

Uncertainty quantification of the rate parameters of an ethyl iodide pyrolysis mechanism

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The optimization of a kinetic mechanism for the pyrolysis of ethyl iodide was carried out based on data obtained from reflected shock wave experiments with H-ARAS and I-ARAS detection. The experiments were conducted in a stainless steel shock tube behind reflected shock waves at temperatures between 957 K and 1397 K, and pressures between 1.3 bar and 1.8 bar with argon as bath gas [1].

The thermal decomposition reaction of C₂H₅I behind the reflected shock wave was monitored using H-ARAS and I-ARAS. In the mechanism optimization study all these measurements were taken into account together with the rate coefficients measured by Michael et al. [2] for reaction H₂ + I → H + HI. The experimental data were interpreted using the following 5-step mechanism: R1: C₂H₅I → C₂H₅ + I; R2: C₂H₅+M → C₂H₄+H+M; R3: C₂H₅I → C₂H₄ + HI; R4: H + HI → H₂ + I; R5: C₂H₅I + H → C₂H₅ + HI.

Arrhenius parameters A and E of reactions R1, R3, R4, and R5 were determined from the experimental data. The joint covariance matrix of the optimized Arrhenius parameters was also calculated. This covariance matrix was converted to the temperature dependent uncertainty parameters f of the rate coefficients and to the temperature dependent correlation coefficients between pairs of rate coefficients. Each fitted rate coefficient was determined with much lower uncertainty compared to the estimated uncertainty of the data available in the literature.

The C₂H₅I decomposition branching ratio, $k_{R1} / (k_{R1} + k_{R3})$, was calculated from the optimized rate parameters. The value obtained was 0.965 at 900 K, decreasing nearly linearly to 0.905 at 1400 K, and the value extrapolated to 2000 K was 0.840. This is in good agreement with the branching ratios determined by Kumaran *et al.* (0.87 ± 0.11 at 950 K-2050 K) [3], Yang and Tranter (larger than 0.87) [4], and Miyoshi *et al.* (0.92 ± 0.06 at 950 K-1400 K) [5].

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