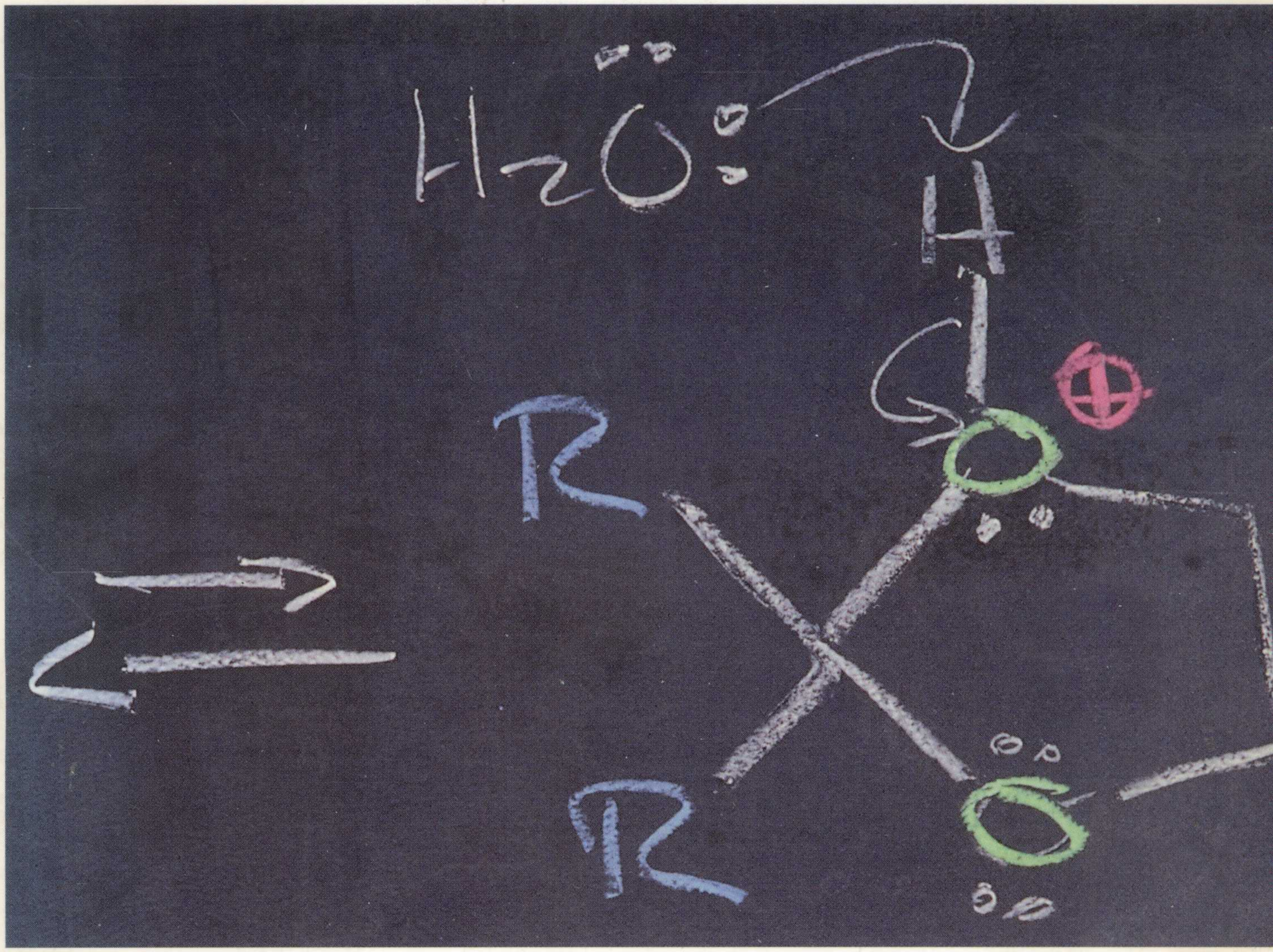
Organic Chemistry

study guide / solutions manual



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HENRY L. GINGRICH

Study Guide/Solutions Manual for Jones's Organic Chemistry

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Introduction

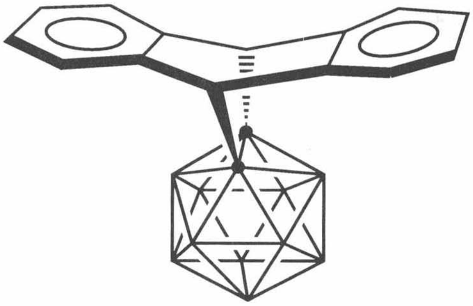
In this Study Guide we try to go beyond straightforward "bare bones" answers to problems. Once one gets past simple questions, problem solving in organic chemistry becomes very hard to teach. The answers to many problems are intuition-intensive, and therefore it becomes difficult to explain in explicit terms how to proceed. Nonetheless there are things that can be said that may help; there are techniques of problem solving that can be learned. In this collection of comments on solutions to all of the problems that are not solved in the text itself, we try to help you to do that. As in the text, we seek in these pages to show you how to approach problems in organic chemistry in general, not just how we got from here to there in specific cases.

The exercises in these chapters become much easier when we have an idea of where we are going. What exactly are we trying to do in this problem? What tasks must be accomplished? What bonds are we trying to make or break? What rings must be closed or opened? Such questions seem simple, but it is amazing how few people really start problems with the simple question: "What happens in this reaction?" Analyze! Once a goal is in mind, the path to that goal becomes much, much easier. In a sense, a good problem solver has learned, first and foremost, to avoid "thrashing." We know that is a flip remark, but it is, nonetheless, true. A person solving a tough problem is like a bacterium swimming up a food gradient—he or she (or it) is following a pathway that "feels good." We will try to show you how to do that in this Study Guide, but there can be no denying that experience is important, and experience can be gained only by practice. Practice and more practice will teach you what feels good in terms of problem solving—of how to swim up that food gradient—but we will try to give you some hints along the way.

The problems solved in the Study Guide will recapitulate each chapter, and thus will generally start off with the easier examples and then go on to tougher stuff. Don't worry if the hard problems at the end of the sections do not come so easily; they are meant to tax you, to demand some hard work and careful thought. Some difficult problems will be dealt with best over time. If a problem resists solution, and some will, come back to it after a while; let your subconscious work on it for a while. Most research chemists carry unsolved problems around in their heads for a long time, sometimes for years, returning to them now and then. There is nothing wrong with emulating that process. People think at vastly different rates, and it is a rare situation that requires a *rapid* solution of a problem. (Hour exams may be an exception, unfortunately.)

Many of us who actually do organic chemistry for a living (believe it or not there are such people) typically get great pleasure from problem solving. We hope that you will be similarly stimulated. In a fundamental way that is what we humans are about. We have evolved to be curious and to turn over rocks to see what is underneath. Perhaps, thinks our ancestral hunter-gatherer, I will find something good to eat! From such imperatives we humans have become problem solvers, and it gives us pleasure to work out what's happening in unknown situations.

The two of us have solved a good many problems together, and it is great fun. Here is one favorite example, which makes an important point about problem solving. This lesson is so simple as to be trivially obvious and yet at the same time so profound as to be most difficult in practice. We had been working for some time on the synthesis of the pterodactyl-shaped compound shown below.



One of us (MJ) had become entrapped in devising increasingly clever "solutions" that a series of graduate students and undergraduates had not been able to make work—and for good reasons. Those clever solutions were complicated, and extraordinarily hard to carry out in a practical sense. While MJ was away one July, HG had the wit to avoid all the foolish "cleverness" and to do what we beseech our students to do—to "think simple." HG went back to basics, did the work himself, and solved the problem. MJ arrived back in Princeton and was presented with a vial containing exquisitely beautiful crystals of the long-sought compound. What's the lesson? Don't be too clever. If you ground yourself in the basics, analyze what you want to do, and then apply those basics, you will prosper.

Remember, think simple.

Maitland Jones, Jr.
Henry L. Gingrich

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Chapter 1 Outline

1.1 Atoms and Atomic Orbitals
1.2 Covalent Bonds and Lewis Structures
1.3 Introduction to Resonance Forms
1.4 More on Atomic Orbitals

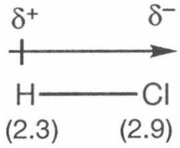
Contents

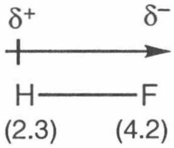
1

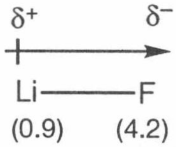
Atoms, Atomic Orbitals, and Bonding

In this chapter, you are learning a bit about atomic structure and acquiring skills that you will need throughout your study of organic chemistry. In a sense, you are learning vocabulary and grammar that will enable you to write sentences a little later, and eventually to compose whole paragraphs and short stories. The problems of this chapter concentrate on tool building and require less thought and imagination than those of later chapters. That does not mean that they are unimportant. Even though much of this chapter may review what you already know, please do not skip past it until you are certain that you can write Lewis structures easily, determine the position of charges without error, and use the arrow formalism to write resonance forms with ease. These skills will be as necessary in Chapter 26 as they are now.

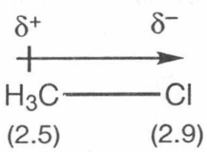
Problem 1.1 A bond dipole will result when two atoms of different electronegativities are attached to each other. This problem requires you only to look up the electronegativities of the two atoms in the bond. The electronegativity (Table 1.2, p 15) of each atom in the bond is shown in parentheses. As you see below, the atom of greater electronegativity will be at the negative end of the dipole. The answer uses an arrow to represent the direction of the dipole, $\delta^{+} \mapsto \delta^{-}$.

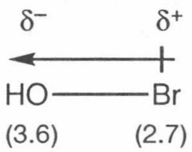


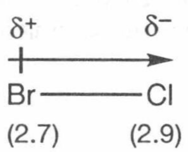




In fact, LiF can well be described as an ionic compound: $Li^{+}F^{-}$







Problem 1.2 This classic problem is asked in many textbooks. It requires you to estimate the net dipole in a molecule by summing the bond dipoles. In carbon tetrachloride (CCl_4), the four dipoles cancel, and there is no net dipole. In chloroform ($CHCl_3$), the dipoles do not cancel, and a net dipole exists.

Here, the four dipoles cancel..............................but in this molecule they do not

Problem 1.3 In each part of this problem, we will first determine the number of electrons available for bonding on each atom. For atoms in the second row of the periodic table, this will be the atomic number of the atom less the two 1*s* electrons. Then we will see how many bonds between atoms are possible using these electrons. Finally, be careful to write the left over nonbonding (lone pair) electrons as dots.

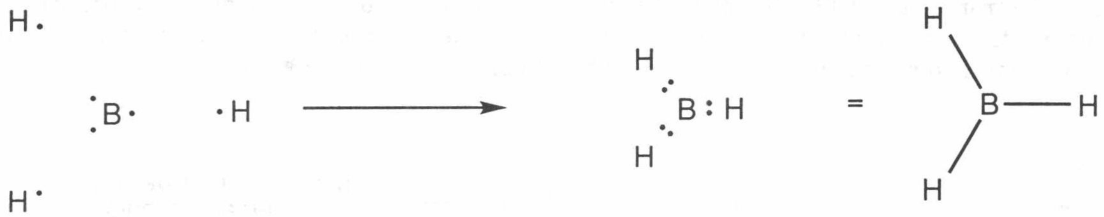
(b) H_2Be

Beryllium ($_4Be$) has two electrons available for bonding (4 – 2 1*s* electrons), and each hydrogen contributes one electron. Two beryllium-hydrogen single bonds are formed. There are no nonbonding electrons.

$$\mathrm{H\cdot} \quad \mathrm{\cdot Be\cdot} \quad \mathrm{\cdot H} \longrightarrow \mathrm{H\!:\!Be\!:\!H} = \mathrm{H{-}Be{-}H}$$

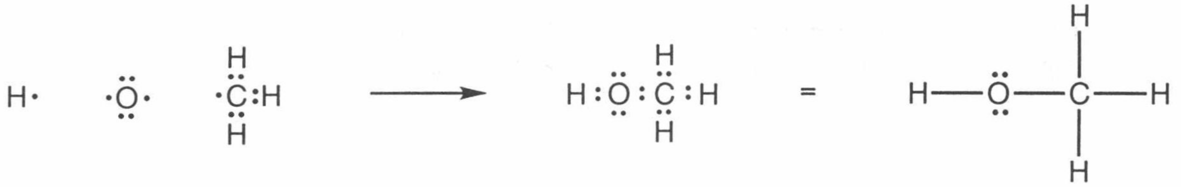
(c) BH_3

As in BF_3 (a), boron ($_5B$) has three electrons available for bonding, and each hydrogen contributes one electron. Three boron-hydrogen single bonds are formed.



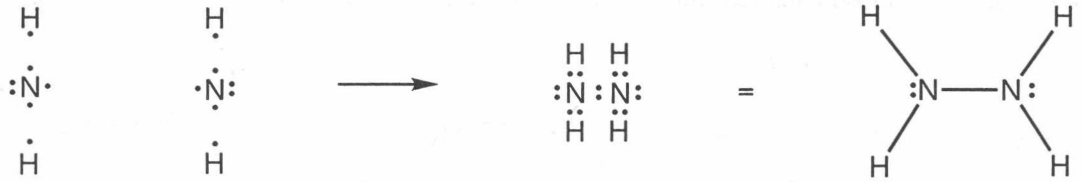
(e) $HOCH_3$

Oxygen ($_8O$) has six electrons available for bonding (8 – 2 1*s* electrons). Carbon forms three covalent single bonds with the three hydrogens, which leaves one carbon electron available for covalent bond formation between carbon and oxygen. Oxygen forms the carbon-oxygen bond as well as one covalent bond with hydrogen, leaving oxygen with two pairs of nonbonding electrons.



(f) $H_2N—NH_2$

Nitrogen has five electrons available for bonding. In this molecule, each nitrogen forms covalent bonds with two hydrogens and a third with the other nitrogen. This uses three of the available electrons, leaving a nonbonding pair of electrons on each nitrogen.



Problem 1.4

(c) Br

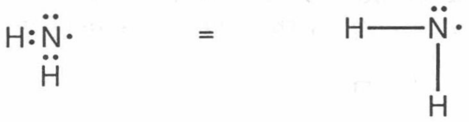
($_{35}$Br) is in the fourth row of the periodic table, so we can ignore the 28 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* electrons. This leaves seven electrons. Like the other halogens, (F, Cl, and I), Br has three nonbonding pairs and a single odd electron.

(d) OH

Oxygen ($_8$O) has six electrons available for bonding. One electron is used in forming a covalent bond with hydrogen, leaving two pairs of nonbonding electrons and a single odd electron on oxygen.

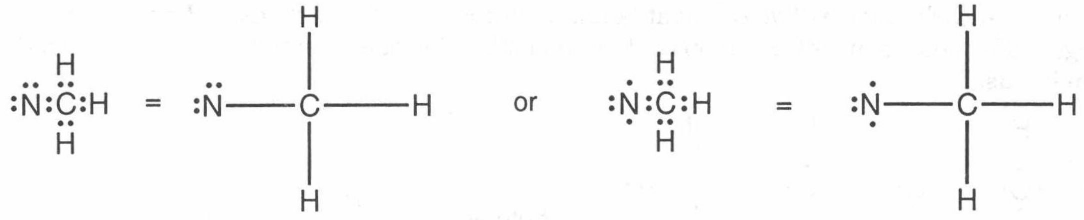
(e) NH_2

Nitrogen has five electrons available for bonding. Two covalent bonds are formed to hydrogens, leaving a nonbonding pair and a single odd electron remaining on nitrogen.



(f) $H_3C—N$

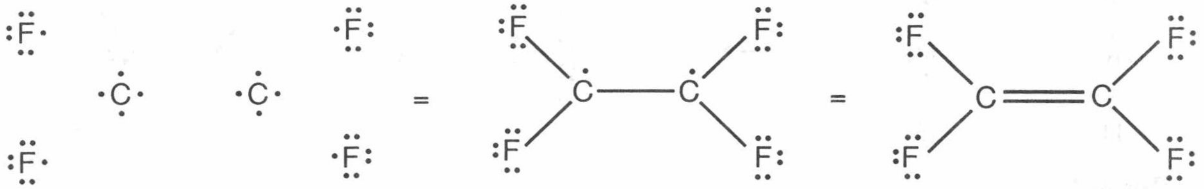
There are two possible answers to this one, and both kinds of molecule are known. Carbon has four electrons available for bonding. Three are used in forming single bonds to the three hydrogens, and the fourth is used in the single bond to nitrogen. Nitrogen has five electrons available for bonding. One covalent bond is formed to carbon, leaving four electrons. These can be used either as two pairs of nonbonding electrons or as one nonbonding pair and two odd electrons



Problem 1.5 The question itself helps with the hard part—working out the connectivity of the atoms. Once again, this is an exercise in electron counting. First, determine the number of electrons available for bonding (atomic number less two 1*s* electrons for most atoms, or a single 1*s* electron for hydrogen), then make single bonds. Finally, we look to see where multiple bonds can be formed.

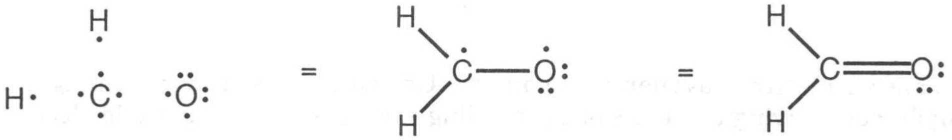
(a) F_2CCF_2

Carbon has four electrons available for bonding and fluorine seven, including a single odd electron. As in ethylene (Fig. 1.13), each carbon forms three covalent bonds, two with fluorines and one with the other carbon atom. Thus, there are three nonbonding pairs remaining on each fluorine, and a single electron left over on each carbon. These are shared in a second covalent carbon-carbon bond.



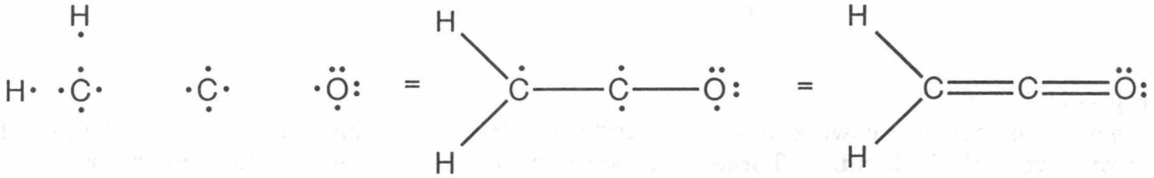
(c) H_2CO

Once again, carbon has four electrons available for bonding, and oxygen six. Carbon uses two electrons to form bonds to hydrogen, and one to bind to oxygen. Oxygen uses one electron in the bond to carbon, leaving one unshared electron on carbon, and five on oxygen. Formation of a second carbon-oxygen bond leaves two nonbonding electron pairs on oxygen.



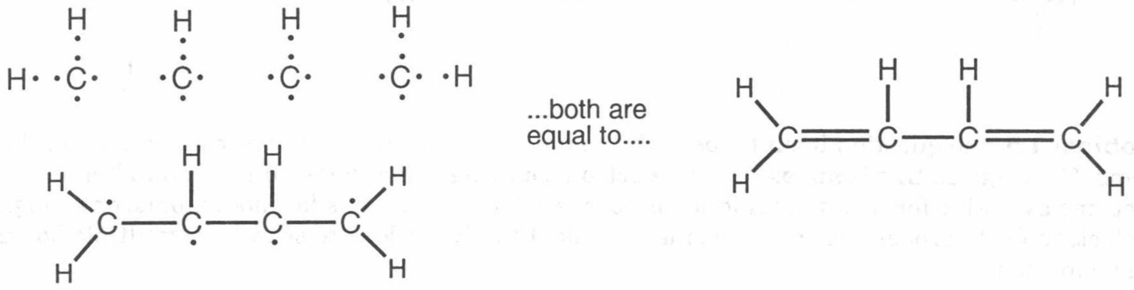
(d) H_2CCO

Each carbon has four available electrons, and the single oxygen six. The left-hand carbon uses three electrons to form three covalent bonds to the two hydrogens and the adjacent carbon. The right-hand carbon uses two electrons in forming covalent bonds with the left-hand carbon and the oxygen, leaving the left-hand carbon with one electron, the right-hand carbon with two, and the oxygen with five. Formation of a second carbon-carbon bond and a second carbon-oxygen bond completes the picture, leaving the oxygen with two nonbonding pairs of electrons.

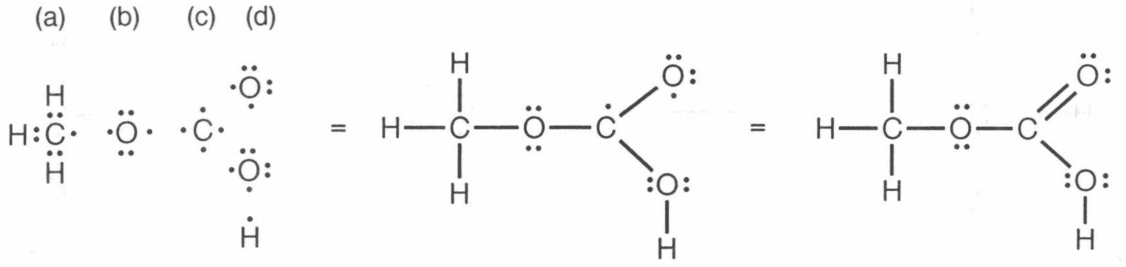


(e) $H_2CCHCHCH_2$

Each of the four carbons has four electrons available for bonding. The two terminal carbons form two covalent bonds with the two hydrogens and a third covalent bond with the adjacent carbon. Each internal carbon forms two covalent bonds with the adjacent carbons and a third to a hydrogen. This leaves one electron on each carbon, allowing the formation of two additional carbon-carbon bonds.



(g) $H_3COCOOH$
Each carbon has four available electrons for bonding, and each oxygen has six. The left-hand carbon (a) forms three bonds to hydrogen and a fourth to one oxygen (b). Oxygen (b) forms two bonds to a pair of carbons. The remaining carbon (c) forms covalent bonds with oxygen (b) and the two other oxygens (d). Each oxygen (d) forms a covalent bond with carbon (c), and one oxygen (d) forms a bond to hydrogen. This process leaves one odd electron on carbon (c) four electrons on the oxygen (d) bound to hydrogen, and five electrons on the non-hydrogen bound oxygen (c). Oxygen (b) has four electrons remaining. Formation of a carbon (c) oxygen (d) bond completes the picture.

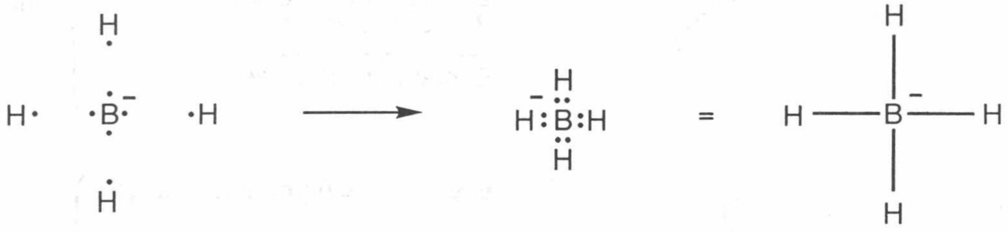


Problem 1.6 This problem is just like Problem 1.4 except that you need to make an adjustment for the charge. First, calculate the number of available electrons on the neutral atom, then add one electron for a negative charge or subtract one electron for a positive charge.

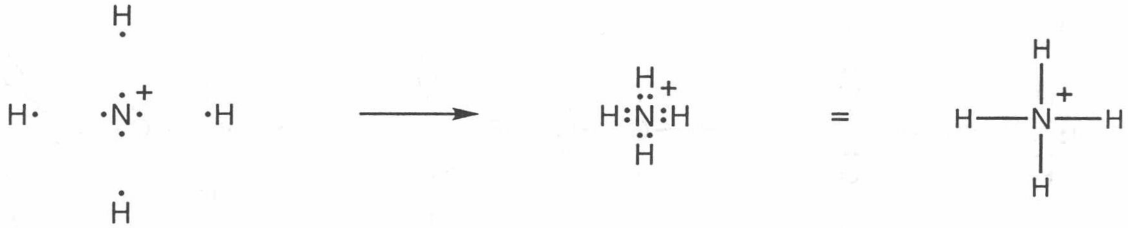
(a) HO^-
Neutral oxygen ($_8O$) has six electrons available for bonding ($8 - 2\ 1s = 6$). Therefore, negatively charged oxygen must have seven electrons.

One covalent bond can be made to the lone hydrogen, which supplies a single electron.

(b) $^-BH_4$
Neutral boron ($_5B$) has three electrons available for bonding ($5 - 2\ 1s$). Therefore, negatively charged boron must have four electrons, allowing four covalent bonds to be made to the four hydrogens, each of which supplies a single electron. Notice that there is no pair of electrons on the negatively charged boron atom. In most negatively charged species, there is a nonbonding pair of electrons. This molecule is an exception.

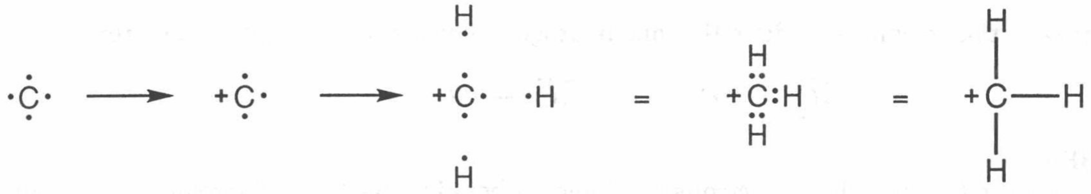


(c) $^{+}NH_4$
Neutral nitrogen ($_7N$) has five electrons available for bonding (7 – 2 1*s*). Positively charged nitrogen must have four electrons for bonding, allowing four single bonds to the four hydrogens, each of which supplies its single electron.



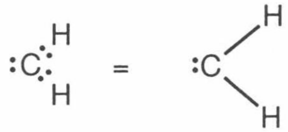
(d) ^{-}Cl
Neutral chlorine ($_{17}Cl$) has seven electrons available for bonding (ignore the 10 1*s*, 2*s*, and 2*p* electrons). Therefore, negatively charged chlorine must have 8 electrons.

(e) $^{+}CH_3$
Neutral carbon ($_6C$) has four electrons available for bonding (6 – 2 1*s*). Positively charged carbon must have only three electrons for bonding, allowing three single bonds to the hydrogens, each of which supplies its single electron.



Problem 1.7
In these examples we will first show a full Lewis structure in which each bonding electron appears as a dot, then a more schematic Lewis structure in which bonds are shown as lines and nonbonding electrons as dots. These structures will be followed by the charge calculation.

(a)



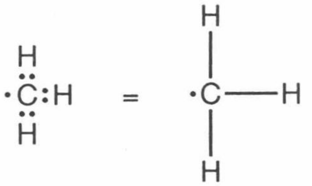
$_6C$ **6 protons = 6 positive charges**

2 1*s* electrons
2 nonbonding electrons
2 shared electrons

6 negative charges

neutral

(b)



$_6C$ **6 protons = 6 positive charges**

2 1*s* electrons
1 nonbonding electrons
3 shared electrons

6 negative charges

neutral

(c)

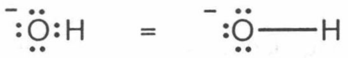
$_6$C **6 protons = 6 positive charges**

2 1*s* electrons
3 nonbonding electrons
1 shared electron

6 negative charges

neutral

(d)



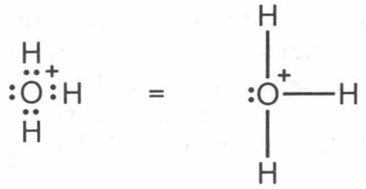
$_8$O **8 protons = 8 positive charges**

2 1*s* electrons
6 nonbonding electrons
1 shared electron

9 negative charges

net 1$^-$

(e)



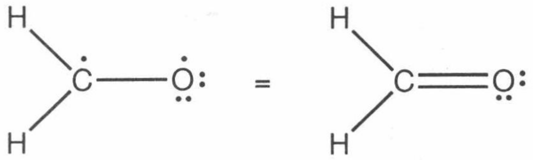
$_8$O **8 protons = 8 positive charges**

2 1*s* electrons
2 nonbonding electrons
3 shared electrons

7 negative charges

net 1$^+$

(f)



$_8$O **8 protons = 8 positive charges**

2 1*s* electrons
4 nonbonding electrons
2 shared electrons

8 negative charges

neutral

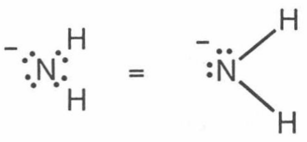
$_6$C **6 protons = 6 positive charges**

2 1*s* electrons
0 nonbonding electrons
4 shared electrons

6 negative charges

neutral

(g)



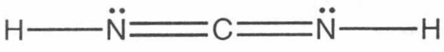
$_7$N **7 protons = 7 positive charges**

2 1*s* electrons
4 nonbonding electrons
2 shared electrons

8 negative charges

net 1$^-$

(h)



$_6C$ **6 protons = 6 positive charges**

2 1*s* electrons
0 nonbonding electrons
4 shared electrons

6 negative charges

neutral

$_7N$ **7 protons = 7 positive charges**

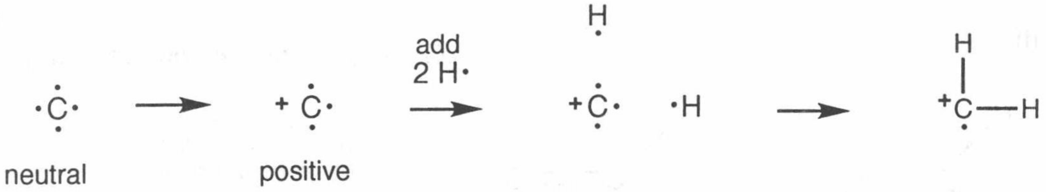
2 1*s* electrons
2 nonbonding electrons
3 shared electrons

7 negative charges

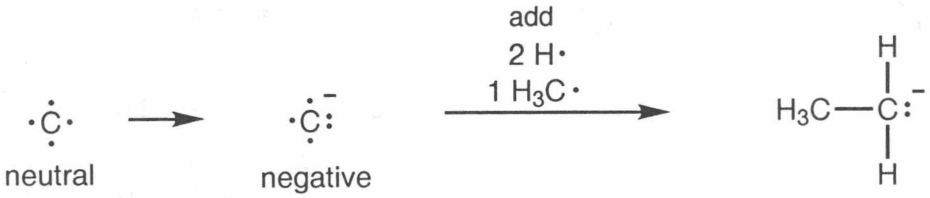
neutral

Problem 1.8 The task here is to work out the number of nonbonding electrons (if any) on the charged atom. Each answer first shows the neutral atom, then the atom with an electron added or removed to get the proper charge. Finally, electrons are used to make the bonds to the available hydrogen atoms or other groups. In (a) for example, we first see carbon with four bonding electrons ($_6C$; 6 electrons – 2 1*s* electrons = 4 bonding electrons), then with one electron removed to get ^+C; finally two of the remaining three electrons form single bonds to the two available hydrogens. This leaves $^+CH_2$ with a single nonbonding electron.

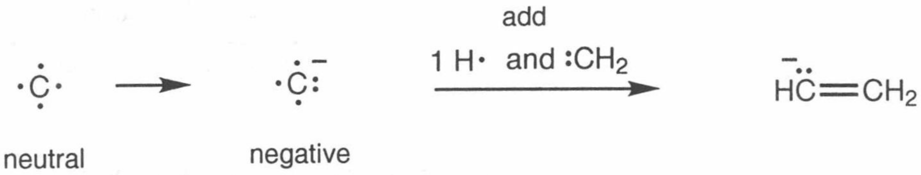
(a) $^+CH_2$



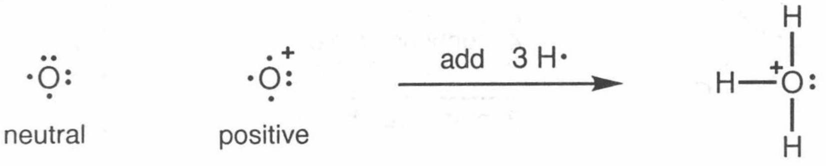
(b) $CH_3\bar{C}H_2$



(c) $H\bar{C}{=}CH_2$



(d) H_3O^+



(e) HO^-