# Reaction Mechanism between Carbonyl Oxide and Hydroxyl Radical: A Theoretical Study

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## (Supplementary material)

**Table S1.** Schematic description of the active spaces used in the CASSCF calculations.

| ***Species*** | ***State*** | ***Space[a]*** | ***Description*** |
|---|---|---|---|
| **$H_2COO$** | ($X^1$A') | (8,7) | Two bonding σ(C-O) and σ(O-$O_t$) and two π orbitals plus the two antibonding σ*(C-O) and σ*(O-$O_t$) and one π* orbitals. |
| **HO** | ($X^2\Pi$) | (3,3) | The bonding σ(O-H) orbital, the p(HO) orbital which contains the unpaired electron and the corresponding antibonding σ*(O-H) orbital. |
| **TS1, M1** | ($^2$A) | (11,10) | Two combined bonding orbitals ( σ(C-O) ± σ(O-H) ) and their corresponding antibonding σ* orbitals; the σ(O-$O_t$) bonding and the corresponding antibonding σ*(O-$O_t$); the π(O-$O_t$) bonding orbital; two combined bonding orbitals ( π(C-O) ± p(HO) ) and one π*(C-O) antibonding orbital. |
| **TS2, TS3** | ($^2$A'), ($^2$A) | (11,10) | One bonding π(O-$O_t$) orbital, four bonding σ(C-O), σ(C-H), σ(O-$O_t$) and π(C-O) orbitals and the corresponding σ* and π* orbitals, and the p(HO) orbital. |
| **TS4** | ($^2$A) | (11,10) | Five bonding σ(O-H), σ($O_t$-H), σ(O-$O_t$), σ($O_t$-$O_{(HO)}$) and π(C-O) orbitals and the corresponding σ* and π* antibonding orbitals. |
| **TS5, TS6** | ($^2$A), ($^2$A) | (11,10) | Two combined bonding orbitals ( σ(C-O) ± σ(O-H) ) and their corresponding antibonding σ* orbitals; the σ(O-$O_t$) bonding orbital and the corresponding antibonding σ*(O-$O_t$); two π(C-O) and π(O-H) orbitals; and two σ(C-H) and σ(H-$O_{(HO)}$) orbitals. |
| **TS7** | ($^2$A'') | (11,10) | Four bonding σ(C-O), σ(C-H), σ(O-$O_t$) and π(C-O) orbitals and the corresponding σ* and π* antibonding orbitals; the bonding σ($H_{(H2COO)}$-$O_{(HO)}$) orbital describing the H migration; and the p(HO) orbital. |

a) (*x*,*x*) denotes the number of active electrons and the number of active orbitals.

**Table S2.** Absolute values of the Energies, Enthalpies and Free Energies (in hartree) for the stationary points and the $T_1$ diagnostic (T1D) of the corresponding CCSD wave-function.

| Compound | E[a] | H[a] | G[a] | E[b] | T1D |
|---|---|---|---|---|---|
| **$H_2COO$** | -189.65490 | -189.61954 | -189.64783 | -189.33143 | 0.0432 |
| **HO** | -75.76506 | -75.75329 | -75.77352 | -75.64558 | 0.0101 |
| **$H_2CO$** | -114.54794 | -114.51759 | -114.54306 | -114.34272 | 0.0154 |
| **$HO_2$** | -150.96670 | -150.94874 | -150.97471 | -150.72655 | 0.0299 |
| ***anti*-HCOO** | -188.96890 | -188.94764 | -188.97630 | -188.63889 | 0.0595 |
| **$H_2O$** | -76.46256 | -76.43743 | -76.45885 | -76.34230 | 0.0100 |
| **HCO** | -113.89716 | -113.88038 | -113.90583 | -113.69231 | 0.0216 |
| **C1** | -265.43270 | -265.38359 | -265.42081 | -264.98893 | 0.0388 |
| **TS1** | -265.43082 | -265.38282 | -265.41638 | -264.98625 | 0.0435 |
| **M1** | -265.54277 | -265.48883 | -265.52190 | -265.10167 | 0.0263 |
| **TS8** | -265.51940 | -265.47198 | -265.50399 | -265.07462 | 0.0255 |
| **C3** | -265.52602 | -265.47521 | -265.51134 | -265.08173 | 0.0267 |
| **C2** | -265.43541 | -265.38622 | -265.42320 | -264.98612 | 0.0401 |
| **TS2** | -265.42168 | -265.37882 | -265.41292 | -264.96842 | 0.0562 |
| **TS3** | -265.41199 | -265.36743 | -265.40244 | -264.95999 | 0.0450 |
| **TS4** | -265.42032 | -265.37558 | -265.40884 | -264.96722 | 0.0354 |
| **TS5** | -265.41584 | -265.37177 | -265.40716 | -264.95795 | 0.0563 |
| **TS6** | -265.41428 | -265.37032 | -265.40593 | -264.95585 | 0.0564 |
| **TS7** | -265.40006 | -265.35947 | -265.39154 | -264.94539 | 0.0358 |

a) Values computed at B3LYP/6-311+G(2df,2p) level.

b) Single point CCSD(T)/aug-cc-pVTZ values at the B3LYP/6-311+G(2df,2p) optimized geometries.

**Table S3.** Absolute values of the Energies, Enthalpies and Free Energies (in hartree) for the stationary points and the $T_1$ diagnostic (T1D) of the corresponding CCSD wave-function. [a]

| compound | E[b] | H[b] | G[b] | E[c] | T1D |
|---|---|---|---|---|---|
| **$H_2COO$** | -189.18182 | -189.14654 | -189.17491 | -189.33189 | 0.0458 |
| **HO** | -75.59329 | -75.58138 | -75.60161 | -75.64558 | 0.0100 |
| **$H_2CO$** | -114.25541 | -114.22506 | -114.25053 | -114.34289 | 0.0157 |
| **$HO_2$** | -150.68907 | -150.67088 | -150.69686 | -150.72660 | 0.0305 |
| ***anti*-HCOO** | -188.49819 | -188.47483 | -188.50345 | -188.64047 | 0.0519 |
| **$H_2O$** | -76.28155 | -76.25605 | -76.27747 | -76.34228 | 0.0100 |
| ***syn*-HCOO** | -188.50300 | -188.48138 | -188.51070 | -188.65107 | 0.0634 |
| **HCO** | -113.61024 | -113.59346 | -113.61891 | -113.69250 | 0.0221 |
| **C1** | -264.78618 | -264.73672 | -264.77422 | -264.99046 | 0.0363 |
| **TS1** | -264.77892 | -264.72999 | -264.76441 | -264.98497 | 0.0442 |
| **M1** | -264.89674 | -264.84280 | -264.87587 | -265.10191 | 0.0269 |
| **TS2** | -264.75990 | -264.71554 | -264.74984 | -264.96972 | 0.0441 |
| **TS3** | -264.75546 | -264.70891 | -264.74244 | -264.96539 | 0.0385 |
| **TS4** | -264.75301 | -264.70750 | -264.74055 | -264.96816 | 0.0316 |
| **TS5** | -264.75676 | -264.71020 | -264.74383 | -264.96734 | 0.0364 |
| **TS6** | -264.75581 | -264.70917 | -264.74274 | -264.96652 | 0.0354 |
| **TS7** | -264.74520 | -264.70254 | -264.73532 | -264.94678 | 0.0370 |

a) For **TS8** and **C3**, see reference 78

b)Values computed at QCISD/6-311+G(d,p) level.

c) Single point CCSD(T)/aug-cc-pVTZ values at the QCISD/6-311+G(d,p) optimized geometries.

**Table S4.** Absolute values of the Energies, Enthalpies and Free Energies (in hartree) for the stationary points.

| Compound | space[a] | E[b] | H[b] | G[b] | space[c] | E[d] |
|---|---|---|---|---|---|---|
| **$H_2COO$** | (8,7) | -188.76209 | -188.72631 | -188.75466 | (12,9) | -189.27664 |
| **HO** [e] | (3,3) | -75.43722 | -75.42547 | -75.44570 | (5,5) | -75.62541 |
| ***anti*-HCOO** | (9,9) | -188.13239 | -188.11031 | -188.13920 | (11,8) | -188.59586 |
| **$H_2O$** | (6,6) | -76.14987 | -76.12467 | -76.14610 | (6,6) | -76.31635 |
| ***syn*-HCOO** | (9,9) | -188.13665 | -188.11466 | -188.14380 | (11,8) | -188.58307 |
| **HCO** | (7,7) | -113.40481 | -113.38725 | -113.41201 | (11,8) | -113.65478 |
| **C1** | (11,10) | -264.20757 | -264.15763 | -264.19586 | (17,14) | -264.91135 |
| **TS1** | (11,10) | -264.19656 | -264.14825 | -264.18390 | (17,14) | -264.91274 |
| **M1** | (11,10) | -264.30109 | -264.24516 | -264.27787 | (17,14) | -265.02664 |
| **TS2** | (11,10) | -264.15513 | -264.11135 | -264.14578 | (17,14) | -264.89417 |
| **TS3** | (11,10) | -264.15444 | -264.10659 | -264.14006 | (17,14) | -264.88680 |
| **TS4** | (11,10) | -264.13040 | -264.08411 | -264.11716 | (17,14) | -264.89359 |
| **TS5** | (11,10) | -264.15553 | -264.10759 | -264.14113 | (17,14) | -264.88845 |
| **TS6** | (11,10) | -264.15428 | -264.10650 | -264.14003 | (17,14) | -264.88803 |
| **TS7** | (11,10) | -264.14077 | -264.09515 | -264.12787 | (17,14) | -264.87489 |

a) (*x*,*x*) denotes the number of active electrons and the number of active orbitals of the CASSCF.

b) Values computed at CASSCF(*x*,*x*)/6-311+G(2df,2p) level.

c) (*y*,*y*) denotes the number of active electrons and the number of active orbitals of the CASPT2.

d) Single point CASPT2(*y*,*y*)/6-311+G(2df,2p) values at the CASSCF(*x*,*x*)/6-311+G(2df,2p) optimized geometries.

e) The Single point CASPT2(*3*,*3*)/6-311+G(2df,2p) values at the CASSCF(*3*,*3*)/6-311+G(2df,2p) optimized geometries is -75.62650 hartree

**Table S5.** Calculated topological properties at the *bcp* for the pre-reactive complexes in the $H_2COO$ + HO reaction.

| x-y | $r_x$ | $r_y$ | $\rho$ | $\nabla^2\rho$ | $\varepsilon$ |
|---|---|---|---|---|---|
| | | | **C1**[a] | | |
| **O2-C1** | 1.600811 | 0.797228 | 0.344847 | 0.196388 | 0.101474 |
| **O3-O2** | 1.209984 | 1.368286 | 0.337589 | 0.005049 | 0.043857 |
| **H5-C1** | 0.698070 | 1.352914 | 0.287795 | -1.026076 | 0.031737 |
| **H4-C1** | 0.681558 | 1.374787 | 0.287284 | -1.034757 | 0.023389 |
| **H7-O6** | 3.624182 | 1.488880 | 0.350102 | -2.451725 | 0.037424 |
| **H7-O3** | 1.286428 | 2.383382 | 0.027113 | 0.086729 | 0.038783 |
| **O6-H4** | 2.841124 | 1.847971 | 0.009689 | 0.030801 | 0.593230 |
| | | | **C1**[b] | | |
| **O2-C1** | 1.598368 | 0.786419 | 0.356202 | -0.035945 | 0.281484 |
| **O3-O2** | 1.209452 | 1.398273 | 0.302455 | 0.283764 | 0.044915 |
| **H5-C1** | 0.692258 | 1.330586 | 0.312355 | -1.329146 | 0.035959 |
| **H4-C1** | 0.672411 | 1.352652 | 0.312852 | -1.348361 | 0.028550 |
| **H7-O6** | 0.365412 | 1.480309 | 0.357707 | -2.578767 | 0.040418 |
| **H7-O3** | 1.412934 | 2.518565 | 0.018624 | 0.069515 | 0.050796 |
| **O6-H4** | 2.962271 | 1.940352 | 0.007192 | 0.027016 | 0.484609 |
| | | | **TS1**[a] | | |
| **O2-O3** | 1.375288 | 1.240634 | 0.324336 | 0.022942 | 0.018485 |
| **C1-O2** | 0.776595 | 1.595654 | 0.351738 | 0.413381 | 0.066143 |
| **H5-C1** | 0.693093 | 1.358591 | 0.286954 | -1.028386 | 0.035160 |
| **H4-C1** | 0.686161 | 1.366048 | 0.286959 | -1.027358 | 0.033093 |
| **O6-C1** | 2.159957 | 2.210800 | 0.033153 | 0.095399 | 0.223331 |
| **H7-O6** | 0.375777 | 1.467603 | 0.355896 | -2.403344 | 0.039379 |
| | | | **TS1**[b] | | |
| **O2-O3** | 1.338024 | 1.199630 | 0.338551 | 0.215339 | 0.041144 |
| **C1-O2** | 0.806847 | 1.649983 | 0.325048 | -0.106022 | 0.220418 |
| **H5-C1** | 0.689463 | 1.326002 | 0.309975 | -1.293732 | 0.044949 |
| **H4-C1** | 0.683113 | 1.333832 | 0.309458 | -1.294444 | 0.037357 |
| **O6-C1** | 2.165357 | 2.238407 | 0.030501 | 0.098210 | 0.184144 |
| **H7-O6** | 0.384588 | 1.457788 | 0.359383 | -2.464322 | 0.043580 |
| | | | **TS2**[a] | | |
| **H5-C1** | 0.695835 | 1.373394 | 0.278749 | -0.982375 | 0.000677 |
| **O2-C1** | 1.558225 | 0.766726 | 0.369538 | 0.510304 | 0.005513 |
| **O3-O2** | 1.235806 | 1.396563 | 0.309141 | 0.100450 | 0.035541 |
| **H4-C1** | 0.767702 | 1.729896 | 0.156590 | -0.243103 | 0.019025 |
| **O6-H4** | 1.604675 | 0.588048 | 0.193405 | -0.271602 | 0.037343 |
| **H7-O6** | 0.355180 | 1.490990 | 0.347163 | -2.417583 | 0.027427 |
| **H7-O3** | 1.410902 | 2.381666 | 0.026786 | 0.083760 | 0.048649 |
| | | | **TS2**[b] | | |
| **H5-C1** | 0.685580 | 1.341954 | 0.306549 | -1.295733 | 0.026795 |
| **O2-C1** | 1.587827 | 0.774545 | 0.369825 | 0.093317 | 0.250521 |

| | | | | | |
|---|---|---|---|---|---|
| **O3-O2** | 1.219031 | 1.414079 | 0.285514 | 0.360789 | 0.039487 |
| **H4-C1** | 0.857607 | 1.740323 | 0.131852 | -0.151231 | 0.033816 |
| **O6-H4** | 1.556770 | 0.603220 | 0.203164 | -0.344202 | 0.040865 |
| **H7-O6** | 0.314123 | 1.484334 | 0.376070 | -2.968432 | 0.028398 |
| **H7-O3** | 1.662388 | 2.658668 | 0.014650 | 0.055334 | 0.268888 |
| | | | **TS4**[a] | | |
| **O6-H7** | 1.454044 | 0.369385 | 0.360423 | -2.442035 | 0.010056 |
| **C1-H4** | 1.782770 | 0.678818 | 0.166577 | -0.327184 | 0.008621 |
| **H5-C1** | 0.711303 | 1.361007 | 0.280501 | -0.984817 | 0.018128 |
| **O2-C1** | 1.597630 | 0.776330 | 0.344447 | 0.519356 | 0.201511 |
| **O3-O2** | 1.299977 | 1.408053 | 0.287303 | 0.110691 | 0.084189 |
| **ring** | | | 0.052606 | 0.221232 | |
| | | | **TS4**[b] | | |
| **O6-H7** | 1.454274 | 0.378726 | 0.356662 | -2.435858 | 0.007985 |
| **C1-H4** | 1.794815 | 0.673116 | 0.161680 | -0.355455 | 0.002766 |
| **H5-C1** | 0.701517 | 1.343099 | 0.299340 | -1.217204 | 0.023778 |
| **O2-C1** | 1.576958 | 0.755437 | 0.371557 | 0.563792 | 0.146581 |
| **O3-O2** | 1.375393 | 1.481228 | 0.218130 | 0.309390 | 0.109902 |
| **ring** | | | 0.057617 | 0.239884 | |

a) Obtained from the QCISD/6-311+G(d, p) wave function. Atom numbering is as shown in Figure 3 and Figure 5.

b) Obtained from the CASSCF(11,10)/6-311+G(2df,2p) wave function. Atom numbering as shown in Figure 3 and Figure 5.

**Table S6.** Cartesian coordinates of the optimized stationary points.

**B3LYP/6-311+G(2df,2p)**

**$H_2COO$**

| | | | |
|---|---|---|---|
| O | -1.177141 | -0.197774 | 0.000000 |
| O | 0.000000 | 0.456746 | 0.000000 |
| C | 1.069093 | -0.197622 | 0.000000 |
| H | 1.029444 | -1.280025 | 0.000000 |
| H | 1.973123 | 0.393985 | 0.000000 |

**HO**

| | | | |
|---|---|---|---|
| O | 0.000000 | 0.000000 | 0.108248 |
| H | 0.000000 | 0.000000 | -0.865985 |

**$H_2CO$**

| | | | |
|---|---|---|---|
| C | -0.000002 | 0.526698 | 0.000000 |
| O | -0.000002 | -0.672885 | 0.000000 |
| H | 0.000015 | 1.111446 | 0.938206 |
| H | 0.000015 | 1.111446 | -0.938206 |

**$HO_2$**

| | | | |
|---|---|---|---|
| O | 0.055269 | -0.608442 | 0.000000 |
| O | 0.055269 | 0.717284 | 0.000000 |
| H | -0.884305 | -0.870735 | 0.000000 |

***a*-HCOO**

| | | | |
|---|---|---|---|
| O | -1.126690 | -0.434493 | 0.000000 |
| O | 0.000000 | 0.299460 | 0.000000 |
| C | 1.194290 | 0.028485 | 0.000000 |
| H | 1.847781 | 0.909359 | 0.000000 |

**$H_2O$**

| | | | |
|---|---|---|---|
| O | 0.000000 | 0.000000 | 0.117791 |
| H | 0.000000 | 0.760331 | -0.471163 |
| H | 0.000000 | -0.760331 | -0.471163 |

**HCO**

| | | | |
|---|---|---|---|
| C | 0.061636 | 0.582600 | 0.000000 |
| O | 0.061636 | -0.589339 | 0.000000 |
| H | -0.862898 | 1.219110 | 0.000000 |

**C1**

| | | | |
|---|---|---|---|
| O | 0.000000 | 1.154571 | 0.000000 |
| O | -1.160213 | 0.438832 | 0.000000 |
| C | -1.127396 | -0.811008 | 0.000000 |
| H | -2.098912 | -1.286795 | 0.000000 |
| H | -0.174864 | -1.333008 | 0.000000 |
| O | 2.104477 | -0.670687 | 0.000000 |
| H | 1.484045 | 0.104120 | 0.000000 |

**TS1**

| | | | |
|---|---|---|---|
| O | -0.706866 | -1.124756 | 0.159598 |
| O | -0.989901 | 0.125686 | -0.297764 |

| | | | |
|---|---|---|---|
| C | -0.348073 | 1.088273 | 0.190535 |
| H | -0.537035 | 2.047643 | -0.270858 |
| H | 0.295401 | 0.939586 | 1.049442 |
| O | 1.839759 | -0.088383 | -0.104158 |
| H | 1.186136 | -0.817237 | 0.016791 |

**M1**

| | | | |
|---|---|---|---|
| O | -1.388272 | -0.544392 | 0.132094 |
| O | -0.752787 | 0.518993 | -0.310616 |
| C | 0.604901 | 0.561517 | 0.250054 |
| H | 1.020703 | 1.485056 | -0.142505 |
| H | 0.476710 | 0.592542 | 1.333235 |
| O | 1.369765 | -0.492382 | -0.185211 |
| H | 1.043533 | -1.304460 | 0.218816 |

**TS8**

| | | | |
|---|---|---|---|
| C | -0.888126 | 0.999985 | 0.069202 |
| H | -1.700416 | 1.684598 | -0.136551 |
| H | 0.107464 | 1.287082 | 0.393161 |
| O | 2.046614 | 0.302175 | -0.028899 |
| H | 1.526891 | -0.495830 | -0.271001 |
| O | -1.159382 | -0.204111 | -0.124822 |
| O | -0.212880 | -1.157534 | 0.103618 |

**C3**

| | | | |
|---|---|---|---|
| C | -0.992472 | -1.051460 | 0.000000 |
| O | -1.441614 | 0.075478 | 0.000000 |
| H | -0.800663 | -1.598014 | 0.935614 |
| H | -0.800663 | -1.598014 | -0.935614 |
| O | 1.390256 | -0.136380 | 0.000000 |
| O | 0.995877 | 1.114815 | 0.000000 |
| H | 0.000000 | 1.073479 | 0.000000 |

**C2**

| | | | |
|---|---|---|---|
| C | -1.005213 | -0.894318 | 0.007976 |
| O | -1.069181 | 0.354352 | 0.005358 |
| O | 0.073707 | 1.089108 | -0.016930 |
| O | 1.727040 | -0.469350 | -0.033345 |
| H | -1.969551 | -1.385178 | 0.023987 |
| H | -0.028989 | -1.368664 | 0.006390 |
| H | 2.177294 | 0.326869 | 0.281106 |

**TS2**

| | | | |
|---|---|---|---|
| C | -1.046318 | 0.449097 | 0.000000 |
| H | -1.968770 | 1.028102 | 0.000000 |
| O | 0.000000 | 1.112296 | 0.000000 |
| O | 1.234808 | 0.547876 | 0.000000 |
| H | -0.846157 | -0.825440 | 0.000000 |
| O | -0.189410 | -1.833634 | 0.000000 |
| H | 0.729651 | -1.509554 | 0.000000 |

**TS3**

| | | | |
|---|---|---|---|
| C | -0.148749 | 0.858014 | 0.292821 |
| H | -0.448162 | 1.769880 | -0.223361 |
| O | 0.952080 | 0.433331 | -0.258201 |
| O | 1.377995 | -0.790290 | 0.096062 |

| | | | |
|---|---|---|---|
| H | -1.015853 | 0.026044 | 0.713297 |
| O | -1.725772 | -0.520767 | -0.093054 |
| H | -2.477912 | 0.077801 | -0.205320 |

**TS4**

| | | | |
|---|---|---|---|
| H | -1.838732 | 0.092317 | 0.735960 |
| O | -1.615493 | -0.350822 | -0.092859 |
| H | -0.560699 | -0.975267 | 0.020312 |
| C | 0.780192 | -0.973256 | 0.012261 |
| H | 1.687139 | -1.583457 | 0.033310 |
| O | 1.094465 | 0.238356 | 0.006302 |
| O | 0.024920 | 1.150710 | -0.021337 |

**TS5**

| | | | |
|---|---|---|---|
| C | 0.110459 | 0.648368 | 0.202798 |
| H | -0.132129 | 1.365488 | -0.582294 |
| O | -0.743686 | -0.291585 | 0.368514 |
| O | -1.920223 | -0.138502 | -0.311319 |
| H | 1.305035 | 0.376950 | 0.499039 |
| O | 2.182296 | -0.137781 | -0.183978 |
| H | 2.017235 | -1.089708 | -0.119266 |

**TS6**

| | | | |
|---|---|---|---|
| C | -0.099906 | 0.577869 | -0.297168 |
| H | 0.154833 | 1.435049 | 0.329200 |
| O | 0.765625 | -0.364048 | -0.292728 |
| O | 1.947663 | -0.060907 | 0.319968 |
| H | -1.279129 | 0.228635 | -0.541941 |
| O | -2.178243 | -0.274431 | 0.142164 |
| H | -2.556622 | 0.464193 | 0.640508 |

**TS7**

| | | | |
|---|---|---|---|
| C | 0.344677 | -1.171513 | 0.000000 |
| H | 1.194786 | -0.176333 | 0.000000 |
| O | 1.407815 | 1.122134 | 0.000000 |
| H | 0.000000 | 1.057269 | 0.000000 |
| O | -1.024112 | 0.687276 | 0.000000 |
| O | -0.833640 | -0.757793 | 0.000000 |
| H | 0.336650 | -2.264795 | 0.000000 |

**QCISD/6-311+G(d,p)**

**$H_2COO$**

| | | | |
|---|---|---|---|
| O | -1.176015 | -0.203652 | 0.000000 |
| O | 0.000000 | 0.478260 | 0.000000 |
| C | 1.069571 | -0.210837 | 0.000000 |

| | | | |
|---|---|---|---|
| H | 1.001331 | -1.295915 | 0.000000 |
| H | 1.989360 | 0.364073 | 0.000000 |

**HO**

| | | | |
|---|---|---|---|
| O | 0.000000 | 0.000000 | 0.107922 |
| H | 0.000000 | 0.000000 | -0.863374 |

**$H_2CO$**

| | | | |
|---|---|---|---|
| C | -0.000007 | 0.530556 | 0.000000 |
| O | -0.000007 | -0.677336 | 0.000000 |
| H | 0.000048 | 1.117675 | 0.938520 |
| H | 0.000048 | 1.117675 | -0.938520 |

**$HO_2$**

| | | | |
|---|---|---|---|
| O | 0.055254 | -0.613592 | 0.000000 |
| O | 0.055254 | 0.721072 | 0.000000 |
| H | -0.884064 | -0.859845 | 0.000000 |

***a*-HCOO**

| | | | |
|---|---|---|---|
| O | -1.117706 | -0.500659 | 0.000000 |
| O | 0.000000 | 0.339777 | 0.000000 |
| C | 1.177624 | 0.062033 | 0.000000 |
| H | 1.875903 | 0.914857 | 0.000000 |

**$H_2O$**

| | | | |
|---|---|---|---|
| H | 0.000000 | 0.756586 | -0.468730 |
| O | 0.000000 | 0.000000 | 0.117182 |
| H | 0.000000 | -0.756586 | -0.468730 |

***s*-HCOO**

| | | | |
|---|---|---|---|
| O | -0.975776 | -0.530761 | 0.000000 |
| O | 0.000000 | 0.597697 | 0.000000 |
| C | 1.102116 | 0.081610 | 0.000000 |
| H | 1.193515 | -1.025150 | 0.000000 |

**HCO**

| | | | |
|---|---|---|---|
| C | 0.061383 | 0.586848 | 0.000000 |
| O | 0.061383 | -0.593996 | 0.000000 |
| H | -0.859360 | 1.230880 | 0.000000 |

**C1**

| | | | |
|---|---|---|---|
| C | -1.050424 | -0.860325 | 0.000000 |
| O | -1.147843 | 0.406977 | 0.000000 |
| O | 0.000000 | 1.136101 | 0.000000 |
| H | -2.002817 | -1.381134 | 0.000000 |
| H | -0.065894 | -1.323070 | 0.000000 |
| O | 1.928472 | -0.603022 | 0.000000 |
| H | 2.126224 | 0.345706 | 0.000000 |

**TS1**

| | | | |
|---|---|---|---|
| O | -1.212563 | -0.852858 | 0.184602 |
| O | -0.767159 | 0.302781 | -0.433291 |
| C | -0.003721 | 1.028917 | 0.248441 |
| H | 0.374555 | 1.912154 | -0.256988 |
| H | 0.154821 | 0.804715 | 1.299099 |
| O | 1.773596 | -0.416696 | -0.068762 |
| H | 1.141957 | -1.156190 | 0.006852 |

**M1**

| | | | |
|---|---|---|---|
| O | -1.376476 | -0.550273 | 0.131852 |
| O | -0.743699 | 0.528172 | -0.314280 |
| C | 0.593971 | 0.561102 | 0.254588 |
| H | 1.021702 | 1.489065 | -0.125467 |
| H | 0.467450 | 0.577069 | 1.342577 |
| O | 1.361622 | -0.494963 | -0.187605 |
| H | 1.015452 | -1.296244 | 0.215624 |

**TS8**

| | | | |
|---|---|---|---|
| C | -0.898944 | -0.673672 | 0.000000 |
| O | -1.165163 | 0.573924 | 0.000000 |
| O | 0.961084 | -0.579130 | 0.000000 |
| O | 1.126019 | 0.699283 | 0.000000 |
| H | 0.000000 | 0.993149 | 0.000000 |
| H | -0.990929 | -1.251869 | 0.928085 |
| H | -0.990929 | -1.251869 | -0.928085 |

**C3**

| | | | |
|---|---|---|---|
| O | -1.481277 | 0.013602 | 0.000000 |
| O | -0.967537 | 1.234267 | 0.000000 |
| H | 0.000000 | 1.092994 | 0.000000 |
| O | 1.485575 | -0.067361 | 0.000000 |
| C | 1.017183 | -1.183701 | 0.000000 |
| H | 0.801404 | -1.717429 | 0.934479 |
| H | 0.801404 | -1.717429 | -0.934479 |

**TS2**

| | | | |
|---|---|---|---|
| C | -1.037535 | 0.459875 | 0.000000 |
| H | -1.973820 | 1.027646 | 0.000000 |
| O | 0.000000 | 1.119257 | 0.000000 |
| O | 1.247018 | 0.499582 | 0.000000 |
| H | -0.854439 | -0.849041 | 0.000000 |
| O | -0.202104 | -1.808596 | 0.000000 |
| H | 0.694151 | -1.419803 | 0.000000 |

**TS3**

| | | | |
|---|---|---|---|
| C | -0.253337 | 0.772548 | 0.369258 |
| H | -0.657920 | 1.667530 | -0.113046 |
| O | 0.832135 | 0.431381 | -0.356802 |
| O | 1.449098 | -0.658979 | 0.142832 |
| H | -1.014849 | -0.145025 | 0.826026 |
| O | -1.580782 | -0.536701 | -0.133845 |
| H | -2.410816 | -0.043397 | -0.146004 |

**TS4**

| | | | |
|---|---|---|---|
| H | -1.837457 | -0.013254 | 0.741434 |
| O | -1.558205 | -0.402584 | -0.096095 |
| H | -0.467194 | -1.018696 | 0.022793 |
| C | 0.832200 | -0.935261 | 0.014111 |
| H | 1.769461 | -1.504297 | 0.028282 |
| O | 1.084150 | 0.295413 | 0.005261 |
| O | -0.083196 | 1.125648 | -0.018813 |

**TS5**

| | | | |
|---|---|---|---|
| C | -0.266133 | 0.798079 | 0.153567 |

| | | | |
|---|---|---|---|
| H | -0.089366 | 0.757184 | 1.230358 |
| O | 0.727584 | 0.185195 | -0.529133 |
| O | 1.627128 | -0.447269 | 0.270600 |
| H | -1.458426 | 0.662249 | -0.299412 |
| O | -1.768697 | -0.391997 | 0.105880 |
| H | -1.543523 | -0.975329 | -0.631123 |

**TS6**

| | | | |
|---|---|---|---|
| C | -0.263807 | 0.751317 | 0.287998 |
| H | -0.112684 | 0.480028 | 1.336665 |
| O | 0.759800 | 0.311489 | -0.471449 |
| O | 1.602001 | -0.522352 | 0.192285 |
| H | -1.424968 | 0.701189 | -0.247799 |
| O | -1.696601 | -0.437485 | -0.156029 |
| H | -2.201110 | -0.502337 | 0.664689 |

**TS7**

| | | | |
|---|---|---|---|
| C | 0.382650 | -1.159065 | 0.000000 |
| H | 1.192593 | -0.148817 | 0.000000 |
| O | 1.359238 | 1.157359 | 0.000000 |
| H | 0.000000 | 1.042319 | 0.000000 |
| O | -1.025041 | 0.655281 | 0.000000 |
| O | -0.820461 | -0.773205 | 0.000000 |
| H | 0.401618 | -2.254597 | 0.000000 |

**CASSCF/6-311+G(2df,2p)**

**$H_2COO$ (8,7)**

| | | | |
|---|---|---|---|
| O | 0.006535 | -0.000538 | 0.000000 |
| O | 1.356004 | 0.004510 | 0.000000 |
| C | 1.951254 | 1.134119 | 0.000000 |
| H | 1.372495 | 2.033675 | 0.000000 |
| H | 3.018211 | 1.078813 | 0.000000 |

**HO (3,3)**

| | | | |
|---|---|---|---|
| O | 0.000000 | 0.000000 | 0.053647 |
| H | 0.000000 | 0.000000 | -0.919470 |

***a*-HCOO (9,9)**

| | | | |
|---|---|---|---|
| O | -1.010728 | -0.536881 | 0.000000 |
| O | -0.016290 | 0.502909 | 0.000000 |
| C | 1.171538 | -0.025283 | 0.000000 |
| H | 1.791301 | 0.875263 | 0.000000 |

**$H_2O$ (6,6)**

| | | | |
|---|---|---|---|
| O | 0.000000 | 0.000000 | 0.066737 |
| H | 0.000000 | 0.756977 | -0.529584 |
| H | 0.000000 | -0.756977 | -0.529584 |

***s*-HCOO (9,9)**

| | | | |
|---|---|---|---|
| O | -1.130821 | -0.433696 | 0.000000 |
| O | -0.026880 | 0.518505 | 0.000000 |
| C | 1.093982 | 0.037452 | 0.000000 |
| H | 1.383574 | -0.998865 | 0.000000 |

**C1 (11,10)**

| | | | |
|---|---|---|---|
| C | -1.199083 | -0.808466 | 0.000000 |
| O | -1.264770 | 0.451312 | 0.000000 |
| O | -0.081636 | 1.160836 | 0.000000 |
| H | -2.145568 | -1.308475 | 0.000000 |
| H | -0.245934 | -1.298193 | 0.000000 |
| O | 2.268941 | -0.695534 | 0.000000 |
| H | 1.693917 | 0.093967 | 0.000000 |

**C1 (17,14)**

| | | | |
|---|---|---|---|
| C | -1.202537 | -0.817475 | 0.000000 |
| O | -1.249211 | 0.457147 | 0.000000 |
| O | -0.092164 | 1.157500 | 0.000000 |
| H | -2.161071 | -1.291665 | 0.000000 |
| H | -0.259479 | -1.323643 | 0.000000 |
| O | 2.301912 | -0.673812 | 0.000000 |
| H | 1.688416 | 0.087395 | 0.000000 |

**TS1 (11,10)**

| | | | |
|---|---|---|---|
| O | -1.489435 | -0.717709 | 0.230608 |
| O | -0.864145 | 0.278147 | -0.417363 |
| C | 0.007932 | 0.964883 | 0.258171 |
| H | 0.426403 | 1.785966 | -0.278671 |
| H | 0.091004 | 0.803445 | 1.309936 |
| O | 1.916394 | -0.343529 | -0.017167 |
| H | 1.373332 | -1.148380 | -0.105562 |

**TS1 (17,14)**

| | | | |
|---|---|---|---|
| O | -1.480851 | -0.727159 | 0.224652 |
| O | -0.856165 | 0.271829 | -0.414185 |
| C | 0.009630 | 0.968952 | 0.261665 |
| H | 0.428212 | 1.786619 | -0.281447 |
| H | 0.428212 | 1.786619 | -0.281447 |
| O | 1.903259 | -0.342973 | -0.010520 |
| H | 1.361714 | -1.147999 | -0.114228 |

**M1 (11,10)**

| | | | |
|---|---|---|---|
| O | -1.417993 | -0.500790 | 0.194321 |
| O | -0.726195 | 0.505201 | -0.361535 |

| | | | |
|---|---|---|---|
| C | 0.582898 | 0.559920 | 0.254307 |
| H | 1.011234 | 1.479075 | -0.103663 |
| H | 0.441825 | 0.561640 | 1.322804 |
| O | 1.401095 | -0.485670 | -0.174561 |
| H | 1.047157 | -1.305447 | 0.185617 |

**TS2 (11,10)**

| | | | |
|---|---|---|---|
| C | -1.000270 | 0.489105 | 0.000000 |
| H | -1.972636 | 0.942593 | 0.000000 |
| O | 0.010158 | 1.223908 | 0.000000 |
| O | 1.264773 | 0.618237 | 0.000000 |
| H | -0.786550 | -0.868939 | 0.000000 |
| O | -0.249128 | -1.877669 | 0.000000 |
| H | 0.647456 | -1.558492 | 0.000000 |

**TS3 (11,10)**

| | | | |
|---|---|---|---|
| C | -0.235503 | 0.765803 | 0.369635 |
| H | -0.643720 | 1.652392 | -0.090151 |
| O | 0.839499 | 0.435647 | -0.380763 |
| O | 1.495344 | -0.639901 | 0.156671 |
| H | -1.023867 | -0.136083 | 0.810040 |
| O | -1.639853 | -0.554798 | -0.111164 |
| H | -2.428372 | -0.035703 | -0.165849 |

**TS4 (11,10)**

| | | | |
|---|---|---|---|
| H | -1.804427 | -0.088221 | 0.785340 |
| O | -1.566305 | -0.353474 | -0.128027 |
| H | -0.478254 | -0.982039 | 0.006133 |
| C | 0.843872 | -0.926209 | 0.033206 |
| H | 1.745494 | -1.524541 | 0.054892 |
| O | 1.134880 | 0.278814 | -0.009217 |
| O | -0.135502 | 1.142639 | -0.045355 |

**TS5 (11,10)**

| | | | |
|---|---|---|---|
| c | -0.254910 | 0.819968 | 0.150769 |
| H | -0.082506 | 0.763972 | 1.210215 |
| O | 0.755968 | 0.221391 | -0.542485 |
| O | 1.627179 | -0.471075 | 0.294713 |
| H | -1.465597 | 0.648837 | -0.277914 |
| O | -1.777325 | -0.414489 | 0.103457 |
| H | -1.574243 | -0.980492 | -0.638018 |

**TS6 (11,10)**

| | | | |
|---|---|---|---|
| C | -0.246451 | 0.761145 | 0.283739 |
| H | -0.104840 | 0.488535 | 1.315473 |
| O | 0.778989 | 0.320723 | -0.477877 |
| O | 1.615323 | -0.526840 | 0.210988 |
| H | -1.420542 | 0.696254 | -0.227474 |
| O | -1.752892 | -0.430072 | -0.161098 |
| H | -2.206957 | -0.527896 | 0.662607 |

**TS7 (11,10)**

| | | | |
|---|---|---|---|
| C | 0.365863 | -1.155216 | 0.000000 |
| H | 1.181259 | -0.158224 | 0.000000 |

| | | | |
|---|---|---|---|
| O | 1.423793 | 1.156576 | 0.000000 |
| H | -0.050489 | 1.034486 | 0.000000 |
| O | -1.029943 | 0.672930 | 0.000000 |
| O | -0.820505 | -0.796366 | 0.000000 |
| H | 0.420618 | -2.234912 | 0.000000 |