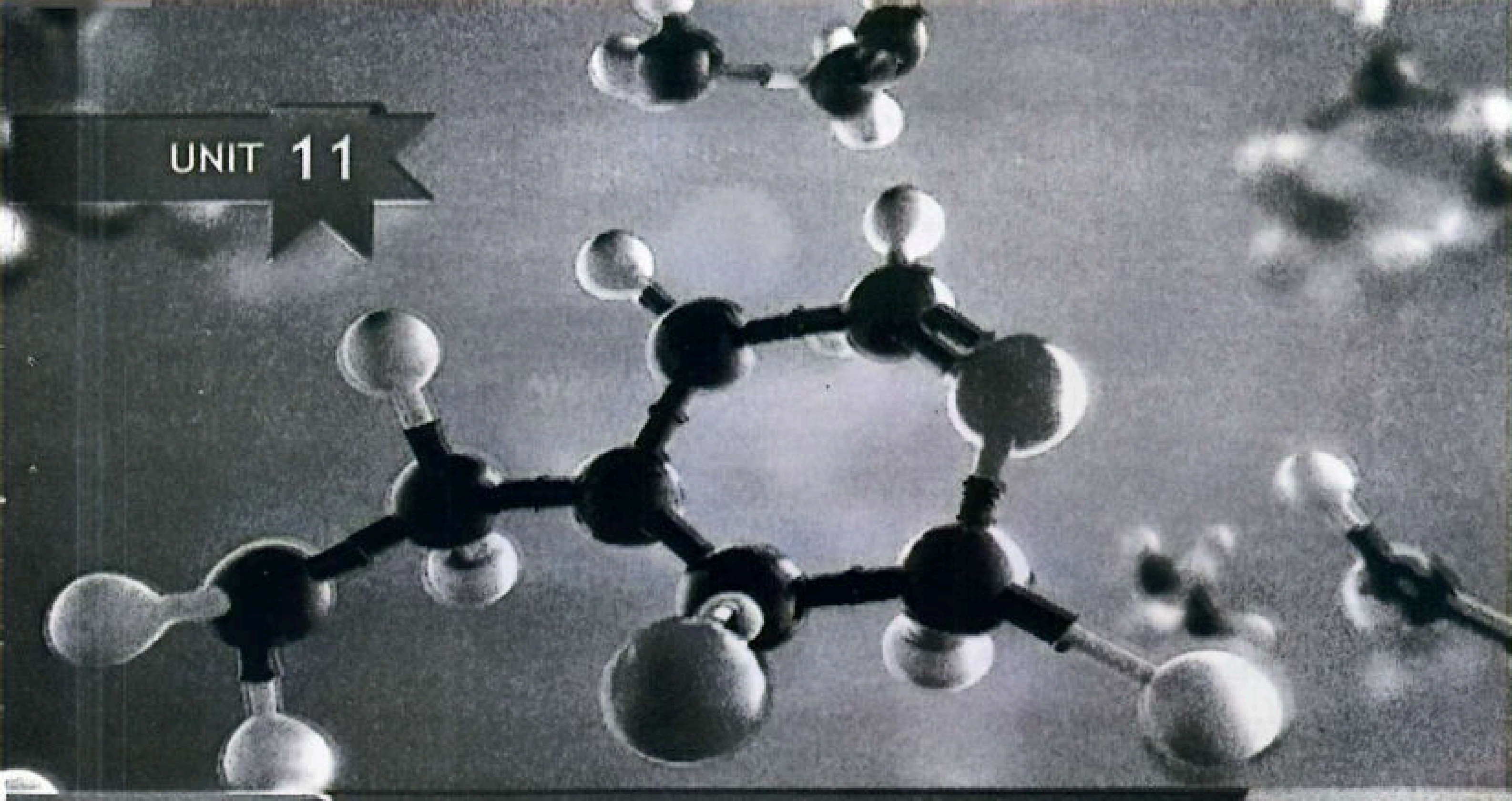


UNIT 11

CARBONYL COMPOUNDS

Student Learning Outcomes (SLOs)

- State the reactions by which benzoic acid can be produced: reaction of an alkylbenzene with hot alkaline $KMnO4$ and then dilute acid, exemplified by methyl benzene.
- Describe the reaction of carboxylic acids with PCl_3,, and heat, PCl_5, or $SOCl_2$ to form acyl chlodides.
- Recognise that some carboxylic acids can be further oxidized: a. the oxidation of methanoic acid with Fehling`s solution or Tollen`s reagent or acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ to carbon dioxide and water. b. the oxidation of ethanedioic acid with warm acidified $KMnO_4$ to carbon dioxide.
- Explain the relative acidities of carboxylic acids, phenols and alcohols.
- Explain the relative acidities of chlorine-substituted carboxylic acids.
- Recall the reactions by which esters can be produced: reaction of alcohols with acyl chlorides using the formation of ethyl ethanoate and phenyl benzoate as examples.
- Recall the reactions(reagents and conditions) by which acyl chlorides can be produced: reaction of carboxylic acids with PCl_3 and heat, PCl_5, or $SOCl_2$.
- Describe the following reactions of acyl chlorides: (check either bullets or add a,b, c,d): a. hydrolysis on addition of water at room temperature to give the carboxylic acid and HCl. b. reaction with an alcohol at room temperature to produce an ester and HCl. c. reaction with phenol at room temperature to produce an ester and HCl. d. reaction with ammonia at room temperature to produce an amide and HCl. e. reaction with a primary or secondary amine at room temperature to produce an amide and HCl.
- Describe the addition-elimination mechanism of acyl chlorides in reactions.
- Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and halogenoarenes (aryl chlorides).

Carbonyl compounds are a class of organic substances characterized by the presence of a carbonyl group ($C=O$). A carbonyl group consists of a carbon atom doubly bonded to an oxygen atom. This functional group is very reactive and acts as the main structural feature of many organic molecules. Carbonyl compounds can be broadly divided into two main types based on the nature of the atoms or groups attached to the carbonyl carbon:

Aldehydes: In aldehydes, the carbonyl group is attached to at least one hydrogen atom and one alkyl or aryl group. The general formula for aldehydes is RCHO, where R can be hydrogen, alkyl or aryl.

Example: Formaldehyde ($HCHO$), Acetaldehyde (CH_3CHO)

Ketones: In ketones, a carbonyl group is attached to two alkyl or aryl groups. The general formula for ketones is RCOR', where R and R' can be alkyl or aryl.

Example: acetone (CH_3COCH_3), butanone ($CH_3COC_2H_5$)

In addition to aldehydes and ketones, the carbonyl group is also present in several other important classes of compounds:

Carboxylic acids: These contain a carbonyl group. attached to a hydroxyl group (-OH) and an alkyl or aryl group. The general formula is RCOOH.

Example: acetic acid (CH_3COOH), benzoic acid (C_6H_5COOH)

Esters: Recall that Esters formed by the reaction of carboxylic acids and alcohols have a carbonyl group attached to an alkoxy group (-OR) and an alkyl or aryl group. The general formula is RCOOR'.

Aliphatic carboxylic acids have the carboxyl group attached to an open chain of carbon atoms.

Example: ethyl acetate ($CH_3COOCH_2CH_3$), methyl benzoate $C_6H_5COOCH_3$

Amides: Contains a carbonyl group attached to a nitrogen atom (which can be attached to hydrogen atoms or alkyl groups) and an alkyl or aryl group. The general formula is RCONR'R".

Example: Acetamide (CH_3CONH_2), N,N-Dimethylacetamide $CH_3CON(CH_3)_2$

Anhydrides: Anhydrides formed by the reaction of two carboxylic acids contain two carbonyl groups linked to an oxygen atom. The general formula is $(RCO)_2O$.

This chapter focuses on the properties and reactions of carboxylic acids, acyl chlorides and related compounds such as esters and alkylbenzenes. It introduces the key chemical changes involved in the conversion of alkylbenzenes to benzoic acid and explores how carboxylic acids can react with chlorinating agents such as PCl_3, PCl_5 and $SOCl_2$ to form acyl chlorides. Overall, the chapter provides a comprehensive overview of the chemical behaviour and transformations of carboxylic acids and their derivatives.

11.1 Acidity

Carboxylic acids are acidic simple organic compounds (pK_a ~ 5). But they are weak acids compared to mineral acids like HCl or H_2SO_4. (Remember the lower the pK_a, the stronger the acid)

Table 11.1: pK_a value of organic acids

Carboxylic Acid	Structure	pKa
Ethanoic acid	CH_3CO_2H	4.7
Propanoic acid	$CH_3CH_2CO_2H$	4.9
Fluoroethanoic acid	CH_2FCO_2H	2.6
Chloroethanoic acid	CH_2ClCO_2H	2.9
Dichloroethanoic acid	$CHCl_2CO_2H$	1.3
Trichloroethanoic acid	CCl_3CO_2H	0.9
Nitroethanoic acid	$O_2NCH_2CO_2H$	1.7

Acidity order of chlorine substituted acetic acid is:

$$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$$

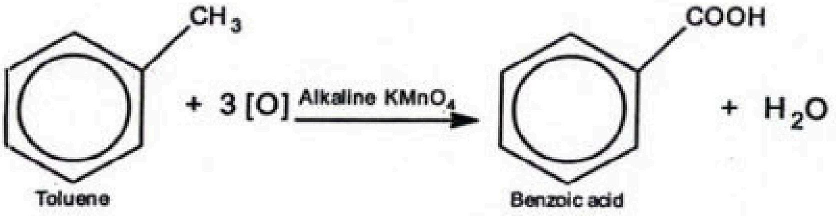
The electron-withdrawing group bonded to the carbon atom next to the carboxyl group (COOH) makes the acid stronger. Due to electron withdrawing group electrons will move away from oxygen. Hence decreases the charge density on the oxygen atom of the carboxylate ion which stabilizes the group and makes it less likely to bond with an H^+ ion. For example, chloroacetic acid is 100 times stronger acid than acetic acid.

The electron-donating group (Alkyl) strengthens the O—H bond in the acid's —COOH group. It donates a negative charge towards the group of the carboxylate ion, making it more likely to accept an H+ ion, hence acidic strength decreases. For example, formic acid is more acidic than acetic acid.

11.2 Preparation of Benzoic Acids

By the oxidation of Alkyl Benzenes

Benzoic acid can be prepared by the oxidation of alkyl benzene, when treated with hot alkaline $KMnO_4$. The mixture is finally hydrolyzed with dilute acid.



11.3 Reactivity

The carboxyl group shows the chemistry of both the carbonyl ($-\overset{O}{\overset{\|}{C}}-$) and the hydroxyl of an (–OH) groups. In most reactions, the carboxyl group is retained. However, the reactivity of these molecules is due to the presence of the carbonyl group.

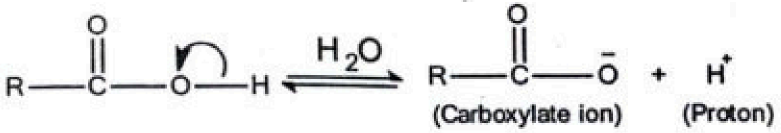
11.4 Reactions of Carboxylic Acids

Carboxylic acids undergo the following types of reactions.

1. The reaction in which hydrogen atom of –OH group of the carboxyl group is involved (salt formation).
2. The reaction in which the OH group is replaced by another group.
3. The reactions involving carboxyl group as a whole.

11.4.1 Reaction involving H-atom of the carboxyl group (Acidic properties of Carboxylic acid)

Carboxylic acids are weaker acids than mineral acids. They produce H^+ ion when dissolved in water



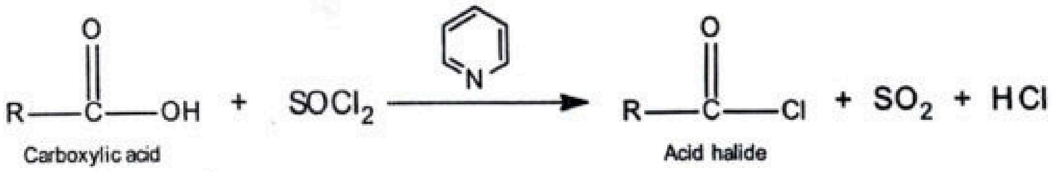
11.4.2 Reaction involving the OH group of Carboxylic acid

(Preparation of derivatives of Carboxylic acid)

The addition of a nucleophile to the carboxyl group is always followed by the displacement of the –OH group by some other group producing a carboxylic acid derivative. The –OH group can thus be replaced by X, OR, and NH_2 to form halides, esters, and amides respectively.

1. Reaction with Thionyl Chloride (Preparation of Acyl Chlorides)

- Acyl chlorides are prepared by treating the carboxylic acid with thionyl chloride, ($SOCl_2$), in the presence of a base (Pyridine).



2. Reaction with Phosphorus halides

Phosphorus(III) chloride reacts with carboxylic acids at room temperature producing acyl chloride and phosphorus acid.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

ethanoic acid → ethanoyl chloride

Phosphorus(V) chloride reacts with carboxylic acids in a cold state producing acyl chloride and phosphorus oxychloride with the evolution of fumes of hydrogen chloride.

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

ethanoic acid ethanoyl chloride

11.4.3 Oxidation Reactions

Some carboxylic acids like methanoic acid and ehandioic acid can be further oxidized by some oxidizing agents. For example;

(i) Methanoic acid is oxidized to carbon dioxide and water by the Tollen`s reagent with the formation of a silver mirror.

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

(ii) Methanoic acid is also oxidized to carbon dioxide and water by Fehling`s solution with the formation of red precipitates of copper(I)oxide.

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

(iii) Etanedioic acid is oxidized to carbon dioxide by warm potassium manganate(VII) solution acidified with dilute sulphuric acid. In this reaction, the purple colour of $KMnO_4$ is changed into a light pink colour due to its reduction into manganese(II) ions.

$$(COOH)_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

11.4.4 Comparing Strengths of Carboxylic acids, Phenols and Alcohols

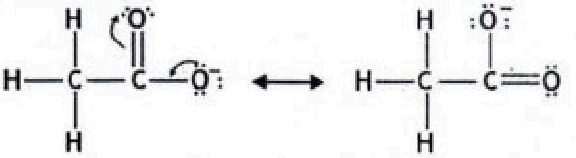
The relative strengths of weak acids are compared by their pK_a values. The smaller the pK_a value, the stronger the acid. The pK_a value of an acid depends on the stability of it conjugate base it forms after donating a proton.

$$CH_3COOH \qquad CH_3COO^- + H^+ \qquad pK_a = 4.76$$

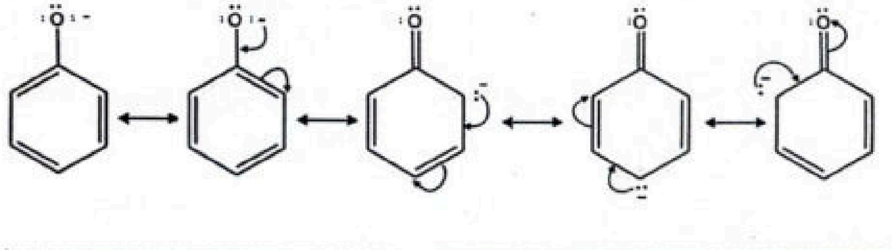
$$C_6H_5OH \qquad C_6H_5O^- + H^+ \qquad pK_a = 10$$

$$CH_3CH_2OH \qquad CH_3CH_2O^- + H^+ \qquad pK_a = \text{about } 16$$

Ethanoate ion is stabilized due to resonance. It spreads over the whole of the COO^- group between the two electronegative atoms.



Phenoxide ion is also stabilized due to resonance. A negative charge spreads over the ring but between less electronegative atoms. So, it is less stable than ethanoate ion. Phenols are, therefore, less acidic than carboxylic acids.



Ethoxide ion on the other hand has no delocalization of the negative charge. It will readily combine with H^+ to reform ethanol. So, ethanol is less likely to lose H^+ ions. It is hardly acidic. The acidic strength of these compounds is in the following order.

etanoic acid > phenol > ethanol

11.5 Reaction of Acyl chlorides

1. **Reaction of Acyl chlorides with alcohols (Formation of esters)**

Acyl halides react vigorously with alcohols at room temperature to produce esters. For example,

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$$

ethanoyl chloride   ethanol   ethylethanoate

$$C_6H_5COCl + CH_3CH_2OH \rightarrow C_6H_5COOCH_2CH_3 + HCl$$

benzoyl chloride   ethanol   ethyl benzoate

2. **Reaction of acyl chloride with phenol**

Acyl chloride reacts with phenol at room temperature to produce an ester.

$$CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$$

phenylethanoate

3. **Reaction with water (Hydrolysis)**

Acyl halides hydrolyse with water at room temperature to produce carboxylic acids and hydrochloric acid.

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$

4. **Reaction with ammonia (Formation of amides)**

Acyl halides react with ammonia at room temperature to produce amides. The hydrogen chloride produced reacts with excess ammonia to give ammonium chloride.

$$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$$

ethanamide

$$HCl + NH_3 \rightarrow NH_4Cl$$

5. **Reaction with primary and secondary amines (Formation of N-substituted amides)**

Primary and secondary amines react in a similar way as ammonia at room temperature to produce N-substituted amides. The hydrogen chloride reacts with excess amine to give ammonium salt.

$$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$$

ethanoyl chloride   methanamide   N-methylmethanamide

$$HCl + CH_3NH_2 \rightarrow [CH_3NH_3]Cl$$

Methyl ammonium chloride

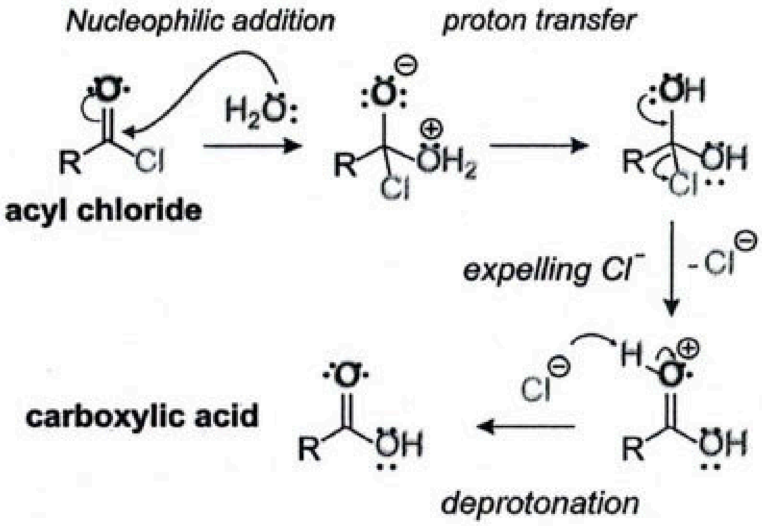
$$CH_3COCl + (CH_3)_2NH \rightarrow CH_3CONH(CH_3)_2 + HCl$$

N-methylmetanamide   N,N-dimethylmethanamide

$$HCl + (CH_3)_2NH \rightarrow [(CH_3)_2NH_2]^{+}Cl^{-}$$

dimethyl ammonium chloride

11.5.1 General mechanism of the reactions of acyl chlorides with nucleophiles



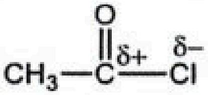
11.5.2 Comparison of Hydrolysis of Acyl chlorides , Alkyl chlorides, and Aryl chlorides

The ease of hydrolysis of these compounds is in the following order.

Acyl chlorides > Alkyl chlorides > Aryl chlorides

This trend can be explained on the basis of the strength of the C—Cl bond.

- In acyl chlorides, the carbonyl carbon atom is attached to two electronegative atoms (O and Cl), pulling electrons away. The carbonyl carbon is highly electron deficient. The nucleophile can easily attack it and displace the chlorine atom. So, the hydrolysis occurs most readily.

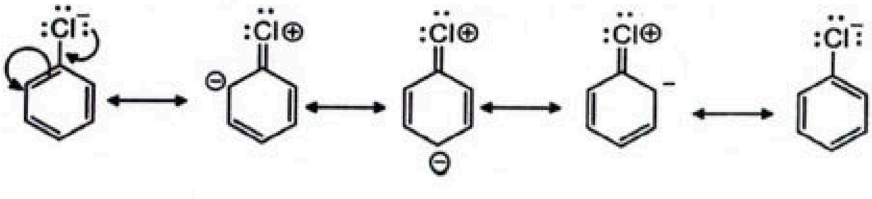


$CH_3—\overset{O}{\overset{\|}{C}}{}^{\delta+}—Cl^{\delta-}$

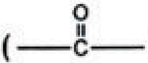
- In alkyl chlorides, the carbon atom is attached to only one electronegative atom, which pulls electrons away. The carbon atom is therefore less electron deficient than the carbonyl carbon atom. Hydrolysis requires a stronger nucleophile than water.

$$\overset{}{CH_3}—\overset{\delta+}{CH_2}—\overset{\delta-}{Cl}$$

- In aryl chlorides, the lone pair of chlorine is involved in resonance and is delocalized over the ring. The C-Cl bond, therefore has some double bond character. As a result, the C-Cl bond is difficult to break, even by a strong nucleophile. So, hydrolysis will not occur.



KEY POINTS

- Carboxylic acids are the most acidic simple organic compounds (pK_a ~ 5).
- The electron-withdrawing group bonded to the carbon atom next to the carboxyl group (COOH) makes the acid stronger.
- The carboxyl group shows the chemistry of both the carbonyl ( $-\overset{\overset{O}{\|}}{C}-$) and the hydroxyl of an ($-OH$) group.
- The $-OH$ group of carboxylic acids can be replaced by X, OR, and NH_2 to form halides, esters, and amides respectively.
- Phosphorus(III)chloride reacts with carboxylic acids at room temperature producing acyl chloride and phosphorus acid.
- Methanoic acid is oxidized to carbon dioxide and water by Tollen`s reagent with the formation of a silver mirror.
- Methanoic acid is also oxidized to carbon dioxide and water by Fehling`s solution with the formation of red precipitates of copper(I)oxide.
- Phenoxide ion is stabilized due to resonance. Ethoxide ion on the other hand has no delocalization of the negative charge.
- Acyl halides react vigorously with alcohols at room temperature to produce esters.
- Acyl chloride reacts with phenol at room temperature to produce an ester.
- Acyl halides hydrolyse with water at room temperature to produce carboxylic acids and hydrochloric acid.
- Acyl halides react with ammonia at room temperature to produce amides.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which reagent would you use to convert toluene to benzoic acid?

a) $KMnO_4$ and dilute acid
b) Fehling's solution
c) PCl_5
d) $SOCl_2$

ii. What is the main product of the reaction between acetic acid and PCl_5?

a) Ethyl acetate
b) Acetyl chloride
c) Acetic anhydride
d) Acetone

iii. Which of the following is a strong oxidizing agent for the oxidation of methanoic acid?

a) PCl_5 b) $SOCl_2$ c) $KMnO_4$ d) PCl_3

iv. In terms of acidity, which of the following is the most acidic?

a) Methanol b) Phenol c) Formic acid d) Benzoic acid

v. What happens when benzoyl chloride reacts with water?

a) Benzoic acid and HCl are formed.
b) Benzene and water are formed.
c) Phenol and water are formed.
d) Benzoate and water are formed.

vi. The mechanism by which acyl chlorides react with alcohols is:

a) Addition b) Elimination

c) Addition-elimination d) Substitution

vii. Which of the following acyl chlorides is expected to hydrolyze most readily?

a) Methyl chloride b) Acetyl chloride

c) Phenyl chloride d) Benzyl chloride

viii. When formic acid is oxidized, which of the following is formed?

a) Water only b) Carbon dioxide only

c) Methanol only d) Water and carbon dioxide

ix. The relative acidity of chlorinated carboxylic acids is primarily due to:

a) Increased stability of the conjugate base.

b) Electron-donating effects of the chlorine atom.

c) Lowering of the carboxylate pK_a.

d) Increased electron density around the carbonyl group.

x. The addition-elimination reaction mechanism of acyl chlorides involves:

a) Nucleophilic attack on the carbonyl carbon.

b) Addition of HCl to the carbonyl group.

c) Electrophilic substitution on the benzene ring.

d) Radical addition to the carbonyl group.

xi. Why are carboxylic acids more acidic than phenols and alcohols?

a) Carboxylic acids have a lower molecular weight.

b) Carboxylic acids are better at forming hydrogen bonds.

c) The carboxylate anion is resonance-stabilized.

d) Carboxylic acids have a higher boiling point.

xii. How does chlorine substitution affect the acidity of carboxylic acids?

a) It increases acidity by donating electrons.

b) It decreases acidity by withdrawing electrons.

c) It increases acidity by withdrawing electrons.

xiii. Which of the following statements about the addition-elimination mechanism of acyl chlorides is correct?

a) The nucleophile attacks the carbonyl carbon, forming a tetrahedral intermediate.

b) The nucleophile attacks the chlorine atom directly.

c) The reaction involves a free radical intermediate.

d) The acyl chloride first forms a carbocation intermediate.

xiv. What is the major difference in the oxidation products of ethanedioic acid and methanoic acid when treated with warm acidified $KMnO_4$?

a) Ethanedioic acid produces carbon dioxide, while methanoic acid produces formaldehyde.

b) Ethanedioic acid produces carbon monoxide, while methanoic acid produces carbon dioxide and water.

c) Ethanedioic acid produces carbon dioxide, while methanoic acid produces carbon dioxide and water.

d) Ethanedioic acid produces acetic acid, while methanoic acid produces carbon dioxide.

2. Short Answer Questions

i. Write the equation for the reaction of acetic acid with $SOCl_2$.

ii. Explain why methanoic acid can be oxidized while other carboxylic acids cannot.

iii. What products are formed when ethanedioic acid is oxidized with warm acidified $KMnO_4$?

iv. Describe the mechanism of acyl chloride hydrolysis with water.

v. What is the difference in reactivity between acyl chlorides and alkyl chlorides?

vi. Explain the influence of chlorine substitution on the acidity of carboxylic acids.

vii. What product results from the reaction of acyl chlorides with phenol?

viii. Methylbenzene can be oxidized to benzoic acid using hot, alkaline KMnO4 and then dilute acid.

  a. Describe the role of potassium permanganate in the oxidation of methylbenzene.
  b. Explain why the reaction mixture needs to be acidified after oxidation.

ix. Carboxylic acids can be converted to acyl chlorides using PCl_3, PCl_5 or $SOCl_2$.

  a. Write the balanced chemical equation for the reaction of acetic acid with PCl5.
  b. Compare the by-products formed when using PCl_3 and $SOCl_2$ for this conversion.

x. Methanoic acid can be oxidized by Fehling's solution, Tollen's reagent, acidified $KMnO_4$, or acidified $K_2Cr_2O_7$.

  a. Outline the changes observed when methanoic acid is treated with Tollen's reagent.
  b. Write the balanced chemical equation for the oxidation of methanoic acid with acidified $KMnO_4$.

xi. Carboxylic acids are generally more acidic than phenols and alcohols.

  a. Explain why carboxylic acids are more acidic than alcohols.
  b. Discuss the effect of electron-withdrawing groups on the acidity of carboxylic acids.

3. Long Answer Questions

i. Describe the process of converting toluene to benzoic acid using hot alkaline $KMnO_4$ and then dilute acid. Include the mechanism and discuss the reasons for the choice of reagent.

ii. Explain the relative acidities of carboxylic acids, phenols, and alcohols. Provide examples and discuss how substituents can affect acidity.

iii. Compare the reactivity and hydrolysis of acyl chlorides with alkyl and aryl chlorides. Explain the factors that affect their reactivity.

iv. Esters can be formed from alcohols and acyl chlorides, exemplified by the formation of phenyl benzoate. Write the balanced chemical equation for the formation of phenyl benzoate from benzoyl chloride and phenol.

v. Acyl chlorides hydrolyze rapidly in water, while aryl chlorides are resistant. Analyze the electronic structures of these compounds to explain this contrast in reactivity.

vi. Given three compounds: ethanoyl chloride, chloromethane, and chlorobenzene, predict which one hydrolyzes the fastest and explain your reasoning with reference to bond polarity and resonance.