Thermochemical Property Measurements of Hydrogen Peroxide and the Hydroxyl Radical in Aqueous Solution

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Photo-induced decomposition of hydrogen peroxide leads to the prompt formation of reactive hydroxyl radicals. The photoacoustic signal generated by pulsed irradiation of an aqueous hydrogen peroxide solution is proportional to the combined photo-induced volume changes from both the enthalpy and the molecular transformation of the dissociation reaction. The magnitude of the photoacoustic signal arising from enthalpy of the reaction is due to local heating of the solution and is dependent on the thermoelastic properties of the solution. One the other hand, the magnitude of the photoacoustic signal arising from the molecular volume change is independent of the thermoelastic properties of the solution since no heat is evolved in molecular transformations. Because the thermoelastic properties of aqueous solutions change substantially over a narrow temperature range variable temperature photoacoustic calorimetry provides an experimental approach to measure these two thermodynamic properties simultaneously. This presentation will demonstrate how the thermochemical properties of a short-lived transient hydroxyl radical can be measured by a variation of the thermoelastic properties of an aqueous solution as a function of temperature.