Supplementary Information

Theoretical investigations of the mechanism, kinetics and subsequent degradation products of the NO$_3$ radical initiated oxidation of 4-hydroxy-3-hexanone

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Fig. S1  Optimized geometries of all reactants (R), reaction complexes (ER/EP), transition states (TS), and products (P) at the BH&HLYP/6-311++G(d,p) level for the reaction of 4-hydroxy-4-methyl-2-pentanone (4H4M2P) with NO$_3$ radical. Bond lengths are in angstroms, and angles are in degrees.

(a)  

(b)
Fig. S2  Calculated TST, CVT, and CVT/SCT rate constants as a function of $10^{3/T}$ for title reactions in the temperature range of 260-330 K. (a) For reaction path 2. (b) For reaction path 4. (c) For reaction path 5.
Fig. S3  Classical potential energy curve ($V_{\text{MPE}}$), ground-state vibrational adiabatic energy curve ($V^0$), and zero-point energy curve (ZPE) as functions of $s$ (amu)$^{1/2}$ bohr at the CCSD(T)//BH&HLYP/6-311++G(d,p) level for the reactions. (d) For reaction path1, (e) For reaction path2. (f) For reaction path4. (g) For reaction path5.
Fig. S4 IRC plots of transition states (TS1-TS5) of title reaction obtained at the BH&HLYP/6-311++G(d,p) level of theory.
<table>
<thead>
<tr>
<th>Species</th>
<th>BH&amp;HLYP/6-311++G(d, p)</th>
<th>&lt;s^2&gt;</th>
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<tr>
<td>CH₃CH₂C(O)CH(OH)C₂H₅</td>
<td>27, 87, 100, 182, 213, 237, 239, 260, 323, 326, 436, 533, 565, 664, 786, 810, 845, 923, 1033, 1039, 1084, 1103, 1126, 1175, 1187, 1213, 1275, 1323, 1339, 1371, 1437, 1438, 1462, 1473, 1481, 1499, 1536, 1545, 1550, 1553, 1562, 1878, 3085, 3103, 3118, 3123, 3126, 3147, 3156, 3181, 3186, 3192, 3199, 4023</td>
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<td>491, 641, 731, 837, 1016, 1409, 1459, 1862, 3899, 1300i, 21, 29, 41, 57, 87, 94, 148, 169, 222, 234, 239, 264, 337, 356, 415, 438, 489, 500, 563, 695, 715, 791, 808, 820, 837, 877, 926, 1018, 1031, 1037, 1080, 1107, 1140, 1166, 1199, 1208, 1248, 1263, 1323, 1339, 1371, 1413, 1441, 1443, 1446, 1464, 1472, 1487, 1503, 1536, 1551, 1562, 1763, 1887, 3067, 3091, 3104, 3127, 3157, 3169, 3182, 3192, 3195, 3197, 3252, 4026</td>
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<td>1322i, 17, 30, 51, 64, 87, 100, 128, 170, 205, 214, 231, 258, 278, 321, 343, 367, 467, 536, 586, 685, 713, 778, 799, 837, 853, 871, 936, 1020, 1034, 1078, 1095, 1107, 1132, 1162, 1184, 1209, 1226, 1257, 1326, 1350, 1387, 1434, 1441, 1451, 1459, 1474, 1482, 1502, 1543, 1545, 1553, 1761, 1887, 3105, 3115, 3119, 3127, 3149, 3163, 3176, 3194, 3197, 3202, 4021</td>
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<td>EP3</td>
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<td>26, 93, 101, 156, 188, 234, 236, 263, 323, 342, 427, 458, 534, 563, 665, 781, 812, 899, 944, 1034, 1041, 1101, 1124, 1153, 1169, 1211, 1225, 1285, 1338, 1370, 1436, 1438, 1461, 1469, 1482, 1499, 1536, 1550, 1562, 1882, 3079, 3087, 3088, 3104, 3119, 3156, 3182, 3186, 3242, 3358, 4024</td>
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<td>35, 56, 98, 177, 216, 224, 239, 325, 341, 361, 416, 540, 581, 629, 778, 818, 827, 929, 1024, 1055, 1102, 1119, 1128, 1148, 1231, 1319, 1327, 1371, 1419, 1430, 1468, 1471, 1516, 1529, 1544, 1549, 1550, 1553, 1569, 1675, 3076, 3109, 3115, 3124, 3140, 3169, 3190, 3194, 3199, 3210, 3998</td>
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<th>C₂H₅C(O)CH(OH)CH₂CH₃</th>
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<td>20, 79, 85, 122, 182, 211, 217, 247, 305, 319, 428, 487, 541, 640, 652, 784, 840, 917, 1020, 1034, 1062, 1103, 1118, 1163, 1180, 1221, 1262, 1318, 1340, 1398, 1436, 1450, 1473, 1477, 1500, 1530, 1542, 1545, 1553, 1882, 3013, 3030, 3124, 3126, 3130, 3149, 3189, 3192, 3200, 3278, 4022</td>
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<th>C₂H₅C(O)CH(OH)CH₂CH₂</th>
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<td>26, 88, 117, 151, 185, 220, 246, 313, 326, 343, 429, 521, 547, 574, 674, 786, 848, 870, 919, 1035, 1084, 1101, 1110, 1162, 1174, 1197, 1271, 1291, 1325, 1356, 1430, 1436, 1470, 1477, 1498, 1511, 1523, 1546, 1553, 1877, 3079, 3084, 3123, 3126, 3146, 3147, 3192, 3199, 3217, 3326, 3989</td>
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**Table S2** The relative energy ($\Delta E$), enthalpy ($\Delta H$), and Gibbs free energy ($\Delta G$) of the H-abstraction reaction of 4H4M2P with the NO$_3$ radical calculated at CCSD(T)//BH&HLYP/6–311++G(d,p) levels (kcal/mol).

<table>
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<tr>
<th>Pathways</th>
<th>Stationary points</th>
<th>$\Delta E$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
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<tbody>
<tr>
<td></td>
<td>4H4M2P+NO$_3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Path1</td>
<td>ER1</td>
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<td>-1.26</td>
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<td></td>
<td>TS1</td>
<td>5.97</td>
<td>6.03</td>
<td>15.72</td>
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<td></td>
<td>EP1</td>
<td>-7.49</td>
<td>-6.85</td>
<td>1.93</td>
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<td></td>
<td>P1</td>
<td>-1.47</td>
<td>-1.18</td>
<td>-1.86</td>
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<tr>
<td></td>
<td>ER2</td>
<td>-0.63</td>
<td>-1.04</td>
<td>9.87</td>
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<td>Path2</td>
<td>TS2</td>
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<td>8.22</td>
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<td>-16.84</td>
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<td>-7.08</td>
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<td>15.68</td>
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<td></td>
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<td>-0.87</td>
<td>10.03</td>
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<td>Path4</td>
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<td>7.74</td>
<td>17.42</td>
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<td>-14.71</td>
<td>-5.30</td>
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<tr>
<td></td>
<td>P4</td>
<td>-1.03</td>
<td>-0.65</td>
<td>-1.65</td>
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</table>
**Table S3**  Calculated CVT/SCT rate constant values (in cm$^3$ molecule$^{-1}$ s$^{-1}$) for the H atom abstraction reaction of 4H4M2P with the NO$_3$ radical at BH&HLYP/6-311++G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>$k_{\text{path1}}$ ($\times 10^{-17}$)</th>
<th>$k_{\text{path2}}$ ($\times 10^{-18}$)</th>
<th>$k_{\text{path3}}$ ($\times 10^{-16}$)</th>
<th>$k_{\text{path4}}$ ($\times 10^{-18}$)</th>
<th>$k_{\text{total}}$ ($\times 10^{-16}$)</th>
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<tbody>
<tr>
<td>260</td>
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<td>1.33</td>
<td>3.03</td>
<td>0.67</td>
<td>3.13</td>
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<tr>
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<td>1.88</td>
<td>3.42</td>
<td>1.18</td>
<td>3.60</td>
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<tr>
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<td>2.60</td>
<td>2.60</td>
<td>3.88</td>
<td>2.02</td>
<td>4.19</td>
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<tr>
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<td>4.47</td>
<td>3.55</td>
<td>4.41</td>
<td>3.38</td>
<td>4.93</td>
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<tr>
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<td>4.89</td>
<td>5.02</td>
<td>5.66</td>
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<td>5.53</td>
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<td>10.80</td>
<td>7.43</td>
<td>21.60</td>
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**Table S4**  The T1 diagnostic and $<s^2>$ values of the main species for the reaction of CH$_3$CH$_2$C(O)(OO•)(OH)CH$_2$CH$_3$ with NO radical on the singlet surface at the CCSD(T)/BH&HLYP/6-311++G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>A</th>
<th>NO</th>
<th>IM1</th>
<th>IM2</th>
<th>IM3</th>
<th>Propionic acid</th>
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<tbody>
<tr>
<td>T1</td>
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<td>0.022</td>
<td>0.017</td>
<td>0.017</td>
<td>0.016</td>
<td>0.014</td>
</tr>
<tr>
<td>$&lt;s^2&gt;$</td>
<td>0.758</td>
<td>0.755</td>
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<td>0</td>
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<table>
<thead>
<tr>
<th>Species</th>
<th>TS6</th>
<th>TS7</th>
<th>TS8</th>
<th>TS9</th>
<th>NO$_2$</th>
<th>Propionyl</th>
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<tbody>
<tr>
<td>T1</td>
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<td>0.022</td>
<td>0.040</td>
<td>0.028</td>
<td>0.024</td>
<td>0.018</td>
</tr>
<tr>
<td>$&lt;s^2&gt;$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.757</td>
<td>0.750</td>
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