

4.3.1: Carbocation Structure and Stability

Objectives

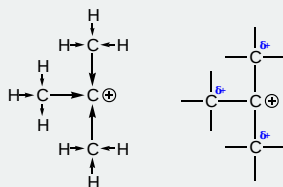
After completing this section, you should be able to

- describe the geometry of a given carbocation.
- arrange a given series of carbocations in order of increasing or decreasing stability.
- explain the relative stability of methyl, primary, secondary and tertiary carbocations in terms of hyperconjugation and inductive effects.

Study Notes

Although [hyperconjugation](#) can be used to explain the relative stabilities of carbocations, this explanation is certainly not the only one, and is by no means universally accepted. A more common explanation, involving the concept of an inductive effect, is given below.

It is a general principle in chemistry that the more a charge is dispersed, the more stable is the species carrying the charge. Put simply, a species in which a positive charge is shared between two atoms would be more stable than a similar species in which the charge is borne wholly by a single atom. In a tertiary carbocation, the positively charged carbon atom attracts the bonding electrons in the three carbon-carbon sigma (σ) bonds, and thus creates slight positive charges on the carbon atoms of the three surrounding alkyl groups (and, indeed, on the hydrogen atoms attached to them). Chemists sometimes use an arrow to represent this inductive release:



Note: These diagrams do not reflect the geometry of the carbocation. The overall charge on the carbocation remains unchanged, but some of the charge is now carried by the alkyl groups attached to the central carbon atom; that is, the charge has been dispersed.

In the tertiary carbocation shown above, the three alkyl groups help to stabilize the positive charge. In a secondary carbocation, only two alkyl groups would be available for this purpose, while a primary carbocation has only one alkyl group available. Thus the observed order of stability for carbocations is as follows:

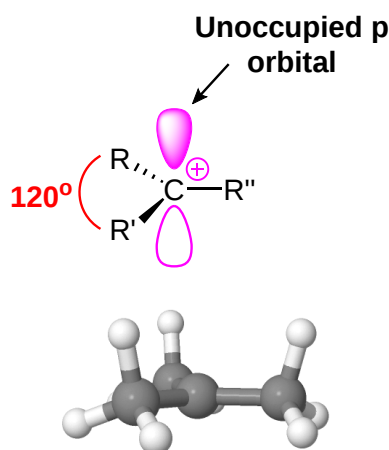
tertiary > secondary > primary > methyl.

Stability of carbocation intermediates

The next step in understanding why Markovnikov's rule is often followed in electrophilic additions, involves understanding the structure and stability of the carboncation intermediate formed during the mechanism.

Carbocation Structure

Carbocations typically have three substituents which makes the carbon sp^2 hybridized and gives the overall molecule a trigonal planar geometry. The carbocation's substituents are all in the same plane and have a bond angle of 120° between them. The carbon atom in the carbocation is electron deficient; it only has six valence electrons which are used to form three sigma covalent bonds with the substituents. The carbocation carbon has an unoccupied p orbital which is perpendicular to the plane created by the substituents. The p orbital can easily accept electron pairs during reactions making carbocations excellent Lewis acids.



Stability of Carbocation Intermediates

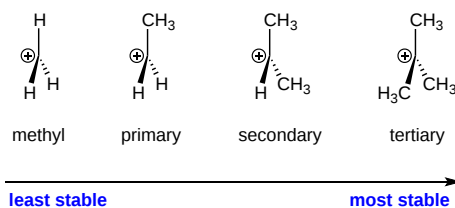
By being a reactive intermediate of the electrophilic addition mechanism, the stability of a carbocation has a direct effect on the reaction. The critical question now becomes, *what stabilizes a carbocation?*

A positively charged species such as a carbocation is very electron-poor, and thus anything which donates electron density will help to stabilize it. Conversely, a carbocation will be *destabilized* by an electron withdrawing group.



Extensive experimental evidence has shown that a carbocation becomes more stable as the number of alkyl substituents increases. Carbocations can be given a designation based on the number of alkyl groups attached to the carbocation carbon. Three alkyl groups is called a tertiary (3°) carbocation, 2 alkyl groups is called secondary (2°), and 1 alkyl group is called primary (1°). No alkyl groups are attached (3 hydrogen substituents) is called a methyl carbocation.

The overall order of stability is as follows:

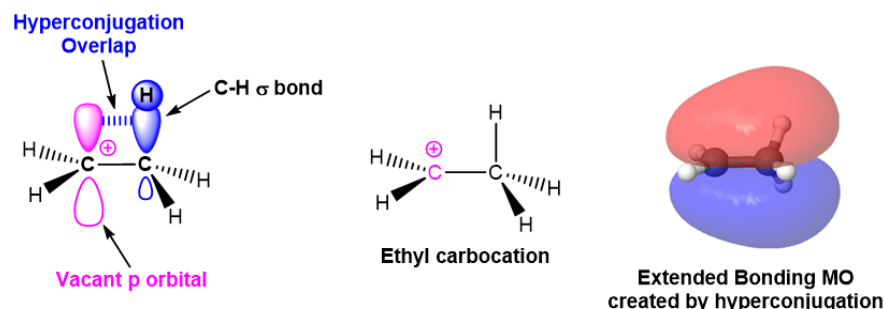


Alkyl groups stabilize carbocations for two reasons. The first is through inductive effects. As discussed in **Section 2-1**, inductive effects occur when the electrons in covalent bonds are shifted towards an nearby atom with a higher electronegativity. In this case, the positively charged carbocation draws in electron density from the surrounding substituents thereby gaining stabilization by slightly reducing its positive charge. Alkyl groups are more effective at inductively donating electron density than a hydrogen because they are larger, more polarizable, and contain more bonding electrons. As more alkyl groups are attached to the carbocation more inductive electron donation occurs and the carbocation becomes more stable.

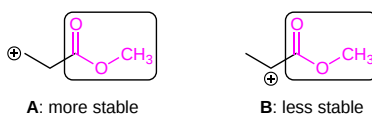
The second reason alkyl groups stabilize carbocations is through hyperconjugation. As previously discussed in **Section 7.6**, hyperconjugation is an electron donation that occurs from the parallel overlap of p orbitals with adjacent hybridized orbitals participating in sigma bonds. This electron donation serves to stabilize the carbocation. As the number of alkyl substituents increases, the number of sigma bonds available for hyperconjugation increases, and the carbocation tends to become more stabilized.

In the example of ethyl carbocation shown below, the p orbital from a sp^2 hybridized carbocation carbon involved interacts with a sp^3 hybridized orbital participating in an adjacent C-H sigma bond. Electron density from the C-H sigma bond is donated into carbocation's p orbital providing stabilization.

The molecular orbital of the ethyl carbocation shows the interaction of electrons in methyl group's C-H sigma bonds with the adjacent empty p orbital from the carbocation. The interaction creates a bonding molecular orbital which extends over the three atom chain (C-C-H) involved in hyperconjugation. The expanded molecular orbital helps to stabilize the carbocation.



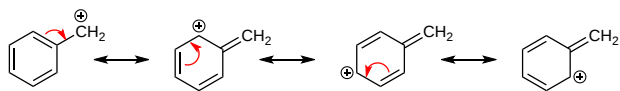
It is not accurate to say, however, that carbocations with higher substitution are *always* more stable than those with less substitution. Just as electron-donating groups can stabilize a carbocation, electron-withdrawing groups act to destabilize carbocations. Carbonyl groups are electron-withdrawing by inductive effects, due to the polarity of the C=O double bond. It is possible to demonstrate in the laboratory that carbocation A below is more stable than carbocation B, even though A is a primary carbocation and B is secondary.



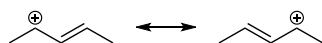
The difference in stability can be explained by considering the electron-withdrawing inductive effect of the ester carbonyl. Recall that inductive effects - whether electron-withdrawing or donating - are relayed through covalent bonds and that the strength of the effect decreases rapidly as the number of intermediary bonds increases. In other words, the effect decreases with distance. In species B the positive charge is closer to the carbonyl group, thus the destabilizing electron-withdrawing effect is stronger than it is in species A.

In the next chapter we will see how the carbocation-destabilizing effect of electron-withdrawing fluorine substituents can be used in experiments designed to address the question of whether a biochemical nucleophilic substitution reaction is S_N1 or S_N2 .

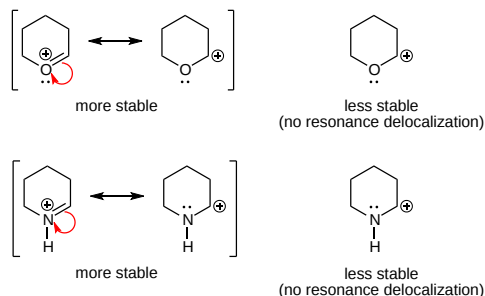
Stabilization of a carbocation can also occur through resonance effects, and as we have already discussed in the acid-base chapter, resonance effects as a rule are more powerful than inductive effects. Consider the simple case of a **benzylic** carbocation:



This carbocation is comparatively stable. In this case, electron donation is a resonance effect. Three additional resonance structures can be drawn for this carbocation in which the positive charge is located on one of three aromatic carbons. The positive charge is not isolated on the benzylic carbon, rather it is delocalized around the aromatic structure: this delocalization of charge results in significant stabilization. As a result, benzylic and **allylic** carbocations (where the positively charged carbon is conjugated to one or more non-aromatic double bonds) are significantly more stable than even tertiary alkyl carbocations.



Because heteroatoms such as oxygen and nitrogen are more electronegative than carbon, you might expect that they would by definition be electron withdrawing groups that destabilize carbocations. In fact, the opposite is often true: if the oxygen or nitrogen atom is in the correct position, the overall effect is carbocation stabilization. This is due to the fact that although these heteroatoms are electron *withdrawing* groups by induction, they are electron *donating* groups by resonance, and it is this resonance effect which is more powerful. (We previously encountered this same idea when considering the relative acidity and basicity of phenols and aromatic amines in [section 7.4](#)). Consider the two pairs of carbocation species below:



In the more stable carbocations, the heteroatom acts as an electron donating group by resonance: in effect, the lone pair on the heteroatom is available to delocalize the positive charge. In the less stable carbocations the positively-charged carbon is more than one bond away from the heteroatom, and thus no resonance effects are possible. In fact, in these carbocation species the heteroatoms actually *destabilize* the positive charge, because they are electron withdrawing by induction.

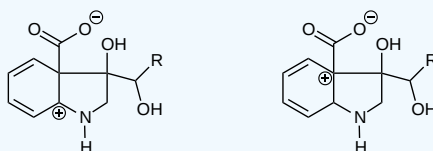
Finally, **vinyllic** carbocations, in which the positive charge resides on a double-bonded carbon, are very unstable and thus unlikely to form as intermediates in any reaction.



a vinyllic carbocation (very unstable)

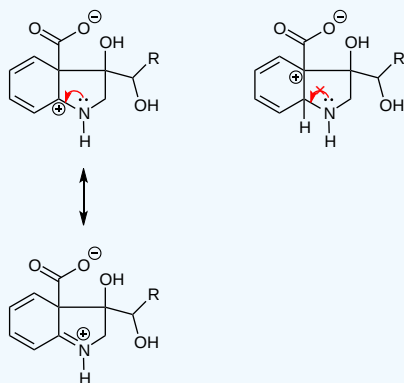
✓ Example 4.3.1.1

In which of the structures below is the carbocation expected to be more stable? Explain.



Answer

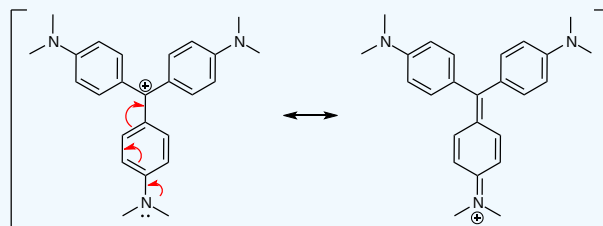
In the carbocation on the left, the positive charge is located in a position relative to the nitrogen such that the lone pair of electrons on the nitrogen can be donated to fill the empty orbital. This is not possible for the carbocation species on the right.



✓ Example 4.3.1.2

Draw a resonance structure of the crystal violet cation in which the positive charge is delocalized to one of the nitrogen atoms.

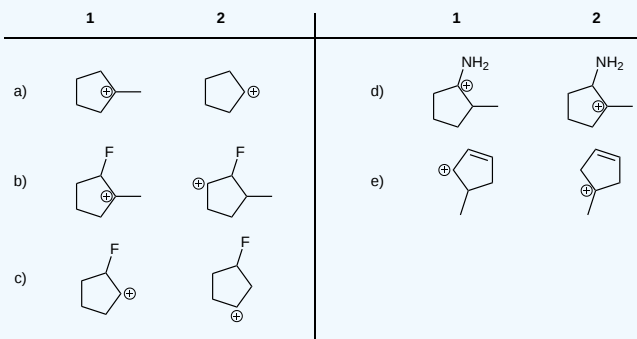
Answer



When considering the possibility that a nucleophilic substitution reaction proceeds *via* an S_N1 pathway, it is critical to evaluate the stability of the hypothetical carbocation intermediate. If this intermediate is not sufficiently stable, an S_N1 mechanism must be considered unlikely, and the reaction probably proceeds by an S_N2 mechanism. In the next chapter we will see several examples of biologically important S_N1 reactions in which the positively charged intermediate is stabilized by inductive and resonance effects inherent in its own molecular structure.

✓ Example 4.3.1.3

State which carbocation in each pair below is more stable, or if they are expected to be approximately equal. Explain your reasoning.



Answer

- 1 (tertiary vs. secondary carbocation)
- 1 (tertiary vs. secondary carbocation)
- 2 (positive charge is further from electron-withdrawing fluorine)
- 1 (lone pair on nitrogen can donate electrons by resonance)
- 1 (allylic carbocation – positive charge can be delocalized to a second carbon)

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