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Carboxylic acid and their derivatives.

⇒ Naming

→ $CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH$: Propanoic Acid

→ $CH_3CH_2-\overset{\overset{O}{\|}}{C}-Cl$: Propanoyl Chloride

⇒ The acidity of carboxylic acid

→ Acids are proton donors

$$CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$$

→ dissociates partially as it is a weak acid.

⇒ The effect of electron donating groups on acidity

Note: Alkyl groups are electron donating (positive inductive effect)

→ HCO_2H : HCO_2^- → no increase in negative charge density

→ CH_3CO_2H : $CH_3CO_2^-$ → increased negative charge density

→ $CH_3CH_2CO_2H$: $CH_3CH_2CO_2^-$ → increased -ve charge density

So as we know alkyl groups are electron donating, they donate electrons to CO_2^- which makes the compound more ready to react with H^+. This means it becomes a weak acid.

∴ HCO_2^- → lowest pH, most acidic, most stable

$CH_3CO_2^-$ → higher pH, less acidic, less stable

$CH_3CH_2CO_2^-$ → highest pH, least acidic, least stable

⇒ The effect of electron withdrawing groups on acidity

→ Note: Cl is a electron withdrawing group (negative inductive effect)

→ $ClCH_2COOH$: $ClCH_2COO^-$ → least acidic, highest pH

→ $Cl_2CHCOOH$: Cl_2CHCOO^- → less acidic, higher pH

→ Cl_3CCOOH : Cl_3CCOO^- → most acidic, lowest pH

→ we know Cl is electron withdrawing group, ∴ it make the compound less ready to bond with H^+, because the no. of free electrons are almost reduced to 0, which also means it almost fully dissociates.

⇒ IF we have both e^- withdrawing and e^- donating

→ $Cl\,CH_2\,COOH$: $Cl\,CH_2\,COO^-$ lowest pH, most acidic

→ $Cl\,CH_2\,CH_2\,COOH$: $Cl\,CH_2\,CH_2\,COO^-$ higher pH, less acidic

→ $Cl\,CH_2\,CH_2\,CH_2\,COOH$: $Cl\,CH_2\,CH_2\,CH_2\,COO^-$ highest pH, least acidic

→ when there is 1 Cl and 1 CH_2 that's when e^- withdrawing group is closest to COO^- which means it wont let H^+ bond.

→ when there is 1 Cl but 2 CH_2 that's when e^- withdrawing group is far and 2 e^- donating groups are present which will make COO^- readily react with H^+.

→ when there is 1 Cl but 3 CH_2 that's when e^- withdrawing group is farthest and has the least effect, and 3 e^- donating groups are present which will make COO^- more readily react with H^+.

⇒ Comparing Acidities

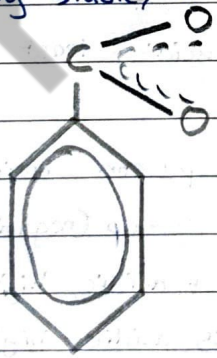
→ in order most acidic to least acidic

$C_6H_5COOH > C_6H_5OH > CH_3CH_2OH$

→ because

* C_6H_5COOH has a resonating structure which makes it very stable, because it has charge spread evenly across it

→ negative inductive electron withdrawing effect of C=O



* in C_6H_5OH, the lone pair of O^- delocalises into the benzene ring and they overlap with pi electron cloud.

* CH_3CH_2OH has 2 electron donating groups → methyl groups

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⇒ Oxidation of Methanoic Acid

→ $HCOOH + [O] \rightarrow CO_2 + H_2O$

→ weak oxidising agents like Fehling's solution and Tollens' reagent can be used for this reaction.

→ $K_2Cr_2O_7$ can also be used.

⇒ Oxidation of Ethanedioic acid

$$H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + [O] \rightarrow 2CO_2 + H_2O$$

→ only strong oxidising agent, $KMnO_4$

→ Reaction: $2MnO_4^- + 6H^+ + 5\,HO_2CCO_2H \rightarrow 10CO_2 + 8H_2O + 2Mn^{2+}$

⇒ Acyl Chlorides

$$R-\overset{O}{\overset{\|}{C}}-Cl$$

→ most reactive group

→ Cl and O are highly electronegative ∴ pulls e^- towards them

$$R-\overset{O\,\delta^-}{\overset{\|}{C}}-\underset{\delta^+}{Cl}\ \ \underset{\delta^-}{}$$

$$\overset{O\ \delta^-}{\overset{\|}{C}}-Cl \quad (\delta^+ \rightarrow \delta^-)$$

→ Formation of acyl chlorides

→ $CH_3CH_2COOH + PCl_5 \rightarrow CH_3CH_2COCl + POCl_3 + HCl$

propanoic acid — phosphorus pentachloride — propanoyl chloride

→ $3CH_3CH_2COOH + PCl_3 \rightarrow 3CH_3CH_2COCl + H_3PO_3$

→ condition: Heat

→ $CH_3CH_2COOH + SOCl_2 \rightarrow CH_3CH_2COCl + SO_2 + HCl$

→ has highest yield because SO_2 and HCl are both gases

% purity ↑

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→ Reactions of acyl chlorides are condensation reactions they follow nucleophilic substitution

→ Acyl chloride + water (hydrolysis, whenever OH is obtained)
→ $CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2COOH + HCl$

→ Acyl chloride + Ammonia
→ $CH_3CH_2COCl + NH_3 \rightarrow CH_3CH_2CONH_2 + HCl$

→ Ease of hydrolysis

$CH_3CH_2COCl > CH_3CH_2CH_2Cl > C_6H_5Cl$
(δ^+ on CH_3CH_2COCl; δ^+ on $CH_3CH_2CH_2Cl$)

lone pair of Cl^- delocalises in the benzene ring. Increases bond strength of C-Cl.

→ Acyl Chloride + Alcohol
$CH_3CH_2COCl + CH_3OH \rightarrow CH_3CH_2COOCH_3 + HCl$

→ Acyl Chloride + Phenol
→ Step 1: $C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$ (sodium phenoxide)
→ Step 2: $CH_3CH_2COCl + C_6H_5O^-Na^+ \rightarrow CH_3CH_2COOC_6H_5 + NaCl$
(phenyl propanoate)

→ Acyl Chlorides + Amines
$CH_3CH_2COCl + CH_3NH_2 \rightarrow CH_3CH_2CONHCH_3 + HCl$