

Chapter 20

Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution

Chapter 20 suggested problems: none

Class Notes

I. The functional derivatives of carboxylic acids

A. Acyl group: R-CO-

B. Closely related to each other and a number of other chemical families

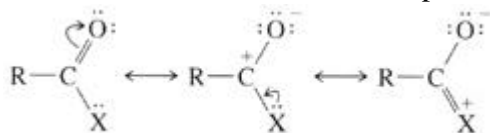
1. Acyl chlorides
2. Carboxylic acid anhydrides
3. Carboxylic acid esters
4. Amides (carboxamides)

C. Nomenclature

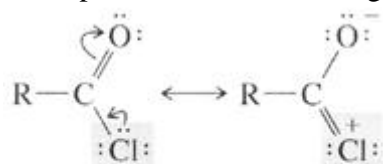
1. Acid halides: change "ic acid" to "yl halide"
 - a. Propanoic acid to propanoyl chloride
2. Acid anhydrides: change "acid" to anhydride
 - a. Benzoic acid to benzoic anhydride
3. Esters: change "ic acid" to "ate," preceded by name of alcohol or phenol group
 - a. Methyl ethanoate
4. Amides: change "ic acid" of common name or "oic acid" of IUPAC name to "amide"
 - a. Acetamide and ethanamide

D. Structure, electron delocalization, and resonance

1. All of the acid derivatives feature an atom attached to the acyl group with one or more lone pairs of electrons
2. Electron release (of a non-bonding pair) by the substituent results in resonance stabilization of the compound

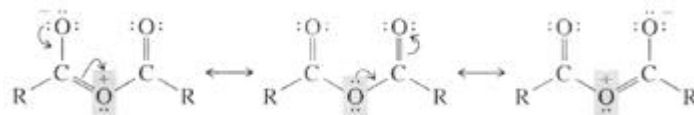


3. This stabilizes the carbonyl and decreases its electrophilic character
4. The extent of stabilization depends on the ability of the substituent to share its non-bonding pairs
5. In acid chlorides the long C-Cl bond length (180 pm) results in poor orbital overlap and ineffective sharing of chlorine's nbp

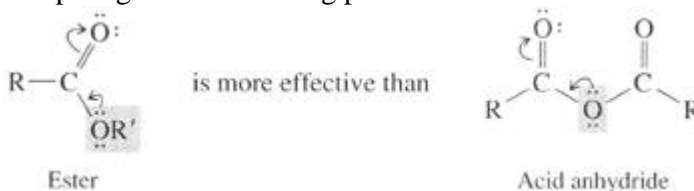


Weak resonance stabilization

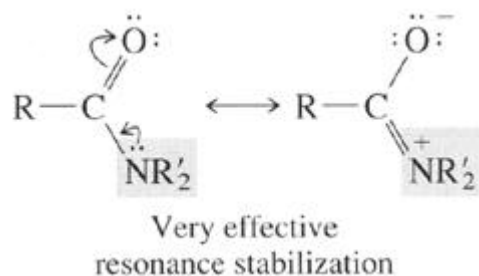
- a. At the same time, the EN of Cl effects electron distribution on the carbonyl carbon, making it relatively more susceptible to nucleophilic attack than the other acid derivatives
6. Acid anhydrides are better stabilized than acyl chlorides but the twin carbonyls both vie for the non-bonding pair



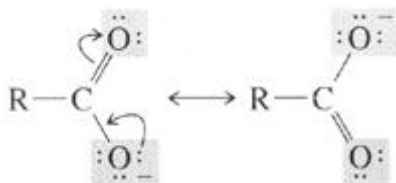
7. Esters are better stabilized than anhydrides because only one carbonyl is competing for non-bonding pair



8. Amides are better stabilized than esters



9. Carboxylate ions exhibit the greatest resonance stabilization of the acid derivatives



10. One acid derivative can be converted to another if the conversion results in a more stabilized carbonyl group

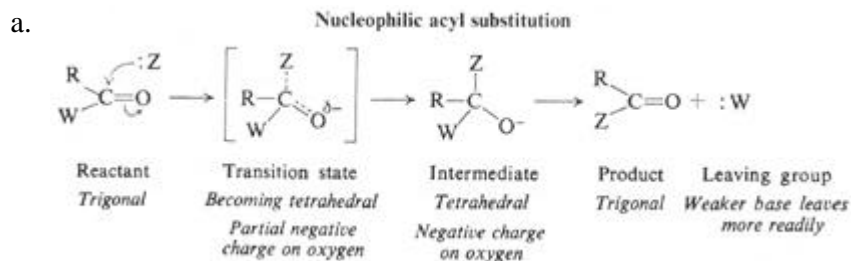
E. Physical properties

1. The acid derivatives are polar due to the carbonyl group
2. BP
 - a. Acid chlorides, anhydrides, and esters are similar to comparably sized aldehydes and ketones
 - b. Amides (1° & 2°) are capable of H-bonds and have high BP
3. Solubility
 - a. Aqueous solubility: 3-5 carbons for esters, 5-6 carbons for amides
 - b. Varying solubility in other polar solvents
4. Volatile esters have pleasant odors

II. Nucleophilic acyl substitution

A. Common denominators

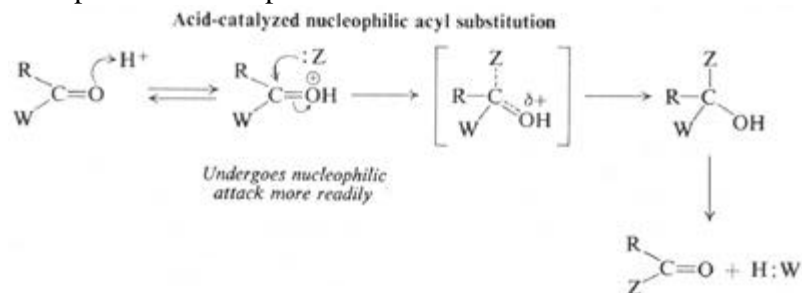
1. Each derivative is prepared (directly or indirectly) from the corresponding carboxylic acid and can be converted back by hydrolysis
2. Much of the chemistry of these compounds involves the conversion of the substances into their parent acids and into each other, although each class also has its distinct reactions
3. Acid derivatives retain the acid carbonyl group (although it may be temporarily lost during transition states), which determines the characteristic



i. The rate of the first step (from reactant to tetrahedral intermediate) is enhanced by electron-withdrawing substituents (on R) and can be hindered by electron-donating or bulky substituents

ii. The rate of the second step depends on the basicity of the leaving group (:W)

b. Acid-catalyzed nucleophilic substitution is enhanced by the protonation of the carbonyl, which makes the carbonyl carbon even more susceptible to nucleophilic attack



C. Nucleophilic substitution: alkyl vs. acyl

1. The carbonyl group makes acyl compounds more reactive than alkyl compounds
2. This is largely a matter of transition state geometry
3. The transition state of S_N2 substitutions involves a geometry change from tetrahedral to essentially trigonal bipyramidal, which is unstable in carbon compounds
4. The transition state of acyl substitutions involves a geometry change from trigonal planar to tetrahedral geometry, both of which are stable

III. Nucleophilic substitution reactions of acyl chlorides

- A. With carboxylic acids to form acid anhydrides
- B. With alcohols to form esters
- C. With ammonia and amines to form amides
- D. With water (hydrolysis) to form carboxylic acids and hydrohalic acid

IV. Nucleophilic substitution reactions of acid anhydrides

- A. With alcohols to form ethers
- B. With ammonia and amines to form amides
- C. With water (hydrolysis) to form two carboxylic acids

V. Nucleophilic substitution reactions of esters

- A. With ammonia and amines to form amides
- B. With water (hydrolysis) to form a carboxylic acid and an alcohol

VI. Nucleophilic substitution reactions of amides

- A. With water (hydrolysis) to form a carboxylic acid and an amine

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