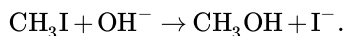


5.6: Mechanisms and Elementary Processes

To see what we mean by an elementary process, let us consider some possible mechanisms for the base hydrolysis of methyl iodide:



In this reaction, a carbon–iodide bond is broken and a carbon–oxygen bond is formed. While any number of reaction sequences sum to this overall equation, we can write down three that are reasonably simple and plausible. The C–I could be broken first and the C–OH bond formed thereafter. Alternatively, the C–OH bond could be formed first and the C–I bond broken thereafter. In the first case, we have an intermediate species, CH_3^+ , of reduced coordination number, and in the second we have an intermediate, $\text{HO}-\text{CH}_3-\text{I}^-$, of increased [coordination number](#). Finally, we can suppose that the bond-forming and bond-breaking steps occur simultaneously, so that no intermediate species is formed at all.

- Heterolytic bond-breaking precedes bond-making



- Bond-making precedes bond-breaking



- Bond-breaking and bond-making are simultaneous



The distinction between mechanism (b) and mechanism (c) is that an intermediate is formed in the former but not in the latter. Nevertheless, mechanism (c) clearly involves an intermediate structure in which both the incoming and the leaving group are bonded to the central carbon atom. The distinction between mechanisms (b) and (c) depends on the nature of the intermediate structure. In mechanism (b), we suppose that the intermediate is a *bona fide* chemical entity; once a molecule of it is formed, that molecule has a finite lifetime. In (c), we suppose that the intermediate structure is transitory; it does not correspond to a molecule with an independent existence.

For this distinction to be meaningful, we must have a criterion that establishes the shortest lifetime we are willing to associate with “real molecules.” It might seem that any minimum lifetime we pick must be wholly arbitrary. Fortunately this is not the case; there is a natural definition for a minimum molecular lifetime. The definition arises from the fact that molecules undergo vibrational motions. If a collection of atoms retains a particular relative orientation for such a short time that it never undergoes a motion that we would recognize as a vibration, it lacks an essential characteristic of a normal molecule. This means that the period of a high-frequency molecular vibration (roughly 10^{-14} s) is the shortest time that a collection of atoms can remain together and still have all of the characteristics of a molecule. If a structure persists for more than a few vibrations, it is reasonable to call it a molecule, albeit a possibly very unstable one.

In mechanism (c) the structure designated $[\text{HO}\cdots\text{CH}_3\cdots\text{I}^-]^\ddagger$ depicts a transitory arrangement of the constituent atoms. The atomic arrangement does not persist long enough for the $\text{HO}-\text{CH}_3$ bond or the CH_3-I bond to undergo vibrational motion. A structure with these characteristics is called an **activated complex** or a **transition state** for the reaction, and a superscript double dagger, \ddagger , is conventionally used to signal that a structure has this character. The distinction between a *bona fide* intermediate and a transition state is clear enough in principle, but it can be very difficult to establish experimentally.

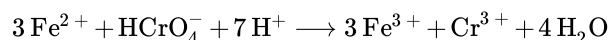
These considerations justify our earlier definition: An elementary reaction is one in which there are no intermediates. Any atomic arrangement that occurs during an elementary reaction does not persist long enough to vibrate before the arrangement goes on to become products or reverts to reactants.

An elementary reaction is one in which there are no intermediates.

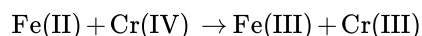
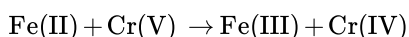
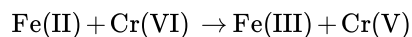
We can distinguish a small number of possible kinds of elementary reaction: termolecular elementary reactions, bimolecular elementary reactions, and unimolecular reactions. A single molecule can spontaneously rearrange to a new structure or break into

smaller pieces. Two molecules can react to form one or more products. Three molecules can react to produce products. Or we can imagine that some larger number of molecules reacts. We refer to these possibilities as **unimolecular**, **bimolecular**, **termolecular**, and **higher-molecularity** processes.

The stoichiometry of many reactions is so complicated as to preclude the possibility that they could occur as a single elementary process. For example, the reaction



can not plausibly occur in a single collision of three ferrous ions, one chromate ion, and seven hydronium ions. It is just too unlikely that all of these species could find themselves in the same place, at the same time, in the proper orientation, and with sufficient energy to react. In such cases, the stoichiometric mechanism **must be a series** of elementary steps. For this reaction, a skeletal representation of one plausible series is



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