

Supplemental Material for

Methylcyclohexane pyrolysis and oxidation in a jet-stirred reactor

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Table S1. Reaction class and rate constant source for MCH pyrolysis and oxidation

Reaction Class – High Temperature	Source	Updates/Comments
1. Unimolecular Fuel Decomposition	Wang et al (1)	
2. H-atom abstraction from the fuel <i>H, O₂</i> <i>OH</i> <i>HO₂</i> <i>CH₃, O, CH₃O₂, C₂H₃, C₂H₅</i>	Wang et al(1), Sivaramakrishnan (2), Aguilera-Iparraguirre (3), Sarathy et al (4)	
3. Alkyl radical decomposition	Wang et al (1)	
4. Alkyl radical isomerization	Wang et al (1)	
5. H-atom abstraction reactions from alkenes	Wang et al (1)	
6. Addition of radical species <i>O</i> and <i>OH</i> to alkenes	Weber et al (5)	Not included in Wang et al (1) mechanism
7. Reactions of alkenyl radicals with <i>HO₂</i>, <i>CH₃O₂</i>, and <i>C₂H₅O₂</i>	Wang et al (1)	
8. Alkenyl radical decomposition	Wang et al (1)	
9. Alkene decomposition	Wang et al (1)	
10. Retroene decomposition reactions	Wang et al (1)	

Reaction Class – Intermediate Temperature	Source	Updates/Comments
MCHENE radical + HO₂ and subsequent decomposition (R + HO₂ = RO + OH)	Weber et al (5) – no reference to where they obtained their rates	Included to improve IDT's, might affect formation of Toluene, Benzene etc.?

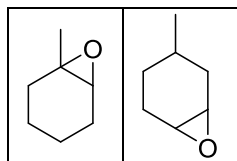
Reaction Class – Low Temperature	Source	Updates/Comments
11. R + O₂ = ROO	*Xing et al (6,7), ~Fernandes et al (8)	*(CYCHEXCH2, MCHR1, MCHR2). ~(MCHR3, MCHR4)
12. R + ROO = RO + RO.	Sarathy et al (4)	
13. R + HO₂ = RO + OH.	Sarathy et al (4)	
14. R + CH₃O₂ = RO + CH₃O.		Not included
15. Alkyl peroxy radical isomerization (ROO = QOOH). <i>CHXCH2OO = CHXJ2CH2Q</i> <i>CHXCH2OO = MCHXQJ3</i> <i>MCH1OO = MCH1QJ2</i> <i>MCH1OO = MCH1QJ4</i> <i>MCH1OO = MCH1QJ3</i> <i>MCH2OO = MCH2QX</i> <i>MCH2OO = MCH2QJ4</i>	Xing et al (6) Xing et al (6) Xing et al (7) Xing et al (7) Xing et al (7) Xing et al (7) Xing et al (7)	Included to form MCHYO12 Included to form MCHYO14

<i>MCH3OO = MCH3QJ1</i>	Fernandes et al (8)	A/4, Ea -2kcal tertiary H
<i>MCH3OO = MCH3QJ5</i>	Fernandes et al (8)	A/2
<i>MCH4OO = MCH4QJ1</i>	Fernandes et al (8)	A/2, Ea -2kcal tertiary H
<i>MCH4OO = MCH4QJ2</i>	Fernandes et al (8)	
16. Concerted eliminations (ROO = alkene + HO₂).		
<i>CHXCH2OO = CHXDCH2 + HO₂</i>	Xing et al (6)	
<i>MCH1OO = CHXDCH2+HO₂</i>	Xing et al (7)	
<i>MCH1OO = MCH1ENE+HO₂</i>	Xing et al (7)	
<i>MCH2OO = MCH2ENE+HO₂</i>	Xing et al (7)	
<i>MCH3OO = MCH2ENE + HO₂</i>	Fernandes et al (8)	A/2
<i>MCH3OO = MCH3ENE + HO₂</i>	Fernandes et al (8)	A/2
<i>MCH4OO = MCH3ENE + HO₂</i>	Fernandes et al (8)	
17. ROO + HO₂ = ROOH + O₂	Sarathy et al (4)	A*4 notable effect of Intermediate temp IDT.
18. ROO + H₂O₂ = ROOH + HO₂.	Sarathy et al (4)	
19. ROO + CH₃O₂ = RO + CH₃O + O₂.	Sarathy et al (4)	
20. ROO + ROO = RO + RO + O₂.	Sarathy et al (4)	
21. ROOH = RO + OH	Jalan et al (9)	
22. RO decomposition.	Weber et al (5)	
23. QOOH = cyclic ether + OH (cyclic ether formation).	*Xing et al (6,7), ~Fernandes et al (8)	*(CYCHEXCH2, MCHR1, MCHR2). ~(MCHR3, MCHR4)
24. QOOH = alkene + HO₂ (radical site beta to OOH group).	*Xing et al (6,7), ~Fernandes et al (8)	*(CYCHEXCH2, MCHR1, MCHR2). ~(MCHR3, MCHR4)
25. QOOH = alkene + carbonyl + OH (radical site gamma to OOH group).	*Xing et al (6,7), ~Fernandes et al (8)	*(CYCHEXCH2, MCHR1, MCHR2). ~(MCHR3, MCHR4)
26. (QOOH + O₂ = OOQOOH).	Rates taken from 1 st O ₂ addition	A/4 (should be A/2, however improvement in IDT's)
27. OOQOOH = KHP + OH.		
<i>MCHXQ2QJ = CHXCHO2Q+OH</i>	MCH2OO = MCH2QX	A*2/3, Ea -3KCAL, alpha H
<i>MCHXQ3QJ = CHXCHO2Q+OH</i>	Butylcyclohexane mech	
<i>MCH2QXQJ = MCH2OXQ+OH</i>	CHXCH2OO = CHXJ2CH2Q	A/4, Ea -3KCAL, alpha H
<i>MCH2Q4QJ = MCH2O4Q+OH</i>	MCH4OO = MCH4QJ2	A /4, Ea-2KCAL (ringstrain)
<i>MCH2Q6QJ = MCH2O6Q+OH</i>	MCH2OO = MCH2QJ6	Ea -2KCAL (ringstrain)
<i>MCH3Q5QJ = MCH3O5Q+OH</i>	MCH3OO = MCH3QJ5	A/2, Ea -2KCAL (ringstrain)
<i>MCH3Q1QJ = MCH3O1Q+OH</i>	MCH1OO = MCH1QJ3	A/2, Ea -2KCAL (ringstrain)
<i>MCH4Q2QJ = MCH4O2Q+OH</i>	MCH2OO = MCH2QJ4	Ea -2KCAL (ringstrain)
<i>MCH4Q1QJ = MCH4O1Q+OH</i>	MCH1OO = MCH1QJ4	Ea -2KCAL (ringstrain)
28. KHP decomposition	Weber et al (5)	
29. Cyclic ether reactions with OH and HO₂.	Weber et al (5)	
30. Decomposition of large carbonyl species and carbonyl radicals.	Weber et al (5)	

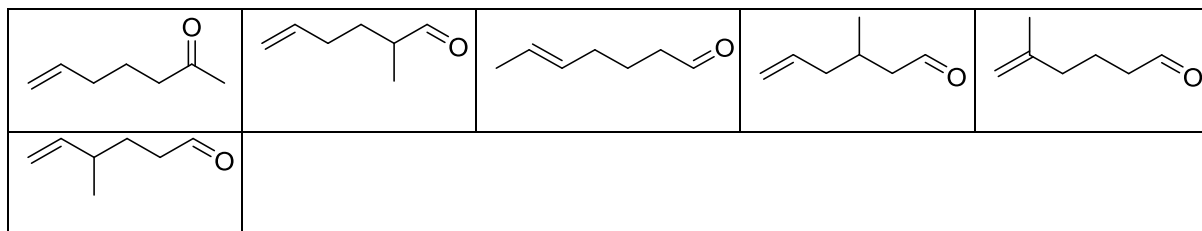
Reaction Class – Alternative Temperature	Source	Updates/Comments
OOQOOH = Olefinic hydroperoxide + HO₂	Class 16. ROO = Olefin + HO ₂	Analogous rates as previous classes. ‘A’ factor corrections applied where necessary.
OOQOOH = P(OOH)₂	Class 15. ROO = QOOH	“
P(OOH)₂ = Olefinic hydroperoxide + HO₂	Class 24. QOOH = Olefin + HO ₂	“
P(OOH)₂ = Hydroperoxy cyclic ether + OH	Class 23. QOOH = cyclic ether + OH	“
P(OOH)₂ + O₂ = OOP(OOH)₂	Class 26. QOOH + O ₂ = OOQOOH	“
OOP(OOH)₂ = Keto-dihydroperoxide + OH	Class 27. OOQOOH = Keto-hydroperoxide + OH	“
OOP(OOH)₂ = Olefinic dihydroperoxide + HO₂	Class 16. ROO = Olefin + HO ₂	“
OOP(OOH)₂ = T(OOH)₃	Class 15. ROO = QOOH	“
T(OOH)₃ = Olefinic dihydroperoxide + HO₂	Class 24. QOOH = Olefin + HO ₂	“
T(OOH)₃ = Dihydroperoxy cyclic ether + OH	Class 23. QOOH = cyclic ether + OH	“

Table S2. Lumped species in the kinetic model

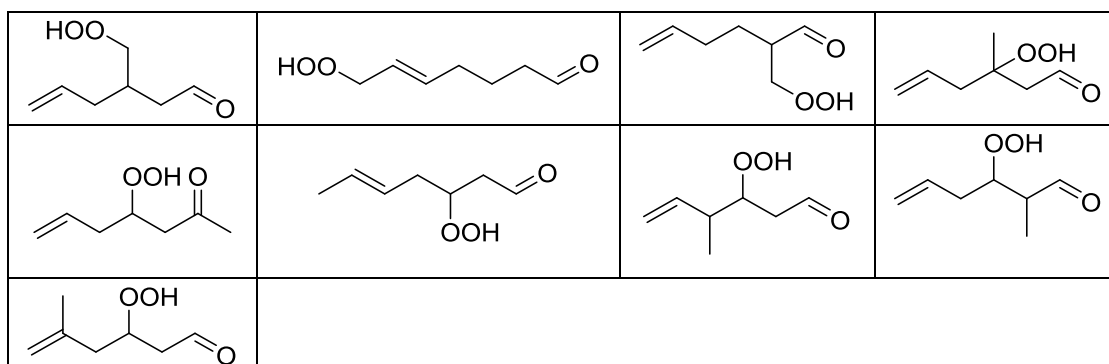
MCHYO12



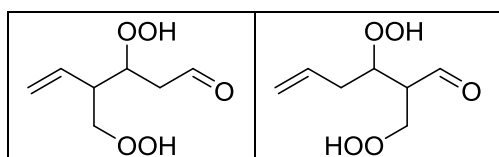
C7ENE-ONE



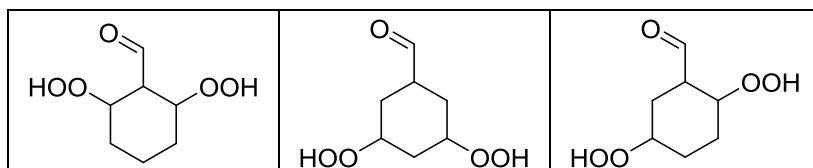
C7ENE-ONEQ



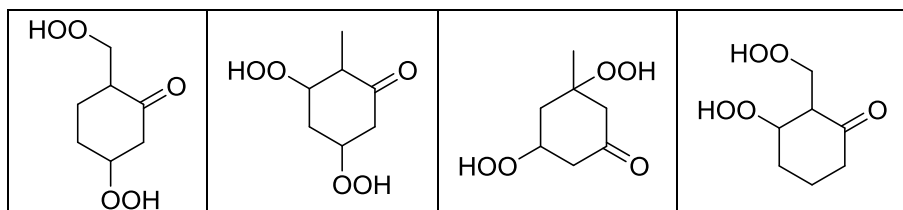
C7ENE-ONEQQ



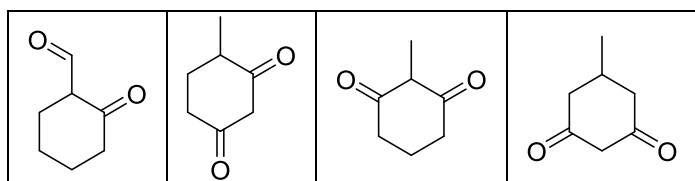
MCHXO2Q6Q



MCH2OXQ4Q



MCH2O4O



References

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