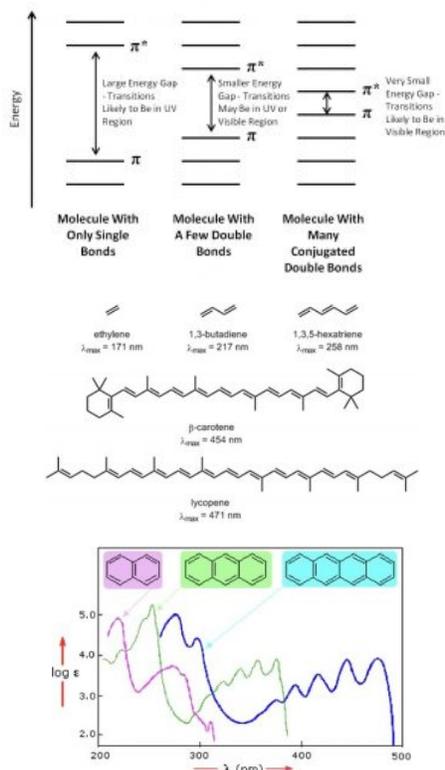


8.4: UV-VIS Spectroscopy and Conjugated Systems- Review

As you probably remember, the more atomic orbitals that combine to produce molecular orbitals, the smaller the energy gap between the MOs becomes. For example, an electron in an isolated pi bond absorbs energy in the far UV (~ 170 nm), a rather high energy. As we increase the number of conjugated double bonds, the energy gap between the orbitals (in fact the gap between the HOMO and LUMO) gets smaller and smaller, so that lower energy photons can bring about this transition. Eventually, the wavelength of light needed to promote an electron from highest occupied to the lowest unoccupied MO (HOMO \rightarrow LUMO) moves into the visible region, and the substance becomes colored. Note that its color does not represent the light that is absorbed, but rather the light that is transmitted or reflected. These conjugated regions of molecules are called chromophores.^[3] The longer the conjugated section of the molecule, the longer the wavelength that is absorbed. The compounds responsible for highly colored fruits and vegetables—such as lycopene and β -carotene, as well as your ability to see visible light (retinals) contain large chromophore regions.



Samples of UV-VIS absorption spectra are shown here (\rightarrow). Note that, in contrast with most other spectroscopic techniques (which usually produce sharp lines), the peaks in these spectra are more broad; the longer the conjugated section of the chromophore is, the longer the wavelength (and lower energy) that it absorbs. This means that each of these compounds has a different color. Moreover, the fact that the peaks in these spectra are not sharp means that UV-VIS spectroscopy is typically not used for identification of compounds. However, the amount of light absorbed is proportional to the concentration of the substance, so UV-VIS spectroscopy can be used to determine the concentration of samples. The visible spectrum runs from about 300 nm to 750 nm.

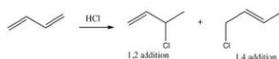
Reactions of Conjugated Systems: Kinetic and Thermodynamic Control of Reactions:

Now let us consider the reaction of 1,3-butadiene with a reagent such as HCl. Just as we saw with isolated alkenes, the first step in the reaction is the addition of the electrophile H^+ to produce the most stable carbocation. In this reaction, the proton adds to C-1; the resulting carbocation is resonance-stabilized with positive charge at both C-2 and C-4. The question, then, is: where does the nucleophile add?



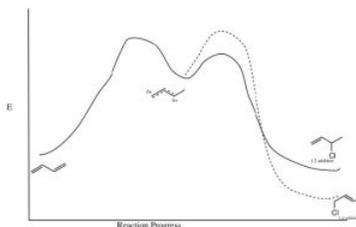
In fact, the position of equilibrium depends upon the conditions under which the reaction occurs. First, let us consider the two potential sites of attack. Attack at C-2 would mean that the reagent has added across the C-1/C-2 pi bond—this is called 1,2

addition. Attack at C-4 is called 1,4-addition and the two products are clearly different.

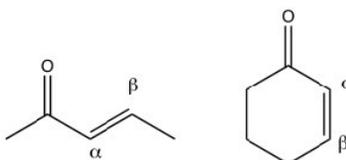


The partial positive charge at C-2 is located on a secondary carbon, whereas that on the C-4 is on a primary carbon. This means that the intermediate carbocation has more partial positive charge on C-2 than on C-4 and the transition state for the reaction to give the 1,2-addition product will have a lower activation energy than the transition state for the 1,4 product because it is more stabilized (by induction and hyper-conjugation). Therefore, the attack of the nucleophile (chloride) would occur faster at C-2; that is, 1,2 addition is the kinetically favored product.

However, if we consider the 1,4-addition product, the alkene product itself is more substituted (there are two alkyl groups on the double bond) and, therefore, it is more stable than the product of 1,2 addition. Even though the 1,4-addition product is formed more slowly through a less-stabilized transition state, the product itself is more stable; it is the thermodynamically favored product.

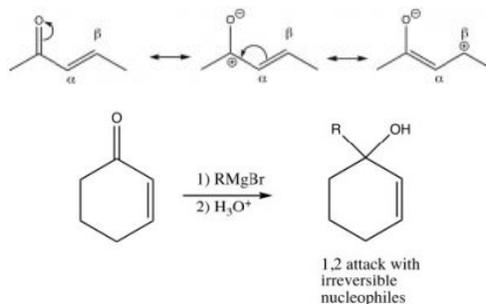


In fact, by controlling the reaction conditions, it is possible to produce either the kinetic or the thermodynamic product. If the reaction is run at relatively low temperature, there will not be enough energy to overcome the activation energy barrier associated with the 1,4-addition product reaction and the kinetic (1,2) product will be produced. However, at higher temperatures, there is enough energy; the 1,4 activation energy barrier will be reached more often, so that even if the kinetic product is formed, the fact that the reaction is reversible will, over time, lead to the most stable product accumulating at equilibrium. It is important to note that the most stable product is not always formed—it depends upon reaction conditions.

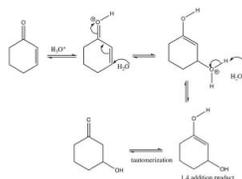


Conjugated carbonyl compounds:

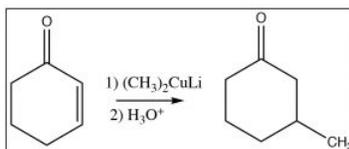
Carbonyl compounds can also be conjugated with carbon-carbon double bonds. These compounds are often referred to as α,β unsaturated carbonyls (the carbon next to the carbonyl carbon is termed the alpha carbon). By drawing resonance forms for this system, we see that there is a partial positive charge on the carbonyl carbon and on the β carbon. This means that α,β unsaturated carbonyl compounds are susceptible to nucleophilic attack at both the $C=O$ and at the β carbon. Which is analogous to the 1,2- and 1,4-additions to conjugated dienes.



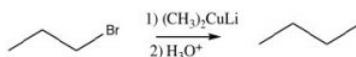
Just as the 1,3-conjugated diene case, attack at the carbonyl carbon is the kinetically preferred product since there is more positive charge there and the reaction is faster. Reagents that attack carbonyls irreversibly, such as grignards, alkyl lithiums, or reducing agents such as LiAlH₄ will, therefore, tend to produce the product of attack at the carbonyl. This is the 1,2-addition product.



If we use a reversible nucleophile (ROH, H₂O, RNH₂), then the most thermodynamically stable product will predominate, that is, the product of 1,4 addition. However, this product undergoes a tautomerism^[4] that regenerates the carbonyl (which is the source of the stability—recall C = O bonds are very strong).



Another reagent that can produce a product resulting from attack at the beta carbon is a reagent that we have not seen yet, an organocuprate, otherwise known as the Gilman^[5] reagent, which consists of a complex of alkyl groups, copper, and lithium and has the generic formula R₂CuLi. The general reaction is shown here. The organocuprate has the two alkyl groups bonded to the copper species (formally Cu²⁺), but the carbon-copper bond is more covalent than ionic (the charge on the carbon is lower than on the equivalent Grignard or alkyl lithium reagent) and this makes attack at the beta carbon more likely.^[6]



Gilman reagents are also very useful because they can accomplish nucleophilic attack on alkyl halides, which does not occur with Grignard or alkyl lithium reagents.

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