Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for Nitrous acid (HONO) as a sink of simplest Criegee intermediate in the atmosphere

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Table S1: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of CH_2OO + HONO reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Coordinates				Frequencies		
CH_2OO	O	1.167175	0.19252	0			
	O	-0.006869	-0.459323	0	538.6581	697.4377	930.256
	C	-1.054273	0.20301	0	1022.0054	1261.2468	1432.3163
	H	-1.971952	-0.368537	0	1628.3226	3140.2607	3291.8233
	H	-0.984853	1.284902	0			
Cis-HONO	N	0.160978	-0.516104	-0.000056			
	O	-1.07062	0.068769	0.000054	685.9664	702.3739	968.0504
	O	1.044674	0.253693	0.000031	1372.3672	1783.8467	3662.3849
	H	-0.919279	1.033028	-0.000287			
Trans-HONO	N	0.162635	0.481149	0.000012			
	O	-1.017717	-0.254818	0.00001	566.847	699.1352	903.683
	O	1.089014	-0.218665	-0.000009	1336.9243	1838.851	3831.4679
	H	-1.708816	0.419817	-0.000084			
TS^{ot}_{cis}	O	0.504986	0.229388	0.029806			
	O	2.143078	0.541864	-0.229448	-663.2394	16.6105	58.8595
	C	2.801427	-0.39967	0.136987	88.6021	220.2522	318.9889
	H	3.89075	-0.360345	0.040246	374.8122	498.61	556.1574
	H	2.303624	-1.276792	0.559109	672.3375	717.1119	995.7475
	N	-1.32616	-0.15476	0.11097	1200.43	1248.0297	1388.5809
	O	-2.115365	0.944601	0.100379	1477.4521	1770.0265	1812.061
	O	-1.871835	-1.155374	-0.157086	3036.7296	3150.0167	3669.7239

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	H	-3.00673	0.63465	-0.147271			
TS^{ot}_{trans}	O	0.473191	0.076115	-0.000471			
	O	2.113655	0.518639	-0.000206	-620.5418	44.2227	109.8342
	C	2.793548	-0.477741	0.000358	118.6033	233.9978	327.3715
	H	3.883412	-0.380836	0.000628	374.7601	512.2669	568.1366
	H	2.313879	-1.460189	0.00058	721.6558	723.4588	1016.0002
	N	-1.404814	-0.229047	-0.000207	1206.5644	1247.6116	1396.502
	O	-1.861126	1.043834	0.000372	1478.4396	1812.3217	1835.3947
	O	-2.240084	-1.039624	0.000049	3040.3908	3154.6059	3692.3565
	H	-1.009976	1.519086	0.000144			
HCHO	O	0.670471	0.000248	0.000034			
	C	-0.525546	0.000027	-0.000138	1213.2946	1273.5648	1539.6997
	H	-1.10717	0.937403	0.000278	1869.1092	2945.9741	3016.5118
	H	-1.103322	-0.939547	0.000278			
HNO3	O	-1.050351	-0.725557	-0.000079			
	N	-0.141242	0.034996	0.000196	504.13	620.9047	705.7992
	O	1.101539	-0.564498	-0.00001	825.1482	981.6791	1357.703
	O	-0.142124	1.236269	-0.000051	1415.7119	1809.3066	3783.6212
	H	1.716189	0.185323	-0.000258			
RC^{ha}_{trans}	O	1.432993	-1.144409	0.153765	29.3392	89.2185	105.997
	O	1.983689	-0.052822	-0.463434	156.3452	166.5127	258.9553
	C	1.875536	1.03995	0.100942	539.422	694.0269	764.4053

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	H	2.309294	1.881652	-0.424708	888.5999	964.2469	1041.582
	H	1.369229	1.102514	1.05852	1090.8326	1266.752	1439.2134
	N	-1.880012	-0.369376	-0.242632	1459.3304	1664.7057	1806.2324
	O	-0.830421	0.084835	0.506977	3091.3709	3135.9082	3281.578
	H	-0.095611	-0.583808	0.382315			
	O	-2.795766	0.355592	-0.187728			
	O	1.582003	-1.021811	-0.042146	-1071.0071	57.8207	110.3758
	O	1.569857	0.291382	-0.572465	130.6253	255.3153	405.6495
	C	1.104964	1.084455	0.277433	479.5819	621.8228	773.964
	H	0.822815	2.061778	-0.099803	879.6014	912.1277	978.7652
TS^{hs}_{trans}	H	1.175843	0.863263	1.333267	1164.654	1246.6493	1400.8277
	N	-1.582704	-0.514879	-0.192657	1442.731	1621.4702	1740.5933
	O	-0.553739	-0.260552	0.643717	1863.0243	3150.3641	3289.2795
	H	0.427111	-0.924012	0.337371			
	O	-2.3452	0.378031	-0.26496			
	O	1.122473	0.220369	-0.081359	192.4534	289.6468	506.4185
	O	-0.06306	-0.558593	-0.06483	686.0443	960.1216	1188.2997
	C	-1.129966	0.262803	0.092831	1230.4988	1407.8125	1448.5031
HPM	H	-2.054352	-0.293563	0.09391	3159.9578	3300.2288	3802.0732
	H	-1.047423	1.256255	-0.322319			
	H	1.406265	0.166279	0.840936			
	N	0	0	0.314204	783.2825	1465.2372	1776.0132
NO_2	O	0	1.090359	-0.137464			

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	O	0	-1.090359	-0.137464			
	O	-1.169711	-0.826679	0.618842	-313.037	174.6028	299.2654
	O	-1.491277	0.260938	-0.10866	361.8911	385.6796	477.9411
	C	-0.495811	1.128652	-0.075574	626.2789	656.696	689.5726
	O	0.402961	-0.991279	-0.643789	939.2824	995.8639	1056.627
TS_{cis}^{oz}	H	-0.626149	1.919735	-0.80322	1192.8857	1250.0115	1303.142
	H	-0.12531	1.400539	0.906528	1379.5712	1498.8799	1544.8227
	O	1.785299	0.257327	0.498908	3140.7424	3251.1331	3739.2324
	H	1.813171	-0.615989	0.923293			
	N	0.813568	0.131621	-0.499366			
	O	-1.255134	-0.747618	0.625401	-385.7238	187.6112	286.1722
	O	-1.492305	0.325742	-0.147628	349.0737	368.0907	482.4623
	C	-0.467592	1.139702	-0.092774	627.4475	639.5433	677.844
	O	0.333685	-1.066925	-0.537496	892.3763	993.7424	1025.6584
TS_{trans}^{oz}	H	-0.530296	1.936327	-0.823055	1173.502	1253.6995	1313.4213
	H	-0.074422	1.355028	0.894457	1322.2866	1501.8346	1541.4953
	O	1.80852	0.105156	0.533071	3138.7109	3257.475	3832.9636
	N	0.833655	0.021366	-0.504293			
	H	2.41655	0.790033	0.228509			
	O	-1.246511	-0.656991	0.335863	180.939	299.1682	393.4956
	O	-0.988417	0.701446	0.515746	467.6818	543.2712	601.5881
	C	-0.155993	1.025015	-0.580881	768.2604	847.1728	864.5643
	O	-0.017442	-1.137467	-0.460047	985.3601	1007.5648	1083.976
PC_{cis}^{oz}							

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	H	-0.695777	0.987672	-1.524708	1133.1579	1171.2588	1265.9597
	H	0.328268	1.972469	-0.37825	1352.427	1437.5683	1490.5777
	O	1.598338	0.016583	0.590233	3121.2006	3224.6477	3734.248
	H	1.001583	0.083689	1.352781			
	N	0.790592	-0.083212	-0.545557			
	O	-0.944568	-0.841633	0.495968	129.5591	330.6492	360.3559
	O	-1.445638	0.411317	0.120286	472.2821	627.7054	710.4092
	C	-0.268564	1.14866	-0.135062	758.3039	858.6207	909.6464
	O	0.019079	-1.027802	-0.557535	965.9493	998.1502	1056.1032
PC_{trans}^{oz}	H	-0.483894	1.825226	-0.955683	1092.9776	1141.6074	1244.2275
	H	0.110262	1.653857	0.749934	1375.6309	1410.9572	1515.5407
	O	1.659386	0.076247	0.527097	3116.1606	3193.7616	3859.8178
	N	0.744311	0.132123	-0.540574			
	H	2.468768	-0.240942	0.113609			
	C	-1.193309	-0.732285	0.526828	-367.5155	141.3451	270.458
	O	-1.513976	0.28228	-0.167922	351.308	428.2711	474.1935
	O	-0.572526	1.24461	-0.054018	591.6537	637.8505	699.5947
	O	0.431106	-1.020822	-0.51681	865.0216	971.1415	1023.3895
$TS1_{cis}^{ca}$	H	-0.638254	-0.573151	1.44158	1098.2192	1244.5385	1307.2821
	H	-1.789375	-1.618171	0.355598	1394.0551	1488.8243	1556.6298
	O	1.778101	0.307701	0.498103	3157.2873	3291.5989	3712.5521
	H	1.676692	-0.459135	1.086744			
	N	0.989879	0.076288	-0.588531			

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	C	-1.108856	-0.695899	0.601221	-1113.325	77.471	92.6719
	O	-1.500513	0.264554	-0.139468	263.1243	378.7331	478.4219
	O	-0.575397	1.253324	-0.167263	525.5072	632.3669	687.7438
	O	0.393726	-1.060499	-0.535039	736.1341	817.8758	973.217
	H	-0.468922	-0.474288	1.445246	1030.2393	1209.814	1369.2895
	H	-1.718078	-1.587801	0.546697	1383.147	1609.6928	1785.9188
	O	1.661779	0.191572	0.600465	2296.033	2983.8823	3786.7627
	N	0.996342	-0.005008	-0.59755			
$TS1^{ca}_{trans}$	H	2.028983	1.080938	0.514028			
	C	-1.132588	-0.645981	0.397835	59.0392	299.3377	383.6305
	O	-1.351938	0.666959	-0.025851	516.6965	578.7609	724.9457
	O	-0.024809	1.149766	-0.055179	761.9152	848.8385	915.0769
	O	-0.074181	-1.06385	-0.440402	978.9984	1051.1897	1061.0284
RC^{ca}_{cis}	H	-0.855498	-0.675265	1.46068	1115.5714	1178.3765	1254.6815
	H	-2.012052	-1.247156	0.173391	1381.773	1431.5154	1527.1454
	O	1.790029	-0.059566	0.362478	3056.2538	3205.956	3716.9294
	H	1.389021	-0.022776	1.250754			
	N	0.794464	0.03923	-0.571458			
	C	-1.324897	-0.469382	0.223056	107.2895	212.9709	298.3223
	O	-0.91601	0.839941	0.476016	530.7612	623.8235	767.1895
	O	0.038221	1.018898	-0.592956	795.5407	903.7279	947.8626
	O	-0.176176	-1.115003	-0.348056	968.2356	1002.6835	1010.8969
RC^{ca}_{trans}	H	-1.581778	-0.927566	1.175138	1120.1252	1152.2812	1225.2681
	H	-2.131327	-0.516396	-0.509818	1399.7619	1417.7264	1539.1563

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	O	1.524923	-0.087369	0.644687	3079.5124	3163.7105	3861.0393
	N	0.780093	-0.125431	-0.538588			
	H	2.434166	-0.113472	0.328928			
	C	-1.506308	0.077121	-0.216413	-1137.6637	50.1784	109.5879
	O	-1.523422	-0.595192	0.81384	297.5107	361.0129	405.5849
	O	1.619841	0.405525	0.772555	492.4626	625.8035	711.9467
	O	-0.372976	1.030192	-0.432235	757.7987	845.6208	996.738
$TS2_{cis}^{ca}$	H	-1.806239	-0.334641	-1.190516	1065.5912	1203.329	1375.2071
	H	-1.893109	1.209762	-0.163132	1410.8533	1601.6868	1730.4316
	O	0.85136	-1.015205	-0.652776	2278.748	3008.0692	3643.8017
	H	1.125286	-1.601257	0.081045			
	N	1.001927	0.237265	-0.205714			
	C	-1.368622	-0.462549	0.222691	-1113.325	77.471	92.6719
	O	-1.71467	0.694851	0.443207	263.1243	378.7331	478.4219
	O	0.861349	1.258171	-0.231827	525.5072	632.3669	687.7438
	O	-0.359605	-0.704437	-0.855492	736.1341	817.8758	973.217
$TS2_{trans}^{ca}$	H	-1.194384	-1.178896	1.040976	1030.2393	1209.814	1369.2895
	H	-1.873053	-1.05911	-0.680633	1383.147	1609.6928	1785.9188
	O	1.58697	-0.535239	0.685142	2296.033	2983.8823	3786.7627
	N	0.959744	0.110729	-0.349771			
	H	1.568606	-1.468577	0.423671			
	C	-0.132538	0.360397	0.000077	516.234	674.3734	1056.6952
	O	-1.167903	-0.219752	0.000032	1141.1362	1289.6114	1430.4637
FA							

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	O	1.051094	-0.277267	-0.000131	1909.948	3024.6264	3864.7757
	H	-0.046287	1.457713	-0.000475			
	H	1.775988	0.356057	0.000811			

Table S2: Absolute energy for the relevant species of CH_2OO + HONO reaction estimated at CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory

Species	Energy in Hartree
CH_2OO	-189.3306315
Cis-HONO	-205.4504807
Trans-HONO	-205.4511513
NO_2	-204.8160967
FA	-189.5107133
CH_2O	-114.3425655
HNO_3	-280.5440445
HPM	-394.8591518
TS^{ha}_{trans}	-394.7802752
$TS1^{ca}_{cis}$	-394.7722702
$TS1^{ca}_{cis}$	-394.7754658
$TS1^{ca}_{trans}$	-394.7795863
$TS1^{ca}_{trans}$	-394.7763635
TS^{ot}_{cis}	-394.7559786
TS^{ot}_{trans}	-394.7660783
TS^{oz}_{cis}	-394.7711454
TS^{oz}_{trans}	-394.7655403
RC^{ha}_{trans}	-394.7984774
RC^{ca}_{cis}	-394.803633
RC^{ca}_{trans}	-394.8136505
PC^{oz}_{cis}	-394.7757968
PC^{oz}_{trans}	-394.7742122

Table S3: ZCT tunneling cofficient for CH_2OO+HONO reaction within the temperature range of 213-320 K.

Temp (K)	trans-HONO				cis-HONO		
	κ_{ot}	κ_{oz}	κ_{ca}	κ_{ha}	κ_{ot}	κ_{oz}	κ_{ca}
213	2.38	1.27	1.83	13.00	2.70	1.13	1.42
216	2.31	1.26	1.80	11.80	2.61	1.13	1.40
219	2.25	1.25	1.77	10.70	2.52	1.12	1.39
224	2.16	1.24	1.72	9.31	2.40	1.12	1.37
235	1.99	1.21	1.63	7.10	2.19	1.11	1.33
250	1.82	1.18	1.54	5.30	1.97	1.09	1.28
259	1.74	1.17	1.49	4.59	1.87	1.09	1.26
280	1.59	1.14	1.40	3.51	1.69	1.07	1.22
290	1.54	1.13	1.37	3.17	1.62	1.07	1.20
298	1.50	1.13	1.35	2.95	1.58	1.06	1.19
300	1.49	1.12	1.34	2.90	1.57	1.06	1.19
310	1.45	1.12	1.32	2.68	1.52	1.06	1.17
320	1.42	1.11	1.29	2.50	1.48	1.06	1.16

Table S4: T1-Diagnostic values for the different TS inovolved in the CH_2OO + HONO reaction, calculated at CCSD(T)/aug-cc-pVTZ level of theory.

Species	T1-Diagnostic
TS_{ha}^{trans}	0.026
TS_{ot}^{cis}	0.027
TS_{ot}^{trans}	0.027
TS_{oz}^{cis}	0.031
TS_{oz}^{trans}	0.030
TS_{ca}^{cis}	0.033
TS_{ca}^{trans}	0.032

1 post-CCSD(T) calculation

To check the accuracy of CCSD(T)/aug-cc-pVTZ method, we have calculate the full CCSDT calculation for the TS of HAT reaction. The contribution accounted for the full triple excitation (ΔE_T) at CCSDT/cc-PVDZ level of theory calculated using MRCC[1] code can be expressed as follows.

$$\Delta E_T = E_{CCSDT} - E_{CCSD(T)} \tag{1}$$

and the final energy barrier can be expressed as below

$$\Delta E_{Final} = \Delta E_T + \Delta E_{CCSD(T)/aug-cc-pVTZ} \tag{2}$$

Table S5: Comparison of the energies of the HAT reaction obtained after including full T correction with the energies obtained at CCSD(T)/aug-cc-pVTZ level of theory.

species	$\Delta E_{CCSD(T)/aug-cc-pVTZ}$	ΔE_T	ΔE_{Final}
CH_2OO+HONO	0.00	0.00	0.00
TS_{ha}	0.11	0.29	0.40

Table S6: Equilibrium constants for the cis-trans-isomerization of HONO

Temp (K)	$K_{eq-HONO}$
213	3.74×10^{-1}
216	3.79×10^{-1}
219	3.83×10^{-1}
224	3.91×10^{-1}
235	4.08×10^{-1}
250	4.29×10^{-1}
259	4.41×10^{-1}
280	4.66×10^{-1}
290	4.77×10^{-1}
298	4.86×10^{-1}
300	4.88×10^{-1}
310	4.98×10^{-1}
320	5.07×10^{-1}

2 Effective rate constant for HAT reaction.

The general expression for the HAT reaction can be expressed as follows.

$$CH_2OO + HONO \underset{}{\overset{K_{eq}}{\rightleftharpoons}} RC_{ha} \xrightarrow[TS_{ha}]{k_{uni}} \text{product}$$

As the HONO exist in cis and trans form, the reaction can proceed through both the isomers and the overall rate can be expressed as follows.

$$\nu = k_{bi}^{cis}[CH_2OO][cis-HONO] + k_{bi}^{trans}[CH_2OO][trans-HONO] \tag{3}$$

for the HAT reaction k_{bi}^{cis} is zero, therefore

$$\nu = k_{bi}^{trans}[CH_2OO][trans-HONO] \tag{4}$$

However, two conformers of HONO are almost degenerate so that an equilibrium can be established between cis-HONO and trans-HONO in the atmosphere thorough

$$\text{trans-HONO} \overset{\text{K}_{eq-HONO}}{\rightleftharpoons} \text{cis-HONO}$$

and the $\text{K}_{eq-HONO}$ can be expressed as follows

$$K_{eq-HONO} = \frac{[cis-HONO]}{[trans-HONO]} \tag{5}$$

Taking into account this equilibrium, and considering the whole concentration of nitrous acid as

$$[HONO] = [cis-HONO] + [trans-HONO] \tag{6}$$

The reaction rate (4) can be written as

$$\nu = \frac{k_{bi}^{trans}}{1+K_{eq-HONO}}[CH_2OO][HONO] = k_{eff}^{ha}[CH_2OO][HONO] \tag{7}$$

where

$$k_{eff}^{ha} = \frac{k_{bi}^{trans}}{1+K_{eq-HONO}} \tag{8}$$

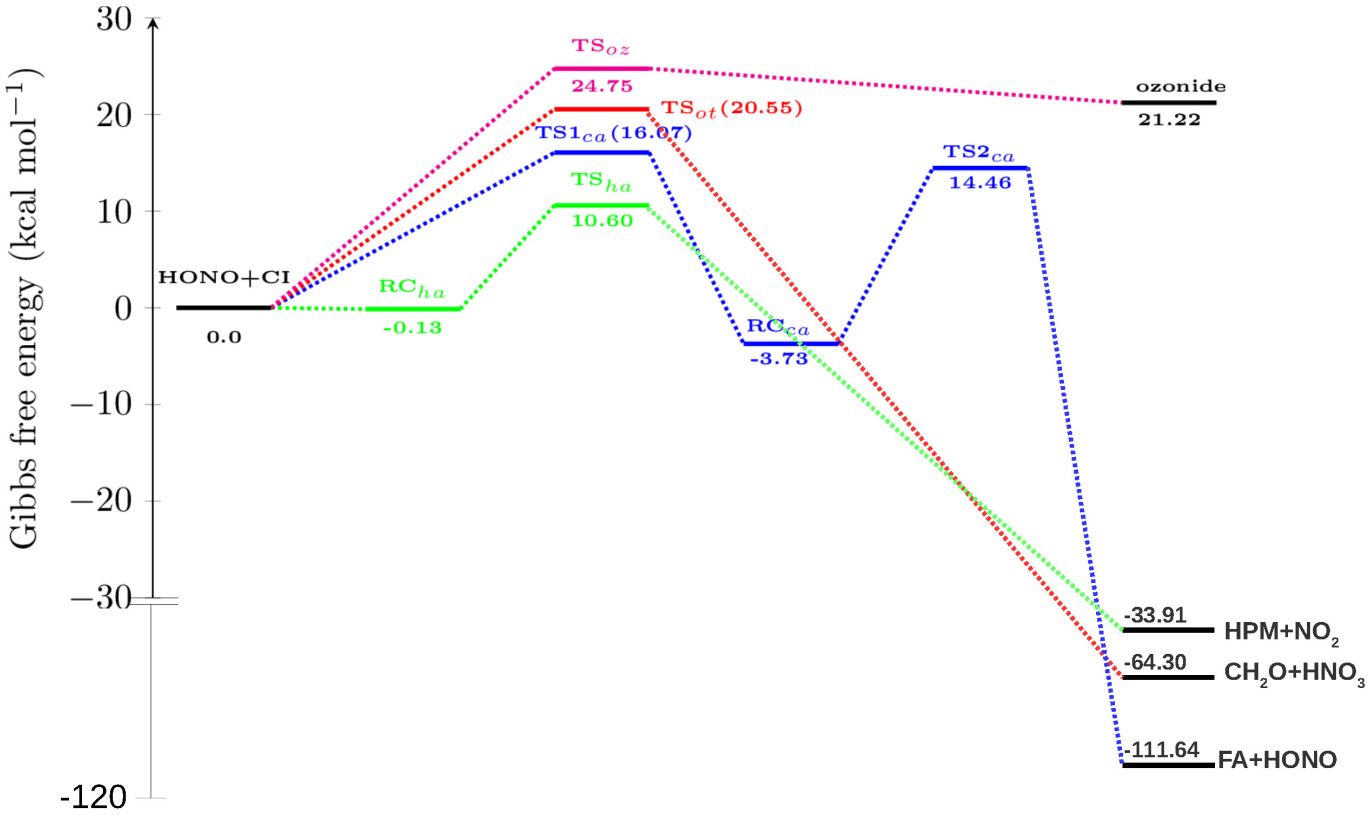

Figure S1: Gibbs free energy profile for CH_2OO + trans-HONO reaction, calculated at CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory.

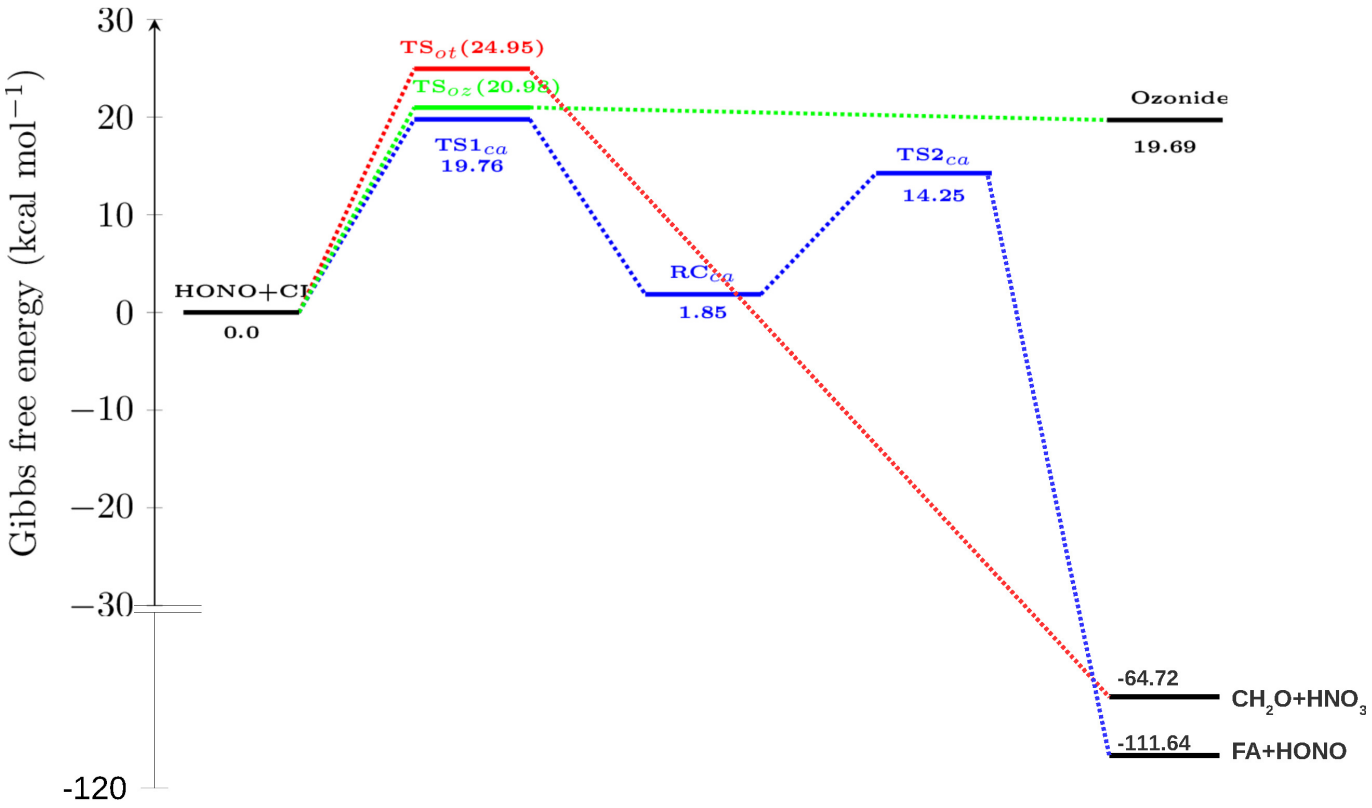

Figure S2: Gibbs free energy profile for CH_2OO + cis-HONO reaction, calculated at CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory.

References

(1) Kállay, M.; Rolik, Z.; Csontos, J.; Ladjánszki, I.; Szegedy, L.; Ladóczki, B.; Samu, G.; Petrov, K.; Farkas, M.; Nagy, *URL: http://www. mrcc. hu, accessed August 26th* **2016**,