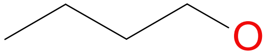
アルコール燃料の燃焼排出物の生成経路

防衛大学校応用化学科　安永健治

Previous combustion studies of butanol isomers

n-Butanol



Spark ignition engine

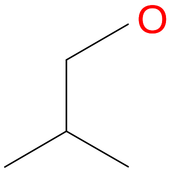
R. W. Rice, A. K. Sanyal, A. C. Elrod, J. Eng. Gas Power 113 (1991) 377-382
T. Wallner, S. A. Miers, S. McConnell, J. Eng. Gas Power 131 (2009) 32802-32809
G. L. Miller, J. L. Smith, J. P. Workman, Trans. ASAE 24 (1981) 538-540
M. Gautam, D. W. Martin, Proc. Inst, Mech. Eng. Part A 214 (2000) 165-182
M. Gautam, D. W. Martin, D. Carder, Proc. Inst, Mech. Eng. Part A 214 (2000) 497-511
Y. Yacoub, R. Bata, M. Gautam, Proc. Inst, Mech. Eng. Part 212 (1998) 363-379
F.N. Alasfour, Appl. Therm. Eng. 17 (1997) 537-549
F.N. Alasfour, Int. J. Energy Res. 21 (1997) 21-30
S. Szwaja, J. D. Naber, Fuel 89 (2010) 1573-1582

Compression ignition engine

G. L. Miller, J. L. Smith, J. P. Workman, Trans. ASAE 24 (1981) 538-540
M. Yao, H. Wang, Z. Zheng, Y. Yue, Fuel 89 (2010) 2191-2201
C. D. Rakopoulos, A. M. Diamaratos, E. G. Giakoumis, D. C. Rakopoulos, Energy 35 (2011) 5173-5184
F. Lujaji, L. Kristóf, A. Bereczky, M. Mbarawa, Fuel 90 (2011) 505-510.
D. C. Rakopoulos, C. D. Rakopoulos, D. T. Hountalas, E. C. Kakaras, E. G. Giakoumis, R. G. Papagiannakis, Fuel 89 (2010) 2781-2790
D. C. Rakopoulos, C. D. Rakopoulos, E. G. Giakoumis, A. M. Diamaratos, D. C. Energ. Convers. Manage. 51 (2010) 1989-1997
O. Doǵan, Fuel 90 (2011) 2467-2472.
P. Saisirirat, F. Foucher, S. Chanchaona, C. Mounaïm-Rousselle, Energ. Fuel. 24 (2010) 5404–5409.
P. Saisirirat, C. Togbé, S. Chanchaona ,F. Foucher, , C. Mounaïm-Rousselle, P. Dagaut, Proc. Combust. Inst. 33 (2010) 3007-3014.
S. Lebedevas, G. Lebedeva, E. Sendzikiene, V. Makareviciene, Energ. Fuel. 24 (2010) 4503–4509.
R.N. Mehta, M. Chakraborty, P. Mahanta, P.A. Parikh, Ind. Eng. Chem. Res 49 (2010) 7660–7665.

Previous combustion studies of butanol isomers

iso-Butanol



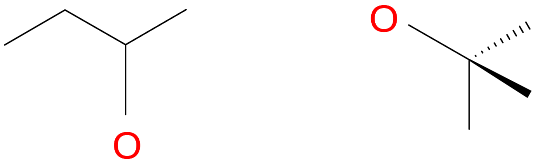
Spark ignition engine

F.N. Alasfour, Appl. Therm. Eng. 18 (1998) 245–256.
F.N. Alasfour, Appl. Therm. Eng. 18 (1998) 609–618.
F.N. Alasfour, Energ. Source. 21 (1999) 379–394.

Compression ignition engine

M. Karabektas, M. Hosoz, Renew. Energ. 34 (2009) 1554–1559.
M.I. Al-Hasan, M. Al-Momany, Transport 23 (2008) 306–310.

sec-Butanol and *tert*-Butanol



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Gas analysis of oxidation of butanol isomers

Jet Stirred Reactor

***n*-Butanol**

P. Dagaut, S.M. Sarathy, M.J. Thomson, Proc. Combust. Inst. 32 (2009) 229–237.

***sec*-Butanol, *iso*-Butanol**

C. Togbè, A. Mzè-Ahmed, P. Dagaut, Energ. Fuel. 24 (2010) 5244–5256.

Premixed laminar low pressure flame

***n*-Butanol**

N. Hansen, M. R. Harper, W. H. Green, Phys Chem. Chem. Phys. 13 (2011) 20262-20274
P. Oßwald, H. Güldenberg, K. Kohse-Höinghaus, B. Yang, T. Yuan, F. Qi, Combust. Flame 158 (1) (2011) 2-15.

***sec*-Butanol, *iso*-Butanol, *tert*-Butanol**

P. Oßwald, H. Güldenberg, K. Kohse-Höinghaus, B. Yang, T. Yuan, F. Qi, Combust. Flame 158 (1) (2011) 2-15.

Flow reactor

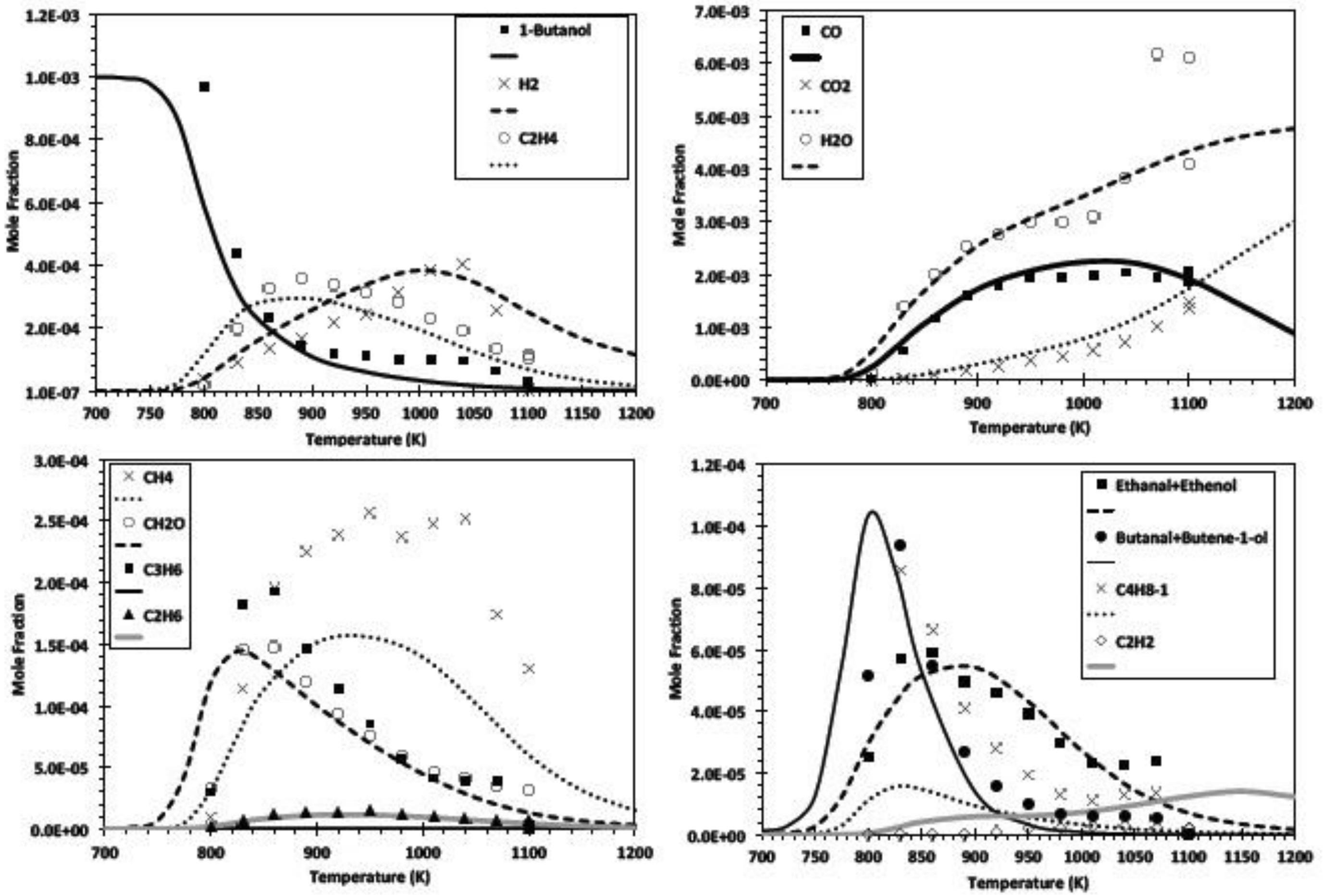
***n*-Butanol**

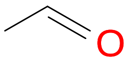
M.R. Harper, K.M. Van Geem, S.P. Pyl, G.B. Marin, W.H. Green, Combust. Flame 158 (2011) 16–41.

***sec*-Butanol**

K.M. Van Geem, S.P. Pyl, G.B. Marin, M.R. Harper, W.H. Green, Ind. & Eng. Chem. Res., 49 (2010) 10399–10420.

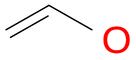
Jet stirred reactor



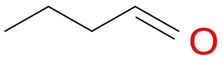


CH_3CHO

↕

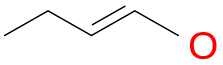


CH_2CHOH



$CH_3CH_2CH_2CHO$

↕



$CH_3CH_2CHCHOH$

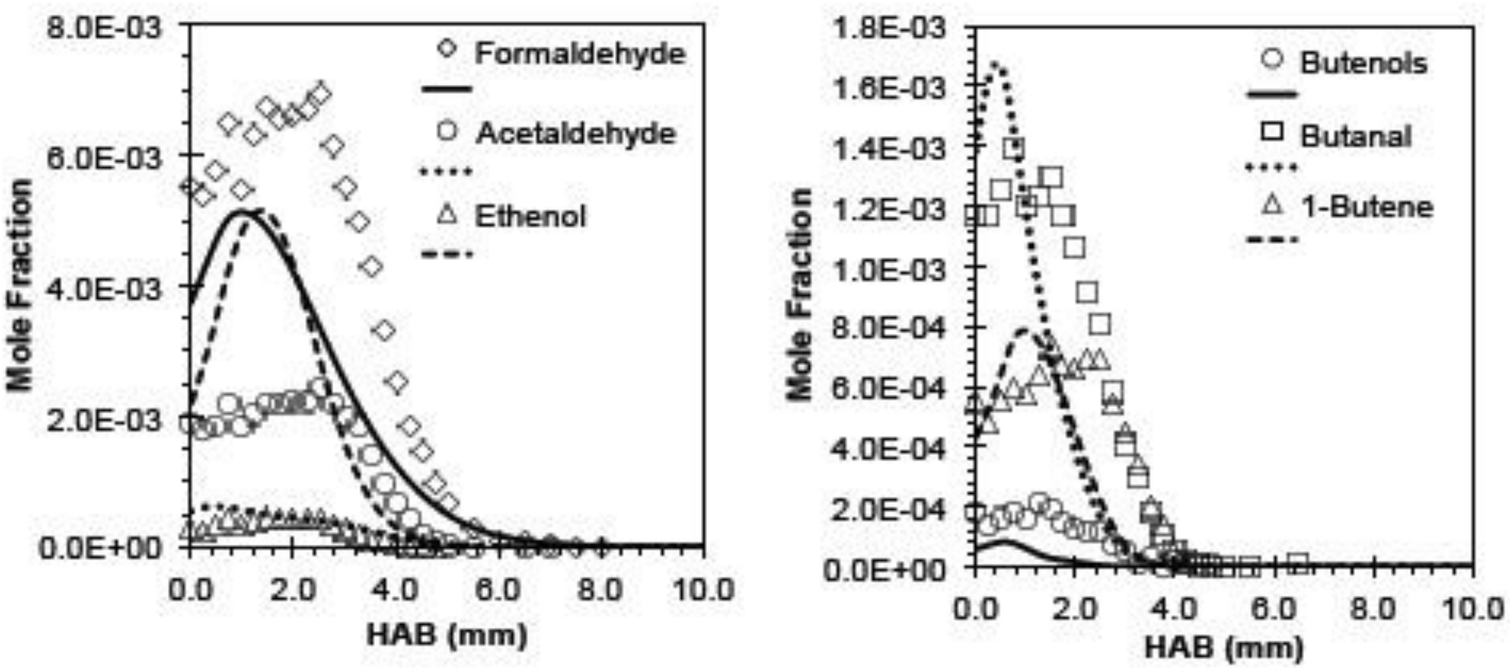
1(*n*)-butanol oxidation in a JSR at 10 atm, τ = 0.7 s and φ = 1. The initial fuel mole fraction was 0.1%.

P. Dagaut, S.M. Sarathy, M.J. Thomson, Proc. Combust. Inst. 32 (2009) 229–237.

Reaction Mechanism

Mani Sarathy, Stijn Vranckx, Kenji Yasunaga, Marco Mehl, Patrick Oßwald, Wayne K. Metcalfe, Charles K. Westbrook, William J. Pitz, Katharina Kohse-Höinghaus, Ravi X. Fernandes, Henry J. Curran, Combustion and Flame, accepted.

Premixed laminar low pressure flame



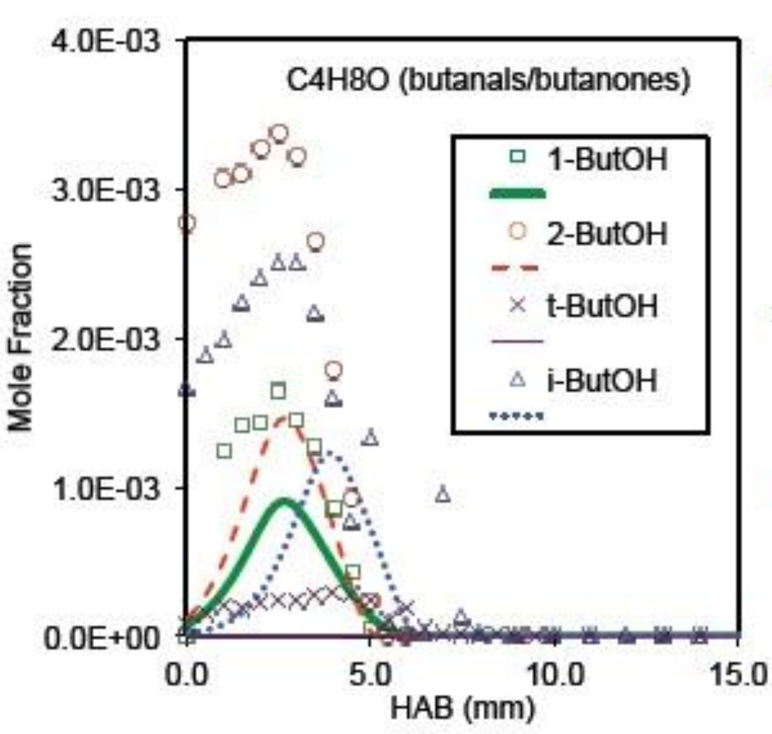
n-Butanol, 42.8% O_2, 50.0%Ar, ϕ =1.0, *p* =15 Torr and *v* = 96.1 cm/s

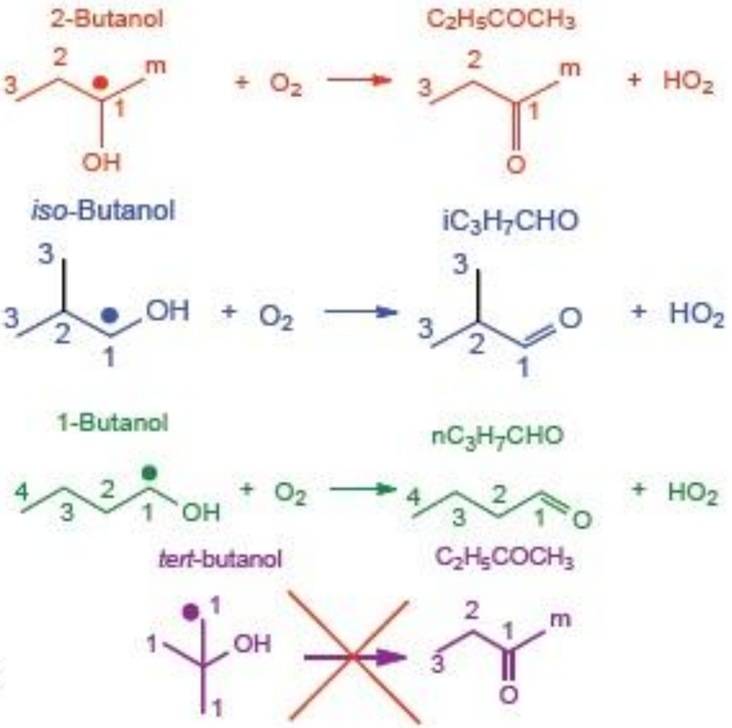
Experimental and predicted profiles for select species measured in stoichiometric 1(*n*)-butanol flames by Hansen et al.

N. Hansen, M. R. W. H. Green, Phys Chem. Chem. Phys. 13 (2011) 20262-20274

Reaction Mechanism
Mani Sarathy, Stijn Vranckx, Kenji Yasunaga, Marco Mehl, Patrick Oßwald, Wayne K. Metcalfe, Charles K. Westbrook, William J. Pitz, Katharina Kohse-Höinghaus, Ravi X. Fernandes, Henry J. Curran, Combustion and Flame, accepted.

Premixed laminar low pressure flame





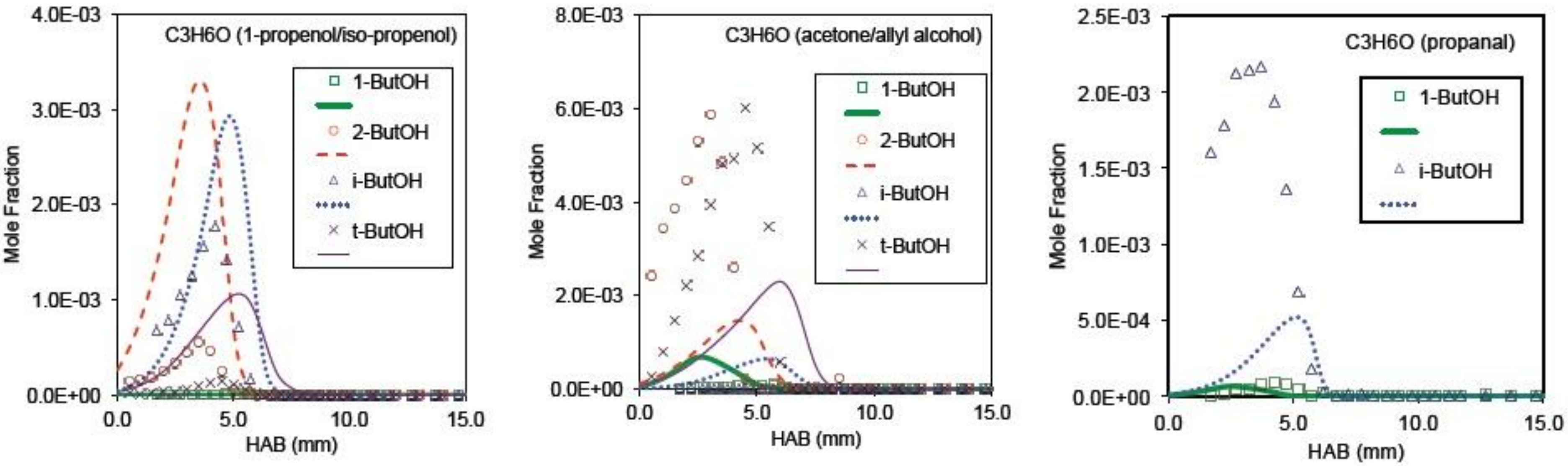
Butanol, 58.1% O_2, 25% Ar, $\phi = 1.7$, $p = 30$ Torr and v = 32.3 cm/s

P. Oßwald, H. Güldenberg, K. Kohse-Höinghaus, B. Yang, T. Yuan, F. Qi, Combust. Flame 158 (1) (2011) 2-15.

Reaction Mechanism

Mani Sarathy, Stijn Vranckx, Kenji Yasunaga, Marco Mehl, Patrick Oßwald, Wayne K. Metcalfe, Charles K. Westbrook, William J. Pitz, Katharina Kohse-Höinghaus, Ravi X. Fernandes, Henry J. Curran, Combustion and Flame, accepted.

Premixed laminar low pressure flame

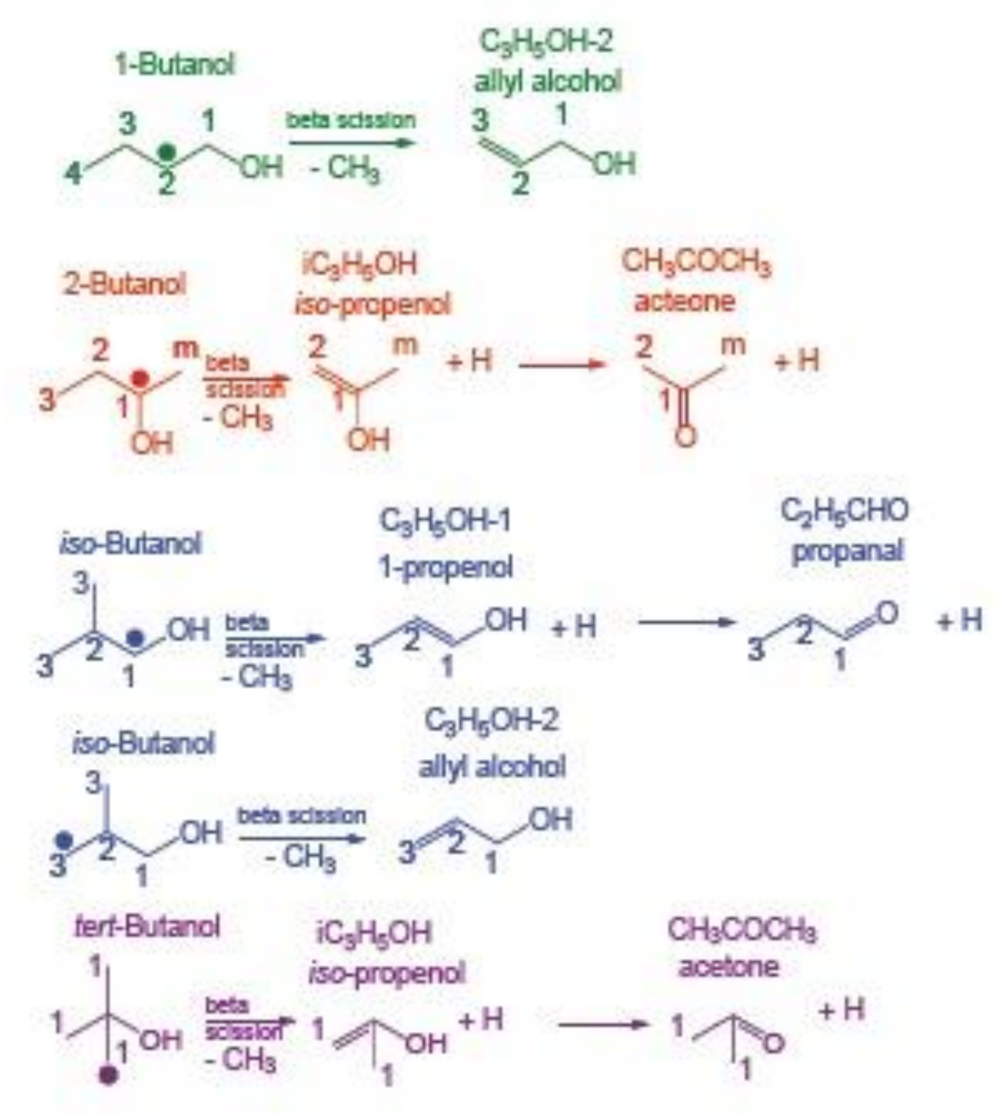


P. Oßwald, H. Güldenberg, K. Kohse-Höinghaus, B. Yang, T. Yuan, F. Qi, Combust. Flame 158 (1) (2011) 2-15.

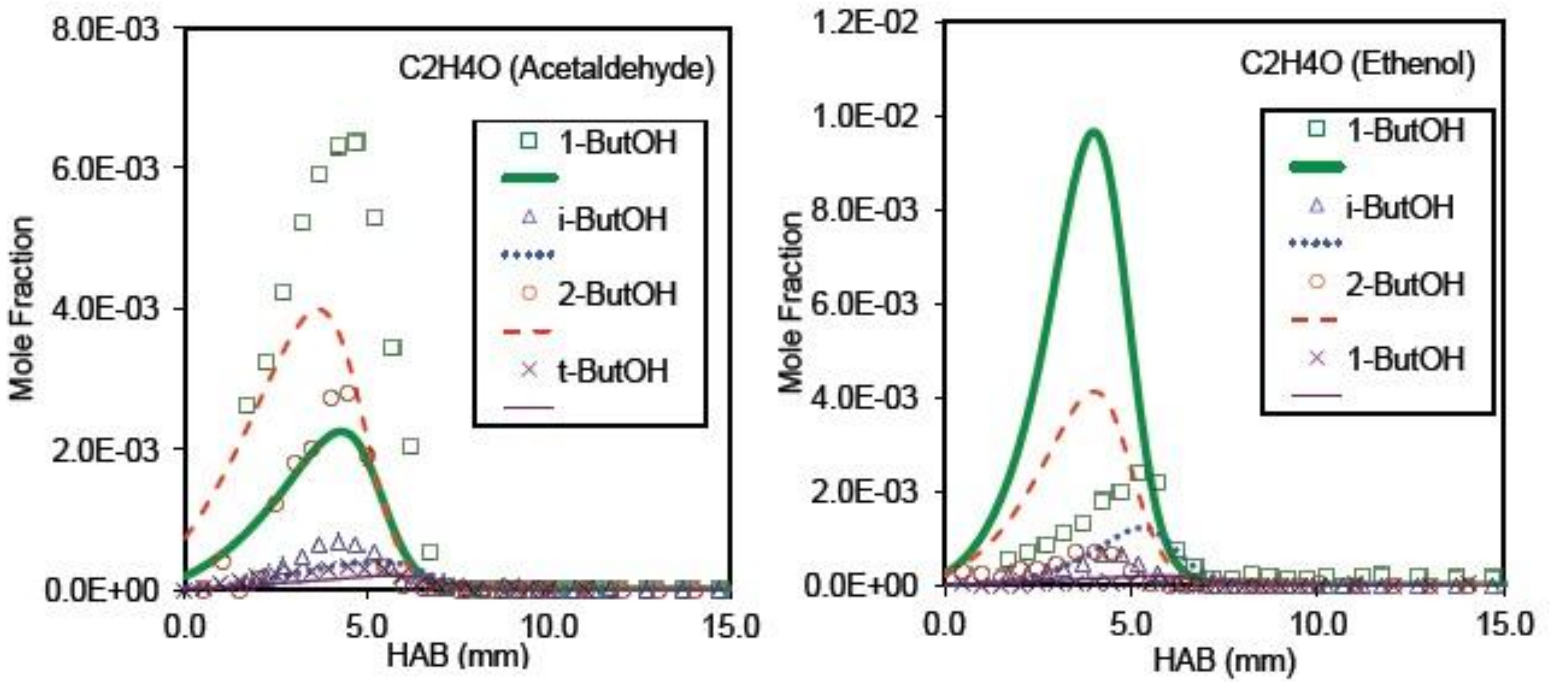
Reaction Mechanism
Mani Sarathy, Stijn Vranckx, Kenji Yasunaga, Marco Mehl, Patrick Oßwald, Wayne K. Metcalfe, Charles K. Westbrook, William J. Pitz, Katharina Kohse-Höinghaus, Ravi X. Fernandes, Henry J. Curran, Combustion and Flame, accepted.

Premixed laminar low pressure flame

Reaction Path



Premixed laminar low pressure flame



P. Oßwald, H. Güldenberg, K. Kohse-Höinghaus, B. Yang, T. Yuan, F. Qi, Combust. Flame 158 (1) (2011) 2-15.

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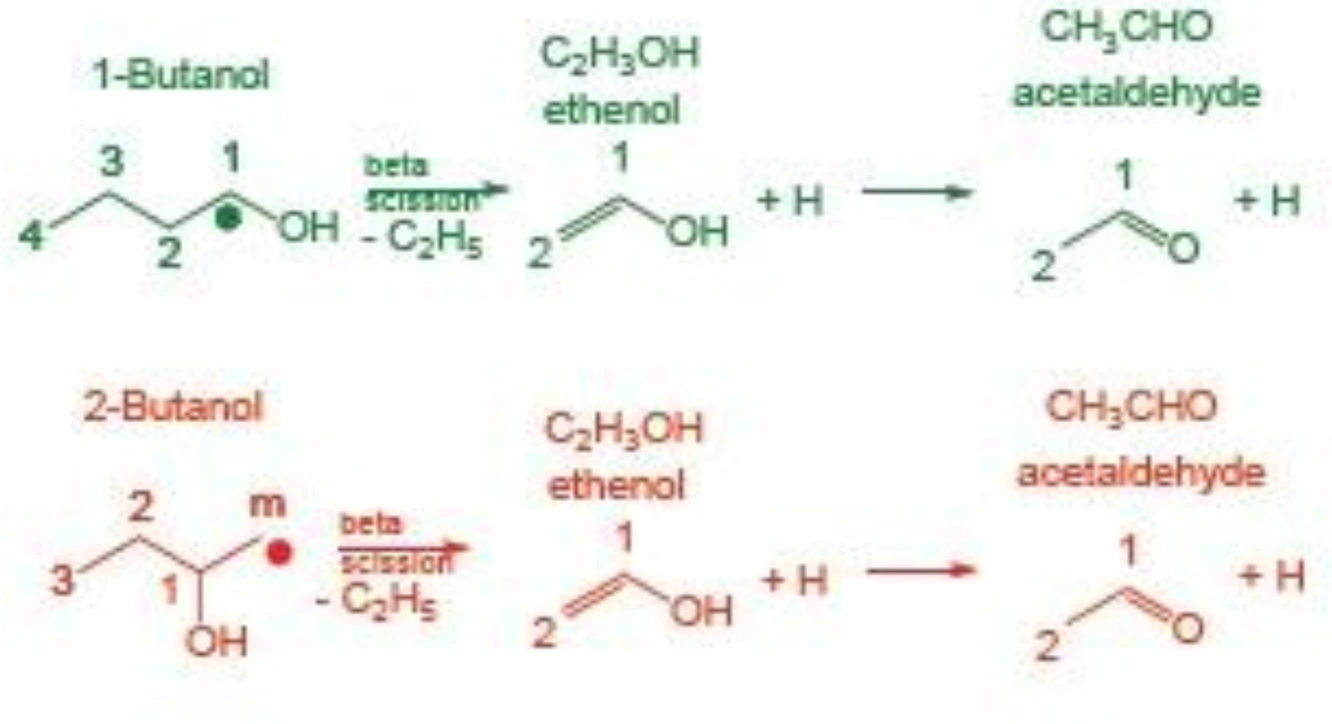
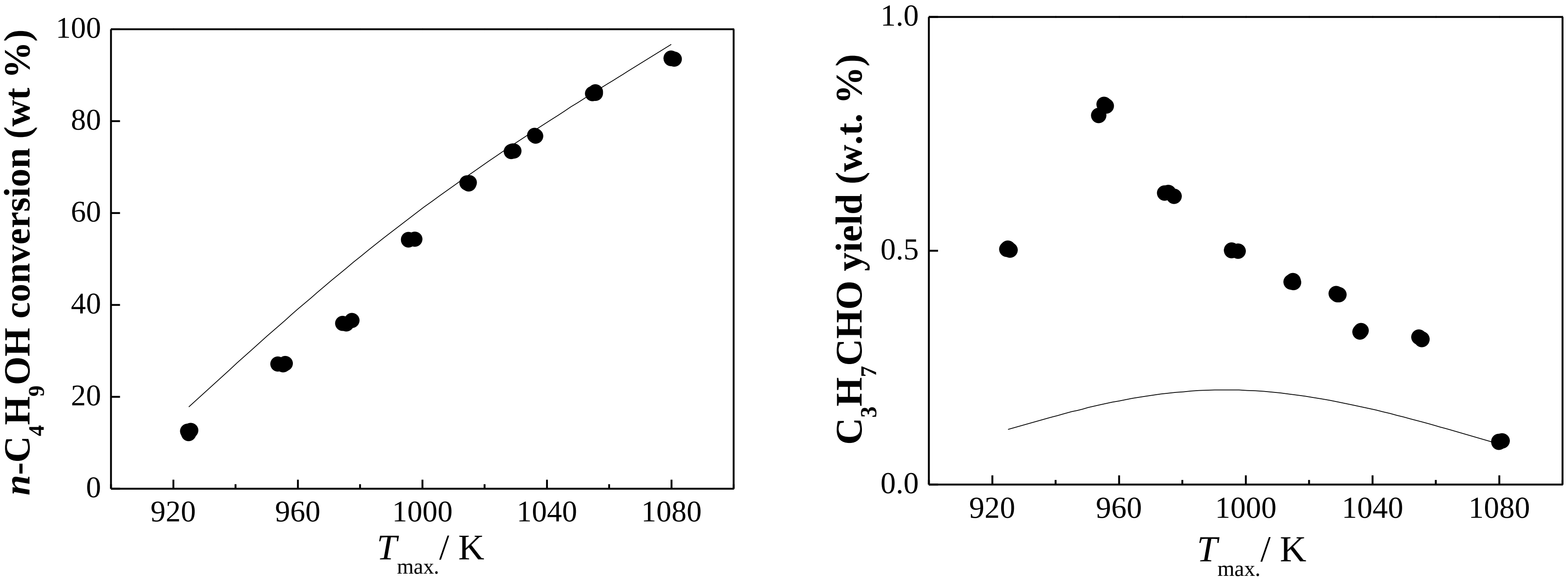
Reaction Path



Flow Reactor



Conversion and yield profiles for n-C_4H_9OH *and* n-butyraldehyde (C_3H_7CHO) in the pyrolysis reactor at 1.7 atm.

M.R. Harper, K.M. Van Geem, S.P. Pyl, G.B. Marin, W.H. Green, Combust. Flame 158 (2011) 16–41.

Reaction Mechanism
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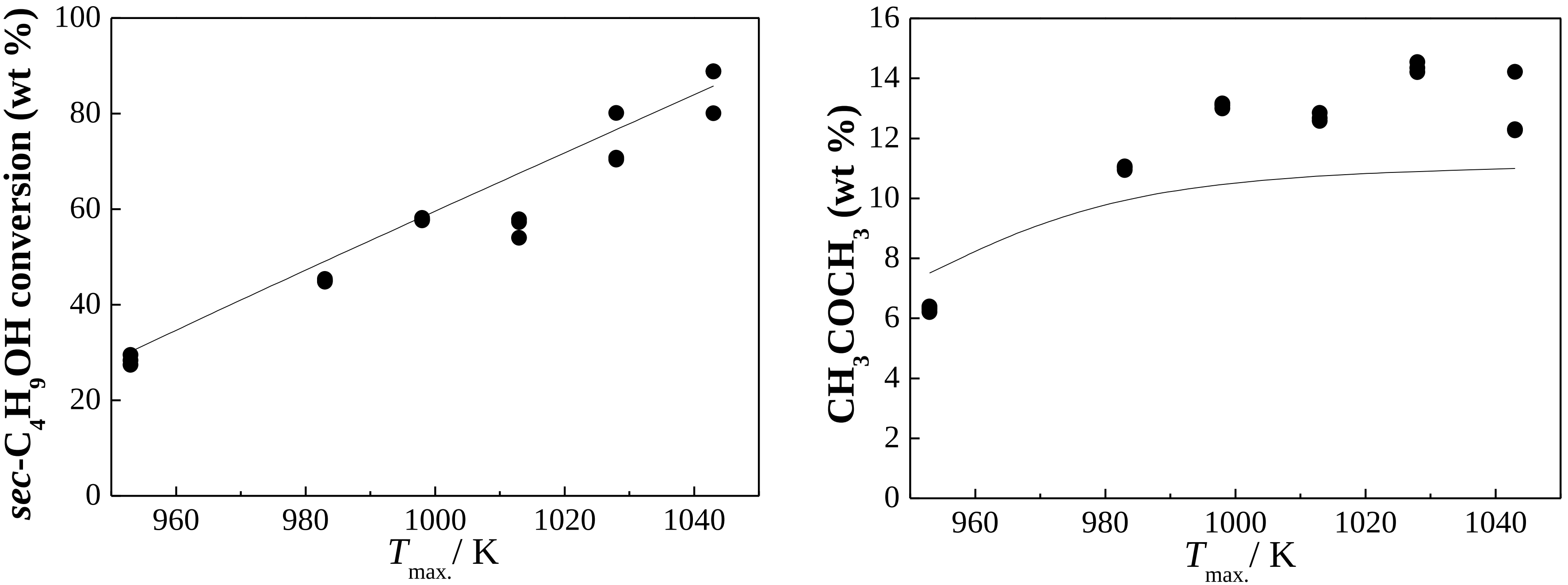


Conversion and yield profiles for *sec*-C_4H_9OH and *acetone* in the pyrolysis reactor at 1.7 atm measured by Van Geem *et al.*

K.M. Van Geem, S.P. Pyl, G.B. Marin, M.R. Harper, W.H. Green, Ind. & Eng. Chem. Res., 49 (2010) 10399–10420.

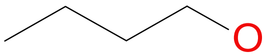
Reaction Mechanism

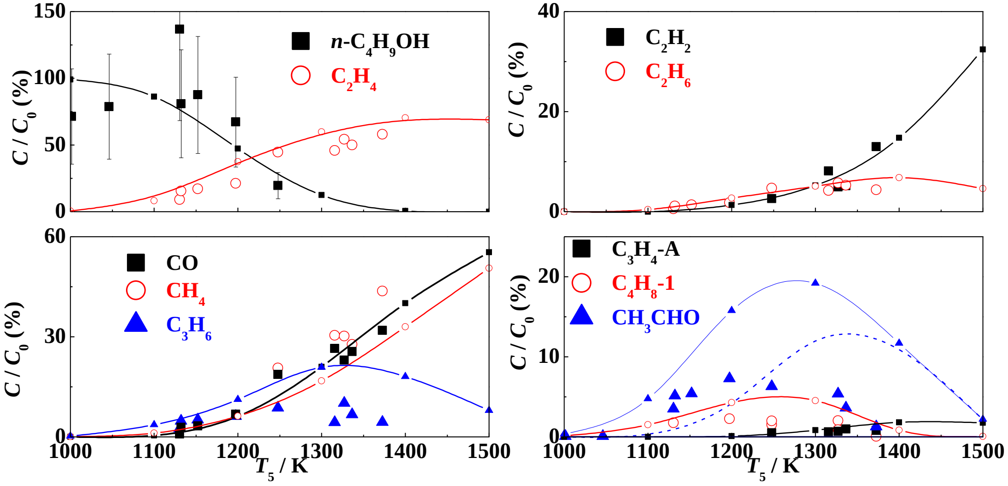
Mani Sarathy, Stijn Vranckx, Kenji Yasunaga, Marco Mehl, Patrick Oßwald, Wayne K. Metcalfe, Charles K. Westbrook, William J. Pitz, Katharina Kohse-Höinghaus, Ravi X. Fernandes, Henry J. Curran, Combustion and Flame, accepted.

Shock tube

Shock tube

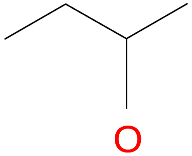
n-Butanol

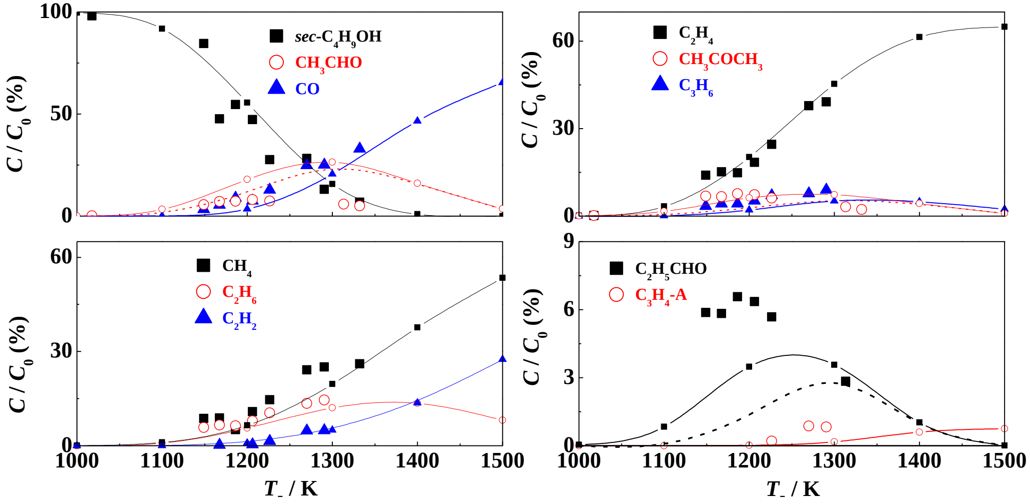




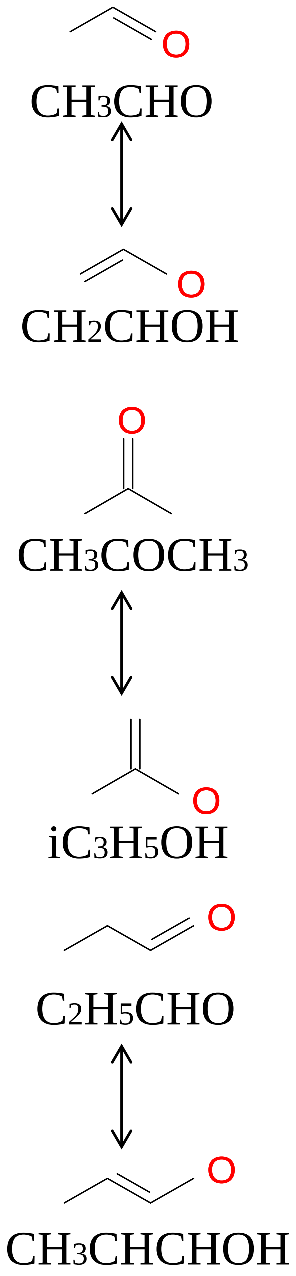
Normalized species concentration profiles for the pyrolysis of 1.5% *n*-C_4H_9OH diluted in Ar, effective heating time = 2.6−3.0 ms, lines simulation.

sec-Butanol





Normalized species concentration profiles for the pyrolysis of 1.5% *sec*-C_4H_9OH in Ar, effective heating time = 2.6−3.0 ms, lines simulation.



CH_3CHO

CH_2CHOH

CH_3COCH_3

iC_3H_5OH

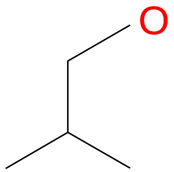
C_2H_5CHO

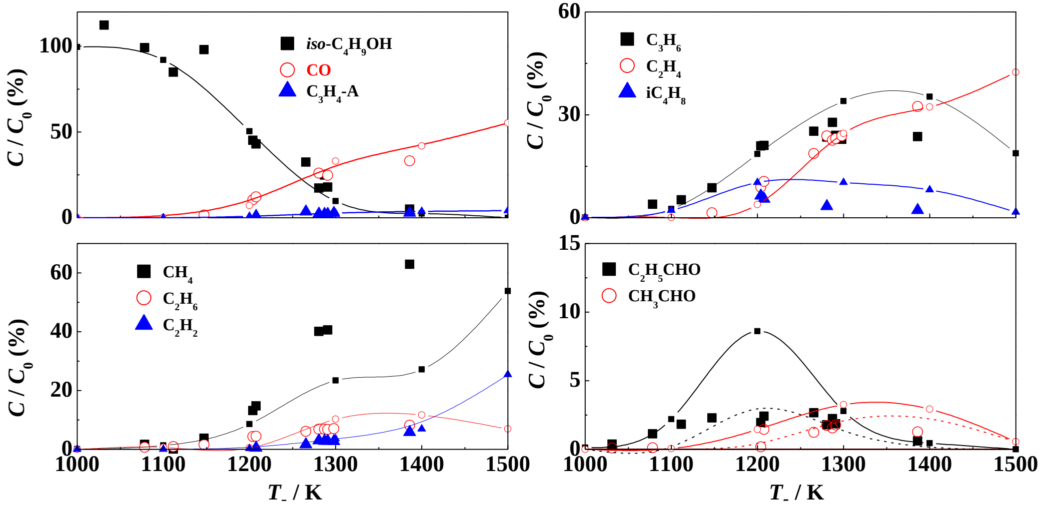
$CH_3CHCHOH$

Shock tube

Shock tube

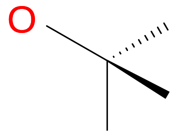
iso-Butanol

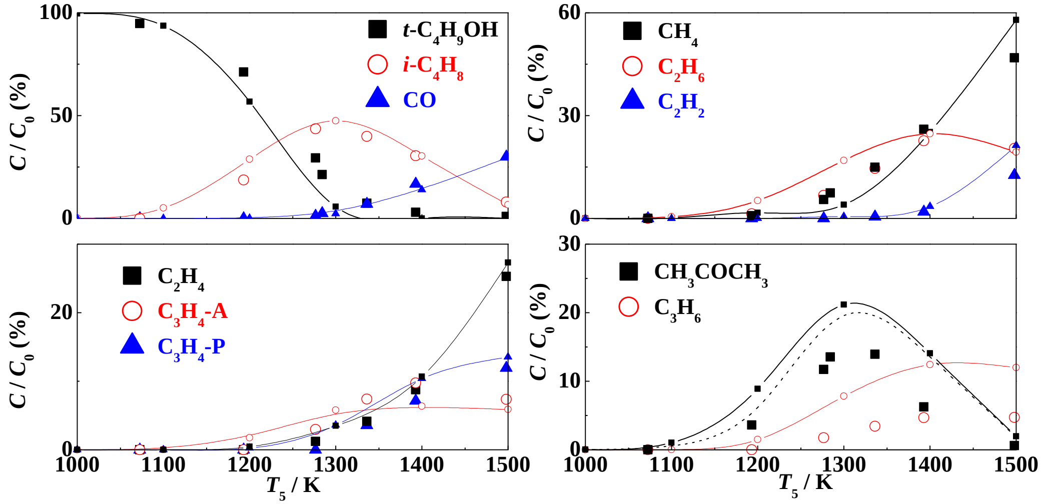




Normalized species concentration profiles for the pyrolysis of 1.5% *iso*-C_4H_9OH diluted in Ar, effective heating time = 2.6−3.0 ms, lines simulation.

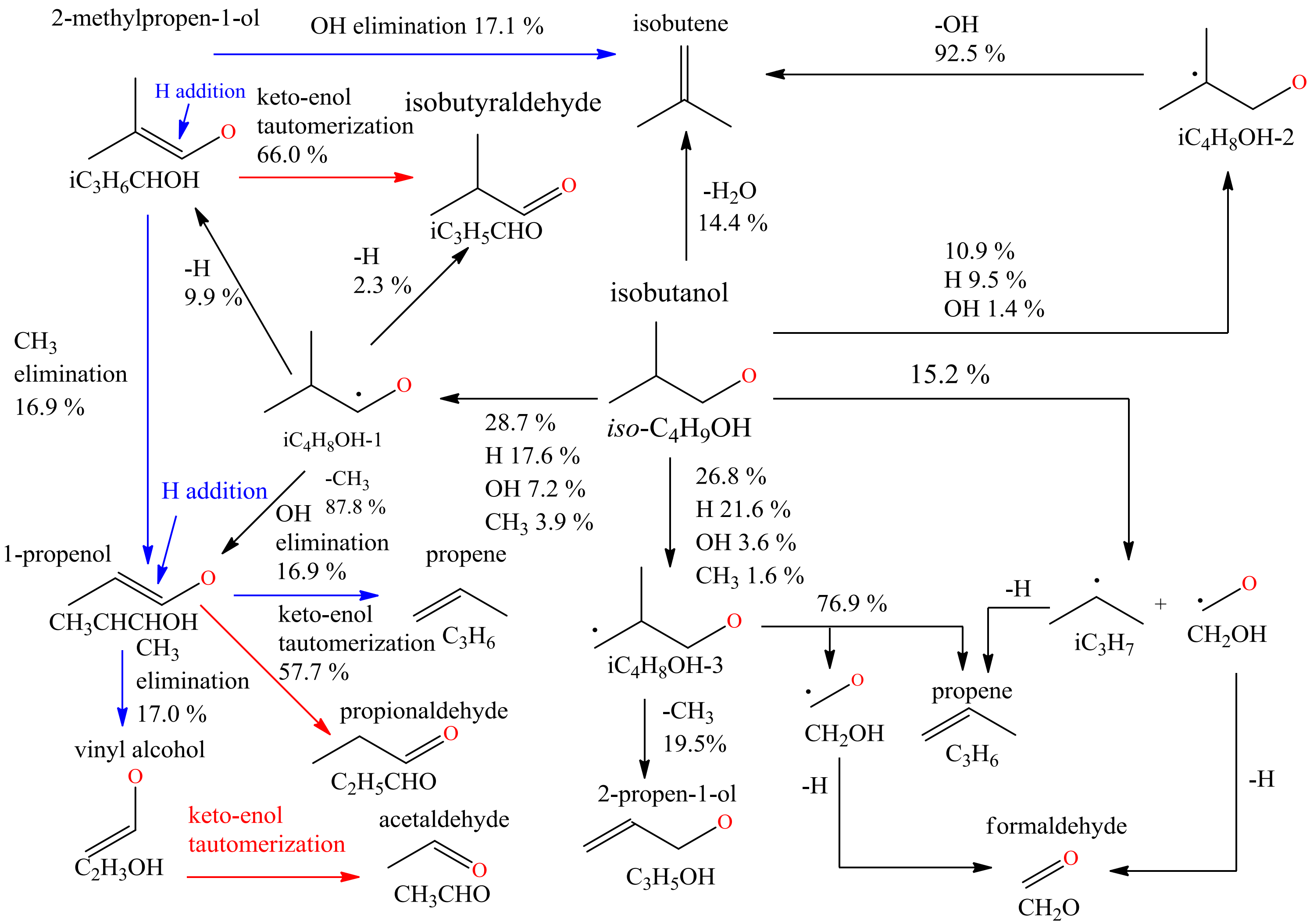
tert-Butanol





Normalized species concentration profiles for the pyrolysis of 1.0% *tert*-C_4H_9OH in Ar, effective heating time = 1.5 − 1.7 ms, lines simulation.

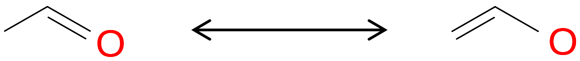
Reaction path analysis



Reaction path analysis for *iso*-C_4H_9OH pyrolysis. Shock conditions: 1.5% *iso*-C_4H_9OH diluted in Ar, 1300 K, 1.9 atm, 20 % consumption

Summary

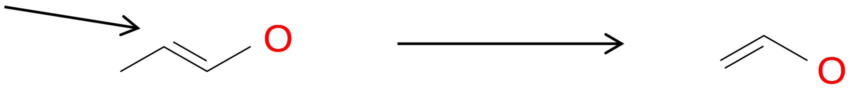
Keto-enol tautomerization



CH_3CHO CH_2CHOH

Hydrogen addition and methyl elimination

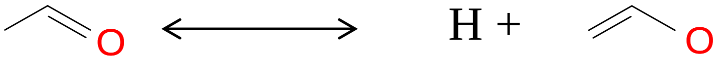
H



$CH_3CHCHOH$ CH_2CHOH + CH_3

Chemically-activated H-atom (HO_2 radical and formic acid) assisted tautomerization reaction

H + H +



CH_3CHO CH_2CHOH

Further reactions