 298 | Difference from CB2002 |
|-----------------|----------|----------|----------|---------------------------|
| Pressure (mbar) | 1013 | 1013 | 491 | |
| CB2002 | 1.57E+04 | 1.96E+04 | 5.19E+03 | |
| CB4 (M3) | 1.68E+04 | 2.29E+04 | 8.15E+03 | +7% to +36% |
| CB4 (M4) | 1.70E+04 | 2.22E+04 | 5.94E+03 | +7% to +13% |
| SAPRC99 | 1.33E+04 | 1.80E+04 | 4.77E+03 | -9% to -18% |

Notes:

- CB2002 used as the reference because it has currently accepted values from Troe (2001) that are consistent with JPL (2003) and IUPAC (2004).
- CB4 (M3) values from Gery et al., (1999).
- CB4 (M4) values from JPL (1994).
- SAPRC99 values from Carter (2000)

MODELING RESULTS FOR CB2002 AND CB4xi

The impacts of the CB2002 and CB4xi mechanism updates were evaluated using three LADCO/MRPO modeling databases. The new mechanisms were compared to CAMx mechanism 4 (M4). Kirk Baker of LADCO performed the model runs and provided results for analysis and inclusion in this report.

- CB2002 predicted lower regional ozone than CB4 (M4) on all days.
- Areas of peak 8-hour ozone above 85 ppb were much reduced using CB2002 and the peak 8-hr ozone levels were reduced by 8 ppb to 9 ppb.
- The lower ozone with CB2002 degraded model performance.

As mentioned above, a sensitivity test showed that the different ozone predictions for CB2002 were not explained simply by a change in the OH + NO₂ reaction rate.

- Compared to CB4 (M4), the CB4xi predicted higher ozone regionally on all days.
- Areas of peak 8-hour ozone above 85 ppb were much greater using CB4xi and the peak 8-hr ozone levels were increased by 3 ppb to 4 ppb.
- The higher ozone with CB4xi improved model performance.

The higher regional ozone with CB4xi than CB4 is due to the NO_x recycling reactions included in CB4xi. These reactions are the photolysis of organic nitrates and nitric acid, discussed in Section 3, that are included in other mechanisms such as SAPRC99 (Carter, 2000) and CBM-Z (Zaveri and Peters, 1999). The effect of these NO_x recycling reactions partially explains why SAPRC99 tends to predict higher regional ozone than CB4. Zaveri and Peters (1999) also concluded that including photolysis of organic nitrates would increase regional ozone predictions.

Including 17 extra inorganic reactions in CB4xi resulted in small difference in 24-hr average predictions for all PM species. The changes are summarized below for each PM species:

- The extra inorganic reactions resulted in slightly higher PM nitrate and sulfate in summer. This is consistent with slightly higher oxidant levels slightly accelerating the oxidation of NO_x and SO₂.
- Adding the NO_x recycling reactions that convert a small amount of nitric acid back to NO_x did not reduce PM nitrate. This is because only a small amount of nitric acid is recycled and the change in oxidant levels is the dominant effect.
- PM ammonium increased slightly along with the PM sulfate and nitrate increases
- Changes in PM sulfate/nitrate/ammonium were smaller in winter than summer because oxidant production is much less active in winter. In winter, oxidant levels are determined mainly by tropospheric background (i.e., CAMx boundary conditions) rather than photochemistry within CAMx.
- There were no changes for soil and EC because they are inert primary PM species.
- There were small decreases in OC that are attributed to differences in secondary organic aerosol (SOA). The chemical reaction updates did not alter any reactions that produce SOA so differences must be due to differences in the oxidants that trigger SOA formation, possibly small spatial and/or temporal shifts.

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