ADVANCED CHEMISTRY BLOC

(HYDROLYSIS)

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HYDROLYSIS AND HYDRATION

NOTE : In this article equations are intensionally not balanced.

If you are ready to consider hydration along with hydrolysis, you will be amazed to see a large number of important chemical reactions of your syllabus comes under this single banner.

In hydrolysis, bonds break during the reaction while in hydration simply water is added. In hydrolysis, you watch more than one product while in hydration, there is only one product unless a disproportionation takes place.

$$CCl_4 + H_2O \longrightarrow \text{No hydrolysis ordinarily}$$

Carbon fails to expand its octet to receive the donation of electron pair from H_2O to form required intermediate. However, carbon uses the third energy shell to expand its octet.

$$CCl_4 + H_2O \xrightarrow[\text{steam}]{\Delta \text{ catalyst}} COCl_2 + HCl$$

$$SiCl_4 + H_2O \longrightarrow Si(OH)_4 + HCl$$

$$SiF_4 + H_2O \longrightarrow H_2SiO_3 + HF$$

But HF subsequently reacts with SiF_4.

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

SiH_4 is stable to water but rapidly hydrolysed by alkali.

$$SiH_4 + OH^- \longrightarrow SiO_4^{4-} + H_2$$

In SiH_4, the hydrogen carries a partial negative charge and in OH^-, it carries a partial positive charge. This facilitates the release of H_2.

$$GeH_4 + OH^- \text{ (30%)} \longrightarrow \text{No hydrolysis}$$

Polarity of H in both GeH_4 and OH^- is positive.

$$BF_3 + H_2O \longrightarrow H^+[BF_3(OH)]^-$$

No hydrolysis, rather an acid-base reaction takes place.

$$BCl_3 + H_2O \longrightarrow B(OH)_3 + HCl$$

The general rule is the central atom produces the oxyacid maintaining its oxidation state while the peripheral atom produces the hydra-acid.

$$AlCl_3 + H_2O \longrightarrow Al(OH)_3 + HCl$$

Again, $NF_3 + H_2O \longrightarrow$ No hydrolysis

N – F bond is too strong to break.

$$NCl_3 + H_2O \longrightarrow NH_3 + HOCl$$
$$\text{(not } HNO_2 \text{ and HCl)}$$

Nitrogen has no room to accept electrons. Therefore, it is the Cl that accepts donated electrons.

$$PF_5 + H_2O \longrightarrow \text{No hydrolysis}$$

P – F bond is again too strong to cleave.

$$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$$
$$PCl_5 + H_2O \longrightarrow H_3PO_4 + HCl$$
$$SF_6 + H_2O \longrightarrow \text{No hydrolysis}$$

Steric factor is the primary reason of the failure as there is no room for H_2O to approach cental S atom, which is crowded by six fluorine atoms.

$$\underset{\substack{\text{does not}\\\text{exist}}}{SCl_6} + H_2O \xrightarrow{\quad\times\quad} \underset{\substack{\text{does not}\\\text{exist either}}}{S(OH)_6} + HCl$$

The lower electronegativity of six Cl^- or six OH^- is responsible for non-existence of these compounds.

$$BiCl_3 + H_2O \longrightarrow \underset{\text{White turbidity}}{BiOCl} + HCl$$

$$SbCl_3 + H_2O \longrightarrow \underset{\text{White turbidity}}{SbOCl} + HCl$$

There are BiO^+ and SbO^+ ions formed due to high positive charge density of Bi^{3+} and Sb^{3+} ions.

$$BrF_5 + H_2O \longrightarrow HBrO_3 + HF$$

Similarly,

$$R-\overset{O}{\overset{\|}{C}}-OR' \quad \begin{cases} \xrightarrow{H_3O^+} RCOOH + R'OH \text{ (reversible)} \\ \xrightarrow{OH^-} RCOO^- + R'OH \text{ (irreversible)} \end{cases}$$

$$R-C\equiv N \quad \begin{cases} \xrightarrow{H_3O^+} RCOOH + NH_4^+ \\ \xrightarrow{OH^-} RCOO^- + NH_3 \\ \xrightarrow[\text{hydrolysis}]{\text{partial}} RCONH_2 \end{cases}$$

$$R-\overset{+}{N}\equiv\overset{-}{C} \quad \begin{cases} \xrightarrow{H_3O^+} R-\overset{+}{N}H_3 + HCOOH \\ \xrightarrow{OH^-} \text{No hydrolysis} \end{cases}$$

OH^- cannot attack either N or C.

$$R-O-R' \quad \begin{cases} \xrightarrow{H_3O^+} R-OH + R'-OH \\ \xrightarrow{OH^-} \text{No hydrolysis} \end{cases}$$
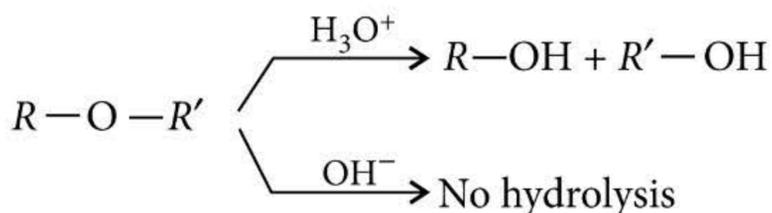
RO^- or $R'O^-$ both are bad leaving groups.

$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-Br \quad \begin{cases} \xrightarrow[H_2O]{Ag^+} (CH_3)_3C-OH(S_N1) \\ \xrightarrow[\Delta]{OH^-} CH_2=C\overset{CH_3}{\underset{CH_3}{\diagdown}} \end{cases}$$

No hydrolysis, rather elimination
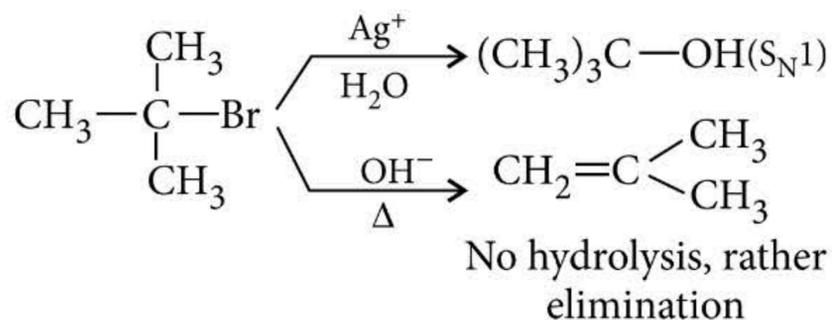
It is not surprising that sometimes hydrolysis reactions give a twist.

$$XeF_4 + H_2O \longrightarrow Xe + HF + O_2 + XeO_3$$
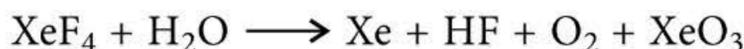
It is a clear cause of disproportionation during hydrolysis.

Whereas, the other two fluorides of Xe behave in different ways :

$$XeF_2 + H_2O \longrightarrow Xe + HF + O_2$$
$$XeF_6 + H_2O \longrightarrow XeOF_4 + HF$$
$$XeOF_4 + H_2O \longrightarrow XeO_3 + HF$$
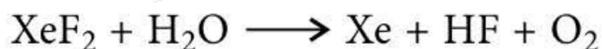
Before we close, check the following two reactions :

$$\overset{CH_3}{\underset{H}{\diagup}}C=NH \xrightarrow{H_2O} \overset{CH_3}{\underset{H}{\diagup}}C=O + NH_3$$

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + HCl$$
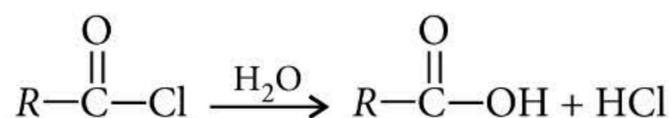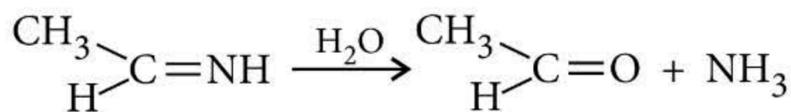
No catalyst even required for these two organic reactions.
We shall be checking hydration in the next episode.

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