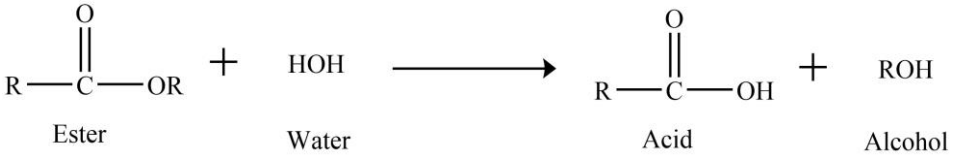
❖ Hydrolysis of Esters and Amides

In this section, we will discuss the mechanism of acid- and base-catalyzed hydrolysis of esters and amides (both are the derivatives of carboxylic acid) in detail.

➢ *Hydrolysis of Esters*

Although the esters are derived from acids, they are generally neutral compounds. In an archetypal ester reaction, the OR group (i.e., alkoxy) of the ester is swapped by another group. One such type of reaction is the ester hydrolysis where the OH group (generated by the water-splitting) replaces the alkoxy group of esters under consideration. The ester hydrolysis can either be catalyzed by an acid or by a base.

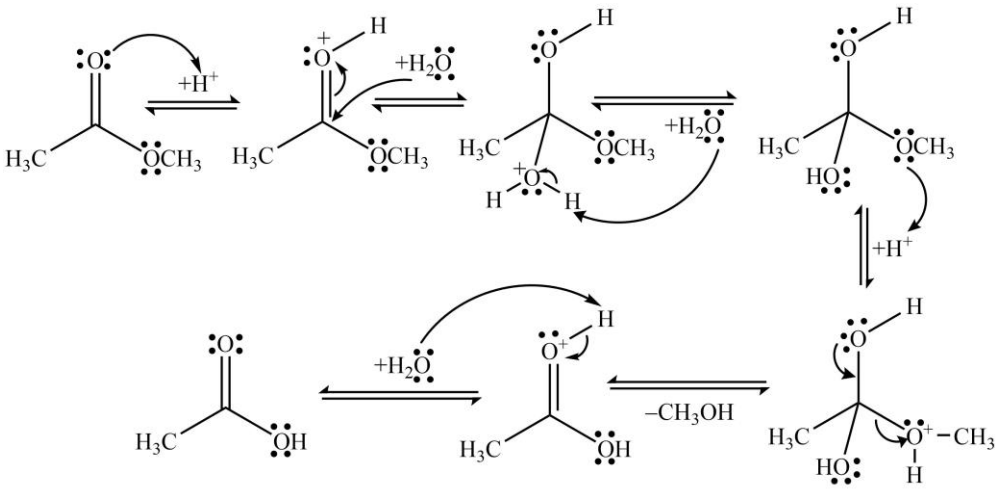
Illustrative Reaction: The typical organic chemical reaction depicting acid hydrolysis of esters is shown below.



Mechanism involved: Since the ester hydrolysis can either be catalyzed by an acid or by a base; a brief overview for both kinds must be understood for a better understanding.

i) Acid-catalyzed mechanism of ester hydrolysis:

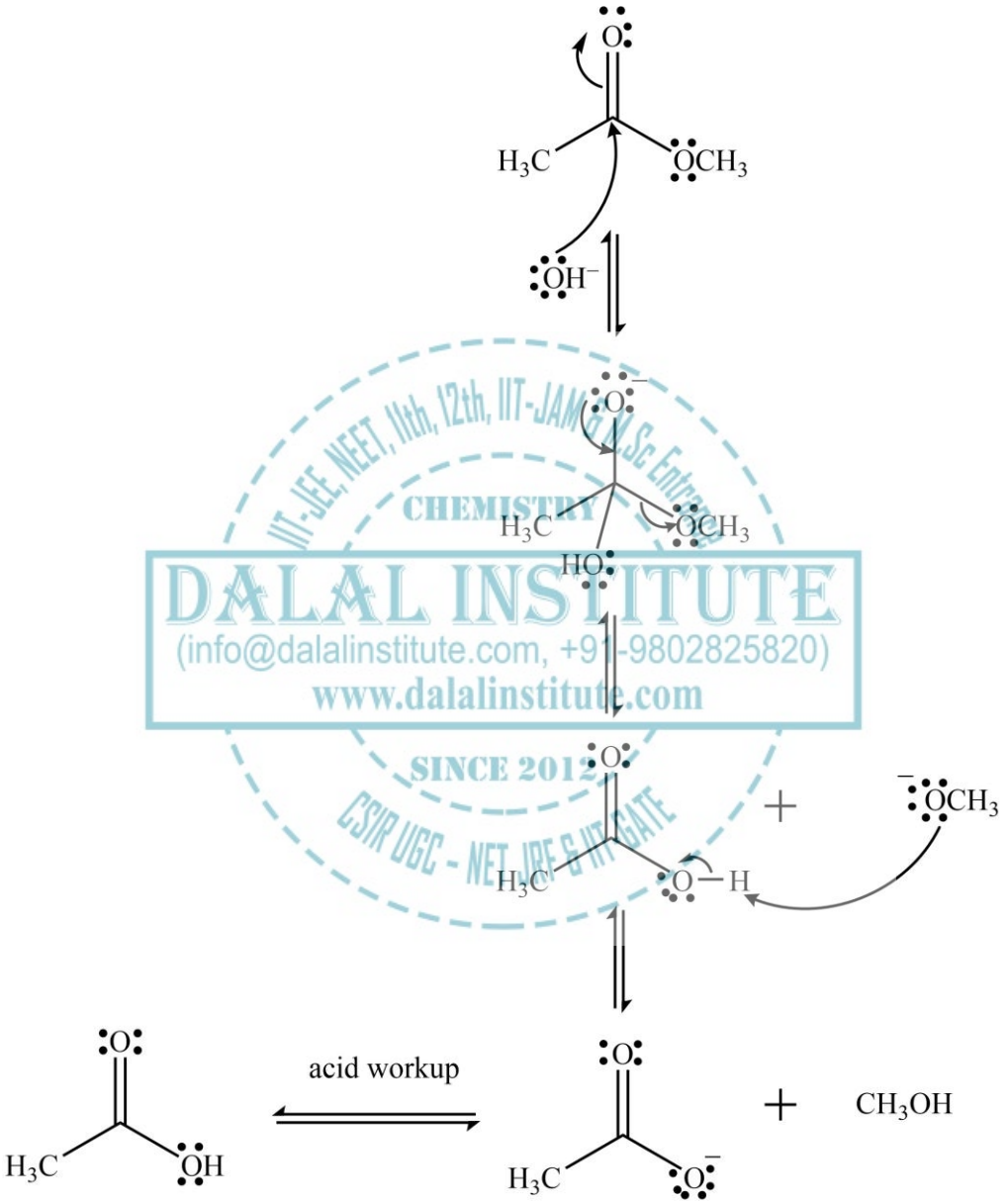
The mechanism for acid-catalyzed ester hydrolysis is a case of 'less reactive system type', and all the steps involved are shown below.



Furthermore, it is also worthy to note that the acidic hydrolysis of esters is just the reverse of esterification where an ester is heated with a large amount of water in the presence of a strongly acidic catalyst. Also, acidic ester hydrolysis is a reversible process and does not complete with 100% yield (like esterification).

ii) Base catalyzed mechanism of ester hydrolysis:

The mechanism for base-catalyzed ester hydrolysis is a case of 'reactive system type', and all the steps involved are shown below.

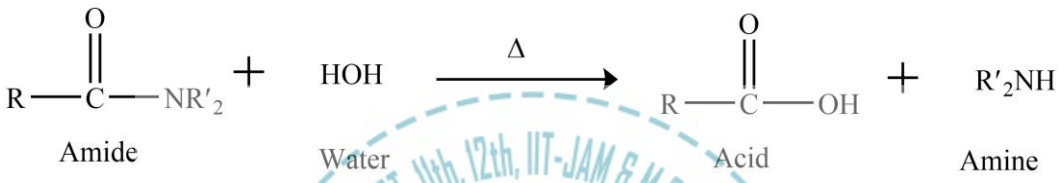


The mechanism given above gives rise to the breakage of the acyl-oxygen bond (second step); and is supported by experimental pieces of evidence through if the compound is isotopically labeled (i.e., ^{18}O). A similar conclusion was drawn if esters of chiral alcohols were used. The base-catalyzed ester hydrolysis is popularly known as the "saponification" process due to its use of soap-synthesis.

➢ ***Hydrolysis of Amides***

Amides are derivatives of carboxylic acid where the OH group has been substituted by NR_2, NH_2, NHR, or amine. Since the reaction between an amine and a carboxylic acid giving amide occurs via the release of the water molecule (condensation reaction), the amides' hydrolysis can be labeled as the reverse of condensation reaction as the amine and acid are being reproduced. The amides' hydrolysis isn't easy and requires conditions like the heating of amide with aqueous acid for a long interval of time. Like the hydrolysis of esters, the amide hydrolysis can either be catalyzed by an acid or by a base.

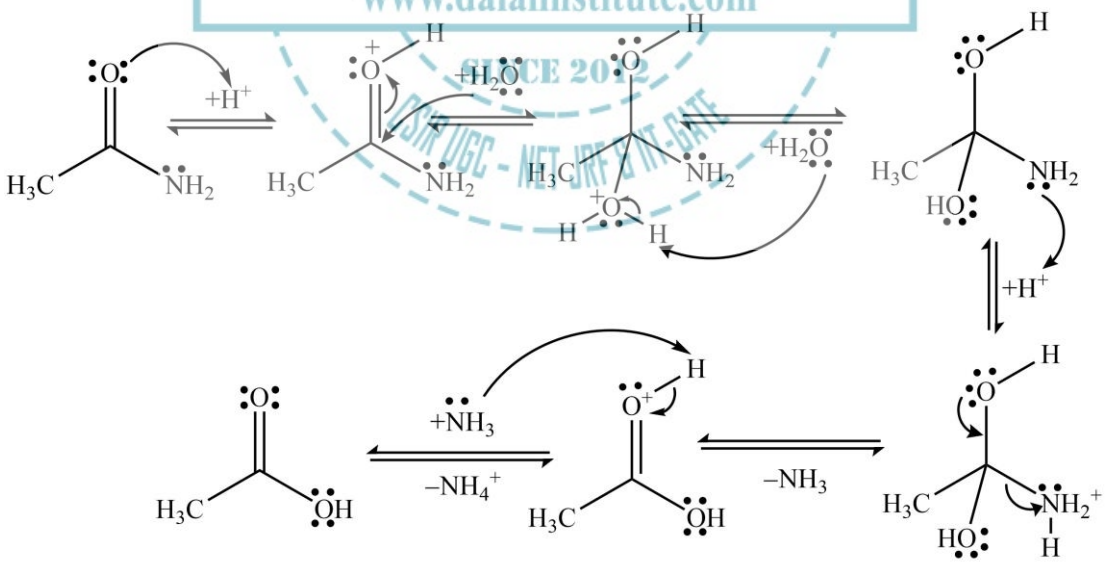
Illustrative Reaction: The typical organic chemical reaction depicting acid hydrolysis of amides is shown below.



Mechanism involved: Since the amide hydrolysis can either be catalyzed by an acid or by a base; a brief overview for both kinds must be discussed for a better understanding.

i) Acid-catalyzed mechanism of amide hydrolysis:

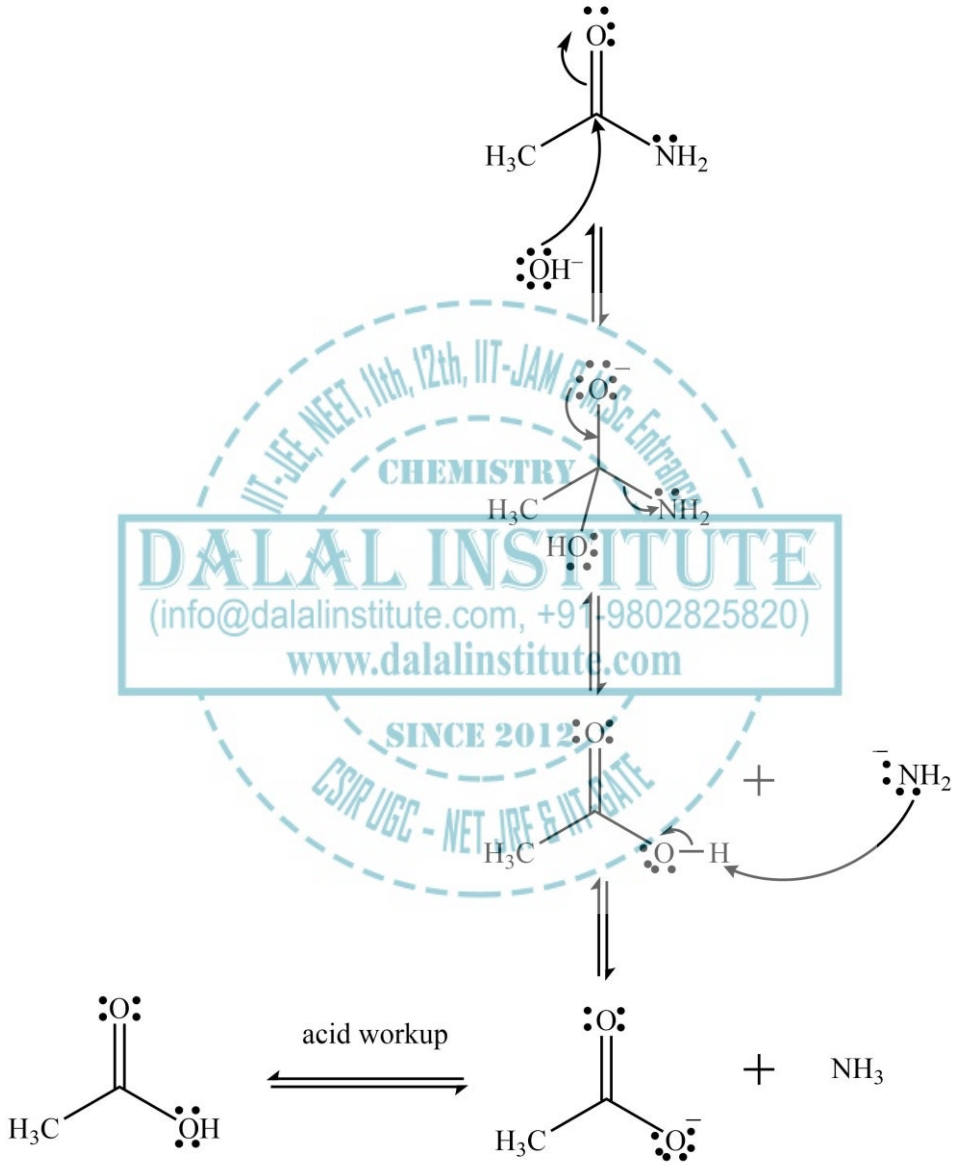
The mechanism for acid catalyzed amide hydrolysis is a case of 'less reactive system type', and all the steps involved are shown below.



It is obvious from the mechanism given above that the acid catalysed amide hydrolysis is quite analogous to the acid catalysed esters' hydrolysis; and proceed via the protonation of the carbonyl group and not the amide one.

ii) Base catalyzed mechanism of amide hydrolysis:

The base-catalyzed amide hydrolysis is extremely difficult to carry out but possible if the amide is heated for a very long span of time. All the steps involved in the base-catalyzed hydrolysis of amide are shown below.



It is obvious that the major problem in the way of substitution to happen is the need for a good leaving group; however, the deprotonated amine so strongly basic that it is almost the opposite of a good leaving group. Consequently, the breaking of amide is proved to be extremely difficult even if we couple very high temperatures with a base like KOH.

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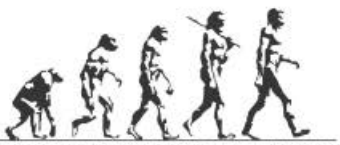

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Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC – NET JRF, IIT-GATE)
Founder & Educator, Dalal Institute
E-Mail: dr.mandeep.dalal@gmail.com
www.mandeepdalal.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK), and Springer (Netherlands).

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