

DRAFT

MEMORANDUM

Date: 29 March 1994

To: Marcia Dodge, U.S. EPA
Edwin Meyer, U.S. EPA
Ken Schere, U.S. EPA
Gary Whitten, SAI
James Killus
Greg Yarwood, SAI

From: Mike Gery

Subject: Summary of Revisions and Versions of the CBM-4 Mechanism

AS IS THE CASE WITH ANY CHEMICAL KINETICS MECHANISM THAT IS USED FOR A NUMBER OF YEARS, various weaknesses and improvements are identified over time. Inevitably, if the use is long enough, it is necessary to update the content of the mechanism. Conversely, because the mechanism is widely distributed and used in regulatory models that must be consistent between all users, the number of updates must necessarily be limited.

Recently, I have had requests for information regarding what "version" of CBM-4 to use for various applications. It seems that, while the mechanism's developers have never formally established version numbers, there are, nevertheless, a number of different CBM-4 version numbers related to mechanism applications (e.g., SAI's UAM models and UNC's research modifications).

In the interest of consistency, I would like to summarize and reach consensus on the issue of basic CBM-4 modifications.....

1. The Original CBM-4 Mechanism - Version 4.0

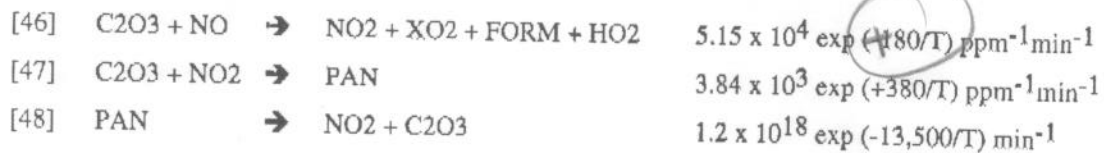
The CBM-4 mechanism was first published in 1988 by the U.S. EPA in the report "Development and Testing of the CBM-IV for Urban and Regional Modeling (EPA/600/3-88-012). The same version of the mechanism was also reported on in the Journal of Geophysical Research in 1989 (Gery, M.W., G.Z. Whitten, J.P. Killus and M.C. Dodge, "A Photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling," Jnl. Geophys. Res., 94:12925-12956 (1989).

A table from the U.S. EPA report, summarizing the CBM-4.0 reactions and rates, is included as Attachment A.

2. The 1991 Update for PAN Chemistry and Radical Termination Reactions - Version 4.1

New measurements for the acetyl peroxy radical with NO and NO₂ were made about 1990 by both SAPRC in California and the LACTOZ project in Europe. In addition, Dr. Marcia Dodge pointed out that the lack of XO₂ operator termination by HO₂ radical could lead to overprediction of hydrogen peroxide concentrations and other problems. Therefore, at the end of 1990, a number of revisions were suggested for the original mechanism. These were (referring to the reaction numbers in Attachment A):

A. Modify the rate constants listed for Reactions 46 through 48 to the following:



B. Add the following reaction:



These reactions were included in the CBM-4.0 and used in a limited set of simulations to assess their impact on calculations. Subsequently, the changes were included in the regulatory versions of EPA's Regional Oxidant Model (ROM) and the Urban Airshed Model (UAM).

Updating CBM-4.0 with these four reactions results in CBM-4.1.

Take these
as $\frac{E_a}{R}$
literally

3. Recent Updates Reactions - Version 4.2

Dr. Greg Yarwood of SAI has recently suggested that the radical operator XO₂N should have originally been given termination reactions similar to its [non-nitrate-forming] counterpart, XO₂. To achieve this, the suggested changes to the CBM-4.1 were:

A. Modify the rate constant listed for Reactions 81 to the following:



B. Add the following reactions:



These reactions are expected to slightly increase the lifetime of NO_x under transport conditions of low NO_x levels. Such conditions are rarely achieved in smog chamber experiments; and therefore, few data sets exist for verifying the changes. Nevertheless, they are felt to be consistent with known kinetics and internally consistent with the formulation of the mechanism.

Updating CBM-4.1 with these four reactions results in CBM-4.2.

Note, however, that since these changes are less significant than those listed earlier and because the U.S. EPA is currently in the midst of regulatory calculations using the CBM-4.1, these changes have not been applied in the U.S. EPA's regulatory models ROM and UAM. The regulatory versions of UAM and ROM utilize CBM-4.1.

4. Other Reactions that may be included in the CBM-4 versions.

From time to time, various research groups have added various reactions or reaction sets to the basic CBM-4 reactions. However, outside of these two basic modifications to the original CBM-4.0, these additional reaction sets should be considered application specific. While it is often useful to enhance the mechanism for specific applications, the user should be aware that these modified mechanisms are not evaluated to the degree that the original CBM-4.0 was, and may carry unintended error or uncertainty.

5. Aggregation of Ambient and Emitted Compounds into Mechanism Species

NED:

I would like to direct the reader to some location where the CBM-4 speciation profiles are kept and updates. Does OAQPS have some sort of data file like this. Perhaps in the UAM preparation database.

Could you provide a reference?

MIKE

4-8-94

TO: Mike Gery
FROM: Ken Schere

After talking with you I was sure that we had referred to the current CB-IV in ROM as CB-4.2 (in fact I have annotated mechanism listings from you with that designation on it). This is my best attempt at reconstructing history:

- CB4.0 - Originally published in EPA report "Development of CBM-X Mechanisms for Urban and Regional AQSMs" by Whitten and Gery (1986), EPA/600/3-86/012 (see enclosed mechanism listing ... 70 reactions, 28 species)
- CB4.1 - Originally published in EPA/600/3-88/012 and in JGR (1989) as you have indicated in your fax (except that you have called this version CB4.0).
- CB4.2 - same as CB4.1, except with the rate constants to PAN chemistry changed, and the addition of the XO_2+HO_2 reaction
- CB4.3 - Then I would call the suggestions for recent updates (XO_2N reactions) as CB4.3.

It all depends on what you want to use as a starting point.

For your info, I have enclosed copies of the note from Kuruvilla John (NY-DEC) on his questions about CB-IV as implemented in UAM-IV, and Marcia Dodge's response to his questions. Apparently, the official version of the code on the EPA bulletin board has the rate constants for reactions 29-31 (PNA chemistry) set to zero.