Uncertainty Analysis of Chemical Thermometry and the Decomposition of Cyclohexene in a Variable Pressure Flow Reactor

Joshua S. Heyne,[1,*] and Frederick L. Dryer[1]

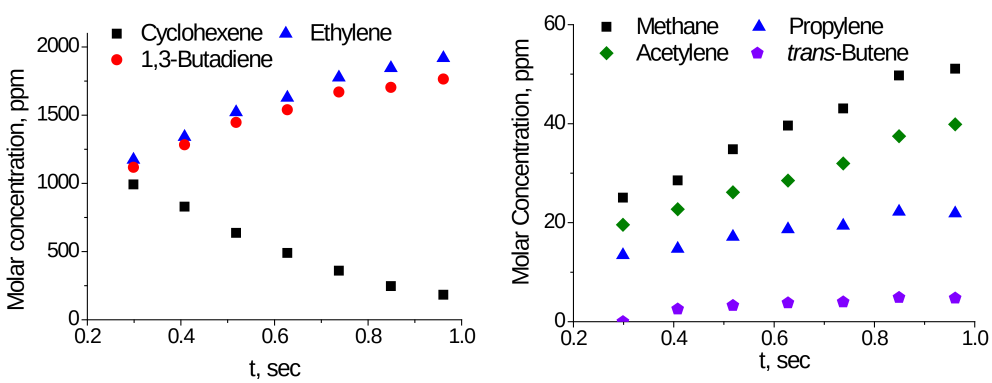
[1] Princeton University, Princeton, NJ, USA
* Corresponding author: jheyne@princeton.edu

TUESDAY

The high temperature dependence of the water elimination reaction decomposition channel for small alcohols, as with most decompositions, emphasizes the importance of accurate temperature measurements when experimentally characterizing their rate constants (1)-(2). While we have recently been studying the referenced reactions using thermocouple methods, we also considered chemical thermometry. Chemical thermometry, i.e. determining temperature by measurement of the thermal decomposition rate of a well studied compound, has been used previously by a number of authors (3,4). If the decomposition rate is well determined, the inversion of the Arrhenius expression (solving for the temperature) should yield determinations with small uncertainties. The use of chemical thermometry alleviates random errors in shock tube experiments (4) and gives a simple approach for dealing with non-idealities (3). Some authors have used this technique exclusively for the temperature determination in their experiments. Through our research, we have concluded that the uncertainty associated with chemical thermometry has not been investigated thoroughly. On the basis of literature data and new experiments that we conducted, the uncertainty analysis of two chemical thermometers: cyclohexene (reverse Diels-Alder reaction) and 1,1,1-trifloroethane (HF elimination) is reported. The work suggests that the uncertainty of chemical thermometry is far greater than expected (σ_T > 20 K). This result is consistent with new pyrolysis data for cyclohexene at 957 K and 6.1 atm in the Variable Pressure Flow Reactor, see Figure 1 and with the disparities between prior modeling studies and experimental results (5).

References

(1) Heyne, J.S.; Dooley, S.; Dryer, F. L. *ESSCI* Storrs, CT, **2011**.
(2) Heyne, J.S.; Serinyel, Z.; Dooley, S.; Dryer, F. L.; Curran, H. *CSSCI* Dayton, OH, **2012**.
(3) Tranter, R. S.; Sivaramakrishman, R.; Srinivasan, N.; Brezinsky, K. *Int. J. Chem. Kin.* **2001,** 722-731.
(4) Tsang, W.; Lifshitz, A. *Int. J. Chem. Kin.***1998**, (30), 621-627.
(5) Metcalfe, W. K.; Dooley, S.; Dryer, F. L. *Energy & Fuels* **2011**, (25) 4915-4936.



(a) (b)

Figure 1: Pyrolysis of cyclohexene at 6.1 atm, and 2300/997700 cyclohexene/N_2 for (a) major species and (b) minor species. The measured temperature is 957 K while chemical thermometry predicts 978 K.