

## ***Interactive comment on “Mainz Isoprene Mechanism 2 (MIM2): an isoprene oxidation mechanism for regional and global atmospheric modelling” by D. Taraborrelli et al.***

### **Anonymous Referee #2**

Received and published: 2 September 2008

The authors present a chemical mechanism of atmospheric isoprene oxidation suitable for use in regional and global models, including under conditions where  $\text{RO}_2 + \text{HO}_2$  and/or  $\text{RO}_2 + \text{RO}_2$  reactions dominate over  $\text{RO}_2 + \text{NO}$ . It is stated that the mechanism is based closely on that in the University of Leeds Master Chemical Mechanism (MCM). The major focus in the mechanism "development" portion of the manuscript concerns the OH radical reaction because isoprene is emitted from vegetation mainly during daylight hours. Apart from the reaction listing in Table 3 of the Supplementary Material (which lists the lumped reactions) and Figure 1 (which provides a summary reaction flow diagram for the OH radical reaction, but with very little detail), there is no detailed discussion of the chemical pathways involved in the OH and  $\text{NO}_3$  radical

and O<sub>3</sub> reactions, nor of the reactions of the first- and later generation products. It appears that the MCM web-site needs to be used in conjunction with this manuscript in order to figure out the details of the reaction scheme; for example, HCOC5 (a 1,2-hydroxyketone) is shown in Figure 1 and is isomeric to the two 1,4-hydroxyaldehydes lumped as LHC4ACCHO - only by diligently searching Table 3 of the Supplementary Material or (easier) the MCM website is it clear that HCOC5 is formed from RO<sub>2</sub> and/or HO<sub>2</sub> reactions with ISOPDO<sub>2</sub>, and not from ISOPDO<sub>2</sub> + NO.

Theoretical calculations (see, for example, Stevens et al., 2000; Lei et al., 2001; Francisco-Marquez et al., 2003; Greenwald et al., 2007) and structure-activity relationships (Peeters et al., 1994) all agree that OH radical addition to isoprene (2-methyl-1,3-butadiene) occurs mainly at the 1- and 4-positions, with percent addition at the 1-, 2-, 3- and 4-positions from the above cited theoretical studies being in the ranges 56-72%, 1%, 2%, and 28-37%, respectively, and from the Peeters et al. (1994) SAR 60%, 5%, 5%, and 30%, respectively. The MCM (from the MCM website) has OH radical addition at the 1- and 4-positions of 65.5% and 34.5%, respectively, and neglects OH addition at the 2- and 3-positions; this is a slight simplification from Jenkin et al. (1998) who used an OH radical addition distribution of 59.4%, 4.7%, 4.7% and 31.3%, respectively. The MCM is therefore consistent with theoretical calculations, including the recent Greenwald et al. (2007) study which calculates OH addition to the 1-, 2- 3- and 4-positions of 67%, 2%, 2% and 29%, respectively. Inspection of Figure 1 shows that MIM2 does follow the MCM, with OH addition to only the 1- and 4-positions, and with the distribution of the four resulting hydroxyp peroxy radicals following that in the MCM. Clearly, the authors need to explicitly state the initial distribution of OH radical addition to the carbon atoms in isoprene and the assumptions made concerning the subsequent position of O<sub>2</sub> addition.

As expected, the mechanism predictions are generally quite similar to those of the MCM, and MIM2 appears to be an improvement over MIM.

## References

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Greenwald, E. E., North, W. W., Georgievskii, Y. and Klippenstein, S. J.: A two transition state model for radical-molecule interactions: applications to isomeric branching in the OH-isoprene reaction, *J. Phys. Chem. A*, 111, 5582-5592, 2007.

Francisco-Marquez, M., Alvarez-Idaboy, J. R. and Vivier-Bunge, A.: Theoretical study of the initial reaction between OH and isoprene in tropospheric conditions, *Phys. Chem. Chem. Phys.*, 5, 1392-1399, 2003. Jenkin, M. E., Boyd, A. A. and Lesclaux, R.: Peroxy radical kinetics resulting from the OH-initiated oxidation of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and isoprene, *J. Atmos. Chem.*, 29, 267-298, 1998.

Lei, W., Zhang, R., McGivern, W. S., Derecskei-Kovacs, A. and North, S. W.: Theoretical study of OH-O<sub>2</sub>-isoprene peroxy radicals, *J. Phys. Chem. A*, 105, 471-477, 2001.

Peeters, J., Boullet, W. and Van Hoeymissen, J.: Site-specific partial rate constants for OH addition to alkenes and dienes. *Proc. EUROTRAC Symposium '94*, SPB Academic Publishing bv, Eds. Borrell P. M., Borrell, P., Cvitas, T. and Seiler, W., The Hague, 1994, pp. 110-114. Stevens, P. S., Seymour, E. and Li, Z.: Theoretical and experimental studies of the reaction of OH with isoprene, *J. Phys. Chem. A*, 104, 5989-5997, 2000.

---

[Interactive comment on Atmos. Chem. Phys. Discuss.](#), 8, 14033, 2008.

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)