

Theory based rate constants for H-abstractions of silanes and the possibility of reactivity analogies and rate rules

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Abstract

Reactivities of hydrocarbons are important in the context of combustion and atmospheric chemistry [1,2]. Since many years, chemists tried to systematically investigate reactivities of specific bonds (for example primary, secondary, and tertiary C-H bonds). In both fields, atmospheric and combustion chemistry, physical chemists tried to establish structure-activity-relationships.

However, chemical kinetics and bond reactivity tendencies can be also important in the context of gas-phase material synthesis. In semiconductor industry, thin films of silicon carbide and SiO₂ are manufactured by thermal decomposition of Si-containing precursor compounds like silane (SiH₄), tri- and tetramethylsilane (Si(CH₃)₃ and Si(CH₃)₄), etc. Accordingly, research on high temperature kinetics of silicon-organic compounds is actively proceeded [3]. Si-containing materials like nanoparticles can be produced at high temperature by spray flame synthesis and CVD systems. Under flame conditions, H-atom abstractions are the most important reaction class, especially H-abstractions by OH-radicals.

However, much time and resources are required to carry out experimental gas phase kinetic studies. Therefore, computational chemistry is a cost effective way to predict chemical kinetic data.

Transition state theory (TST) is a suitable method to calculate rate constant data of H-atom abstractions.

In this work, C-H and Si-H abstraction rate constants for reactions between OH radicals and hydrocarbons/silicon-organic species are calculated based on using computational methods like MP2 and CCSD(T).

Molecular geometries and frequencies were obtained at the MP2/6-311G++ and MP2/aug-cc-pVTZ levels of theory. Single point energies were then calculated at the CCSD(T)/aug-cc-pVXZ(X=T, Q, infinity) level of theory. Where appropriate, low frequency modes in transition states have been treated as free rotors. For a variety of molecules (Si_xC_yH_z), TST-calculations have been performed in order to derive k(T) data for specific types of C-H and Si-H bonds. These data can be used to compare reactivity tendencies towards H-atom abstractions and the possibility of developing structure-activity-relationships will be discussed.

Keywords: *quantum chemistry, computational chemistry, gas dynamic, reaction constant, reaction kinetic, transition state theory*

References

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Biography

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