

Investigation of the isoprene + OH reaction in the presence and absence of oxygen to confirm the Leuven Isoprene Mechanism

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Isoprene comprises about 40% (~500 Tg C/yr) of global VOC emissions. Because of its high emission rates and rapid reaction with hydroxyl, OH, radicals ($k \sim 1.01 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K)⁽¹⁾, it is expected that isoprene would consume considerable amounts of these radicals. However, a large discrepancy is noticed between the concentrations of OH radicals estimated by current models and those observed in several campaigns performed in known isoprene-abundant areas, such as the Amazon Basin and Borneo ($[\text{OH}]_{\text{measured}}/[\text{OH}]_{\text{model}} \sim 10$).^(2; 3) These comparisons evidence significant OH radical propagation from isoprene oxidation.

In order to explain these radical-recycling processes, Peeters *et al.* proposed a mechanism, “*The Leuven isoprene mechanism (LIM)*”, where they presented new pathways for regeneration of OH radicals involving peroxy radicals based on *ab initio* calculations.⁽⁴⁾ Laser flash photolysis experiments with OH detection by laser induced Fluorescence (LFP-LIF) of the isoprene + OH reaction were performed as a function of temperature, in the presence and absence of oxygen, to investigate the potential energy surface in the LIM mechanism. The studies were carried out using an instrument capable of measuring the fast kinetics of radicals in the gas phase at high temperatures (up to ~750 K) and pressures (up to ~2 atm)⁽⁵⁾.

Equation 1 shows the temperature dependence based on measurements in the absence of oxygen:

$$k^\infty(T) = (1.00 \pm 1.62) \times 10^{-10} \left(\frac{T}{298} \right)^{-0.56 \pm 0.28} \quad \text{Eq. 1}$$

The temperature dependence of the isoprene + OH reaction was also evaluated in the presence of oxygen ($[\text{O}_2] \leq 1 \times 10^{19} \text{ cm}^{-3}$) using the same experimental procedure. No major differences were observed between the OH decay traces with/without O_2 below 523 K. Interestingly, the OH traces observed for experiments performed in the presence of oxygen at high temperatures ($T \geq 573 \text{ K}$) showed a deviation from a single exponential decay. The averaged rate coefficient for recycling ($\text{RO}_2 \rightarrow \text{OH}$) at 598 K is $(589 \pm 46) \text{ s}^{-1}$ and the rate constant for the RO_2 consumption excluding OH recycling ($\text{RO}_2 \rightarrow \text{Products}$) is $(723 \pm 40) \text{ s}^{-1}$. These coefficients were estimated via fits of the traces to a biexponential equation. Detailed analysis demonstrated a good agreement between our experimental observations and the LIM1 mechanism regarding the barriers for OH generation. A comparison with the literature was performed and reasonable agreement was observed for most of the analysed investigations.

References

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