



Supplement of

Glyoxal yield from isoprene oxidation and relation to formaldehyde: chemical mechanism, constraints from SENEX aircraft observations, and interpretation of OMI satellite data

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interred from our analysis of DERTER observations.			
Reaction	Base Model Prod- ucts	Revised Model Products	Base & Revised Reaction Rates
$RIO2 \rightarrow$	HPALD	0.5HPALD + 0.5DHPCARP +	$k = 4.07 \times 10^8 \exp\left(\frac{-7694}{T}\right)$
$\Box HPCARP+NO \rightarrow$	no reaction	GLYX + MGLY + NO2 + OH	$k = 2.7 \times 10^{-12} \exp\left(\frac{360}{T}\right)$
$DHPCARP+HO2 \rightarrow$	no reaction	RCOOH	$k = 2.05 \times 10^{-13} \exp\left(\frac{1300}{T}\right)$
$DHPCARP \rightarrow$	no reaction	RCOOH + CO + OH	$k = 2.9 \times 10^7 \exp\left(\frac{-5300}{T}\right)$
$DHPCARP \rightarrow$	no reaction	DHDC	$k = 1.28 \times 10^7 \exp\left(\frac{-5300}{T}\right)$
$DHDC+h\nu \rightarrow$	no reaction	MGLY + GLYX + 2OH	J _{HPALD}
HPALD+OH→	MGLY + CO + CH2O + OH	$\begin{array}{r} 0.365 \mathrm{HPC52O2} \\ + & 0.085 \mathrm{GLYX} \\ + & 0.085 \mathrm{MCO3} \\ + & 0.55 \mathrm{MGLY} \\ + & 0.55 \mathrm{CO} \\ + \\ 0.55 \mathrm{CH2O} \\ + \\ 0.635 \mathrm{OH} \end{array}$	$k = 5.11 \times 10^{-11}$
$HPALD + h\nu \rightarrow$	$\begin{array}{r} 0.25 {\rm GLYX} & + \\ 0.25 {\rm MGLY} \\ + & 0.5 {\rm HAC} & + \\ 0.5 {\rm GLYC} & + & {\rm CH2O} \\ + & {\rm HO2} & + & {\rm OH} \end{array}$	$\begin{array}{cccc} 0.5 {\rm MGLY} & + \\ 0.39 {\rm HAC} & + \\ 0.11 {\rm GLYC} & + \\ 0.11 {\rm MCO3} & + \\ 1.89 {\rm CO} & + 0.89 {\rm HO2} \\ + & 2 {\rm OH} \end{array}$	J _{HPALD}
$HPC52O2+NO \rightarrow$	no reaction	GLYX + MGLY + MO2 + HO2	$k = 2.7 \times 10^{-12} \exp\left(\frac{360}{T}\right)$
$HPC52O2+HO2 \rightarrow$	no reaction	RCOOH	$k = 2.05 \times 10^{-13} \exp\left(\frac{1300}{T}\right)$
RIO2+NO→	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccc} 0.91 \mathrm{NO2} & + \\ 0.82 \mathrm{HO2} & + \\ 0.82 \mathrm{CH2O} & + \\ 0.476 \mathrm{MVK} & + \\ 0.344 \mathrm{MACR} & + \\ 0.009 \mathrm{ISOPND} \\ + & 0.081 \mathrm{ISOPNB} \\ + & 0.058 \mathrm{HC5} & + \\ 0.03 \mathrm{DIBOO}^{\dagger} \end{array}$	$k = 2.7 \times 10^{-12} \exp\left(\frac{350}{T}\right)$
GLYC+OH→	$\begin{array}{r} f(0.732 \text{CH2O} + \\ 0.5 \text{CO} + 0.227 \text{OH} \\ + 0.773 \text{HO2} + \\ 0.134 \text{GLYX} + \\ 0.134 \text{HCOOH} + \\ (1-f)(\text{HCOOH} + \\ \text{OH} + \text{CO}) \end{array}$	$\begin{array}{r} 0.676 \text{CH2O} & + \\ 0.466 \text{CO} & + & 0.21 \text{OH} \\ + & 0.79 \text{HO2} & + \\ 0.2 \text{GLYX} & + \\ 0.124 \text{HCOOH} \end{array}$	$k = 8 \times 10^{-12}$ f = 1 - 11.0729exp ($\frac{-T}{73}$)

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

[†]The revised mechanism has been updated to include the isoprene nitrate yield recommendation by Fisher et al. [2016]. The reaction used in this study preserved the ISOPNB and ISOPND yields from the GEOS-Chem mechanism (RIO2+NO \rightarrow 0.936NO2 + 0.904HO2 + 0.844CH2O + 0.493MVK + 0.351MACR + 0.01ISOPND + 0.056ISOPNB + 0.06HC5 + 0.03DIBOO). The difference CHOCHO production from isoprene over the southeast US due to this change is less than 2%, howeer it is important for isoprene organic nitrates.

S1 Production of CHOCHO from glycolaldehyde

The main two sinks of glycolaldehyde in the atmosphere are via photolysis and OH, with the latter oxidation pathway yielding CHOCHO. Reported yields of CHOCHO via OH initiated GLYC oxidation range from 14 - 29% [Magneron et al., 2005, Butkovskaya et al., 2006, Chan et al., 2009, Galloway et al., 2011]. Here we use a yield of 20%, following MCMv3.3.1, whose yield value is from Magneron et al. [2005]. Li et al. [2016] set the yield in AM3 to 13% citing Butkovskaya et al. [2006], and report an absolute yield from GLYC oxidation of 7.2%. If this yield is constant, this implies that 45% of GLYC in AM3 is lost to photolysis. However photolysis is generally a minor GLYC sink. Figure S1 shows the fraction of GLYC lost to OH simulated by GEOS-Chem over the SENEX period (June 1-July 10 2013). This simulation is from the model as described in the main text, except that it was performed globally at $2^{\circ} \times 2.5^{\circ}$ degree resolution. The model suggests approximately 20% of GLYC is lost to photolysis over the Southeast US, a factor of 2.5 smaller than suggested by the absolute yield from Li et al. [2016].



Fraction of glycolaldehyde lost to OH

Figure S1: The fraction of GLYC lost to oxidation by OH for the period 1 June - 10 July 2013, simulated by GEOS-Chem.

Butkovskaya et al. [2006] observed that the yield of CHOCHO from OH initiated GLYC oxidation decreased with decreasing temperature. Both our GEOS-Chem mechanism and the AM3 mechanism derive from the mechanism presented by Mao et al. [2013]. Here, the CHOCHO yield from GLYC + OH was calculated from a temperature dependent parameterization of the yields from Butkovskaya et al. [2006] (Table S1). Figure S2 shows the CHOCHO yield from OH initiated GLYC oxidation as a function of temperature in the original and revised GEOS-Chem mechanisms. The parameterization tends to underestimate the CHOCHO yield compared to the chamber study it was based on (e.g. 296K Butkovskaya

et al. [2006] report a 14% yield, compared to 10.8% in the parameterization). The yield from the parameterization is approximately half that from the MCMv3.3.1 reaction implemented in this study, and thus could explain the difference in GLYC yields shown here and for AM3, if this is the actual reaction implemented.



Figure S2: CHOCHO yield from the reaction of GLYC with OH as a function of temperature, from the original and revised GEOS-Chem mechanism presented in Table S1

S2 Production of CHOCHO from Isoprene epoxydiols

 β -isoprene epoxydiols (IEPOXB, Figure S3) account for ~ 95% of total IEPOX [Jenkin et al., 2015]. The IEPOXB pathways pertinent to CHOCHO production from MCMv3.3.1 are shown in Figure S3. The H-abstraction pathway leading to CHOCHO production via C58AO2 accounts for 37% of IEPOXB loss to OH, and is based on IEPOX chamber experiments [Bates et al., 2014]. CHOCHO forms as a coproduct to hydroxyacetone (ACE-TOL) via reaction with NO. In MCMv3.3.1 the reaction between C58AO2 and HO₂ leads to the generation of the assocated hydroperoxide (C58AOOH). Li et al. [2016] suggest that MCMv3.3.1 underestimates the CHOCHO yield from this pathway because it does not assume full radical chain propogation (dashed blue arrow, Figure S3), and set a total CHOCHO yield from IEPOX oxidation at 28%.



Figure S3: Left: Pathways of CHOCHO formation from the oxidation of IEPOX in MCMv3.3.1 [Jenkin et al., 2015]. Species are labeled with their names in MCMv3.3.1. The dashed blue arrow indicates the CHOCHO formation pathway from the reaction of the IEPOX peroxy radical (C58AO2) with HO₂ in AM3 [Li et al., 2016]. Right: Branching ratio between the reaction of the C58AO2 with HO₂ and isomerization, at a HO₂ concentration of 1×10^9 molecules cm⁻³

However MCMv3.3.1 does not produce CHOCHO in high yield via this pathway as there is a competing (1,4) H-shift isomerization (red arrow, Figure S3), forming MACROH. The branching ratio as a function of temperature between HO₂ and the isomerization is shown in Figure S3 (right). This has been calculated with a HO₂ concentration of 1×10^9 molecules cm⁻³. HO₂ concentrations simulated by GEOS-Chem over the Southeast US during SENEX were never above this concentration, so the plot in Figure S3 can be regarded as an upper limit for the HO₂ pathway. MCMv3.3.1 suggests that at 296K, HO₂ reactions with C58AO2 account for at most 3% of total loss.

The chamber experiments reported by Bates et al. [2014] also suggest that the majority of C58AO2 is lost via isomerization. The sum of products of the (1,4) H-shift isomerizations of IEPOXB peroxy radicals (including MACROH) were detected using chemical ionization mass spectrometry (CIMS), by monitoring the signal at m/z = 189. Bates et al. [2014] oxidized cis-IEPOXB under low-NO_x conditions and inferred yields of the m/z = 189 products that

were approximately 4 times higher than those formed via the HO₂ pathway (ACETOL and GLYC). Since ACETOL is a coproduced with CHOCHO, we set the yield of CHOCHO from IEPOX + HO₂ equal to the ACETOL yield derived from the low-NO_x cis-IEPOXB oxidation experiment (8.5%). The observed ACETOL yields cannot accomodate the 28% yield assumed in AM3, even when factoring in the reported 30% uncertainty in the measurements.



Figure S4: Cumulative time-dependent molar yields of CHOCHO from IEPOX oxidation in the GEOS-Chem, AM3 and MCMv3.3.1 chemical mechanisms. Results are from box model simulations described in the main text, calculated at two imposed NO_x concentrations (0.1 and 1 ppbv). The AM3 yield does not include contribution from GLYC oxidation. "OH exposure time" is equivalent to time for a constant $[OH]=4 \times 10^6$ molecules cm⁻³

Bates et al. [2014] also derived ACETOL yields from experiments involving the oxidation of cis- and trans-IEPOXB under high-NO_x (~ 570 ppb NO) conditions. At these NO levels, the (1,4) H-shift isomerization pathway should be minor. We combine the observed ACETOL yields with the measured yields of cis- and trans-IEPOXB and estimate a CHOCHO yield of 8.8% for the reaction of IEPOX+NO.

Figure S4 compares the cumulative CHOCHO yield from IEPOX in GEOS-Chem, MCMv3.3.1, and AM3, as a function of OH exposure time (Equation 3, main text). The GEOS-Chem yields are within the range simulated by MCMv3.3.1, however the NO_x -dependence of the yield is weaker. The yield realized by AM3 is approximately 2.5 times higher than GEOS-Chem after 25 hours of OH exposure time.

S3 Production of CHOCHO via isoprene peroxy radical isomerization



Figure S5: Main pathways to CHOCHO formation from the ISOPO2 isomerization in MCMv3.3.1 [Jenkin et al., 2015]. Only species relevant to CHOCHO formation are shown. Key reactions for determining the CHOCHO yield are highlighted in red.

Figure S5 shows the pathways to CHOCHO formation via ISOPO2 isomerization in MCMv3.3.1 [Jenkin et al., 2015]. ISOPO2 isomerization yields dihydroperoxy-formyl peroxy radicals (di-HPCARPs) in addition to HPALDs [Peeters et al., 2014]. In general, yields of CHOCHO via ISOPO2 isomerization in MCMv3.3.1 are negligable, as its formation via di-HPCARPs and HPALDs require NO. In contrast, CHOCHO production in AM3 is much stronger, as HPALD photolysis produces yields 25% CHOCHO. This yield is based on Stavrakou et al. [2010], however no mechanism for CHOCHO formation was provided. As such, we regard the MCMv3.3.1 protocol as more reliable. Nevertheless, analysis of the SENEX observations suggested that MCMv3.3.1 was missing a prompt source of CHOCHO under low-NOx conditions. This lead to our further examination of the MCMv3.3.1 ISOPO₂ pathways for missing reactions.

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 ~ 0.5 s⁻¹ [Crounse et al., 2012]. A (1,5) H-shift isomerization of the di-HPCARP



Figure S6: Transition states for the (1,4) and (1,5) H-shift isomerizations of the di-HPCARP leading to CHOCHO formation. These are compared to the proxy compounds used to determine their rates [Crounse et al., 2012, 2013]. The subsequent steps to CHOCHO formation from the (1,5) H-shift are also shown.

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] (CH₃CH(OO·)CH₂CH(OOH)CH₃, Figure S6) 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) Hshift, based on the ratio of the MACRO2 (1,4)H-shift and CH₃CH(OO·)CH₂CH(OOH)CH₃ (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.

S4 Sensitivity to aerosol reactive uptake

Li et al. [2016] showed that CHOCHO concentrations are sensitive to aerosol reactive uptake. Although we only simulate CHOCHO loss to OH and photolysis, a reasonable estimate of the CHOCHO concentration with aerosol loss ([CHOCHO]_a) can be made assuming steady state;

$$[CHOCHO]_a = \frac{k_{OH}[OH] + J}{k_{aer} + k_{OH}[OH] + J}[CHOCHO]$$
(S1)

where [CHOCHO], k_{aer} , k_{OH} , and J are the simulated concentration, aerosol loss rate to reactive uptake, OH reaction rate, and photolysis rate of CHOCHO respectively. k_{aer} is calculated following Jacob [2000];

$$k_{aer} = \left(\frac{a}{D_g} + \frac{4}{\nu\gamma}\right)^{-1} A \tag{S2}$$

a is the effective aerosol radius, D_g is the gas phase diffusion constant, ν is the mean molecular speed of CHOCHO, γ is the reactive uptake coefficient, and A is the aerosol surface area. We test the sensitivity with $\gamma = 2 \times 10^{-3}$ from Li et al. [2016].

Figure S7 shows the observed and simulated median vertical profiles of CHOCHO (with and without aerosol uptake) along the SENEX flight tracks. Inclusion of aerosol reactive decreases the median mixed layer (< 1 km) CHOCHO concentration by ~ 10%. The difference between observed and simulated median mixed layer CHOCHO concentrations is -13% with the aerosol sink, comparable to that of HCHO (-14%).



Figure S7: Median vertical profiles of CHOCHO concentrations during SENEX (June 1 - July 10 2013). Observed concentrations [Min et al., 2016] are compared to GEOS-Chem model values with and without aerosol uptake (Equation S1), sampled along the flight tracks. Horizontal bars indicate interquartile range. Altitudes are above ground level (AGL).



Figure S8: Median vertical profiles of isoprene, methylvinylketone+methacrolein (MVK+MACR), CO, and O_3 concentrations during SENEX (June 1 - July 10 2013). Observed concentrations are compared to GEOS-Chem model values sampled along the flight tracks. Horizontal bars indicate interquartile range. Altitudes are above ground level (AGL)



Figure S9: Isoprene, methylvinylketone+methacrolein (MVK+MACR), CO, and O₃ concentrations below 1 km AGL during SENEX (June 1 - July 10 2013). The grid squares show daytime aircraft observations compared to the colocated GEOS-Chem model values on the $0.25^{circ} \times 0.3125^{\circ}$ model grid. Background contours in the right panels show the average model-simulated concentrations at 13 - 14 local time for the SENEX period. Comparison statistics between model and observation grid squares are shown as the correlation coefficient r and the normalized mean bias (NMB).



Figure S10: Relationship between CHOCHO and HCHO concentrations in the mixed layer (< 1 km AGL during SENEX (June 1 - July 10 2013). Observed values are compared to GEOS-Chem model values that have been rescaled to account for aerosol uptake (Equation S1). Lines and reported slopes are from reduced major axis regressions.



CHOCHO yield from isoprene and monoterpenes

Figure S11: Cumulative time-dependent molar yields of CHOCHO from the oxidation of isoprene and monoterpenes. Results are from box model simulations described in the main text, calculated at two imposed NO_x concentrations (0.1 and 1 ppbv). The isoprene mechanism is from GEOS-Chem and the α -pinene and β -pinene mechanisms are from MCMv3.3.1. "OH exposure time" is equivalent to time for a constant [OH]=4 × 10⁶ molecules cm⁻³



Figure S12: 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 ($75^{\circ} - 100^{\circ}$ W, $29.5^{\circ} - 45^{\circ}$ N) is shown within the GEOS-Chem panels.

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