Energetics of Free Radicals: Bridges between Gas-Phase and Solution Data

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Solution-phase homolytic bond dissociation enthalpies (BDEs) are crucial for understanding the reactivity of organic free radicals. However, most of the available BDE values refer to the ideal gas phase. To bridge these two sets of data the solvation enthalpies of parent compounds and their fragments (free radicals) are required. While solvation enthalpies of (long-lived) parent compounds can be experimentally obtained by traditional thermochemical methods, the solvation enthalpies of transient species are not easily determined.

This lecture reviews a number of models which have been proposed to deal with the difference between the solvation energetics of a radical and its parent molecule. Based on these models, and on experimental (time-resolved photoacoustic calorimetry) and computational chemistry results, it is concluded that the radical-solvent interaction may be larger than previously anticipated.