

**How humidity makes HONO the dominant sink  
of alkyl substituted Criegee intermediates and a  
key nocturnal source of OH radicals.**

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# S1 Details of the methodology used for the electronic structure theory

To estimate energies at CCSD(T)/CBS level of theory, first we calculated the single point energies at CCSD(T)/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVTZ level of theory, and then extrapolated these energies to corresponding CBS limit using the method of Varandas and Pansini.<sup>1,2</sup> Specifically, for the extrapolation of correlation energies, the following equation is used:

$$\text{CBS(Corr)} = \frac{2.71^3 E_{\text{ATZ}} - 1.91^3 E_{\text{ADZ}}}{2.71^3 - 1.91^3}$$

Where,  $E_{\text{ADZ}}$  and  $E_{\text{ATZ}}$  are correlation energies at CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ level of theory, respectively. For the extrapolation of Hartree-Fock energies, the following equation is used:

$$\text{CBS(HF)} = \frac{2.96^5 E_{\text{ATZ}} - 2.08^5 E_{\text{ADZ}}}{2.96^5 - 2.08^5}$$

Where,  $E_{\text{ADZ}}$  and  $E_{\text{ATZ}}$  are Hartree-Fock energies at CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ level of theory, respectively.

# S2 Details of master equation calculation

The simulation requires two inputs; dissociation rate constants of well separating into the reactants ( $k_r(\text{E})$ ) and unimolecular transformation rate ( $k_{uni}$ ). To compute  $k_r(\text{E})$ , MultiWell uses inverse Laplace transformation (ILT) method. The ILT method requires a pre-exponential factor for the unimolecular dissociation from RC to isolated reactants, which have been estimated using KTOOLS code available in MultiWell suite of programs.<sup>3</sup> For the unimolecular dissociation step, we used Rice-Ramsperger-Kassel-Marcus (RRKM) theory to calculate unimolecular rate constant ( $k_{uni}$ ). To mimic air, we have used  $\text{N}_2$  as the bath

gas, (corresponding Lennard Jones (L-J) parameters are  $\sigma = 3.74 \text{ \AA}$ , and  $\epsilon/kT = 82.0 \text{ K}$ ). To simulate the energy transfer model, a single exponential model was used with maximum energy  $50000 \text{ cm}^{-1}$  and grain size of  $100 \text{ cm}^{-1}$ .

Table S1: Cartesian coordinates and all normal mode frequencies of the optimized geometries calculated at M06-2X/aug-cc-pVTZ level of theory.

Species	Cartesian coordinates (Å)			Frequency (cm <sup>-1</sup> )			
HONO	N	0.000000	0.507841	0.000000	578.25	700.42	905.04
	O	0.882551	-0.567177	0.000000	1342.40	1841.11	3830.82
	O	-1.101711	0.141484	0.000000			
	H	1.753278	-0.149345	0.000000			
CH <sub>2</sub> O	O	-0.670517	-0.000022	0.000001	1213.53	1273.49	1539.85
	C	0.525515	0.000000	-0.000003	1869.05	2945.55	3015.83
	H	1.105357	0.938452	0.000006			
	H	1.105686	-0.938280	0.000006			
HONO-WM	N	0.000000	0.000000	0.000000	54.45	126.99	164.70
	O	0.000000	0.000000	1.362978	214.87	251.07	356.84
	H	0.954537	0.000000	1.577834	743.64	823.39	980.20
	O	-1.082840	-0.000091	-0.440978	1471.28	1614.81	1814.28
	O	2.737695	0.038716	1.197557	3575.40	3846.44	3950.86
	H	2.712604	0.000304	0.236470			
	H	3.416194	-0.580443	1.476227			
RC1	O	-2.290632	-0.005198	0.299978	44.59	70.96	89.08
	O	-1.590609	-0.932425	-0.472859	119.04	142.62	183.84
	C	-0.718236	-1.567441	0.123953	255.30	280.56	305.80
	H	-0.160286	-2.289775	-0.459503	375.27	525.15	561.39
	H	-0.595398	-1.422324	1.190966	741.45	791.57	872.48
	N	1.451568	-0.245451	0.037543	1032.26	1105.71	1118.11
	O	1.690969	1.049961	-0.047199	1135.53	1248.03	1444.44
	H	0.765057	1.482418	-0.030813	1583.43	1646.32	1680.44
	O	2.420049	-0.920451	0.034985	1785.44	2704.73	2994.62

	O	-0.669560	1.995074	0.035543	3143.34	3285.91	3921.56
	H	-1.364055	1.274969	0.146618			
	H	-0.978614	2.581815	-0.657373			
CH <sub>2</sub> OO-WM	O	0.000000	0.000000	0.000000	109.89	171.45	222.30
	O	0.000000	0.000000	1.366796	226.96	435.97	535.20
	C	1.093923	0.000000	1.940039	682.82	714.49	895.96
	H	1.051477	-0.020008	3.021832	1079.95	1270.14	1455.41
	H	2.006762	0.014427	1.356032	1640.64	1662.85	3140.67
	O	1.840976	-1.998828	0.163746	3286.46	3550.81	3937.00
	H	1.145356	-1.413054	-0.192863			
	H	1.693010	-2.861436	-0.226231			
PC1	O	-1.146336	-1.213073	0.689277	57.27	79.58	130.36
	O	-0.465321	-1.202523	-0.562042	161.73	235.96	250.35
	C	0.856368	-1.042565	-0.298790	290.72	329.39	432.06
	H	1.422516	-1.293672	-1.193253	504.28	558.79	601.05
	H	1.202243	-1.591157	0.573659	718.46	822.61	926.83
	N	1.232789	0.417018	-0.007153	969.17	1117.98	1224.96
	O	0.415026	1.286025	-0.201169	1302.74	1375.26	1452.86
	H	-1.571988	1.401111	-0.260506	1506.26	1549.61	1617.12
	O	2.361362	0.583669	0.374153	1712.63	3115.94	3188.45
	O	-2.423202	1.070396	0.056480	3401.48	3790.83	3931.26
	H	-1.741374	-0.435946	0.571156			
	H	-3.011367	1.059964	-0.701825			
CH <sub>2</sub> OO-HONO	O	1.726645	0.149075	-0.424619	65.11	92.16	142.24
	C	1.420994	1.180380	0.176914	166.18	224.27	273.11
	H	1.576944	2.106624	-0.363474	525.70	695.30	769.68
	H	1.036518	1.112184	1.187704	876.31	1010.42	1052.16

	N	-1.275186	0.258091	0.073861	1107.39	1256.42	1448.64
	O	-1.091003	-1.060534	-0.093082	1557.40	1679.05	1793.75
	H	-0.100623	-1.185359	0.034659	2990.53	3141.61	3286.10
	O	-2.398689	0.584560	-0.031905			
WM	O	0.000000	0.116499	0.000000	1620.74	3866.96	3969.44
	H	0.762335	-0.465889	0.000000			
	H	-0.762335	-0.466105	0.000000			
CH <sub>2</sub> OO	C	1.057098	-0.186174	0.000000	538.15	697.71	927.20
	H	1.006167	-1.269154	0.000000	1023.97	1260.68	1433.37
	H	1.966689	0.398409	0.000000	1630.89	3139.98	3290.59
	O	0.000000	0.459688	0.000000			
	O	-1.164430	-0.211215	0.000000			
TS1	O	-2.168499	-0.265149	0.363952	-192.58	61.31	87.13
	O	-1.351239	-1.032554	-0.495819	157.95	169.02	231.95
	C	-0.365843	-1.535524	0.069640	309.04	343.14	396.47
	H	0.262187	-2.177531	-0.536319	473.41	526.96	642.84
	H	-0.302919	-1.493424	1.150480	809.44	849.00	866.93
	N	1.378564	-0.118013	0.039187	1127.14	1206.42	1235.68
	O	1.413544	1.177659	-0.054333	1245.08	1264.33	1432.32
	H	0.397617	1.511818	-0.046159	1547.21	1636.29	1671.08
	O	2.426002	-0.665711	0.071156	1794.83	1960.53	2462.60
	O	-0.942390	1.883534	0.025921	3148.15	3288.49	3941.63
	H	-1.537902	1.043013	0.173589			
	H	-1.293219	2.373119	-0.720741			
OH	O	0.000000	0.000000	0.107992	3769.62		
	H	0.000000	0.000000	-0.863937			
NO <sub>2</sub>	N	0.000000	0.000000	0.314473	783.52	1465.18	1775.31

	O	0.000000	1.090255	-0.137582			
	O	0.000000	-1.090255	-0.137582			
$RC_{syn}$	O	0.000000	0.000000	0.000000	32.18	46.53	66.87
	O	0.000000	0.000000	1.390754	98.38	128.57	149.61
	C	1.117276	0.000000	1.937487	187.69	218.54	235.42
	N	1.596427	-2.629572	2.583009	292.58	330.03	358.06
	O	1.447251	-3.661967	1.755844	474.02	595.53	674.66
	H	1.105091	-3.246428	0.902117	783.83	817.28	899.26
	O	1.993708	-2.934223	3.650061	976.10	1002.41	1036.71
	C	2.375320	0.050311	1.184035	1090.28	1102.59	1120.00
	H	2.366258	0.958108	0.575131	1369.25	1417.43	1448.19
	H	3.226334	0.027169	1.855929	1470.90	1575.83	1672.42
	H	2.406716	-0.783028	0.480652	1677.40	1790.81	2848.30
	H	1.061664	0.003529	3.020857	3037.49	3064.52	3122.66
	O	0.629156	-2.476467	-0.394229	3192.28	3205.02	3919.16
	H	0.320381	-1.521248	-0.308982			
	H	-0.006813	-2.930764	-0.950408			
$Syn-CH_3CHOO$	C	-0.471838	0.672873	-0.000110	165.46	341.56	449.39
	O	0.769424	0.575000	-0.000074	655.13	820.68	897.06
	O	1.343717	-0.657592	0.000139	936.68	1070.13	1162.88
	C	-1.392753	-0.475360	0.000003	1362.09	1418.97	1441.02
	H	-2.039879	-0.413405	-0.877006	1477.33	1660.72	3064.62
	H	-0.827002	-1.399901	-0.000842	3118.90	3186.86	3208.01
	H	-2.038482	-0.414327	0.878122			
	H	-0.812225	1.703289	-0.000157			
$PC_{syn}$	O	0.000000	0.000000	0.000000	34.67	56.10	122.43
	O	0.000000	0.000000	1.424644	155.23	196.14	218.38

	C	1.293499	0.000000	1.870622	234.84	266.18	299.32
	N	1.887569	-1.434722	1.810293	334.80	370.99	460.85
	O	1.169101	-2.353890	1.490545	500.97	585.17	644.75
	H	-0.597347	-2.647733	0.654714	768.61	820.33	892.63
	O	3.043293	-1.536901	2.131876	921.95	997.95	1073.44
	C	2.243188	0.951114	1.179943	1167.51	1229.87	1326.52
	H	1.787705	1.938953	1.190416	1379.80	1414.62	1487.61
	H	3.190013	0.977359	1.709259	1491.56	1502.07	1551.52
	H	2.405099	0.649211	0.149730	1616.11	1698.15	3101.48
	H	1.229220	0.182194	2.943647	3118.33	3181.71	3199.29
	O	-1.246505	-2.392333	-0.014761	3422.67	3791.23	3933.32
	H	-0.513687	-0.823231	-0.167584			
	H	-2.105556	-2.430755	0.411307			
Syn-CH <sub>3</sub> CHOO-WM	O	0.000000	0.000000	0.000000	83.92	133.15	162.21
	O	0.000000	0.000000	1.375845	205.38	237.49	335.65
	C	1.109534	0.000000	1.940049	431.00	479.80	675.82
	H	1.028125	-0.019777	3.022271	743.44	793.63	908.75
	O	1.060319	-2.503447	0.059795	997.22	1093.51	1123.79
	H	0.559664	-1.697102	-0.178781	1363.27	1416.33	1449.34
	H	0.542033	-3.246985	-0.250920	1474.87	1638.61	1668.15
	C	2.380086	0.037828	1.213265	3043.51	3108.79	3181.91
	H	2.507586	-0.925315	0.707096	3195.92	3498.72	3936.79
	H	2.306783	0.789763	0.425811			
	H	3.207799	0.225439	1.889122			
TS <sub>syn</sub>	O	0.000000	0.000000	0.000000	-557.18	33.08	79.47
	O	0.000000	0.000000	1.415367	136.65	175.53	191.23
	C	1.146683	0.000000	1.940809	221.10	255.21	343.03

	N	1.667580	-2.077950	2.423538	376.38	407.87	456.61
	O	1.422701	-3.133422	1.730380	558.74	653.34	669.16
	H	0.875543	-2.806168	0.787499	737.67	899.70	919.09
	O	2.247464	-2.225245	3.449139	978.38	1000.47	1105.65
	C	2.382790	0.274516	1.178627	1153.57	1281.22	1331.84
	H	2.316210	1.307061	0.825746	1365.43	1385.54	1410.64
	H	3.247473	0.149850	1.823027	1455.38	1475.97	1609.32
	H	2.445235	-0.360749	0.300238	1657.59	1677.35	1786.35
	H	1.112446	0.105173	3.020389	1854.45	3070.03	3153.62
	O	0.300092	-2.392448	-0.274703	3188.14	3202.23	3911.00
	H	0.110217	-1.307310	-0.217069			
	H	-0.523801	-2.850519	-0.454678			
Syn-CH <sub>3</sub> CHOO-HONO	O	-1.022440	-1.389816	-0.428953	59.08	58.44	94.51
	O	-1.361403	-0.658104	0.700512	101.68	155.97	196.25
	C	-1.529230	0.565794	0.573519	275.66	349.71	450.14
	N	1.448777	0.299881	0.094664	648.86	774.66	843.77
	O	1.528062	-0.979194	-0.290260	884.97	929.35	1048.56
	H	0.559532	-1.260403	-0.378857	1068.04	1094.67	1175.06
	O	2.502350	0.806017	0.239210	1373.19	1421.79	1436.99
	C	-1.438881	1.318669	-0.681710	1468.15	1569.82	1690.08
	H	-0.742472	2.144927	-0.532145	1786.22	2895.78	3062.70
	H	-1.119835	0.678897	-1.494913	3123.18	3178.70	3219.65
	H	-2.420961	1.753074	-0.886833			
	H	-1.781586	1.046339	1.515168			
PC <sub>anti</sub>	O	0.000000	0.000000	0.000000	55.74	66.12	134.10
	O	0.000000	0.000000	1.423915	160.35	213.53	224.00
	C	1.302184	0.000000	1.832909	237.92	275.09	284.28

	N	1.945819	-1.385508	1.594495	304.47	339.34	504.88
	O	1.226563	-2.358337	1.540060	512.19	544.75	688.66
	H	-0.540230	-2.672175	0.689657	733.83	814.96	896.57
	O	3.146929	-1.398980	1.531463	926.05	1043.25	1092.19
	C	1.352229	0.259677	3.319500	1162.07	1246.11	1336.40
	H	2.378137	0.188906	3.671684	1370.83	1409.49	1488.57
	H	0.971135	1.259385	3.511542	1493.51	1505.64	1546.89
	H	0.731291	-0.466901	3.840440	1617.88	1706.94	3088.26
	H	1.925328	0.666496	1.240311	3140.15	3172.56	3180.89
	O	-1.180160	-2.428698	0.006707	3415.98	3786.11	3930.82
	H	-0.493412	-0.834724	-0.172586			
	H	-2.046570	-2.483207	0.415888			
Anti-CH <sub>3</sub> CHOO-HONO	O	-0.616573	1.844813	0.169480	66.37	74.39	134.85
	O	-1.299339	0.744665	-0.366819	159.68	182.33	235.22
	C	-1.362495	-0.246970	0.371927	257.37	327.69	354.49
	N	1.393025	-0.447478	0.098224	560.10	780.03	871.61
	O	1.707352	0.821541	-0.160293	894.64	982.14	1075.66
	H	0.828954	1.333596	-0.035489	1096.17	1118.35	1181.82
	O	2.304110	-1.188217	-0.001157	1367.46	1417.51	1460.81
	C	-1.978633	-1.488604	-0.119930	1466.55	1603.12	1697.40
	H	-1.214565	-2.269108	-0.092410	1787.98	2685.06	3064.37
	H	-2.777369	-1.791845	0.557855	3126.47	3183.87	3195.75
	H	-2.355182	-1.367322	-1.130703			
	H	-0.950640	-0.141939	1.371512			
Anti-CH <sub>3</sub> CHOO-WM	O	0.000000	0.000000	0.000000	78.06	139.87	171.75
	O	0.000000	0.000000	1.387237	221.16	243.43	293.05
	C	1.108151	0.000000	1.939197	336.10	479.42	563.77

	H	1.983128	0.046899	1.297202	764.58	877.75	898.75
	O	1.673139	-2.093205	0.298476	987.88	1111.64	1179.44
	H	1.025256	-1.465234	-0.088166	1375.81	1423.84	1464.26
	H	1.473886	-2.950620	-0.079666	1468.14	1654.39	1693.53
	C	1.187916	-0.085568	3.407872	3064.91	3125.73	3180.21
	H	1.780132	0.744934	3.793624	3192.28	3443.33	3936.77
	H	0.197898	-0.088165	3.853653			
	H	1.716082	-1.007043	3.662818			
TS <sub>anti</sub>	O	0.000000	0.000000	0.000000	-762.93	49.68	87.08
	O	0.000000	0.000000	1.417936	136.37	150.00	205.50
	C	1.153106	0.000000	1.913403	238.16	247.15	285.42
	N	1.856257	-2.194341	1.934882	336.35	414.34	425.53
	O	1.446136	-3.190921	1.242042	545.85	553.82	642.59
	H	0.610549	-2.824372	0.511591	686.91	895.84	907.80
	O	2.744020	-2.407777	2.701994	941.74	1023.10	1111.61
	C	1.291402	0.180772	3.370702	1181.46	1281.68	1354.39
	H	2.136870	-0.400937	3.730406	1390.22	1418.01	1449.96
	H	1.499252	1.238822	3.548690	1457.43	1479.85	1585.86
	H	0.375450	-0.098838	3.883222	1618.92	1657.70	1753.77
	H	1.980540	0.132313	1.224933	1768.59	3066.58	3144.37
	O	-0.222889	-2.387516	-0.286778	3188.56	3204.82	3914.61
	H	-0.186241	-1.277525	-0.215418			
	H	-1.113629	-2.704655	-0.124114			
CH <sub>3</sub> CHO	O	1.225110	-0.277160	0.000012	157.93	513.52	775.87
	C	0.233225	0.397942	-0.000028	901.03	1138.42	1145.81
	C	-1.162542	-0.147780	0.000016	1380.62	1430.18	1464.97
	H	-1.695786	0.224423	-0.876544	1474.83	1866.20	2944.54

	H	-1.148137	-1.233950	-0.000521	3062.92	3125.06	3180.09
	H	-1.695288	0.223800	0.877120			
	H	0.314228	1.502036	-0.000078			
$RC_{anti}$	O	0.000000	0.000000	0.000000	38.41	74.70	87.30
	O	0.000000	0.000000	1.402033	116.38	150.27	177.34
	C	1.119924	0.000000	1.931327	197.78	235.20	254.28
	N	1.805404	-2.633315	1.891567	293.82	311.05	334.04
	O	1.519935	-3.638411	1.090127	404.14	560.52	571.39
	H	0.864991	-3.239223	0.407996	794.59	887.24	895.89
	O	2.552328	-2.914181	2.767149	988.80	1076.48	1121.26
	C	1.243766	0.029365	3.396390	1132.59	1151.87	1182.72
	H	1.885163	-0.799130	3.703494	1366.77	1421.91	1462.58
	H	1.743736	0.956145	3.685278	1471.76	1577.65	1641.85
	H	0.270482	-0.036932	3.872808	1694.53	1771.22	2626.90
	H	1.975117	0.021873	1.261113	2904.37	3061.68	3122.97
	O	-0.056536	-2.508822	-0.533297	3178.50	3190.37	3925.10
	H	-0.078980	-1.510374	-0.362531			
Anti-CH <sub>3</sub> CHOO	H	-0.964055	-2.805213	-0.621580	167.15	268.67	329.13
	C	-0.370064	0.399514	0.000016	566.06	883.70	900.51
	O	0.566273	-0.412482	-0.000063	985.38	1094.93	1168.55
	O	1.839961	0.076479	-0.000032	1362.72	1421.60	1467.69
	C	-1.762798	-0.093107	0.000051	1469.48	1674.11	3064.67
	H	-2.286611	0.288683	-0.877786	3121.08	3165.13	3183.30
	H	-1.783663	-1.179059	-0.000432			
	H	-2.286246	0.287845	0.878481			
	H	-0.096187	1.452105	0.000090			
RC2	O	-1.518340	1.689900	-0.050877	24.22	42.14	78.71

	O	-1.477583	0.467666	-0.726720	92.78	114.92	156.56
	C	-1.361833	-0.553042	-0.013337	170.33	213.93	226.21
	N	1.488350	-0.702493	-0.033268	237.75	282.24	305.08
	O	2.411776	0.239245	0.062287	340.63	378.69	401.83
	H	1.883679	1.109990	-0.003208	497.86	566.82	602.52
	O	1.924161	-1.801742	0.022284	789.87	824.19	919.29
	O	0.968107	2.335704	-0.063622	954.03	995.68	1061.59
	H	-0.025051	2.135842	-0.078774	1091.69	1104.81	1116.26
	H	1.136366	2.982401	-0.751385	1129.57	1319.28	1387.00
	C	-1.303220	-0.442021	1.454586	1415.04	1448.95	1465.55
	H	-2.230612	0.022346	1.797341	1474.93	1488.51	1574.64
	H	-1.154070	-1.416179	1.909189	1649.44	1665.12	1773.32
	H	-0.506769	0.250690	1.725141	2697.24	2923.85	3062.50
	C	-1.336358	-1.850692	-0.722312	3070.19	3124.98	3131.96
	H	-0.409138	-2.365471	-0.462045	3187.55	3191.06	3923.12
	H	-2.166977	-2.463272	-0.367084			
	H	-1.402375	-1.710554	-1.796739			
PC2	O	1.028164	-1.300551	-0.811183	48.70	49.77	124.27
	O	0.369047	-1.093622	0.433834	154.86	196.15	212.48
	C	-0.814113	-0.425203	0.208940	218.66	240.70	261.32
	N	-0.472760	1.055400	-0.171621	270.36	301.05	334.48
	O	0.577449	1.516056	0.220348	358.72	400.09	502.28
	H	2.409114	0.809454	0.378329	507.80	571.85	597.57
	O	-1.310169	1.669680	-0.778583	751.87	809.88	864.95
	O	3.096128	0.197524	0.079372	894.46	961.87	982.93
	H	1.885966	-0.858770	-0.618474	1030.40	1076.99	1180.42
	H	3.535589	-0.121738	0.870513	1275.49	1315.28	1404.37

	C	-1.668856	-1.016632	-0.889934	1418.43	1478.11	1482.94
	H	-1.810029	-2.070319	-0.655362	1488.76	1497.61	1511.19
	H	-2.632457	-0.518451	-0.927482	1547.67	1617.64	1695.19
	H	-1.178539	-0.931224	-1.854301	3085.29	3097.72	3170.22
	C	-1.509307	-0.333229	1.553804	3172.85	3178.71	3198.67
	H	-1.812204	-1.334066	1.853405	3432.70	3780.65	3931.55
	H	-0.829457	0.075605	2.298389			
	H	-2.389950	0.299392	1.469165			
(CH <sub>3</sub> ) <sub>2</sub> COO-WM	O	0.985885	1.340866	0.335000	57.53	132.61	157.41
	O	-0.160359	0.999263	-0.367179	174.26	211.38	215.89
	C	-0.826053	0.035157	0.067757	316.56	339.16	376.41
	O	2.029418	-0.994346	-0.525791	459.55	507.75	604.75
	H	1.889565	-0.068127	-0.230349	794.77	828.78	916.64
	H	2.767329	-0.974441	-1.136330	950.72	993.44	1090.44
	C	-2.011454	-0.348516	-0.736432	1108.55	1317.19	1387.69
	H	-2.904616	-0.305696	-0.112050	1410.29	1451.19	1464.85
	H	-2.122392	0.298729	-1.600808	1474.16	1492.57	1647.08
	H	-1.889506	-1.384187	-1.058893	1664.15	3054.83	3067.78
	C	-0.437619	-0.663002	1.303744	3120.10	3128.09	3182.46
	H	0.485370	-1.215036	1.102753	3186.46	3418.29	3937.02
	H	-0.191819	0.080609	2.062241			
	H	-1.222729	-1.339954	1.626785			
(CH <sub>3</sub> ) <sub>2</sub> CO	O	0.000013	1.390777	0.000002	39.22	146.55	384.06
	C	-0.000006	0.185947	-0.000013	494.19	541.14	806.77
	C	-1.282412	-0.610523	0.000004	889.07	898.61	1087.27
	H	-2.136940	0.059123	0.000233	1126.38	1251.18	1388.77
	H	-1.315928	-1.258270	-0.877237	1398.10	1462.58	1468.95

	H	-1.315694	-1.258605	0.877009	1473.72	1492.86	1848.60
	C	1.282400	-0.610541	-0.000005	3063.45	3069.03	3125.10
	H	1.315922	-1.258224	0.877284	3131.99	3180.56	3181.53
	H	1.315719	-1.258660	-0.876975			
	H	2.136918	0.059119	-0.000245			
TS2	O	-1.595005	1.539644	0.022326	-983.16	36.93	77.27
	O	-1.428598	0.341242	-0.704379	111.68	129.49	137.93
	C	-1.106546	-0.666828	-0.014578	185.99	199.86	245.44
	N	1.405466	-0.531162	-0.048055	284.79	302.30	354.58
	O	2.151617	0.497828	0.062855	392.09	399.74	473.84
	H	1.398858	1.492147	-0.029300	528.01	589.93	663.57
	O	1.951820	-1.600485	0.010709	704.07	823.12	892.17
	O	0.651678	2.374371	-0.088822	923.70	984.47	1003.26
	H	-0.490929	2.005714	-0.061314	1100.31	1104.19	1269.52
	H	0.833353	2.919187	-0.857362	1322.41	1349.59	1400.73
	C	-1.049803	-0.615071	1.460301	1412.72	1447.28	1454.94
	H	-0.599510	-1.526452	1.841054	1467.43	1474.22	1486.34
	H	-0.511179	0.264675	1.797299	1493.27	1600.41	1629.90
	H	-2.079899	-0.521298	1.817194	1637.47	1761.32	3059.06
	C	-1.038540	-1.942658	-0.754940	3066.78	3125.05	3157.07
	H	-0.088537	-2.425551	-0.519600	3189.68	3206.42	3912.64
	H	-1.846944	-2.582926	-0.393992			
	H	-1.136241	-1.780826	-1.823807			
(CH <sub>3</sub> ) <sub>2</sub> COO-HONO	O	-0.323346	1.788465	-0.127155	40.99	65.31	94.87
	O	-0.933456	0.707341	-0.762464	143.89	165.08	182.43
	C	-1.427404	-0.163929	-0.015067	184.81	254.84	336.26
	N	1.668747	-0.491904	0.103393	357.82	376.50	494.42

	O	2.027385	0.754380	-0.212701	601.23	778.14	824.83
	H	1.149904	1.272513	-0.192924	905.48	949.75	992.83
	O	2.575100	-1.246430	0.120319	1062.31	1084.87	1100.49
	C	-2.010313	-1.343730	-0.692483	1107.66	1317.65	1381.08
	H	-1.444347	-2.223239	-0.376851	1406.82	1448.86	1461.75
	H	-3.040077	-1.483491	-0.362789	1471.93	1488.83	1579.39
	H	-1.962298	-1.240373	-1.771878	1668.58	1779.74	2780.97
	C	-1.402643	-0.006457	1.447276	3065.31	3070.72	3128.64
	H	-0.357500	0.003060	1.763655	3129.22	3189.96	3191.10
	H	-1.801638	0.976862	1.699490			
	H	-1.948582	-0.807358	1.935197			
(CH <sub>3</sub> ) <sub>2</sub> COO	C	0.371062	0.018585	0.000050	161.48	208.25	291.02
	O	-0.558411	-0.817590	-0.000008	329.95	366.36	493.49
	O	-1.838845	-0.328935	-0.000003	609.82	827.33	925.08
	C	0.053885	1.456083	-0.000006	953.09	989.39	1085.66
	H	-0.578150	1.668238	0.865389	1102.01	1316.06	1393.97
	H	0.954341	2.062465	-0.000046	1411.69	1442.13	1466.96
	H	-0.578203	1.668145	-0.865370	1474.33	1486.77	1654.07
	C	1.752599	-0.524309	0.000001	3059.28	3065.43	3109.82
	H	2.288094	-0.158843	0.877727	3121.90	3182.23	3183.88
	H	1.739149	-1.610169	0.000607			
	H	2.287541	-0.159787	-0.878484			

Table S2: Termolecular rate constants ( $k_t$ ) (in  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ) and total termolecular rate constant ( $k_t^{\text{total}}$ ) for the WM catalysed  $\text{CH}_2\text{OO} + \text{HONO}$  reactions over the temperature range of 213–320 K, for all three paths, i.e., Path-A, Path-B, and Path-C.

Temp.	$k_t^{\text{Path-A}}$	$k_t^{\text{Path-B}}$	$k_t^{\text{Path-C}}$	$k_t^{\text{total}}$
213	$8.26 \times 10^{-27}$	$1.09 \times 10^{-29}$	$3.16 \times 10^{-29}$	$8.30 \times 10^{-27}$
216	$5.51 \times 10^{-27}$	$8.73 \times 10^{-30}$	$2.41 \times 10^{-29}$	$5.54 \times 10^{-27}$
219	$3.70 \times 10^{-27}$	$6.98 \times 10^{-30}$	$1.85 \times 10^{-29}$	$3.73 \times 10^{-27}$
224	$1.95 \times 10^{-27}$	$4.85 \times 10^{-30}$	$1.20 \times 10^{-29}$	$1.97 \times 10^{-27}$
235	$5.20 \times 10^{-28}$	$2.28 \times 10^{-30}$	$4.89 \times 10^{-30}$	$5.27 \times 10^{-28}$
250	$1.00 \times 10^{-28}$	$8.67 \times 10^{-31}$	$1.59 \times 10^{-30}$	$1.03 \times 10^{-28}$
259	$4.06 \times 10^{-29}$	$5.03 \times 10^{-31}$	$8.52 \times 10^{-31}$	$4.19 \times 10^{-29}$
265	$2.28 \times 10^{-29}$	$3.54 \times 10^{-31}$	$5.72 \times 10^{-31}$	$2.38 \times 10^{-29}$
278	$7.07 \times 10^{-30}$	$1.71 \times 10^{-31}$	$2.50 \times 10^{-31}$	$7.49 \times 10^{-30}$
280	$5.95 \times 10^{-30}$	$1.53 \times 10^{-31}$	$2.22 \times 10^{-31}$	$6.33 \times 10^{-30}$
290	$2.60 \times 10^{-30}$	$9.02 \times 10^{-32}$	$1.23 \times 10^{-31}$	$2.81 \times 10^{-30}$
298	$1.38 \times 10^{-30}$	$5.96 \times 10^{-32}$	$7.82 \times 10^{-32}$	$1.52 \times 10^{-30}$
300	$1.19 \times 10^{-30}$	$5.40 \times 10^{-32}$	$7.00 \times 10^{-32}$	$1.31 \times 10^{-30}$
310	$5.67 \times 10^{-31}$	$3.33 \times 10^{-32}$	$4.10 \times 10^{-32}$	$6.42 \times 10^{-31}$
320	$2.82 \times 10^{-31}$	$2.06 \times 10^{-32}$	$2.46 \times 10^{-32}$	$3.27 \times 10^{-31}$

Table S3: Termolecular rate constants ( $k_t$ ) (in  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ) and total termolecular rate constant ( $k_t^{\text{total}}$ ) for the WM catalysed  $(\text{CH}_3)_2\text{OO} + \text{HONO}$  reactions over the temperature range of 213–320 K, for all three paths, i.e., Path-A, Path-B, and Path-C.

Temp.	$k_t^{\text{Path-A}}$	$k_t^{\text{Path-B}}$	$k_t^{\text{Path-C}}$	$k_t^{\text{total}}$
213	$1.03 \times 10^{-22}$	$3.79 \times 10^{-29}$	$6.05 \times 10^{-27}$	$1.03 \times 10^{-22}$
216	$6.02 \times 10^{-23}$	$3.13 \times 10^{-29}$	$4.37 \times 10^{-27}$	$6.02 \times 10^{-23}$
219	$3.55 \times 10^{-23}$	$2.60 \times 10^{-29}$	$3.18 \times 10^{-27}$	$3.55 \times 10^{-23}$
224	$1.52 \times 10^{-23}$	$1.93 \times 10^{-29}$	$1.91 \times 10^{-27}$	$1.52 \times 10^{-23}$
235	$2.61 \times 10^{-24}$	$1.04 \times 10^{-29}$	$6.57 \times 10^{-28}$	$2.61 \times 10^{-24}$
250	$2.97 \times 10^{-25}$	$4.84 \times 10^{-30}$	$1.73 \times 10^{-28}$	$2.97 \times 10^{-25}$
259	$9.01 \times 10^{-26}$	$3.16 \times 10^{-30}$	$8.27 \times 10^{-29}$	$9.02 \times 10^{-26}$
265	$4.24 \times 10^{-26}$	$2.39 \times 10^{-30}$	$5.17 \times 10^{-29}$	$4.24 \times 10^{-26}$
278	$9.14 \times 10^{-27}$	$1.35 \times 10^{-30}$	$1.96 \times 10^{-29}$	$9.16 \times 10^{-27}$
280	$7.31 \times 10^{-27}$	$1.24 \times 10^{-30}$	$1.70 \times 10^{-29}$	$7.33 \times 10^{-27}$
290	$2.48 \times 10^{-27}$	$8.13 \times 10^{-31}$	$8.52 \times 10^{-30}$	$2.49 \times 10^{-27}$
298	$1.10 \times 10^{-27}$	$5.86 \times 10^{-31}$	$5.03 \times 10^{-30}$	$1.10 \times 10^{-27}$
300	$9.03 \times 10^{-28}$	$5.40 \times 10^{-31}$	$4.42 \times 10^{-30}$	$9.08 \times 10^{-28}$
310	$3.49 \times 10^{-28}$	$3.62 \times 10^{-31}$	$2.36 \times 10^{-30}$	$3.51 \times 10^{-28}$
320	$1.42 \times 10^{-28}$	$2.44 \times 10^{-31}$	$1.30 \times 10^{-30}$	$1.43 \times 10^{-28}$

Table S4: Termolecular rate constants ( $k_t$ ) (in  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ) and total termolecular rate constant ( $k_t^{total}$ ) for the WM catalysed anti- $\text{CH}_3\text{CHOO} + \text{HONO}$  reactions over the temperature range of 213–320 K, for all three paths, i.e., Path-A, Path-B, and Path-C.

Temp.	$k_t^{Path-A}$	$k_t^{Path-B}$	$k_t^{Path-C}$	$k_t^{total}$
213	$2.90 \times 10^{-23}$	$2.03 \times 10^{-29}$	$1.48 \times 10^{-26}$	$2.90 \times 10^{-23}$
216	$1.69 \times 10^{-23}$	$1.62 \times 10^{-29}$	$1.06 \times 10^{-26}$	$1.70 \times 10^{-23}$
219	$1.00 \times 10^{-23}$	$1.30 \times 10^{-29}$	$7.65 \times 10^{-27}$	$1.00 \times 10^{-23}$
224	$4.33 \times 10^{-24}$	$9.12 \times 10^{-30}$	$4.53 \times 10^{-27}$	$4.33 \times 10^{-24}$
235	$7.96 \times 10^{-25}$	$4.36 \times 10^{-30}$	$1.51 \times 10^{-27}$	$7.97 \times 10^{-25}$
250	$9.54 \times 10^{-26}$	$1.73 \times 10^{-30}$	$3.81 \times 10^{-28}$	$9.58 \times 10^{-26}$
259	$2.99 \times 10^{-26}$	$1.03 \times 10^{-30}$	$1.77 \times 10^{-28}$	$3.00 \times 10^{-26}$
265	$1.44 \times 10^{-26}$	$7.37 \times 10^{-31}$	$1.08 \times 10^{-28}$	$1.45 \times 10^{-26}$
278	$3.25 \times 10^{-27}$	$3.71 \times 10^{-31}$	$3.93 \times 10^{-29}$	$3.29 \times 10^{-27}$
280	$2.62 \times 10^{-27}$	$3.35 \times 10^{-31}$	$3.37 \times 10^{-29}$	$2.65 \times 10^{-27}$
290	$9.25 \times 10^{-28}$	$2.04 \times 10^{-31}$	$1.63 \times 10^{-29}$	$9.42 \times 10^{-28}$
298	$4.22 \times 10^{-28}$	$1.39 \times 10^{-31}$	$9.25 \times 10^{-30}$	$4.31 \times 10^{-28}$
300	$3.48 \times 10^{-28}$	$1.27 \times 10^{-31}$	$8.08 \times 10^{-30}$	$3.57 \times 10^{-28}$
310	$1.39 \times 10^{-28}$	$8.06 \times 10^{-32}$	$4.13 \times 10^{-30}$	$1.44 \times 10^{-28}$
320	$5.85 \times 10^{-29}$	$5.19 \times 10^{-32}$	$2.18 \times 10^{-30}$	$6.08 \times 10^{-29}$

Table S5: Termolecular rate constants ( $k_t$ ) (in  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ) and total termolecular rate constant ( $k_t^{total}$ ) for the WM catalysed syn- $\text{CH}_3\text{CHOO} + \text{HONO}$  reactions over the temperature range of 213–320 K, for all three paths, i.e., Path-A, Path-B, and Path-C.

Temp.	$k_t^{Path-A}$	$k_t^{Path-B}$	$k_t^{Path-C}$	$k_t^{total}$
213	$8.06 \times 10^{-23}$	$3.01 \times 10^{-29}$	$1.79 \times 10^{-26}$	$8.06 \times 10^{-23}$
216	$4.82 \times 10^{-23}$	$2.46 \times 10^{-29}$	$1.25 \times 10^{-26}$	$4.82 \times 10^{-23}$
219	$2.75 \times 10^{-23}$	$2.00 \times 10^{-29}$	$8.64 \times 10^{-27}$	$2.75 \times 10^{-23}$
224	$1.24 \times 10^{-23}$	$1.44 \times 10^{-29}$	$4.87 \times 10^{-27}$	$1.24 \times 10^{-23}$
235	$2.08 \times 10^{-24}$	$7.28 \times 10^{-30}$	$1.51 \times 10^{-27}$	$2.08 \times 10^{-24}$
250	$2.40 \times 10^{-25}$	$3.01 \times 10^{-30}$	$3.50 \times 10^{-28}$	$2.41 \times 10^{-25}$
259	$7.46 \times 10^{-26}$	$1.80 \times 10^{-30}$	$1.55 \times 10^{-28}$	$7.48 \times 10^{-26}$
265	$3.55 \times 10^{-26}$	$1.27 \times 10^{-30}$	$9.44 \times 10^{-29}$	$3.56 \times 10^{-26}$
278	$7.82 \times 10^{-27}$	$6.55 \times 10^{-31}$	$3.31 \times 10^{-29}$	$7.85 \times 10^{-27}$
280	$6.23 \times 10^{-27}$	$5.99 \times 10^{-31}$	$2.84 \times 10^{-29}$	$6.26 \times 10^{-27}$
290	$2.15 \times 10^{-27}$	$3.61 \times 10^{-31}$	$1.35 \times 10^{-29}$	$2.16 \times 10^{-27}$
298	$9.75 \times 10^{-28}$	$2.51 \times 10^{-31}$	$7.60 \times 10^{-30}$	$9.83 \times 10^{-28}$
300	$8.05 \times 10^{-28}$	$2.28 \times 10^{-31}$	$6.67 \times 10^{-30}$	$8.12 \times 10^{-28}$
310	$3.20 \times 10^{-28}$	$1.48 \times 10^{-31}$	$3.51 \times 10^{-30}$	$3.24 \times 10^{-28}$
320	$1.32 \times 10^{-28}$	$9.44 \times 10^{-32}$	$1.92 \times 10^{-30}$	$1.34 \times 10^{-28}$

Table S6: Effective rate constants (in  $\text{s}^{-1}$ ) for reaction of  $\text{CH}_2\text{OO}$  with HONO,  $\text{H}_2\text{O}/(\text{H}_2\text{O})_2/\text{SO}_2$  and for WM catalyzed  $\text{CH}_2\text{OO} + \text{HONO}$  reaction over the temperature range of 213–320 K. The concentration are taken  $[\text{HONO}]=8.9\times 10^{10}$  molecule  $\text{cm}^{-3}$ ,  $[\text{SO}_2]=9.0\times 10^{10}$  molecule  $\text{cm}^{-3}$ , and  $[\text{H}_2\text{O}]$  and  $[(\text{H}_2\text{O})_2]$  corresponding to RH=20% and 100%.

Temp.	$k_{eff}^{\text{H}_2\text{O}(RH=20\%)}$	$k_{eff}^{\text{H}_2\text{O}(RH=100\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=20\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=100\%)}$	$k_{eff}^{\text{HONO}}$	$k_{eff}^{\text{HONO}(RH=20\%)}$	$k_{eff}^{\text{HONO}(RH=100\%)}$	$k_{\text{unimolecular}}$	$k_{eff}^{\text{SO}_2}$
213	$4.91\times 10^{-3}$	$2.45\times 10^{-2}$	$7.42\times 10^{-2}$	1.85	1.04	$5.01\times 10^{-2}$	$2.50\times 10^{-1}$	$5.34\times 10^{-8}$	
216	$7.80\times 10^{-3}$	$3.90\times 10^{-2}$	$1.76\times 10^{-1}$	4.41	1.02	$4.95\times 10^{-2}$	$2.47\times 10^{-1}$	$1.03\times 10^{-7}$	
219	$1.23\times 10^{-2}$	$6.13\times 10^{-2}$	$3.99\times 10^{-1}$	9.97	1.01	$4.88\times 10^{-2}$	$2.44\times 10^{-1}$	$1.94\times 10^{-7}$	
223									5.76
224	$2.53\times 10^{-2}$	$1.26\times 10^{-1}$	$7.34\times 10^{-1}$	$1.83\times 10^1$	0.98	$4.76\times 10^{-2}$	$2.38\times 10^{-1}$	$5.38\times 10^{-7}$	
235	$1.11\times 10^{-1}$	$5.54\times 10^{-1}$	2.11	$5.28\times 10^1$	0.93	$4.45\times 10^{-2}$	$2.22\times 10^{-1}$	$4.37\times 10^{-6}$	
250	$6.69\times 10^{-1}$	3.35	9.66	$2.42\times 10^2$	0.85	$3.97\times 10^{-2}$	$1.98\times 10^{-1}$	$5.65\times 10^{-5}$	
259	1.77	8.87	$2.54\times 10^1$	$6.35\times 10^2$	0.81	$3.68\times 10^{-2}$	$1.84\times 10^{-1}$	$2.28\times 10^{-4}$	4.95
265	3.27	$1.63\times 10^1$	$3.66\times 10^1$	$9.15\times 10^2$	0.78	$3.49\times 10^{-2}$	$1.75\times 10^{-1}$	$5.47\times 10^{-4}$	
266									3.96
275									3.69
278	$1.12\times 10^1$	$5.59\times 10^1$			0.72	$3.11\times 10^{-2}$	$1.55\times 10^{-1}$	$3.21\times 10^{-3}$	
280	$1.25\times 10^1$	$6.26\times 10^1$	$1.04\times 10^2$	$2.60\times 10^3$	0.71	$2.86\times 10^{-2}$	$1.43\times 10^{-1}$	$4.15\times 10^{-3}$	
281									3.69
290	$2.67\times 10^1$	$1.34\times 10^2$	$1.76\times 10^2$	$4.39\times 10^3$	0.67	$2.37\times 10^{-2}$	$1.19\times 10^{-1}$	$1.43\times 10^{-2}$	
296									3.6
298	$4.77\times 10^1$	$2.39\times 10^2$	$2.61\times 10^2$	$6.52\times 10^3$	0.64	$2.04\times 10^{-2}$	$1.02\times 10^{-1}$	$3.61\times 10^{-2}$	
300	$5.40\times 10^1$	$2.70\times 10^2$	$2.82\times 10^2$	$7.05\times 10^3$	0.63	$1.97\times 10^{-2}$	$9.85\times 10^{-2}$	$4.52\times 10^{-2}$	
310	$1.03\times 10^2$	$5.17\times 10^2$	$4.35\times 10^2$	$1.09\times 10^4$	0.60	$1.64\times 10^{-2}$	$8.21\times 10^{-2}$	$1.33\times 10^{-1}$	
316									3.78
320	$1.89\times 10^2$	$9.46\times 10^2$	$6.45\times 10^2$	$1.61\times 10^4$	0.56	$1.37\times 10^{-2}$	$6.86\times 10^{-2}$	$3.65\times 10^{-1}$	

Table S7: Effective rate constants (in  $\text{s}^{-1}$ ) for reaction of  $(\text{CH}_3)_2\text{COO}$  with HONO,  $\text{H}_2\text{O}/(\text{H}_2\text{O})_2/\text{SO}_2$  and for WM catalyzed  $(\text{CH}_3)_2\text{COO} + \text{HONO}$  reaction over the temperature range of 213–320 K. The concentration are taken  $[\text{HONO}]=8.9\times 10^{10}$  molecule  $\text{cm}^{-3}$ ,  $[\text{SO}_2]=9.0\times 10^{10}$  molecule  $\text{cm}^{-3}$ , and  $[\text{H}_2\text{O}]$  and  $[(\text{H}_2\text{O})_2]$  corresponding to RH=20% and 100%.

Temp.	$k_{eff}^{\text{H}_2\text{O}(RH=20\%)}$	$k_{eff}^{\text{H}_2\text{O}(RH=100\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=20\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=100\%)}$	$k_{eff}^{\text{HONO}}$	$k_{eff}^{\text{HONO}(RH=20\%)}$	$k_{eff}^{\text{HONO}(RH=100\%)}$	$k_{\text{unimolecular}}$	$k_{eff}^{\text{SO}_2}$
213	$2.83\times 10^{-5}$	$1.41\times 10^{-4}$	$1.35\times 10^{-6}$	$3.38\times 10^{-5}$	3.80	$6.23\times 10^2$	$3.12\times 10^3$	1.82	
216	$4.80\times 10^{-5}$	$2.40\times 10^{-4}$	$4.11\times 10^{-6}$	$1.03\times 10^{-4}$	3.71	$5.38\times 10^2$	$2.69\times 10^3$	2.18	
219	$8.03\times 10^{-5}$	$4.02\times 10^{-4}$	$1.19\times 10^{-5}$	$2.96\times 10^{-4}$	3.64	$4.64\times 10^2$	$2.32\times 10^3$	2.60	
224	$1.84\times 10^{-4}$	$9.18\times 10^{-4}$	$3.22\times 10^{-5}$	$8.05\times 10^{-4}$	3.50	$3.66\times 10^2$	$1.83\times 10^3$	3.49	
235	$9.98\times 10^{-4}$	$4.99\times 10^{-3}$	$2.07\times 10^{-4}$	$5.17\times 10^{-3}$	3.21	$2.20\times 10^2$	$1.10\times 10^3$	6.73	
250	$7.87\times 10^{-3}$	$3.94\times 10^{-2}$	$2.53\times 10^{-3}$	$6.33\times 10^{-2}$	2.83	$1.15\times 10^2$	$5.73\times 10^2$	$1.65\times 10^1$	
259	$2.42\times 10^{-2}$	$1.21\times 10^{-1}$	$1.14\times 10^{-2}$	$2.85\times 10^{-1}$	2.61	$7.92\times 10^1$	$3.96\times 10^2$	$2.81\times 10^1$	
265	$4.90\times 10^{-2}$	$2.45\times 10^{-1}$	$2.31\times 10^{-2}$	$5.79\times 10^{-1}$	2.47	$6.24\times 10^1$	$3.12\times 10^2$	$4.01\times 10^1$	
278	$2.04\times 10^{-1}$	1.02			2.19	$3.80\times 10^1$	$1.90\times 10^2$	$8.63\times 10^1$	
280	$2.35\times 10^{-1}$	1.17	$1.45\times 10^{-1}$	3.64	2.15	$3.31\times 10^1$	$1.65\times 10^2$	$9.70\times 10^1$	
283									1.71
285									1.63
290	$5.77\times 10^{-1}$	2.89	$3.99\times 10^{-1}$	9.96	1.95	$2.10\times 10^1$	$1.05\times 10^2$	$1.73\times 10^2$	1.46
295									1.31
298	1.13	5.65	$8.54\times 10^{-1}$	$2.13\times 10^1$	1.80	$1.48\times 10^1$	$7.42\times 10^1$	$2.75\times 10^2$	1.22
300	1.33	6.64	1.01	$2.52\times 10^1$	1.77	$1.36\times 10^1$	$6.82\times 10^1$	$3.09\times 10^2$	1.17
303									1.1
310	2.89	$1.44\times 10^1$	2.38	$5.96\times 10^1$	1.60	8.99	$4.50\times 10^1$	$5.45\times 10^2$	
320	5.96	$2.98\times 10^1$	5.30	$1.32\times 10^2$	1.44	6.02	$3.01\times 10^1$	$9.57\times 10^2$	

Table S8: Effective rate constants (in  $\text{s}^{-1}$ ) for reaction of anti- $\text{CH}_3\text{CHOO}$  with  $\text{HONO}$ ,  $\text{H}_2\text{O}/(\text{H}_2\text{O})_2/\text{SO}_2$  and for WM catalyzed anti- $\text{CH}_3\text{CHOO} + \text{HONO}$  reaction over the temperature range of 213–320 K. The concentration are taken  $[\text{HONO}]=8.9\times 10^{10}$  molecule  $\text{cm}^{-3}$ ,  $[\text{SO}_2]=9.0\times 10^{10}$  molecule  $\text{cm}^{-3}$ , and  $[\text{H}_2\text{O}]$  and  $[(\text{H}_2\text{O})_2]$  corresponding to RH=20% and 100%.

Temp.	$k_{eff}^{\text{H}_2\text{O}(RH=20\%)}$	$k_{eff}^{\text{H}_2\text{O}(RH=100\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=20\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=100\%)}$	$k_{eff}^{\text{HONO}}$	$k_{eff}^{\text{HONO}(RH=20\%)}$	$k_{eff}^{\text{HONO}(RH=100\%)}$	$k_{unimolecular}$	$k_{eff}^{\text{SO}_2}$
213	1.80	8.98	$2.99\times 10^{-2}$	$7.48\times 10^{-1}$	8.38	$1.75\times 10^2$	$8.74\times 10^2$	$1.55\times 10^{-3}$	
216	2.64	$1.32\times 10^1$	$8.00\times 10^{-2}$	2.00	8.39	$1.51\times 10^2$	$7.57\times 10^2$	$2.57\times 10^{-3}$	
219	3.83	$1.92\times 10^1$	$2.03\times 10^{-1}$	5.08	8.39	$1.31\times 10^2$	$6.55\times 10^2$	$4.20\times 10^{-3}$	
224	6.98	$3.49\times 10^1$	$4.49\times 10^{-1}$	$1.12\times 10^1$	8.39	$1.05\times 10^2$	$5.23\times 10^2$	$9.25\times 10^{-3}$	
235	$2.38\times 10^1$	$1.19\times 10^2$	1.89	$4.73\times 10^1$	8.32	$6.73\times 10^1$	$3.36\times 10^2$	$4.68\times 10^{-2}$	
250	$1.06\times 10^2$	$5.31\times 10^2$	$1.38\times 10^1$	$3.46\times 10^2$	8.13	$3.69\times 10^1$	$1.85\times 10^2$	$3.40\times 10^{-1}$	
259	$2.39\times 10^2$	$1.19\times 10^3$	$4.71\times 10^1$	$1.18\times 10^3$	7.97	$2.64\times 10^1$	$1.32\times 10^2$	1.00	
265	$3.98\times 10^2$	$1.99\times 10^3$	$7.99\times 10^1$	$2.00\times 10^3$	7.85	$2.13\times 10^1$	$1.07\times 10^2$	1.99	
278	$1.11\times 10^3$	$5.55\times 10^3$	$7.99\times 10^1$	$2.00\times 10^3$	7.55	$1.36\times 10^1$	$6.82\times 10^1$	7.88	
280	$1.21\times 10^3$	$6.04\times 10^3$	$3.32\times 10^2$	$8.30\times 10^3$	7.50	$1.20\times 10^1$	$5.98\times 10^1$	9.64	
290	$2.24\times 10^3$	$1.12\times 10^4$	$7.07\times 10^2$	$1.77\times 10^4$	7.23	7.95	$3.97\times 10^1$	$2.53\times 10^1$	
293									
295									
298	$3.56\times 10^3$	$1.78\times 10^4$	$1.25\times 10^3$	$3.13\times 10^4$	7.01	5.79	$2.89\times 10^1$	$5.22\times 10^1$	6.03
300	$3.98\times 10^3$	$1.99\times 10^4$	$1.41\times 10^3$	$3.53\times 10^4$	6.95	5.35	$2.68\times 10^1$	$6.23\times 10^1$	
310	$6.77\times 10^3$	$3.39\times 10^4$	$2.68\times 10^3$	$6.69\times 10^4$	6.65	3.68	$1.84\times 10^1$	$1.45\times 10^2$	
320	$1.11\times 10^4$	$5.55\times 10^4$	$4.83\times 10^3$	$1.21\times 10^5$	6.35	2.55	$1.27\times 10^1$	$3.20\times 10^2$	

Table S9: Effective rate constants (in  $\text{s}^{-1}$ ) for reaction of syn- $\text{CH}_3\text{CHOO}$  with  $\text{HONO}$ ,  $\text{H}_2\text{O}/(\text{H}_2\text{O})_2/\text{SO}_2$  and for WM catalyzed syn- $\text{CH}_3\text{CHOO} + \text{HONO}$  reaction over the temperature range of 213–320 K. The concentration are taken  $[\text{HONO}]=8.9\times 10^{10}$  molecule  $\text{cm}^{-3}$ ,  $[\text{SO}_2]=9.0\times 10^{10}$  molecule  $\text{cm}^{-3}$ , and  $[\text{H}_2\text{O}]$  and  $[(\text{H}_2\text{O})_2]$  corresponding to RH=20% and 100%.

Temp.	$k_{eff}^{\text{H}_2\text{O}(RH=20\%)}$	$k_{eff}^{\text{H}_2\text{O}(RH=100\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=20\%)}$	$k_{eff}^{(\text{H}_2\text{O})_2(RH=100\%)}$	$k_{eff}^{\text{HONO}}$	$k_{eff}^{\text{HONO}(RH=20\%)}$	$k_{eff}^{\text{HONO}(RH=100\%)}$	$k_{unimolecular}$	$k_{eff}^{\text{SO}_2}$
213	$9.21\times 10^{-7}$	$4.60\times 10^{-6}$	$6.01\times 10^{-8}$	$1.50\times 10^{-6}$	$8.17\times 10^{-1}$	$4.86\times 10^2$	$2.43\times 10^3$	1.15	
216	$1.65\times 10^{-6}$	$8.23\times 10^{-6}$	$1.92\times 10^{-7}$	$4.79\times 10^{-6}$	$8.12\times 10^{-1}$	$4.31\times 10^2$	$2.15\times 10^3$	1.37	
219	$2.89\times 10^{-6}$	$1.45\times 10^{-5}$	$5.78\times 10^{-7}$	$1.45\times 10^{-5}$	$8.08\times 10^{-1}$	$3.59\times 10^2$	$1.80\times 10^3$	1.63	
224	$7.16\times 10^{-6}$	$3.58\times 10^{-5}$	$1.69\times 10^{-6}$	$4.22\times 10^{-5}$	$7.98\times 10^{-1}$	$2.99\times 10^2$	$1.49\times 10^3$	2.17	
235	$4.59\times 10^{-5}$	$2.29\times 10^{-4}$	$1.26\times 10^{-5}$	$3.14\times 10^{-4}$	$7.73\times 10^{-1}$	$1.75\times 10^2$	$8.77\times 10^2$	4.10	
250	$4.42\times 10^{-4}$	$2.21\times 10^{-3}$	$1.84\times 10^{-4}$	$4.61\times 10^{-3}$	$7.29\times 10^{-1}$	$9.27\times 10^1$	$4.64\times 10^2$	9.68	
259	$1.51\times 10^{-3}$	$7.56\times 10^{-3}$	$9.17\times 10^{-4}$	$2.29\times 10^{-2}$	$7.01\times 10^{-1}$	$6.56\times 10^1$	$3.28\times 10^2$	$1.61\times 10^1$	
265	$3.28\times 10^{-3}$	$1.64\times 10^{-2}$	$1.98\times 10^{-3}$	$4.94\times 10^{-2}$	$6.80\times 10^{-1}$	$5.24\times 10^1$	$2.62\times 10^2$	$2.25\times 10^1$	
278	$1.56\times 10^{-2}$	$7.81\times 10^{-2}$	$1.43\times 10^{-2}$	$3.57\times 10^{-1}$	$6.36\times 10^{-1}$	$3.26\times 10^1$	$1.63\times 10^2$	$4.64\times 10^1$	
280	$1.84\times 10^{-2}$	$9.18\times 10^{-2}$	$1.43\times 10^{-2}$	$3.57\times 10^{-1}$	$6.29\times 10^{-1}$	$2.83\times 10^1$	$1.41\times 10^2$	$5.18\times 10^1$	
290	$4.96\times 10^{-2}$	$2.48\times 10^{-1}$	$4.27\times 10^{-2}$	1.07	$5.94\times 10^{-1}$	$1.83\times 10^1$	$9.13\times 10^1$	$8.92\times 10^1$	
293									
298	$1.04\times 10^{-1}$	$5.22\times 10^{-1}$	$9.75\times 10^{-2}$	2.44	$5.66\times 10^{-1}$	$1.32\times 10^1$	$6.60\times 10^1$	$1.37\times 10^2$	2.61
300	$1.25\times 10^{-1}$	$6.24\times 10^{-1}$	$1.17\times 10^{-1}$	2.92	$5.59\times 10^{-1}$	$1.22\times 10^1$	$6.10\times 10^1$	$1.53\times 10^2$	2.16
310	$2.94\times 10^{-1}$	1.47	$2.98\times 10^{-1}$	7.45	$5.25\times 10^{-1}$	8.29	$4.15\times 10^1$	$2.59\times 10^2$	
320	$6.56\times 10^{-1}$	3.28	$7.10\times 10^{-1}$	$1.77\times 10^1$	$4.92\times 10^{-1}$	5.63	$2.82\times 10^1$	$4.37\times 10^2$	

Table S10: The fitting rate constants of reactions in the GEOS-Chem.

Reaction	Rate Coefficient ( $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ )
$\text{CH}_2\text{OO} + \text{HNO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{NO}_2 + \text{OH} + \text{H}_2\text{O}$	GCARR_ac(6.03d-40, 6426.0d0)
$\text{CH}_3\text{CHOO} + \text{HNO}_2 + \text{H}_2\text{O} = \text{ALD2} + \text{NO}_2 + \text{OH} + \text{H}_2\text{O}$	GCARR_ac(4.36d-40, 8448.0d0)

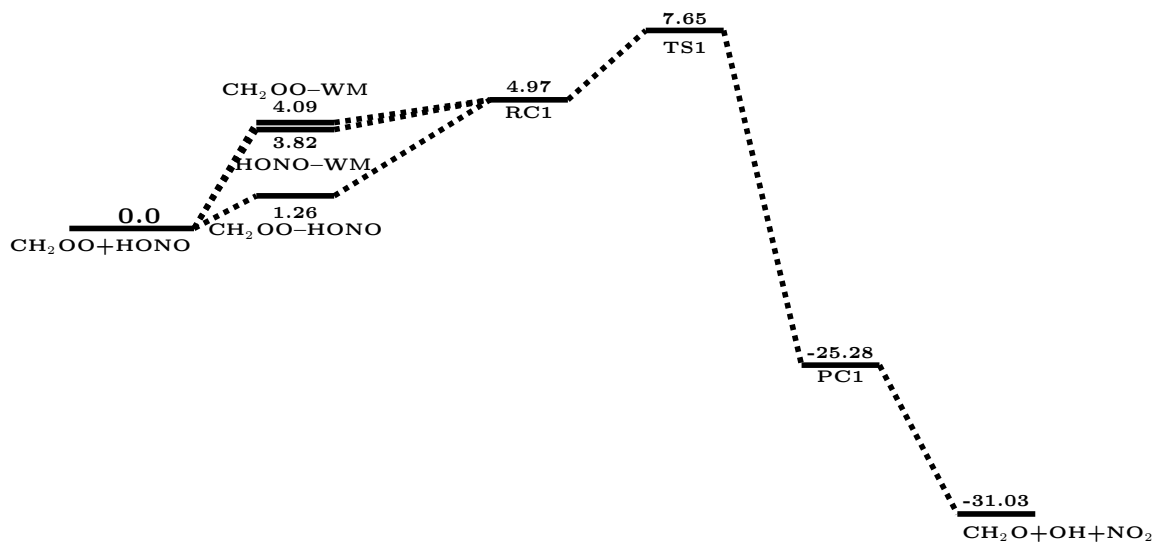


Figure S1: Gibbs energy profile ( $\text{kcal mol}^{-1}$ ) for  $\text{CH}_2\text{OO} + \text{HONO}$  reaction obtained at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory at 298 K.

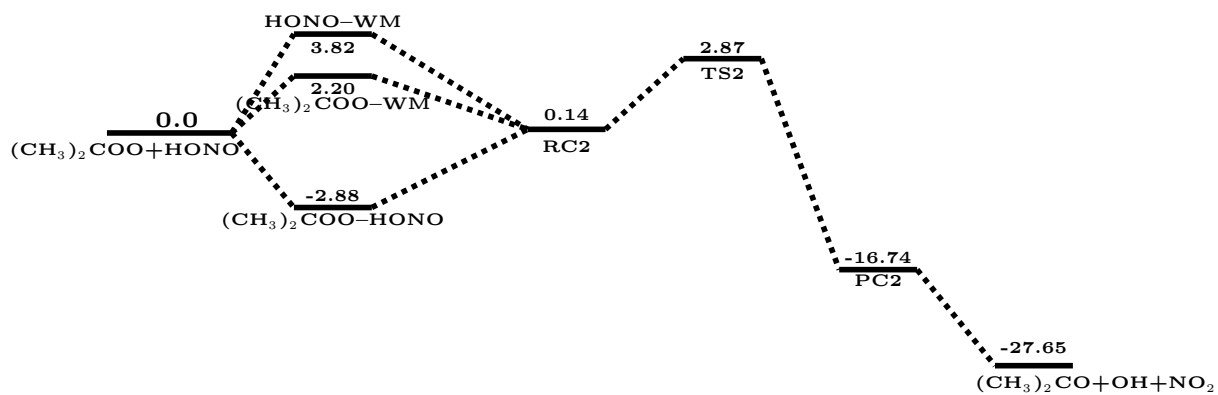


Figure S2: Gibbs energy profile (kcal mol<sup>-1</sup>) for (CH<sub>3</sub>)<sub>2</sub>COO + HONO reaction obtained at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory at 298 K.

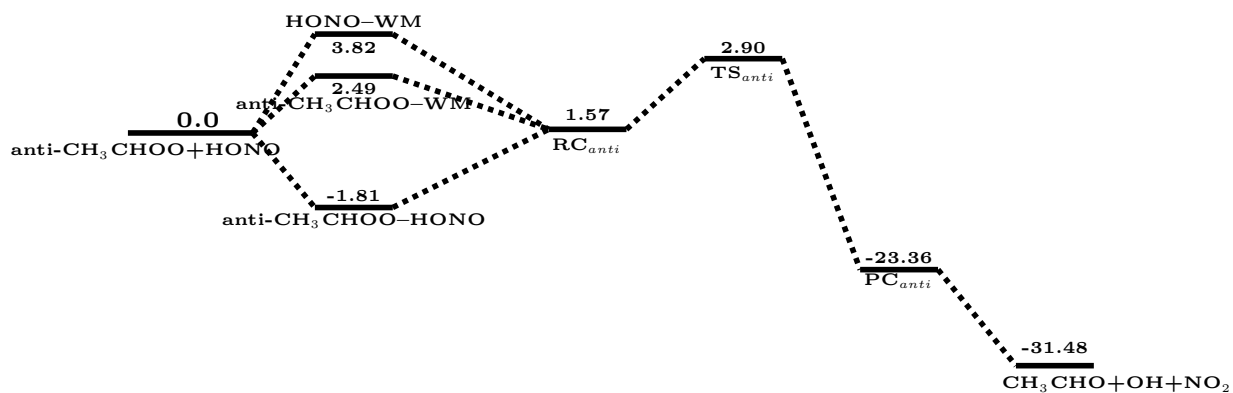


Figure S3: Gibbs energy profile (kcal mol<sup>-1</sup>) for anti-CH<sub>3</sub>CHOO + HONO reaction obtained at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory at 298 K.

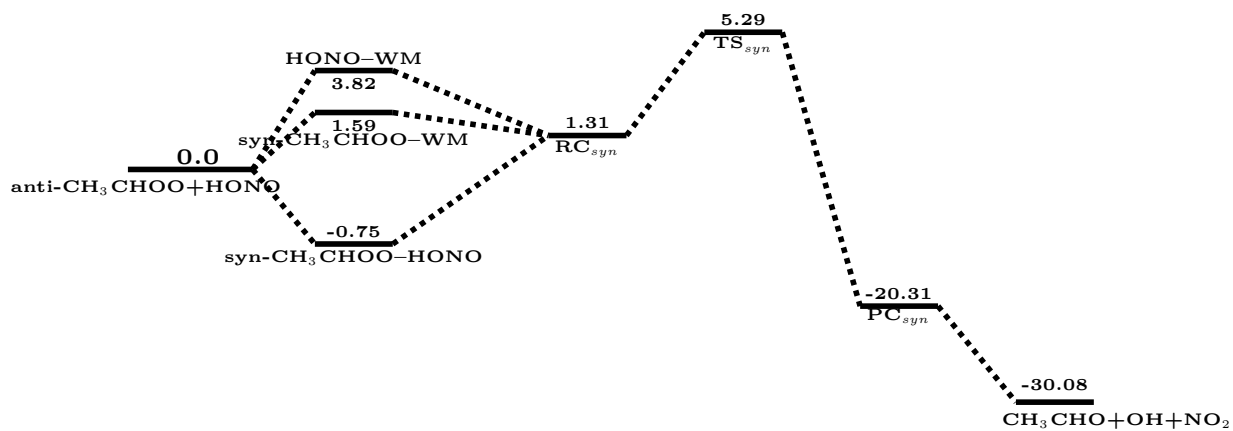


Figure S4: Gibbs energy profile (kcal mol<sup>-1</sup>) for syn-CH<sub>3</sub>CHO + HONO reaction obtained at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory at 298 K.

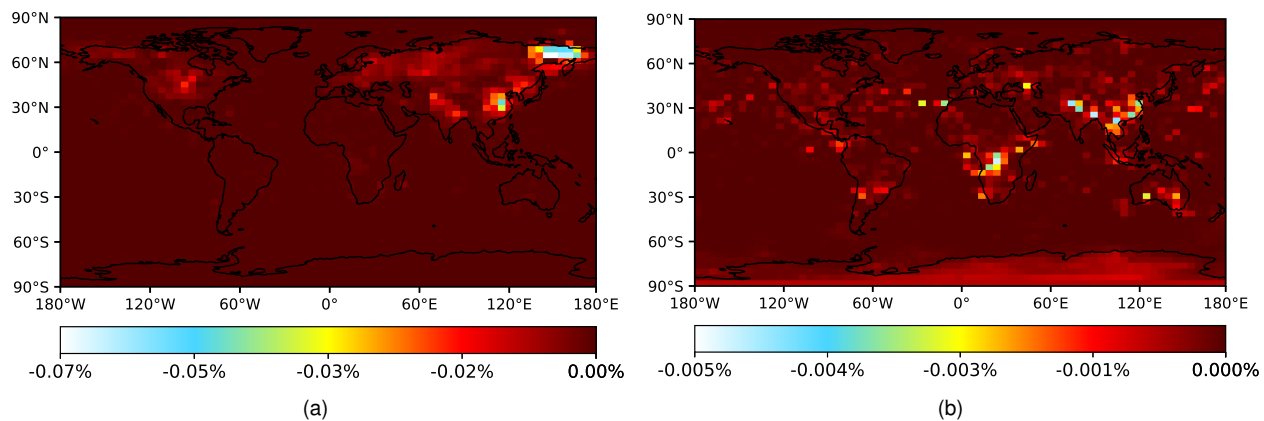


Figure S5: Global relative changes in  $\text{CH}_2\text{OO}$  concentrations resulting from the inclusion of the water catalyzed (WM)  $\text{CI} + \text{HONO}$  reaction in 24-hour simulations. (a)  $\text{CH}_2\text{OO}$  changes in January, (b)  $\text{CH}_2\text{OO}$  changes in June.

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