## SUPPORTING INFORMATION

## H-abstraction Reactions by OH, HO2, O, O2 and Benzyl Radical Addition to O2 and Their Implications for Kinetic Modelling of Toluene Oxidation.

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Figure S 1: Toluene bond dissociation energies in kcal/mol computed using energies determined as E=ECCSD(T)-F12/VTZ-F12 + EMP2-F12/VQZ-F12 - EMP2-F12/VTZ-F12 at geometries optimized at the M06-2X/6-311+G(d,p )level. Structure and names of toluene radicals.



Figure S 2:Potential energy surface for the OH + toluene reaction. Energies are in kcal/mol relative to the reactants.

Table S 1: Rate constant for the H-abstraction reactions of toluene calculated in this study. Units are cm3, s, mol-1, cal. Mean and maximum deviations of the Arrhenius fits are reported for each channel.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Reaction** | **A [cm3/s/mol]** | **n** | **Ea [cal/mol]** | **Average, Max [%]**  **|(kcalc-kfit)/kcalc|** |
| OH+C6H5CH3↔C6H5CH2+H2O | 6.12E+07 | 1.587 | 220.3 | 2, 10 |
| OH+C6H5CH3↔C6H4CH3+H2O | 9.39E+03 | 2.859 | 1326.0 | 2, 5 |
| O2+C6H5CH3↔C6H5CH2+HO2 | 1.81E+02 | 3.365 | 38473.2 | 3, 7 |
| O2+C6H5CH3↔C6H4CH3+HO2 | 1.67E+06 | 2.361 | 53670.7 | <1, 2 |
| O+C6H5CH3↔C6H5CH2+OH | 1.37E+08 | 1.585 | 3949.6 | 7, 16 |
| O+C6H5CH3↔C6H4CH3+OH | 8.08E+06 | 2.208 | 9377.2 | 2, 3 |
| HO2+C6H5CH3↔C6H5CH2+H2O2 | 2.72E+00 | 3.546 | 11323.6 | 6, 15 |
| HO2+C6H5CH3↔C6H4CH3+H2O2 | 1.44E+02 | 3.384 | 22595.3 | 7, 2 |



Figure S 3: Potential energy surface for the reaction HO2+toluene. Energies are in kcal/mol relative to the reactants.



Figure S 4: Potential energy surface for the O(3P) + toluene reaction. Energies are in kcal/mol relative to the reactants.



Figure S 5: Electronic energy profiles along the M06-2X/6-311++G(d,p) IRC around the TS4 structure. The energy profiles are normalized defining the zero at the M06-2X saddle point.

Table S2: Excited state energies for H-abstraction by O(3P) calculated relatively to the ground state at the saddle point at different level of theories and with different basis sets and active spaces. MS-MR is multistate-multireference CASPT2 and SS-SR is single state single reference CASPT2.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | E(T1)-E(T0) kcal/mol | | | | | |
|  | (6e,5o) | | | | (12e,11o) | |
|  | SS-SR | MS-MR | SS-SR | MS-MR | SS-SR | |
| Reaction | cc-pVDZ | | aug-cc-pVTZ | | cc-pVDZ | aug-cc-pVTZ |
| O+C6H5CH3🡪 C6H5CH2+OH | 0.30 | 0.26 | 0.38 | 0.39 | 0.25 | 0.33 |
| O+C6H5CH3🡪 oC6H4CH3+OH | 1.69 | 1.83 | 0.99 | 1.02 | 1.46 | 0.71 |
| O+C6H5CH3🡪 mC6H4CH3+OH | 1.22 | 1.36 | 0.94 | 1.01 | 1.04 | 0.76 |
| O+C6H5CH3🡪 pC6H4CH3+OH | 1.26 | 1.40 | 1.02 | 1.09 | 1.05 | 0.80 |

Table S3: Rate constants for C6H5CH2+O2 calculated in this study. Units are cm3, mol, s, cal. aHigh pressure limit rate constants. Mean and maximum deviations of the Arrhenius fits are reported for each channel.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | A | n | Ea [cal/mol] | *Fitting T [K]* | *Average, Max [%]*  *|(kcalc-kfit)/kcalc|* |
| C6H5CH2+O2= C6H5CH2O2 | 5.55E+07 | 1.251 | -1377.77 | *300-2500a* | <1, <1 |
| 0.1 atm | 2.91E+36 | -8.333 | 5075.92 | *600-800* | 1, 2 |
| 1 atm | 2.01E+47 | -11.2 | 12464.00 | *600-900* | <1, <1 |
| 10 atm | 1.08E+33 | -6.566 | 8493.47 | *600-1100* | 2, 3 |
| 100 atm | 4.41E+22 | -3.266 | 5146.57 | *600-1500* | 4, 7 |
| 1000 atm | 3.36E+14 | -0.766 | 1938.88 | *600-2100* | 4, -8 |
| C6H5CH2O2= C6H5CH2+O2 | 2.04E+12 | 0.203 | 20421.31 | *300-2500 a* | 3, -5 |
| 0.1 atm | 5.52E+05 | 1.465 | 12764.58 | *600-800* | 4, 5 |
| 1 atm | 7.00E+41 | -9.164 | 30314.23 | *600-900* | 1, 3 |
| 10 atm | 4.26E+33 | -6.398 | 28695.20 | *600-1100* | <1, 3 |
| 100 atm | 7.79E+23 | -3.31 | 25519.46 | *600-1500* | <1, 4 |
| 1000 atm | 1.21E+18 | -1.507 | 23336.99 | *600-2100* | 3, 5 |
| C6H5CH2+O2=C6H5CHO+OH |  |  |  |  |  |
| 0.1 atm | 4.31E+05 | 1.65 | 15929.05 | *600-2500* | <1, 8 |
| 1 atm | 2.66E+07 | 1.156 | 17382.76 | *600-2500* | <1, 2 |
| 10 atm | 8.66E+13 | -0.635 | 22883.04 | *600-2500* | <1, 6 |
| 100 atm | 2.05E+17 | -1.474 | 28281.88 | *600-2500* | <1, 11 |
| 1000 atm | 7.76E+06 | 1.524 | 25276.76 | *600-2500* | 2, 20 |
| C6H5CH2O2= C6H5CHO +OH | 2.72E+00 | 3.395 | 31375.15 | *300-2500 a* |  |
| 0.1 atm | 1.31E+02 | 0.753 | 16871.05 | *600-800* | <1, 3 |
| 1 atm | 1.06E+44 | -10.953 | 44007.04 | *600-900* | <1, 3 |
| 10 atm | 3.41E+43 | -10.059 | 48218.50 | *600-1100* | 1, 8 |
| 100 atm | 1.05E+28 | -4.934 | 44480.63 | *600-1500* | <1, 6 |
| 1000 atm | 1.25E+16 | -1.182 | 40386.24 | *600-2100* | <1, 8 |
| C6H5CH2+O2=C6H5O+CH2O |  |  |  |  |  |
| 0.1 atm | 1.24E+09 | 0.503 | 20441.72 | *600-2500* | <1, 3 |
| 1 atm | 4.86E+09 | 0.341 | 20948.09 | *600-2500* | <1, 7 |
| 10 atm | 7.46E+14 | -1.076 | 25511.69 | *600-2500* | 1, 7 |
| 100 atm | 4.11E+21 | -2.856 | 33389.10 | *600-2500* | <1 |
| 1000 atm | 1.11E+10 | 0.484 | 30361.05 | *600-2500* | 3, 14 |
| C6H5CH2O2= C6H5O+CH2O |  |  |  |  |  |
| 0.1 atm | *Negligible* | | | |  |
| 1 atm | 1.56E+08 | -0.06 | 34235.39 | *800-900* | <1, <1 |
| 10 atm | 1.84E+100 | -26.829 | 82244.39 | *600-1100* | <1, 15 |
| 100 atm | 1.24E+33 | -6.531 | 50368.99 | *600-1500* | <1, 7 |
| 1000 atm | 2.64E+22 | -3.074 | 48400.26 | *600-2100* | <1, 15 |