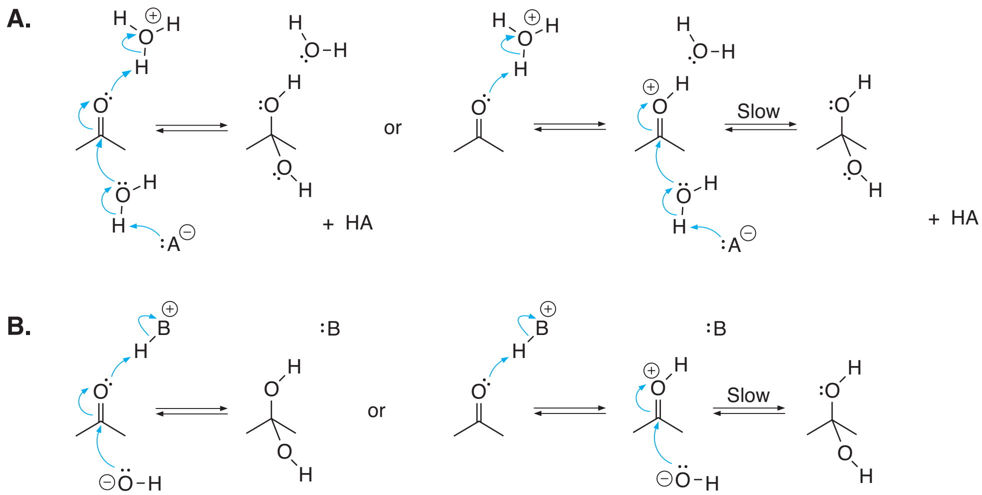

Figure 9.10
A. Examples of possible mechanisms involving the specific-acid–general-base-catalyzed hydration of acetone (type-n mechanisms). These are kinetically equivalent to the mechanism given in Figure 9.8 **A** (type-e mechanism). **B.** Examples of possible mechanisms involving the specific-base–general-acid-catalyzed hydration of acetone. These are kinetically equivalent to the mechanism given in Figure 9.8 **B.** Do not take these scenarios as the correct mechanisms for these hydration reactions, but consider them, instead, as simply possibilities highlighting our discussion.

a combination of HO^- and HB^+. The two possible mechanisms cannot be distinguished by a kinetic analysis. Examples of mechanisms that cannot be distinguished by pH and concentration experiments are shown in Figure 9.10. With acid catalysis, the standard general catalyzed path has been termed the **type-e** mechanism, while the kinetically equivalent combination of specific and general catalysis is called the **type-n** mechanism. In summary:

- A general-acid-catalyzed reaction is kinetically equivalent to a reaction that uses a specific acid and a general base in steps prior to or at the rate-determining step.
- A general-base-catalyzed reaction is kinetically equivalent to a reaction that uses a specific base and a general acid in steps prior to or at the rate-determining step.

9.3.4 Concerted or Sequential General-Acid–General-Base Catalysis

Sometimes both a general-acid and a general-base catalyst are required for a reaction. This is often the case with enzymes. In the following reaction scenario (Eq. 9.34) an acid HA and a base B are involved in the mechanism to make an intermediate that then forms the product and regenerates the two catalysts. Now both [HA] and [B] are present in the kinetic expression (Eq. 9.35). The k_{obs} rate constant would equal k[HA][B]. This means that the rate dependence upon pH is a combination of that observed for general-acid and general-base catalysis. Imagine combining the plots shown in Figures 9.9 **C** and **D**; a bell-shaped plot would result. The largest k_{obs} is found at a pH where the product of the concentrations of HA and B is at a maximum (Figure 9.11).

$$\mathrm{R} + \mathrm{HA} + \mathrm{B} \xrightarrow{\text{Slow}} \mathrm{I} \xrightarrow{\text{Fast}} \mathrm{P} + \mathrm{HA} + \mathrm{B} \qquad \text{(Eq. 9.34)}$$

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{R}][\mathrm{HA}][\mathrm{B}] \qquad \text{(Eq. 9.35)}$$