

Summary Sheet: Two Key Concepts for Nucleophilic Substitution on Carbonyls plus a third bonus concept

Predicting the rate of reaction at a carbonyl and the fate of the resulting tetrahedral intermediate depend on understanding two key concepts: 1. The electronic nature of the atoms adjoining the carbonyl; 2. Steric bulk around the carbonyl.

Key Concept #1: The importance of electronic factors

Take the simplest carbonyl, formaldehyde. It undergoes one type of reaction: nucleophilic addition.



What happens when you substitute one of the hydrogens on formaldehyde for a different functional group?



The rate of the reaction will depend on two key factors:

1) Electronegative functional groups make the carbonyl carbon more electrophilic, which increases the rate of reaction with nucleophiles.



2) Donation of σ electrons by the R group makes the carbonyl carbon less electrophilic, which decreases the rate of reaction with nucleophiles.



Does this discussion seem familiar from electrophilic aromatic substitution? It should! It's the same principle! Recall from electrophilic aromatic substitution:

Strongly activating
NH₂, NHR, NR₂, OH, O⁻

Moderately deactivating
CO₂H, CO₂R, CH₃, OH, OR, OAr

Moderately activating
NHCO₂R, NHCO₂, OCH₃, OR

Strongly Deactivating
CF₃, CO₂

Weakly activating
CH₃, C₂H₅, R, C₆H₅

Trial of NO₂ and SO₃H, which are important in electrophilic aromatic substitution but not here. In general, carbonyl groups attached to these functional groups are too unstable toward hydrolysis to be synthetically useful.

Weakly Deactivating
F, Cl, Br, I

deactivating due to electronegativity but are *ortho*-directors

Note: look at the position of OH and O⁻. They are extremely strong σ -donors. This is why carbonyl groups are resistant to attack under basic conditions. Strong σ -donation by O⁻ into the carbonyl makes it extremely resistant toward nucleophilic attack.

Just like with electrophilic aromatic substitution, σ -donation humps electrophilicity. The stronger the σ -donor, the more resistant the carbonyl will be towards nucleophilic attack.

The presence of donating groups makes the carbonyl carbon less electrophilic and the carbonyl oxygen **more nucleophilic**. Recall these resonance forms:



The carbonyl is the most nucleophilic (and Lewis basic) site. Therefore, it is protonated first.

A good proxy for donating ability is pK_a, especially when the atom attached to the carbonyl is the same.

Example:



The tetrahedral intermediate can undergo further reaction:



How can you predict what will happen?

Leaving group ability is directly related to the pK_a of the conjugate acid.



Remember, however, that under basic conditions OH will be O⁻, which means it would have to leave as O⁻, an extremely bad leaving group.

Advice: Know your pK_a's cold. They are a great measure of leaving group ability and also of the electron donating ability of the conjugate base, which comes up **again and again** when discussing chemical reactivity.

Acidolyses and estolyses:

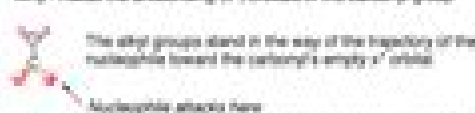


Key Concept #2: The importance of steric factors

Formaldehyde again, as the hydrogens are replaced with progressively bulkier groups, the reaction rate goes down.



Why? Recall the antibonding (π^*) orbitals of the carbonyl group:



The same concept applies for the rate of reaction of nucleophiles with esters and amides.



A final important concept: Lewis acids make carbonyls more electrophilic!



For example, in the Fischer esterification, the first step is protonation of the carbonyl and



The protonated carbonyl, which is now more electrophilic, reacts with the relatively weak nucleophile, the alcohol.



Note in this example that the reaction between the Lewis acid (HCl) and nucleophile (EtOH) is reversible under the reaction conditions, whereas using, say, a Grignard reagent would result in irreversible protonation of the nucleophile (i.e. no reaction). Compatibility between Lewis acids and nucleophiles is treated with more detail in advanced level organic chemistry courses.

In general: more nucleophilic = less electrophilic = faster rate of reaction with electrophiles = higher electron density = more Lewis basic (= less Lewis acidic) = more electron rich = less electrophilic
more electrophilic = less nucleophilic = faster rate of reaction with nucleophiles = lower electron density = less Lewis basic (= more Lewis acidic) = less electron rich = more electrophilic

* Recall: acylfluorides are the result of a thermodynamic equilibrium, while nucleophilicity is measured by reaction rate

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 - The Rise of Digital Reading Master Organic Chemistry Reaction Guide
 - Advantages of eBooks Over Traditional Books
2. Identifying Master Organic Chemistry Reaction Guide
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Master Organic Chemistry Reaction Guide
 - User-Friendly Interface
4. Exploring eBook Recommendations from Master Organic Chemistry Reaction Guide
 - Personalized Recommendations
 - Master Organic Chemistry Reaction Guide User Reviews and Ratings
 - Master Organic Chemistry Reaction Guide and Bestseller Lists
5. Accessing Master Organic Chemistry Reaction Guide Free and Paid eBooks
 - Master Organic Chemistry Reaction Guide Public Domain eBooks
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 - Master Organic Chemistry Reaction Guide Budget-Friendly Options
6. Navigating Master Organic Chemistry Reaction Guide eBook Formats

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 - Master Organic Chemistry Reaction Guide Enhanced eBook Features
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 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Master Organic Chemistry Reaction Guide
 9. Balancing eBooks and Physical Books Master Organic Chemistry Reaction Guide
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 - Creating a Diverse Reading Collection Master Organic Chemistry Reaction Guide
 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Master Organic Chemistry Reaction Guide
 - Setting Reading Goals Master Organic Chemistry Reaction Guide
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Master Organic Chemistry Reaction Guide
 - Fact-Checking eBook Content of Master Organic Chemistry Reaction Guide
 - Distinguishing Credible Sources
 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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