High Temperature Kinetics of O-substitution in Ethers and Peroxides Reaction Class

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Reliable estimates of high-pressure-limit reaction rates as a function of temperature are essential for the development of reaction sets that can be used to model complex chemical processes.
This work reports a series (more than 100) of rate coefficients computed for representative radical O-substitution reactions in ethers ($R_1OR_2+R_3 \rightarrow R_1OR_3+R_2$) and peroxides ($R_1OOR_2+R_3 \rightarrow R_1OR_3+OR_2$) up to c4. This class of reactions was previously omitted from our kinetics libraries of the Reaction Mechanism Generator software [1] due to very scanty data available in the literature [2]. Rate coefficients were calculated using transition state theory and CBS-QB3 computational chemistry calculations. The effect of hindered internal rotations was included via rotor potential energy scans and solution of the one-dimensional Schrodinger equation. This work highlights fast reactions that may be important for hydrocarbons oxidation and therefore should be taken into account in the kinetic models. The effects of branching and double and triple bonds conjugate to oxygen atom under radical attack are also analyzed.

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