

Criegee + HONO reaction: the dominant sink of Criegee, and the missing non-photolytic source of OH•

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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 ⁻¹)		
CH ₂ OO	C	1.057098	-0.186174	0	538.15	697.71	927.20
	H	1.006167	-1.269154	0	1023.97	1260.68	1433.37
	H	1.966689	0.398409	0	1630.89	3139.98	3290.59
	O	0	0.459688	0			
	O	-1.16443	-0.211215	0			
HONO	N	0	0.507841	0	578.24	700.42	905.04
	O	0.882551	-0.567177	0	1342.39	1841.11	3830.83
	O	-1.101711	0.141484	0			
	H	1.753278	-0.149345	0			
RC1	O	1.498972	-1.038397	0.244942	65.11	92.16	142.24
	O	1.726641	0.149063	-0.424616	166.18	224.27	273.11
	C	1.420998	1.180384	0.176904	525.70	695.30	769.68
	H	1.576962	2.106616	-0.363492	876.31	1010.42	1052.16
	H	1.036523	1.112197	1.187687	1107.39	1256.42	1448.64
	N	-1.27518	0.258091	0.073874	1557.40	1679.05	1793.75
	O	-1.091011	-1.060536	-0.093095	2990.53	3141.61	3286.10
	H	-0.100636	-1.185364	0.034644			
	O	-2.398675	0.584571	-0.031904			
TS1	O	1.650665	-0.899517	0.185806	-248.25	103.69	196.24
	O	1.542624	0.364395	-0.446018	243.30	340.61	400.60
	C	0.909591	1.185914	0.23834	522.64	776.50	782.50
	H	0.706837	2.142819	-0.228811	880.96	1088.56	1139.31
	H	0.750931	0.992577	1.29178	1183.44	1244.33	1437.18
	N	-1.137944	0.151896	0.035635	1635.17	1684.49	1795.32
	O	-0.807104	-1.120664	-0.039819	1974.20	3146.01	3282.87
	H	0.257887	-1.162149	0.072964			
	O	-2.287134	0.386785	-0.051896			
PC1	O	-1.891229	0.38775	0.49254	76.22	188.29	332.59
	O	-1.329506	-0.452034	-0.504135	421.52	455.14	553.61
	C	-0.157737	-0.957206	-0.020654	605.00	738.56	930.50
	H	0.182808	-1.741835	-0.690912	972.37	1116.88	1203.36
	H	-0.218591	-1.294705	1.012421	1297.85	1374.49	1439.18
	N	0.95063	0.094534	-0.02322	1452.24	1502.00	1713.12
	O	0.652686	1.231141	-0.303473	3113.19	3190.86	3755.70
	H	-1.488438	1.239765	0.262016			
	O	2.045078	-0.307073	0.277935			
OH	O	0	0	0.107992	3769.62		
	H	0	0	-0.863937			
NO ₂	N	0	0	0.314473	783.52	1465.18	1755.31
	O	0	1.090255	-0.137582			
	O	0	-1.090255	-0.137582			
HCHO	O	-0.670517	0.0000227	-0.000001	1213.53	1273.49	1539.85
	C	0.525515	0	0.000003	1869.05	2945.55	3015.83
	H	1.105357	-0.938452	-0.000006			
	H	1.105686	0.93828	-0.000006			

Species	Cartesian coordinates (Å)				Frequency (cm ⁻¹)		
(CH ₃) ₂ COO	C	0.371062	0.018585	0.00005	161.4785	208.2494	291.0197
	O	-0.558411	-0.81759	-0.000008	329.946	366.3571	493.4939
	O	-1.838845	-0.328935	-0.000003	609.8208	827.3278	925.0805
	C	0.053885	1.456083	-0.000006	953.0914	989.3886	1085.6587
	H	-0.57815	1.668238	0.865389	1102.011	1316.0578	1393.969
	H	0.954341	2.062465	-0.000046	1411.6898	1442.1269	1466.9645
	H	-0.578203	1.668145	-0.86537	1474.3344	1486.7659	1654.0743
	C	1.752599	-0.524309	0.000001	3059.282	3065.4337	3109.8178
	H	2.288094	-0.158843	0.877727	3121.9032	3182.2265	3183.8812
	H	1.739149	-1.610169	0.000607			
	H	2.287541	-0.159787	-0.878484			
RC2	O	-0.323346	1.788465	-0.127155	40.9916	65.3092	94.8686
	O	-0.933456	0.707341	-0.762464	143.887	165.0795	182.4321
	C	-1.427404	-0.163929	-0.015067	184.8149	254.8398	336.26
	N	1.668747	-0.491904	0.103393	357.8193	376.4962	494.4218
	O	2.027385	0.75438	-0.212701	601.2322	778.1414	824.8282
	H	1.149904	1.272513	-0.192924	905.477	949.7473	992.8326
	O	2.5751	-1.24643	0.120319	1062.3121	1084.8706	1100.4914
	C	-2.010313	-1.34373	-0.692483	1107.6633	1317.6543	1381.0831
	H	-1.444347	-2.223239	-0.376851	1406.8156	1448.8553	1461.7488
	H	-3.040077	-1.483491	-0.362789	1471.93	1488.8255	1579.3946
	H	-1.962298	-1.240373	-1.771878	1668.5843	1779.7402	2780.974
	C	-1.402643	-0.006457	1.447276	3065.3064	3070.7206	3128.6412
	H	-0.3575	0.00306	1.763655	3129.2175	3189.9646	3191.0969
	H	-1.801638	0.976862	1.69949			
	H	-1.948582	-0.807358	1.935197			
TS2	O	0.550552	-1.91232	-0.157936	-875.0178	88.1328	110.2442
	O	1.027394	-0.718099	-0.761686	141.1228	161.9634	176.0151
	C	1.025985	0.293662	0.000171	241.0089	299.2742	320.3139
	N	-1.317937	0.33477	-0.010799	370.0784	395.3556	489.6676
	O	-1.645557	-0.916254	-0.068479	558.7228	604.2866	812.5142
	H	-0.607076	-1.53411	-0.103381	895.2549	933.636	968.2391
	O	-2.206625	1.124555	0.016787	990.135	1094.7045	1099.1694
	C	1.032531	0.192244	1.478444	1245.2764	1289.6521	1326.3627
	H	2.072829	-0.000888	1.762063	1404.0109	1419.8947	1454.66
	H	0.720659	1.139428	1.908866	1457.975	1469.165	1490.2106
	H	0.422449	-0.627005	1.835792	1618.1624	1686.0865	1860.5208
	C	1.35894	1.574774	-0.666744	3054.66	3071.2572	3137.5137
	H	0.578987	2.294941	-0.418211	3156.4911	3191.39	3222.9338
	H	2.30335	1.947896	-0.267396			
	H	1.423516	1.449212	-1.742853			

Species	Cartesian coordinates (Å)				Frequency (cm ⁻¹)		
PC2	O	1.985793	-0.726895	0.25413	52.4597	162.8702	213.6543
	O	1.28194	0.118675	-0.639404	234.9484	262.3477	282.2477
	C	0.100634	0.559106	-0.067175	326.5011	355.8608	396.5205
	N	-0.876611	-0.653207	0.010107	462.1167	477.6842	583.8607
	O	-0.484791	-1.727573	-0.385388	617.808	757.3543	860.24
	H	1.618317	-1.589659	0.007351	893.1847	962.7302	982.8632
	O	-1.970236	-0.431354	0.465927	1032.5788	1070.5757	1186.0233
	C	0.242791	1.111547	1.33574	1277.0505	1305.6178	1405.298
	H	0.963065	1.92676	1.298642	1412.3545	1436.5532	1478.2497
	H	-0.716779	1.486469	1.679701	1484.8552	1486.8893	1499.1822
	H	0.606302	0.351478	2.020882	1513.7957	1692.8757	3087.5924
	C	-0.498782	1.533219	-1.060518	3094.1386	3167.6738	3174.1824
	H	0.143496	2.409662	-1.110279	3184.9593	3190.5432	3760.4604
	H	-0.555824	1.076113	-2.046571			
	H	-1.491803	1.82556	-0.730883			
(CH ₃) ₂ CO	O	0.021464	1.382277	0.000011	111.9307	175.4067	384.5896
	C	-0.005455	0.177931	-0.000082	497.2894	531.5722	796.9533
	C	1.277228	-0.627419	-0.000037	883.6212	934.5994	1075.7547
	H	1.100747	-1.700338	-0.00297	1116.1008	1245.1935	1382.726
	H	1.862521	-0.350951	-0.876226	1390.7895	1465.3831	1477.3376
	H	1.859411	-0.355511	0.87968	1482.7335	1483.9292	1847.1097
	C	-1.300425	-0.59294	-0.000001	3061.2825	3075.9873	3122.6717
	H	-1.338462	-1.24216	-0.876626	3149.0436	3166.3195	3181.8401
	H	-1.338009	-1.242613	0.876335			
	H	-2.146009	0.087933	0.000439			

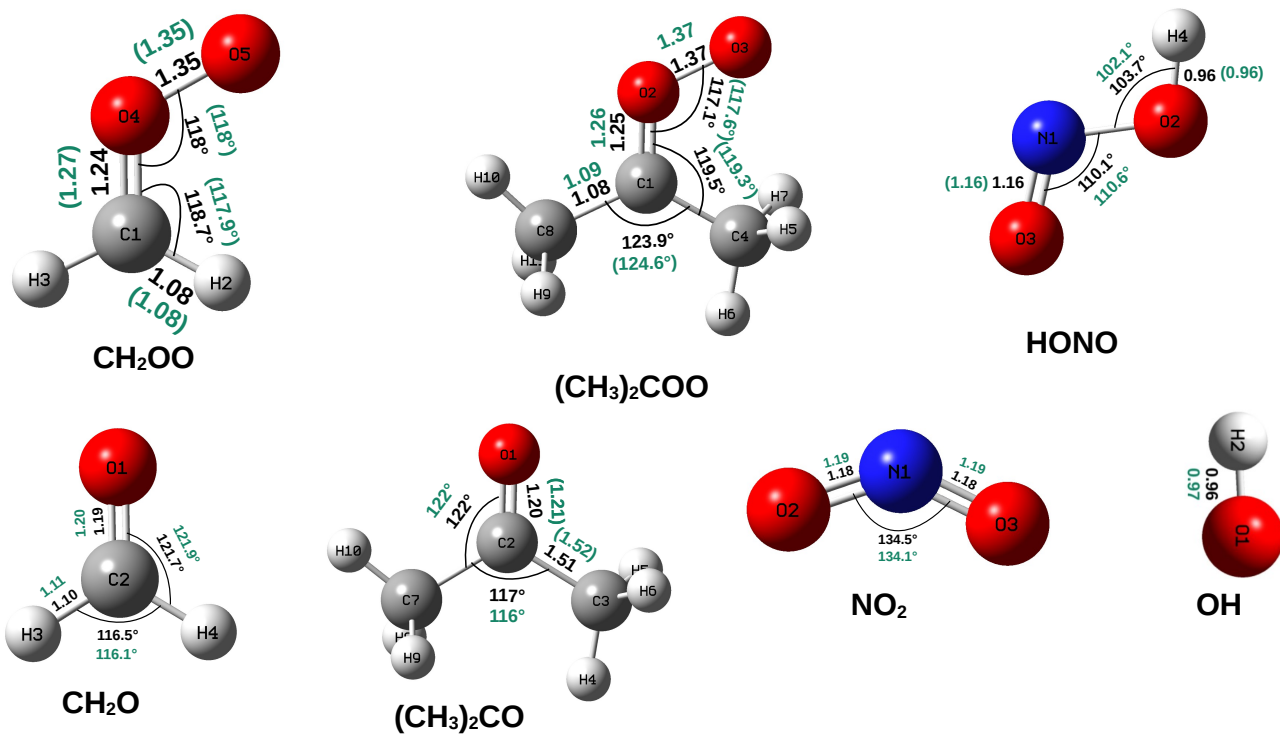


Figure S1: Comparison of geometrical parameters of the isolated species, obtained at M06-2X/aug-cc-pVTZ level of theory (values in bold black) with the available experimental data (values in bold green).¹

Table S2: Comparison of frequencies (in cm^{-1}) of the isolated species, obtained at M06-2X/aug-cc-pVTZ level of theory with the available experimental data.

Species	Experimental				(M06-2X/aug-cc-pVTZ)			
CH_2OO	848				538.15	1023.97	1630.89	
	908				697.71	1260.68	3139.98	
	1241				927.20	1433.37	3290.59	
	1286							
	1435							
HONO	543	1263			578.24	1342.39		
	596	1700			700.42	1841.11		
	790	3591			905.04	3830.83		
OH	3738				3769.62			
NO_2	750				783.52			
	1318				1465.18			
	1666				1755.31			
HCHO	1167	1249			1213.53	1869.05		
	1500	1746			1273.49	2945.55		
	2782	2843			1539.85	3015.83		
$(\text{CH}_3)_2\text{COO}$	77	877	1364	2937	111.9307	175.4067	384.5896	497.2894
	125	891	1410	2937	531.5722	796.9533	883.6212	934.5994
	385	1066	1426	2963	1075.7547	1116.1008	1245.1935	1382.7261
	484	1091	1435	2972	1390.7895	1465.3831	1477.3376	1482.7335
	530	1216	1454	3019	1483.9292	1847.1097	3061.2825	3075.9873
	777	1364	1731	3019	3122.6717	3149.0436	3166.3195	3181.8401

Table S3: The bimolecular rate constant along with its capture rate and gamma for both, $\text{CH}_2\text{OO} + \text{HONO}$ and $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction.

Temp.	k_f	γ	$k_{bi}^{\text{CH}_2\text{OO}}$	k'_f	γ'	$k_{bi}^{(\text{CH}_3)_2\text{OO}}$
213	2.78×10^{-11}	1.42×10^{-01}	3.94×10^{-12}	2.58×10^{-11}	8.42×10^{-01}	2.17×10^{-11}
216	2.87×10^{-11}	1.37×10^{-01}	3.94×10^{-12}	2.67×10^{-11}	8.34×10^{-01}	2.23×10^{-11}
219	2.96×10^{-11}	1.33×10^{-01}	3.94×10^{-12}	2.77×10^{-11}	8.25×10^{-01}	2.28×10^{-11}
224	3.12×10^{-11}	1.26×10^{-01}	3.93×10^{-12}	2.93×10^{-11}	8.11×10^{-01}	2.38×10^{-11}
235	3.47×10^{-11}	1.13×10^{-01}	3.90×10^{-12}	3.31×10^{-11}	7.77×10^{-01}	2.57×10^{-11}
250	3.97×10^{-11}	9.63×10^{-02}	3.83×10^{-12}	3.89×10^{-11}	7.28×10^{-01}	2.83×10^{-11}
259	4.29×10^{-11}	8.77×10^{-02}	3.76×10^{-12}	4.26×10^{-11}	6.97×10^{-01}	2.97×10^{-11}
265	4.50×10^{-11}	8.25×10^{-02}	3.71×10^{-12}	4.53×10^{-11}	6.76×10^{-01}	3.06×10^{-11}
278	4.97×10^{-11}	7.21×10^{-02}	3.58×10^{-12}	5.13×10^{-11}	6.31×10^{-01}	3.24×10^{-11}
280	5.04×10^{-11}	7.07×10^{-02}	3.56×10^{-12}	5.23×10^{-11}	6.24×10^{-01}	3.26×10^{-11}
290	5.41×10^{-11}	6.38×10^{-02}	3.45×10^{-12}	5.74×10^{-11}	5.89×10^{-01}	3.38×10^{-11}
298	5.70×10^{-11}	5.89×10^{-02}	3.35×10^{-12}	6.17×10^{-11}	5.61×10^{-01}	3.46×10^{-11}
300	5.77×10^{-11}	5.77×10^{-02}	3.33×10^{-12}	6.28×10^{-11}	5.54×10^{-01}	3.47×10^{-11}
310	6.13×10^{-11}	5.21×10^{-02}	3.20×10^{-12}	6.85×10^{-11}	5.19×10^{-01}	3.56×10^{-11}
320	6.48×10^{-11}	4.72×10^{-02}	3.06×10^{-12}	7.45×10^{-11}	4.86×10^{-01}	3.62×10^{-11}

Table S4: The bimolecular rate constant, average concentration in the polluted environment and effective rate constant for $\text{CH}_2\text{OO} + \text{X}$ (where $\text{X} = \text{SO}_2, \text{NO}_2, \text{NO}, \text{CO}, \text{H}_2\text{O}$, and $(\text{H}_2\text{O})_2$).

Reaction	k_{bi}^{298K}	$[\text{X}]$ (molecule cm^{-3})	k_{eff} (sec^{-1})
$\text{CH}_2\text{OO} + \text{SO}_2^{2,3}$	3.72×10^{-11}	9.00×10^{10}	3.35
$\text{CH}_2\text{OO} + \text{NO}_2^{3,4}$	1.00×10^{-12}	9.00×10^{11}	0.90
$\text{CH}_2\text{OO} + \text{NO}^{3,5}$	$< 6.00 \times 10^{-14}$	9.00×10^{10}	0.01
$\text{CH}_2\text{OO} + \text{CO}^{3,6}$	$< 2.0 \times 10^{-16}$	3.00×10^{13}	0.01
$\text{CH}_2\text{OO} + \text{H}_2\text{O} (RH=20\%)^{7-9}$	3.13×10^{-16}	1.53×10^{17}	47.73
$\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2 (RH=20\%)^{7-9}$	5.48×10^{-12}	4.76×10^{13}	260.96
$\text{CH}_2\text{OO} + \text{H}_2\text{O} (RH=100\%)^{7-9}$	3.13×10^{-16}	7.63×10^{17}	238.64
$\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2 (RH=100\%)^{7-9}$	5.48×10^{-12}	1.19×10^{15}	6524.00

1 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.^{10,11} 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_{ADZ} and E_{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_{ADZ} and E_{ATZ} are Hartree-Fock energies at CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ level of theory, respectively.

2 Details of the methodology used for the kinetics calculations

To calculate γ , we have used master equation approach as implemented in MultiWell code, where simulations are started from the RC well. The simulation requires two inputs; dissociation rate constants of well separating into the reactants ($k_r(E)$) and unimolecular transformation rate (k_{uni}). To compute $k_r(E)$, MultiWell uses Inverse Laplace Transform (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.¹² 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 N₂ as the bath gas, (corresponding Lennard Jones (L-J) parameters are $\sigma = 3.74$ Å, and $\epsilon/kT = 82.0$ K). The Lennard Jones (L-J) parameters for RC was not known, therefore, L-J parameters of RC are estimated with the help of combining rule¹³ which requires L-J parameters of CI and HONO to calculate the L-J parameters of RC using the combining rule (see following equations).

$$\sigma_{RC} = \frac{1}{2}(\sigma_{CH_2OO} + \sigma_{HONO})$$

$$(\epsilon/k_B)_{RC} = [(\epsilon/k_B)_{CH_2OO}(\epsilon/k_B)_{HONO}]^{1/2}$$

The L-J parameters for RC using above equations turns out to be, $\sigma = 4.68$ Å and $\epsilon = 246.15$ K. To simulate the energy transfer model, a single exponential model was used with maximum energy 50000 cm⁻¹ and grain size of 100 cm⁻¹.

3 Details of kinetic modelling

The kinetic model has been developed using a ReactionSystem module from chempy.¹⁴ This model requires two key components: first, a list of relevant reactions along with their rate coefficients, and second, a list of realistic initial concentrations of the reactive species involved in the reactions. In principle, we solve a system of ordinary differential equations (ODEs) that describe the time-dependent changes in the concentrations of OH• and HO₂•. We have performed this kinetic modeling at room temperature. The system is simulated for 60 minutes using a high-resolution time grid with 50,000 time steps to capture rapid chemical kinetics. Stringent absolute (atol=1e-8) and relative (rtol=1e-8) tolerances are applied to maintain numerical stability and precision. We first tracked the change in concentration of OH• and HO₂• using kinetic model consisting of CH₂OO + HONO reaction (M-1), followed

by the second model consisting of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction (M-2). The reaction mechanism included three bimolecular reactions which can be initiated from the title reaction as mentioned in the box (main manuscript). Initial concentrations of relevant species (HCHO , $(\text{CH}_3)_2\text{CO}$, and $\text{HO}_2^\bullet$) were chosen based on literature values representing polluted urban conditions.³ Although the average concentration of NO_2 , and $\text{OH}^\bullet$ are found to be $\sim 10^6$ and $\sim 10^{12}$ molecules cm^{-3} in the atmosphere, we have used modelled value of them in the present work. In $\text{CH}_2\text{OO} + \text{HONO}$ reaction model, the initial OH radical concentration was set to $\sim 10^4$ molecules cm^{-3} , while in $(\text{CH}_3)_2\text{COO} + \text{HONO}$ model, it was set to $\sim 10^5$ molecules cm^{-3} . Similarly, the concentration of NO_2 was kept to be $\sim 10^{10}$ molecules cm^{-3} for both the kinetic modelling in order to observe a clear numerical change in the values of $\text{HO}_2^\bullet$.

Table S5: List of all reactions and their corresponding rate coefficients, along with the model concentrations of the relevant species at 298 K.

Reactions	k_{298}	Species	Concentration
$\text{CH}_2\text{OO} + \text{HONO} \rightarrow \text{HCHO} + \text{NO}_2 + \text{OH}$	3.34×10^{-12}	$\text{CH}_2\text{OO}/\text{C}_2\text{H}_6\text{COO}^{15}$	1.00×10^5
$\text{C}_2\text{H}_6\text{COO} + \text{HONO} \rightarrow \text{C}_2\text{H}_6\text{CO} + \text{NO}_2 + \text{OH}$	3.46×10^{-11}	$\text{HCHO}/\text{C}_2\text{H}_6\text{O}^3$	5.10×10^{11}
$\text{HCHO} + \text{HO}_2 \rightarrow \text{HOCH}_2\text{OO}^{16}$	6.27×10^{-14}	HONO^{17}	8.90×10^{10}
$\text{C}_2\text{H}_6\text{CO} + \text{HO}_2 \rightarrow \text{HOC}_2\text{H}_6\text{COO}^{18}$	4.40×10^{-13}	NO_2 (M-1/M-2)	1.00×10^{10}
$\text{NO}_2 + \text{HO}_2 \rightarrow \text{HNO}_4^{19}$	5.40×10^{-12}	OH(M-1)	2.30×10^4
		OH(M-2)	2.30×10^5
		HO_2^3	7.00×10^8

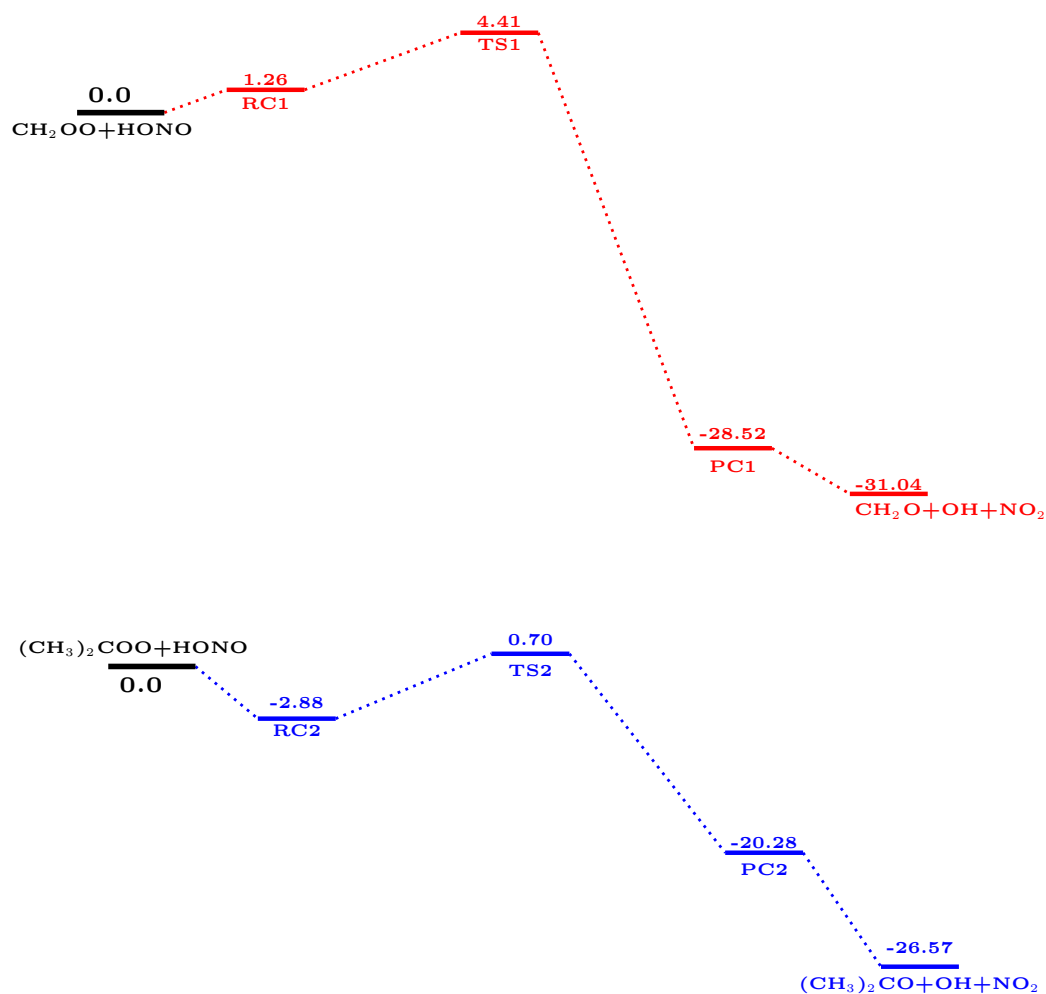


Figure S2: Top panel: Gibbs free energy profile (kcal mol⁻¹) for CH₂OO + HONO reaction obtained at CCSD(T)/CBS level of theory at 298 K. Bottom panel: Gibbs free energy profile (kcal mol⁻¹) for (CH₃)₂COO + HONO reaction obtained at same level of theory at 298 K.

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