Inhibition and Promotion of Pyrolysis by Hydrogen Sulfide (H2S) and Sulfanyl Radical (SH)

This study resolves the interaction of sulfanyl radical (SH) with aliphatic (C1–C4) hydrocarbons, using CBS-QB3 based calculations. We obtained the C–H dissociation enthalpies and located the weakest link in each hydrocarbon. Subsequent computations revealed that H abstraction by SH from the weakest C–H sites in alkenes and alkynes, except for ethylene, appears noticeably exothermic. Furthermore, abstraction of H from propene, 1-butene, and iso-butene displays pronounced spontaneity (i.e., $\Delta G^0 < -20$ kJ mol$^{-1}$ between 300–1200 K) due to the relatively weak allylic hydrogen bond. However, an alkyl radical readily abstracts H atom from H$_2$S, with H$_2$S acting as a potent scavenger for alkyl radicals in combustion processes. That is, these reactions proceed in the opposite direction than those involving SH and alkene or alkynyl species, exhibiting shallow barriers and strong spontaneity. Our findings demonstrate that the documented inhibition effect of hydrogen sulfide (H2S) on pyrolysis of alkanes does not apply to alkenes and alkynes. During interaction with hydrocarbons, the inhibitive effect of H$_2$S and promoting interaction of SH radical depend on the reversibility of the H abstraction processes. For the three groups of hydrocarbon, Evans–Polanyi plots display linear correlations between the bond dissociation enthalpies of the abstracted hydrogens and the relevant activation energies. In the case of methane, we demonstrated that the reactivity of SH radicals toward abstracting H atoms exceeds that of HO$_2$ but falls below those of OH and NH$_2$ radicals.