Molecularity

If a chemical reaction proceeds by more than one step or stage, its overall velocity or rate is limited by the slowest step, the rate-determining step. This "bottleneck concept" has analogies in everyday life. For example, if a crowd is leaving a theater through a single exit door, the time it takes to empty the building is a function of the number of people who can move through the door per second. Once a group gathers at the door, the speed at which other people leave their seats and move along the aisles has no influence on the overall exit rate. When we describe the mechanism of a chemical reaction, it is important to identify the rate-determining step and to determine its "molecularity". The molecularity of a reaction is defined as the number of molecules or ions that participate in the rate-determining step. A mechanism in which two reacting species combine in the transition state of the rate-determining step is called bimolecular. If a single species makes up the transition state, the reaction would be called unimolecular. The relatively improbable case of three independent species coming together in the transition state would be called termolecular.

Kinetics

One way of investigating the molecularity of a given reaction is to measure changes in the rate at which products are formed or reactants are lost, as reactant concentrations are varied in a systematic fashion. This sort of study is called kinetics, and the goal is to write an equation that correlates the observed results. Such an equation is termed a kinetic expression, and for a general reaction of the type:

\[ A + B \rightarrow C + D \]

it takes the form:

\[ \text{Reaction Rate} = k[A]^n[B]^m \]

where the rate constant \( k \) is a proportionality constant that reflects the nature of the reaction, \( [A] \) is the concentration of reactant A, \( [B] \) is the concentration of reactant B, and \( n \) & \( m \) are exponential numbers used to fit the rate equation to the experimental data. Chemists refer to the sum \( n + m \) as the kinetic order of a reaction. In a simple bimolecular reaction \( n \) & \( m \) would both be 1, and the reaction would be termed second order, supporting a mechanism in which a molecule of reactant A and one of B are incorporated in the transition state of the rate-determining step. A bimolecular reaction in which two molecules of reactant A (and no B) are present in the transition state would be expected to give a kinetic equation in which \( n=2 \) and \( m=0 \) (also second order). The kinetic expressions found for the reactions shown at the beginning of this section are written in blue in the following equations. Each different reaction has its own distinct rate constant, \( k \). All the reactions save 7 display second order kinetics, reaction 7 is first order.

It should be recognized and remembered that the molecularity of a reaction is a theoretical term referring to a specific mechanism. On the other hand, the kinetic order of a reaction is an experimentally derived number. In ideal situations these two should be the same, and in most of the above reactions this is so. Reaction 7 above is clearly different from the other cases reported here. It not only shows first order kinetics (only the alkyl halide concentration influences the rate), but
the chiral 3º-alkyl bromide reactant undergoes substitution by the modest nucleophile water with extensive racemization. Note that the acetonitrile cosolvent does not function as a nucleophile. It serves only to provide a homogeneous solution, since the alkyl halide is relatively insoluble in pure water.

One of the challenges faced by early workers in this field was to explain these and other differences in a rational manner.

Contributors