77g High-Temperature Water; Specific or General Acid/Base Catalyst?

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High-temperature water (HTW), defined here as liquid water above 200 ºC, is a useful and environmentally benign medium for chemical reactions. Relative to water at room temperature, HTW has a low dielectric constant, increased solubility for small organic compounds, and an increased ion product. All of these properties are temperature dependent and can be manipulated to optimize the reaction environment. HTW, which has elevated levels of both hydronium and hydroxide ions, is an interesting medium for acid/base-catalyzed reactions, because such reactions can occur with no added acid or base. This paper will describe our recent investigations into the pH dependence of the rates of several different classes of reactions (e.g., aldol condensations, rearrangements, and triglyceride hydrolyses) in HTW. These investigations have brought into question the hypothesis that most acid/base-catalyzed reactions in HTW act via specific acid/base catalysis. Rather, we found that many of these reactions occur via general acid/base catalysis at near neutral pH. In reactions where general acid/base catalysis is the predominatant route to reaction, the addition of weak acids/bases (CO2 and NH3) to HTW may be less effective at increasing reaction rates than one would expect from the conventional wisdom in the field.