

5E06: A KINETIC MODELING STUDY ON THE OXIDATION OF PRIMARY REFERENCE FUEL-TOLUENE MIXTURES INCLUDING CROSS REACTIONS BETWEEN AROMATICS AND ALIPHATICS.

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You showed the importance of cross reactions between benzyl radicals and allene molecules. However allene is usually a minor species in combustion species, especially at low temperature. What could be the importance of reactions of benzyl radicals and more abundant species, such as propene or isobutene?

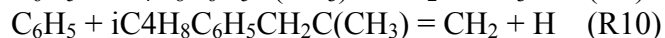
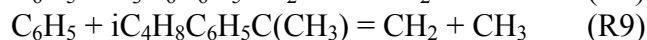
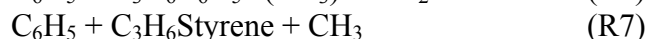
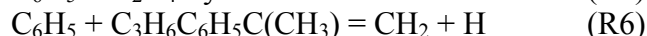
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We have already included alkene (C₂H₄, C₃H₆, C₄H₈, C₃H₄) + benzyl reactions in the model. Figure 1 shows simulated time profiles of intermediate species in the oxidation of *n*-heptane and iso-octane at 1500 K with the current PRF/Toluene mechanism. You see that ethylene (C₂H₄) is produced from *n*-heptane, and propene (C₃H₆), iso-butene (iC₄H₈) and allene (aC₃H₄) are produced from iso-octane at high temperatures. On the other hand, benzyl radical, benzaldehyde, benzene are dominant intermediates during the induction period of toluene oxidation. Therefore, reactions between these intermediates are expected to be important cross reactions.

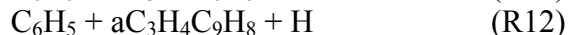
For the reactions of benzyl (phenyl) radical and alkene included in the model, the rate constants were derived as follows.

As indicated by Fahr et al. [1], addition reactions of phenyl radical to alkenes proceed by the combination of addition and β -scission. The displacement reactions of C₂H₄, C₃H₆ and iC₄H₈ with phenyl radicals (R5)–(R10), and their subsequent reactions were considered

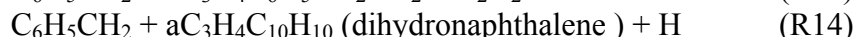
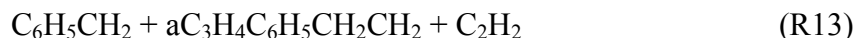


Rate constants of these reactions were taken from the estimates of Tsang [2]. For the benzyl radicals, corresponding reactions are endothermic, and therefore not considered in the present model. Vereecken et al. [3] calculated the potential energy barrier heights for the reaction of aC₃H₄ + C₆H₅. They also derived the channel specific rate constants of this reaction based on the RRKM-master equation analysis. At high temperatures, dominant reaction channels are H atom abstraction, (R11) and (R12). The reaction (R11)

produces benzyl radical and acetylene by the addition to double bond followed by H atom transfer and β -scission. The reaction (R12) produce indenenes (C_9H_8) and H atom by the addition to double bond followed by H atom transfer and ring formation.



Corresponding benzyl reactions with allene were included in the present model. In case of benzyl radical, H atom abstraction reactions (R3), (R13) and (R14) are need to be considered.



Reactions (R13) and (14) are exothermic, and their rate constants are assumed to be equal to those of corresponding $aC_3H_4 + C_6H_5$ reactions. Subsequent reactions of $C_{10}H_{10}$ are taken from Da Costa et al [4].

From the comparison between measured and simulated ignition delay times in shock tube, we have concluded that C_2H_4 , C_3H_6 , and $C_4H_8 +$ benzyl reactions do not affect to ignition of PRF/toluene mixtures, but $C_3H_4 +$ benzyl reactions affects to ignition at high temperatures.

Next, we discuss about benzyl + allene reactions at low temperatures. Vanhove et al. [5] investigated the oxidation of surrogate fuel mixtures composed of *n*-heptane, iso-octane, toluene, and 1-hexene by using a RCM below 900 K. In their study, it is noted that the extrapolation of the ignition delay times of iso-octane/toluene mixture (iso-octane 65%, toluene 35%) to higher temperatures ($T > 1100$ K) are shorter than those of pure iso-octane. Such acceleration effect of toluene addition was not observed in *n*-heptane/toluene mixtures. Figure 2 shows the comparison between measured and simulated (no heat loss) ignition delay times in RCM by Vanhove et al. [5]. You see that there are no differences for simulated ignition delay times between with and without cross reactions. Thus, we have concluded that benzyl + allene reactions do not affect to ignition PRF/Toluene mixtures at low temperatures. Although the kinetics of benzyl + allene reactions are not well understood (their rate constants and reaction path), we think that the possibilities of benzyl + allene reactions as cross reactions were shown.

References:

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- [5] G. Vanhove, G. Petit, R. Minetti, *Combust. Flame* 145 (2006) 521–532