1 Discussion of (1,5)-H Shift Isomerization of the di-HPCARP

The (1,4) H-shift di-HPCARP isomerization was included in the MCMv3.3.1 protocol to be consistent with the updated chemistry of the methacrolein-derived α-formyl peroxy radical (MACRO2) [Crounse et al., 2012]. Chamber experiments suggest MACRO2 isomerization rates of $\sim 0.5\ s^{-1}$ [Crounse et al., 2012]. A (1,5) H-shift isomerization of the di-HPCARP is also possible. Generally (1,5) H-shift isomerization rates are expected to be three orders of magnitude slower then the (1,4) H-shift. However recent work has shown that it can be strongly enhanced by the presence of functional groups with oxygen moities [Crounse et al., 2013], such as the terminal peroxide group in di-HPCARP. The closest structural proxy for the di-HPCARP from Crounse et al. [2013] ($CH_3CH(OO^{\cdot})CH_2CH(OOH)CH_3$) is predicted to have a isomerization rate of $0.22\ s^{-1}$, suggesting that the (1,5) H-shift isomerization of the di-HPCARP is competitive with the (1,4) H-shift. Here we include the di-HPCARP (1,5)H-shift in our revised mechanism, scaling the rate to 44% of the (1,4) H-shift, based on the ratio of the MACRO2 (1,4)H-shift and $CH_3CH(OO^{\cdot})CH_2CH(OOH)CH_3$ (1,5)H-shift rates.

The di-hydroperoxide dicarbonyl compound (DHDC) produced from the (1,5) H-shift isomerization can potentially lead to the production of CHOCHO via photolysis. Recent studies of the photolysis of HPALDs [Peeters et al., 2014], and carbonyl nitrates [Müller et al., 2014] have suggested mechanisms by which photon absorption on carbonyl chromophores can lead to dissociation of weaker bonds (e.g. O−OH) at near unity quantum yields. The same mechanisms are possible for DHDC. Assuming no interaction between the carbonyl chromophores, we estimate the cross section of DHDC to be twice the value of butenal, available from the 2006 IUPAC recommendations [Atkinson et al., 2006]. Combined with unity quantum yields, this yields a lifetime of ~ 2.8 hours at midday. The actual photolysis rate may be faster than this estimate, as interactions between the peroxide and carbonyl groups may enhance the cross section analagous to the effect of nitrate groups adjacent to carbonyl chromophores [Müller et al., 2014]. In the revised mechanism we set the DHDC photolysis rate equal to the HPALD photolysis rate. DHDC accounts for 26% of CHOCHO production from isoprene over the Southeast US in our simulations.

Table S1: Summary of the suggested changes to the GEOS-Chem chemical mechanism inferred from our analysis of SENEX observations.

Reaction	Base Model Products	Revised Model Products	Base & Revised Reaction Rates
RIO2→	HPALD	0.5HPALD + 0.5DHPCARP	$k = 4.07 \times 10^{8}\exp\left(\frac{-7694}{T}\right)$
DHPCARP+NO→	no reaction	GLYX + MGLY + NO2 + OH	$k = 2.7 \times 10^{-12}\exp\left(\frac{360}{T}\right)$
DHPCARP+HO2→	no reaction	RCOOH	$k = 2.05 \times 10^{-13}\exp\left(\frac{1300}{T}\right)$
DHPCARP→	no reaction	RCOOH + CO + OH	$k = 2.9 \times 10^{7}\exp\left(\frac{-5300}{T}\right)$
DHPCARP→	no reaction	DHDC	$k = 1.28 \times 10^{7}\exp\left(\frac{-5300}{T}\right)$
DHDC+$h\nu$ →	no reaction	MGLY + GLYX + 2OH	J_{HPALD}
HPALD+OH→	MGLY + CO + CH2O + OH	0.365HPC52O2 + 0.085GLYX + 0.085MCO3 + 0.55MGLY + 0.55CO + 0.55CH2O + 0.635OH	$k = 5.11 \times 10^{-11}$
HPALD+$h\nu$ →	0.25GLYX + 0.25MGLY + 0.5HAC + 0.5GLYC + CH2O + HO2 + OH	0.5MGLY + 0.39HAC + 0.11GLYC + 0.11MCO3 + 1.89CO + 0.89HO2 + 2OH	J_{HPALD}
HPC52O2+NO→	no reaction	GLYX + MGLY + NO2 + HO2	$k = 2.7 \times 10^{-12}\exp\left(\frac{360}{T}\right)$
HPC52O2+HO2→	no reaction	RCOOH	$k = 2.05 \times 10^{-13}\exp\left(\frac{1300}{T}\right)$
RIO2+NO→	0.93NO2 + 0.855HO2 + 0.71CH2O + 0.414MVK + 0.296MACR + 0.023ISOPND + 0.047ISOPNB + 0.145HC5 + 0.075DIBOO	0.936NO2 + 0.904HO2 + 0.844CH2O + 0.493MVK + 0.351MACR + 0.01ISOPND + 0.056ISOPNB + 0.06HC5 + 0.03DIBOO	$k = 2.7 \times 10^{-12}\exp\left(\frac{350}{T}\right)$
GLYC+OH→	f(0.732CH2O + 0.5CO + 0.227OH + 0.773HO2 + 0.134GLYX + 0.134HCOOH) + (1-f)(HCOOH + OH + CO)	0.676CH2O + 0.466CO + 0.21OH + 0.79HO2 + 0.2GLYX + 0.124HCOOH	$k = 2.05 \times 10^{-13}\exp\left(\frac{1300}{T}\right)$ $f = 1 - 11.0729\exp\left(\frac{-T}{73}\right)$

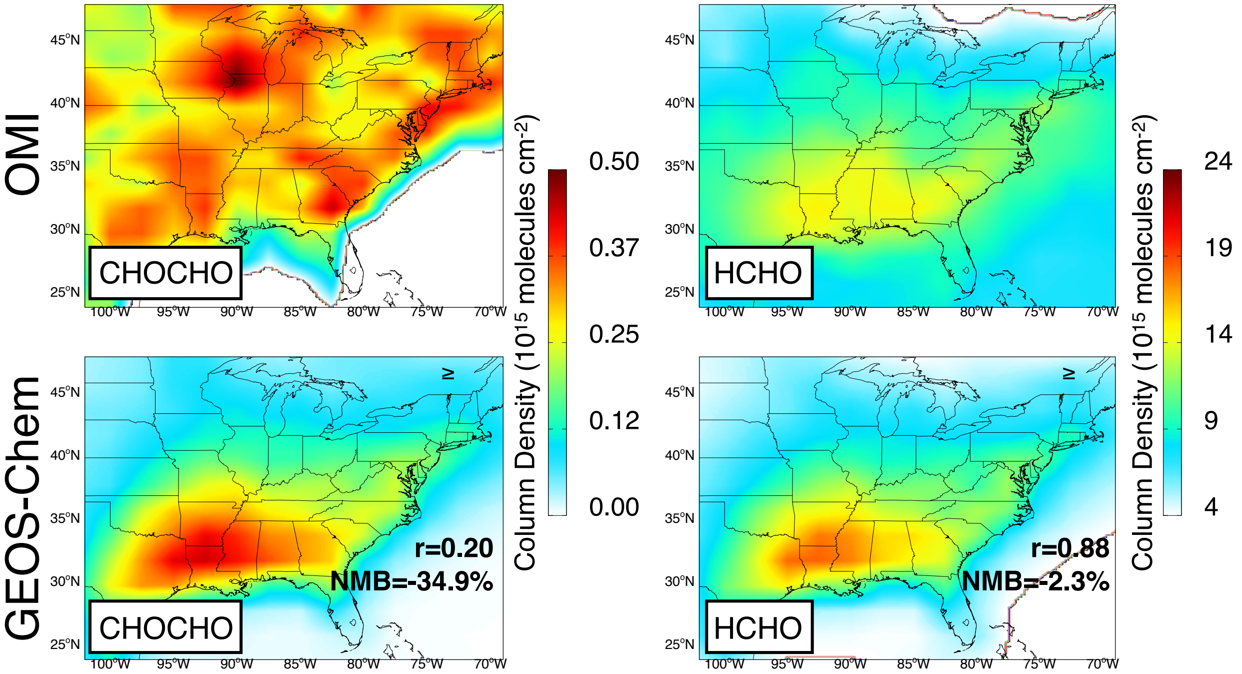

Figure S1: Mean CHOCHO and HCHO columns in summer (JJA) 2013. OMI satellite observations (top) are compared to GEOS-Chem model values (bottom). The OMI HCHO observations have been scaled up by a factor of 1.67 to correct for retrieval bias [Zhu et al., 2016]. The normalized mean bias (NMB) and spatial correlation (r) between GEOS-Chem and OMI in the eastern US (75° – 100°W, 29.5° – 45°N) is shown within the GEOS-Chem panels.

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