⇒ Complex Reactions

Reactions in which some side reactions accompanying the main chemical reaction is called complex reactions.

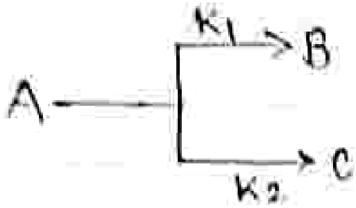
Complex reactions proceed in a series of steps instead of a single step.

⇒ Complex reactions are of following types

I Kinetics of Parallel or Side reactions

The reactions in which the maximum yield of the products is obtained is called the main or major reaction while the other reaction or reactions are called side or parallel reaction.

Let us consider a general reaction



In the reaction the reactant A gives two products B and C separately in two different reactions with rate constants K_1 and K_2.

If $K_1 > K_2$

The reaction $A \rightarrow B$ will be the major reaction and.

$A \rightarrow C$ will be the side or parallel reaction.

Let us assume that both these reactions are of first order and concentration of A is [A] at the time t.

The differential rate expressions are.

$$r_1 = \frac{-d[A]}{dt} = K_1[A] \quad \text{——— (1)}$$

and

$$r_2 = \frac{-d[A]}{dT} = K_2[A] \quad \text{——— (2)}$$

The total rate of disappearance of A is given by

$$\frac{-d[A]}{dT} = r_1 + r_2$$

$$\text{or} \quad -\frac{d[A]}{dT} = K_1[A] + K_2[A]$$

$$= (K_1 + K_2)[A]$$

$$\therefore \quad -d[A]/dT = K'[A] \quad \text{——— (3)}$$

Where K' is the first order rate constant. It is equal to the sum of the two constants K_1 and K_2 of two side reactions.

Integrating equation (3), we get

$$\int \frac{-d[A]}{dT} = \int K'[A]$$

Applying the limits $[A]_0$ & $[A]_t$ and 0 & t, we have

$$\int_{[A]_0}^{[A]_t} \frac{-d[A]}{dt} = K' \int_0^t dt$$

$$\ln \frac{[A]_0}{[A]_t} = K't + (K_1 + K_2)t \quad \text{——— (4)}$$

Where $[A]_0$ is the initial concentration of the reactant A and $[A]_t$ is the concentration of A at time t.

The ratio of the rates of two side reactions is obtained by dividing equations (1) by (2), we get.

$$\frac{r_1}{r_2} = \frac{K_1[A]}{K_2[A]} = \frac{K_1}{K_2} \quad \text{——— (5)}$$

from equations (4) and (5) we can calculate the individual rate constant K_1 and K_2.

Teacher's Signature :

⇒ Examples of side reactions or Parallel reactions

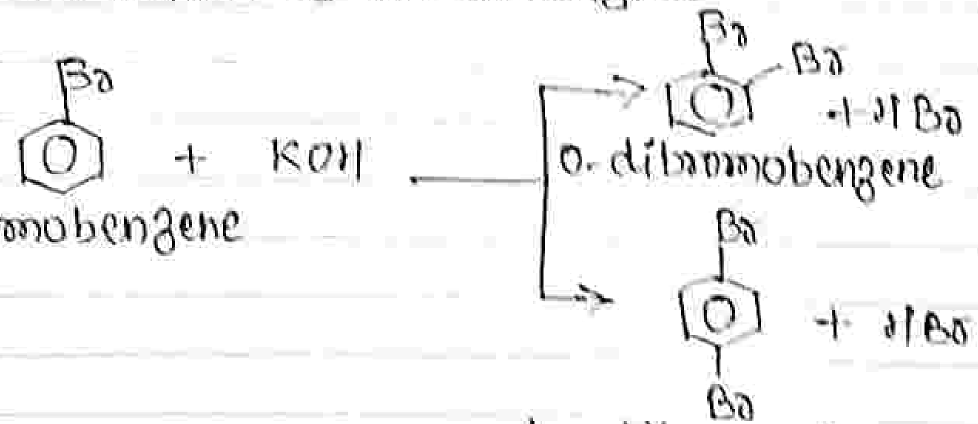
① Reaction of Ethyl bromide with Potassium hydroxide

CH_3CH_2Br (Ethyl bromide) + KOH (Potassium hydroxide) →
- → $CH_2=CH_2$ (Ethylene) + KBr + H_2O
- → CH_3CH_2OH (Ethyl alcohol) + KBr

② Dehydration of 2-methyl-2-butanol

$CH_3-C(CH_3)(OH)-CH_2-CH_3$ (2-methyl 2-butanol) →
- → $CH_3-C(CH_3)=CH-CH_3$ (2-methyl 2-butene)
- → $CH_2=C(CH_3)-CH_2-CH_3$ (2-methyl 1-butene)

③ Bromination of bromobenzene



Bromobenzene → o-dibromobenzene ; p-dibromobenzene.