# Chapter 14

# CARBON

## 14-1 Introduction

There are more known compounds of carbon than of any other element except hydrogen. Most are best regarded as organic chemicals. This chapter considers certain compounds traditionally considered "inorganic." Chapter 29 discusses organometallic or, more precisely, organoelement compounds in which there are bonds to carbon such as Fe—C, P—C, Si—C, and Al—C.

The electronic structure of C in its ground state is $1s^2 2s^2 2p^2$, so that to accommodate the normal four covalence the atom must be promoted to a valence state $2s2p_x2p_y2p_z$ (see Section 3-2). The ion $C^{4+}$ does not arise in any normal chemical process, but $C^{4-}$ may possibly exist in some carbides of the most electropositive metals.

Some cations, anions, and radicals have been detected as transient species in organic reactions. Certain stable species of these types are known. The ions are known as *carbonium* ions [e.g., $(C_6H_5)_3C^+$] or *carbanions* [e.g., $(NC)_3C^-$]. These species can be stable only when the charge is extensively delocalized onto the attached groups.

Divalent carbon species or *carbenes* ($:CR_1R_2$) play a role in many reactions, but they are highly reactive. Carbenes can be trapped by binding to transition metals and many metal carbene compounds are known (Section 29-17).

The divalent species of some other Group IVB(14) elements, such as $:SiF_2$ or $:SnCl_2$, can be considered to have carbene-like behavior.

A unique feature of carbon is its propensity for bonding to itself in chains or rings, not only with single bonds (C—C), but also with multiple bonds (C=C or C≡C). Sulfur and silicon are the elements next most inclined to *catenation*, as this self-binding is called, but they are far inferior to carbon. The reason for the thermal stability of carbon chains is the intrinsic high strength of the C—C single bond ($356$ kJ mol$^{-1}$). The Si—Si bond ($226$ kJ mol$^{-1}$) is weaker but another important factor is that Si—O bonds ($368$ kJ mol$^{-1}$) are much stronger than C—O bonds ($336$ kJ mol$^{-1}$). Hence, given the necessary activation energy, compounds with Si—Si links are converted very exothermically into ones with Si—O bonds.

## 14-2 The Chemistry and Physical Properties of Diamond, Graphite, the Fullerenes, and Carbides

### Diamond

Diamond differs from graphite in its physical and chemical properties because of differences in the arrangement and bonding of the atoms (Section 8-5). Diamond ($3.51$ g cm$^{-3}$) is denser than graphite ($2.22$ g cm$^{-3}$), but graphite is

more stable, by 2.9 kJ mol$^{-1}$ at 300 K and 1 atm pressure. From the densities, it follows that to transform graphite into diamond, pressure must be applied. From the thermodynamic properties of the allotropes it is estimated that they would be in equilibrium at 300 K under a pressure of about 15,000 atm. Because equilibrium is attained extremely slowly at this temperature, the diamond structure persists under ordinary conditions.

Diamonds can be produced from graphite only by the action of high pressure, and high temperatures are necessary for an appreciable rate of conversion. Naturally occurring diamonds must have been formed when those conditions were provided by geological processes.

In 1955 a successful synthesis of diamonds from graphite was reported. Although graphite can be directly converted into diamond at about 3000 K and pressures above 125 kbar, in order to obtain useful rates of conversion, a transition metal catalyst, such as Cr, Fe, or Pt, is used. It appears that a thin film of molten metal forms on the graphite, which dissolves some graphite and reprecipitates it as diamond, which is less soluble. Diamonds up to 0.1 carat (20 mg) of high industrial quality can be routinely produced at competitive prices. Some gem quality diamonds have also been made but the cost, thus far, has been prohibitive. Diamond will burn in air at 600–800 °C but its chemical reactivity is much lower than that of graphite or amorphous carbon.

### Graphite

Many forms of amorphous carbon (including charcoals, certain soots, and lampblack) are all actually microcrystalline forms of graphite. The physical properties of such materials are mainly determined by the nature and extent of their surface areas. The finely divided forms, which present relatively vast surfaces with only partially saturated attractive forces, readily absorb large amounts of gases and solutes from solution. Active forms of carbon impregnated with palladium, platinum, or other metals are widely used as industrial catalysts.

An important aspect of graphite technology is the production of very strong fibers by pyrolysis, at 1500 °C or above, of oriented organic polymer fibers (e.g., those of polyacrylonitrile, polyacrylate esters, or cellulose). When incorporated into plastics the reinforced materials are light and of great strength. Other forms of graphite, such as foams, foils, or whiskers, can also be made.

The loose layered structure of graphite allows many molecules and ions to penetrate the layers to form what are called *intercalation* or *lamellar compounds*. Some of these may be formed spontaneously when the reactant and graphite are brought together. The alkali metals, halogens, and metal halides and oxides (e.g., $FeCl_3$ and $MoO_3$) are examples of reactants.

### Fullerenes

The sootlike substances known as the fullerenes have already been introduced (Section 8-5). In the last few years there has been a remarkable explosion of papers in the chemical research literature on the fullerenes, and no doubt the topic will grow in scope as new discoveries are made. The reactions listed below represent only a portion of the emerging chemistry of the fullerenes. For this reason, the list of *Supplementary Reading* materials at the end of this chapter is more extensive than usual. The interested student is encouraged to consult not

only these sources, but also the latest research and review literature, as advances in this area are expected to be unusually rapid.

The unsaturation of $C_{60}$ is indicated by its reduction by Li in $NH_3(\ell)/$ $t$-BuOH (Birch reduction) to give a light cream solid composed of $C_{60}H_{36}$ and $C_{60}H_{18}$. Reaction with primary and secondary amines (e.g., $n$-PrNH$_2$, $t$-BuNH$_2$, ethylenediamine, morpholine, and $n$-dodecylamine) results in the multiple addition of H and NR$_2$ groups across the C=C double bonds to give $C_{60}H_6(NR_2)_6$. Each such addition results in the rehybridization of the carbon atoms from $sp^2$ to $sp^3$.

The first derivative structure of $C_{60}$ was that of the remarkable osmium compound made as in Reaction 14-2.1.



$$C_{60} \xrightarrow[\text{4-}t\text{-Bupy}]{\text{OsO}_4} C_{60} \qquad (14\text{-}2.1)$$
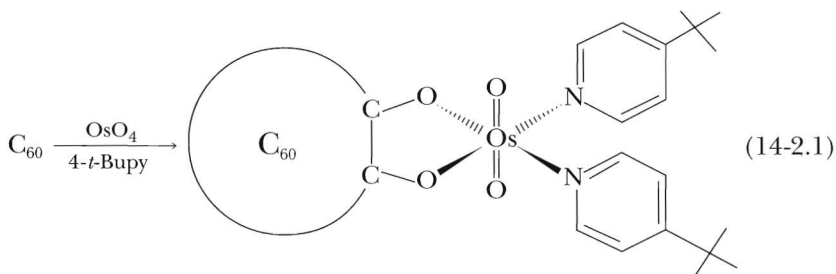
This reaction of OsO$_4$ is characteristic of the C=C double bonds of alkenes. Two similar pyridine (py) derivatives have been prepared by reacting either 2 equivalents of OsO$_4$ and 5 equivalents of py, or 1 equivalent of OsO$_4$ and 2.2 equivalents of py, with $C_{60}$ in toluene, at 0 °C, giving Structures 14-Ia and 14-Ib, respectively.
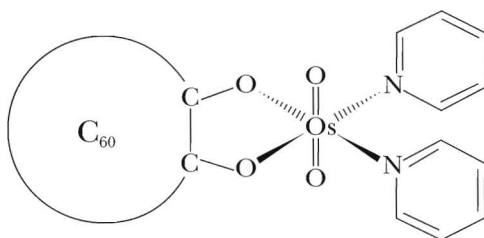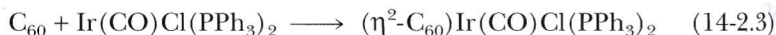


14-Ia
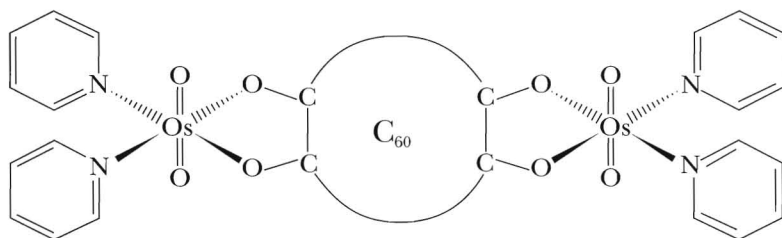


14-Ib

Such *osmylations* are typical of pyridine-activated polycyclic aromatic hydrocarbons, and underscore the "aromaticity" of $C_{60}$. Nevertheless, certain facts are best interpreted by regarding the $C_{60}$ structure as a series of isolated alkenes. This is consistent with the two distinct C—C bond lengths in $C_{60}$, and with the fact that only small ring currents are detectable in $C_{60}$. The high reactivity of $C_{60}$ is attributable to the nonplanarity of the C=C groups, which causes high-strain

energy, and because each C=C double bond is attached to four electron-with-drawing groups.

That $C_{60}$ can behave as an alkene towards transition metals is also shown by Reactions 14-2.2 and 14-2.3, in which a side-on, $\eta^2$ connection to either Pt or Ir is made by the $\pi$ electrons of a C=C group, a classic bonding situation typical

$$C_{60} + (\eta^2\text{-}C_2H_4)Pt(PPh_3)_2 \longrightarrow C_2H_4 + (\eta^2\text{-}C_{60})Pt(PPh_3)_2 \quad (14\text{-}2.2)$$

$$C_{60} + Ir(CO)Cl(PPh_3)_2 \longrightarrow (\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2 \quad (14\text{-}2.3)$$

of simple alkenes, as discussed further in Chapter 29. Although such compounds could be formulated as in Structure 14-IIa, analogous to the bonding of ethyl-ene to transition metals (Section 29-12), it is probably more like Structure 14-IIb,



14-IIa                    14-IIb
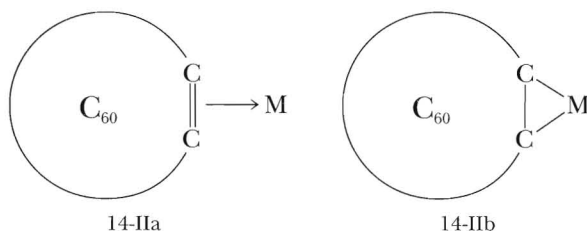
more typical of the bonding to transition metals by alkenes containing electron-withdrawing substituents, such as $C_2F_4$ or $C_2(CN)_4$. This formulation of the bond between $C_{60}$ and Ir is also better for the product of Reaction 14-2.3, in that the reaction is then understood to be both an oxidation of iridium from Ir(I) to Ir(III), as well as an addition of the new C=C ligand. (See oxidative addition re-actions, in Chapter 30.) The three-membered ring with single bonds (Structure 14-IIb) is likely to be the correct form of the epoxide, $C_{60}O$ (Structure 14-IIc), which is made by photochemical oxidation in benzene.



14-IIc
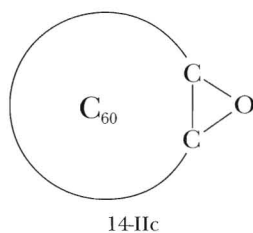
Reactions such as those in Equations 14-2.2 and 14-2.3 may be further un-derstood by appreciating more about the details of the structure of $C_{60}$, which is composed of 20 six-membered rings interconnected with 12 five-membered rings, such that no five-membered rings share an edge with other five-membered rings. Thus we find six-membered rings fused both to other six-membered rings (6–6 fusions) and to five-membered rings (6–5 fusions), but we find five-mem-bered rings fused only to six-membered rings. Although all carbon atoms are the same, as discussed in Chapter 8, there are two types of C—C bonds, one longer than the other by about 0.1 Å. These two types of C—C bonds appear in the sphere at regular locations, one at the 6–6 ring fusions and the other at the 6–5

ring fusions. Consequently, when $C_{60}$ reacts by simple addition to a transition metal to form an $\eta^2$ attachment, increasing the coordination number of the metal from four to six, as in Reaction 14-2.3, the metal atom is found attached specifically to the two carbon atoms (designated $C_1$—$C_2$) of a 6–6 ring fusion. The coordinated carbon atoms $C_1$ and $C_2$ are pulled away from the $C_{60}$ sphere, and the $C_1$—$C_2$ bond is somewhat elongated. Reaction 14-2.3 may be reversed by dissolving the product in $CH_2Cl_2$. Thus $C_{60}$ behaves like tetracyanoethylene and $O_2$, both of which reversibly add to $IrCOCl(PPh_3)_2$, as discussed in Chapter 30. A similar reaction has been reported for $C_{70}$.

Partial *halogenation* of $C_{60}$ and $C_{70}$ may be accomplished by reaction with $Cl_2$ or $Br_2$, although the extent of halogenation is sometimes uncertain. Reaction of $C_{60}$ with $Br_2$ gives $C_{60}Br_2$ and $C_{60}Br_4$. In each case, the bromination can be reversed at 150 °C, giving a quantitative recovery of bromine. Chlorination of $C_{60}$ gives mixtures of $C_{60}Cl_n$, the average value of $n$ being 24. The chloro derivatives are dechlorinated only at temperatures above 400 °C and are thus more stable than the bromo derivatives. The chlorine atoms of $C_{60}Cl_n$ can be replaced by $OCH_3$ groups, using methanolic KOH, as well as by $C_6H_5$ groups, in a Friedel–Crafts reaction (Section 13-4) with benzene, catalyzed by $AlCl_3$. Partially fluorinated derivatives, $C_{60}F_6$ and $C_{60}F_{42}$, have been isolated, but prolonged (12 days) interaction with $F_2$ gives colorless $C_{60}F_{60}$.

Anions, known as *fullerides*, are readily obtained, and these can be either diamagnetic or, like the radical $C_{60}^{\div}$, paramagnetic. From bulk electrolysis, the salt $(Ph_4P)^+C_{60}^{\div}(Ph_4PCl)_2$ has been obtained. The anion is also formed in THF solvent, using the tetraphenylporphyrin complex of $Cr^{2+}$ as a reducing agent, as in Reaction 14-2.4, where TPP = tetraphenylporphyrin.

$$Cr^{II}(TPP) + C_{60} \longrightarrow [Cr^{III}(TPP)]^+C_{60}^{\div} \qquad (14\text{-}2.4)$$
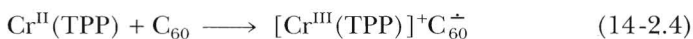
Reduction of $C_{60}/C_{70}$ mixtures by Li gives red-brown solutions which, on treatment with $CH_3I$, gives polymethylated fullerenes with 1–24 methyl groups. Direct interaction with other alkali metals gives black materials such as $(K^+)_3C_{60}^{3-}$. Also, films of $C_{60}$ doped with K, Rb, or Cs metal vapor can be prepared, which are superconducting and may be of value since the critical temperature for superconductivity is relatively high. For instance, $T_c$ for $Rb_nC_{60}$ is 30 K.

Heterofullerenes can be expected, since BN is isoelectronic with CC. As already discussed, $\alpha$-BN is an analog of graphite and $\beta$-BN is an analog of diamond. Not surprisingly, then, calculations have suggested that $C_{12}B_{24}N_{24}$ should be stable. So far, laser vaporization of graphite has given $C_{58}B_2$ and $C_{59}B$.

Large metal atoms may be inserted into the center of certain fullerenes, giving compounds such as $La_2C_{80}$ and $LaC_{82}$. These are obtained by the arc-vaporization of $La_2O_3$ and graphite, which yields solvent-extractable products. The similar $LaC_{60}$ is not solvent extractable, but it can be sublimed. The details on such compounds are still forthcoming. Since the heavy atoms are thought to be encapsulated within the fullerene sphere, these substances have been called the "endohedral metallofullerenes." Interestingly, certain small fullerene compounds appear to be especially stable, for instance, $MC_{28}$ (M = U, Zr, Hf, and Ti) and $KC_{44}$. It should be noted, however, that no one has, as yet, isolated a pure endohedral metallofullerene; the materials claimed to date have been characterized principally by mass spectrometry.

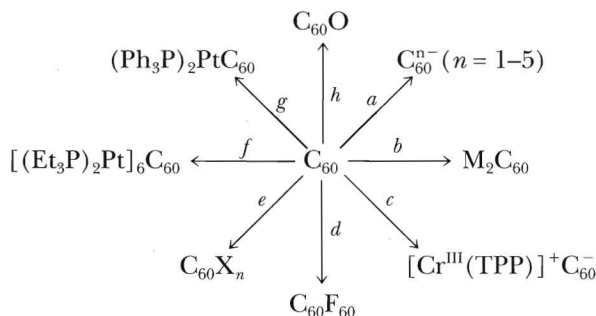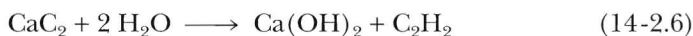Reactions of $C_{60}$ are listed in Fig. 14-1.

$$C_{60}O$$

$$(Ph_3P)_2PtC_{60}$$

$$C_{60}^{n-} \; (n = 1\text{--}5)$$

$$[(Et_3P)_2Pt]_6C_{60} \xleftarrow{\;\;f\;\;} C_{60} \xrightarrow{\;\;b\;\;} M_2C_{60}$$

$$C_{60}X_n$$

$$[Cr^{III}(TPP)]^+C_{60}^-$$

$$C_{60}F_{60}$$

**Figure 14-1**    Some reactions of $C_{60}$: (*a*) electrochemical reduction ($E°$ depends on the solvent); (*b*) alkali metals; (*c*) $Cr^{II}(TPP)$; (*d*) $F_2$, 70 °C; (*e*) $Cl_2$, $Br_2$; (*f*) $Pt(Et_3P)_4$; (*g*) $Pt(C_2H_4)(PPh_3)_2$; and (*h*) $C_6H_6$, $O_2$, *hv*.

## Carbides

Solid compounds of carbon with elements other than hydrogen are generally called carbides. However, there are quite diverse types of carbides, which may be classified as follows.

*Ionic Carbides.* These are formed by the most electropositive metals, such as the alkali and alkaline earth metals and aluminum. While it is a bit of an oversimplification to call them ionic, these carbides behave in many ways as though the carbon atoms were present in anionic form, for example, as $C^{4-}$ or $C_2^{2-}$ ions. This is particularly evident in their reactions with water, as in Reactions 14-2.5 and 14-2.6.

$$Al_4C_3 + 12 \, H_2O \longrightarrow 4 \, Al(OH)_3 + 3 \, CH_4 \tag{14-2.5}$$

$$CaC_2 + 2 \, H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \tag{14-2.6}$$

*Interstitial Carbides.* The transition metals form carbides in which carbon atoms occupy tetrahedral holes in the close-packed arrays (Chapter 4) of metal atoms. Such materials are commonly very hard, electrically conducting, and have very high melting points (3000–4800 °C). Tungsten carbide (WC) is so hard that it is used to make tool bits for machining steel. The smaller metals Cr, Mn, Fe, Co, and Ni give carbides that are intermediate between typically ionic and interstitial carbides, and these are hydrolyzed by water or dilute acids.

*Covalent Carbides.* The metalloids, especially silicon and boron, form SiC and $B_4C$, which are also extremely hard, infusible, and chemically inert. Silicon carbide has a diamond-like structure (Chapters 4 and 8) in which C and Si atoms are each tetrahedrally surrounded by four of the other kind of atoms. Under the name *carborundum,* it is used in cutting tools and abrasives.

## 14-3    Carbon Monoxide

This colorless toxic gas (bp −190 °C) is formed when carbon is burned in a deficiency of oxygen. The following equilibrium is found at all temperatures

$$2\,CO(g) = C(s) + CO_2(g) \qquad (14\text{-}3.1)$$
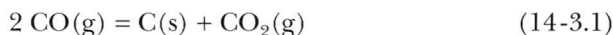
but this equilibrium is rapidly attained only at elevated temperatures. Carbon monoxide is made commercially along with hydrogen (Section 9-1) by steam re-forming or partial combustion of hydrocarbons and by Reaction 14-3.2.

$$CO_2 + H_2 = CO + H_2O \qquad (14\text{-}3.2)$$

A mixture of CO and $H_2$ (synthesis gas) is very important commercially, being used in the hydroformylation process (Section 30-9) and for the synthesis of methanol. Carbon monoxide is also formed when carbon is used in reduction processes, for example, of phosphate rock to give phosphorus (Section 17-2) and in automobile exhausts. Carbon monoxide is also released by certain marine plants and it occurs naturally in the atmosphere.

Carbon monoxide is formally the anhydride of formic acid ($HCO_2H$), but this is not an important aspect of its chemistry. Although CO is an exceedingly weak base, one of its important properties is its ability to act as a ligand toward transition metals. The metal—CO bond involves a certain type of multiple bonding ($d\pi$–$p\pi$ bonding discussed in Chapter 28). The toxicity of CO arises from this ability to bind to the Fe atom in hemoglobin (Section 31-4) in the blood. Only iron and nickel react directly with CO (Chapter 28) under practical conditions.

## 14-4  Carbon Dioxide and Carbonic Acid

Carbon dioxide is present in the atmosphere (300 ppm), in volcanic gases, and in supersaturated solution in certain spring waters. It is released on a large scale by fermentation processes, limestone calcination, and all forms of combustion of carbon and carbon compounds. It is involved in geochemical cycles as well as in photosynthesis. In the laboratory it can be made by the action of heat or acids on carbonates. Solid $CO_2$ (sublimes $-78.5\ °C$) or "dry ice" is used for refrigeration.

Carbon dioxide is the anhydride of the most important simple acid of carbon, *carbonic acid*. For many purposes, the following acid dissociation constants are given for aqueous carbonic acid:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.16 \times 10^{-7}$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.84 \times 10^{-11}$$

The equilibrium quotient in the first equation is incorrect because not all the $CO_2$ dissolved and undissociated is present as $H_2CO_3$. The greater part of the dissolved $CO_2$ is only loosely hydrated, so that the correct first dissociation constant, using the real concentration of $H_2CO_3$, has the much larger value of about $2 \times 10^{-4}$, more in keeping (see Section 7-12) with the structure $(HO)_2CO$.

The rate at which $CO_2$ comes into equilibrium with $H_2CO_3$ and its dissociation products when passed into water is measurably slow. This explains why we

can analytically distinguish between $H_2CO_3$ and the loosely hydrated $CO_2(aq)$. This slowness is of great importance in biological, analytical, and industrial chemistry.

The slow reaction can be shown by addition of a saturated aqueous solution of $CO_2$, on the one hand, and of dilute acetic acid, on the other, to solutions of dilute NaOH containing phenolphthalein indicator. The acetic acid neutralization is instantaneous, whereas with the $CO_2$ neutralization, it takes several seconds for the color to fade.
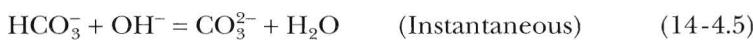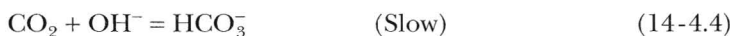
The hydration of $CO_2$ occurs by two paths. For pH < 8, the principal mechanism is direct hydration of $CO_2$ according to Eq. 14-4.1, followed by a rapid acid–base reaction to give bicarbonate:

$$CO_2 + H_2O = H_2CO_3 \qquad \text{(Slow)} \qquad (14\text{-}4.1)$$

$$H_2CO_3 + OH^- = HCO_3^- + H_2O \qquad \text{(Instantaneous)} \qquad (14\text{-}4.2)$$

The rate law for this process is first order.

$$\frac{-d[CO_2]}{dt} = k_{CO_2}[CO_2] \qquad k_{CO_2} = 0.03 \ s^{-1} \qquad (14\text{-}4.3)$$

At pH > 10, the predominant reaction of $CO_2$ is by direct attack with $OH^-$, as in Reaction 14-4.4, followed by a rapid acid–base reaction to give carbonate:

$$CO_2 + OH^- = HCO_3^- \qquad \text{(Slow)} \qquad (14\text{-}4.4)$$

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O \qquad \text{(Instantaneous)} \qquad (14\text{-}4.5)$$

for which the rate law is

$$\frac{-d[CO_2]}{dt} = k_{OH^-}[OH^-][CO_2] \qquad k_{OH^-} = 8500 \ M^{-1} \ s^{-1} \qquad (14\text{-}4.6)$$

Because $k_{OH^-}$ is so much larger than $k_{CO_2}$, it can be considered that the mechanism given by Reactions 14-4.4 and 14-4.5 represents base catalysis of the $CO_2$ hydrolysis mechanism given by Reactions 14-4.1 and 14-4.2. Both mechanisms operate in the pH range 8–10.

For each hydration process there is a corresponding dehydration reaction.

$$H_2CO_3 \longrightarrow H_2O + CO_2 \qquad k_{H_2CO_3} = 20 \ s^{-1} \qquad (14\text{-}4.7)$$

$$HCO_3^- \longrightarrow CO_2 + OH^- \qquad k_{HCO_3} = 2 \times 10^{-4} \ s^{-1} \qquad (14\text{-}4.8)$$

Hence, for the overall equilibrium represented by Reaction 14-4.9

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O \qquad (14\text{-}4.9)$$

the equilibrium constant can be determined to be

$$K = \frac{[CO_2]}{[H_2CO_3]} = \frac{k_{H_2CO_3}}{k_{CO_2}} = \text{about } 660 \qquad (14\text{-}4.10)$$

It follows from the large value of $K$ in Reaction 14-4.10 that the true ionization constant ($K_a$) of $H_2CO_3$ is greater than the apparent constant, as noted previously.

## 14-5  Compounds with C—N Bonds; Cyanides and Related Compounds

An important area of "inorganic" carbon chemistry is that of compounds with C—N bonds. The most important species are the cyanide, cyanate, and thio-cyanate ions and their derivatives.

*Cyanogen, (CN)₂.* This flammable gas (bp −21°C) is stable despite the fact that it is highly endothermic ($\Delta H_f^\circ = 297$ kJ mol$^{-1}$). It can be obtained by cat-alytic gas-phase oxidation of HCN by $NO_2$

$$2\ HCN + NO_2 \longrightarrow (CN)_2 + NO + H_2O \tag{14-5.1}$$

$$NO + \tfrac{1}{2}O_2 \longrightarrow NO_2 \tag{14-5.2}$$
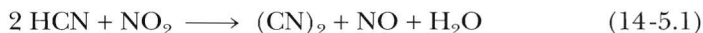
Cyanogen can also be obtained from $CN^-$ by aqueous oxidation using $Cu^{2+}$ (cf. the $Cu^{2+}$–$I^-$ reaction):

$$Cu^{2+} + 2\ CN^- \longrightarrow CuCN + \tfrac{1}{2}(CN)_2 \tag{14-5.3}$$
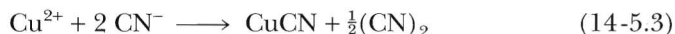
or acidified peroxodisulfate. Dry $(CN)_2$ is made by the reaction

$$Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2 \tag{14-5.4}$$

Although pure $(CN)_2$ is stable, the impure gas may polymerize at 300–500 °C. Cyanogen dissociates into CN radicals and, like halogens, can oxidatively add to lower valent metal atoms (Chapter 30) giving dicyano complexes, for example,

$$(Ph_3P)_4Pd + (CN)_2 \longrightarrow (Ph_3P)_2Pd(CN)_2 + 2\ Ph_3P \tag{14-5.5}$$
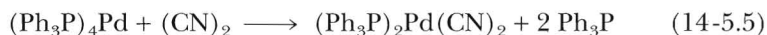
A further resemblance to the halogens is the disproportionation in basic solu-tion.

$$(CN)_2 + 2\ OH^- \longrightarrow CN^- + OCN^- + H_2O \tag{14-5.6}$$

Thermodynamically this reaction can occur in acid solution but is rapid only in base. A stoichiometric mixture of $O_2$ and $(CN)_2$ burns producing one of the hottest flames (~5050 K) known from a chemical reaction.
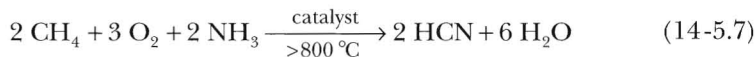
*Hydrogen Cyanide.* Like the hydrogen halides, HCN is a covalent, molecular substance, but is capable of dissociation in aqueous solution. It is an extremely poisonous (though less so than $H_2S$), colorless gas and is evolved when cyanides are treated with acids. Liquid HCN (bp 25.6 °C) has a very high dielectric con-stant (107 at 25 °C) that is due (as for $H_2O$) to association of the polar molecules by hydrogen bonding. Liquid HCN is unstable and can polymerize violently in the absence of stabilizers. In aqueous solutions polymerization is induced by ul-traviolet light.

Hydrogen cyanide is thought to have been one of the small molecules in the earth's primeval atmosphere and to have been an important source or interme-

diate in the formation of biologically important chemicals. For example, under pressure, with traces of water and ammonia, HCN pentamerizes to adenine.
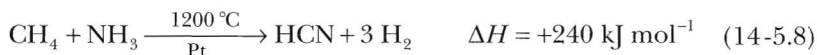
In aqueous solution, HCN is a very weak acid ($pK_{25°C} = 9.21$) and solutions of soluble cyanides are extensively hydrolyzed, but the pure liquid is a strong acid.

Hydrogen cyanide is made industrially from $CH_4$ and $NH_3$ by the reactions

$$2\ CH_4 + 3\ O_2 + 2\ NH_3 \xrightarrow[>800\ °C]{catalyst} 2\ HCN + 6\ H_2O \qquad (14\text{-}5.7)$$

$$\Delta H = -475\ kJ\ mol^{-1}$$

or

$$CH_4 + NH_3 \xrightarrow[Pt]{1200\ °C} HCN + 3\ H_2 \qquad \Delta H = +240\ kJ\ mol^{-1} \qquad (14\text{-}5.8)$$

Hydrogen cyanide has many industrial uses. It may be added directly to alkenes; for example, butadiene gives adiponitrile, $NC(CH_2)_4CN$ (for nylon), in the presence of zero-valent Ni alkylphosphite catalysts that operate by oxidative–addition and transfer reactions (Chapter 30).

*Cyanides.* Sodium cyanide is manufactured by the fusion of calcium cyanamide with carbon and sodium carbonate.

$$CaCN_2 + C + Na_2CO_3 \longrightarrow CaCO_3 + 2\ NaCN \qquad (14\text{-}5.9)$$

The cyanide is leached with water. The $CaCN_2$ is made in an impure form contaminated with $CaO$, $CaC_2$, C, and so on, by the interaction

$$CaC_2 + N_2 \xrightarrow{\sim 1100\ °C} CaNCN + C \qquad (14\text{-}5.10)$$

The linear $NCN^{2-}$ ion is isostructural and isoelectronic with $CO_2$. Cyanamide itself ($H_2NCN$) can be made by acidification of CaNCN. The commercial product is the dimer, $H_2NC(=NH)NHCN$, which also contains much of the tautomer containing the substituted *carbodiimide group*, $H_2N-C(=NH)-N=C=NH$. Organocarbodiimides are important synthetic reagents in organic chemistry and $CH_3N=C=NCH_3$ is stable enough to be isolated.

Sodium cyanide can also be obtained by the reaction

$$NaNH_2 + C \xrightarrow{500-600\ °C} NaCN + H_2 \qquad (14\text{-}5.11)$$

Cyanides of electropositive metals are water soluble but those of $Ag^I$, $Hg^I$, and $Pb^{II}$ are very insoluble. The cyanide ion is of great importance as a ligand (Chapter 28), and many cyano complexes of transition metals are known (e.g., Zn, Cd, or Hg); some, like $Ag(CN)_2^-$ and $Au(CN)_2^-$, are of technical importance and others are employed analytically. The complexes sometimes resemble halogeno complexes [e.g., $Hg(CN)_4^{2-}$ and $HgCl_4^{2-}$], but other types exist. Fusion of alkali cyanides with sulfur gives the *thiocyanate* ion ($SCN^-$).

## 14-6　Compounds with C—S Bonds

*Carbon disulfide* ($CS_2$) is a very toxic liquid (bp 46 °C), usually pale yellow, and is prepared on a large scale by the interaction of methane and sulfur over silica or alumina catalysts at about 1000 °C.

$$CH_4 + 4\,S = CS_2 + 2\,H_2S \tag{14-6.1}$$

In addition to its high flammability in air, $CS_2$ is a very reactive molecule and has an extensive chemistry, much of it organic in nature. It is used to prepare carbon tetrachloride industrially.

$$CS_2 + 3\,Cl_2 \longrightarrow CCl_4 + S_2Cl_2 \tag{14-6.2}$$

Carbon disulfide is one of the small molecules that readily undergo the "insertion reaction" (Chapter 30), where the $-S-\overset{\displaystyle \|}{\underset{\displaystyle S}{C}}-$ group is inserted between

Sn—N, Co—Co, and other bonds. Thus dithiocarbamates are obtained with titanium dialkylamides.

$$Ti(NR_2)_4 + 4\,CS_2 \longrightarrow Ti(S_2CNR_2)_4 \tag{14-6.3}$$

The $CS_2$ molecule can also serve as a ligand, being either bound as a donor through sulfur or added oxidatively (Chapter 30) to give a three-membered ring, as in Structure 14-III.
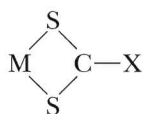
$$(C_6H_5)_3P \diagdown \qquad S$$
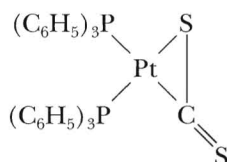
14-III

Important reactions of $CS_2$ involve nucleophilic attacks on carbon by the ions $RO^-$ and $HS^-$ and by primary or secondary amines, which lead, in basic solution, respectively, to xanthates, thiocarbonates, and dithiocarbamates. For example,
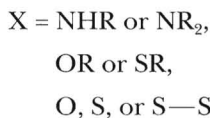
| | | | |
|---|---|---|---|
| $RO^-$ | | $ROCS_2^-$  Xanthate | (14-6.4) |
| $HS^-$ | $+\ C$ $\longrightarrow$ | $CS_3^{2-}$      Thiocarbonate | (14-6.5) |
| $R_2HN$ | | $R_2NCS_2^-$  Dithiocarbamate | (14-6.6) |

*Dithiocarbamates* are normally prepared as Na salts by the action of primary or secondary amines on $CS_2$ in the presence of NaOH. The Zn, Mn, and Fe dithiocarbamates are used as agricultural fungicides, and Zn salts are used as accelerators in the vulcanization of rubber.
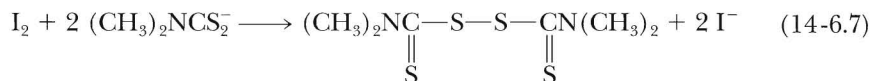
Dithiocarbamates form many complexes with metals. The $CS_2^-$ group in dithiocarbamates, as well as in xanthates, thioxanthates, and thiocarbonates, is usually chelated (as in Structure 14-IV), but monodentate and bridging dithiocarbamates are known.

$$M \diagup^{\textstyle S}_{\textstyle S} \diagdown C-X \qquad \begin{aligned} &X = NHR\ or\ NR_2, \\ &\qquad OR\ or\ SR, \\ &\qquad O,\,S,\ or\ S-S \end{aligned}$$

14-IV

On oxidation of aqueous solutions by $H_2O_2$, $Cl_2$, or $S_2O_8^{2-}$, *thiuram disulfides* are obtained, for example,

$$I_2 + 2 \ (CH_3)_2NCS_2^- \longrightarrow (CH_3)_2NC-S-S-CN(CH_3)_2 + 2 \ I^- \qquad (14\text{-}6.7)$$

with the two C atoms doubly bonded to S (shown below each NC as $\|$ S).

Thiuram disulfides, which are strong oxidants, are used as polymerization initiators (for, when heated, they give radicals) and as vulcanization accelerators. Tetraethylthiuram disulfide is "Antabuse," the agent for rendering the body allergic to ethanol.

## STUDY GUIDE

### Scope and Purpose

Most of the chemistry of the element carbon constitutes the field of organic chemistry. The inorganic chemist, however, is legitimately concerned with certain aspects of carbon that are very important and that have traditionally not been included in the realm of organic chemistry. These include nearly all of the chemistry of the element itself, of compounds in which carbon is combined with metals and metalloids, and much of the chemistry of the simple, binary compounds with nonmetals (oxides, cyanides, or halides). The field of organometallic chemistry, which we examine in Chapters 29 and 30, is a truly interdisciplinary one.

### Study Questions

#### A. Review

1. The electronic structure of C in its ground state is $1s^2 2s^2 2p_x 2p_y$. Why does carbon usually form four single bonds and not two?

2. Give examples of a stable carbonium ion, a carbanion, and a free radical. What is a carbene?

3. What is meant by catenation? Why does silicon have much less tendency to catenation than carbon? Could the same be said for nitrogen?

4. Describe the synthesis and main properties of diamond.

5. What is graphite? Draw its structure and explain why its properties differ from those of diamond.

6. List ways in which CO can be made.

7. List ways in which $CO_2$ can be made.

8. On which side is the equilibrium in the reaction

$$CO_2(aq) + 2 \ H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$
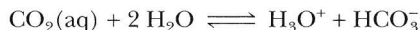
9. Why does $CaCO_3$ dissolve to some extent in $CO_2$ saturated water? Write balanced equations for the reactions involved.

10. How could you make cyanogen in the laboratory? Write balanced equations.

11. List similarities between $(CN)_2$ and $CN^-$ and $Cl_2$ and $Cl^-$.

12. Why are solutions of KCN in water alkaline?

13. Give the industrial synthesis and major properties of hydrogen cyanide.

14. How is $CS_2$ prepared? Write equations for its reaction with $C_2H_5ONa$ in ethanol and with $(C_2H_5)_2NH$ in the presence of aqueous NaOH.

15. How would you convert $BaCO_3$ labeled with $^{13}C$ or $^{14}C$, which is the usual source of labeled carbon compounds, to (a) $Ni(*CO)_4$, (b) $*C_2H_2$, (c) $*CH_4$, (d) $*CS_2$, and (e) $*CH_3OH$?

## B. Additional Exercises

1. The C—C bond length in graphite is 1.42 Å. How does this compare with the C—C bond length in (a) diamond, (b) ethylene, and (c) benzene? What do you expect is the C—C bond order in graphite? Explain.

2. Write down the structures, the Lewis diagrams, and the MO's for the isoelectronic molecules carbon dioxide and allene. What sort of differences in chemistry do you expect?

3. Hydrogen cyanide (HCN) can give dimers, trimers, tetramers, pentamers, and polymers on polymerization. Write some plausible structures for these molecules.

4. Explain why HCN is a weak acid in aqueous solution yet as the pure liquid it is a strong acid. Recall the material of Chapter 7.

5. Zinc dithiocarbamates are dimeric. Propose a structure.

6. Draw the Lewis diagrams for each reactant and product of Reaction 14-6.3.

7. Identify the oxidizing and reducing agents in Reactions 14-5.1 and 14-5.2. Draw the Lewis diagram for each reactant and product.

## C. Questions from the Literature of Inorganic Chemistry

1. Consider the paper by A. L. Balch, V. J. Catalano, and J. W. Lee, "Accumulating Evidence for the Selective Reactivity of the 6–6 Ring Fusion of $C_{60}$. Preparation and Structure of $(\eta^2-C_{60})Ir(CO)Cl(PPh_3)_2 \cdot 5\ C_6H_6$," *Inorg. Chem.,* **1991,** *30,* 3980–3981.

   (a) List all of the significant structural changes to the $C_{60}$ framework that occur upon formation of the $\eta^2$ attachment to Ir in the title compound.

   (b) How was the formation of the title compound shown to be reversible?

   (c) What conclusions do the authors reach regarding the two types of ring fusions in the $C_{60}$ framework?

   (d) Five benzene molecules are found in the crystal. What effects do these have on the structure of the coordination compound?

2. Consider the paper by P. J. Fagan, J. C. Calabrese, and B. Malone, "A Multiply-Substituted Buckminsterfullerene ($C_{60}$) with Octahedral Array of Platinum Atoms," *J. Am. Chem. Soc.,* **1991,** *113,* 9408–9409.

   (a) Explain how NMR spectroscopy has been used to determine the structure of the title compound.

   (b) What structural features make this compound similar to that of Question 1C above?

# SUPPLEMENTARY READING

Ansell, M. F., "Diamond Cleavage," *Chem. Ber.,* **1984,** 1017–1021.

Baum, R. M., "Flood of Fullerene Discoveries Continues," *Chem. Eng. News,* **June 1, 1992,** 25–33.

Diederich, F. and Whetten, R. L., "$C_{60}$: From Soot to Superconductors," *Angew. Chem. Int. Ed. Engl.,* **1991,** *30,* 678–680.