

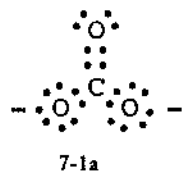
Electron Pushing

7

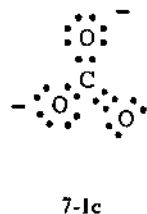
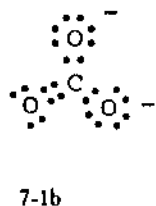
Electron pushing is an extremely powerful tool for understanding organic reaction mechanisms. The ability to push electrons can save you from having to fully memorize mechanisms — and can even help you work out mechanisms that are unfamiliar. Besides, this simple tool also serves to help organize and integrate the plethora of mechanisms encountered in a year-long course in organic chemistry.

Resonance Theory

Before using electron pushing in the context of reaction mechanisms, let us look at a simpler application in writing resonance structures. You may recall that there are occasions when a single Lewis structure does not adequately describe a molecule or ion. For example, the carbonate ion CO_3^{2-} (7-1) is known to have a planar structure in which all three carbon-oxygen bonds are identical. However, it's impossible to write a Lewis structure for this ion in which the octet rule is satisfied *and* all C-O bonds are the same. The best we can do is a structure such as 7-1a



which describes one C-O bond as a double bond and the other two as single bonds. Then, with a little fiddling around, we find that there are two more ways to write this ion, as shown in 7-1b and 7-1c:



These representations differ from 7-1a only in the placement of the double and single bonds. This situation arises because Lewis structures are not sophisticated enough to represent bonds that are *delocalized*, that is, those in which a given electron pair is associated with more than two nuclei. The concept of **resonance** saves us from having to discard or limit the use of this otherwise valuable theory. Ion 7-1 is described as being a (resonance) **hybrid** of the three contributing structures, 7-1a, 7-1b, and 7-1c. This relationship is generally denoted by double-headed arrows connecting the contributing structures.

⇒ When we say that a species is a resonance hybrid, this does not mean that the species switches back and forth among electron distributions. The species is a hybrid of constant structure in the same sense that a glass of pineapple-orange juice is a "hybrid" of pineapple juice and orange juice. (I suspect your friends would look at you strangely if you tried to convince them that your glass of pineapple-orange juice keeps switching back and forth between pineapple juice and orange juice...I know mine would.)

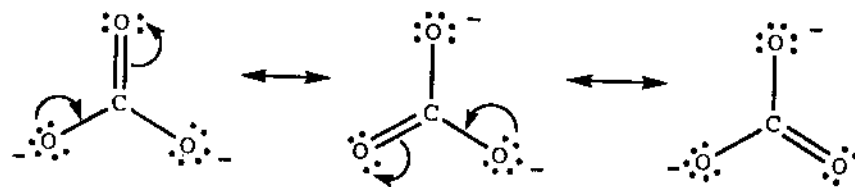
Electron Distribution

Between Single and Multiple Bonds

Electron pushing can help us recognize the existence of resonance contributors. In this role, it is simply a device for electronic bookkeeping. For example, starting with one of the carbonate ion resonance contributors, say 7-1a, and using a single line to represent each electron pair that represents a bond, we can generate a second contributor simply by shifting electron pairs between bonding and nonbonding positions, as indicated by the curved arrows shown in 7-1d.

⇒ Each curved arrow is an instruction to take the electron pair at the tail end of the arrow and move it to the head of the arrow.

For 7-1d this entails moving an electron pair from a nonbonding position on oxygen to a position in which it becomes a bond (actually part of a double bond) and then moving a second electron pair from a position in which it is part of a bond to a nonbonding position on another oxygen. In fact, those two curved arrows in 7-1d are the instructions for drawing another contributor, 7-1e. Likewise, the curved arrows on 7-1e instruct us in drawing yet another contributor, 7-1f.



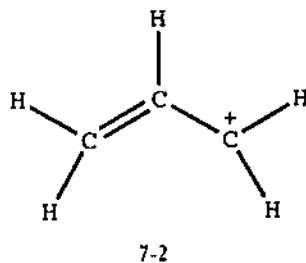
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Notice that in each case one of the curved arrows appears to chase the other, as do the arrows in 7-1d. You will find this "chasing" phenomenon to be generally true when you push electrons: A curved arrow that moves an electron pair away from a nucleus necessarily creates an electron deficiency at that nucleus, and the second curved arrow moves another pair in to satisfy the local deficiency. (See how the arrows in 7-1d and 7-1e that move a pair away from carbon to a non-bonding position on oxygen create an electron deficiency at carbon, which is in turn filled by moving a nonbonding pair to a bonding position on carbon.)

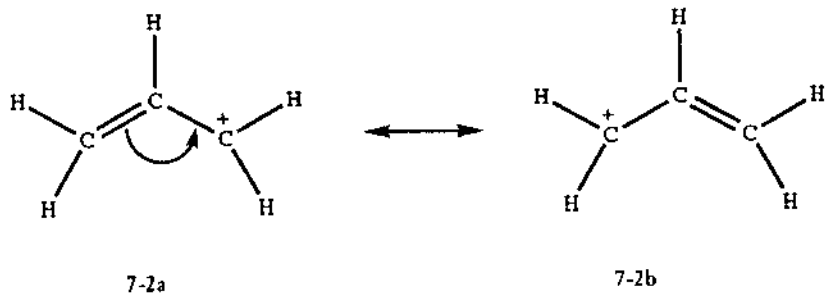
Before going on, put this book aside and try writing the structure of the carbonate ion, then putting in the curved arrows to generate the second (and then third) resonance contributor.

In Carbocations and Carbanions

Consider carbocation 7-2:

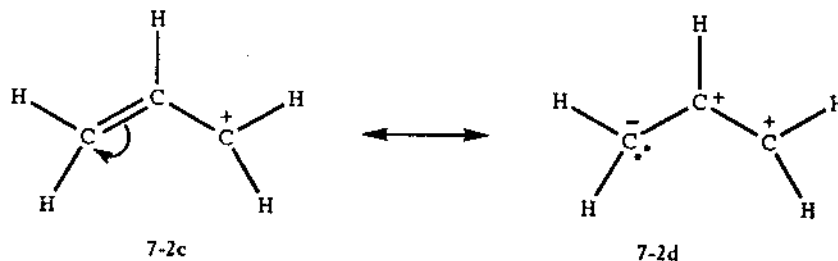


Clearly, there are pushable electrons in this species, but this time there is an already existing electron deficiency because the carbon at the right end has only six electrons around it. Pushing two electrons of the double bond toward the positively charged carbon, as in 7-2a, satisfies *this* electron deficiency but creates a new one at the leftmost carbon as in 7-2b:

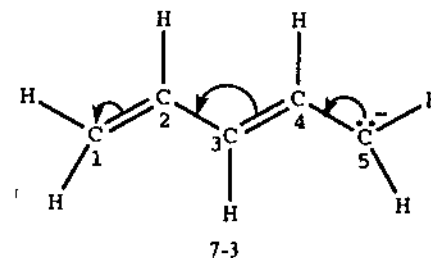


Lewis structures 7-2a and 7-2b are of *equal importance* in their contribution to the description of the actual structure of this ion. But what happens if we take the res-

onance structure 7-2a and try pushing electrons as in 7-2c? This generates the resonance contributor 7-2d, which is a much less important contributor because it has two additional (formal) charges and two like charges on contiguous carbon atoms.



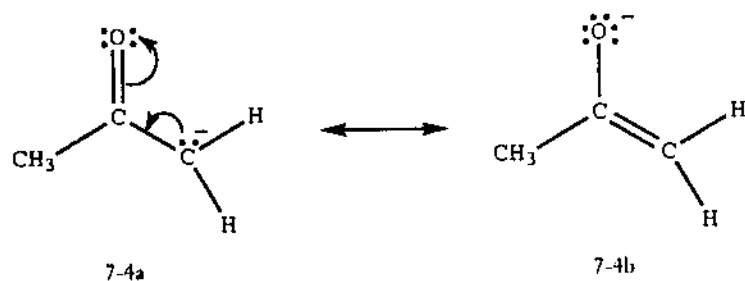
It will take some practice for you to get comfortable with electron pushing. The first step is to recognize the meaning of the curved arrow so that you can read another person's electron pushing. Try, for example, to draw the structure that the curved arrows in 7-3 direct you to draw:



If you have come up with a structure with the negative charge on carbon 1 and double bonds between carbons 2 and 3 and between 4 and 5, continue reading. Otherwise, stop and do Problems 7-1 through 7-4 for more practice.

Example 7-1: Describe the structure of the anion formed when 2-propanone $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$ is treated with a strong base.

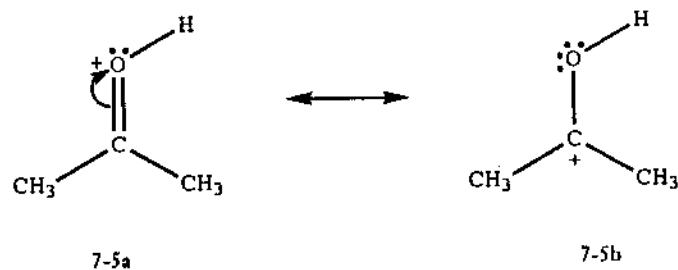
Solution: A strong base will remove a proton (hydrogen) from 2-propanone, leaving the electron pair that constituted the bond between that hydrogen and carbon. The anion 7-4a is generated, and a second resonance contributor, 7-4b, can be written as the curved arrows in 7-4a direct:



Both contributors 7-4a and 7-4b are important, although 7-4b appears to be more important because it places the negative charge on the more electronegative atom (oxygen rather than carbon). The existence of these two important contributors suggests that there are two sites of high electron density rather than one.

Example 7-2 When 2-propanone is treated with a strong acid, a cation results. Describe the structure of this cation.

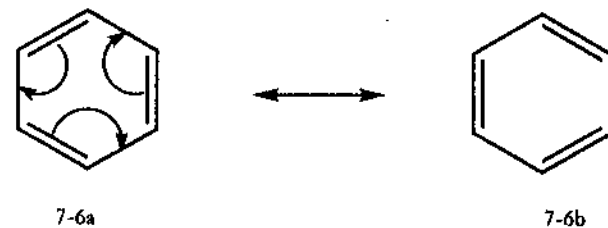
Solution: 2-Propanone will acquire a proton at its most basic site under these conditions, yielding cation 7-5a; pushing one electron pair of the carbon-oxygen double bond out onto oxygen generates a second resonance contributor 7-5b:



Both of these contributors are important. Contributor 7-5a has the advantage that all atoms (other than hydrogen) have a complete octet of electrons, but suffers from the disadvantage of having a positive charge on the highly electronegative oxygen. Contributor 7-5b is better in having the positive charge on carbon, but poorer in having a carbon with only six electrons around it. An interesting prediction that arises from this analysis is that protonation of 2-propanone (or any ketone) creates a cation having a highly electrophilic carbon, and therefore protonated 2-propanone is expected to be more reactive toward nucleophiles than is 2-propanone itself.

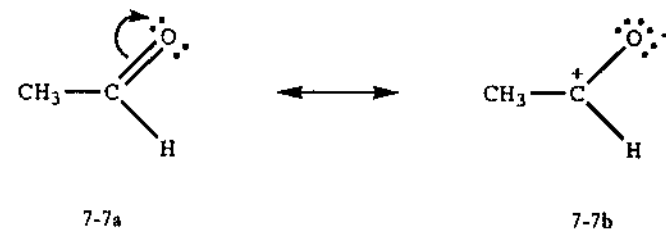
In Neutral Molecules

Electron pushing can also be used to generate resonance contributors for neutral molecules. The pushable electrons often come from double (or triple) bonds in this case. Benzene is a neutral molecule that can be represented by the two resonance contributors 7-6a and 7-6b:



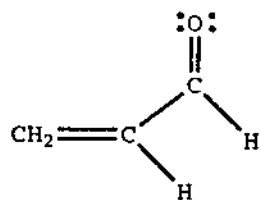
The two contributors are of equal importance, and the known structural parameters for benzene support this picture beautifully. For example, all six carbon-carbon bonds in benzene are of equal length and have a length between the normal values for carbon-carbon single and double bonds.

In some instances you may generate one or more resonance contributors from a neutral molecule but find that all of them have formal charges. (Of course the charges would have to add up to zero because the molecule is uncharged.) These charged contributors can be expected to make only minor contributions to the actual structure. However, they may provide additional insight into the electron distribution of the molecule in question. Ethanal (acetaldehyde), for example, is adequately represented by structure 7-7a, whereas 7-7b is of only minor importance:



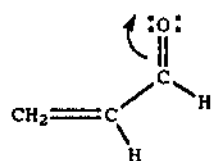
Still, 7-7b does emphasize the electrophilic nature of the carbonyl carbon in this compound.

Example 7-3 The carbonyl carbon in proenal, 7-8a, is not the only electrophilic site in this molecule. Locate a second electrophilic site.

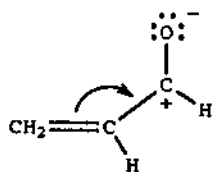


7-8a

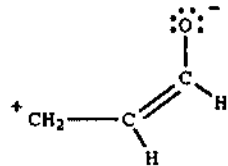
Solution: Pushing electrons as illustrated generates two more contributors, 7-8b and 7-8c:



7-8a



7-8b



7-8c

One of them (7-8c) suggests that the leftmost carbon (carbon 3) is also an electrophilic site.

Before going on, do the first four problems at the end of this chapter.

Mechanisms of Organic Reactions

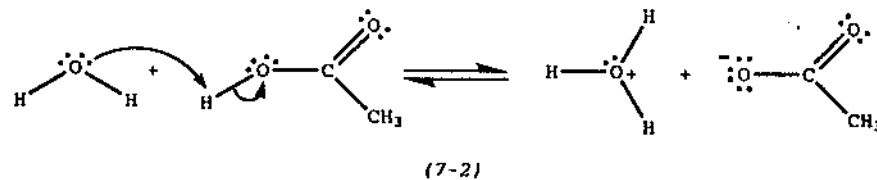
Acid-base theory à la G. N. Lewis

Now let us apply electron pushing to some chemical reactions. First, consider the acid-base reaction that occurs when a ketone is treated with a strong acid, as in equation (7-1):

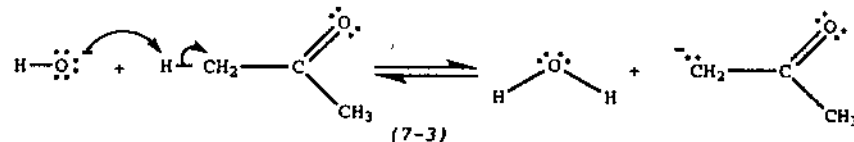


Notice that the curved arrow illustrates the direction of *electron pair movement* and that the Lewis octet rule is satisfied for all atoms (except hydrogen) in the products. Actually, the electrons don't leave the ketone. As a molecule of HCl approaches the ketone, the nonbonding electrons on oxygen form a bond to hydrogen. The H-Cl bond breaks, so the electrons of that bond end up on chlorine, which promptly leaves as a chloride ion.

There are an enormous number of chemical reactions with steps that resemble equation (7-1). In fact, most of the acid-base reactions you have already learned can be illustrated with curved arrows such as the ones drawn here. Notice the similarity to equation (7-1) of equations (7-2) and (7-3), emphasized by the curved arrows, despite the great differences in structure of the reactants:

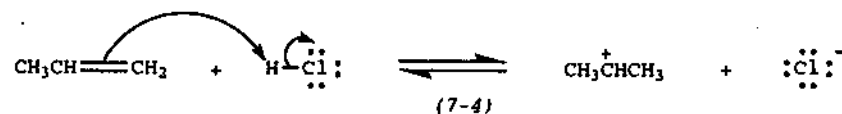


(7-2)



(7-3)

Also, as you encounter more organic reactions, you will see examples in which a double (or triple) bond functions as a base as in equation 7-4:



(7-4)

As you begin to use electron pushing in the context of chemical reactions, the primary rule to remember is that

it is always electrons that are being pushed.

With some practice, it will be easy to recognize (and avoid) incorrect uses of the curved arrows such as that illustrated in (partial) equation (7-5):



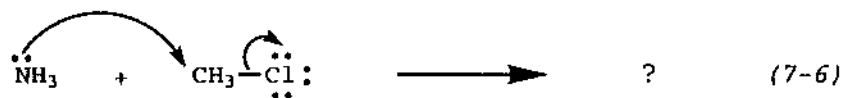
(7-5)

The key here is practice. Watch out for arrows that appear to push positive charge. This is a bit like moving a hole in the ground by trying to physically move the hole itself. Instead, you dig a second hole and throw the earth from creation of this new hole into the old one, thereby effectively "moving" it. At first, you should check your work to be sure that you have the same number of valence electrons on both sides of any equation. You should also make a habit of checking to see that the sum of the charges on the left side of the equation is equal to that on the right side.

Nucleophilic Substitution

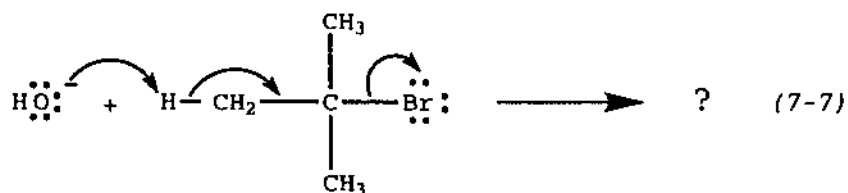
Let us look at a couple of examples illustrating the role of electron pushing in nucleophilic substitution.

Example 7-4 Complete equation (7-6) by filling in the reaction products, using the curved arrows as a guide.



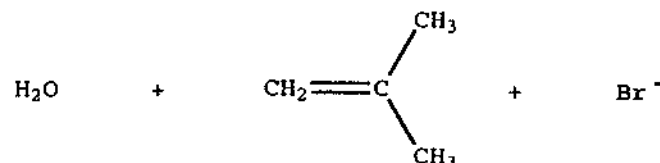
Solution: This is an example of a nucleophilic substitution reaction encountered in Chapter 5. One curved arrow moves the nonbonding electron pair on the nitrogen of ammonia toward the carbon of chloromethane, forming a carbon-nitrogen bond. The other arrow expresses the movement of one of the existing electron pairs around carbon (the one that constitutes the carbon-chlorine bond) away from carbon, a necessity because carbon would otherwise have ten valence electrons. This latter electron pair is pushed onto chlorine, which departs as chloride. This emphasizes that the leaving group serves to carry away the electron pair just as the nucleophile carries in a new electron pair. The products of this reaction, then, are CH_3NH_3^+ and Cl^- .

Example 7-5 Partial equation (7-7) illustrates the chemistry that occurs when 2-bromo-2-methylpropane is treated with potassium hydroxide (typically in a solvent such as ethanol). Fill in the products of this reaction.



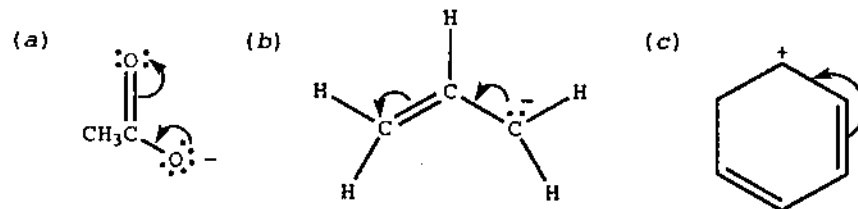
Solution: Since the curved arrows provide a "road map" to the product, you

need not be familiar with a particular reaction to write the products under these circumstances. This set of arrows says that hydroxide acquires a proton, thereby releasing an electron pair to form a new carbon-carbon double bond, which in turn requires the ejection of an electron pair. The products are water, 2-methylpropene, and bromide ion:

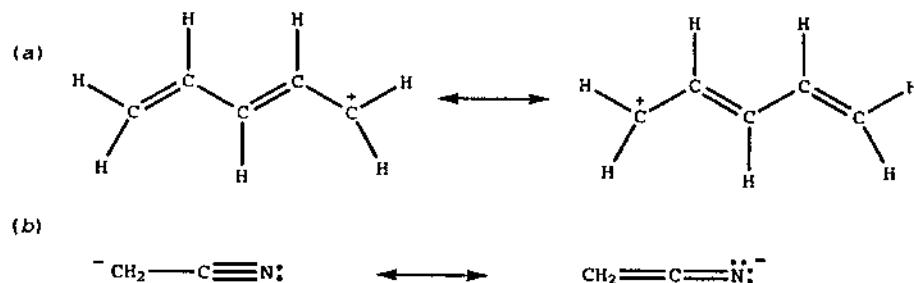


Problems

Problem 7-1: Use the instructions embodied in the curved arrows to draw a second resonance contributor for each of the following:

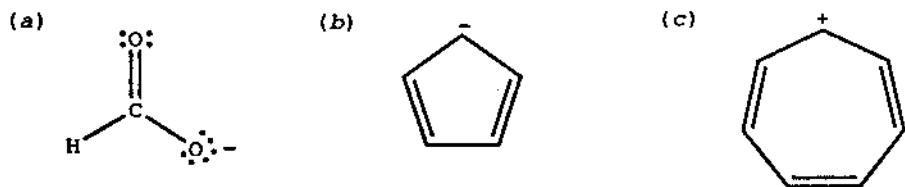


Problem 7-2: Fill in the curved arrows to show how the second resonance contributor is derived from the first. (The double-headed arrow is used to indicate that two structures are related as resonance contributors.)

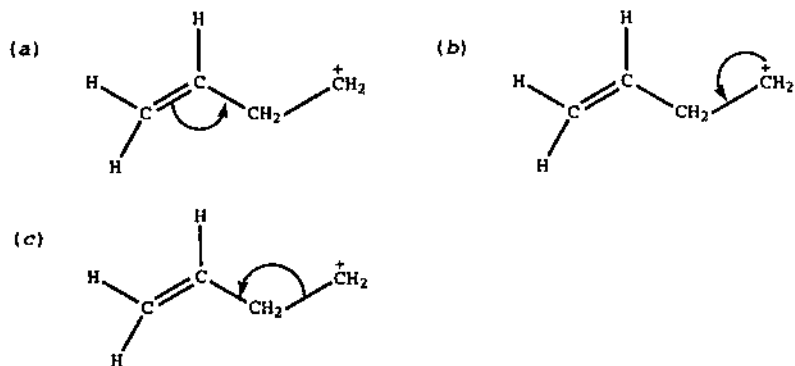




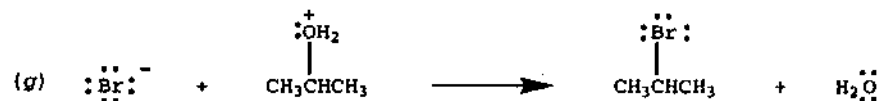
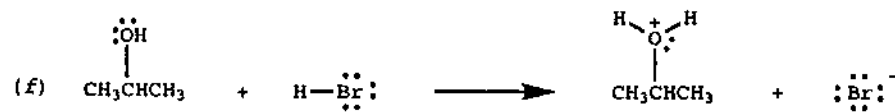
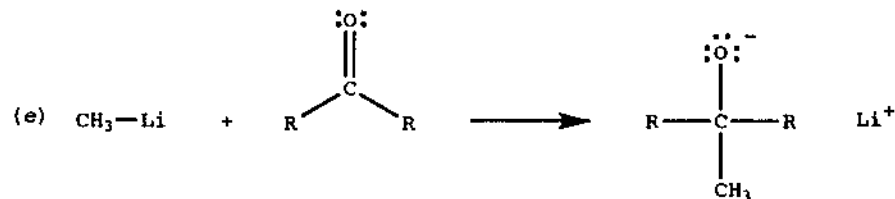
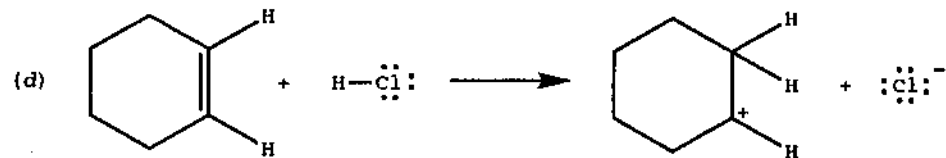
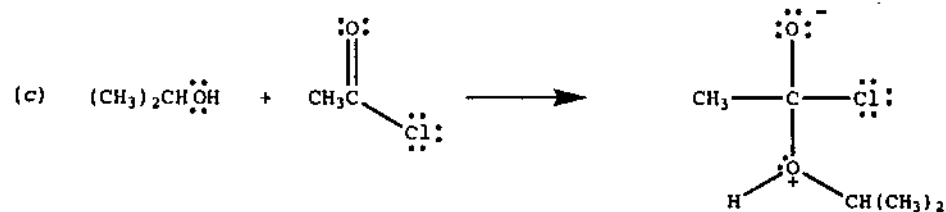
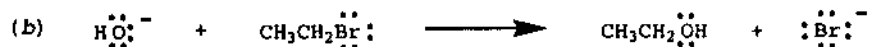
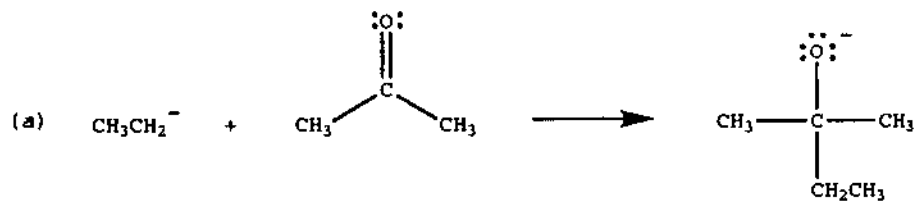
Problem 7-3: How many additional (important) resonance contributors can you draw for each of the following ions? Use curved arrows in generating your answers.



Problem 7-4: Explain why the electron pushing below is incorrect:

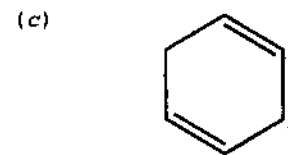
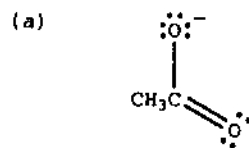


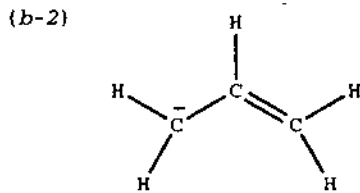
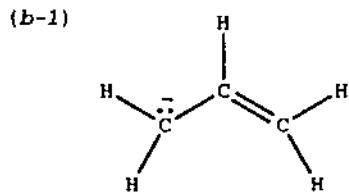
Problem 7-5: Some of the following equations appeared in Chapter 5. Fill in curved arrows as required for each:



Solutions

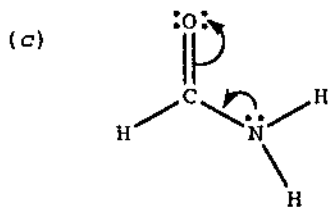
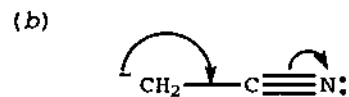
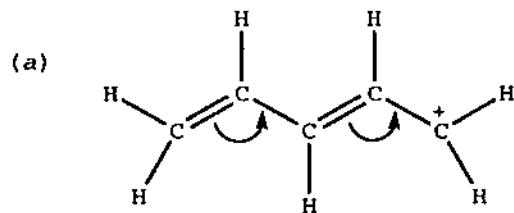
7-1:



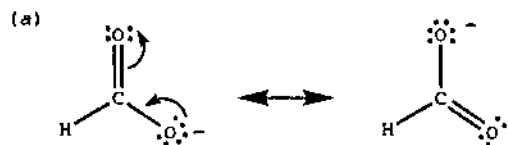


Notice that in (a) and (b-1) unshared pairs of electrons are shown even when a negative charge is also shown. Some chemists consider this redundant and use only the negative charge to represent the electron pair in question, as in (b-2). Often, individuals (including instructors, authors, and me) are not entirely consistent in this practice; this means that you will need to watch out for negative charges that are used to represent electron pairs. Watch for this in the remaining problems in this chapter, stopping to count how many electrons are around each atom in a given structure.

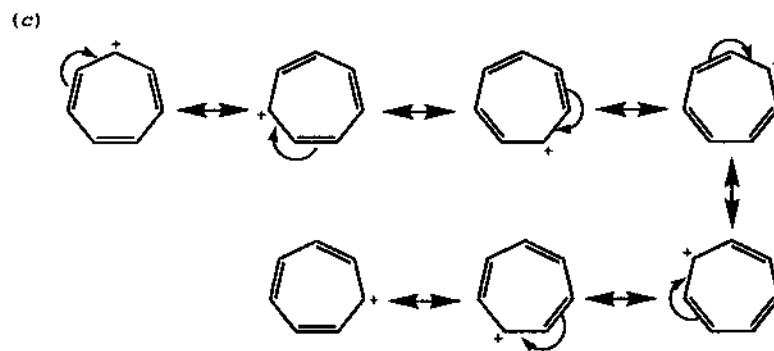
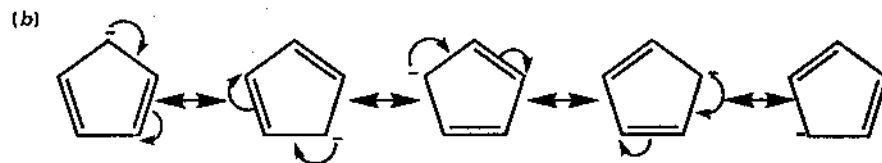
7-2:



7-3:



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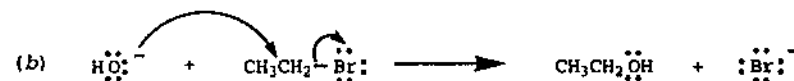
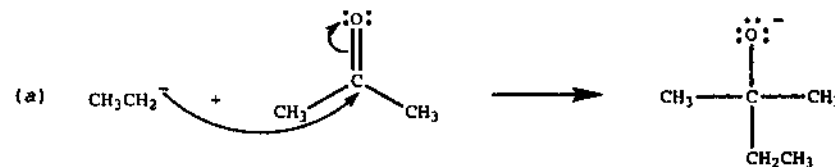
7-4:

(a) Electrons are being pushed toward a carbon that already has eight electrons around it.

(b) There are no electrons to push. Notice that the tail of the arrow is on a carbon that has only six electrons around it.

(c) The arrow appears to be indicating that the electron pair of one of the carbon-carbon bonds is being pushed in a way that suggests that these carbons are no longer bonded.

7-5:



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