



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
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MEMORANDUM

SUBJECT: Comments on Modifications to the CB4

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TO: Ken Schere

I have read the comments made by the NY Department of Environmental Conservation regarding SAI's proposed changes to the CB4. My thoughts on their comments are as follows:

- (1) It doesn't matter that the rate constant for Reaction 81 has been increased by a factor of 12. It's a dummy reaction anyway and it seems more logical that its rate constant should be identical to the rate constant for the other similar dummy reaction (Reaction 79). Increasing k_{81} won't have much (if any) effect on predictions because as long as there is any NO in the system, XO₂N will react with it rather than with itself or with HO₂ or XO₂ radicals.
- (2) There is no point in adding a reaction between NTR and OH. For one thing, it would mean adding a species to the mechanism as NTR presently is not included in the CB4. And secondly, nitrates react with OH so slowly that inclusion of an NTR + OH reaction would have a negligible effect on predictions. For example, the rate constant for reaction of methyl nitrate with OH is $3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$; k_{OH} for ethane, which is considered to be non-reactive, is only slightly lower than this ($2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$). The rate constant for the n-propyl nitrate + OH reaction is only $7.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$, making it considerably less reactive than the propane + OH reaction ($k_{\text{OH}} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$) and propane reacts exceedingly slowly.
- (3) PNA chemistry is of little importance except at high altitudes and/or low temperatures. It might be safe to eliminate Reactions 29-31 from the

mechanism, but if this is what SAI has done (and it's news to me), they should justify it. What do predictions look like in the aloft layers when these three reactions are deleted?

- (4) The OH + HO₂ reaction probably should be included in future mechanism development work. I am opposed, however, to adding it to the CB4 unless the CB4 is re-evaluated against smog chamber data to make sure that the inclusion of this reaction does not alter predictions to the extent that the CB4 no longer is able to reproduce the chamber data.
- (5) It's hard to believe that the surface resistances for H₂O₂ and HNO₃ could vary by a factor of 10²⁰. This looks like a coding error to me.