

Supplementary Material

Combustion of n -C₃–C₆ linear alcohols: an experimental and kinetic modeling study.

Part I: reaction classes, rate rules, model lumping and validation.

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1. Structure and size of the kinetic models attached.

Table S1 describes the attached kinetic models. The modular structure of the CRECK model (Version 2003, March 2020 [1]) allows to easily reduce the number of species and reactions by including/excluding kinetic subsets. The octanol model is provided as a separate module.

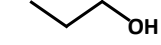


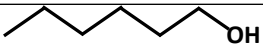

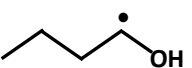
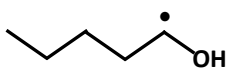
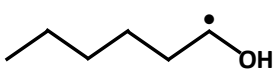
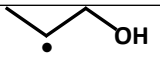

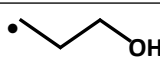
Table S1: CRECK2003 (March 2020) kinetic models attached to this study [1].

Model	Description	Number of Species	Number of Reactions	References
Model1	HT and LT, complete CRECK2003 model	491	17888	[2-9]
Model2	HT and LT including NO _x (<i>Model1 with NO_x</i>)	536	18348	[2-10]
Model3	HT only, complete CRECK2003 HT model (<i>Model1 without LT</i>)	367	14453	[2-9]
Model4	HT only, TPRF and alcohols	253	7559	[2-6, 8, 9]
Model5	HT with PAHs and NO _x (<i>Model 3 with NO_x</i>)	412	14913	[2-10]
Octanol subset	Octanol HT and LT subsets only			[8, 9]

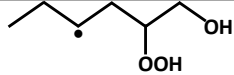
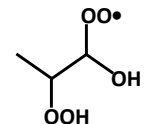
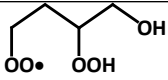
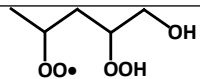
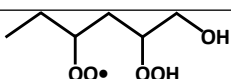
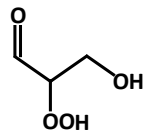
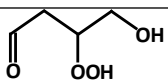
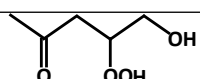
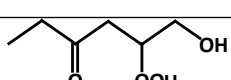
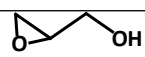

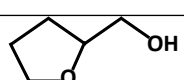
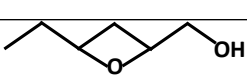
2. Nomenclature for alcohols and related molecules

Table S2 shows the nomenclature of species in the kinetic models for alcohols pyrolysis and oxidation.

Table S2: Species nomenclature. *denotes lumped species for which only one representative isomer is pictured.

	Species Name	Species Formula	Representation	Model name
1	n-propanol	C ₃ H ₈ O ₁		NC3H7OH
2	n-butanol	C ₄ H ₁₀ O ₁		N1C4H9OH
3	n-pentanol	C ₅ H ₁₂ O ₁		C5H11OH
4	n-hexanol	C ₆ H ₁₄ O ₁		C6H13OH
5	α-radical, n-propanol	C ₃ H ₇ O ₁		CH3CH2CHOH
6	α-radical, n-butanol	C ₄ H ₉ O ₁		CH3CH2CH2CHOH
7	α-radical, n-pentanol	C ₅ H ₁₁ O ₁		RPENT1OHA
8	α-radical, n-hexanol	C ₆ H ₁₃ O ₁		RHEX1OHA
9	β-radical, n-propanol	C ₃ H ₇ O ₁		CH3CHCH2OH
10	β-radical, n-butanol	C ₄ H ₉ O ₁		CH3CH2CHCH2OH
11	γ-radical, n-propanol	C ₃ H ₇ O ₁		CH2CH2CH2OH

12	γ -radical, n-butanol	C4H9O1		CH3CHCH2CH2OH
13	δ -radical, n-butanol	C4H9O1		CH2CH2CH2CH2OH
14	alkoxy radical, n-propanol	C3H7O1		CH3CH2CH2O
15	alkoxy radical, n-butanol	C4H9O1		CH3CH2CH2CH2O
16	n-pentanol radicals*	C5H11O1		RPENT1OHB
17	n-hexanol radicals*	C6H13O1		RHEX1OHB
18	n-propanal	C3H6O1		C2H5CHO
19	n-butanal	C4H8O1		C3H7CHO
20	n-pentanal	C5H10O1		C4H9CHO
21	n-hexanal	C6H12O1		ALDC6
22	1-propenol isomers*	C3H6O1		C3H5OH
23	1-butenol isomers*	C4H8O1		NC4H7OH
24	1-pentenol isomers*	C5H10O1		C5H9OH
25	hydroxyalkyl-peroxy radicals ($\dot{R}O_2$), n-propanol*	C3H7O3		RNC3OHOOX
26	hydroxyalkyl-peroxy radicals ($\dot{R}O_2$), n-butanol*	C4H9O3		RBU1OOX
27	hydroxyalkyl-peroxy radicals ($\dot{R}O_2$), n-pentanol*	C5H11O3		RPENT1OOX
28	hydroxyalkyl-peroxy radicals ($\dot{R}O_2$), n-hexanol*	C6H13O3		RC6OHOOX
29	hydroperoxyl-alkylhydroxy radicals ($\dot{Q}OOH$), n-propanol*	C3H7O3		QNC3OHOOX
30	hydroperoxyl-alkylhydroxy radicals ($\dot{Q}OOH$), n-butanol*	C4H9O3		QBU1OOX
31	hydroperoxyl-alkylhydroxy radicals ($\dot{Q}OOH$), n-pentanol*	C5H11O3		QPENT1OOX

32	hydroperoxyl-alkylhydroxy radicals (\dot{Q} OOH), n-hexanol*	C6H13O3		QC6OHOOX
33	(\dot{O}_2 QOOH), n-propanol*	C3H7O5		ZNC3OHOOX
34	(\dot{O}_2 QOOH), n-butanol*	C4H9O5		ZBU1OOX
35	(\dot{O}_2 QOOH), n-pentanol*	C5H11O5		ZPENT1OOX
36	(\dot{O}_2 QOOH), n-hexanol*	C6H13O5		ZC6OHOOX
37	carbonyl hydroxyalkyl hydroperoxide (CHHP), n-propanol*	C3H6O4		KEHYNC3OH
38	carbonyl hydroxyalkyl hydroperoxide (CHHP), n-butanol*	C4H8O4		KEHYBU1
39	carbonyl hydroxyalkyl hydroperoxide (CHHP), n-pentanol*	C5H10O4		KEHYP1OH
40	carbonyl hydroxyalkyl hydroperoxide (CHHP), n-hexanol*	C6H12O4		KEHYC6OH
41	epoxy alcohols, n-propanol*	C3H6O2		C3OHCYETH
42	epoxy alcohols, n-butanol*	C4H8O2		C4OHCYETH
43	epoxy alcohols, n-pentanol*	C5H10O2		C5OHCYETH
44	epoxy alcohols, n-hexanol*	C6H12O2		C6OHCYETH

3. Reference kinetic parameters for H-atom abstraction reactions by \dot{H} , \dot{OH} , \dot{O} , \dot{HO}_2 and \dot{CH}_3

Table S3: Reference kinetic parameters for H-atom abstraction reactions by most important radicals. Units are cal, cm³, mol, s.

	Site	A	n	Ea
R=\dot{H}	O	3.00e+06	2.00	6349.34
	α	1.05e+07	2.00	4000.00
	β	4.50e+06	2.00	4000.00
	Secondary	6.60e+06	2.00	4000.00
	Primary	9.00e+06	2.00	6349.34
R=\dot{OH}	O	1.50e+09	1.00	1540.75
	α	5.25+09	1.00	50.00
	β	2.25+09	1.00	50.00

	Secondary	3.30e+09	1.00	50.00
	Primary	4.50e+09	1.00	1540.75
R=Ö	O	2.35e+06	2.00	4691.70
	α	8.23e+06	2.00	2500.00
	β	3.53e+06	2.00	2500.00
	Secondary	5.17e+06	2.00	2500.00
	Primary	7.05e+06	2.00	4691.70
R=HÖ₂	O	9.60e+05	2.00	19190.53
	α	1.02e+07	2.00	16000.00
	β	2.40e+06	2.00	16000.00
	Secondary	1.76e+06	2.00	16000.00
	Primary	2.40e+06	2.00	19190.53
R=ĊH₃	O	3.00e+04	2.00	7443.70
	α	1.05e+05	2.00	5000.00
	β	4.50e+04	2.00	5000.00
	Secondary	6.60e+04	2.00	5000.00
	Primary	9.00e+04	2.00	7443.70

4. Comparison of radical decomposition and isomerization rate constants (CRECK vs Sarathy et al.)

Figure S1 compares high pressure limit rate constants for alcohol radicals decomposition and isomerization reactions. The rate constants selected in this work are compared with those proposed by Sarathy et al. [11].

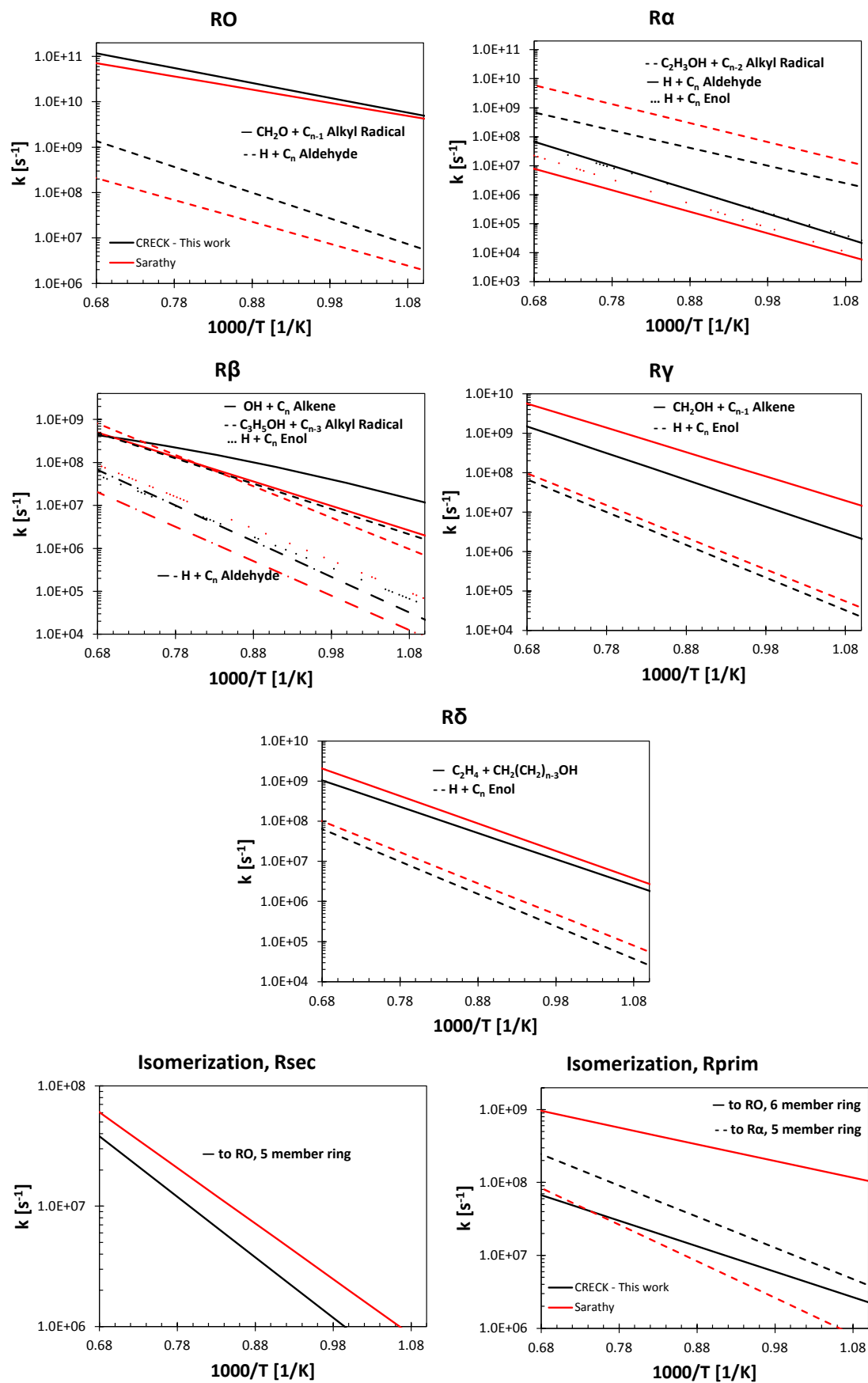


Figure S1: Comparison of radical decomposition and isomerization rate constants. Black lines: this work (CRECK model), red lines: Sarathy et al. [11].

5. Rate of production analysis

Figure S2 compares results from a rate of production analysis performed with the present model and that of Sarathy et al. [11], for a n-pentanol/air mixtures ($\phi=1.0$) at $p=10$ bar and $T=748$ K.

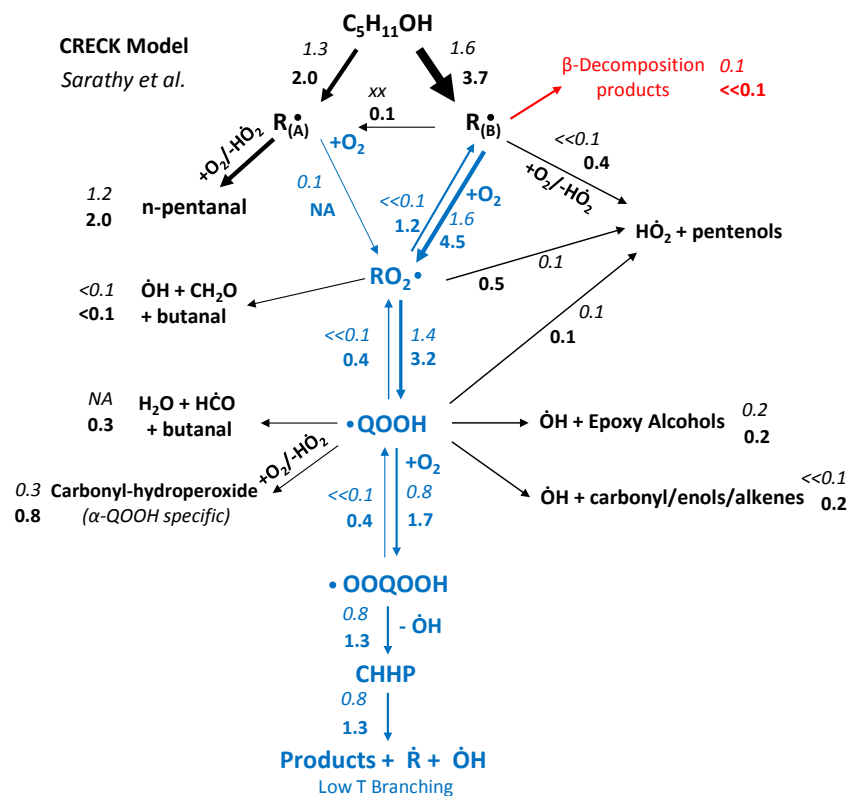


Figure S2: reactive fluxes analysis of n-pentanol oxidation in an adiabatic constant volume batch reactor at $T = 748$ K, $p = 10$ bar and $\phi = 1.0$ (fuel conversion $\sim 20\%$). Numbers are rates of production/consumption in $10^{-4} \text{ mol cm}^{-3} \text{ s}^{-1}$. Bold: CRECK model, italics: Sarathy et al. [11]

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