

D.B. College (Jaigarh) lect - 7

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Isotope Effects!

The next question which comes up is how do we ascertain the presence of two discrete steps in the mechanism and also that the formation of σ -Complex is the rate determining step. Answer to this question can be obtained from the study of kinetic isotope effect. If the rate of reaction depends on a step which involves breaking of a C-H bond, then a kinetic isotope effect. If the rate of (k_H/k_D) of 6 to 7 is expected. Absence of any significant isotope effect in aromatic electrophilic substitution (except sulphonation) suggests that the proton is lost in the last step, subsequent to σ -C. We see that the isotope effect study has provided two pieces of important information regarding

the mechanism. Firstly, it has shown that the reaction takes place in two steps and secondly, that the first step is slower than the second step.

Nitration:

Nitration reaction is generally carried out with a mixture of concentrated nitric acid and sulphuric acid. The reagents which cause nitration are called nitrating agents.

(a) The various nitrating agents which are commonly employed are:

N_2O_5 in CCl_4 in the presence of P_2O_5 is used when anhydrous conditions are required.

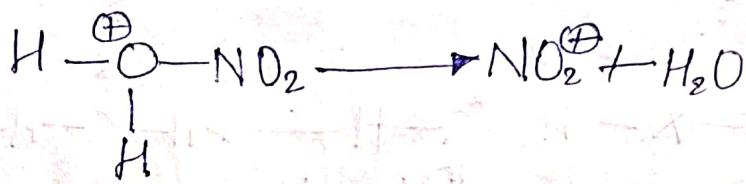
(b) Ethyl nitrate ($\text{C}_2\text{H}_5\text{ONO}_2$) is used to carry out nitration in alkaline medium.

(c) In the case of polycyclic hydrocarbons N_2O_4 and nitronium salts such as $\text{NO}_2^+ \text{BF}_4^-$, $\text{NO}_2^+ \text{PF}_6^-$, $\text{NO}_2^+ \text{SO}_4^-$, can be used. The electrophile involved in nitration reaction is nitronium ion (NO_2^+).

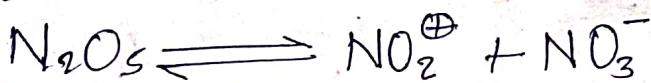
Mechanism

Generation of electrophile from nitrating agent.

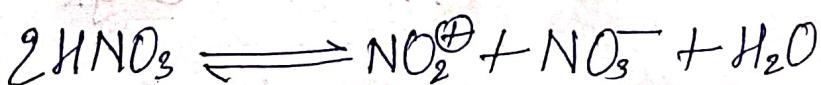
- (a) In a mixture of nitric acid and sulphuric acid, base reaction takes place in which nitric acid acts as the base.



- (b) N_2O_5 in CCl_4 when used, results in a spontaneous dissociation reaction.



- (c) With Concentrated HNO_3 alone



The electrophile generated in this case is obtained by the behaviour of one nitric acid as the base and other molecule as the acid, but the equilibrium lies in the reactant side.