## The RACM2\_Berkeley2.1 Mechanism

The gas phase chemistry is based on the original RACM2 (Regional Atmospheric Chemistry Mechanism) mechanism (Goliff et al., 2013), and its upgraded versions, which are named RACM2\_Berkeley (Browne et al., 2014) and RACM2\_Berkeley2 (Zare et al., 2018). The original RACM2 is available in CMAQ v5.0.2 and later versions (Sarwar et al., 2013). In RACM2\_Berkeley, Browne et al. (2014) modified RACM2 to be consistent with the recent parameterization for hydroxyl radical (OH) oxidation of isoprene. They also reclassified the lumped organic nitrates from monoterpenes and anthropogenic VOC precursors into new species and added oxidation reactions for the new organic nitrate species. The RACM2\_Berkeley2 mechanism described in Zare et al. (2018) is an updated version of RACM2\_Berkeley that reflects more recent advances in the understanding of atmospheric organic chemistry in both low- and high-NOx conditions, with a focus on detailed representation of isoprene nitrates from NO3 oxidation and production and fate of the most important individual organic nitrates. The RACM2\_Berkeley2 mechanism was used within the WRF-Chem model.

Here, further explicit representation of multifunctional isoprene nitrates that are subject to reactive uptake to the aerosol phase are implemented to RACM2\_Berkeley2 (hereafter referred to as RACM2\_Berkeley2.1). The newly introduced species into the mechanism include C5 hydroxy nitrooxy dihydroperoxide (IHDPN), C5 dihydroxy nitrooxy hydroperoxide (IDHPN), C5 hydroxy nitrooxyperoxy radical (IHNO2), C5 hydroxy nitrooxyalkoxy radical (IHNO), C5 hydroxy hydroperoxide nitrate (IHPN) and INO2IN. INO2IN is a ROOR from INO2+INO2 reaction, where INO2 is produced from NO3 addition to isoprene and subsequent O2 addition.

IHDPN and IDHPN are 2nd generation nitrates produced from oxidation of δ and β isomers of C5 nitrooxy hydroperoxide (INPD and INPB) and C5 hydroxy nitrate (IHND and IHNB), respectively (Schwantes et al.,2015**)**. OH oxidation of the 1st generation isoprene nitrates (INPD, INPB and IHND, IHNB) produces RO2 radicals (INPHO2s and IDHNO2s), which react with HO2 to form IDHPN and IHDPN. Pye et al. (2015) showed the dominant peroxy radical (RO2) fate is reaction with HO2 and to a small extent reaction with other RO2. The RO2+NO3 reaction is negligible. Therefore, in this study where we add the RO2+HO2 reactions to form IDHPN and IHDPN, we omit RO2+NO3 reactions to save computational time.

Schwantes et al. (2015) showed that INO2 can react with itself or with another RO2 radical to form C5 hydroxy nitrates, C5 carbonyl nitrates, INO2IN and alkoxy radicals (INO). INO can either react with O2 or rapidly undergo a [1,5]-H-shift to form a C5 dihydroxy nitrate, a C5 hydroxy carbonyl nitrate or a C5 hydroxy hydroperoxide nitrate (Kwan et al., 2012; Schwantes et al., 2015). We implement these reactions into the scheme and use the lumped IHPN indicator as a surrogate for these 3 products. In total the updated reaction set includes 28 lumped organic nitrate surrogate species, in contrast to only three organic nitrate species (two isoprene-derived nitrates and one lumped terpene nitrate) were included in the original RACM2 mechanism. All new introduced species and modifications implemented into the RACM2\_Berkeley2.1 mechanism are listed in Table 1 and 2.

**Table 1.** Species added to the RACM2\_Berkeley2.1.

|  |  |
| --- | --- |
| Abbreviation | Description |
| IHDPN | C5 hydroxy nitrooxy dihydroperoxide |
| IDHPN | C5 dihydroxy nitrooxy hydroperoxide |
| INO2IN | Product from INO2 and INO2 |
| IHNO2 | C5 hydroxy nitrooxyperoxy radical (1,5 H shift product) |
| IHNO | C5 hydroxy nitrooxyalkoxy radical |
| IHPN | C5 hydroxy hydroperoxide nitrate |

**Table 2.** Reactions that are added, removed or modified in the RACM2\_ Berkeley2.1.

|  |  |  |  |
| --- | --- | --- | --- |
| Reactants | Products | Rate (s-1) | Status |
| INO2+INO2 | 0.39 INO+0.67ICN+0.10 MACR+0.616 IHND+0.154 IHNB+0.035 INO2IN | 5.2D-12 | Modified |
| ICN+NO3 | 0.1INHED + 0.1NO2  + 0.9 NC4CO3 +0.9 HNO3 | 6.3D-12exp(-1860/T) | Modified |
| NH4CO3+NO | PROPNN+CO+HO2+NO2 | 7.5D-12exp(-690/T) | Removed |
| NH4CO3+NH4CO3 | 0.3 R4N+0.7 PROPNN+0.7 HO2+0.7 CO | 1.0D-11 | Removed |
| NC4CO3+NO3 | PROPNN+CO+HO2+NO2 | 4.0D-12 | Added |
| IDHNO2D+NO3 | HO2+NO2+0.12 HAC+0.12 ETHLN+0.8 GLYC+0.80 PROPNN+0.08 R4N+0.08 HCHO | 2.3D-12 | Removed |
| IDHNO2B+NO3 | HO2+NO2+0.76 HAC+0.76 ETHLN+0.23 R4N+0.23 HCHO | 2.3D-12 | Removed |
| IDHNO2D+HO2 | 0.27IDHPN +0.73 OH + 0.73 HO2 + 0.09 HAC+ 0.09 ETHLN + 0.58 PROPNN+ 0.58GLYC + 0.06 R4N + 0.06 HCHO | 2.04D-13 \*exp(1300/Temp) | Added |
| IDHNO2B + HO2 | 0.27IDHPN + 0.73 OH+ 0.73 HO2 + 0.56 HAC + 0.17 HCHO + 0.56 ETHLN + 0.17 R4N | 2.04D-13 \* exp(1300/Temp) | Added |
| INPD+HO | 0.37 INHED+0.08IEPOX + 0.08NO2+0.37 HO +0.55 INPHO2D | 1.1D-10 | Modified |
| INPHO2B+NO3 | NO2+HO2+HCHO+R4NO | 2.3D-12 | Removed |
| INPHO2D+NO3 | NO2+HO2+0.92 PROPNN+0.92 GLY+0.08 HAC+0.08 ETHLN | 2.3D-12 | Removed |
| INPHO2B+ HO2 | 0.27IHDPN  + 0.73 OH + 0.73 HO2 + 0.73 hcho+ 0.73 R4NO | 2.04D-13 \* exp(1300/Temp) | Added |
| INPHO2D+ HO2 | 0.27IHDPN + 0.06 ETHLN + 0.73 OH + 0.73 HO2+ 0.67 PROPNN + 0.67 GLYC  + 0.06 HAC | 2.04D-13 \* exp(1300/Temp) | Added |
| INHED+HO | 0.27 HAC+0.73 CO+0.27 NO2+0.27 HCHO+0.17 PROPNN+0.17 GLY+0.46 R4N+0.1 INHED | 8.4D-12 | Modified |
| INHEB+HO | 0.08 INHEB  0.22PROPNN+0.22 GLY  0.31 GLYC+0.31 MGLY  0.09 HAC+0.43 NO2+0.39 HCHO+0.01 ETHLN+0.01 HAC+0.12 KET+0.26 R4N | 1.25D-11 | Modified |
| INO | IHNO2 | 2.0D5 | Added |
| IHNO2 + NO3 | IHNO + NO2 | 2.3D-12 | Added |
| IHNO2 + HO2 | IHPN | 2.91D-13\*exp(1300/T )\*0.706 | Added |
| IHNO + O2 | IHPN + HO2 | 2.5D-12\*exp(-300/TEMP) | Added |
| IHNO2 + IHNO2 | 0.46IHNO + 1.54IHPN | 2\*5.0 D-12 | Added |
| IHPN + hv | IHNO + HO | j(Pj\_ch3o2h) | Added |

Browne, E. C., Wooldridge, P. J., Min, K.-E. and Cohen, R. C.: On the role of monoterpene chemistry in the remote continental boundary layer, Atmos. Chem. Phys., 14(3), 1225–1238, doi:10.5194/acp-14-1225-2014, 2014.

Eddingsaas, N. C., VanderVelde, D. G. and Wennberg, P. O.: Kinetics and products of the acid-catalyzed ring-opening of atmospherically relevant butyl epoxy alcohols, J Phys Chem A, 114(31), 8106–8113, doi:10.1021/jp103907c, 2010.

Goliff, W. S., Stockwell, W. R. and Lawson, C. V.: The regional atmospheric chemistry mechanism, version 2, Atmospheric Environment, 68, 174–185, doi:10.1016/j.atmosenv.2012.11.038, 2013.

Jacobs, M. I., Burke, W. J. and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14(17), 8933–8946, doi:10.5194/acp-14-8933-2014, 2014.

Kwan, A. J., Chan, A. W. H., Ng, N. L., Kjaergaard, H. G., Seinfeld, J. H. and Wennberg, P. O.: Peroxy radical chemistry and OH radical production during the NO3-initiated oxidation of isoprene, Atmos. Chem. Phys., 12(16), 7499–7515, doi:10.5194/acp-12-7499-2012, 2012.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H. and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, Atmos. Chem. Phys., 9(4), 1479–1501, doi:10.5194/acp-9-1479-2009, 2009.

Pye, H. O. T., Luecken, D. J., Xu, L., Boyd, C. M., Ng, N. L., Baker, K. R., Ayres, B. R., Bash, J. O., Baumann, K., Carter, W. P. L., Edgerton, E., Fry, J. L., Hutzell, W. T., Schwede, D. B. and Shepson, P. B.: Modeling the Current and Future Roles of Particulate Organic Nitrates in the Southeastern United States, Environ. Sci. Technol., 49(24), 14195–14203, doi:10.1021/acs.est.5b03738, 2015.

Sarwar, G., Godowitch, J., Henderson, B. H., Fahey, K., Pouliot, G., Hutzell, W. T., Mathur, R., Kang, D., Goliff, W. S. and Stockwell, W. R.: A comparison of atmospheric composition using the Carbon Bond and Regional Atmospheric Chemistry Mechanisms, Atmospheric Chemistry and Physics, 13(19), 9695–9712, doi:10.5194/acp-13-9695-2013, 2013.

Schwantes, R. H., Teng, A. P., Nguyen, T. B., Coggon, M. M., Crounse, J. D., St. Clair, J. M., Zhang, X., Schilling, K. A., Seinfeld, J. H. and Wennberg, P. O.: Isoprene NO3 Oxidation Products from the RO2 + HO2 Pathway, J. Phys. Chem. A, doi:10.1021/acs.jpca.5b06355, 2015.

Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X. and Seinfeld, J. H.: Gas-Phase Reactions of Isoprene and Its Major Oxidation Products, Chem. Rev., 118(7), 3337–3390, doi:10.1021/acs.chemrev.7b00439, 2018.

Zare, A., Romer, P. S., Nguyen, T., Keutsch, F. N., Skog, K. and Cohen, R. C.: A comprehensive organic nitrate chemistry: insights into the lifetime of atmospheric organic nitrates, Atmospheric Chemistry and Physics, 18(20), 15419–15436, doi:https://doi.org/10.5194/acp-18-15419-2018, 2018.