

Supplementary Information

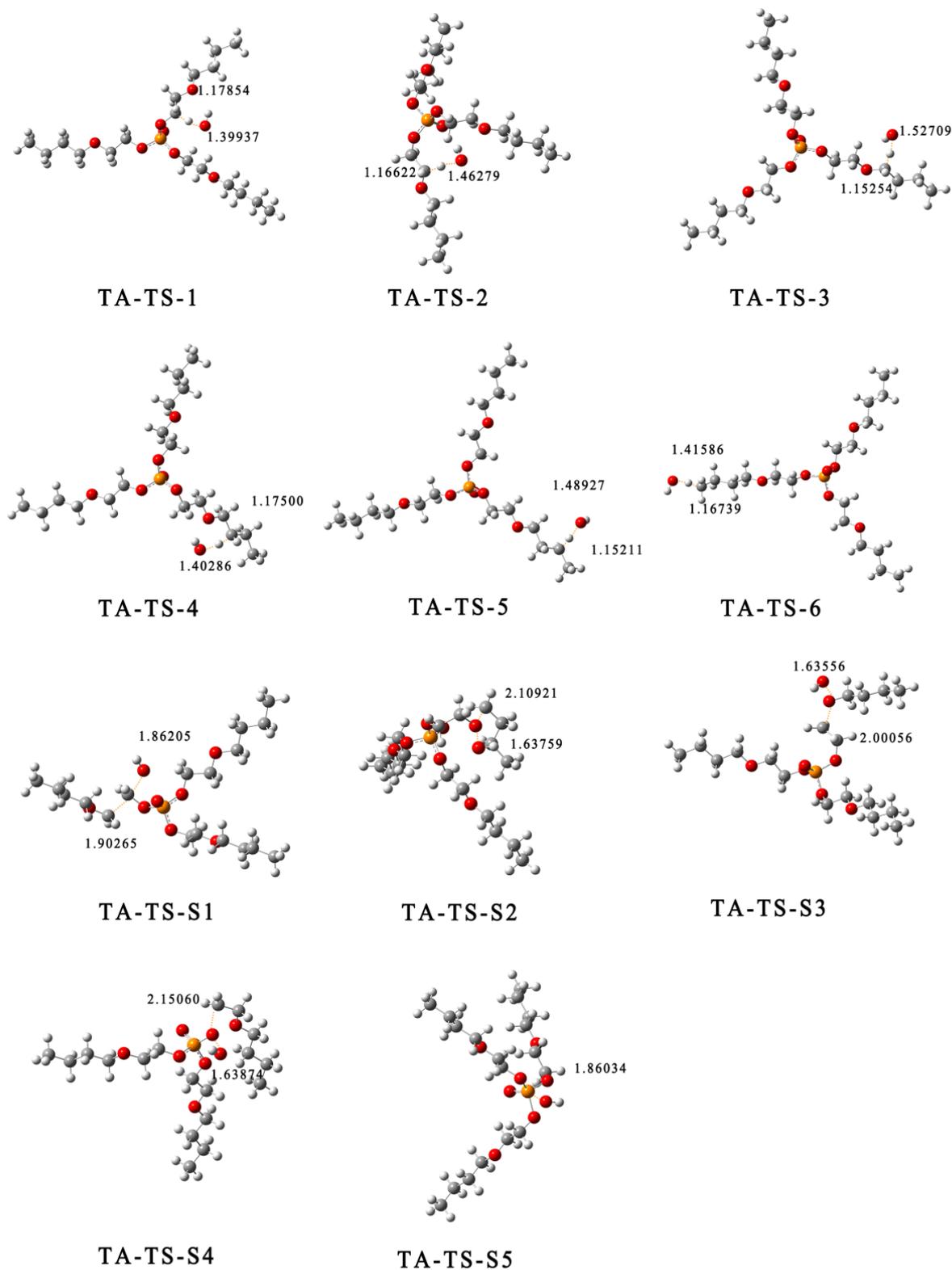


Figure S1: Geometrical parameters of transition states in the reaction of TBOEP with $\cdot\text{OH}$ in the atmosphere obtained at M06-2X/6-311++G(d,p) levels of theory with bond lengths in Å.

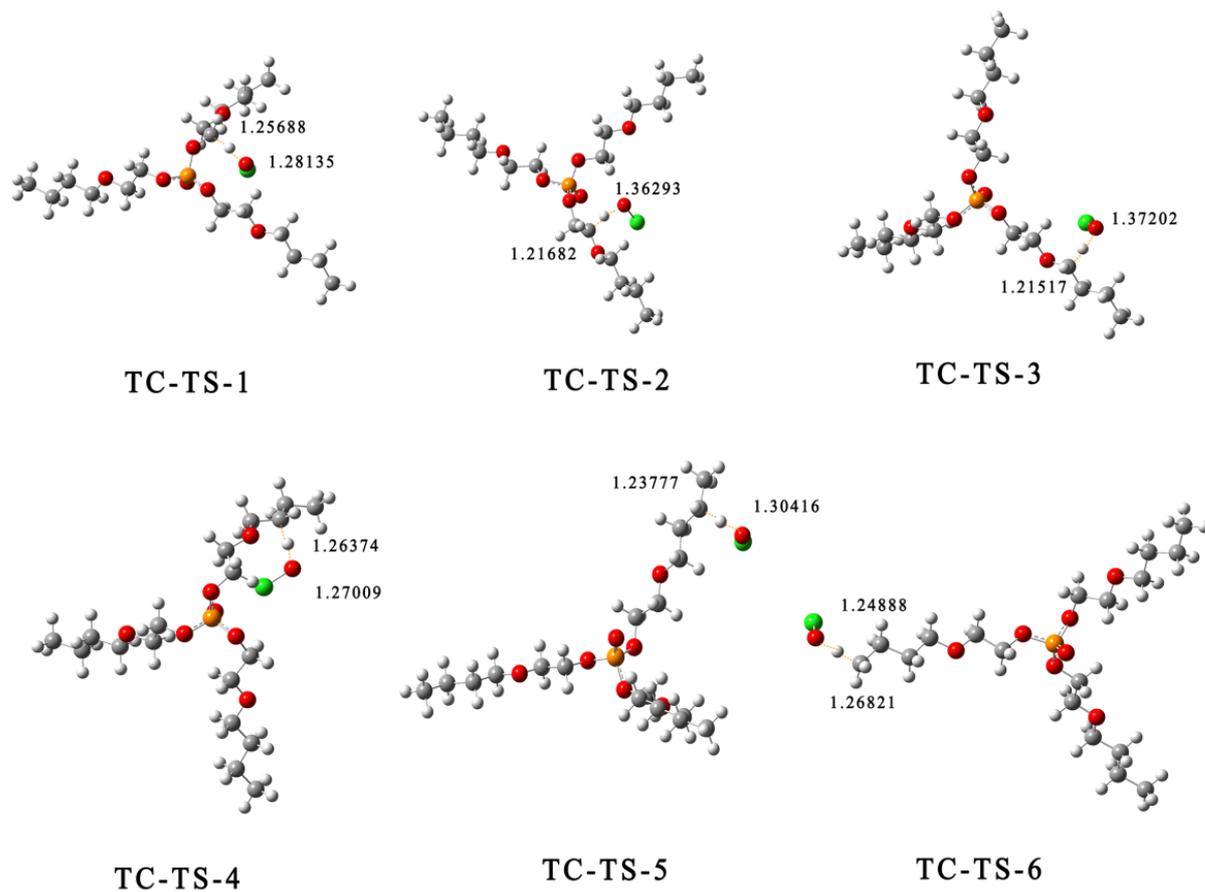
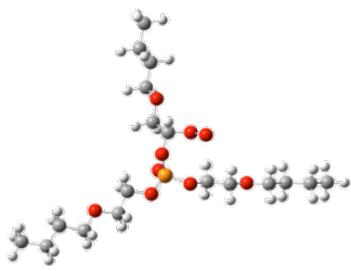
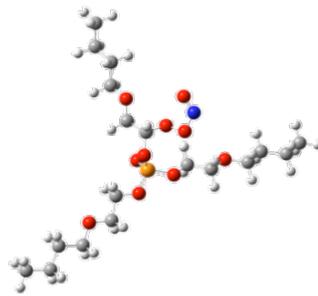


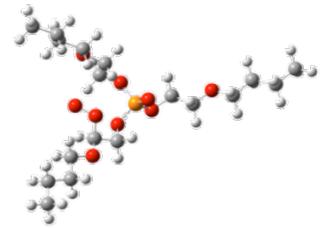
Figure S2: Geometrical parameters of transition states in the reaction of TBOEP with $\cdot\text{ClO}$ in the atmosphere obtained at M06-2X/6-311++G(d,p) levels of theory with bond lengths in Å.



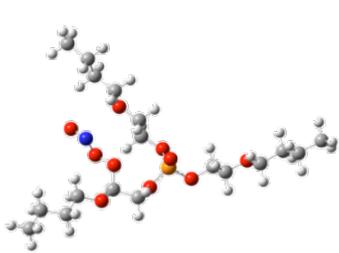
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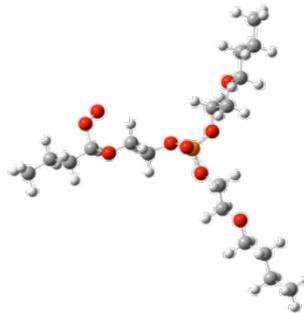
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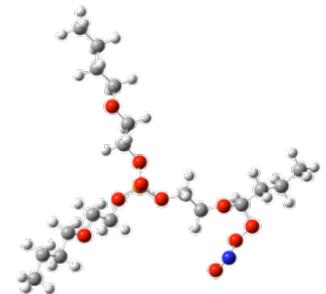
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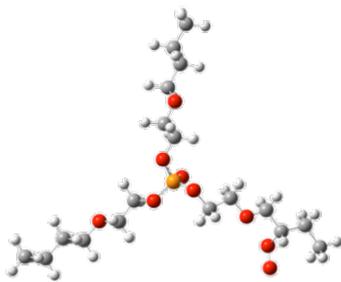
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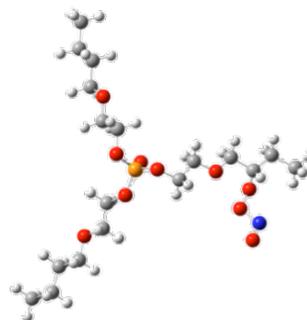
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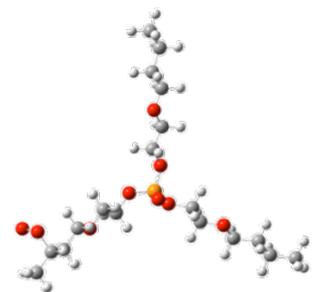
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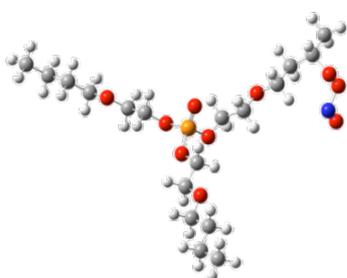
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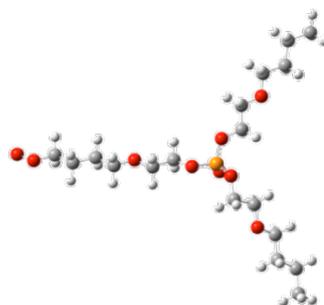
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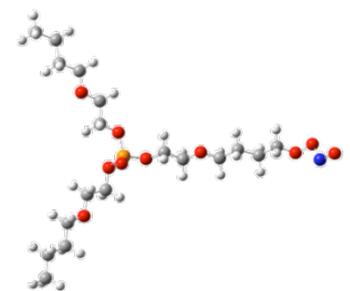
TAP5-IM-1



TAP5-IM-2



TAP6-IM-1



TAP6-IM-2

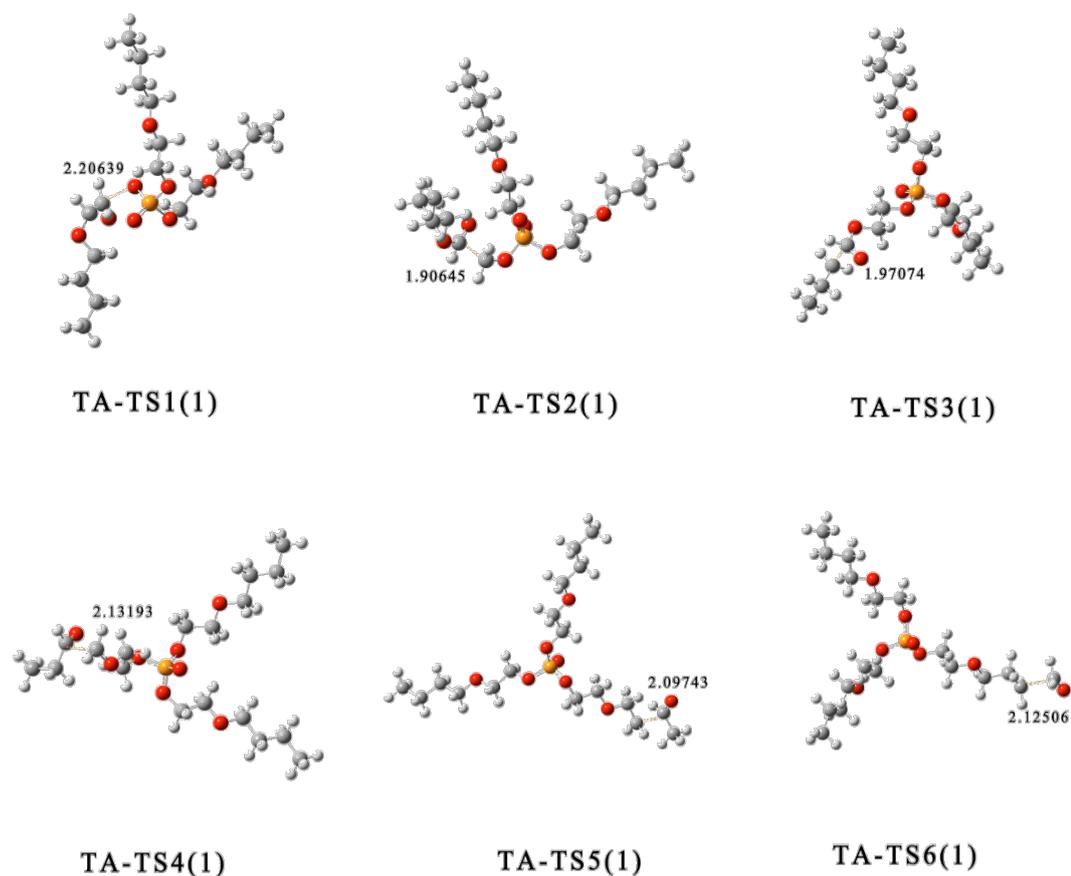


Figure S3: Geometrical parameters of each species in the subsequent reactions for TBOEP at the M06-2X/6-311++G(d,p) levels of theory. (bond lengths in Å)

Table S1: The relative energy (ΔE), reaction enthalpy (ΔH), reaction Gibbs free energy (ΔG) and free energy correction (G_{corre}) in the reaction of TBOEP+OH at the M06-2X/6-311++G(3df,2pd)/M06-2X/6-311++G(d,p) levels of theory under atmospheric conditions, the unit is in kJ/mol

| Species | M06-2X/6-311++G(d,p) | | | | M06-2X/6-311++G(3df,2pd) | |
|------------------------|----------------------|------------|------------|--------------------|--------------------------|------------------------------|
| | ΔE | ΔH | ΔG | G_{corre} | ΔE | $\Delta(E+G_{\text{corre}})$ |
| TBOEP+OH | 0 | 0 | 0 | 1297.2 | 0 | 0 |
| TA-TS-1 | -8.9 | -13.5 | 34.7 | 1339.0 | -4.0 | 36.8 |
| TA-P1+H ₂ O | -73.0 | -71.1 | -24.3 | 1285.3 | -75.3 | -87.2 |
| TA-TS-2 | -30.0 | -35.8 | 13.8 | 1341.1 | -29.8 | 14.1 |
| TA-P2+H ₂ O | -107.1 | -107.4 | -43.2 | 1305.1 | -110.3 | -102.4 |
| TA-TS-3 | -6.0 | -8.7 | 26.0 | 1326.9 | -4.2 | 25.5 |
| TA-P3+H ₂ O | -92.5 | -91.0 | -38.8 | 1292.2 | -96.2 | -101.2 |
| TA-TS-4 | -7.6 | -11.6 | 28.8 | 1330.2 | -3.9 | 29.0 |
| TA-P4+H ₂ O | -76.2 | -73.7 | -27.6 | 1283.7 | -75.6 | -89.1 |
| TA-TS-5 | 0.7 | -1.3 | 29.7 | 1321.2 | 4.9 | 28.9 |
| TA-P5+H ₂ O | -82.2 | -79.7 | -32.4 | 1285.2 | -81.3 | -93.3 |
| TA-TS-6 | 9.4 | 7.1 | 40.3 | 1322.3 | 13.7 | 38.8 |
| TA-P6+H ₂ O | -67.6 | -65.3 | -15.4 | 1288.0 | -66.7 | -75.9 |
| TA-TS-S1 | 137.4 | 132.7 | 132.7 | 1344.7 | 132.5 | 180.0 |

| | | | | | | |
|-------------------|-------|-------|-------|--------|-------|-------|
| TA-S1-P1+TA-S1-P2 | -67.1 | -71.5 | -75.2 | 1295.4 | -82.1 | -83.9 |
| TA-TS-S2 | 220.3 | 214.5 | 271.6 | 1350.9 | 227.6 | 281.2 |
| TA-S2-P1+TA-S2-P2 | 185.6 | 182.6 | 174.7 | 1281.9 | 184.9 | 169.6 |
| TA-TS-S3 | 248.2 | 245.0 | 284.8 | 1334.6 | 251.3 | 288.6 |
| TA-S3-P1+TA-S3-P2 | 180.5 | 177.8 | 172.0 | 1286.5 | 177.5 | 166.8 |
| TA-TS-S4 | 263.7 | 260.0 | 310.0 | 1342.0 | 272.8 | 317.7 |
| TA-S4-P1+TA-S4-P2 | 224.4 | 222.8 | 212.3 | 1279.9 | 221.9 | 204.5 |
| TA-TS-S5 | 124.4 | 117.0 | 168.2 | 1352.2 | 117.7 | 172.8 |
| TA-S5-P1+TA-S5-P2 | -47.5 | -52.5 | -55.6 | 1287.7 | -48.6 | -58.1 |

Table S2: The relative energy (ΔE), reaction enthalpy (ΔH), reaction gibbs free energy (ΔG) and free energy correction (G_{corre}) in the reaction of TBOEP+ClO at the M06-2X/6-311++G(3df,2pd)//M06-2X/6-311++G(d,p) levels of theory under atmospheric conditions, the unit is in kJ/mol

| Species | M06-2X/6-311++G(d,p) | | | | M06-2X/6-311++G(3df,2pd) | |
|------------|----------------------|------------|------------|--------------------|--------------------------|------------------------------|
| | ΔE | ΔH | ΔG | G_{corre} | ΔE | $\Delta(E+G_{\text{corre}})$ |
| TBOEP+ClO | 0.0 | 0.0 | 0.0 | 1267.0 | 0.0 | 0.0 |
| TC-TS-1 | 13.4 | 11.5 | 58.0 | 1299.6 | 36.0 | 68.5 |
| TC-P1+HOCl | 7.9 | 9.8 | -0.9 | 1249.8 | 21.3 | 4.0 |
| TC-TS-2 | 2.0 | -1.0 | 46.5 | 1300.7 | 22.4 | 56.1 |
| TC-P2+HOCl | -26.2 | -26.4 | -19.8 | 1269.6 | -13.8 | -11.2 |
| TC-TS-3 | -1.0 | -4.8 | 46.0 | 1304.6 | 15.9 | 53.5 |
| TC-P3+HOCl | -11.6 | -10.1 | -15.5 | 1256.6 | 0.4 | -10.0 |
| TC-TS-4 | 5.6 | 2.5 | 58.7 | 1309.2 | 28.4 | 70.6 |
| TC-P4+HOCl | 4.7 | 7.2 | -4.3 | 1248.1 | 21.0 | 2.1 |
| TC-TS-5 | 12.6 | 11.1 | 56.6 | 1299.0 | 33.0 | 65.0 |
| TC-P5+HOCl | -1.4 | 1.3 | -9.0 | 1249.7 | 15.2 | -2.1 |
| TC-TS-6 | 31.8 | 29.0 | 73.7 | 1295.0 | 54.2 | 82.2 |
| TC-P6+HOCl | 13.3 | 15.6 | 8.0 | 1252.5 | 29.8 | 15.3 |

Table S3: The relative energy (ΔE), reaction enthalpy (ΔH), reaction Gibbs free energy (ΔG) and free energy correction (G_{corre}) in the subsequent reactions of TBOEP free radicals with O_2 and NO at the M06-2X/6-311++G(3df,2pd)//M06-2X/6-311++G(d,p) levels of theory under atmospheric conditions, the units are kJ/mol

| Species | M06-2X/6-311++G(d,p) | | | | M06-2X/6-311++G(3df,2pd) | |
|-----------------------|----------------------|------------|------------|--------------------|--------------------------|------------------------------|
| | ΔE | ΔH | ΔG | G_{corre} | ΔE | $\Delta(E+G_{\text{corre}})$ |
| TA-P1+ O_2 +NO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TAP1-IM-1+NO | -310.2 | -315.0 | -259.1 | 1264.6 | -325.1 | -256.2 |
| TAP1-IM-2 | -402.1 | -410.4 | -304.8 | 1321.0 | -434.6 | -309.4 |
| TAP1-1+ NO_2 | -362.9 | -369.3 | -319.3 | 1254.2 | -377.6 | -319.2 |
| TA-TS1(1)+ NO_2 | -288.2 | -295.3 | -243.0 | 1282.7 | -290.7 | -242.5 |
| TAP1-2+TAP1-3+ NO_2 | -417.2 | -422.9 | -423.3 | 1235.9 | -397.1 | -395.7 |
| TA-P2+ O_2 +NO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TAP2-IM-1+NO | -293.0 | -297.1 | -253.0 | 1271.3 | -308.7 | -253.0 |
| TAP2-IM-2 | -368.7 | -374.4 | -294.8 | 1313.5 | -406.9 | -309.1 |
| TAP2-1+ NO_2 | -335.7 | -340.9 | -304.1 | 1260.0 | -351.8 | -307.5 |
| TA-TS2(1)+ NO_2 | -320.1 | -325.7 | -289.3 | 1293.1 | -333.5 | -294.7 |
| TAP2-2+TAP2-3+ NO_2 | -349.2 | -351.9 | -372.4 | 1231.6 | -362.3 | -384.9 |

| | | | | | | |
|-------------------------------|--------|--------|--------|--------|--------|--------|
| TA-P3+O ₂ +NO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TAP3-IM-1+NO | -307.4 | -311.8 | -265.2 | 1261.7 | -323.4 | -264.4 |
| TAP3-IM-2 | -383.2 | -390.8 | -299.1 | 1313.5 | -415.4 | -304.6 |
| TAP3-1+NO ₂ | -352.0 | -357.5 | -316.6 | 1251.6 | -366.0 | -317.1 |
| TA-TS3(1)+NO ₂ | -326.0 | -331.4 | -296.1 | 1278.5 | -367.1 | -329.9 |
| TAP3-2+TAP3-3+NO ₂ | -365.7 | -367.7 | -386.2 | 1220.2 | -371.7 | -392.8 |
| TA-P4+O ₂ +NO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TAP4-IM-1+NO | -301.2 | -306.8 | -254.3 | 1261.5 | -320.7 | -253.4 |
| TAP4-IM-2 | -374.9 | -385.8 | -279.6 | 1319.4 | -410.8 | -285.6 |
| TAP4-1+NO ₂ | -333.9 | -341.2 | -289.9 | 1257.1 | -355.3 | -292.4 |
| TA-TS4(1)+NO ₂ | -306.2 | -313.5 | -261.4 | 1289.9 | -324.8 | -267.7 |
| TAP4-2+TAP4-3+NO ₂ | -312.3 | -316.4 | -321.2 | 1227.5 | -324.0 | -329.3 |
| TA-P5+O ₂ +NO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TAP5-IM-1+NO | -301.1 | -306.5 | -258.1 | 1258.9 | -320.9 | -257.8 |
| TAP5-IM-2 | -377.5 | -386.4 | -288.0 | 1315.6 | -413.4 | -293.5 |
| TAP5-1+NO ₂ | -332.1 | -340.8 | -287.9 | 1255.7 | -350.2 | -290.2 |
| TA-TS5(1)+NO ₂ | -270.5 | -278.1 | -229.5 | 1282.1 | -282.7 | -235.0 |
| TAP5-2+TAP5-3+NO ₂ | -298.0 | -302.3 | -303.7 | 1225.6 | -301.9 | -310.7 |
| TA-P6+O ₂ +NO | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TAP6IM-1+NO | -295.5 | -300.0 | -257.2 | 1257.6 | -317.5 | -258.4 |
| TAP6-IM-2 | -373.0 | -381.1 | -289.1 | 1313.7 | -413.3 | -298.1 |
| TAP6-1+NO ₂ | -338.3 | -345.7 | -298.3 | 1252.3 | -355.1 | -301.4 |
| TA-TS6(1)+NO ₂ | -264.8 | -270.0 | -231.4 | 1278.1 | -278.8 | -237.8 |
| TAP6-2+TAP6-3+NO ₂ | -282.1 | -283.3 | -291.6 | 1225.2 | -271.8 | -283.8 |

Table S4: Ecotoxicity values (logLC₅₀, logEC₅₀, and logChV) of TBOEP and degraded products to fish, daphnid and green algae (unit in mg/L)

| Species | Acute toxicity | | | Chronic toxicity | | |
|-----------|---------------------|---------------------|---------------------|------------------|---------|-------------|
| | Fish | Daphnid | Green algae | Fish | Daphnid | Green algae |
| | logLC ₅₀ | logLC ₅₀ | logEC ₅₀ | logChV | logChV | logChV |
| TBOEP | 1.62 | 1.42 | 1.45 | 0.66 | 0.52 | 0.96 |
| TAP1-IM-2 | 1.97 | 1.76 | 1.74 | 1.00 | 0.82 | 1.22 |
| TAP2-IM-2 | 1.97 | 1.76 | 1.74 | 1.00 | 0.82 | 1.22 |
| TAP3-IM-2 | 1.97 | 1.76 | 1.74 | 1.00 | 0.82 | 1.22 |
| TAP4-IM-2 | 1.97 | 1.76 | 1.74 | 1.00 | 0.82 | 1.22 |
| TAP5-IM-2 | 1.97 | 1.76 | 1.74 | 1.00 | 0.82 | 1.22 |
| TAP6-IM-2 | 1.91 | 1.69 | 1.69 | 0.93 | 0.76 | 1.17 |
| TAP1-2 | 2.62 | 2.37 | 2.20 | 1.60 | 1.33 | 1.59 |
| TAP2-3 | 2.55 | 2.28 | 2.04 | 1.51 | 1.19 | 1.39 |
| TAP3-2 | 3.13 | 2.85 | 2.61 | 2.09 | 1.76 | 1.96 |
| TAP4-3 | 3.18 | 2.87 | 2.46 | 2.09 | 1.67 | 1.73 |
| TAP5-3 | 3.50 | 3.17 | 2.68 | 2.39 | 1.92 | 1.91 |
| TAP6-3 | 2.87 | 2.56 | 2.16 | 1.79 | 1.37 | 1.43 |