SUPPLEMENTARY MATERIAL

Is Either Direct Photolysis or Photocatalyzed H-shift of Peroxyl Radicals A Competitive Pathways in the Troposphere?

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S1. Data for the photolysis cross section calculation

Table S1. $d_{\text{if}}$ is the electronic transition dipole moment of the strongest transition to a dissociative state, $R_0$ is the equilibrium bond length in the ground electronic state, $E_{\text{if}}$ is the dissociation energy at the first dissociation limit, $A$ and $B$ are parameters fitted to the
dissociative excited state with the largest transition dipole moment, \(m\) is reduced mass and \(\omega\) is wavenumber corresponding to the vibration along the breaking bond.

|        | \(d_1^f\) (a.u.) | \(R_0\) (Å) | \(E_0\) (eV) | \(A\) (a.u) | \(B\) (a.u) | \(m\) (A.u.) | \(\omega\) (cm\(^{-1}\)) |
|--------|------------------|-------------|-------------|-----------|----------|------------|-----------------|
| CH\(_3\)OO | 0.66             | 1.3         | 2.7         | 3.74      | 1.39     | 10.6       | 1090            |
| HC(O)CH\(_2\)O\(_2\) | 1                | 1.3         | 2.7         | 3.74      | 1.39     | 12.6       | 928             |
| CH\(_3\)CH\(_2\)O\(_2\) | 0.67             | 1.3         | 2.7         | 3.74      | 1.39     | 11.8       | 959             |
| HC(O)O\(_2\) | 0.59             | 1.31        | 2.7         | 3.75      | 1.42     | 11.8       | 961             |
| CH\(_3\)C(O)O\(_2\) | 0.64             | 1.32        | 2.7         | 3.74      | 1.43     | 12.6       | 928             |

Fig. S1. The computed cross sections of photolysis at CH\(_3\)OO.
S2. Data for the calculations on H-shifts in the D₀ state, and OH loss or H-shifts in the D₁ state.

Table S2.1. Activation barriers ($E_0$) for H-shifts in the D₀ state, activation barriers ($E_1$) in for H-shift or OH loss reactions the D₁ state, imaginary frequency ($\omega_0$) and reduced mass ($m_0$) in the D₀ state, imaginary frequency ($\omega_1$) and reduced mass ($m_1$) in D₁ state, Eckart correction factor ($\kappa_0$) in the D₀ state, Eckart correction factor ($\kappa_1$) in the D₁ state, and the rate constant of the H-shift in the D₀ state, $k_{H-shift}$, all computed at the XMCQPDT2/CASSCF(11,7)/6-311++G(d,p) level of theory.

| Compound                  | $E_0$ (kcal/mol) | $E_1$ (kcal/mol) | $\omega_0$ (cm⁻¹) and $m_0$ | $\omega_1$ (cm⁻¹) and $m_1$ | $\kappa_0$ | $\kappa_1$ | $k_{H-shift}$ (s⁻¹) |
|---------------------------|------------------|------------------|------------------------------|------------------------------|-------------|-------------|---------------------|
| CH₃OÔ                     | 48               | 35*              | 2054, 1.1                    | 1146, 4.1                    | 9.10⁵       | 5.8         | 1.0·10⁻¹⁶          |
| HC(O)CH₂OØ                | 25               | 33               | 2802, 1.1                    | 1981, 2.5                    | 1.1·10⁷     | 3.0·10⁴     | 4.8                |
| CH₃CH₂OØ                  | 42               | 30               | 2800, 1.1                    | 1910, 1.1                    | 1.1·10¹¹    | 7.8·10³     | 8.5·10⁴           |
| HC(O)OÔ                   | 42               | 42**             | 2110, 1.1                    | 1133, 1.3                    | 1.1·10⁶     | 5.5         | 1.0·10⁻¹²         |
| CH₃C(O)OÔ                 | 35.6             | 28               | 2353, 1.1                    | 1047, 2.9                    | 1.1·10⁷     | 5.7         | 5.0·10⁻⁸         |

*Activation barriers and other data for the D₁ state correspond to the OH loss reaction, as a transition state for the 1,3 H-shift could not be found in this state for CH₃OO.

**Activation barriers and other data for the D₁ state correspond to the HO₂ loss reaction, as a transition state for the 1,3 H-shift could not be found in this state for HC(O)OÔ.

Table S2.2. The activation barrier ($E_0$) in the D₀ state, activation barrier ($E_1$) in the D₁ state, imaginary frequency ($\omega_0$) and reduced mass ($m_0$) in the D₀ state, imaginary frequency ($\omega_1$) reduced mass ($m_1$) in D₁ state, computed at XMCQPDT2/CASSCF(11,7)/6-311++G(d,p) and at XMCQPDT2/CASSCF(11,7)/cc-pvTZ level of theory for CH₃OÔ.

|          | $E_0$ (kcal/mol) | $E_1$ (kcal/mol) | $\omega_0$ (cm⁻¹) and $m_0$ | $\omega_1$ (cm⁻¹) and $m_1$ |
|----------|------------------|------------------|------------------------------|------------------------------|
| 6-311++G(d,p) | 48               | 35               | 2054, 1.1                    | 1146, 4.1                    |
| cc-pvTZ    | 47               | 34               | 2155, 1.1                    | 1643, 1.5                    |
S3. Cartesian coordinates of atoms in Å for reactant molecule and transition state

1. $D_0$ state

1.1. CH$_3$OØ

RC

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| O    | -0.002677551 | 0.559911422 | 0.328918530 |
| O    | -1.063994811  | 0.419442733  | -0.463472202 |
| C    | 0.941203967   | -0.500749997 | 0.071759500  |
| H    | 0.457687702   | -1.459877309 | 0.255082600  |
| H    | 1.762752712   | -0.338245616 | 0.768263184  |
| H    | 1.283306944   | -0.432241771 | -0.960826754 |

TS

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| O    | -0.002677551 | 0.628380861 | 0.068186899 |
| O    | -0.996925440  | -0.554369017 | 0.121763838 |
| C    | 0.995828602   | -0.313712407 | 0.012861199 |
| H    | 0.114300895   | -1.235262885 | 0.056000481 |
| H    | 1.593375879   | -0.411230187 | 0.918560785  |
| H    | 1.502270882   | -0.396190282 | -0.949869251 |
1.2. HC(O)\text{CH}_2\text{O}\text{O}

\text{RC}

\begin{align*}
\text{O} & : 1.559390647, 0.372554965, -0.026951945 \\
\text{O} & : 1.823016194, -0.933754877, -0.013854552 \\
\text{C} & : 0.137982290, 0.679717803, -0.023760234 \\
\text{H} & : -0.033212914, 1.305362218, -0.933754877 \\
\text{H} & : -0.043710708, 1.277802670, -0.920688756 \\
\text{C} & : -0.847707453, -0.481215899, -0.000547708 \\
\text{O} & : -2.037089748, -0.228460073, 0.005152663 \\
\text{H} & : -0.456980063, -1.507315812, 0.009303672 \\
\end{align*}

1.3. CH\text{}_3\text{CH}_2\text{O}\text{O}

\text{RC}

\begin{align*}
\text{O} & : 1.286349711, 0.421756799, -0.345037978 \\
\text{O} & : 1.334333149, -0.937738167, 0.160586635 \\
\text{C} & : 0.122036636, 0.947766985, 0.220589957 \\
\text{H} & : 0.183632441, 1.068766540, 1.310029660 \\
\text{H} & : -0.134268274, 1.883030342, -0.286355345 \\
\text{C} & : -0.894138130, -0.215961328, -0.016159758 \\
\text{O} & : -2.065409917, -0.261922365, -0.089938135 \\
\text{H} & : 0.216457588, -1.105756568, 0.014799610 \\
\end{align*}
1.4. HC(O)OÖ
RC
1.5. CH$_3$C(O)O$\dot{O}$

RC

O  
0.711969103  1.202660830  -0.890714102
C  
-0.502952942  1.037925795  -0.109089454
|    | X         | Y         | Z          |
|----|-----------|-----------|------------|
| O  | -0.870926074 | -0.089890478 | 0.005117795 |
| C  | -1.110531481  | 2.295750627   | 0.427452358  |
| H  | -0.409395890  | 2.795822619   | 1.098915565  |
| H  | -2.018183931  | 2.018318391   | 0.962138289  |
| O  | 1.121188792   | 2.473538284   | -0.949998263 |
| H  | -1.334772882  | 2.984471404   | -0.389971087 |

**TS**

```
O 0.711969051  1.279678359  -1.058467574
C -0.127715275  0.957017985   0.001539743
O -0.246791545  -0.165495818  0.387914661
C -0.810980732  2.196243382   0.496557106
H -0.570958440  2.465712264   1.524715111
H -1.880276643  2.210064927   0.290586694
O  0.643128002  2.737133307  -1.222551606
H -0.239207018  2.940814888  -0.275942670
```

1. **D₁ state**

1.1. CH₃OØ

```
O -0.002677551  0.574130387   0.361837849
O -1.086618126  0.373075206  -0.517012866
```
|   | C     | H     | H     | H     |
|---|-------|-------|-------|-------|
|   | 0.914028184 | -0.490343130 | 0.076279360 |       |
| H | 0.450719071  | -1.458694996  | 0.281475616 | 0.758055969 |
| H | 1.745438883  | -0.317061603  | 0.758055969 |       |
| H | 1.251768627  | -0.432855497  | -0.960906897 |       |

**TS**

![TS diagram]

|   | O    | H     | O     |       |
|---|------|-------|-------|-------|
|   | -0.002677551 | 0.483794308 | 0.015930118 |       |
| O | -1.246911933  | -0.287749861  | 0.086431664 |       |
| C | 0.999735251   | -0.537283901  | 0.003233442 |       |
| H | -0.673602184  | -1.170120954  | 0.071597475 |       |
| H | 1.606235378   | -0.321341039  | 0.890590059 |       |
| H | 1.563216666   | -0.388050283  | -0.928232921 |       |

**1.2. HC(O)CH₂OÖ**

![RC diagram]

|   | O    | H     | O     |       |
|---|------|-------|-------|-------|
| O | 1.551878638  | 0.405488172  | -0.027927570 |       |
| O | 1.782357607  | -0.983943490  | -0.012472563 |       |
| C | 0.140177869   | 0.721933811   | -0.023952671 |       |
| H | -0.055560838  | 1.333828957   | 0.860714325 |       |
| H | -0.066867791  | 1.307209438   | -0.923994178 |       |
| C | -0.818187964  | -0.460495009  | -0.001231405 |       |
| O | -2.014121058  | -0.263921822  | 0.005413051 |       |
| H | -0.389128517  | -1.477908895  | 0.007960800 |       |
1.3. CH₃CH₂OȮ

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| O       | 0.935604147| 0.500704873| -0.318533180|
| O       | 1.581284209| -0.627577911| 0.221993962|
| C       | -0.377518304| 0.558483660| 0.283636757|
| H       | -0.262348022| 0.624274291| 1.370323710|
| H       | -0.758775336| 1.509156158| -0.091970714|
| C       | -1.262365422| -0.602889633| -0.128591543|
| H       | -1.298592680| -0.679271734| -1.217715340|
| H       | -0.894779227| -1.547427561| 0.276550091|
| H       | -2.276800593| -0.436326774| 0.246656092|

TS

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| O       | 1.355829819| 0.491477830| -0.026621639|
| O       | 1.476311436| -1.029311132| -0.009913560|
| C       | 0.020190742| 0.952971552| -0.026964063|
| H       | -0.102420620| 1.560028922| 0.876103327|
| H       | -0.112170789| 1.534117266| -0.945752501|
| C       | -0.955278514| -0.324478801| 0.000018036|
| O       | -2.147764783| -0.168107887| 0.005721167|
| H       | 0.369700003| -1.161059872| -0.002610223|
O  0.832864904  0.660282648  -0.047204860
O  1.134071537 -0.782157284  -0.013394609
C -0.605047278  0.804475266  0.041140210
H -0.836497991  1.315372973  0.979375118
H -0.926063849  1.414803966  -0.807719129
C -1.177115409 -0.595140950  -0.008861678
H -1.571071496 -0.922547302  -0.968110186
H -0.081557720 -1.166379067   0.064846472
H -1.787687728  -0.903478074  0.836390828

1.4. HC(O)OÓ
RC

O  -0.692384500 -0.373302673  -0.393404048
O  -1.440983475  0.593283298  0.288450742
C  0.368036108 -0.863316138  0.349566525
H  0.424209099 -0.407725065  1.344167099
O  1.095149401 -1.687740209  -0.110271794
1.5. CH₃C(O)OȮ
RC

TS
| At  | X    | Y    | Z    |
|-----|------|------|------|
| O   | -0.531533135 | -0.900733729 | -0.212448980 |
| C   | 0.633044793  | 0.060775020  | 0.013447009  |
| O   | 1.657665326  | -0.506639262 | 0.223685701  |
| C   | 0.127253391  | 1.413830702  | 0.066966878  |
| H   | 0.017644153  | 1.909367015  | -0.898010764 |
| H   | 0.570974608  | 2.019119630  | 0.852212991  |
| O   | -1.706355781 | -0.164219966 | -0.120243837 |
| H   | -1.189447386 | 0.845184927  | 0.136013008  |