# ワークショップ
# 「トルエン詳細反応モデルの改良と着火過程の反応論的考察」

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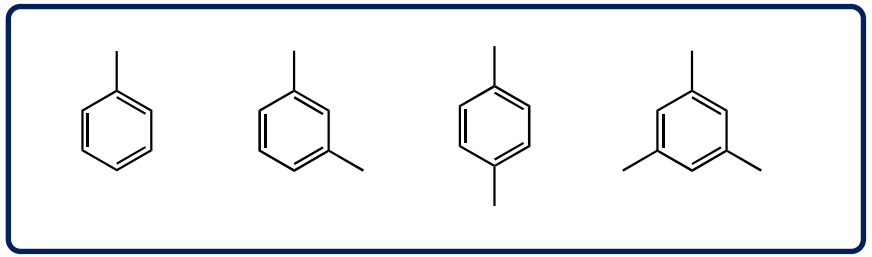
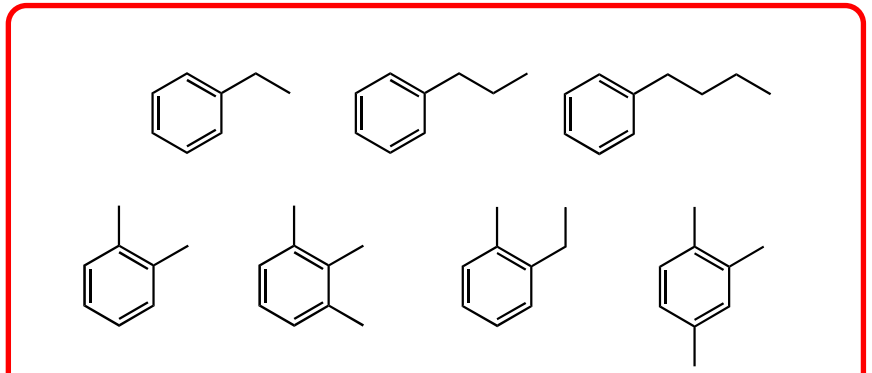
スライド一部抜粋　　**2010/12/03**

# 芳香族燃料の反応性（RCMデータ）

**Low Reactivity**



**High Reactivity = second $O_2$ addition??**

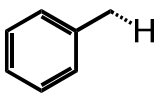
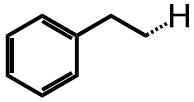
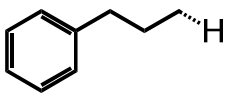
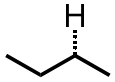
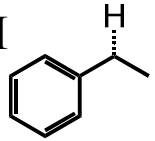
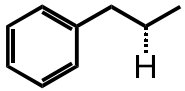
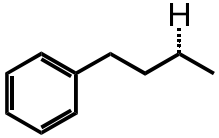
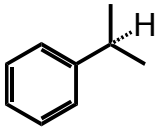
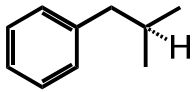
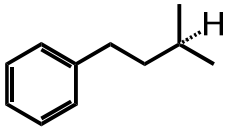


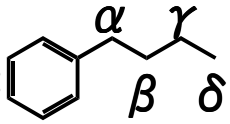
◇$-C_2H_5$, $-C_3H_7$, $-C_4H_9$
◇Side chain at ortho position

Ref. Results from RCM experiments, A. Roubaud *et al.*, *Combustion and Flame 121* (2000) 535-541.

# Bond Dissociation Energy in Aromatics

**C-H bond dissociation energies in kJ mol$^{-1}$, calculated by CBS-QB3 method.**

| | α | β | γ |
|---|---|---|---|
| **primary C-H**  **419[a]** |  **375** |  **422** |  **421** |
| **secondary C-H**  **407[a]** |  **364** |  **409** |  **408** |
| **tertiary C-H**  **399[b]** |  **361** |  **401** |  **398** |

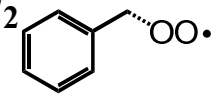
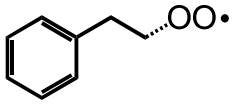
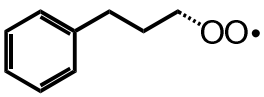
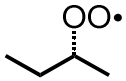
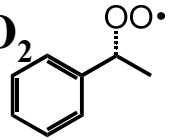
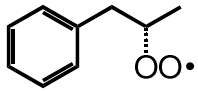
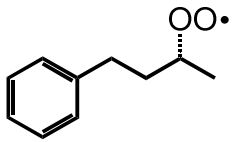
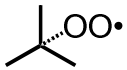
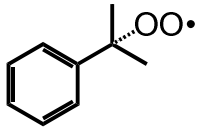
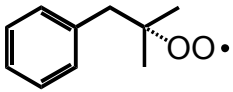
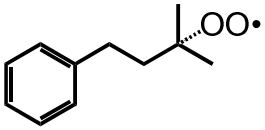
**Notations:** 

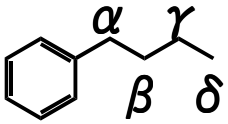


**a) A. Miyoshi, *Int. J. Chem. Kinet.*, 42, 273-288 (2010).**
**b) A. Miyoshi, private communication.**

# Bond Dissociation Energy in Aromatics

**R-$O_2$ bond dissociation energies in kJ $mol^{-1}$, calculated by CBS-QB3 method.**

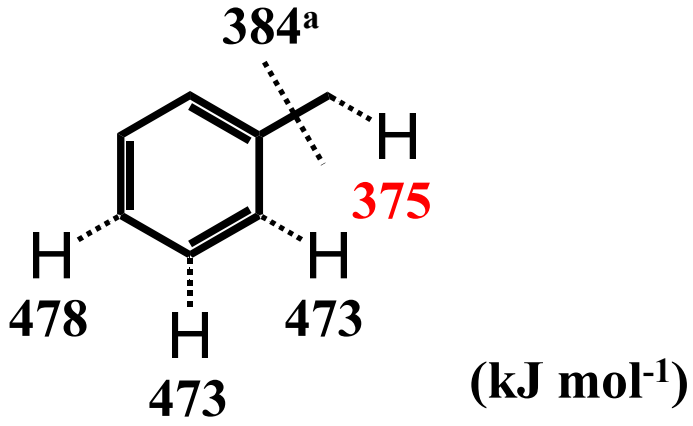
| | α | β | γ |
|---|---|---|---|
| **primary R-$O_2$**  **146[a]** |  **93** |  **147** |  **144** |
| **secondary R-$O_2$**  **153[a]** |  **103** |  **153** |  **154** |
| **tertiary R-$O_2$**  **158[b]** |  **109** |  **152** |  **149** |

**Notations:** 



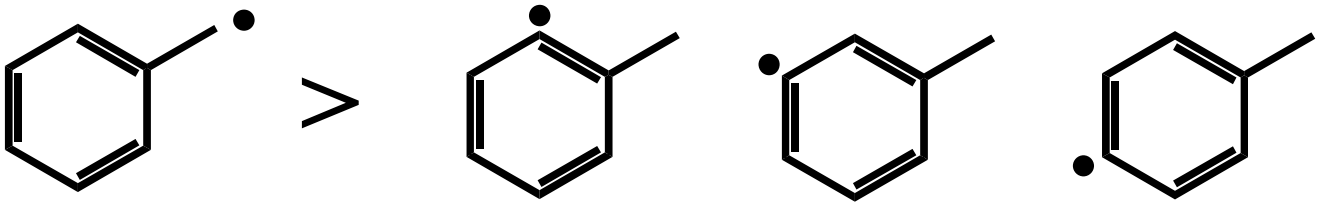
**a) A. Miyoshi, *Int. J. Chem. Kinet.*, 42, 273-288 (2010).**
**b) A. Miyoshi, private communication.**

# Bond Dissociation Energy in Toluene

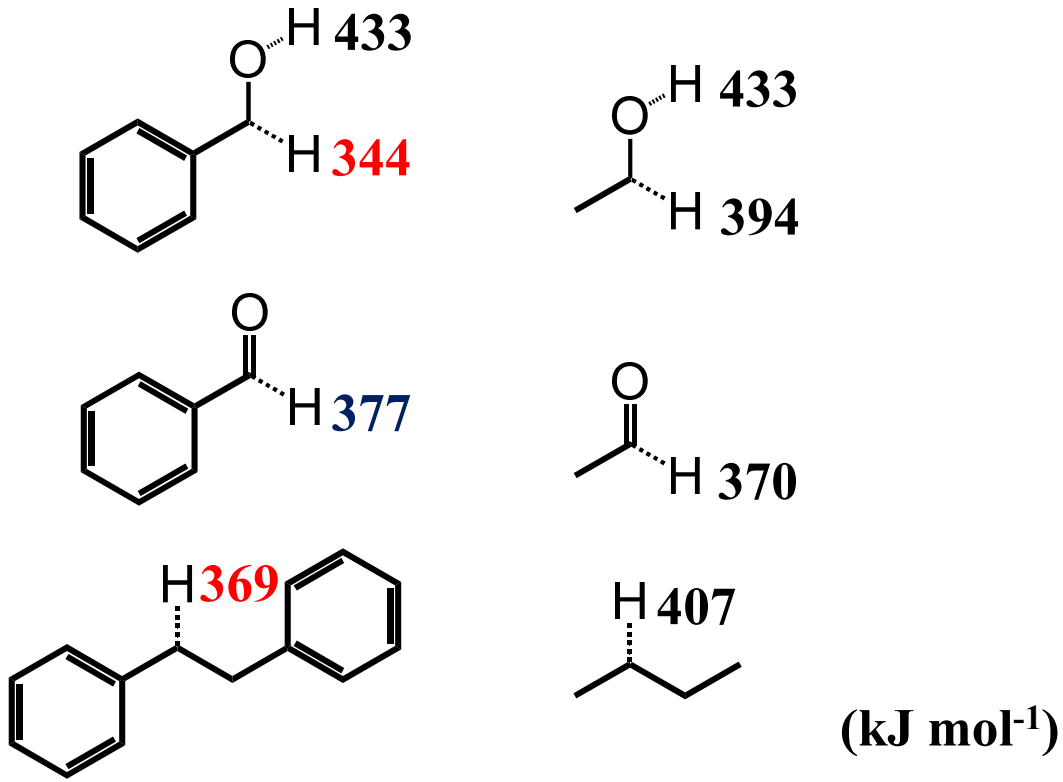


**C-H and C-C bond dissociation energies in toluene calculated by CBS-QB3 method.**

**a) G. Silva *et al.*, *J. Phys. Chem. A.*, 113, 6111-6120 (2009).**



# Bond Dissociation Energy in Intermediates

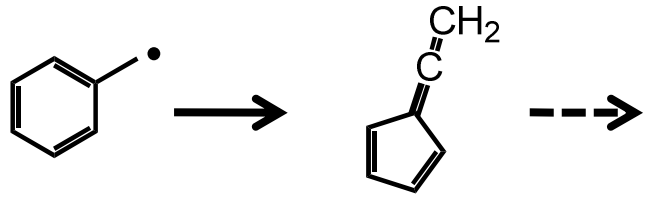



**C-H bond dissociation energies in benzylalcohol, benzaldehyde and bibenzyl calculated by CBS-QB3 method.**

# Toluene Model Updates

➢**Benzyl Radical Thermal Decomposition**

**Gabriel da Silva *et al*. (2009), Lidong Zhang *et al*. (2010)**

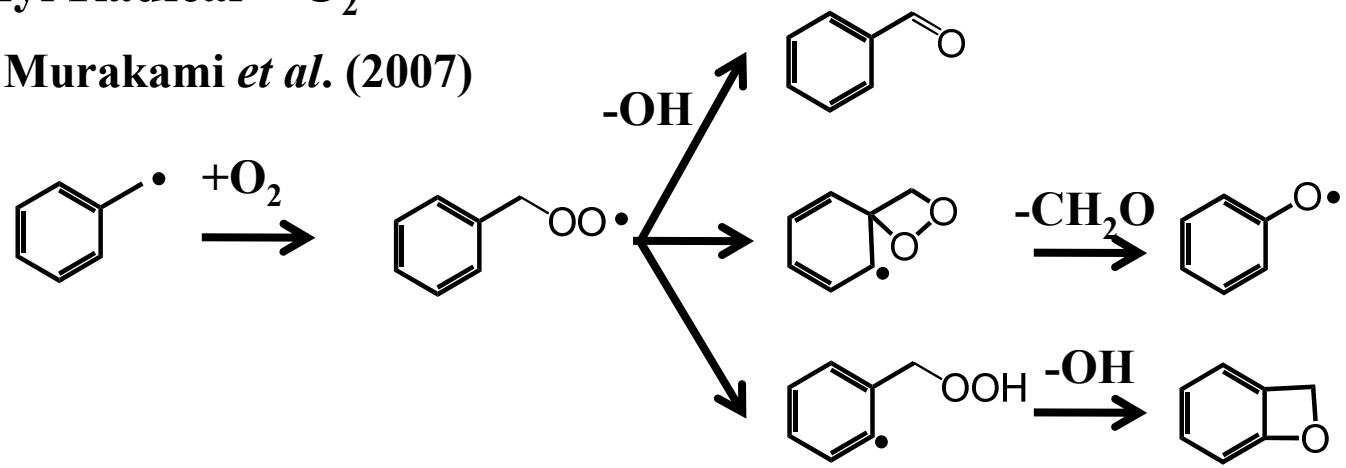



```
C6H5CH2J=C7H6+H                    4.38E+13   0.078   75900.0   !L.Zhang (2010)
C7H5+H=C7H6                        2.00E+12   0.00      0.0     !L.Zhang (2010)
C7H6+H=C7H5+H2                     1.90E+08   1.847   4965.0    !G.Silva,JPCAletter2009
C7H6+OH=C7H5+H2O                   1.20E+05   2.621   -515.0    !G.Silva,JPCAletter2009
C7H6+CH3=C7H5+CH4                  1.87E+04   2.724   6008.0    !G.Silva,JPCAletter2009
C7H5(+M)=C4H2+C3H3(+M)             3.0E+12   -0.075   62300.0   !L.Zhang (2010)
                          LOW  /1.00E+45   8.4    47500.0/      !L.Zhang (2010)
C7H5(+M)=C5H3+C2H2(+M)             3.0E+12   -0.075   62300.0   !L.Zhang (2010)
                          LOW  /1.00E+45   8.4    47500.0/      !L.Zhang (2010)
```

# Toluene Model Updates

- **Benzyl Radical + $O_2$**

  **Y. Murakami *et al*. (2007)**

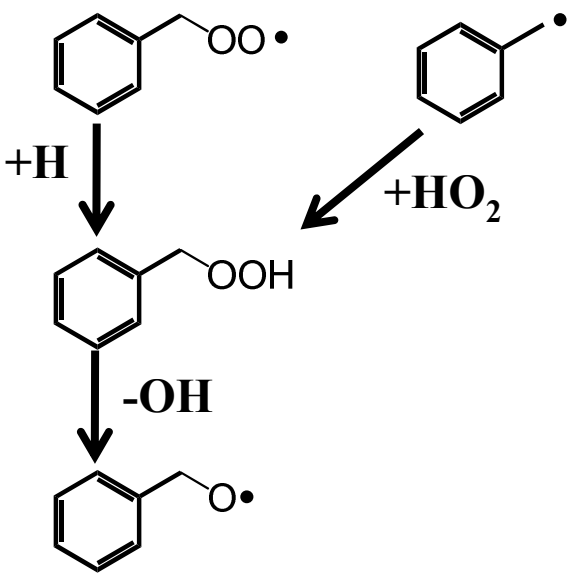



```
C6H5CH2J+O2=C6H5CH2OOJ                    7.455E+31  -6.389    6668.5
                                          REV/ 4.200E+26  -4.127   27225.2/
C6H5CH2OOJ=C6H5CHO+OH                     3.019E+45 -10.053   52808.1
C6H5CH2OOJ=C6H4CH2OOH                     4.982E+22  -3.410   36255.6
!C6H4CH2OOH=>C6H4OH+CH2O                  7.531E+11   0.053   24035.5
C6H4CH2OOH=>C6H5OJ+CH2O                   3.765E+11   0.053   24035.5 !est.sakai
C6H4CH2OOH=>C6H4+OH+CH2O                  3.765E+11   0.053   24035.5 !est.sakai
C6H4CH2OOH=C6H5CYCH2O+OH                  2.747E+12   0.181   21423.9
!est. alkane cyclic ether + OH
C6H5CYCH2O+OH=C6H4+HCO+H2O                5.730E+10   0.510    -437.0
C6H5CH2OOJ=C6H5ACH2OO                     3.555E+32  -6.588   37140.3 !
C6H5ACH2OO=C6H5OJ+CH2O                    4.523E+11   0.502   12990.7 !
```

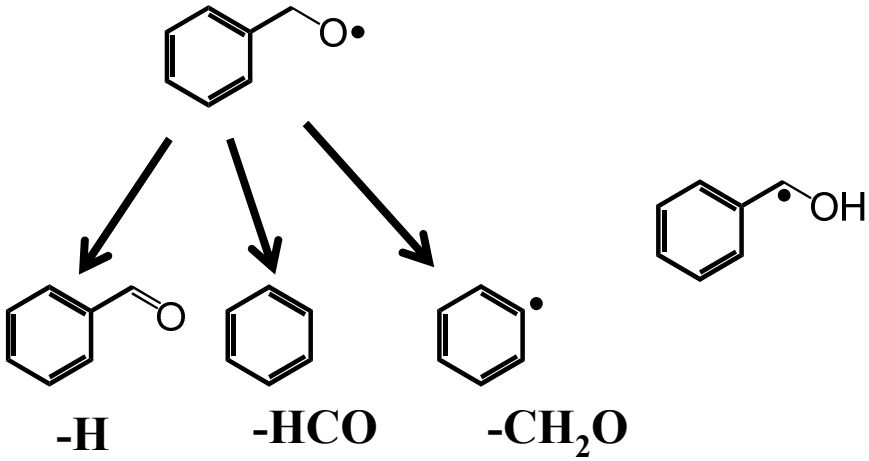
# Toluene Model Updates

- **Benzyl Radical + $HO_2$, Benzoxyl Radical Decomposition**

  **Gabriel da Silva *et al*. (2009), S. Skonov *et al*. (2005)**




**benzyl-OOH system**



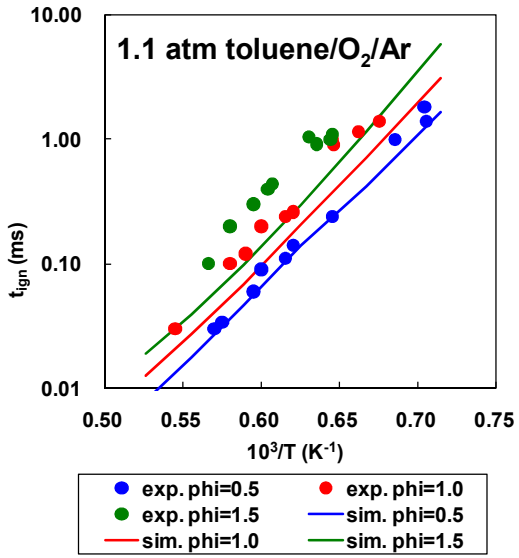

**benzyl-O system**

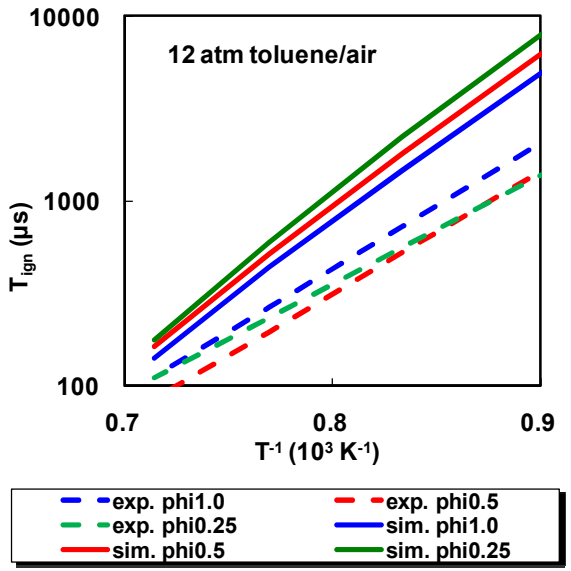
- **Benzylperoxy Radical Reactions**

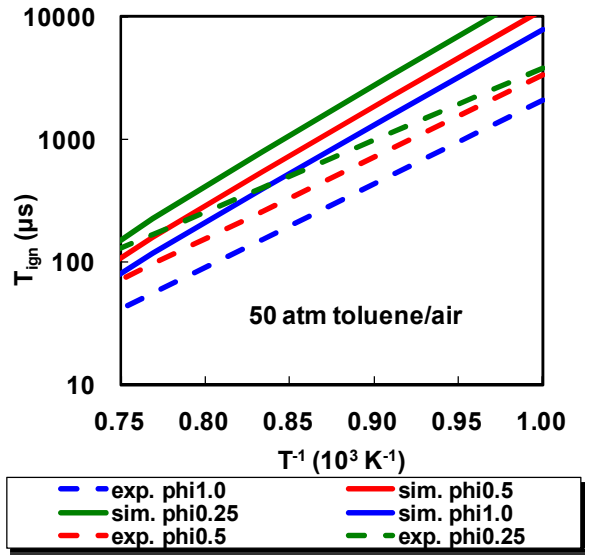
**Estimated from alkane model**

| | | | |
|---|---|---|---|
| C6H5CH2OOJ+HO2=C6H5CH2OOH+O2 | 1.75E+10 | 0.00 | -3275.0 |
| C6H5CH2OOJ+H2O2=C6H5CH2OOH+HO2 | 2.40E+12 | 0.00 | 10000.0 |
| 2C6H5CH2OOJ=>2C6H5CH2OJ+O2 | 1.400E+16 | -1.610 | 1860.0 |
| C6H5CH2OOJ+CH3OO=>C6H5CH2OJ+CH3O+O2 | 1.400E+16 | -1.610 | 1860.0 |

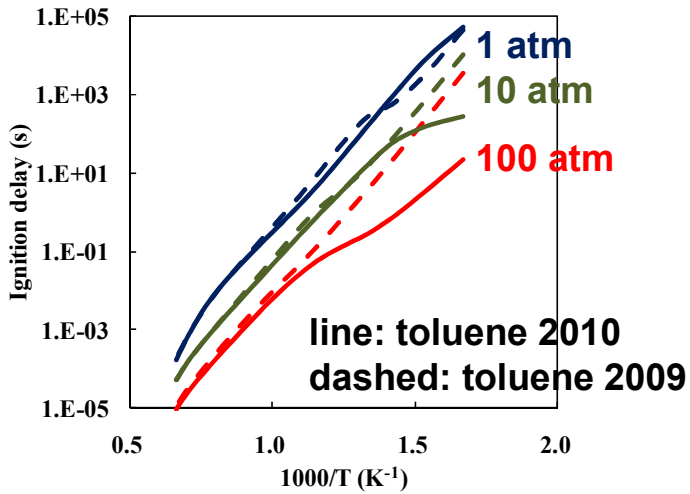
# Toluene Model (2010)



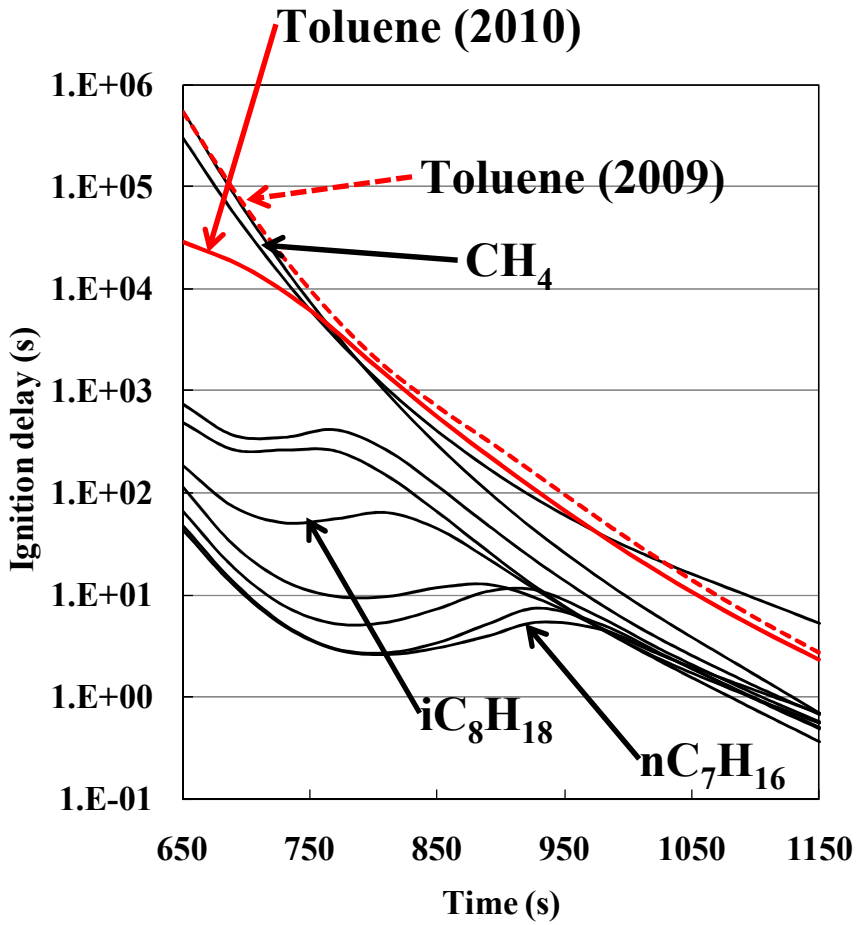




- **Model predictions are drastically changed at low temperatures.**



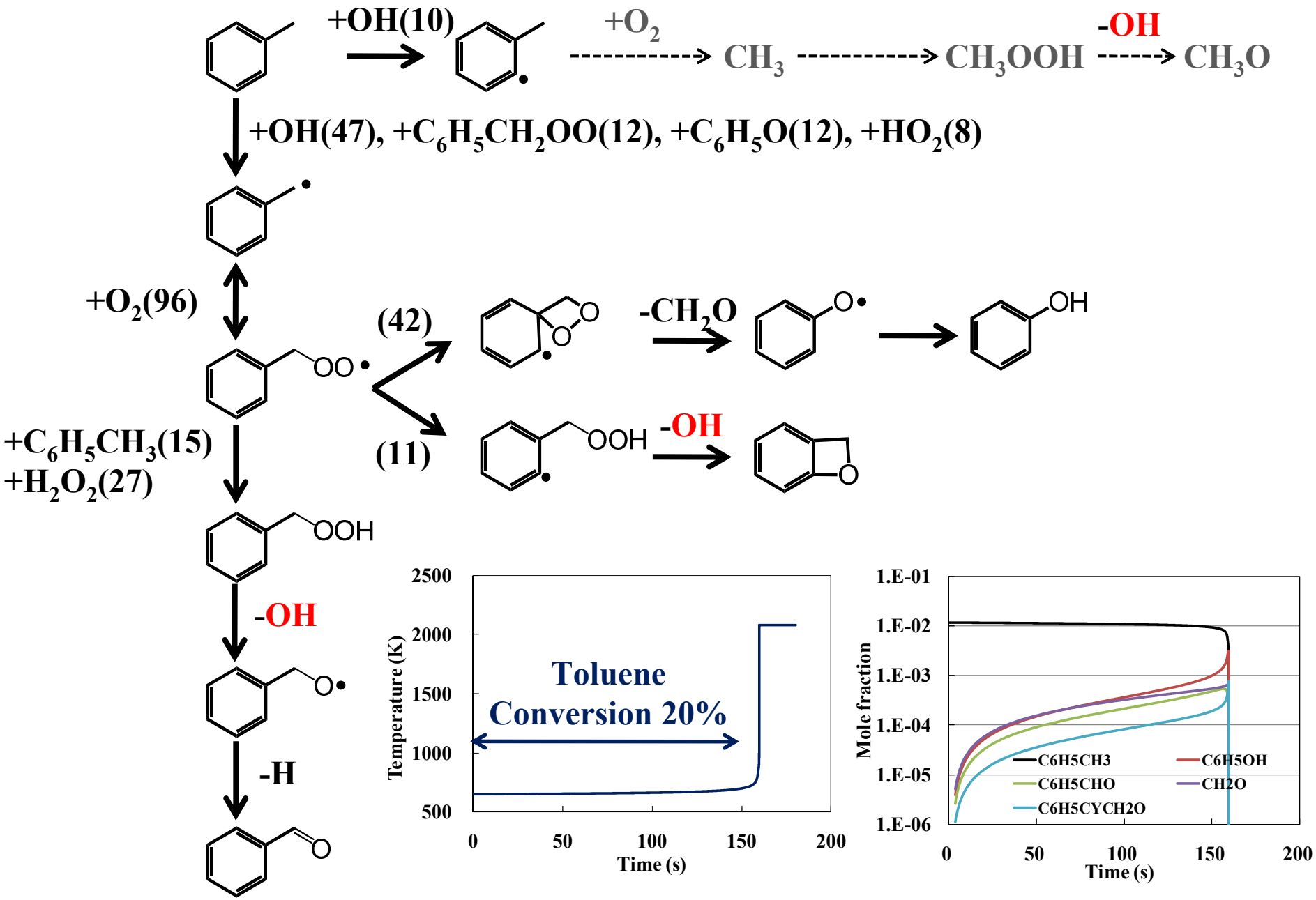
# Toluene Model (2010)



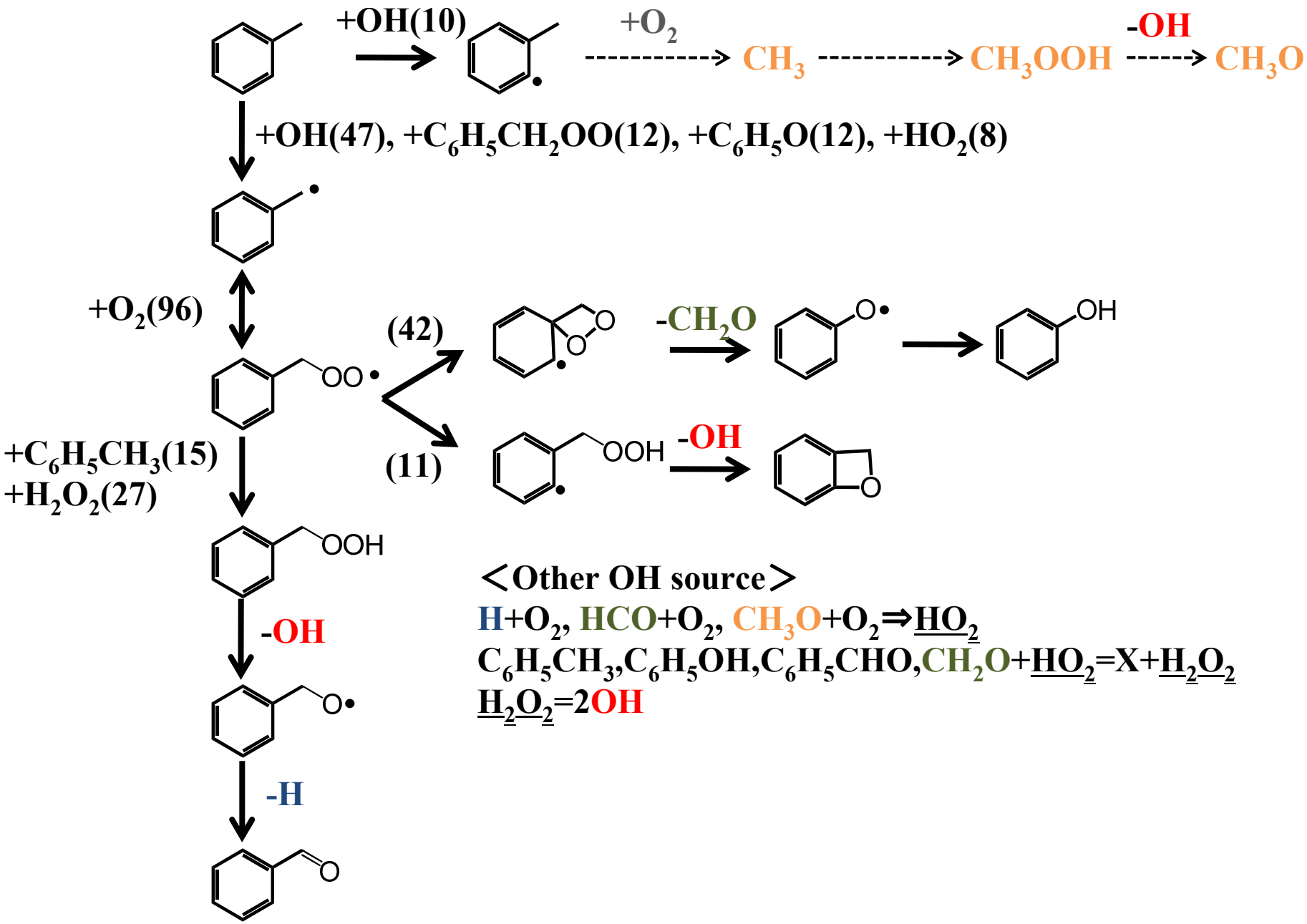

- **Prediction at low temperature is improved??.**

**$iC_8H_{18}$ (RON=100), Toluene(RON~120),$CH_4$(RON~130)**

# Reaction Flow at 650 K



# Reaction Flow at 650 K



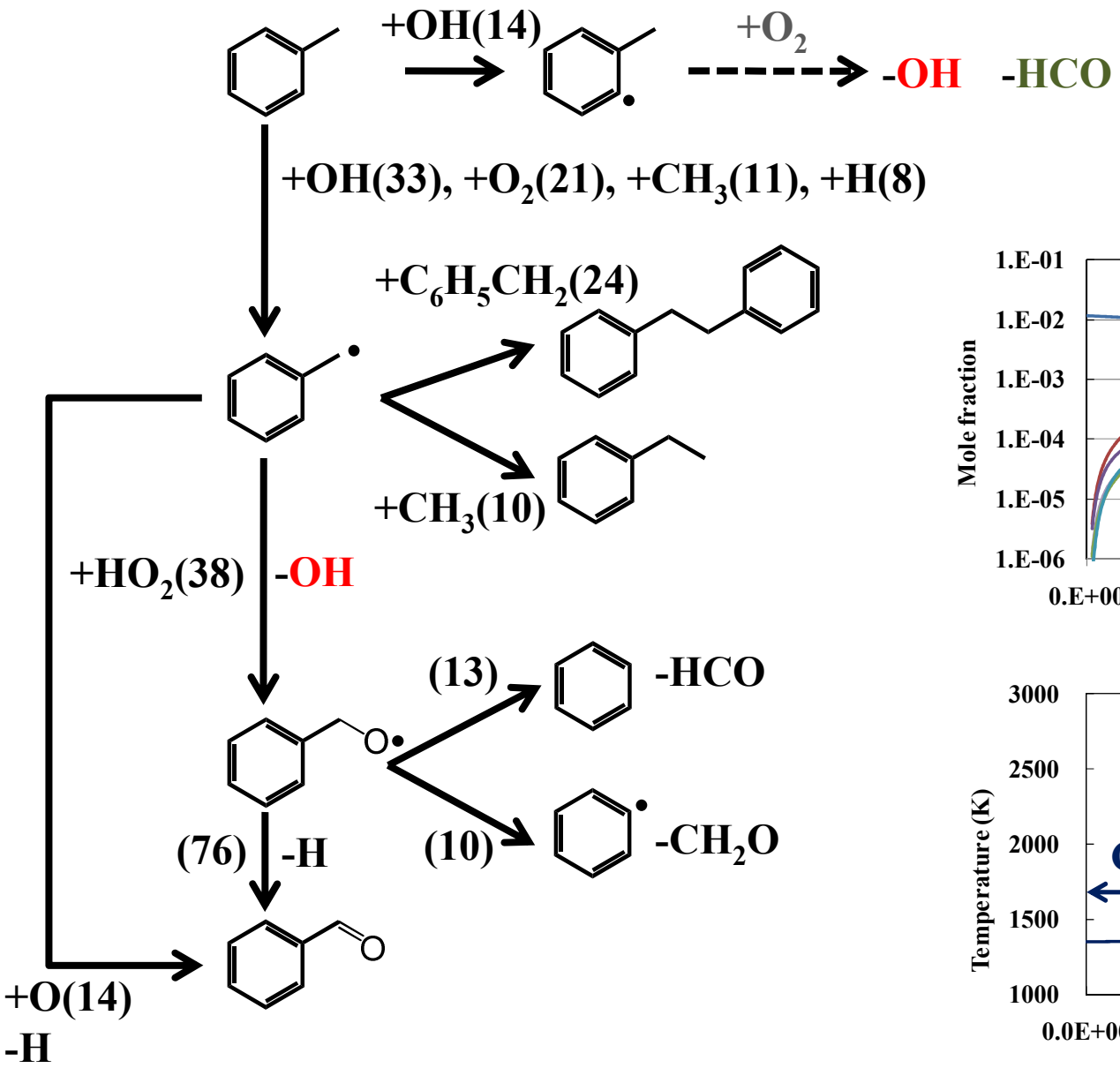

＜Other OH source＞

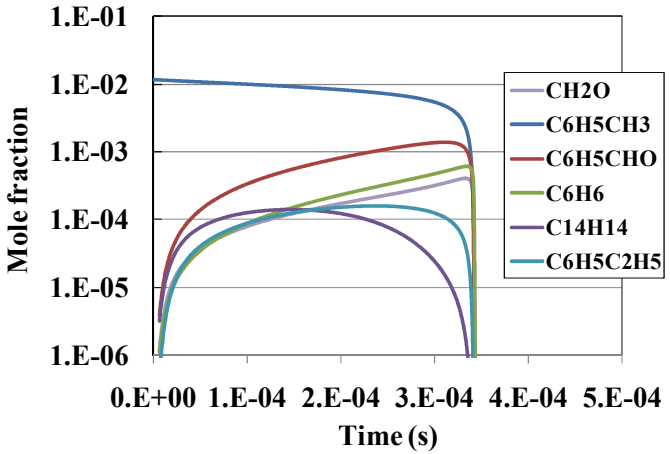
H+$O_2$, HCO+$O_2$, $CH_3O$+$O_2$⇒$\underline{HO_2}$

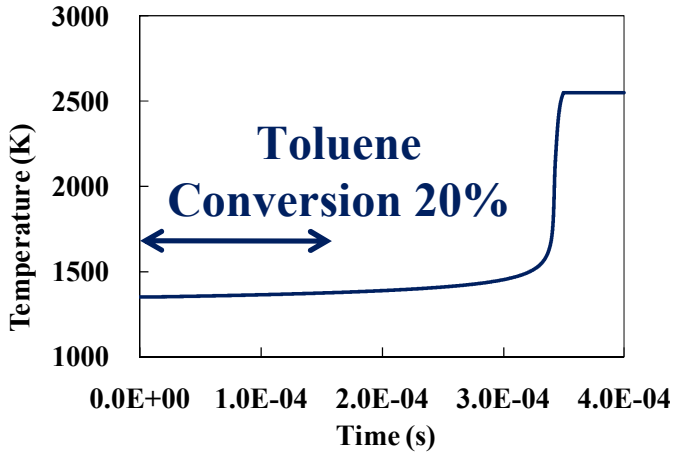
$C_6H_5CH_3$,$C_6H_5OH$,$C_6H_5CHO$,$CH_2O$+$\underline{HO_2}$=X+$\underline{H_2O_2}$

$\underline{H_2O_2}$=2OH

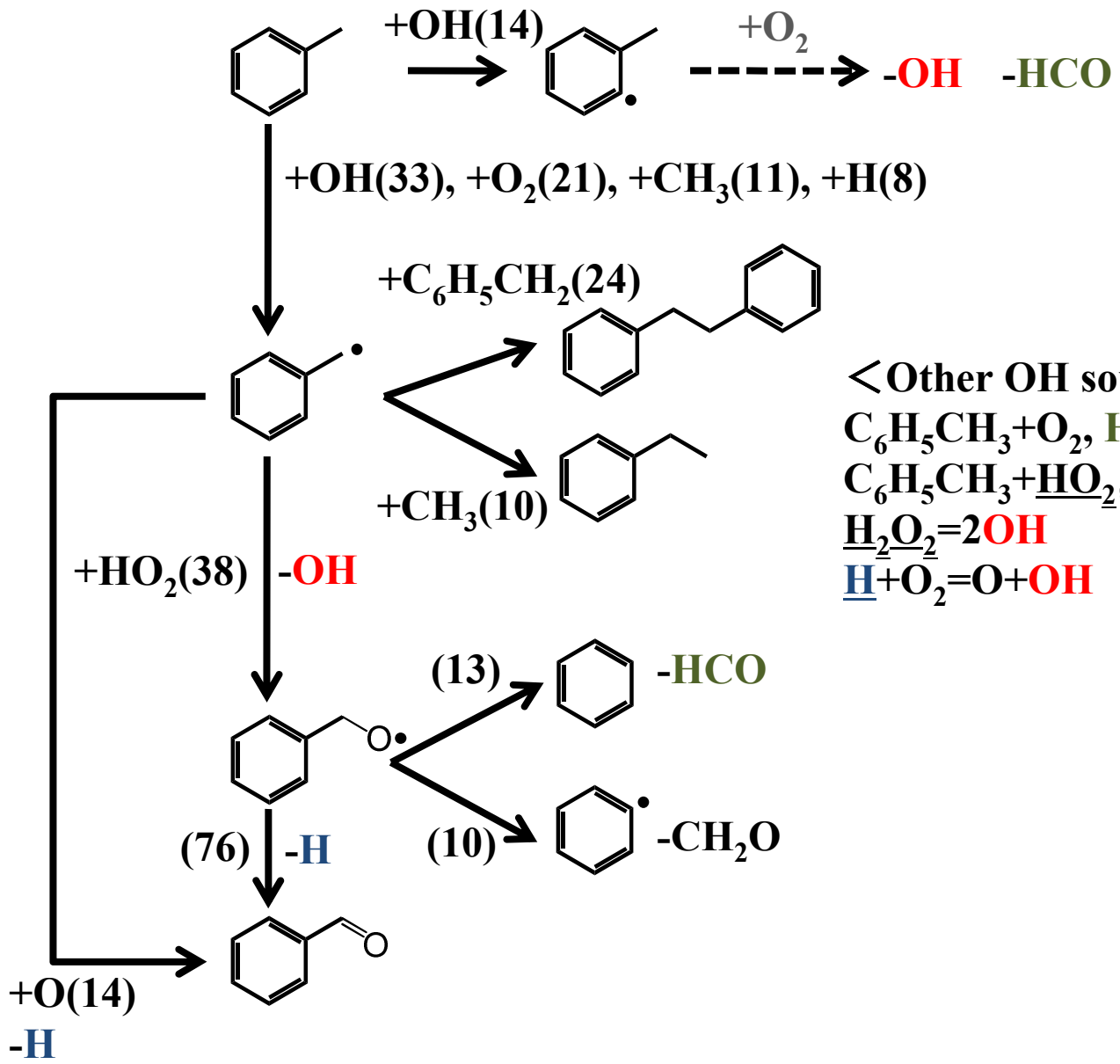
# Reaction Flow at 1350 K



# Reaction Flow at 1350 K




＜Other OH source＞

$C_6H_5CH_3+O_2$, HCO$+O_2 \Rightarrow \underline{HO_2}$

$C_6H_5CH_3+\underline{HO_2}$, $\underline{HO_2}+\underline{HO_2} \Rightarrow \underline{H_2O_2}$

$\underline{H_2O_2}=2OH$

$\underline{H}+O_2=O+OH$