Autoignition of *trans*-Decalin, a Diesel Surrogate Compound: Rapid Compression Machine Experiments and Chemical Kinetic Modeling

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Supplement Material

Table S1: Rates rules applied for key reaction classes in the low temperature chemistry of *trans*-decalin.

Reaction class	Example	Reference (analogous species)	Tunings
Addition of fuel radical to oxygen	DCL-2R+O2<=>DCL-2O2R	R + O2 = RO2 [1] (acyclic alkanes)	None
Isomerization of alkylperoxy radical to hydroperoxyalkyl radical	DCL-2O2R<=>DCLOOH2-4R	RO2 = QOOH [2] (cyclohexane)	None
Formation of ketohydroperoxide from hydroperoxyalkylperoxy radical	DCLOOH2-4O2R=>DCLKET2-4+OH	RO2 = QOOH [2] (cyclohexane)	A × 0.5, Ea –2 kcal/mol
Concerted HO2 elimination from alkylperoxy radical	DCL-2O2R<=>DCLD2+HO2	RO2 = Alkene + HO2 [2] (cyclohexane)	A × 1.15
Formation of cyclic ethers from hydroperoxyalkyl radical	DCLOOH2-4R<=>DCLO2-4+OH	QOOH = Cyclic ether + OH [3] (acyclic alkanes)	None

References

[1] A. Miyoshi, Molecular size dependent falloff rate constants for the recombination reactions of alkyl radicals with O2 and implications for simplified kinetics of alkylperoxy radicals, Int. J. Chem. Kinet. 44 (2012) 59-74, doi: 10.1002/kin.20623.

[2] R.X. Fernandes, J. Zador, L.E. Jusinski, J.A. Miller, and C.A. Taatjes, Formally direct pathways and low-temperature chain branching in hydrocarbon autoignition: the cyclohexyl+ O2 reaction at high pressure, Phys. Chem. Chem. Phys. 11 (2009) 1320-1327, doi: 10.1039/b819825j.

[3] S.M. Villano, L.K. Huynh, H.H. Carstensen, and A.M. Dean, High-pressure rate rules for alkyl + O2 reactions. 2. The isomerization, cyclic ether formation, and β-scission reactions of hydroperoxy alkyl radicals, J. Phys. Chem. A 116 (2012) 5068-5089, doi: 10.1021/jp3023887.

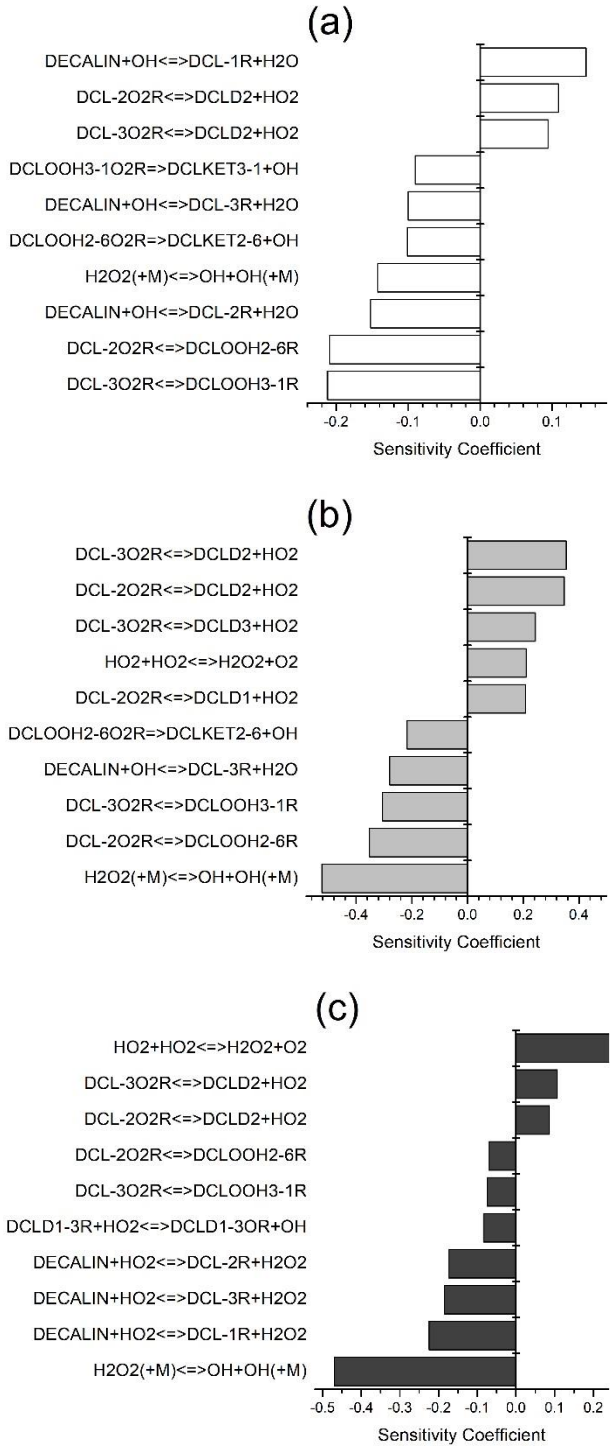

Figure S1: Sensitivity analysis at ϕ=0.5 in air, initial pressure of 15 bar with initial temperatures of (a) 680 K, (b) 780 K, and (c) 940 K.

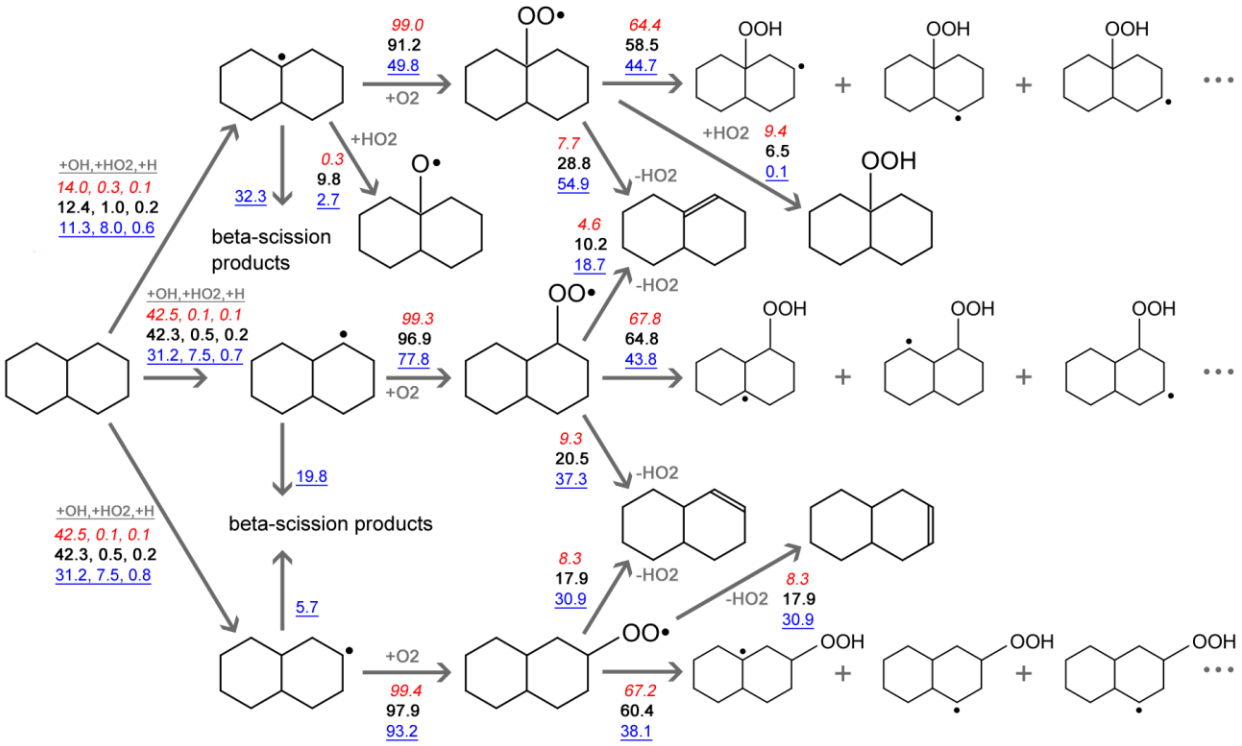

Figure S2: Simplified reaction pathway diagram showing the consumption of fuel-derived radicals and alkyl peroxy radicals; results from rate-of-production analysis at initial temperatures of 680 K, 780 K, and 940 K, under ϕ=0.5 in air, initial pressure of 15 bar (constant volume assumption), and at fuel consumption of 20%. Numbers denotes percentage of contribution. Red italic numbers: 680 K; Black numbers: 780 K; Blue underlined numbers: 940 K.

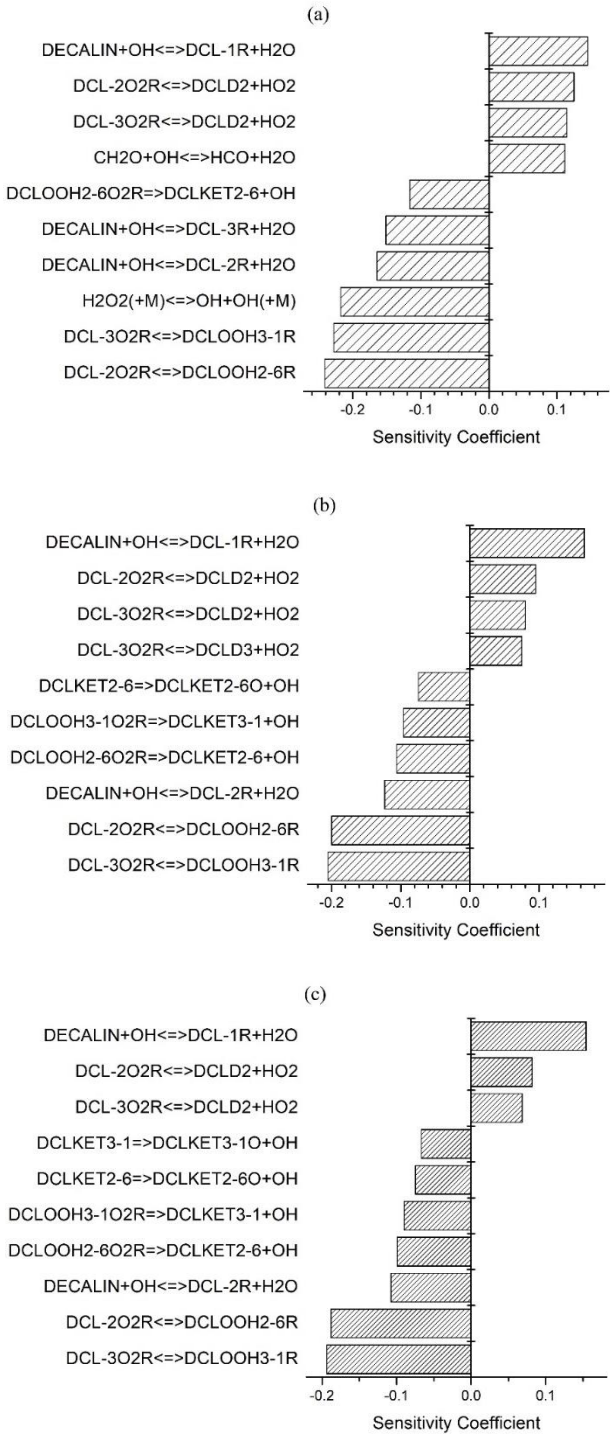

Figure S3: Sensitivity analysis with an initial pressure of 10 bar and an initial temperature of 680 K for *trans*-decalin/air mixtures of (a) ϕ=0.5, (b) ϕ=1.0, and (c) ϕ=2.0.

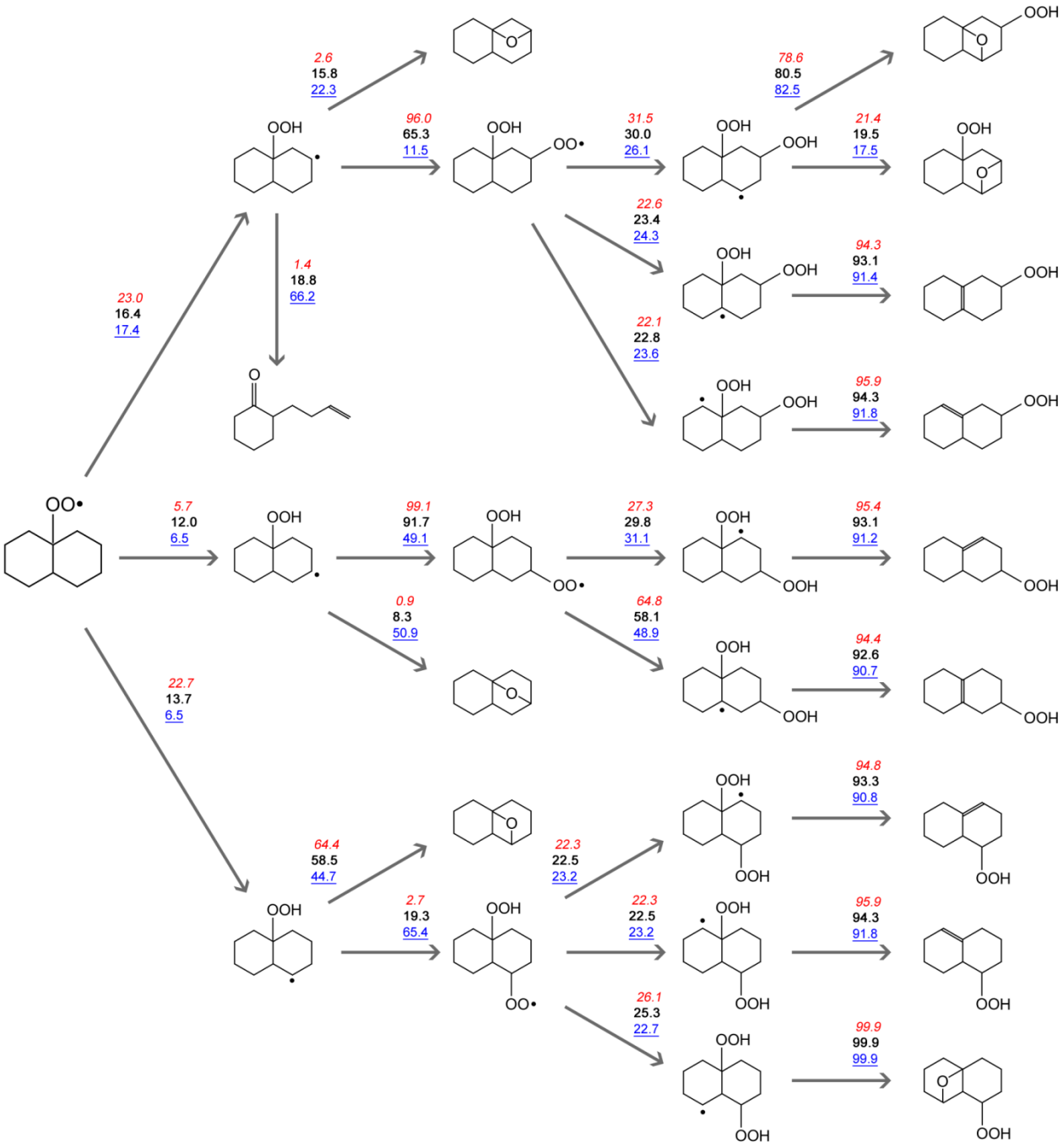

Figure S4: Detailed reaction pathway diagram showing the consumption of alkyl peroxy radical (site 1) initiated by isomerization; results from rate-of-production analysis at initial temperatures of 680 K, 780 K, and 940 K, under ϕ=1.0 in air, initial pressure of 10 bar (CONV assumption), and at fuel consumption of 20%. Numbers denotes percentage of contribution. Red italic numbers: 680 K; Black numbers: 780 K; Blue underlined numbers: 940 K.

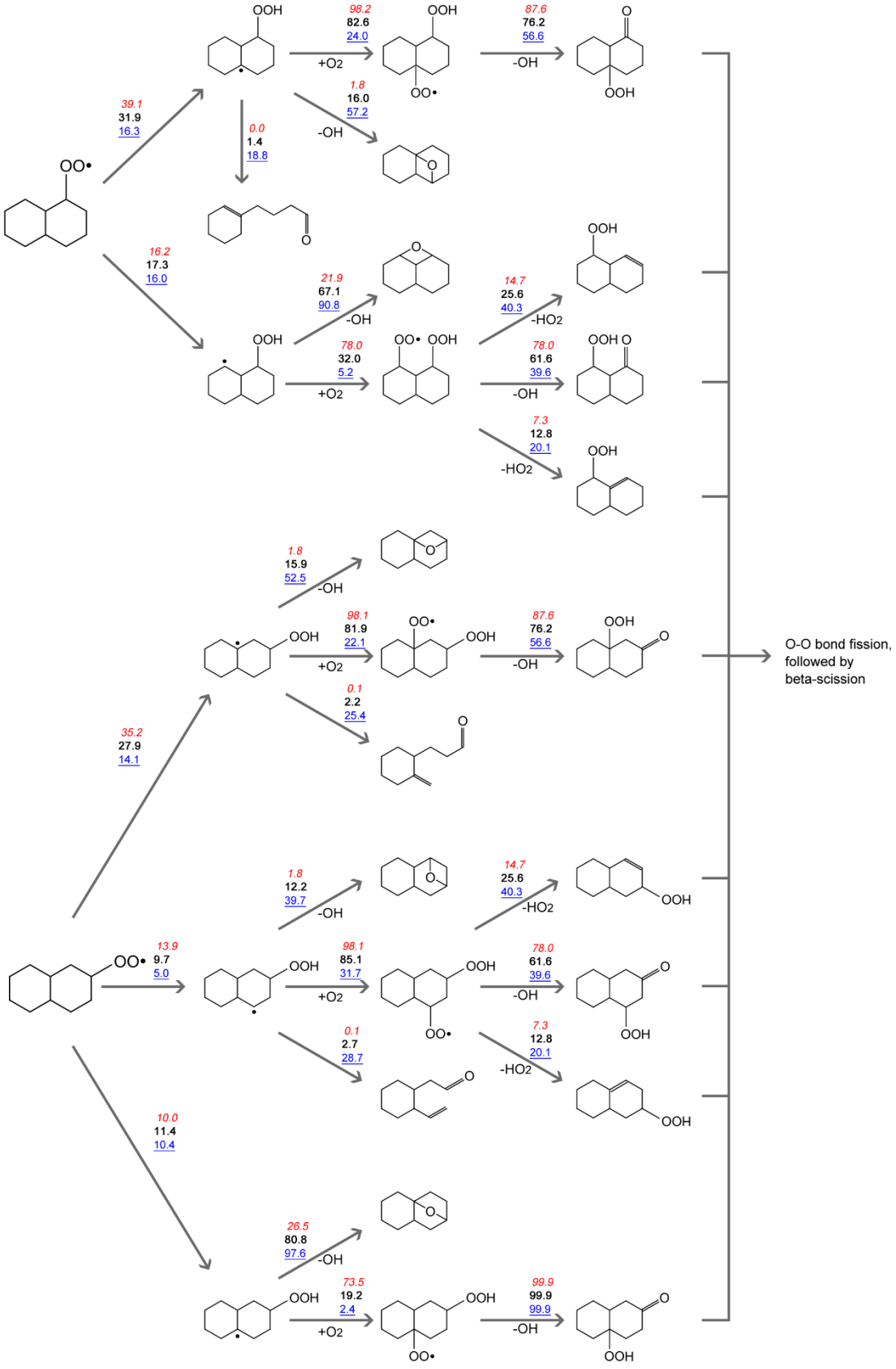

Figure S5: Detailed reaction pathway diagram showing the consumption of alkyl peroxy radical (site 2, site3) initiated by isomerization; results from rate-of-production analysis at initial temperatures of 680 K, 780 K, and 940 K, under ϕ=1.0 in air, initial pressure of 10 bar (CONV assumption), and at fuel consumption of 20%. Numbers denotes percentage of contribution. Red italic numbers: 680 K; Black numbers: 780 K; Blue underlined numbers: 940 K.