Electronic Supplementary Material (ESI) for Faraday Discussions.


# SUPPORTING INFORMATION

## A systematic mechanistic survey on the reactions between OH radical and $CH_3OH$ on ice

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**Table S1** Computed binding energies (eV).

| | $CH_2OH$ | $CH_3OH$ |
|---|---|---|
| A | 0.64 | 0.36 |
| B | 0.58 | 0.37 |
| C | 0.53 | 0.47 |
| D | 0.34 | 0.72 |
| E | 0.69 | 0.30 |
| F | 0.29 | 0.35 |
| G | 0.69 | 0.52 |
| H | 0.58 | 0.15 |
| I | 0.37 | 0.42 |
| J | 0.38 | 0.28 |
| K | 0.58 | 0.38 |
| L | 0.59 | 0.6 |
| M | 0.59 | 0.62 |
| N | 0.29 | 0.32 |
| O | 0.35 | 0.17 |
| P | 0.37 | 0.38 |

**Table S2.** Computed binding energies (eV**,** without ZPE) from and ωB97X-D/Def2-TZVP and ONIOM(ωB97X-D/Def2-TZVP:AMOEBA09) methods. Binding energies are shown in ascending order.

| $CH_2OH$ binding energy | QM | ONIOM (QM:MM) | Discrepancy | $CH_3OH$ binding energy | QM | ONIOM (QM:MM) | Discrepancy |
|---|---|---|---|---|---|---|---|
| N | 0.30 | 0.25 | 0.05 | H | 0.16 | 0.18 | -0.02 |
| J | 0.35 | 0.37 | -0.02 | J | 0.30 | 0.34 | -0.04 |
| D | 0.36 | 0.38 | -0.02 | N | 0.31 | 0.37 | -0.06 |
| F | 0.38 | 0.41 | -0.03 | E | 0.32 | 0.38 | -0.06 |
| O | 0.46 | 0.42 | 0.04 | B | 0.43 | 0.43 | 0.00 |
| I | 0.47 | 0.46 | 0.01 | A | 0.44 | 0.44 | 0.00 |
| M | 0.47 | 0.46 | 0.01 | F | 0.46 | 0.44 | 0.02 |
| P | 0.49 | 0.47 | 0.02 | O | 0.50 | 0.46 | 0.04 |
| C | 0.61 | 0.61 | 0.00 | K | 0.51 | 0.48 | 0.03 |
| B | 0.64 | 0.66 | -0.02 | P | 0.51 | 0.48 | 0.03 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| K | 0.65 | 0.67 | -0.02 | I | 0.52 | 0.52 | 0.00 |
| L | 0.65 | 0.69 | -0.04 | M | 0.58 | 0.59 | -0.01 |
| H | 0.67 | 0.70 | -0.03 | C | 0.64 | 0.61 | 0.03 |
| A | 0.84 | 0.77 | 0.07 | G | 0.67 | 0.66 | 0.01 |
| G | 0.85 | 0.80 | 0.05 | L | 0.70 | 0.69 | 0.01 |
| E | 0.87 | 0.81 | 0.06 | D | 0.87 | 0.89 | -0.02 |

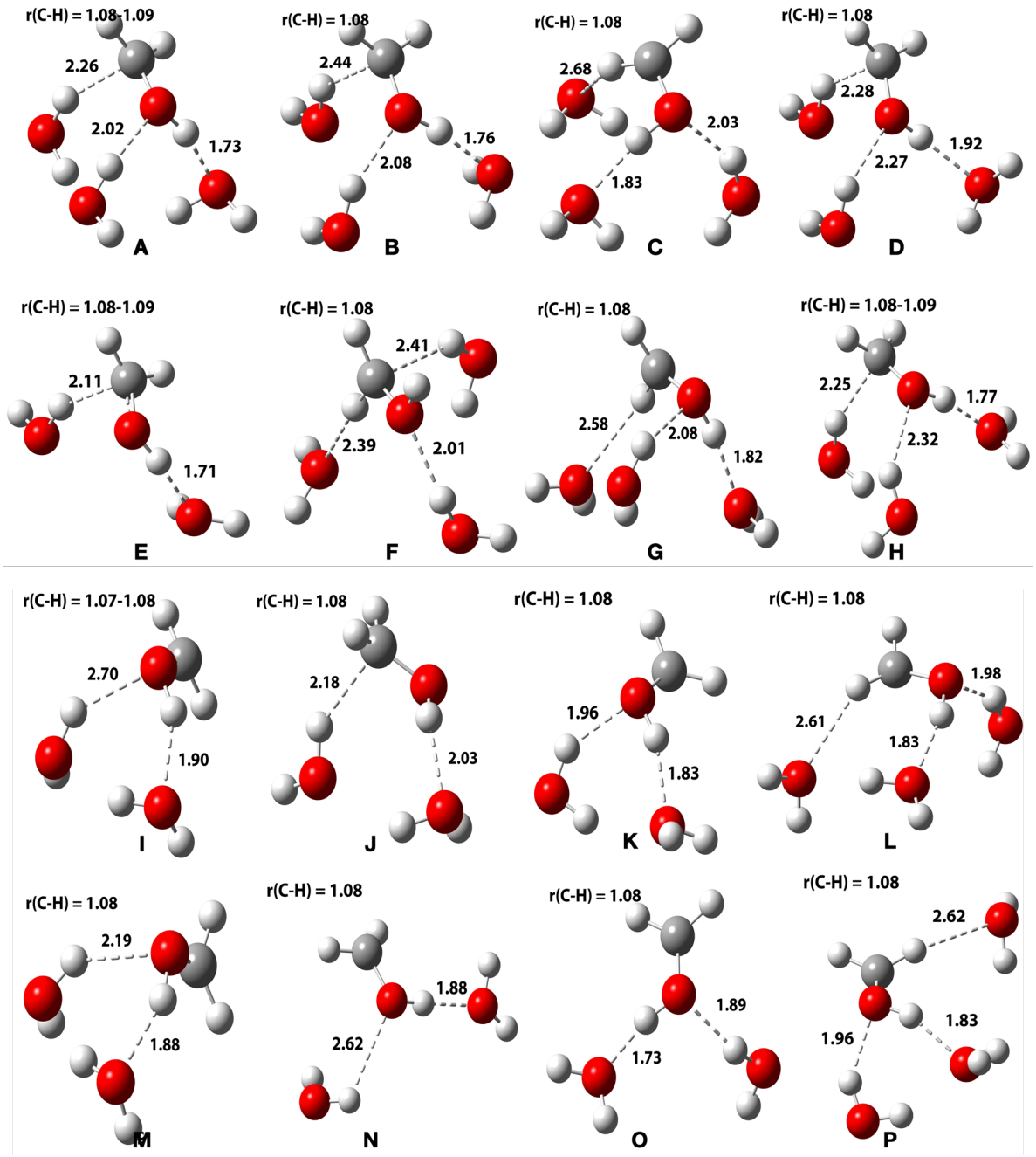


**Figure S1.** Optimized structures of $CH_2OH$ radical on ice. For simplicity, only the $CH_2OH$ radical and a few water molecules in the binding site are shown.

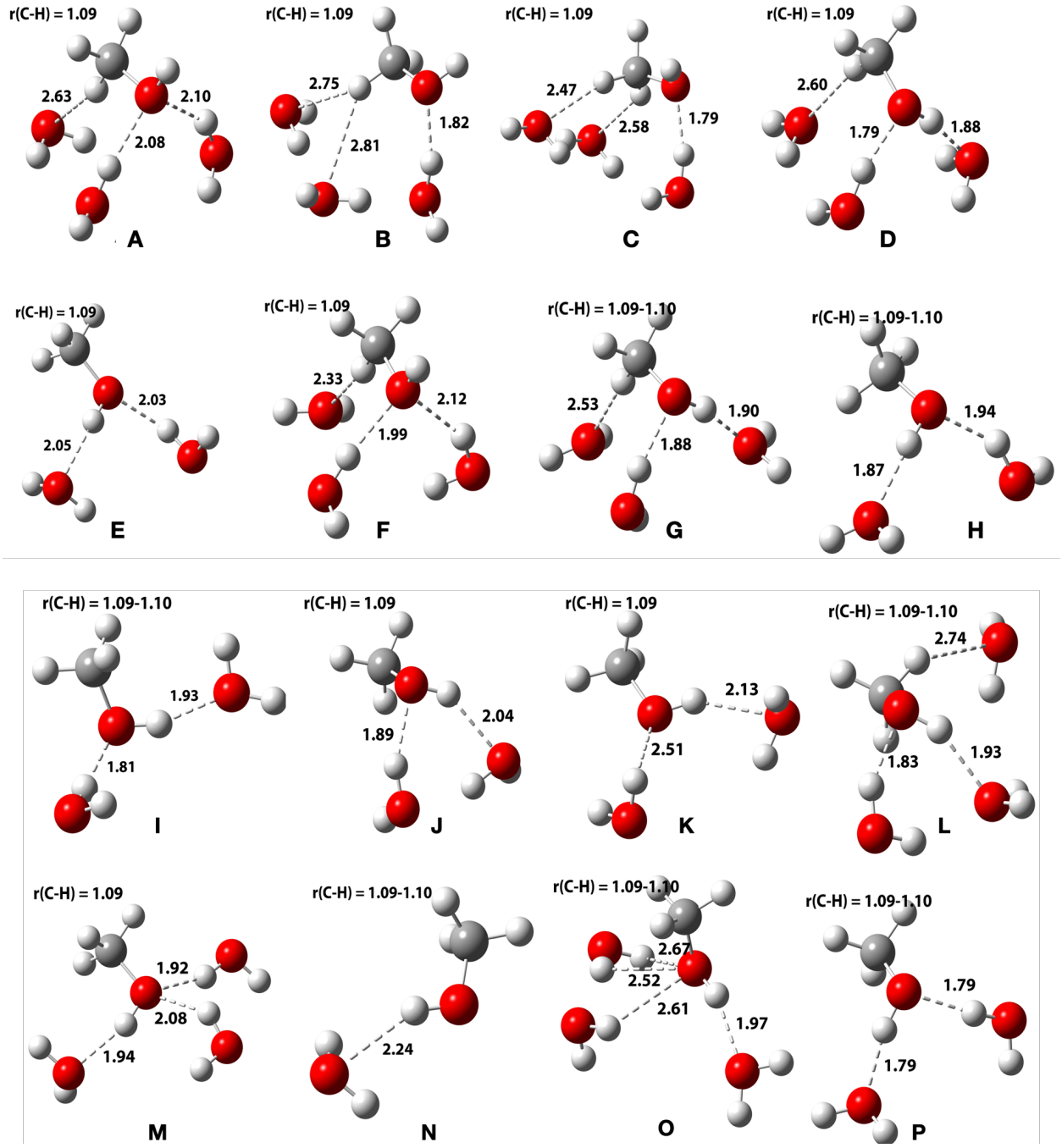


**Figure S2.** Optimized structures of $CH_3OH$ molecule on ice. For simplicity, only the $CH_3OH$ molecule and a few water molecules in the binding site are shown.

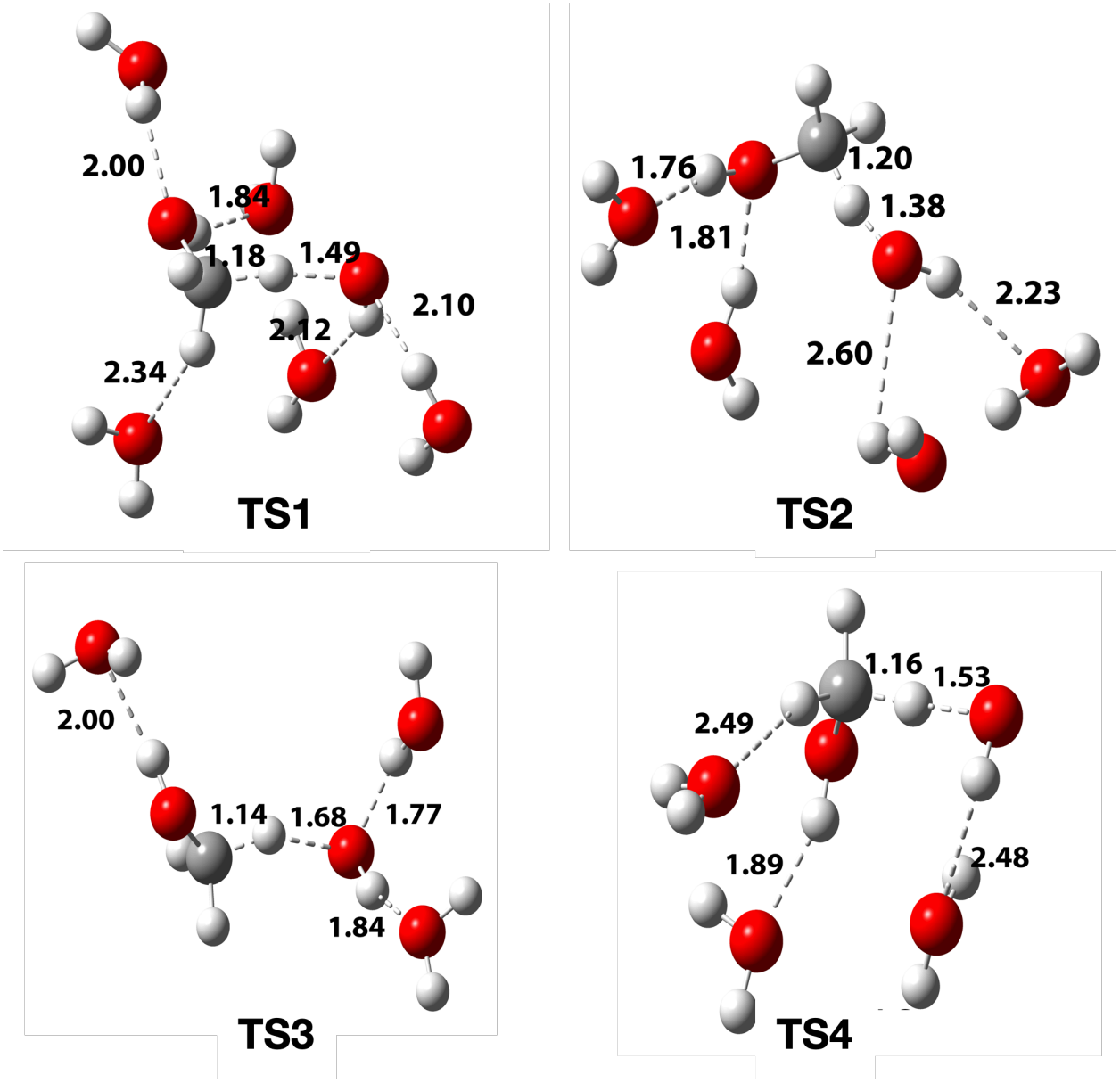


**Figure S3.** Optimized transition state structures of $CH_3OH + OH \rightarrow CH_2OH + H_2O$. For simplicity, only the $CH_3OH$---OH unit and a few water molecules in the binding site are shown.

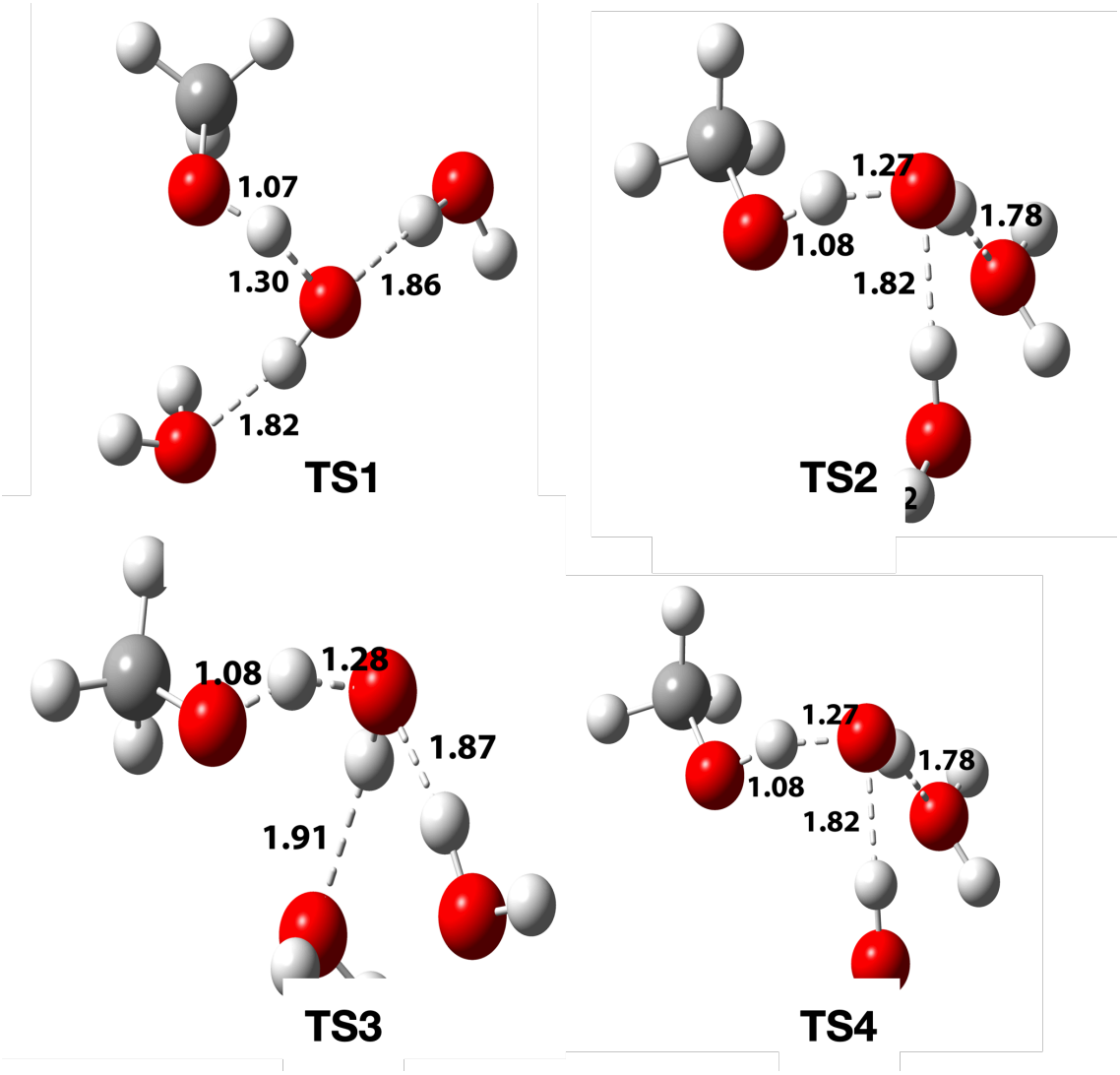


**Figure S4** Optimized transition state structures of $CH_3OH + OH \rightarrow CH_3O + H_2O$. For simplicity, only the $CH_3OH$---OH unit and a few water molecules in the binding site are shown.

**Table S3** Computed energies of the optimized structures.

| $CH_2OH$-ice complex | Zero-point energy/AU | Potential energy/AU |
|---|---|---|
| A | 1.34154 | -3786.89542 |
| B | 1.34112 | -3786.89307 |
| C | 1.34031 | -3786.88591 |

| | | |
|---|---|---|
| D | 1.33971 | -3786.87608 |
| E | 1.30047 | -3671.79168 |
| F | 1.23026 | -3480.93792 |
| G | 1.23484 | -3480.97995 |
| H | 1.22950 | -3480.94311 |
| I | 1.35876 | -3862.92004 |
| J | 1.35916 | -3862.92070 |
| K | 1.35872 | -3862.92776 |
| L | 1.35858 | -3862.92798 |
| M | 1.35858 | -3862.92798 |
| N | 1.35745 | -3862.91255 |
| O | 1.35787 | -3862.91845 |
| P | 1.35917 | -3862.92049 |
| $CH_3OH$-ice complex | Zero-point energy/AU | Potential energy/AU |
| A | 1.35440 | -3787.54773 |
| B | 1.35347 | -3787.54689 |
| C | 1.35439 | -3787.54705 |
| D | 1.35778 | -3787.55976 |
| E | 1.35324 | -3787.53790 |
| F | 1.24446 | -3481.60389 |
| G | 1.24771 | -3481.64782 |
| H | 1.24559 | -3481.62022 |
| I | 1.37349 | -3863.58592 |
| J | 1.37200 | -3863.57937 |
| K | 1.37357 | -3863.58464 |
| L | 1.37326 | -3863.59248 |
| M | 1.37281 | -3863.59271 |
| N | 1.37164 | -3863.58068 |
| O | 1.37099 | -3863.57425 |
| P | 1.37219 | -3863.58313 |

**Table S4.** Computed energies of LMs and TSs of the reaction paths.

| **$CH_3OH + OH \rightarrow CH_2OH + H_2O$** | **Zero-point energy/AU** | **Potential energy/AU** |
|---|---|---|
| R1 | 0.91897 | -4778.64615 |
| TS1 | 0.91755 | -4778.64324 |
| P1 | 0.92118 | -4778.68839 |
| | | |
| R2 | 0.92231 | -4778.64948155 |
| TS2 | 0.92041 | -4778.64359539 |
| P2 | 0.92285 | -4778.68294891 |
| | | |
| R2 | 0.92194 | -4778.64948 |
| TS2 | 0.91743 | -4778.64359 |
| P2 | 0.92216 | -4778.68294 |
| | | |
| R4 | 0.92048 | -4778.65103 |
| TS4 | 0.91706 | -4778.64319 |
| P4 | 0.92048 | -4778.68478 |
| **$CH_3OH + OH \rightarrow CH_3O + H_2O$** | | |
| R1’ | 0.92114 | -4778.64830 |
| TS1’ | 0.91582 | -4778.64181 |
| P1’ | 0.91967 | -4778.67809 |

| | | |
|---|---|---|
| R2’ | 0.92143 | -4778.64601 |
| TS2’ | 0.91667 | -4778.63734 |
| P2’ | 0.92069 | -4778.67300 |
| | | |
| R3’ | 0.92009 | -4778.65464 |
| TS3’ | 0.91471 | -4778.63716 |
| P3’ | 0.91918 | -4778.67008 |
| | | |
| R4’ | 0.92111 | -4778.65623 |
| TS4’ | 0.92040 | -4778.63944 |
| P4’ | 0.92020 | -4778.67481 |