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12 ORGANIC AIR POLLUTANTS

12.1. ORGANIC COMPOUNDS IN THE ATMOSPHERE

Organic pollutants may have a strong effect upon atmospheric quality. The effects of organic pollutants in the atmosphere may be divided into two major categories. The first consists of **direct effects**, such as cancer caused by exposure to vinyl chloride. The second is the formation of **secondary pollutants**, especially photochemical smog (discussed in detail in Chapter 13). In the case of pollutant hydrocarbons in the atmosphere, the latter is the more important effect. In some localized situations, particularly the workplace, direct effects of organic air pollutants may be equally important.

This chapter discusses the nature and distribution of organic compounds in the atmosphere. Chapter 13 deals with photochemical smog and addresses the mechanisms by which organic compounds undergo photochemical reactions in the atmosphere.

Loss of Organic Substances from the Atmosphere

Organic contaminants are lost from the atmosphere by a number of routes. These include dissolution in precipitation (rainwater), dry deposition, photochemical reactions, formation of and incorporation into particulate matter, and uptake by plants. Reactions of organic atmospheric contaminants are particularly important in determining their manner and rates of loss from the atmosphere. Such reactions are discussed in this chapter.

Forest trees present a large surface area to the atmosphere and are particularly important in filtering organic contaminants from air. Forest trees and plants contact the atmosphere through plant cuticle layers, the biopolymer "skin" on the leaves and needles of the plants. The cuticle layer is lipophilic, meaning that it has a particular affinity for organic substances, including those in the atmosphere. A study of the uptake of organic substances (lindane, triadimenol, bitertanol, 2,4-dichlorophenoxyacetic acid, and pentachlorophenol) by conifer needles[1] has shown that the pro-

cess consists of two phases: (1) adsorption onto the needle surfaces and (2) transport through the cuticle layer into the needle and plant. Uptake increases with increasing lipophilicity of the compounds and with increasing surface area of the leaves. This phenomenon points to the importance of forests in atmospheric purification.

Global Distillation and Fractionation of Persistent Organic Pollutants

On a global scale, it is likely that persistent organic pollutants undergo a cycle of distillation and fractionation in which they are vaporized into the atmosphere in warmer regions of the Earth and condense and are deposited in colder regions.[2] The theory of this phenomenon holds that the distribution of such pollutants is governed by their physicochemical properties and the temperature conditions to which they are exposed. As a result, the least volatile persistent organic pollutants are deposited near their sources, those of relatively high volatility are distilled into polar regions, and those of intermediate volatility are deposited predominantly at mid latitudes. This phenomeonon has some important implications regarding the accumulation of persistent organic pollutants in environmentally fragile polar regions far from industrial sources.

12.2. ORGANIC COMPOUNDS FROM NATURAL SOURCES

Natural sources are the most important contributors of organics in the atmosphere, and hydrocarbons generated and released by human activities consitute only about 1/7 of the total hydrocarbons in the atmosphere. This ratio is primarily the result of the huge quantities of methane produced by anaerobic bacteria in the decomposition of organic matter in water, sediments, and soil:

$$2\{CH_2O\} \ \text{(bacterial action)} \qquad CO_2(g) \ + \ CH_4(g) \qquad\qquad (12.2.1)$$
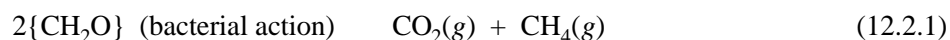
Flatulent emissions from domesticated animals, arising from bacterial decomposition of food in their digestive tracts, add about 85 million metric tons of methane to the atmosphere each year. Anaerobic conditions in intensively cultivated rice fields produce large amounts of methane, perhaps as much as 100 million metric tons per year. Methane is a natural constituent of the atmosphere and is present at a level of about 1.4 parts per million (ppm) in the troposphere.

Methane in the troposphere contributes to the photochemical production of carbon monoxide and ozone. The photochemical oxidation of methane is a major source of water vapor in the stratosphere.

Atmospheric hydrocarbons produced by living sources are called **biogenic hydrocarbons**. Vegetation is the most important natural source of non-methane biogenic compounds. A compilation of organic compounds in the atmosphere[3] documented a total of 367 different compounds that are released to the atmosphere from vegetation sources. Other natural sources include microorganisms, forest fires, animal wastes, and volcanoes.

One of the simplest organic compounds given off by plants is ethylene, C_2H_4. This compound is produced by a variety of plants and released to the atmosphere in its role as a messenger species regulating plant growth. Because of its double bond,

ethylene is highly reactive with hydroxyl radical, HO•, and with oxidizing species in the atmosphere. Ethylene from vegetation sources should be considered as an active participant in atmospheric chemical processes.

Most of the hydrocarbons emitted by plants are **terpenes**, which constitute a large class of organic compounds found in essential oils. Essential oils are obtained when parts of some types of plants are subjected to steam distillation. Most of the plants that produce terpenes are conifers (evergreen trees and shrubs such as pine and cypress), plants of the genus *Myrtus*, and trees and shrubs of the genus *Citrus*. One of the most common terpenes emitted by trees is -pinene, a principal component of turpentine. The terpene limonene, found in citrus fruit and pine needles, is encountered in the atmosphere around these sources. Isoprene (2-methyl-1,3-butadiene), a hemiterpene, has been identified in the emissions from cottonwood, eucalyptus, oak, sweetgum, and white spruce trees. Linalool is a terpene with the chemical formula $(CH_3)_2C=CHCH_2CH_2C(CH_3)(OH)CH=CH_2$, that is given off by some plant species common to Italy and Austria, including the pine *Pinus pinea* and orange blossoms.[4] Other terpenes that are known to be given off by trees include -pinene, myrcene, ocimene, and -terpinene.

As exemplified by the structural formulas of -pinene, -pinene, ^{3}-carene, isoprene, and limonene, shown in Figure 12.1, terpenes contain alkenyl (olefinic) bonds, in some cases two or more per molecule. Because of these and other structural features, terpenes are among the most reactive compounds in the atmosphere. The reaction of terpenes with hydroxyl radical, HO•, is very rapid, and terpenes also react with other oxidizing agents in the atmosphere, particularly ozone, O_3. Turpentine, a mixture of terpenes, has been widely used in paint because it reacts with atmospheric oxygen to form a peroxide, then a hard resin. It is likely that compounds such as -pinene and isoprene undergo similar reactions in the atmos-
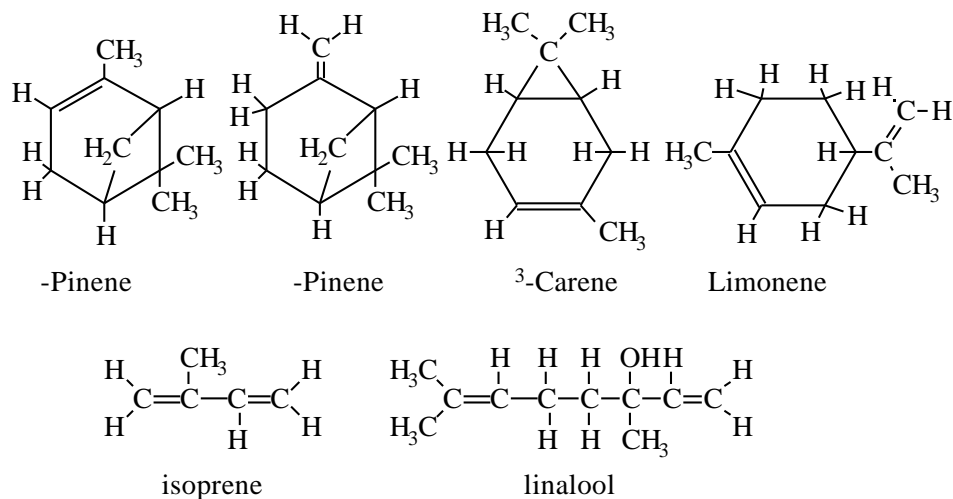

Figure 12.1. Some common terpenes emitted to the atmosphere by vegetation, primarily trees such as pine and citrus trees. These reactive compounds are involved in the formation of much of the small particulate matter encountered in the atmosphere.

phere to form particulate matter. The resulting Aitken nuclei aerosols (see Chapter 10) are a cause of the blue haze in the atmosphere above some heavy growths of vegetation.

Laboratory and smog-chamber experiments have been performed in an effort to determine the fates of atmospheric terpenes. Oxidation initiated by reaction with NO_3 of the four cyclic monoterpenes listed above, -pinene, -pinene, ^{3}-carene, and limonene, has given products containing carbonyl (C=O) functionality and organically bound nitrogen as organic nitrate.[5] When a mixture of -pinene with NO and NO_2 in air is irradiated with ultraviolet light, pinonic acid is formed:
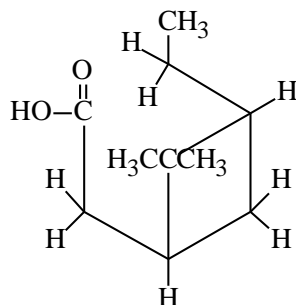
Found in forest aerosol particles, this compound is produced by photochemical processes acting upon -pinene.

Although terpenes are highly reactive with hydroxyl radical, it is now believed that much of the atmospheric aerosol formed as the result of reactions of unsaturated biogenic hydrocarbons is the result of processes that start with reactions between the them and ozone. Pinonic acid (see above) is produced by the reaction of -pinene with ozone.[6] Two of the products of the reaction of limonene with ozone are formaldehyde and 4-acetyl-1-methylcyclohexene:

Limonene   4-acetyl-1-methylcyclohexene
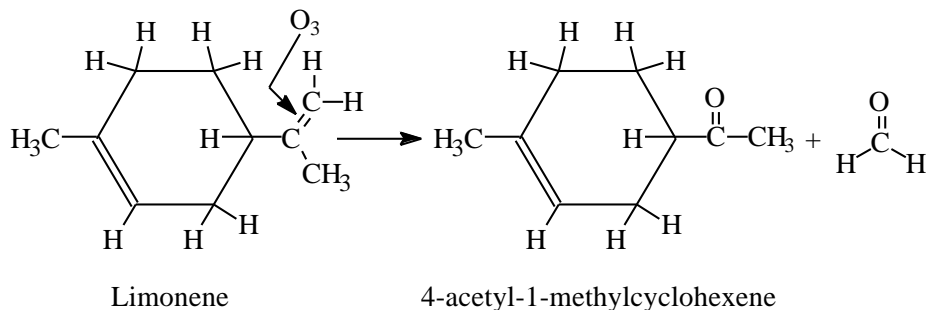
Perhaps the greatest variety of compounds emitted by plants consists of **esters**. However, they are released in such small quantities that they have little influence upon atmospheric chemistry. Esters are primarily responsible for the fragrances associated with much vegetation. Some typical esters that are released by plants to the atmosphere are shown below:

Citronellyl formate

Cinnamyl acetate

Ethyl acrylate

**Coniferyl benzoate**
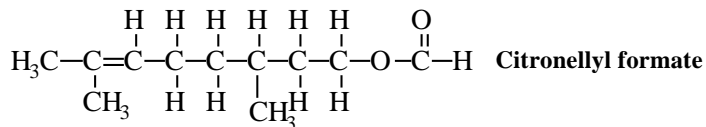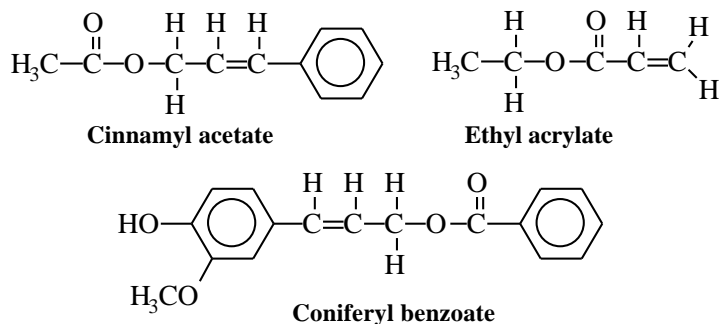
12.3. POLLUTANT HYDROCARBONS

Ethylene and terpenes, which were discussed in the preceding section, are **hydrocarbons**, organic compounds containing only hydrogen and carbon. The major classes of hydrocarbons are **alkanes** (formerly called paraffins), such as 2,2,3-trimethylbutane;
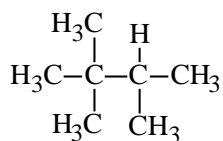
 alkenes (olefins, compounds with double bonds between adjacent carbon atoms), such as ethylene; **alkynes** (compounds with triple bonds), such as acetylene;

$$H-C\equiv C-H$$

and **aryl** (aromatic) **compounds**, such as naphthalene:
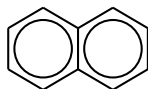
Because of their widespread use in fuels, hydrocarbons predominate among organic atmospheric pollutants. Petroleum products, primarily gasoline, are the source of most of the anthropogenic (originating through human activities) pollutant hydrocarbons found in the atmosphere. Hydrocarbons may enter the atmosphere either directly or as by-products of the partial combustion of other hydrocarbons. The latter are particularly important because they tend to be unsaturated and relatively reactive (see Chapter 13 for a discussion of hydrocarbon reactivity in photochemical smog formation). Most hydrocarbon pollutant sources produce about 15% reactive hydrocarbons, whereas those from incomplete combustion of gasoline are about 45% reactive. The hydrocarbons in uncontrolled automobile exhausts are only about 1/3 alkanes, with the remainder divided approximately equally between more reactive alkenes and aromatic hydrocarbons, thus accounting for the relatively high reactivity of automotive exhaust hydrocarbons.

Investigators who study smog formation in smog chambers have developed synthetic mixtures of hydrocarbons that mimic the smog-forming behavior of hydro-

carbons in a polluted atmosphere. The compounds so used provide a simplified idea of the composition of pollutant hydrocarbons likely to lead to smog formation. A typical mixture consists of 0.556 mole fraction of alkanes, including 2-methylbutane, *n*-pentane, 2-methylpentane, 2,4-dimethylpentane, and 2,2,4-trimethylpentane, and 0.444 mole fraction alkenes, including 1-butene, *cis*-2-butene, 2-methyl-1-butene, 2-methyl-2-butene, ethene (ethylene), and propene (propylene).

Alkanes are among the more stable hydrocarbons in the atmosphere. Straight-chain alkanes with 1 to more than 30 carbon atoms, and branched-chain alkanes with 6 or fewer carbon atoms, are commonly present in polluted atmospheres. Because of their high vapor pressures, alkanes with 6 or fewer carbon atoms are normally present as gases, alkanes with 20 or more carbon atoms are present as aerosols or sorbed to atmospheric particles, and alkanes with 6 to 20 carbon atoms per molecule may be present either as vapor or particles, depending upon conditions.

In the atmosphere, alkanes (general formula C_xH_{2x+2}) are attacked primarily by hydroxyl radical, $HO^\bullet$, resulting in the loss of a hydrogen atom and formation of an **alkyl radical**,

$$C_xH_{2x+1}{}^\bullet$$
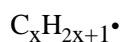
Subsequent reaction with O_2 causes formation of **alkylperoxyl radical**,

$$C_xH_{2x+1}O_2{}^\bullet$$
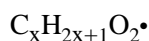
These radicals may act as oxidants, losing oxygen (usually to NO forming NO_2) to produce **alkoxyl radicals**:

$$C_xH_{2x+1}O^\bullet$$
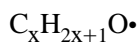
As a result of these and subsequent reactions, lower-molecular-mass alkanes are eventually oxidized to species that can be precipitated from the atmosphere with particulate matter to ultimately undergo biodegradation in soil.

Alkenes enter the atmosphere from a variety of processes, including emissions from internal combustion engines and turbines, foundry operations, and petroleum refining. Several alkenes, including the ones shown below, are among the top 50 chemicals produced each year, with annual worldwide production of several billion kg:

Ethylene   Propylene   Styrene
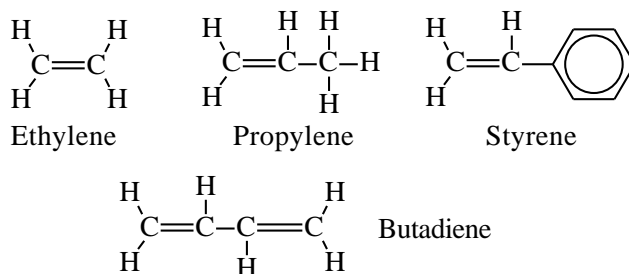
Butadiene

These compounds are used primarily as monomers, which are polymerized to create polymers for plastics (polyethylene, polypropylene, polystyrene), synthetic rubber

(styrenebutadiene, polybutadiene), latex paints (styrenebutadiene), and other applications. All of these compounds, as well as others manufactured in lesser quantities, are released into the atmosphere. In addition to the direct release of alkenes, these hydrocarbons are commonly produced by the partial combustion and "cracking" at high temperatures of alkanes, particularly in the internal combustion engine.

Alkynes occur much less commonly in the atmosphere than do alkenes. Detectable levels are sometimes found of acetylene used as a fuel for welding torches, and 1-butyne used in synthetic rubber manufacture:

$$H-C\equiv C-H \qquad\qquad H-C\equiv C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

Acetylene   **1-Butyne**
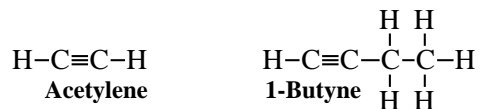
Unlike alkanes, alkenes are highly reactive in the atmosphere, especially in the presence of NO_x and sunlight. Hydroxyl radical reacts readily with alkenes, adding to the double bond and, to a much lesser extent, by abstracting a hydrogen atom. If hydroxyl radical adds to the double bond in propylene, for example, the product is:

$$HO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\displaystyle \bullet}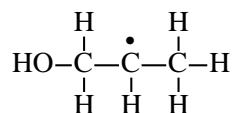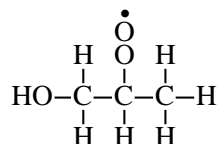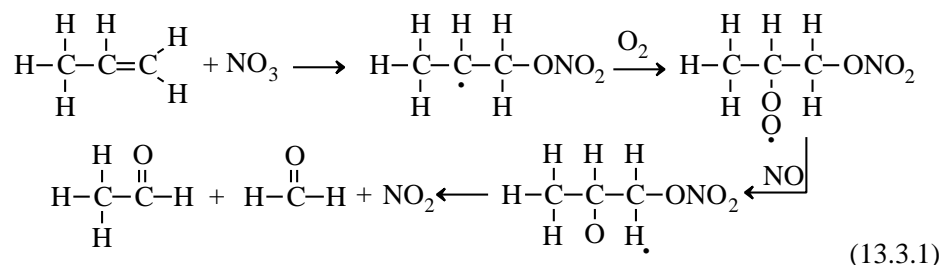{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

Addition of molecular O_2 to this radical results in the formation of a peroxyl radical:

$$HO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle \overset{\bullet}{O}}{\overset{\displaystyle O}{|}}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

These radicals then participate in reaction chains, such as those discussed for the formation of photochemical smog in Chapter 13.

Ozone, O_3, adds across double bonds and is rather reactive with alkenes. As shown for the natural alkene limonene in Section 12.2, aldehydes are among the products of reactions between alkenes and ozone.

Although the reaction of alkenes with NO_3 is much slower than that with $HO\bullet$, the much higher levels of NO_3 relative to $HO\bullet$, especially at night, make it a significant reactant for atmospheric alkenes. The initial reaction with NO_3 is addition across the alkene double bond which, because NO_3 is a free radical species, forms a radical species. A typical reaction sequence is the following:

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}=C\overset{\displaystyle H}{\underset{\displaystyle H}{}} + NO_3 \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \bullet}{}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-ONO_2 \overset{O_2}{\longrightarrow} H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \overset{O}{\overset{\bullet}{O}}}{}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-ONO_2$$

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H + H-\overset{\overset{\displaystyle O}{\|}}{C}-H + NO_2 \longleftarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-ONO_2 \overset{NO}{\longleftarrow}$$
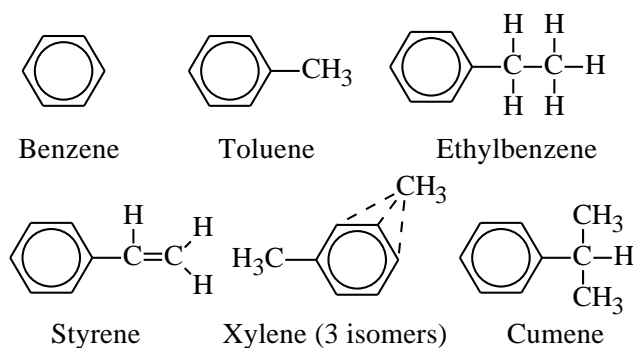
(13.3.1)

12.4. ARYL HYDROCARBONS

Aryl (**aromatic**) **hydrocarbons** may be divided into the two major classes of those that have only one benzene ring and those with multiple rings. As discussed in Chapter 10, the latter are *polycyclic aryl hydrocarbons*, *PAH*. Aryl hydrocarbons with two rings, such as naphthalene, are intermediate in their behavior. Some typical aryl hydrocarbons are:

Benzene   2,6-Dimethylnaphthalene   Pyrene
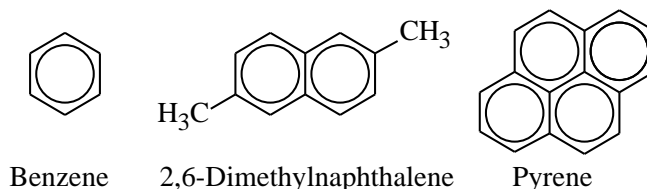
The following aryl hydrocarbons are among the top 50 chemicals manufactured each year:

Benzene   Toluene   Ethylbenzene

Styrene   Xylene (3 isomers)   Cumene

Single-ring aryl compounds are important constituents of lead-free gasoline, which has largely replaced leaded gasoline. Aryl solvents are widely used in industry. Aryl hydrocarbons are raw materials for the manufacture of monomers and plasticizers in polymers. Styrene is a monomer used in the manufacture of plastics and synthetic rubber. Cumene is oxidized to produce phenol and acetone, which are valuable by-products. Because of these applications, plus production of these compounds as combustion by-products, aryl compounds are common atmospheric pollutants.

Many hydrocarbons containing a single benzene ring and a number of hydrocarbon derivatives of naphthalene have been found as atmospheric pollutants. In addition, several compounds containing two or more *unconjugated* rings (not sharing the same   electron cloud between rings) have been detected as atmospheric pollutants. One such compound is biphenyl,
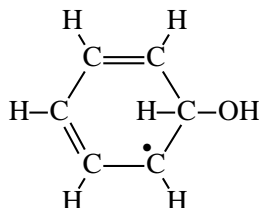
          Biphenyl

which occurs in diesel smoke. It should be pointed out that many of these aryl hydrocarbons have been detected primarily as ingredients of tobacco smoke and are, therefore, of much greater significance in an indoor environment than in an outdoor one.

As discussed in Section 10.8, polycyclic aryl hydrocarbons are present as aerosols in the atmosphere because of their extremely low vapor pressures. These compounds are the most stable form of hydrocarbons having low hydrogen-to-carbon ratios and are formed by the combustion of hydrocarbons under oxygen-deficient conditions. The partial combustion of coal, which has a hydrogen-to-carbon ratio less than 1, is a major source of PAH compounds.

Reactions of Atmospheric Aryl Hydrocarbons

As with most atmospheric hydrocarbons, the most likely reaction of benzene and its derivatives is with hydroxyl radical. Addition of HO$^\bullet$ to the benzene ring results in the formation of an unstable radical species,

$$
\begin{array}{ccc}
& \text{H} \quad\quad \text{H} & \\
& \text{C}=\text{C} & \\
\text{H}-\text{C} & & \text{H}-\text{C}-\text{OH} \\
& \text{C}-\overset{\bullet}{\text{C}} & \\
& \text{H} \quad\quad \text{H} &
\end{array}
$$

where the dot denotes an unpaired electron in the radical. The electron is not confined to one atom; therefore, it is **delocalized** and may be represented in the aryl radical structure by a half-circle with a dot in the middle. Using this notation for the radical above, its reaction with O_2 is,

$$
\underset{\text{(OH, H, }\bullet\text{)}}{\bigcirc} + O_2 \longrightarrow \underset{\text{(OH)}}{\bigcirc} + HO_2\bullet \tag{12.4.1}
$$
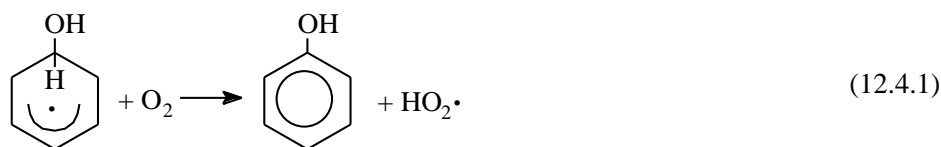
to form stable phenol and reactive hydroperoxyl radical, HOO$^\bullet$. Alkyl-substituted aryls may undergo reactions involving the alkyl group. For example, abstraction of alkyl H by HO$^\bullet$ from a compound such as *p*-xylene can result in the formation of a radical,

$$
\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\bigcirc-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\bullet
$$
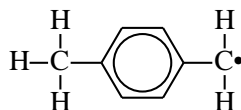
which can react further with O_2 to form a peroxyl radical, then enter chain reactions involved in the formation of photochemical smog (Chapter 13).

Although reaction with hydroxyl radical is the most common fate of aryl compounds during daylight, they react with NO_3 at night. This oxide of nitrogen is formed by the reaction of ozone with NO_2,
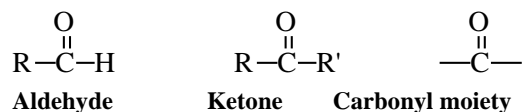
$$
NO_2 + O_3 \quad\quad NO_3 + O_2 \tag{12.4.2}
$$

and can remain in the atmosphere for some time as its addition product with NO_2:

$$
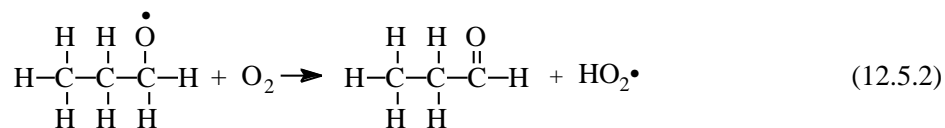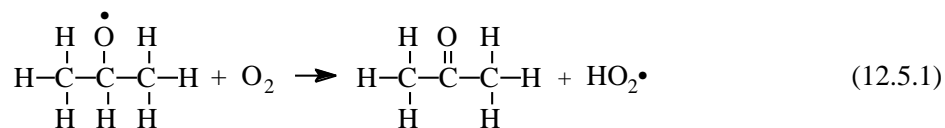NO_2 + NO_3 + M \quad\quad N_2O_5 + M \tag{12.4.2}
$$

The importance of aryl compounds in the formation of secondary air pollutants was emphasized in a study of the aerosol formation potential of gasoline vapor.[7] This study showed that the potential of gasoline vapor to form atmospheric aerosols could be attributed entirely to the aromatic hydrocarbon fraction of the gasoline.

12.5. ALDEHYDES AND KETONES

Carbonyl compounds, consisting of aldehydes and ketones that have a carbonyl moiety, C=O, are often the first species formed, other than unstable reaction intermediates, in the photochemical oxidation of atmospheric hydrocarbons. The general formulas of aldehydes and ketones are represented by the following, where R and R' represent the hydrocarbon *moieties* (portions), such as the –CH$_3$ group.

$$\underset{\textbf{Aldehyde}}{R-\overset{\overset{\textstyle O}{\|}}{C}-H} \qquad \underset{\textbf{Ketone}}{R-\overset{\overset{\textstyle O}{\|}}{C}-R'} \qquad \underset{\textbf{Carbonyl moiety}}{-\overset{\overset{\textstyle O}{\|}}{C}-}$$

Carbonyl compounds are byproducts of the generation of hydroperoxyl radicals from organic alkoxyl radicals (see Section 12.3) by reactions such as the following:

$$\underset{\underset{\textstyle H\ \ H\ \ H}{|\ \ \ |\ \ \ |}}{\overset{\overset{\textstyle H\ \ \overset{\bullet}{O}\ \ H}{|\ \ \ |\ \ \ |}}{H-C-C-C-H}} + O_2 \longrightarrow \underset{\underset{\textstyle H\ \ \ \ \ \ H}{|\ \ \ \ \ \ \ \ |}}{\overset{\overset{\textstyle H\ \ O\ \ H}{|\ \ \ \|\ \ \ |}}{H-C-C-C-H}} + HO_2\bullet \qquad (12.5.1)$$

$$\underset{\underset{\textstyle H\ \ H\ \ H}{|\ \ \ |\ \ \ |}}{\overset{\overset{\textstyle H\ \ H\ \ \overset{\bullet}{O}}{|\ \ \ |\ \ \ |}}{H-C-C-C-H}} + O_2 \longrightarrow \underset{\underset{\textstyle H\ \ H}{|\ \ \ |}}{\overset{\overset{\textstyle H\ \ H\ \ O}{|\ \ \ |\ \ \ \|}}{H-C-C-C-H}} + HO_2\bullet \qquad (12.5.2)$$

The simplest and most widely produced of the carbonyl compounds is the lowest aldehyde, **formaldehyde**:

$$\overset{\overset{\textstyle O}{\|}}{\underset{H\diagup{}^{C}{}\diagdown H}{C}} \qquad \text{Formaldehyde}$$
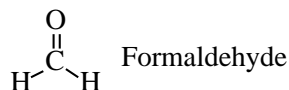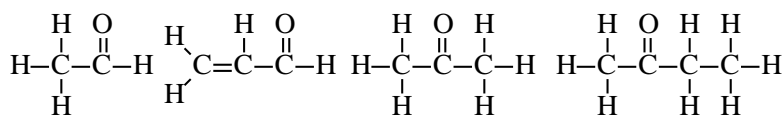
Formaldehyde is produced in the atmosphere as a product of the reaction of atmospheric hydrocarbons beginning with their reactions with hydroxyl radical. For example, formaldehyde is the product of the reaction of methoxyl radical with O$_2$:

$$H_3CO\bullet + O_2 \qquad H-\overset{\overset{\textstyle O}{\|}}{C}-H + HOO\bullet \qquad (12.5.3)$$
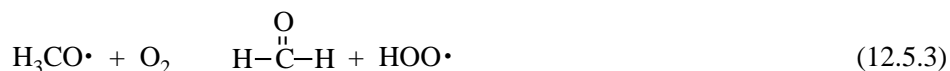
With annual global industrial production exceeding 1 billion kg, formaldehyde is used in the manufacture of plastics, resins, lacquers, dyes, and explosives. It is uniquely important because of its widespread distribution and toxicity. Humans may be exposed to formaldehyde in the manufacture and use of phenol, urea, and melamine resin plastics, and from formaldehyde-containing adhesives in pressed wood products such as particle board, used in especially large quantities in mobile

home construction. However, significantly improved manufacturing processes have greatly reduced formaldehyde emissions from these synthetic building materials. Formaldehyde occurs in the atmosphere primarily in the gas phase.

The structures of some important aldehydes and ketones are shown below:

$$
\begin{array}{cccc}
\underset{\text{Acetaldehyde}}{\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}-H}} &
\underset{\text{Acrolein}}{\mathrm{\overset{\displaystyle H}{\underset{\displaystyle H}{>}}C=\overset{\displaystyle H}{C}-\overset{\displaystyle O}{C}-H}} &
\underset{\text{Acetone}}{\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}} &
\underset{\text{Methylethyl ketone}}{\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}}
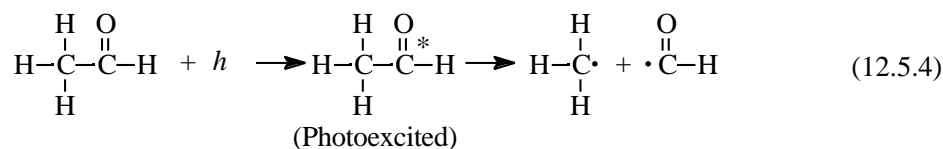\end{array}
$$

Acetaldehyde is a widely produced organic chemical used in the manufacture of acetic acid, plastics, and raw materials. Approximately a billion kg of acetone are produced each year as a solvent and for applications in the rubber, leather, and plastics industries. Methylethyl ketone is employed as a low-boiling solvent for coatings and adhesives, and for the synthesis of other chemicals.

In addition to their production from hydrocarbons by photochemical oxidation, carbonyl compounds enter the atmosphere from a large number of sources and processes. These include direct emissions from internal combustion engine exhausts, incinerator emissions, spray painting, polymer manufacture, printing, petrochemicals manufacture, and lacquer manufacture. Formaldehyde and acetaldehyde are produced by microorganisms, and acetaldehyde is emitted by some kinds of vegetation.

Aldehydes are second only to NO_2 as atmospheric sources of free radicals produced by the absorption of light. This is because the carbonyl group is a **chromophore**, a molecular group that readily absorbs light. It absorbs well in the near-ultraviolet region of the spectrum. The activated compound produced when a photon is absorbed by an aldehyde dissociates into a formyl radical,

$$H\overset{\bullet}{C}O$$

and an alkyl radical. The photodissociation of acetaldehyde illustrates this two-step process:

$$
\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}-H} + h \longrightarrow \mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}{}^{*}-H} \longrightarrow \mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{\cdot}} + \mathrm{{\cdot}\overset{\displaystyle O}{C}-H} \qquad (12.5.4)
$$

(Photoexcited)

Photolytically excited formaldehyde, CH_2O^*, may dissociate in two ways. The first of these produces an H atom and HCO radical; the second produces chemically stable H_2 and CO.

As a result of their reaction with HO· followed by O_2 then NO_2, aldehydes are precursors to the production of strongly oxidizing peroxyacyl nitrates (PANs) such as peroxyacetyl nitrate. This process is discussed in Chapter 13, Section 13.5.

$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}-OO-NO_2} \quad \text{Peroxyacetyl nitrate}$$
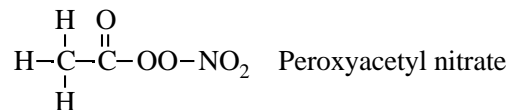
Because of the presence of both double bonds and carbonyl groups, olefinic aldehydes are especially reactive in the atmosphere. The most common of these found in the atmosphere is acrolein,

$$H_2C=CH-\overset{\overset{\displaystyle O}{\|}}{C}-H$$
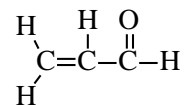
a powerful lachrymator (tear producer) used as an industrial chemical and produced as a combustion byproduct.

The most abundant atmospheric ketone is acetone, $CH_3C(O)CH_3$. About half of the acetone in the atmosphere is generated as a product of the atmospheric oxidation of propane, isobutane, isobutene, and other hydrocarbons. Most of the remainder comes about equally from direct biogenic emissions and biomass burning, with about 3% from direct anthropogenic emissions.

Acetone photolyzes in the atmosphere,

$$CH_3COCH_3 + h\nu \longrightarrow CH_3CO\cdot + \cdot CH_3 \qquad (12.5.5)$$
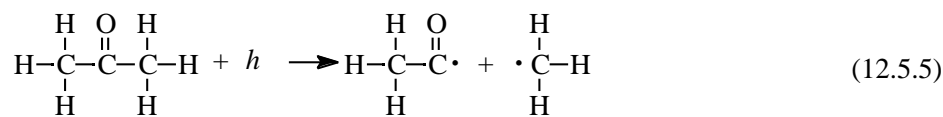
to produce the PAN precursor acetyl radical. It is believed that the mechanism for the removal of the higher ketones from the atmosphere involves an initial reaction with HO· radical.

12.6. MISCELLANEOUS OXYGEN-CONTAINING COMPOUNDS

Oxygen-containing aldehydes, ketones, and esters in the atmosphere were covered in preceding sections. This section discusses the oxygen-containing organic compounds consisting of **aliphatic alcohols**, **phenols**, **ethers**, and **carboxylic acids**. These compounds have the general formulas given below, where R and R' represent hydrocarbon moieties, and Ar stands specifically for an aryl moiety, such as the phenyl group (benzene less an H atom):

R−OH	Ar−OH	R−O−R'	$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$
Aliphatic alcohols	Phenols	Ethers	Carboxylic acids
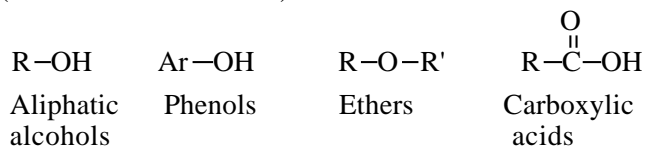
These classes of compounds include many important organic chemicals.

Alcohols

Of the alcohols, methanol, ethanol, isopropanol, and ethylene glycol rank among the top 50 chemicals with annual worldwide production of the order of a billion kg or more. The most common of the many uses of these chemicals is for the manufacture of other chemicals. Methanol is widely used in the manufacture of formaldehyde (see Section 12.5) as a solvent, and mixed with water as an antifreeze formulation. Ethanol is used as a solvent and as the starting material for the manu-

facture of acetaldehyde, acetic acid, ethyl ether, ethyl chloride, ethyl bromide, and several important esters. Both methanol and ethanol can be used as motor vehicle fuels, usually in mixtures with gasoline. Ethylene glycol is a common antifreeze compound.

Numerous aliphatic alcohols have been reported in the atmosphere. Because of their volatility, the lower alcohols, especially methanol and ethanol, predominate as atmospheric pollutants. Among the other alcohols released to the atmosphere are 1-propanol, 2-propanol, propylene glycol, 1-butanol, and even octadecanol, chemical formula $CH_3(CH_2)_{16}CH_2OH$, which is evolved by plants. Alcohols can undergo photochemical reactions, beginning with abstraction of hydrogen by hydroxyl radical. Mechanisms for scavenging alcohols from the atmosphere are relatively efficient because the lower alcohols are quite water soluble and the higher ones have low vapor pressures.

Some alkenyl alcohols have been found in the atmosphere, largely as by-products of combustion. Typical of these is 2-buten-1-ol,

$$\begin{array}{ccccc} & H & H & & H \\ & | & | & & | \\ H- & C & -C & =C- & C & -OH \\ & | & & | & | \\ & H & & H & H \end{array}$$
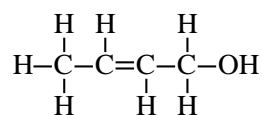
which has been detected in automobile exhausts. Some alkenyl alcohols are emitted by plants. One of these, *cis*-3-hexen-1-ol, $CH_3CH_2CH=CHCH_2CH_2OH$, is emitted from grass, trees and crop plants to the extent that it is known as "leaf alcohol." In addition to reacting with HO• radical, alkenyl radicals react strongly with atmospheric ozone, which adds across the double bond.

Phenols

Phenols are aryl alcohols that have an –OH group bonded to an aryl ring. They are more noted as water pollutants than as air pollutants. Some typical phenols that have been reported as atmospheric contaminants are the following:

phenol   *o*- cresol   *m*- cresol   *p*- cresol   naphthol
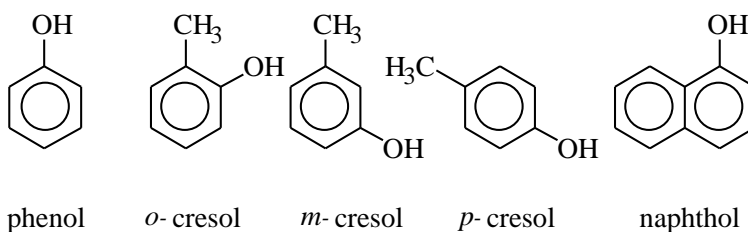
The simplest of these compounds, phenol, is among the top 50 chemicals produced annually. It is most commonly used in the manufacture of resins and polymers, such as Bakelite, a phenol-formaldehyde copolymer. Phenols are produced by the pyrolysis of coal and are major by-products of coking. Thus, in local situations involving coal coking and similar operations, phenols can be troublesome air pollutants.

Ethers

Ethers are relatively uncommon atmospheric pollutants; however, the flamma-bility hazard of diethyl ether vapor in an enclosed work space is well known. In addition to aliphatic ethers, such as dimethyl ether and diethyl ether, several alkenyl ethers, including vinylethyl ether, are produced by internal combustion engines. A cyclic ether and important industrial solvent, tetrahydrofuran, occurs as an air con-taminant. Methyltertiarybutyl ether, MTBE, became the octane booster of choice to replace tetraethyllead in gasoline. Because of its widespread distribution, MTBE has the potential to be an air pollutant, although its hazard is limited by its low vapor pressure. Largely because of its potential to contaminate water, MTBE was proposed for phaseout by both the state of California and the U.S. Environmental Protection Agency in 1999. Another possible air contaminant because of its potential uses as an octane booster is diisopropyl ether (DIPE). The structural formulas of the ethers mentioned above are given below:

Dimethyl ether   Diethyl ether   Vinylethyl ether

Tetrahydrofuran   Methyltertiarybutyl ether (MTBE)   Diisopropyl ether (DIPE)
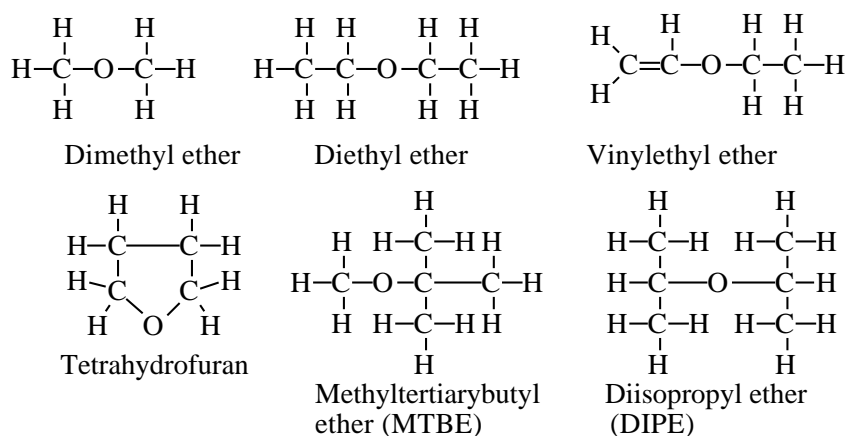
Ethers are relatively unreactive and not as water-soluble as the lower alcohols or carboxylic acids. The predominant process for their atmospheric removal begins with hydroxyl radical attack.

Oxides

Ethylene oxide and propylene oxide,

Ethylene oxide   Propylene oxide
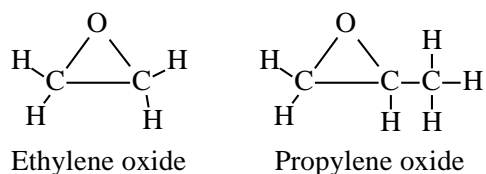
rank among the 50 most widely produced industrial chemicals and have a limited potential to enter the atmosphere as pollutants. Ethylene oxide is a moderately to highly toxic, sweet-smelling, colorless, flammable, explosive gas used as a chemical intermediate, sterilant, and fumigant. It is a mutagen and a carcinogen to experi-mental animals. It is classified as hazardous for both its toxicity and ignitability.

Carboxylic Acids

Carboxylic acids have one or more of the functional groups,
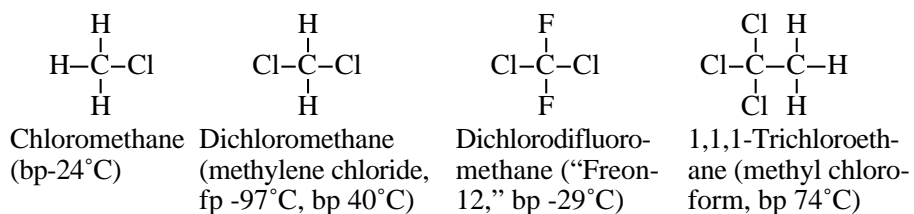
$$\begin{array}{c} O \\ \parallel \\ -C-OH \end{array}$$
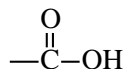
attached to an alkane, alkene, or aryl hydrocarbon moiety. A carboxylic acid, pinonic acid, produced by the photochemical oxidation of naturally-produced -pinene, was discussed in Section 12.2. Many of the carboxylic acids found in the atmosphere probably result from the photochemical oxidation of other organic compounds through gas-phase reactions or by reactions of other organic compounds dissolved in aqueous aerosols. These acids are often the end products of photochemical oxidation because their low vapor pressures and relatively high water solubilities make them susceptible to scavenging from the atmosphere. The sources of relatively abundant atmospheric formic acid, HCOOH, and acetic acid, H_3CCOOH, are not known with certainty.

12.7. ORGANOHALIDE COMPOUNDS

Organohalides consist of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I. They may be saturated (**alkyl halides**), unsaturated (**alkenyl halides**), or aryl (**aryl halides**). The organohalides of environmental and toxicological concern exhibit a wide range of physical and chemical properties. Although most organohalide compounds of pollution concern are from anthropogenic sources, it is now known that a large variety of such compounds are generated by organisms, particularly those in marine environments.[8]

Structural formulas of several alkyl halides commonly encountered in the atmosphere are given below:

$$\begin{array}{cccc} H & H & F & Cl\ \ H \\ | & | & | & |\ \ \ | \\ H-C-Cl & Cl-C-Cl & Cl-C-Cl & Cl-C-C-H \\ | & | & | & |\ \ \ | \\ H & H & F & Cl\ \ H \end{array}$$

Chloromethane (bp-24°C)   Dichloromethane (methylene chloride, fp -97°C, bp 40°C)   Dichlorodifluoromethane ("Freon-12," bp -29°C)   1,1,1-Trichloroethane (methyl chloroform, bp 74°C)

Volatile **chloromethane** (methyl chloride) is consumed in the manufacture of silicones. **Dichloromethane** is a volatile liquid with excellent solvent properties for nonpolar organic solutes. It has been used as a solvent for the decaffeination of coffee, in paint strippers, as a blowing agent in urethane polymer manufacture, and to depress vapor pressure in aerosol formulations. **Dichlorodifluoromethane** is one of the chlorofluorocarbon compounds once widely manufactured as a refrigerant and involved in stratospheric ozone depletion. One of the more common industrial chlorinated solvents is **1,1,1-trichloroethane**.

Viewed as halogen-substituted derivatives of alkenes, the **alkenyl** or **olefinic organohalides** contain at least one halogen atom and at least one carbon-carbon double bond. The most significant of these are the lighter chlorinated compounds.

Vinyl chloride is consumed in large quantities as a raw material to manufacture pipe, hose, wrapping, and other products fabricated from polyvinyl chloride plastic. This highly flammable, volatile, sweet-smelling gas is known to cause angiosarcoma, a rare form of liver cancer. **Trichloroethylene** is a clear, colorless, nonflammable, volatile liquid. It is an excellent degreasing and dry-cleaning solvent, and has been used as a household solvent and for food extraction (for example, in decaffeination of coffee). **Allyl chloride** is an intermediate in the manufacture of allyl alcohol and other allyl compounds, including pharmaceuticals, insecticides, and thermosetting varnish and plastic resins.

Some commonly used aryl halide derivatives of benzene and toluene are shown below:

| Chloro-benzene | Bromo-benzene | Hexachloro-benzene | 1-Chloro-2-methylbenzene |
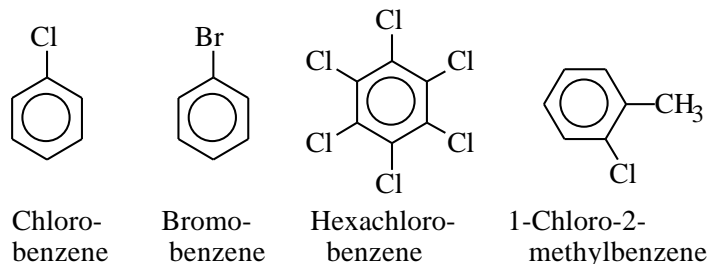
Aryl halide compounds have many uses. The inevitable result of all these uses has been widespread occurrences of human exposure and environmental contamination. Polychlorinated biphenyls, PCBs, a group of compounds formed by the chlorination of biphenyl,

$$+ \ xCl_2 \ \longrightarrow \ \quad + \ xHCl \qquad (12.7.1)$$
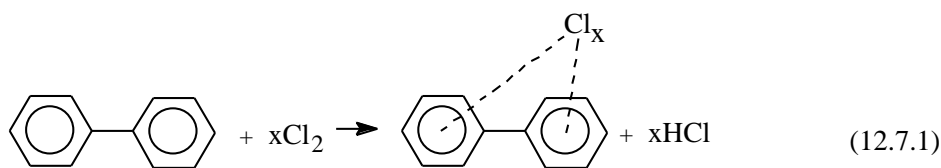
have extremely high physical and chemical stabilities and other qualities that have led to their being used in many applications, including heat transfer fluids, hydraulic fluids, and dielectrics.

As expected from their high vapor pressures and volatilities, the lighter organohalide compounds are the most likely to be found at detectable levels in the atmosphere. On a global basis, the three most abundant organochlorine compounds in the atmosphere are methyl chloride, methyl chloroform, and carbon tetrachloride, which have tropospheric concentrations ranging from a tenth to several tenths of a part per billion. Methyl chloroform is relatively persistent in the atmosphere, with residence times of several years. Therefore, it may pose a threat to the stratospheric ozone layer in the same way as chlorofluorocarbons. Also found are methylene chloride; methyl bromide, CH_3Br; bromoform, $CHBr_3$; assorted chlorofluorocarbons; and halogen-substituted ethylene compounds such as trichloroethylene, vinyl chloride, perchloroethylene, (CCl_2=CCl_2), and solvent ethylene dibromide ($CHBr$=$CHBr$).

Chlorofluorocarbons

Chlorofluorocarbons (**CFC**s), such as dichlorodifluoromethane, commonly called Freons, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon. These compounds are notably stable and nontoxic. They have been widely used in recent decades in the fabrication of flexible and rigid foams and as fluids for refrigeration and air conditioning. The most widely manufactured of these compounds are CCl_3F (CFC-11, bp 24°C), CCl_2F_2 (CFC-12, bp - 28°C), $C_2Cl_3F_3$ (CFC-113), $C_2Cl_2F_4$ (CFC-114), and C_2ClF_5 (CFC-115).

Halons are related compounds that contain bromine and are used in fire extinguisher systems. The major commercial halons are $CBrClF_2$ (Halon-1211), $CBrF_3$ (Halon-1301), and $C_2Br_2F_4$ (Halon-2402), where the sequence of numbers denotes the number of carbon, fluorine, chlorine, and bromine atoms, respectively, per molecule. Halons are particularly effective fire extinguishing agents because of the way in which they stop combustion. Halons act by chain reactions that destroy hydrogen atoms which sustain combustion. The basic sequence of reactions involved is outlined below:

$$CBrClF_2 + H\cdot \longrightarrow CClF_2\cdot + HBr \qquad (12.7.2)$$

$$HBr + H\cdot \longrightarrow Br\cdot + H_2 \qquad (12.7.3)$$

$$Br\cdot + H\cdot \longrightarrow HBr \qquad (12.7.4)$$

Halons are used in automatic fire extinguishing systems, particularly those located in flammable solvent storage areas, and in specialty fire extinguishers, particularly those on aircraft. Because of their potential to destroy stratospheric ozone discussed below, the use of halons in fire extinguishers was severely curtailed in a ban imposed in developed nations on January 1, 1994. Since that time, however, the atmospheric burden of halons has increased.[9] The ban on halons has caused concern because of the favorable properties of halons in fire extinguishers, particularly on aircraft. It is possible that hydrogen-containing analogs of halons may be effective as fire extinguishers without posing a threat to ozone.

The nonreactivity of CFC compounds, combined with worldwide production of approximately one-half million metric tons per year and deliberate or accidental release to the atmosphere, has resulted in CFCs becoming homogeneous components of the global atmosphere. In 1974 it was convincingly suggested, in a classic work that earned the authors a Nobel Prize, that chlorofluoromethanes could catalyze the destruction of stratospheric ozone that filters out cancer-causing ultraviolet radiation from the sun.[10] More recent data on ozone levels in the stratosphere and on increased ultraviolet radiation at earth's surface have shown that the threat to stratospheric ozone posed by chlorofluorocarbons is real.[11] Although quite inert in the lower atmosphere, CFCs undergo photodecomposition by the action of high-energy ultraviolet radiation in the stratosphere, which is energetic enough to break their very strong C-Cl bonds through reactions such as,

$$Cl_2CF_2 \; + \; h \qquad Cl\cdot \; + \; ClCF_2\cdot \qquad\qquad\qquad (12.7.5)$$

thereby releasing Cl atoms. The Cl atoms are very reactive species. Under the rarefied conditions of the stratosphere, one of the most abundant reactive species available for them to react with is ozone, which they destroy through a process that generates ClO:

$$Cl \; + \; O_3 \qquad ClO \; + \; O_2 \qquad\qquad\qquad\qquad (12.7.6)$$

In the stratosphere, there is an appreciable concentration of atomic oxygen by virtue of the reaction

$$O_3 \; + \; h \qquad O_2 \; + \; O \qquad\qquad\qquad\qquad (12.7.7)$$

Nitric oxide, NO, is also present. The ClO species may react with either O or NO, regenerating Cl atoms and resulting in chain reactions that cause the net destruction of ozone:

$$ClO \; + \; O \qquad Cl \; + \; O_2 \qquad\qquad\qquad\qquad (12.7.8)$$

$$\frac{Cl + O_3 \qquad ClO + O_2}{O_3 \; + \; O \qquad 2O_2} \qquad\qquad\qquad\qquad \begin{array}{l}(12.7.9)\\[4pt](12.7.10)\end{array}$$

$$ClO \; + \; NO \qquad Cl \; + \; NO_2 \qquad\qquad\qquad (12.7.11)$$

$$\frac{O_3 + Cl \qquad ClO + O_2}{O_3 \; + \; NO \qquad NO_2 \; + \; O_2} \qquad\qquad\qquad \begin{array}{l}(12.7.12)\\[4pt](12.7.13)\end{array}$$

Both ClO and Cl involved in the above chain reactions have been detected in the 25-45-km altitude region.

The effects of CFCs on the ozone layer may be the single greatest threat to the global atmosphere and is discussed as such in Chapter 14. U. S. Environmental Protection Agency regulations, imposed in accordance with the 1986 Montreal Protocol on Substances that Deplete the Ozone Layer, curtailed production of CFCs and halocarbons in the U. S. starting in 1989. The substitutes for these halocarbons are hydrogen-containing chlorofluorocarbons (HCFCs) and hydrogen-containing fluorocarbons (HFCs). These include CH_2FCF_3 (HFC-134a, 1,1,1,2-tetrafluoroethane, a substitute for CFC-12 in automobile air conditioners and refrigeration equipment), $CHCl_2CF_3$ (HCFC-123, substitute for CFC-11 in plastic foam-blowing), CH_3CCl_2F (HCFC-141b, substitute for CFC-11 in plastic foam-blowing) $CHClF_2$ (HCFC-22, air conditioners and manufacture of plastic foam food containers). Because of the more readily broken H-C bonds they contain, these compounds are more easily destroyed by atmospheric chemical reactions (particularly with hydroxyl radical) before they reach the stratosphere. As of 1999 the HFC 134a market was growing at about a 10 or 15% annual rate with increases of several tens of thousands of metric tons per year.[12] This compound and related compounds containing only

fluorine and hydrogen bound to carbon are favored because they cannot generate any ozone-destroying chlorine atoms.

Atmospheric Reactions of Hydrofluorocarbons and Hydrochlorofluorocarbons

The atmospheric chemistry of hydrofluorocarbons and hydrochlorofluorocarbons is important, even though these compounds do not pose much danger to the ozone layer. Of particular importance is the photooxidation of these compounds and the fates and effects of their photooxidation products. Hydrofluorocarbon 134a, CF_3CH_2F, reacts as follows with hydroxyl radical in the troposphere:

$$CF_3CH_2F + HO^{\bullet} \quad CF_3CHF^{\bullet} + H_2O \qquad (12.7.14)$$

The alkyl radical produced by this reaction forms a peroxy radical with molecular oxygen,

$$CF_3CHF^{\bullet} + O_2 + M \quad CF_3CHFO_2^{\bullet} + M \qquad (12.7.15)$$
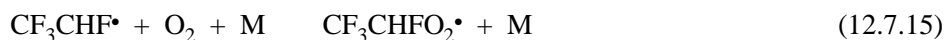
and the peroxy radical reacts with NO:

$$CF_3CHFO_2^{\bullet} + NO \quad CF_3CHFO^{\bullet} + NO_2 \qquad (12.7.16)$$

The product of that reaction can either decompose,

$$CF_3CHFO^{\bullet} \quad CF_3^{\bullet} + HC(O)F \qquad (12.7.17)$$

or react with molecular O_2:

$$CF_3CHFO^{\bullet} + O_2 \quad CF_3C(O)F + HO_2^{\bullet} \qquad (12.7.18)$$
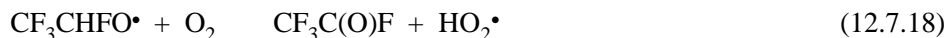
These latter two processes are thought to occur to about equal extents.

Perfluorocarbons

**Perfluorocarbons** are completely fluorinated organic compounds, the simplest examples of which are carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6). Several hundred metric tons of these compounds are produced annually as etching agents in the electronics industry. However, about 30,000 metric tons of CF_4 and about 10% that amount of C_2F_6 are emitted to the global atmosphere each year from aluminum production.[13]

Nontoxic perfluorocarbons do not react with hydroxyl radical, ozone, or other reactive substances in the atmosphere, and the only known significant mechanism by which they are destroyed in the atmosphere is photolysis by radiation less than 130 nm in wavelength. Because of their extreme lack of reactivity, they are involved in neither photochemical smog formation nor ozone layer depletion. As a result of this stability, perfluorocarbons are very long-lived in the atmosphere; the lifetime of CF_4 is estimated to be an astoundingly long 50,000 years! The major atmospheric

concern with these compounds is their potential to cause greenhouse warming (see Chapter 14). Taking into account their nonreactivity and ability to absorb infrared radiation, perfluorocarbons have a potential to cause global warming over a very long time span with an aggregate effect per molecule several thousand times that of carbon dioxide.

Chlorinated Dibenzo-*p*-dioxins and Dibenzofurans

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are pollutant compounds with the general formulas shown below:

PCDFs　　　　　　**PCDDs**　　　　　　**TCDD, a PCDD**
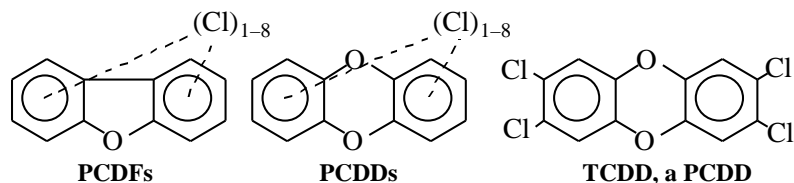
As discussed in Chapters 7 and 22, these compounds are of considerable concern because of their toxicities. One of the more infamous environmental pollutant chemicals is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, TCDD, often known simply as "dioxin."

PCDDs and PCDFs enter the air from numerous sources, including automobile engines, waste incinerators, and steel and other metal production. A particularly important source may well be municipal solid waste incinerators. The formation of PCDDs and PCDFs in such incinerators results in part because of the presence of both chlorine (such as from polyvinylchloride plastic in municipal waste) and catalytic metals. Furthermore, PCDDs and PCDFs are produced by *de novo* synthesis on carbonaceous fly ash surfaces in the post-combustion region of an incinerator at relatively low temperatures of around 300°C in the presence of oxygen and sources of chlorine and hydrogen.
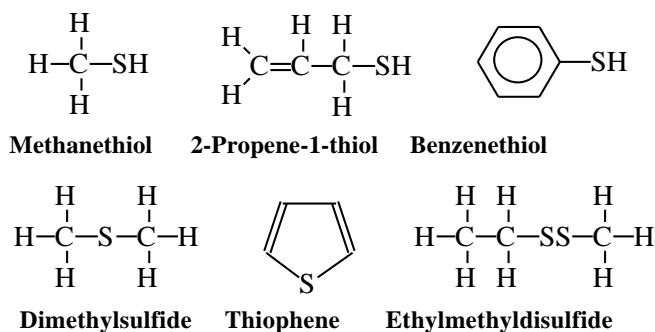
Atmospheric levels of PCDDs and PCDFs are quite low, in the range of 0.4–100 picograms per cubic meter of air. Because of their lower volatilities, the more highly chlorinated congeners of these compounds tend to occur in atmospheric particulate matter, in which they are relatively protected from photolysis and reaction with hydroxyl radical, which are the two main mechanisms by which PCDDs and PCDFs are eliminated from the atmosphere. Furthermore, the less highly chlorinated congeners are more reactive because of their C-H bonds, which are susceptible to attack from hydroxyl radical.

12.8. ORGANOSULFUR COMPOUNDS

Substitution of alkyl or aryl hydrocarbon groups such as phenyl and methyl for H on hydrogen sulfide, H_2S, leads to a number of different organosulfur thiols (mercaptans, R–SH) and sulfides, also called thioethers (R–S–R). Structural formulas of examples of these compounds are shown at the top of the following page.

The most significant atmospheric organosulfur compound is dimethylsulfide, produced in large quantities by marine organisms and introducing quantities of

sulfur to the atmosphere comparable in magnitude to those introduced from pollution sources. Its oxidation produces most of the SO_2 in the marine atmosphere.

H—C—SH   C=C—C—SH   ⬡—SH

Methanethiol   **2-Propene-1-thiol**   **Benzenethiol**

H—C—S—C—H   (thiophene ring with S)   H—C—C—SS—C—H

Dimethylsulfide   **Thiophene**   **Ethylmethyldisulfide**

Methanethiol and other lighter alkyl thiols are fairly common air pollutants that have "ultragarlic" odors; both 1- and 2-butanethiol are associated with skunk odor. Gaseous methanethiol and volatile liquid ethanethiol are used as odorant leak-detecting additives for natural gas, propane, and butane, and are also employed as intermediates in pesticide synthesis. Allyl mercaptan (2-propene-1-thiol) is a toxic, irritating volatile liquid with a strong garlic odor. Benzenethiol (phenyl mercaptan) is the simplest of the aryl thiols. It is a toxic liquid with a severely "repulsive" odor.

Alkyl sulfides or thioethers contain the C-S-C functional group. The lightest of these compounds is dimethyl sulfide, a volatile liquid (bp 38°C) that is moderately toxic by ingestion. Cyclic sulfides contain the C-S-C group in a ring structure. The most common of these compounds is thiophene, a heat-stable liquid (bp 84°C) with a solvent action much like that of benzene that is used in the manufacture of pharmaceuticals, dyes, and resins.

Although not highly significant as atmospheric contaminants on a large scale, organic sulfur compounds can cause local air pollution problems because of their bad odors. Major sources of organosulfur compounds in the atmosphere include microbial degradation, wood pulping, volatile matter evolved from plants, animal wastes, packing house and rendering plant wastes, starch manufacture, sewage treatment, and petroleum refining.

Although the impact of organosulfur compounds on atmospheric chemistry is minimal in areas such as aerosol formation or production of acid precipitation components, these compounds are the worst of all in producing odor. Therefore, it is important to prevent their release into the atmosphere.

As with all hydrogen-containing organic species in the atmosphere, reaction of organosulfur compounds with hydroxyl radical is a first step in their atmospheric photochemical reactions. The sulfur from both mercaptans and sulfides ends up as SO_2. In both cases there is thought to be a readily oxidized SO intermediate, and HS• radical may also be an intermediate in the oxidation of mercaptans. Another possibility is the addition of O atoms to S, resulting in the formation of free radicals as shown below for methyl mercaptan:

$$CH_3SH \ + \ O \qquad H_3C• \ + \ HSO• \tag{12.8.1}$$

The HSO• radical is readily oxidized by atmospheric O_2 to SO_2.
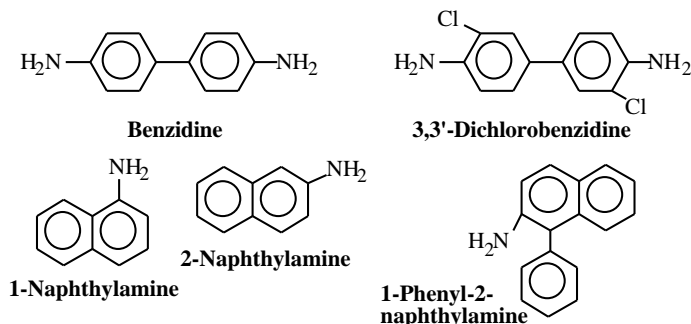
12.9. ORGANONITROGEN COMPOUNDS

Organic nitrogen compounds that may be found as atmospheric contaminants may be classified as **amines**, **amides**, **nitriles**, **nitro compounds**, or **heterocyclic nitrogen compounds**. Structures of common examples of each of these five classes of compounds reported as atmospheric contaminants are:

Methylamine   **Dimethylformamide**   **Acrylonitrile**

Nitrobenzen   **Pyridin**   **Aniline**
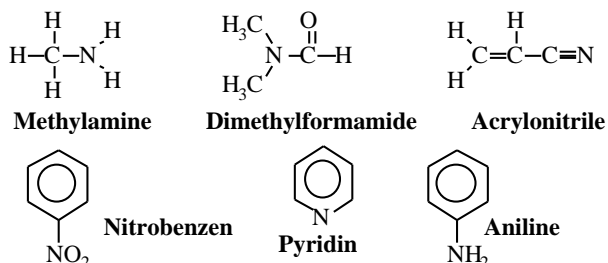
The organonitrogen compounds listed above can come from anthropogenic pollution sources. Significant amounts of anthropogenic atmospheric nitrogen may also come from reactions of inorganic nitrogen with reactive organic species. Examples include nitrates produced by the reaction of atmospheric NO_3.

Amines consist of compounds in which one or more of the hydrogen atoms in NH_3 has been replaced by a hydrocarbon moiety. Lower-molecular-mass amines are volatile. These are prominent among the compounds giving rotten fish their characteristic odor—an obvious reason why air contamination by amines is undesirable. The simplest and most important aryl amine is aniline, used in the manufacture of dyes, amides, photographic chemicals, and drugs. A number of amines are widely used industrial chemicals and solvents, so industrial sources have the potential to contaminate the atmosphere with these chemicals. Decaying organic matter, especially protein wastes, produce amines, so rendering plants, packing houses, and sewage treatment plants are important sources of these substances.

Aryl amines are of special concern as atmospheric pollutants, especially in the workplace, because some are known to cause urethral tract cancer (particularly of the bladder) in exposed individuals. Aryl amines are widely used as chemical intermediates, antioxidants, and curing agents in the manufacture of polymers (rubber and plastics), drugs, pesticides, dyes, pigments, and inks. In addition to aniline, some aryl amines of potential concern are the following:

Benzidine   **3,3'-Dichlorobenzidine**

**1-Naphthylamine**   **2-Naphthylamine**   **1-Phenyl-2-naphthylamine**

In the atmosphere, amines can be attacked by hydroxyl radicals and undergo further reactions. Amines are bases (electron-pair donors). Therefore, their acid-base chemistry in the atmosphere may be important, particularly in the presence of acids in acidic precipitation.

The amide most likely to be encountered as an atmospheric pollutant is dimethylformamide. It is widely used commercially as a solvent for the synthetic polymer, polyacrylonitrile (Orlon, Dacron). Most amides have relatively low vapor pressures, which limit their entry into the atmosphere.

Nitriles, which are characterized by the $-C\equiv N$ group, have been reported as air contaminants, particularly from industrial sources. Both acrylonitrile and acetonitrile, CH_3CN, have been reported in the atmosphere as a result of synthetic rubber manufacture. As expected from their volatilities and levels of industrial production, most of the nitriles reported as atmospheric contaminants are low-molecular-mass aliphatic or olefinic nitriles, or aryl nitriles with only one benzene ring. Acrylonitrile, used to make polyacrylonitrile polymer, is the only nitrogen-containing organic chemical among the top 50 chemicals with annual worldwide production exceeding 1 billion kg.

Among the nitro compounds, RNO_2, reported as air contaminants are nitromethane, nitroethane, and nitrobenzene. These compounds are produced from industrial sources. Highly oxygenated compounds containing the NO_2 group, particularly peroxyacetyl nitrate (PAN, discussed in Chapter 13), are end products of the photochemical oxidation of hydrocarbons in urban atmospheres.

A large number of **heterocyclic nitrogen compounds** have been reported in tobacco smoke, and it is inferred that many of these compounds can enter the atmosphere from burning vegetation. Coke ovens are another major source of these compounds. In addition to the derivatives of pyridine, some of the heterocyclic nitrogen compounds are derivatives of pyrrole:

Pyrrole
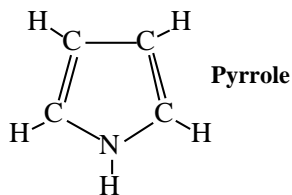
Heterocyclic nitrogen compounds occur almost entirely in association with aerosols in the atmosphere.

Nitrosamines, which contain the N-N=O group, and having, therefore, the general formula,

$$\begin{array}{c} R \\ \diagdown \\ N-N=O \\ \diagup \\ R'' \end{array}$$
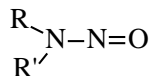
deserve special mention as atmospheric contaminants because some are known carcinogens. As discussed in Chapter 22, nitrosamines include compounds that can attach alkyl groups to DNA resulting in modified DNA that can lead to cancer. Both N-nitrosodimethylamine and N-nitrosodiethylamine have been detected in the atmosphere.

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QUESTIONS AND PROBLEMS

1. Match each organic pollutant in the left column with its expected effect in the right column, below:

   (a) CH_3SH 1. Most likely to have a secondary effect in the atmosphere

   (b) $CH_3CH_2CH_2CH_3$ 2. Most likely to have a direct effect

   (c) $\underset{H}{\overset{H}{>}}C=\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$ 3. Should have the least effect of these three

2. Why are hydrocarbon emissions from uncontrolled automobile exhaust particularly reactive?

3. Assume an accidental release of a mixture of gaseous alkanes and alkenes into an urban atmosphere early in the morning. If the atmosphere at the release site is monitored for these compounds, what can be said about their total and relative concentrations at the end of the day? Explain.

4. Match each radical in the left column with its type in the right column, below:

   (a) $H_3C^{\bullet}$ 1. Formyl radical
   (b) $CH_3CH_2O^{\bullet}$ 2. Alkylperoxyl radical
   (c) $H\overset{\bullet}{C}O$ 3. Alkyl radical
   (d) $CH_xCH_{2x+1}O_2^{\bullet}$ 4. Alkoxyl radical

5. When reacting with hydroxyl radical, alkenes have a reaction mechanism not available to alkanes, which makes the alkenes much more reactive. What is this mechanism?

6. What is the most stable type of hydrocarbon that has a very low hydrogen-to-carbon ratio?

7. In the sequence of reactions leading to the oxidation of hydrocarbons in the atmosphere, what is the first stable class of compounds generally produced?

8. Give a sequence of reactions leading to the formation of acetaldehyde from ethane starting with the reaction of hydroxyl radical.

9. What important photochemical property do carbonyl compounds share with NO_2?