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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impacts of electronically photo-excited NO_2 on air pollution control strategies in the South Coast Air Basin of California" *by* J. J. Ensberg et al.

Anonymous Referee #3

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GENERAL COMMENTS: This paper examines the extent to which a new pathway for formation of HONO and OH involving photo-excited NO2 may be important for ozone and particulate matter (PM) control strategies in southern California. The authors incorporate the new pathway into a photochemical air quality model and simulate the impacts on ozone and PM for a two day episode. The topic addressed by this paper is an important one, since there is currently much uncertainty regarding the rate of this process and its potential importance for control strategies has not been fully characterized. The authors consider the range of reaction rates reported by two conflicting papers that examined these reactions. However, inadequate and inaccurate photochemical modeling and a questionable method for incorporating the new mechanism

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undermine the ability of this paper to provide reliable or meaningful results. The authors are encouraged to resubmit this work with a more robust modeling episode and more careful incorporation of the new reactions.

SPECIFIC COMMENTS: The photochemical modeling applied here is inadequate for addressing the questions at hand. Among the most serious flaws in the modeling approach: (1) Only 2 days are simulated, which is inadequate to fully characterize summertime ozone formation and wholly unsuited to characterizing nitrate formation that occurs year-round, (2) The underlying chemical mechanism is not described and may be outdated given the age of the model, (3) An unconventional and likely inadequate approach is applied to initialize the model, using the episode days themselves rather than previous spin-up days for initialization, (4) A very old (1987) episode is considered, which is unrepresentative of current South Coast conditions as emission and pollutant levels have fallen dramatically. The first three flaws are in part reflected in the unacceptably high levels of error for ozone reported in Table 2, which far exceed error ranges typically allowed in regulatory modeling; model performance for PM is not reported. The outdated episode likely leads to severe overestimates of the importance of photo-excited NO2 to current or future South Coast control strategies, since the results (Figure 3) show that impacts of this pathway diminish as emissions are reduced.

The method for incorporating Reactions 6-8 in the model is suspect. Page 18997 refers to these reactions causing a “deactivation” of NO2 that would slow other reactions involving NO2. Similarly, p. 18992 reports decreases in NO because some of the NO2 is not in its ground state to enable photolysis. However, in fact, the rate constants for NO2 photolysis and (NO2+OH) were probably computed in laboratory studies that ignored the state of NO2, so it is dubious to assume that some of the NO2 is unavailable for those reactions. The way R6-R8 were incorporated could significantly bias the results.

It would be helpful for the authors to describe the extent to which the new mechanism causes any shifts between NOx-limited and VOC-limited chemistry, or the per-ton ef-

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fectiveness of NOx and VOC controls. It is difficult to deduce this information from Figure 3.

The authors present no data to assess the PM model performance, or the speciation of the PM. Without this information, it is impossible to know whether the percentage changes in total PM are meaningful, since presumably this mechanism would be more significant for some components (i.e., nitrate) than others. Discussion of PM results should be omitted unless the performance of the PM modeling can be demonstrated.

TECHNICAL COMMENTS: p. 18987: There are also other sources of OH, such as acetone.

p. 18987: Typo in sentence "For nm, . . ."

p. 18988, line 18: The term "negative" is ambiguous.

p. 18990: Was the 60 ppb threshold applied for bias, or only for error?

p. 18995, line 9: It is not true that the Los Angeles and Riverside results were functions "only of whether or not R6-R8 are included".

p. 18996, line 7: Authors claim "reactions between NOx and OH dominate." Do you mean reaction of NO2 and OH? And are you sure this is true, given that OH+CO is important to HOx cycling.

p. 18996, line 10: Reaction 9 always results in termination. The threshold ratio just indicates the relative importance of this reaction among HOx termination processes.

p. 18997: The discussion from lines 4-10 could be deleted.

p. 19000: Authors claim that this study is first to incorporate excited NO2 pathway in 3-D model. However, these results have already been reported by Wennberg and Dabdub (Science 2008, 319, 1624-1625).

p. 19000: Authors claim that "model predictions . . . improve" by including new mecha-

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nism. But given the similar and unacceptably high levels of error in all cases (Table 2), this conclusion is not justified. Similarly, the claim of “increased accuracy” (p. 18995, line 12) is not justified.

p. 19001: Is it R6 or R7 reaction rate that is uncertain, or both?

Table 1: How was Reaction rate R6 (J NO2-> NO2*) determined?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18985, 2009.