

Computational Kinetics of Reactions $C_2H_6 \rightleftharpoons CH_3 + CH_3$ and $H + O_2 \rightleftharpoons HO_2 \rightleftharpoons HO + O$ in Supercritical CO_2

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Fuel oxy-combustion is an emergent technology where habitual nitrogen diluent is replaced by high-pressure supercritical CO_2 (s CO_2), which increases the efficiency of energy conversion in the newly designed Allam power cycle. The chemical kinetics of ethane association/dissociation reactions ($C_2H_6 \rightleftharpoons CH_3 + CH_3$) and the reactions between hydrogen atom and oxygen molecule ($H + O_2 \rightleftharpoons HO_2 \rightleftharpoons HO + O$) play an important role for combustion in s CO_2 environment. Here we predict these reaction rates at 30-1000 atm and 1000-2000 K. We adopt multiscale approach, where reactive complex is treated by quantum mechanical CCSD method and the transition state is determined by canonical variational transition state theory in rigid rotor/harmonic oscillator approximation. Further, RRKM theory is performed in the addition reaction of a hydrogen atom to an oxygen molecule because of the deep well on the potential energy surface. Environment effects at different densities of CO_2 are taken into account by potential of mean force (PMF), produced with classical molecular dynamics (MD). Accelerated sampling techniques, such as boxed MD and umbrella sampling, are applied for description of rare events. Multi-state empirical valence bond model is applied to accurately describe covalent bond breaking at the cost of classical force field. The free energy of activation $\Delta G^*(r) = \Delta G_{gas}(r) + \Delta G_{sol}(r)$ is applied in the study of gas and condensed phase and the rate constant is derived from the general form of the Eyring-Polanyi equation $k = \kappa \left(\frac{k_B T}{h} \right) \exp\left(-\frac{\Delta G^*}{RT}\right)$. Predicted rates at low densities agree well with the available literature data, while the rates at supercritical conditions are reported for the first time. Extended Arrhenius equation $k = AT^n \exp\left(-\frac{E_a}{RT}\right)$ is fitted by linear least square regression model to obtain k under different temperatures and pressures. Rate constants at 300 atm are predicted to be $2.41 \times 10^{14} T^{-0.20} \exp(-77.03 \text{ kcal/mol}/RT)$ 1/s for ethane dissociation and $8.44 \times 10^{-19} T^{1.42} \exp(19.89 \text{ kcal/mol}/RT)$ $cm^3/\text{molecule/s}$ for methyl-methyl recombination. Rate constants is $4.23 \times 10^{-7} T^{0.73} \exp(-21.86 \text{ kcal/mol}/RT)$ $cm^3/\text{molecule/s}$ for pressure-independent $H + O_2 \rightleftharpoons HO + O$ and $5.22 \times 10^{-2} T^{-2.86} \exp(-7.25 \text{ kcal/mol}/RT)$ $cm^3/\text{molecule/s}$ for pressure-dependent $H + O_2 \rightleftharpoons HO_2$ at 300 atm. Pressure increase leads to increased rate constants for all reactions considered, except for $H + O_2 \rightleftharpoons HO + O$ one.