Supporting Information

Production and Fate of C_4 Dihydroxycarbonyl Compounds from Isoprene Oxidation

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Table S1. Estimated CIMS sensitivities (in normalized counts per ppbv in the inlet flow), along with their constituent parameters, for species relevant to this study.[a]

compound	dipole (D)	polarizability (Å^3)	sensitivity
cis-β-IEPOX	2.47	8.98	0.371
trans-β-IEPOX	1.00	9.01	0.231
IEPOXO	1.93	8.57	0.303
DHBO	2.35	7.49	0.358
DHMP	2.09	7.52	0.331
DHBA	2.22	8.69	0.353
HBDO	2.14	7.22	0.335
HMPD	1.00	8.35	0.233
HOBA	1.08	7.27	0.228

[a] The parameters, dipole and polarizability, of the molecules are calculated with use of density functional theory at the B3LYP level, with the basis sets: 6-31G(d), 6-31+G(d) or cc-pVTZ. The sensitivity is related to the relative collision rate and depends mostly on the dipole moment of the molecule colliding with the ion. The dipole moments listed in Table S1 are the dipole moment averaged over the possible conformers with a Boltzmann abundance larger than 0.1%. The polarizability is similar for different conformers, and the collision rate has a weak dependence on the polarizability, and is thus only calculated for the lowest energy conformer. The calculated sensitivities are estimated to have an error of less than 10%.

Table S2. Reactions in the low-NO isoprene oxidation pathway edited or added to GEOS-Chem for the simulations performed in this study. Standard GEOS-Chem notation is used for product abbreviations.

reactants	products	rate coefficient $k = A*e^{(r/t)}$		reference
		A	r	
$RIO_2 + HO_2$	0.629*(1,2)-ISOPOOH +	2.06E-13	1300	[1]

	0.272*(4,3)-ISOPOOH + 0.037*δ-ISOPOOH + 0.063*(OH + HO_2 + CH_2O) + 0.025*MACR + 0.038*MVK			
(1,2)-ISOPOOH + OH	0.75*RIO_2 + 0.25*HC_5OO + 0.125*(OH + HO_2)	6.13E-12	200	[1]
(1,2)-ISOPOOH + OH	0.85*OH + 0.15*HC_5OO + 0.578*_trans_-β-IEPOX + 0.272*_cis_-β-IEPOX	1.70E-11	390	[1]
(4,3)-ISOPOOH + OH	0.48*RIO_2 + 0.52*HC_5OO + 0.26*(OH + HO_2)	4.14E-12	200	[1]
(4,3)-ISOPOOH + OH	OH + 0.68* _trans_-β-IEPOX + 0.32* _cis_-β-IEPOX	2.97E-11	390	[1]
δ-ISOPOOH + OH	0.25*RIO_2 + 0.75*HC_5OO + 0.375*(OH + HO_2)	5.11E-12	200	[1]
δ-ISOPOOH + OH	0.5*(OH + δ-IEPOX + HC_5OO)	2.92E-11	390	[1]
trans-β-IEPOX + OH	0.83*OH + 0.45*CO + 0.36*DHBO + 0.09*DHMP + 0.08*(HBDO + CH_2O) + 0.17*(IEPOXO + HO_2) + 0.16*(HAC + GLYX) + 0.14*(GLYC + MGLY)	3.73E-11	-400	[2]
cis-β-IEPOX + OH	0.8*OH + 0.48*CO + 0.43*DHBO + 0.05*DHMP + 0.08*(HBDO + CH_2O) + 0.2*(IEPOXO + HO_2) + 0.08*(HAC + GLYX) + 0.16*(GLYC + MGLY)	5.79E-11	-400	[2]
δ-IEPOX + OH	0.6*(IEPOXO + HO_2) + 0.4*IEPOXDOO	3.20E-11	-400	[2-4]
IEPOXO + OH	OH + 1.5*CO + 0.5*(CH_2O + MGLY + HAC)	9.85E-12	410	[3-5]
IEPOXDOO + HO_2	HO_2 + OH + HAC + GLYX	2.06E-13	1300	[3-4]
IEPOXDOO + NO	NO_2 + HO_2 + HAC + GLYX	2.70E-12	350	[3-4]
DHBO + OH	HO_2 + 0.609*HBDO + 0.391*HOBA	8.70E-12	70	this work
DHMP + OH	0.838*(HAC + CO_2 + OH) + 0.162*(HMPD + HO_2)	7.49E-12	410	this work
DHBA + OH	1.528*CO_2 + 0.764*(ALD_2 + OH) + 0.236*(HOBA + HO_2)	9.38E-12	410	this work
HBDO + OH	2*CO + MCO_3 + HO_2	2.13E-12	70	[4-5]
HMPD + OH	CO_2 + OH + MGLY	1.06E-11	410	[4-5]
HOBA + OH	CO_2 + OH + MGLY	6.27E-12	410	[4-5]

Table S3. Rate coefficients for the reactions of $C_4H_6O_3$ hydroxydicarbonyl compounds with OH, as used in the Master Chemical Mechanism v3.2 (MCM)[4] and calculated by structure-activity relationship (SAR).[5]

compound	k_{OH} (10^{-11} cm^3 molec^{-1} s^{-1})	
	MCM[4]	SAR[5]
HBDO	0.27	0.27
HMPD	13.2	4.18
HOBA	2.45	2.48

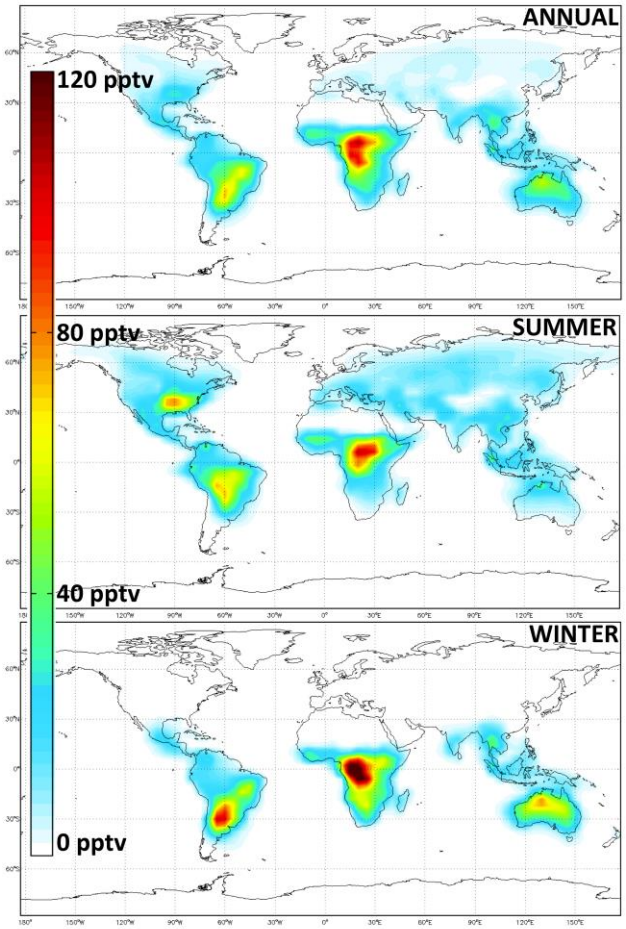

Figure S1. Annual and seasonal average mixing ratios of $C_4H_6O_3$ dihydroxycarbonyl compounds in the lowest 1 km of the atmosphere, as simulated using GEOS-Chem and including photolysis of HBDO.

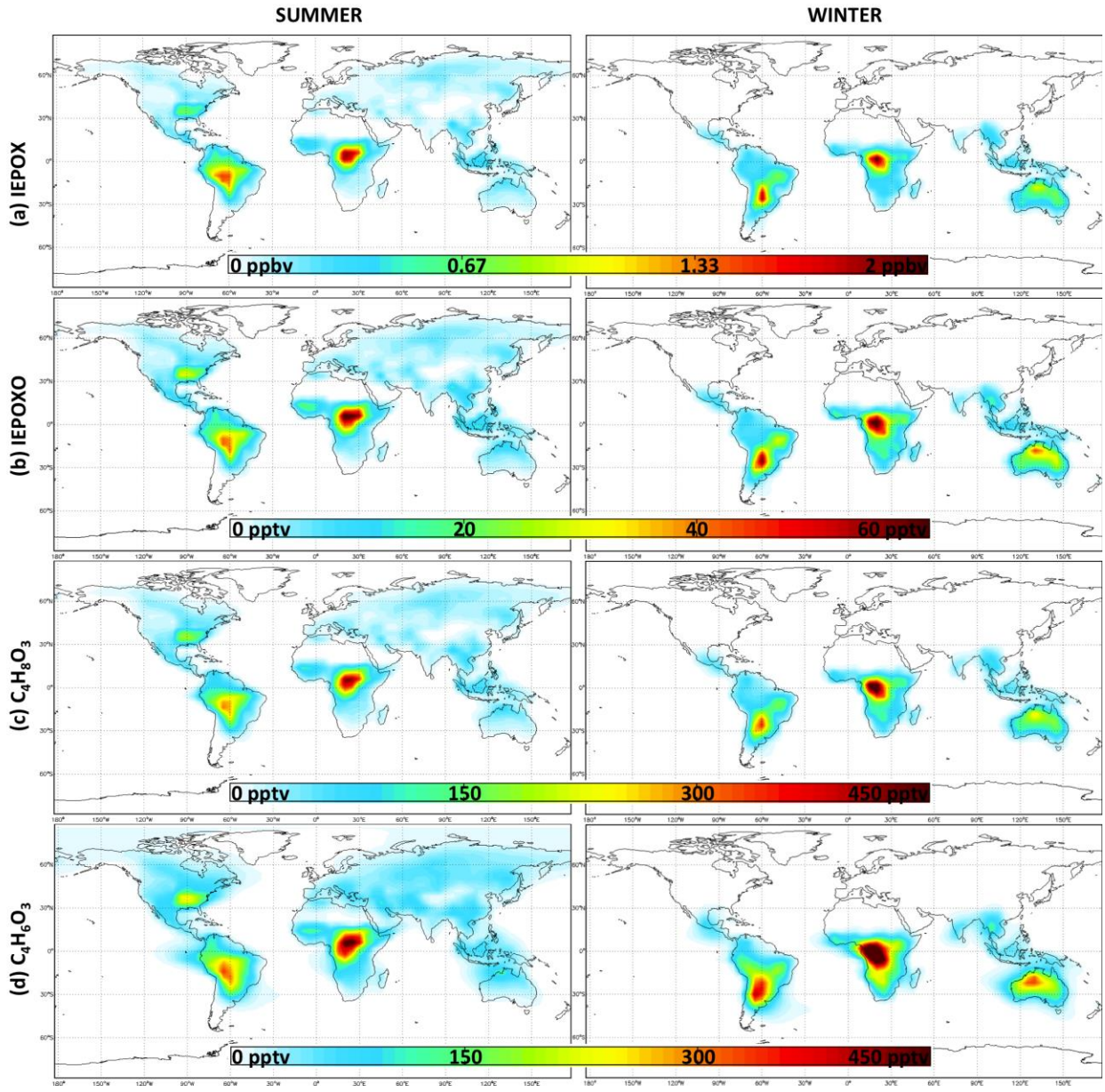

Figure S2. Seasonal average mixing ratios of IEPOX, IEPOXO, $C_4H_8O_3$ dihydroxycarbonyl compounds, and their $C_4H_6O_3$ products in the lowest 1 km of the atmosphere, as simulated using GEOS-Chem.

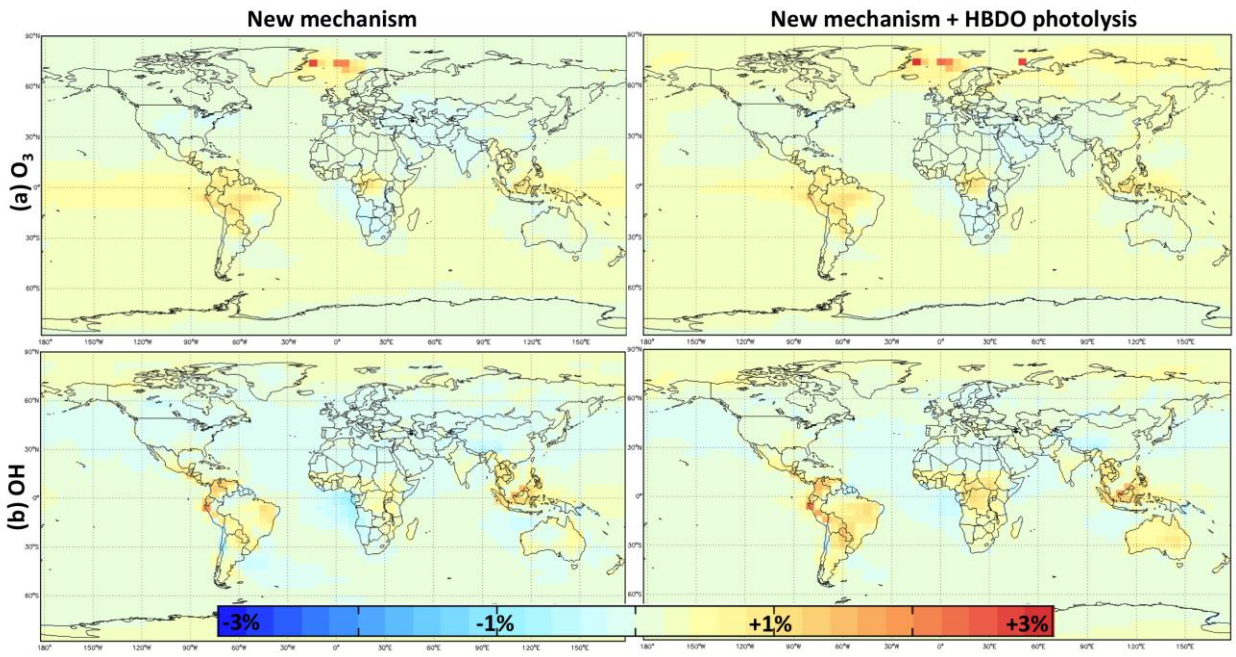

Figure S3. Percent changes in annual average OH and O_3 mixing ratios in the lowest 1 km of the atmosphere caused by the inclusion of the $C_4H_8O_3$ and $C_4H_6O_3$ compounds and their coproducts and products, as compared with a mechanism using the products of IEPOX + OH originally included in GEOS-Chem v.9-02.[6]

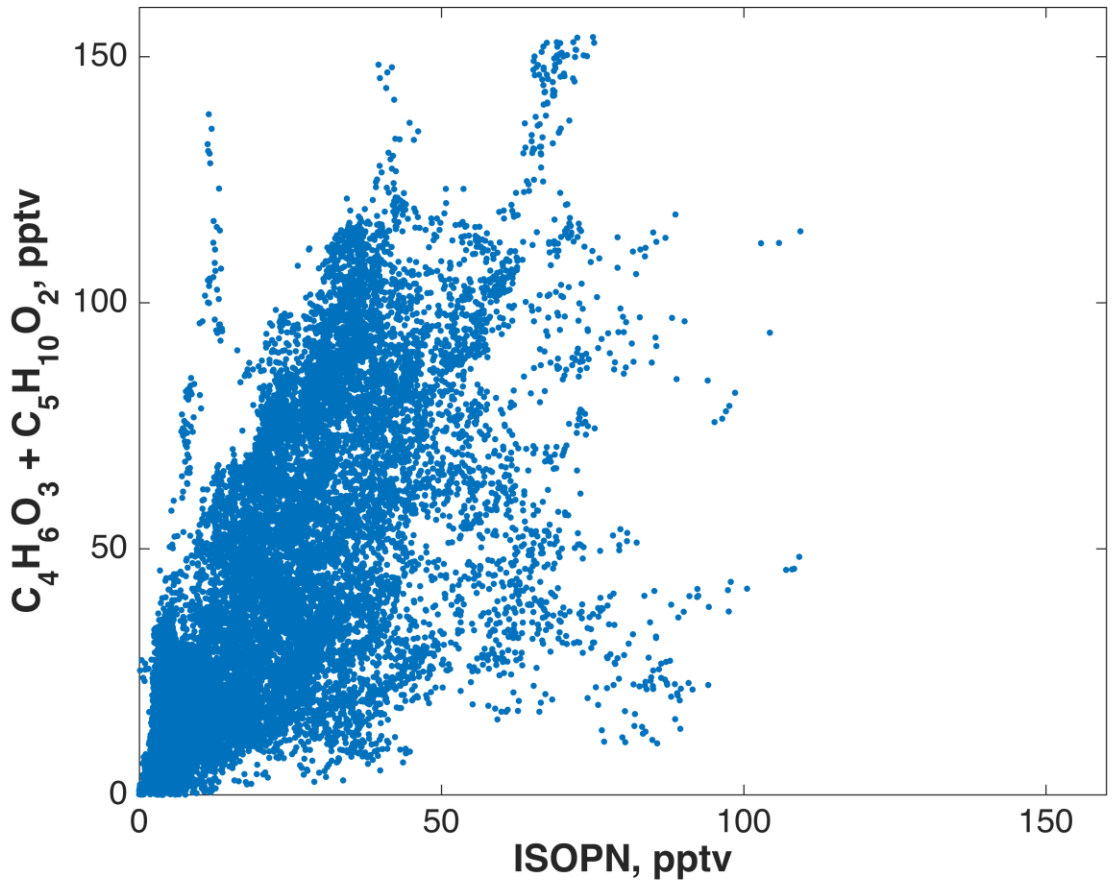

Figure S4. Correlation between isoprene nitrates and $C_4H_6O_3$ + $C_5H_{10}O_2$ during the entire SOAS campaign.

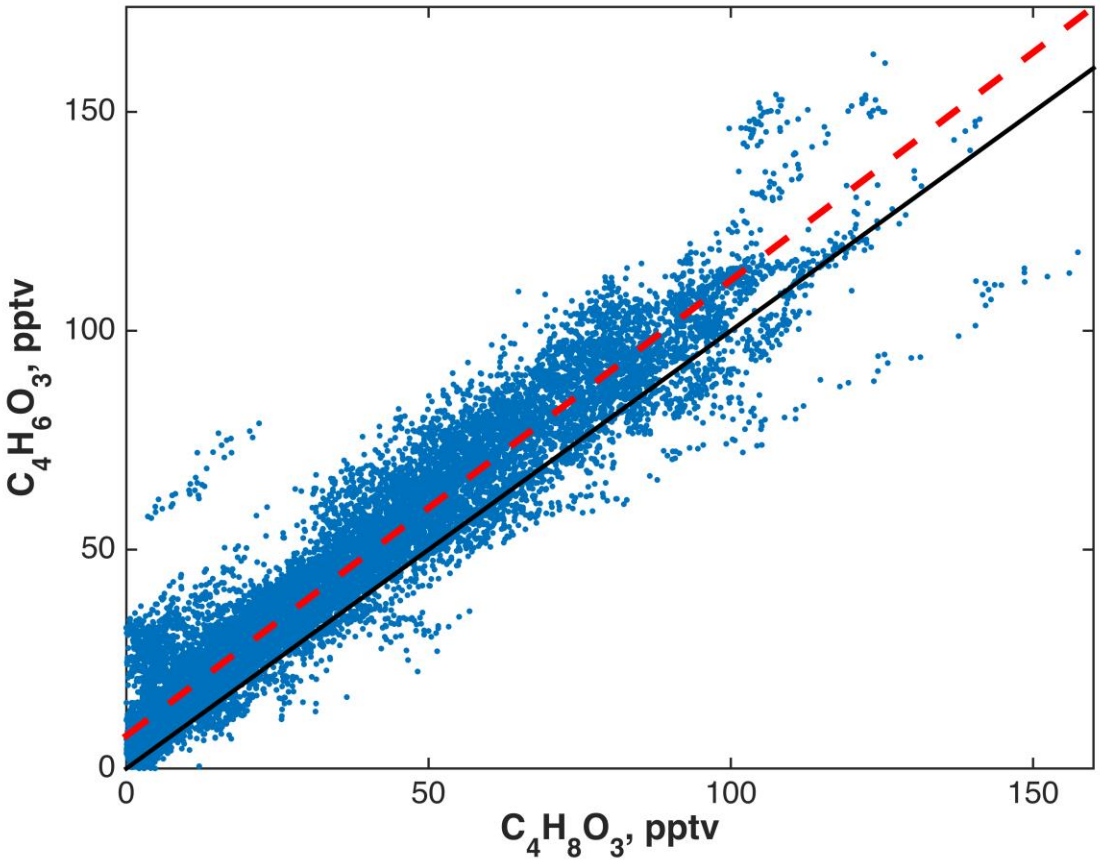

Figure S5. Correlation between $C_4H_8O_3$ and $C_4H_6O_3$ during the entire SOAS campaign, overlaid with a line of best fit (red, dashed; $r^2 = 0.92$) and a 1:1 line (black, solid).

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