Kinetics of H atom attack on unsaturated hydrocarbons using spectral uncertainty propagation and minimization techniques

<u>David A. Sheen*</u>, Claudette M. Rosado-Reyes, Jeffrey A. Manion, and Wing Tsang

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Unsaturated hydrocarbons are an important component of hydrocarbon fuels and intermediates in their oxidation. Under rich conditions, H atom attack is one of the principle pathways of the decomposition of these unsaturated compounds. Consequently, it is critical to understand the H atom attack mechanisms as part of chemical model development. Previous studies have examined the kinetics of H atom attack on various unsaturated hydrocarbons in single pulse shock-tubes. These studies have noted that there are multiple pathways by which H atom attack can proceed, so it is straightforward to measure relative rates but absolute rates are more difficult to estimate. In addition, there is a confounding influence from secondary chemistry. A multiparameter optimization and uncertainty minimization technique [1] is used to constrain a chemical model for the oxidation of H_2/CO/C_1-C_4 hydrocarbons against a range of measurements of the H atom attack process on toluene [2], trimethylbenzene (TMB) [3], propyne [4], and propene [5]. The recommended rate constant expressions, with 2σ uncertainties, are as follows:

$k(CH_4+H \leftrightarrow CH_3+H_2) = 10^{8.82\pm0.21}$ s^{-1} cm^3 mol^{-1} K$^{-1.6}$ $T^{1.6}$exp(-5400 ± 500 K/T)

$k(C_2H_2+CH_3 \leftrightarrow p\text{-}C_3H_4+H) = 10^{11.40\pm0.18}$ s^{-1} cm^3 mol^{-1} K$^{-0.6}$ $T^{0.6}$exp(-7200 ± 400 K/T)

$k(p\text{-}C_3H_4+H \leftrightarrow a\text{-}C_3H_4+H) = 10^{18.29\pm0.21}$ s^{-1} cm^3 mol^{-1} K T^{-1}exp(-6100 ± 500 K/T)

$k(C_3H_6+H \leftrightarrow C_2H_4+CH_3) = 10^{24.52\pm0.20}$ s^{-1} cm^3 mol^{-1} K^3 T^{-3}exp(-7400 ± 700 K/T)

$k(C_3H_6+H \leftrightarrow a\text{-}C_3H_5+H_2) = 10^{5.24\pm0.19}$ s^{-1} cm^3 mol^{-1} K$^{-2.5}$ $T^{2.5}$exp(-1300 ± 200 K/T)

$k(C_6H_5CH_3+H \leftrightarrow C_6H_6+CH_3) = 10^{6.29\pm0.19}$ s^{-1} cm^3 mol^{-1} K$^{-2.2}$ $T^{2.2}$exp(-2000 ± 400 K/T)

$k(C_6H_5CH_3+H \leftrightarrow C_6H_5CH_2+H_2) = 10^{14.10\pm0.25}$ s^{-1} cm^3 mol^{-1} exp(-4500 ± 500 K/T)

$k(TMB+H \leftrightarrow m\text{-xylene}+CH_3) = 10^{13.83\pm0.18}$ s^{-1} cm^3 mol^{-1} exp(-3900 ± 400 K/T)

$k(TMB+H \leftrightarrow (CH_3)_2CH_2C_6H_3+H_2) = 10^{4.57\pm0.25}$ s^{-1} cm^3 mol^{-1} exp(-4300 ± 600 K/T)

In addition, we quantify the effect of secondary chemistry on these rate estimates and the contribution to their uncertainty. Furthermore, we demonstrate how the detailed measurements constrain the model's predictions of global properties such as ignition delay time in propene oxidation.

References

1. D. A. Sheen, H. Wang, Combust. Flame 158 (2011), 2358-2374.
2. D. Robaugh, W. Tsang, J. Phys. Chem 90 (1986), 4159-4163.
3. W. Tsang, J. P. Cui, J. A. Walker, International Symposium on Shock Waves and Shock Tubes 17 (1989), 63-73.
4. C. M. Rosado-Reyes, J. A. Manion, W. Tsang, J. Phys. Chem. A 114 (2010), 5710-5717.
5. C. Rosado-Reyes, J. Manion, W. Tsang, J. Phys. Chem. A 115 (2011), 2727-2734.