

5.5: Other Factors that Affect Reaction Rates

A reaction that occurs in one solvent usually occurs also in a number of similar solvents. For example, a reaction that occurs in water will often occur with a low molecular weight alcohol—or an alcohol-water mixture—as the solvent. Typically, the same rate law is observed in a series of solvents, but the rate constants are solvent-dependent.

Other chemical species that are present in the reaction medium (but which are neither products nor reactants) can also affect observed reaction rates. Any such species meets the usual definition of a **catalyst**. However, common practice restricts use of the word “catalyst” to a chemical species that substantially increases the rate of the reaction. A chemical species that decreases the rate of the reaction is usually called an **inhibitor**. If we think that the rate effect of the non-reacting species results from a non-specific or a greater-than-bonding-distance interaction with one or more reacting species, we call the phenomenon a **medium effect**. A solvent effect is a common kind of medium effect; altering the solvent affects the reaction rate even though the solvent does not form a chemical bond to any of the reactants or products. Dissolved salts can affect reaction rates in a similar way. Such effects often occur when the degree of charge separation along the path of an elementary reaction is significantly different from that in the reactants.

Isotopic substitution in a reactant can affect the reaction rate. (Replacement of a hydrogen atom with a deuterium atom is the most common case.) The effect of an isotopic substitution on a reaction rate is called a **kinetic isotope effect**. Kinetic isotope effects can provide valuable information about the reaction mechanism. A kinetic isotope effect is expected if the energy needed make or break a chemical bond to the isotopically substituted atom is a significant component of the activation energy for the reaction. Kinetic isotope effects are usually small in comparison to other factors that affect reaction rates. A ten-fold change in the reaction rate is a big kinetic isotope effect. Effects much smaller than this are often useful; indeed, the absence of a kinetic isotope effect can help distinguish among alternative mechanisms.

In studies of reaction rates that are focused on finding the reaction mechanism, many characteristics of the reaction that are not strictly rate-related can be important. These include the stereochemistry of the product; the **Walden inversion** that accompanies S_N2 reactions at tetrahedral carbon centers is a notable example. Isotopic substitution that occurs incidental to a reaction can help establish that an intermediate is formed. The effects of competing reactions are often significant. The study of competing reactions is frequently helpful when the reaction involves a short-lived and otherwise undetectable intermediate. The use of isotopic substitution and competing reactions is illustrated in [Section 5.16](#), in which we review the base hydrolysis of cobalt (III)cobalt pentaammine complexes, $Co(NH_3)_5X^{n+}$.

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