

2B01: KINETIC MODELING OF THE BENZYL + HO<sub>2</sub> REACTION.

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Mixtures of alkanes and toluene are surrogates of gasolines often considered in engine modeling. When mixing with a reactive alkane, toluene reacts even at temperatures as low as 700 K leading mainly to benzyl radicals. What could be under these conditions the importance of the reactions of benzyl radicals with oxygen molecules?

**Reply by Gabriel da Silva**

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Benzylperoxy radicals and the benzylhydroperoxide molecule are known to be important intermediates in the low temperature oxidation and autoignition of toluene fuel blends, and the chemistry is expected to involve some of the reactions discussed in this talk.

At low temperatures benzyl will associate with molecular oxygen, forming the collisionally stabilized benzylperoxy radical. Hydrogen atom addition and H-abstraction reactions in the benzylperoxy radical then form benzylhydroperoxide, which dissociates to benzoyl + OH. In this study we calculate the high-pressure limit rate constant for this reaction to be  $k = 3.29 \times 10^{13} T^{0.42} \exp(-39890/RT) \text{ s}^{-1}$ , giving a half-life for benzylhydroperoxide of less than 4 ms at 700 K. For the benzylperoxy + H reaction, where benzylhydroperoxide is formed with around 85 kcal mol<sup>-1</sup> of excess vibrational energy, direct dissociation of the activated adduct to benzoyl + OH is expected to be the dominant process at even low temperatures. We are currently investigating the kinetics and products of this chemically activated reaction.

Importantly, the overall reaction of benzyl + O<sub>2</sub> + H → benzoyl + OH is chain propagating and produces a highly reactive hydroxyl radical from the relatively stable benzyl radical. This process is expected to be involved in the low-temperature ignition of substituted aromatic hydrocarbons, which at present is poorly understood.