Carboxylic Acids & Acyl Compounds

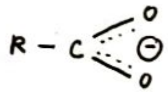
ACIDITY

- → C. acid = weak acid.
  - ↳ due to ionizable H atom

$CH_3C(=O)OH + H_2O \rightleftharpoons CH_3C(=O)O^- + H_3O^+$

← eqm

- → c. acid stronger than alcohols & phenols
  - ∵ O-H bond weakened by e⁻ ~~releasing~~ withdrawing C=O
  - ↳ e⁻ in CO & O-H bonds are drawn towards C=O ∴ release H^+ easily
  - ↳ also, carboxylate ion stabilized by delocalisation of e⁻ around $RCOO^-$ group. ∴ -ve charge spread out & cannot accept back RCOOH.



- → Acid strength : ethanol < H_2O < phenol < ethanoic acid.
  - ↳ Eg $CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$
    - → alkyl group e⁻ releasing ∴ H in O-H less δ+ ∴ not easily deprotonated by H_2O molecules.

STRENGTH OF C. ACID

- → GREATER e⁻ ~~donating~~ donating effect, weaker the acid.
  - ↳ reduces polarisation of O-H bond, strengthening H.
  - ↳ intensifies -ve charge on O atom, ∴ carboxylat ion less stable. → H can combine back.
- → GREATER e⁻ ~~releasing~~ ~~withdrawing~~ withdrawing effect, stronger the acid.
  - ↳ ↑ polarisation, OH bond weaken ∴ dissociates readily
  - ↳ stabilises carboxylate ion by reducing -ve charge on O.

OXIDATION OF METHANOIC ACID

- → HCOOH stronger red. agent ∴ further oxidation w/ mild oxi agents.

WEAK :

→ Reagent : Tollen's reagent / Fehling's solution
Conditions : water bath (60°C) / water bath (warm)
observation : silver mirror / brick red ppt.

$$HCOOH + 2OH^- + 2Ag(NH_3)_2^+ \rightarrow CO_2 + 2H_2O + 2Ag + 4NH_3$$

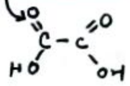
$$HCOOH + 4OH^- + 2Cu^{2+} \rightarrow CO_2 + 3H_2O + Cu_2O$$

STRONG :

→ Reagent : $K_2Cr_2O_7$ in H_2SO_4 (aq) / $KMnO_4$ in H_2SO_4 (aq)
Conditions : heat
observation : orange → green / purple → colourless

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

OXIDATION OF ETHANEDOIC ACID



- → only by stronger oxi agents
- → Reagent : $KMnO_4$ in H_2SO_4 (aq)
  Conditions : heat
  Observation : purple → colourless
- → autocatalysis.

$$(COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e^-$$

Eqn : $2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

ACYL CHLORIDES (ACID CHLORIDES)

- → acyl group : $R-\overset{|}{C}=O$

→

ACID DERIVATIVE	G.FORMULA	EG.
Ester	RCOOR	$CH_3COOC_2H_5$ Ethyl ethanoate
Acid chloride	RCOCl	CH_3COCl Ethanoyl chloride
Acid anhydride	RCOOCOR'	$CH_3COOCOCH_3$ Ethanoic anhydride

other examples (Ester, Acid anhydride)

→ naming depends on R group.

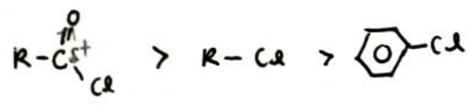
PREPARATON OF ACYL CHLORIDES

- → Replace OH of c. acid with Cl atom
- → ① Reagent : thionyl chloride, $SOCl_2$
  Conditions : dry conditions
  $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
- → ② Reagent : phosphorus (V) chloride, PCl_5
  Conditions : dry conditions
  $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

(ref AS notes)

Carboxylic Acids & Acyl Compounds

EASE OF HYDROLYSIS OF ACYL CHLORIDES

→ 

With H_2O : ✓ vigorous × ×

ppt : immediately slow ×

→ How to test for ease of hydrolysis
  ↳ warm NaOH (aq), Excess dilute HNO_3 , $AgNO_3$ (aq)

→ Ethanoyl chloride gives IMMEDIATE ppt of AgCl

$CH_3COCl + OH^- \rightarrow CH_3CO_2^- + H^+ + \underbrace{Cl^-}_{\text{produce HCl}}$

→ chloroethane white ppt (slow), chlorobenzene no ppt

→ why ? → chlorobenzene has no reaction ∵ C–Cl bond strengthened by overlapping of p-orbital of Cl w/ π orbitals of benzene ring
  → ↑ e^- density on aromatic ring . repels OH^-

→ Ethanoyl chloride > chloroethane ∵ C atom carries larger +ve charge (bonded to O & Cl).
  ↳ Cl bond weaker than C–O ∴ Cl leaves.

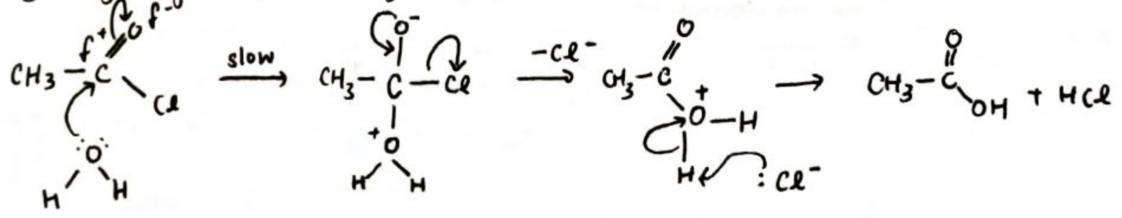
REACTIONS OF ACID CHLORIDES

→ depends on → magnitude of δ+ on C of carbonyl
  → how good nucleophiles compared to C.

→ Ammonia > 1° amines > alcohol > water

→ mechanism → addition - elimination.

→ Eg. hydrolysis of ethanoyl chloride.



ACYL CHLORIDES W/ WATER

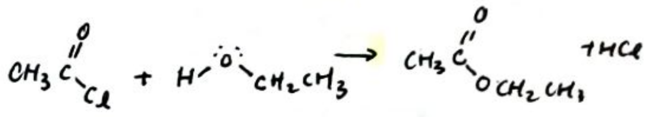
→ forms parent c. acid & HCl.
→ Reagent : H_2O
Conditions : room temp ⇧
→ addition - elimination

$CH_3COCl + H_2O \rightarrow CH_3COOH + \underset{\text{fumes}}{\underset{\uparrow}{HCl}}$

→ violent

ACID CHLORIDE W/ ALCOHOL

→ forms esters & HCl
→ Reagent : Alcohol
Conditions : room temp ⇧

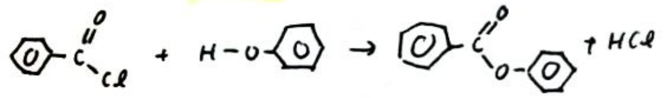


$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

→ goes to completion (⇌ ×)
→ easy to separate products.

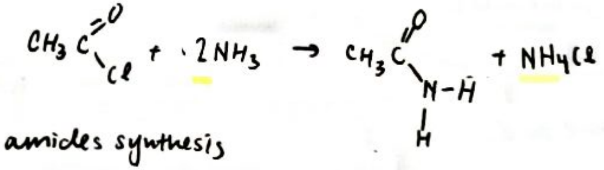
ACID CHLORIDE W/ PHENOL

→ forms phenyl esters
→ Reagent : phenol in NaOH (aq)
Conditions : warm



ACID CHLORIDE W/ AMMONIA & PRIMARY AMINES

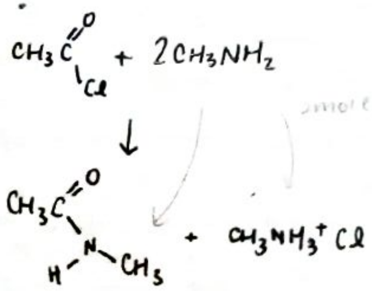
→ form amides
→ Reagent : ammonia
Conditions : room temp



$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

→ amides synthesis

→ Reagent : ammonia, 1° amines
Conditions : room temp



$CH_3COCl + 2CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3NH_3^+Cl^-$

* All room temp except phenol