

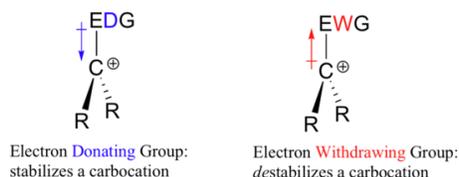
5.7: REACTIVE INTERMEDIATES - CARBOCATIONS

Learning Objective

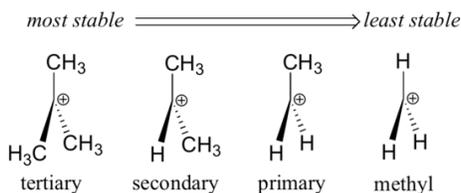
- describe the structure & relative stabilities of carbocations

CARBOCATIONS AND THEIR STABILITY

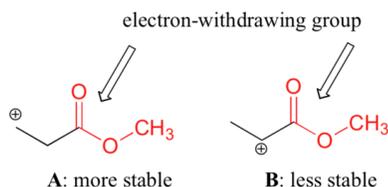
A **carbocation** is an ion with a positively-charged carbon atom. A carbocation is very electron-poor, and thus anything which donates electron density to the center of electron poverty will help to stabilize it. Conversely, a carbocation will be *destabilized* by an electron withdrawing group.



Alkyl groups are electron donating and carbocation-stabilizing because the electrons around the neighboring carbons are drawn towards the nearby positive charge, thus slightly reducing the electron poverty of the positively-charged carbon. What this means is that, in general, *more substituted carbocations are more stable*: a tert-butyl carbocation, for example, is more stable than an isopropyl carbocation. Primary carbocations are highly unstable and not often observed as reaction intermediates; methyl carbocations are even less stable.

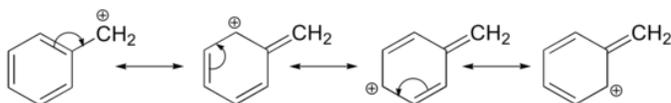


It is not accurate to say, however, that carbocations with higher substitution are *always* more stable than those with less substitution. Just as electron-donating groups can stabilize a carbocation, electron-withdrawing groups act to destabilize carbocations. Carbonyl groups are electron-withdrawing by inductive effects, due to the polarity of the C=O double bond. It is possible to demonstrate in the laboratory (see [section 16.1D](#)) 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.

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:

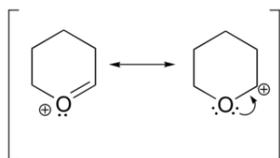


This carbocation is comparatively stable. In this case, electron donation is a resonance effect. Three additional resonance structures can be drawn for this carbocation in which the positive charge is located on one of three aromatic carbons. The positive charge is not isolated on the benzylic carbon, 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.



an allylic carbocation

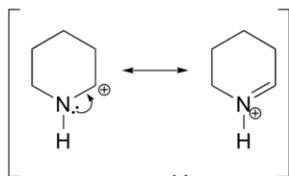
Because heteroatoms such as oxygen and nitrogen are more electronegative than carbon, you might expect that they would by definition be electron withdrawing groups that destabilize carbocations. In fact, the opposite is often true: if the oxygen or nitrogen atom is in the correct position, the overall 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:



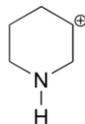
more stable



less stable
(no resonance delocalization)



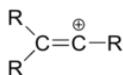
more stable



less stable
(no resonance delocalization)

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.

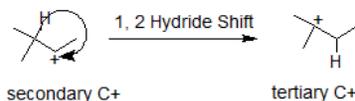
Finally, **vinylic** carbocations, in which the positive charge resides on a double-bonded carbon, are very unstable and thus unlikely to form as intermediates in any reaction.



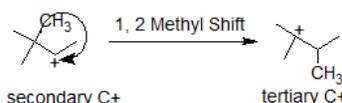
a vinylic carbocation
(very unstable)

CARBOCATION REARRANGEMENTS

Carbocations typically undergo rearrangement reactions from less stable structures to equally stable or more stable ones with rate constants in excess of 10^9 /sec. This fact complicates synthetic pathways to many compounds, so it is important to look for carbocation rearrangements anytime they are formed. It is possible for either a neighboring hydrogen atom or methyl group to shift to the carbocation to create a more stable intermediate. In the 1,2-hydride shift shown below, the secondary carbocation rearranges to a more stable tertiary carbocation. The numbers, 1,2- refer to the vicinal location of the rearrangement, not the nomenclature numbers.

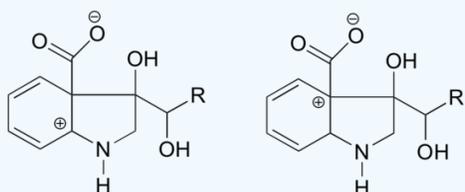


In this next example, the methyl group shifts to stabilize the carbocation.

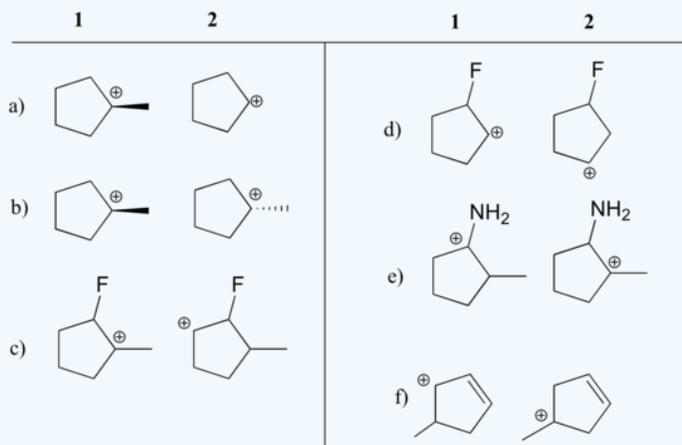


Exercise

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

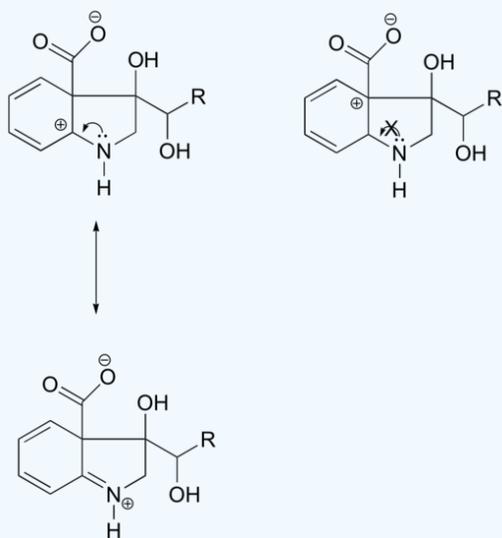


2. Draw a resonance structure of the crystal violet cation in which the positive charge is delocalized to one of the nitrogen atoms. State which carbocation in each pair below is more stable, or if they are expected to be approximately equal. Explain your reasoning.

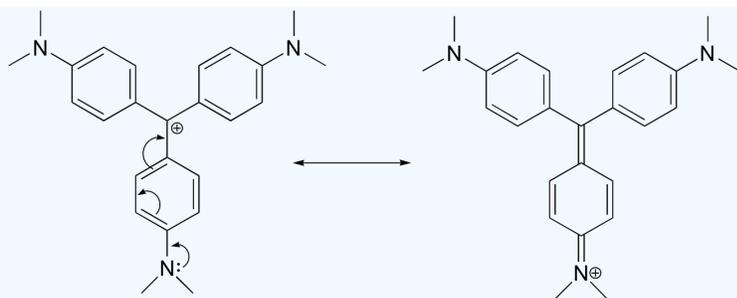


Answer

1. 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.



2.

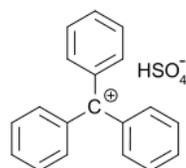


- 3.
- 1 (tertiary vs. secondary carbocation)
 - equal
 - 1 (tertiary vs. secondary carbocation)
 - 2 (positive charge is further from electron-withdrawing fluorine)
 - 1 (lone pair on nitrogen can donate electrons by resonance)
 - 1 (allylic carbocation – positive charge can be delocalized to a second carbon)

HISTORY

The history of carbocations dates back to 1891 when G. Merling[8] reported that he added bromine to tropyliene (cycloheptatriene) and then heated the product to obtain a crystalline, water-soluble material, C_7H_7Br . He did not suggest a structure for it; however, Doering and Knox[9] convincingly showed that it was tropylium (cycloheptatrienylium) bromide. This ion is predicted to be aromatic by Hückel's rule.

In 1902, Norris and Kehrman independently discovered that colorless triphenylmethanol gives deep-yellow solutions in concentrated sulfuric acid. Triphenylmethyl chloride similarly formed orange complexes with aluminium and tin chlorides. In 1902, Adolf von Baeyer recognized the salt-like character of the compounds formed.



He dubbed the relationship between color and salt formation halochromy, of which malachite green is a prime example.

Carbocations are reactive intermediates in many organic reactions. This idea, first proposed by Julius Stieglitz in 1899,[10] was further developed by Hans Meerwein in his 1922 study[11][12] of the Wagner-Meerwein rearrangement. Carbocations were also found to be involved in the S_N1 reaction, the $E1$ reaction, and in rearrangement reactions such as the Whitmore 1,2 shift. The chemical establishment was reluctant to accept the notion of a carbocation and for a long time the Journal of the American Chemical Society refused articles that mentioned them.

The first NMR spectrum of a stable carbocation in solution was published by Doering et al.[13] in 1958. It was the heptamethylbenzenium ion, made by treating hexamethylbenzene with methyl chloride and aluminium chloride. The stable 7-norbornadienyl cation was prepared by Story et al. in 1960[14] by reacting norbornadienyl chloride with silver tetrafluoroborate in sulfur dioxide at -80°C . The NMR spectrum established that it was non-classically bridged (the first stable non-classical ion observed).

In 1962, Olah directly observed the tert-butyl carbocation by nuclear magnetic resonance as a stable species on dissolving tert-butyl fluoride in magic acid. The NMR of the norbornyl cation was first reported by Schleyer et al.[15] and it was shown to undergo proton-scrambling over a barrier by Saunders et al.[16]

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