

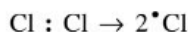
TYPES OF ORGANIC REACTIONS

The common organic reactions may be classified into three categories, viz., substitution reactions, addition reactions and elimination reactions. A brief description of these is in order.

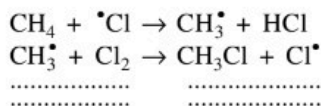
1. Substitution Reactions In these reactions, an atom attached to carbon atom of a molecule is replaced by another atom. These reactions may be initiated by free radical, electrophile or nucleophile.

Free-radical substitution One of the common examples is the reaction between CH_4 and Cl_2 . The reaction is initiated by the homolytic cleavage of Cl_2 by sunlight. The mechanism of the reaction is as follows.

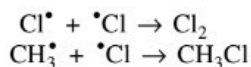
(a) *Initiation step*



(b) *Propagation steps*



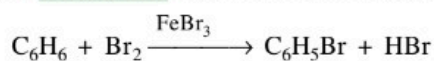
(c) *Termination steps*



Inductive and Resonance Effects 20.5

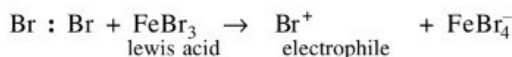
The reactivity of X_2 ($=\text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2$) with CH_4 decreases from F_2 to I_2 . Though initiation step is endothermic, the rate of reaction is not determined by this step but seems to be decided by the first reaction in the propagation step as the activation energy increases from F_2 to I_2 . This energy which decides the fraction of collisions of sufficient energy for the reaction to proceed in the forward direction.

Electrophilic Substitution Reactions The reaction initiated by an electrophile is known as electrophilic substitution reaction. Aromatic substitution reactions are the examples of this type of reaction. For example,

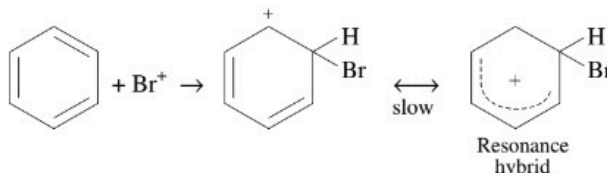


The mechanism of this reaction is as follows.

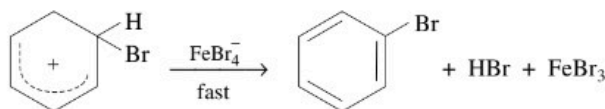
(a) *Formation of an electrophile*



(b) *Electrophilic attack*

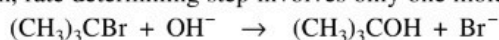


(c) *Elimination of proton*

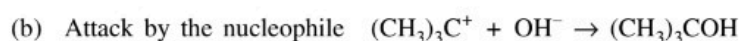
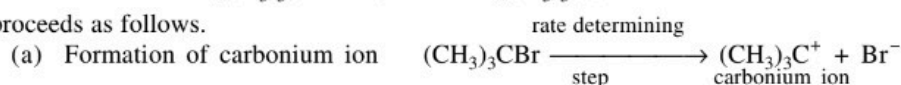


Nucleophilic Substitution Reactions The reaction involves an attack by a nucleophile. The reaction can proceed either via S_N1 or S_N2 mechanism.

In S_N1 mechanism, rate determining step involves only one molecule. For example, the reaction

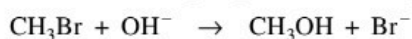


proceeds as follows.

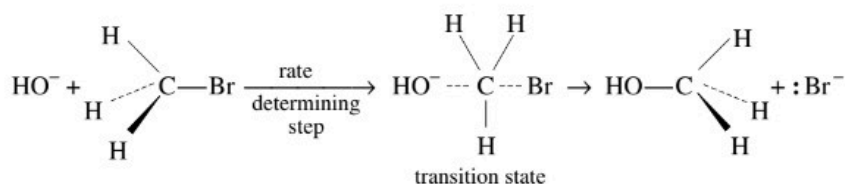


The stability of carbonium ion is the controlling factor for this mechanism. The formation of 3° carbonium ion as an intermediate proceeds via this mechanism. In an optically active compound, substitution at chiral atom via S_N1 produces racemic mixture.

In S_N2 mechanism, rate determining step involves two species. For example, the reaction



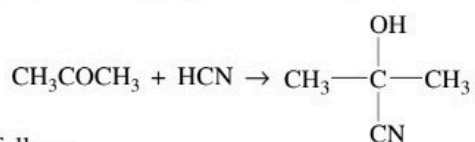
proceeds via this mechanism which may be represented as follows.



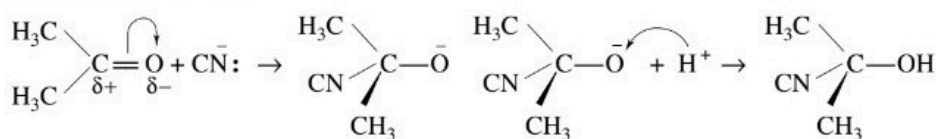
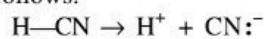
Since 1° carbonium ion is less stable than the transition state formed above, the reaction involving primary alkyl halides proceed via S_N2 mechanism. During the reaction, configuration of carbon is inverted. This is known as Walden inversion.

Secondary alkyl halides may undergo hydrolysis by either S_N1 or S_N2 mechanism depending upon the comparative stability of 2° carbonium ion and the transition state. In general, S_N2 mechanism is strongly inhibited by increasing steric bulk of the reagents. In such a case, S_N1 is favoured.

across $\text{C}=\text{O}$ (carbon-oxygen) double bond proceeds via this mechanism. For example, the reaction



proceeds as follows.



3. Elimination Reactions In these reactions, atoms or group of atoms attached to adjacent carbon atoms are eliminated to generate double or triple bond. For example



The reaction may proceed via E1 or E2 mechanism.