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UPDATES TO THE CARBON BOND MECHANISM FOR VERSION 6 (CB6)

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1. INTRODUCTION

The Carbon Bond (CB) mechanism (Gery et al., 1989) describes tropospheric oxidant chemistry in a concise manner suitable for use in complex 3-dimensional atmospheric models. Existing versions (CB4 and CB05) are used in photochemical grid models for ozone and particulate matter (PM) such as CMAQ, CAMx and WRF-Chem. This paper describes the development and evaluation of version 6 of the Carbon Bond mechanism (CB6).

The development of CB6 was performed for the Texas Commission on Environmental Quality (TCEQ) which is responsible for developing the Texas State Implementation Plan (SIP) for ozone. Ozone SIP development in Texas relies upon modeling using the Comprehensive Air Quality Model with Extensions (CAMx) photochemical model (ENVIRON, 2010) and the CB05 chemical mechanism (Yarwood et al., 2005). The chemical mechanism is a critical component in ozone SIP development because it forms the linkage between emissions of ozone precursors, namely Nitrogen Oxides (NOx) and Volatile Organic Compounds (VOC), and ozone concentrations in the photochemical model. Research in atmospheric chemistry continually provides new information that should be evaluated and potentially incorporated into chemical mechanisms to maintain their accuracy and thereby provide the best possible strategies for improving ozone air quality.

2. MECHANISM DESIGN

As tighter ozone standards are adopted, ozone modeling will be required to focus on lower ozone concentrations and longer time periods. Two aspects of the CB6 design address these needs: (1) several organic compounds that are long-lived and relatively abundant, namely propane, acetone, benzene and ethyne (acetylene), are added explicitly in CB6 so as to improve oxidant formation from these compounds as they are slowly oxidized. (2) Attention is given to the fate of organic nitrates and the extent to which their degradation produces NOx that may then actively participate in oxidant formation.

Gas-phase chemistry influences PM formation by producing aerosol precursors including sulfuric acid, nitric acid and semi-volatile organic compounds. Sulfur dioxide (can be oxidized to sulfuric acid by hydrogen peroxide and organic hydroperoxides. CB6 includes several updates to peroxy radical chemistry that will improve formation of peroxides and therefore sulfate aerosol. Updates to reactions of dinitrogen pentoxide with water vapor will affect nighttime formation of nitric acid although heterogeneous reactions on aerosol (and other) surfaces may dominate nitric acid formation at night.

Secondary organic aerosol (SOA) is very complex and uncertain and a wide variety of modeling approaches have been implemented for SOA. In general, formation of SOA precursors is excluded from CB6 and modelers can add SOA formation to the mechanism according to their preferred methodology (e.g., using the volatility basis set; Robinson et al., 2007). An exception is formation of alpha-dicarbonyl compounds (glyoxal and analogues) which can form SOA via aqueous-

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phase reactions (Carlton et al., 2007). Glyoxal and glycolaldehyde are added in CB6 (in addition to methylglyoxal) to support modeling of aqueous-phase SOA formation. Precursors to alpha-dicarbonyls included in CB6 are aromatics, alkenes and ethyne.

The main constraint in developing CB6 was maintaining backwards compatibility with previous CB mechanisms so that existing modeling databases can be used with CB6. CB6 can be used with emissions developed for the CB05 (and even CB4) mechanisms although doing so forgoes the benefit of some CB6 mechanism improvements.

In summary, the main updates from CB05 to CB6 are:

(1) Incorporating new scientific information released since the previous mechanism update in 2005 (CB05) especially as evaluated by IUPAC (Atkinson et al., 2010) and NASA (Sander et al., 2006) review panels.

(2) Reviewing and updating reactions for alkanes, alkenes and aromatics with the most changes resulting for isoprene and aromatics.

(3) Adding explicitly several long-lived VOCs that form ozone at regional scales, specifically propane, benzene, acetone and other ketones.

(4) Adding explicitly acetylene and benzene because they are precursors to SOA formation and useful as anthropogenic emission tracers.

(5) Adding explicitly VOC degradation products that can produce SOA via aqueous-phase reactions, specifically glyoxal, glycolaldehyde and methylglyoxal.

Table 1 compares the size of the CB6 and CB05 mechanisms. The number of reactions is about 40% greater and the number of species about 50% greater in CB6 than CB05.

Table 1. Summary comparison of the size of the CB6 and CB05 chemical mechanisms.

	CB6	CB05
Gas-phase reactions	218	156
Photolysis reactions	28	23
Gas-phase species	77	51
Emissions species for ozone	21	16

There are 5 new VOC model species in CB6 that should be considered in emissions processing:

- PRPA representing propane (represented as 1.5 PAR + 1.5 NR in CB05)
- BENZ representing benzene (represented as 1 PAR + 5 NR in CB05)
- ETHY representing ethyne (represented as ALDX in CB05)
- ACET representing acetone (represented as 3 PAR in CB05)
- KET representing ketone groups (represented as PAR in CB05)

The usage of the KET species is illustrated by methylethylketone ($CH_3C(O)CH_2CH_3$) which is represented as 3 PAR + KET in CB6 and 4 PAR in CB05.

3. MECHANISM EVALUATION

The CB6 mechanism was evaluated by simulating chamber experiments in which mixtures of VOC and NOx were irradiated to form ozone. A database of experiments compiled by the University of California at Riverside (UCR) was the basis for the evaluation. About 2000 experiments are available in the UCR chamber database (Carter, 2010). Chamber data used for this study are from the April 23, 2010 version of the UCR database. Data were measured using 8 different environmental chambers: EC, ETC, OTC (outdoor), DTC, XTC, CTC and EPA (7 chambers at UCR) and the TVA chamber at the Tennessee Valley Authority.

Indoor chamber experiments are sometimes performed using fluorescent lamps that emit primarily ultra-violet (UV) radiation, namely blacklights. In evaluating CB6, non-blacklight chamber experiments were preferred in order to utilize light conditions most relevant to the atmosphere and thereby minimize the consequences of uncertain photolysis data. However, in some cases only backlight simulations were available and therefore had to be utilized to evaluate MEOH (methanol), ETOH (ethanol), ETHA (ethane) and PRPA (propane). The uncertainty introduced by blacklights is suggested by the results for ethene (ETH). The ETH chemistry of CB6 showed significantly different performance in simulating Max(O_3) against non-blacklight experiments and blacklight experiments: average model bias for 11 non-blacklight experiments and 22 blacklight experiments were -13% (± 17%) and +28% (± 17%), respectively.

Other selection criteria were also used to determine which experiments to use in the CB6 evaluation. In most cases, experiments were not used if the initial NOx was greater than 300 ppb or the final O_3 was less than the initial NOx. After applying these criteria to UCR and TVA experiments, 194 experiments of “single test compound – NOx” or “special mixture – NOx” and 145 experiments of “surrogate mixture – NOx” were selected (339 in total).

Statistical performance metrics and graphical comparisons were used for evaluating CB6. The statistical metrics were the following: The maximum ozone concentration (Max(O_3)), the Maximum Δ(O_3-NO), and the NOx crossover time (i.e., the time when the NO_2 concentration becomes equal to the NO concentration). Means and standard deviations of these metrics were used to characterize performance over multiple experiments. The performance of CB6 in simulating 339 chamber experiments is summarized graphically in Figure 1 for Max(O_3) and the NOx crossover time.

The performance of CB6 and CB05 in simulating chamber studies was comparable for alkanes, alkenes, alcohols and aldehydes with both CB6 and CB05 performing well and exhibiting 20% or less bias for maximum ozone. For species that were explicitly added in CB6 (ethyne, benzene and ketones) CB6 performed much better than CB05. For aromatics, CB6 improved upon CB05 by reducing under prediction bias in maximum ozone to about 10% for benzene, toluene and xylene. For isoprene, both CB05 and CB6 show little bias for maximum ozone (less than 5%) but CB6 tended to form ozone too slowly.

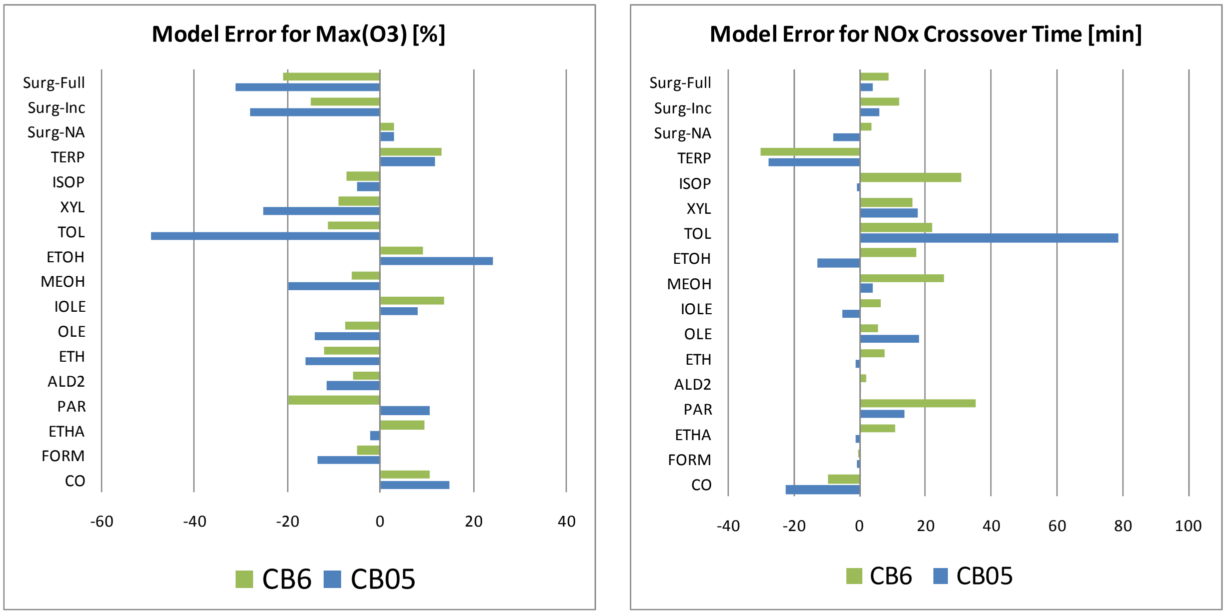

Figure 1. Mechanism performance in simulating Max(O3) and NOx crossover time for 194 single test compound (or special VOC mixture) - NOx experiments and 145 surrogate VOC mixture - NOx experiments.

4. SUMMARY & CONCLUSIONS

A new version of the CB chemical mechanism has been developed ,CB6, as an update to the previous version (CB05; Yarwood et al., 2005). CB6 is backward compatible with CB05 and CB4 and can be used with emission inventories (or other model inputs such as boundary conditions) that were prepared for CB05 or CB4. However, updating model inputs to CB6 is preferable to take full advantage of mechanism improvements.

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5. REFERENCES

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