OZONE

1. Introduction

Ozone [10028-15-6], O_3, is an allotropic form of oxygen whose pungent odor is detectable at low concentrations (0.01–0.05 ppm). It is thermally unstable and explosive in the gas, liquid, and solid phases. In addition to being an excellent disinfectant, ozone is a powerful oxidant not only thermodynamically, but also kinetically, and has many useful synthetic applications in research and industry. Its strong oxidizing and disinfecting properties and its innocuous by-product, oxygen, make it ideal for the treatment of water. Indeed, the most important application of ozone is in the treatment of drinking water, which began in Europe in 1903. In the mid-1990s, there were well over 2000 such water-treatment installations, primarily in Europe. In the U.S. there were over 300 water treatment plants in operation in 2000. Establishment of the Clean Water Act (eg, the Surface Water Treatment Rule and the Disinfection Byproducts Rule) has provided the impetus for using ozone in water treament as a disinfectant and oxidant in the U. S. The treatment of swimming pool water also was developed in Europe during the 1960s (see WATER, TREATMENT OF SWIMMING POOLS, SPAS, AND HOT TUBS).

Another important application of ozone is for odor control in industrial processes and municipal wastewater-treatment plants. Ozone also is used on a large scale for the treatment of municipal secondary effluents (see WATER, MUNICIPAL WATER TREATMENT). Industrial high quality water supplies also are treated with ozone (see WATER, INDUSTRIAL WATER TREATMENT). In addition, ozone has applications in the treatment of cooling-tower water and in pulp bleaching. Advanced oxidation processes employing ozone in combination with ultraviolet (uv) or H_2O_2 greatly improves the reactivity of ozone toward organic contaminants via generation of hydroxyl radicals.

Ozone, which occurs in the stratosphere (15–50 km) in concentrations of 1–10 ppmv, is formed by the action of solar radiation on molecular oxygen. It absorbs biologically damaging ultraviolet radiation (230–320 nm), prevents the radiation from reaching the surface of the earth, and contributes to thermal equilibrium on earth. The concentration of ozone in the stratosphere is being depleted by release of chlorine and bromine containing substances (eg, bromo- and chlorofluorocarbons and methyl bromide), which are photolyzed forming chlorine and bromine atoms that catalytically destroy ozone. The production and use of such substances are being phased out according to recommendations of the Montreal protocol. Ozone also is present in the troposphere. Although concentrations in remote areas are low, much higher levels occur in urban areas due to increased concentrations of carbon monoxide, hydrocarbons, and nitrogen oxides released primarily by internal combustion engines.

2. Properties

2.1. Gas–Liquid–Solid.

At ordinary temperatures, pure ozone is a pale blue gas [$d^{0^\circ C} = 2.1415\,g\,L^{-1}$ at 101.3 kPa (1 atm)] that condenses to an indigo blue liquid ($d^{-112^\circ C} = 1.354\,kg\,L^{-1}$; bp $= -111.9^\circ C$) and freezes to a deep blue-violet solid ($d^{-195.8^\circ C} = 1.728\,kg\,L^{-1}$; mp $= -192.5^\circ C$) (1). At the critical point,

$T_c = -12.1^\circ$C, $P_c = 5532.8$ kPa, and $\rho_c = 0.436$ kg L^{-1} (1). The vapor pressure of the liquid is given by log P(kPa) = 7.378–814.94/T–0.00197T, for T = 90–243 K, and log P(kPa) = 7.6689–867.6/T, for T = 85–95 K (2). Additional property data on ozone and ozone–oxygen mixtures are given in Ref. 1.

2.2. Henry's Law Constant. The equilibrium partitioning of ozone between the gas and liquid phases is governed by a modified form of Henry's law: $P = K_H C$, where P is the ozone partial pressure (kPa), C is the concentration of ozone in solution (molarity M instead of mol fraction), and K_H (kPa M^{-1}) is Henry's law constant. Henry's law constant as a function of the kelvin temperature and molar ionic strength (μ) measured in acidic water (pH 3.5) is given by: $\log_e K_H = -2297/T + 2.659\,\mu - 688\,\mu/T + 16.808$ (3). The effect of pH and temperature is expressed by: $K_H = (7.01 \times 10^7)[10^{(\mathrm{pH}-14)}]^{0.035} \exp\,(-2428/T)$; T in kelvins (4). Calculated values are in good agreement with data in Ref. 3 at pH 3.5 and 0 ionic strength. Additional data on the effect of pH on K_H at 21°C are given in Ref. 5.

2.3. Liquid–Gas Distribution Constant. Substituing the expression for P from the ideal gas equation ($P = nRT/V$) into Henry's law, the following relationship can be derived: $H = [\mathrm{O_3}]_{\mathrm{aq}}/[\mathrm{O_3}]_{\mathrm{g}} = \mathrm{R}T/K_H$, where H (also called the solubility ratio S) is a dimensionless distribution or equilibrium constant, $[\mathrm{O_3}]_{\mathrm{aq}}$ and $[\mathrm{O_3}]_{\mathrm{g}}$ are the aqueous and gas phase concentrations in similar units (eg, mol L^{-1} or mg L^{-1}), R is the gas constant (8.31 L kPa mol^{-1} K^{-1}), and T is the kelvin temperature. Based on published data (3), the calculated constant H in pure water at pH 3.5 can be expressed by the equation $H = 0.495 \exp(-0.0242T)$, where T is in degree celcius (°C). Calculated values of 0.50 and 0.31 at 0 and 20°C are in good agreement with 0.49–0.53 and 0.29–0.35 at the same temperatures listed or calculated from data in Ref. 1.

2.4. Ozone Absorption in Pure Water. Under dynamic conditions, in demand-free water, the equilibrium fraction (α) of ozone dissolved at atmospheric pressure in a single-stage absorber depends only on H at a given temperature and the relative gas and water flow rates (V_g and V_{aq}, L min^{-1}): $\alpha = (HV_{\mathrm{aq}}/V_g)/(1 + HV_{\mathrm{aq}}/V_g)$.

2.5. Solubility. The solubility of ozone varies directly with pressure, inversely with temperature, and ionic strength. The saturation solubility of pure ozone in pure water at pH 3.5 and atmospheric pressure is expressed by the following equation derived from the data in Ref. 3: $[\mathrm{O_{3(aq)}}]_{\max} = 48H/(RT) = (289.54/T_{\mathrm{K}}) \exp(-0.0242T_{\mathrm{C}})$, where T_{K} and T_{C} are kelvin and centigrade temperatures. This equation gives a value of 1.06 g L^{-1} at 0°C, which is in agreement with values of 1.13 and 1.05 g L^{-1} listed or calculated from data in Ref. 1. Data on the solubility of ozone in organic solvents are given in Refs. 1 and 6.

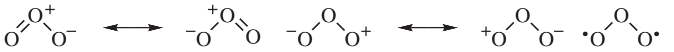
2.6. Adsorptivity. Gaseous ozone can be adsorbed by porous solid substrates, eg, silica gel, and is often used in this form in organic synthesis (7).

2.7. Flammability and Explosivity. Ozone is endothermic, thus it can burn or detonate by itself and represents the simplest combustible and explosive system. The concentration threshold for spark-initiated explosion of liquid ozone in oxygen at −183°C is 18.6 mol% $\mathrm{O_3}$ and the concentration limit for shock wave-initiated detonation of gaseous ozone–oxygen at 25°C is 9.2 mol% $\mathrm{O_3}$ (1). Explosions of gaseous ozone can be initiated by shock wave, electrical spark, heat, or sufficiently intense light flash. Explosion of pure liquid ozone and concentrated solutions in oxygen can be initiated by impurities, sudden change in temperature or pressure, heat, electrical spark, or mechanical shock.

2.8. Thermodynamic Values. Values for gaseous ozone are $\Delta H_f^{\circ} = 142.7\,\text{kJ mol}^{-1}$, $\Delta G_f^{\circ} = 163.2\,\text{kJ mol}^{-1}$, $S^{\circ} = 238.9\,\text{J K}^{-1}\,\text{mol}^{-1}$, and $C_p = 39.2\,\text{J K}^{-1}\,\text{mol}^{-1}$ (8). Aqueous heat of solution is $\Delta H^{\circ}{}_{\text{soln}} = -19.1\,\text{kJ mol}^{-1}$ (3). The heat of vaporization of liquid ozone is $\Delta H^{\circ}{}_v = 10.84\,\text{kJ mol}^{-1}$ (8). The standard reduction potential of ozone is 2.07 V for the half-cell reaction: $O_3 + 2\,H^+ + 2\,e^- \rightarrow O_2 + H_2O$ (8).

2.9. Spectral Data. Gaseous ozone exhibits three principal absorptions in the infrared (ir) at 710, 1043, and $2105\,\text{cm}^{-1}$ (9). Ozone has a diffuse absorption band in the visible region centered at ~600 nm with an absorption cross-section (σ) of $489 \times 10^{-20}\,\text{cm}^2$ and molar absorptivity of $2.94\ M^{-1}\,\text{cm}^{-1}$ (10–12). The uv spectrum shows a single broad absorption centered at 253.7 nm with absorption cross-section of $(1147 \pm 20) \times 10^{-20}\,\text{cm}^2$ and molar absorptivity of $3000 \pm 52\ M^{-1}\,\text{cm}^{-1}$ at 273 K (10–12). The molar absorptivity of aqueous ozone at 260 nm is $3135 \pm 22\ M^{-1}\,\text{cm}^{-1}$ at 25°C (13).

2.10. Structure. Ozone is a triangular molecule with a bond angle of 116.8° established by microwave spectroscopy (14). The bond length of the ozone molecule (0.1278 nm) is intermediate to that of a single and double oxygen bond, corresponding to a bond order of 1.7. Ozone is diamagnetic with C_{2v} symmetry and a low dipole moment of $1.77 \times 10^{-30}\,\text{C m}$ (0.53 D) (15). The structure of ozone based on Pauling resonance concepts is a hybrid, principally of form (**1**), with a small contribution from (**2**) (14).



(**1**) (**2**) (**3**)

The bonding in **1** consists of two σ-bonds and one three-center–four-electron π-bond. Molecular orbital and valence bond calculations indicate that the 1,3-diradical **3**, having two σ-bonds and weak bonding between the singly occupied π-atomic orbitals on the terminal O atoms, may contribute significantly to the ground-state structure of ozone (16–18). Other studies suggest that ozone may have a hypervalent structure, with bonding similar to **1**, and negligible diradical character (19,20).

3. Thermochemical Decomposition

3.1. Gas Phase. The decomposition of gaseous ozone is sensitive not only to homogeneous catalysis by light, trace organic matter, nitrogen oxides, mercury vapor, and peroxides, but also to heterogeneous catalysis by metals and metal oxides.

Decomposition Mechanism. The mechanism of the homogeneous decomposition of gaseous ozone is represented by the following reactions, where M represents the weighted sum of all molecular and atomic species present in the gas phase, including ozone:

$$O_3 + M \underset{2}{\overset{1}{\rightleftharpoons}} O + O_2 + M - 106.5\ \text{kJ}$$

$$O_3 + O \xrightarrow{3} 2\,O_2 + 391.8\ \text{kJ}$$

Reaction 1 is the rate-controlling step. The decomposition rate of pure ozone decreases markedly as oxygen builds up due to the effect of reaction 2, which reforms ozone from oxygen atoms.

Rate Constants. Temperature-dependent equations for the three rate constants obtained by measuring the decomposition of concentrated and dilute ozone have been reported (21–23). The ratio k_2/k_3 has been estimated by measuring the steady-state ozone concentration, formed by means of electric discharge (24), photochemically (25,26), and low temperature reaction of molecular oxygen and glow-discharge generated oxygen atoms (27). The reaction of ozone with glow discharge-generated oxygen atoms has been studied in rapid flow systems (28–30). The preferred temperature-dependent equation (T in kelvin) for k_3 determined by laser photolysis of ozone and monitoring the oxygen atom concentration by time-resolved resonance fluoresence is $4.8\times\ 10^9\exp(-2060/T)\ M^{-1}\,s^{-1}$ (10–12). For k_2 ($M = O_2$), the preferred equation is $2.2\times\ 10^8(T/300)^{-2.8}\ M^{-2}\,s^{-1}$ (10–12), which is based on the generation of oxygen atoms by flash photolysis and measurement of ozone by uv spectrometry.

Ozone Decomposition. The calculated half-life of 1 mol% (1.5 wt%) of pure gaseous ozone diluted with oxygen at 25, 100, and 250°C (based on rate constants from Ref. 23) is 19.3 year, 5.2 h, and 0.1 s, respectively. Although pure ozone−oxygen mixtures are stable at ordinary temperatures in the absence of catalysts and light, ozone produced on an industrial scale from air by electric discharge is less stable due to the presence of impurities; however, ozone produced from oxygen is more stable. At 20°C, 1 mol% ozone produced from air is ~30% decomposed in 12 h.

3.2. Aqueous Phase. Although, ozone decomposes very slowly at room temperature in pure water (eg, double distilled water), its decomposition can be initiated by hydroxyl ion, trace metals (eg, Fe^{2+}), $H_2O_2/HO_2{}^-$, organic matter, heat, and uv light. The listed second-order rate constants in the following sections are in units of $M^{-1}\,s^{-1}$ unless stated otherwise.

Hydroxyl Ion Initiated Decomposition. This radical chain thermal decompostion of ozone is propagated mainly via HO and O_2^- radicals and also involves the following intermediates: O_3^-, O^-, H_2O_2, HO_2^-, HO_2, HO_3 (proposed). The most probable primary step involving an O-atom transfer is

$$O_3 + OH^- \longrightarrow O_2 + HO_2^- \qquad k = 48\ (31-33); 140\ (34); 180\ (35)$$

Another proposed initiation step: $O_3 + HO^- \rightarrow O_2{}^- + HO_2$ $k = 70$ (36–38), is considered less likely from a thermodynamic and mechanistic standpoint.

The reaction of hydroperoxide anion HO_2^- with ozone is generally presumed to occur as follows (31–34):

$$O_3 + HO_2^- \longrightarrow O_3^- + HO_2 \qquad HO_2 \rightleftarrows O_2^- + H^+ \quad pK_a = 4.8$$

An alternative pathway (representing the sum of the above two reactions and the products of reaction of $O_3{}^- + H^+$ discussed below) has been proposed:

$O_3 + HO_2^- \rightarrow O_2^- + O_2 + HO$ $k = 2.8 \times 10^6$ (36–38). The superperoxide radical anion reacts with ozone forming ozonide anion (36–38).

$$O_3 + O_2^- \longrightarrow O_2 + O_3^- \qquad k = 1.6 \times 10^9$$

Ozonide anion reportedly rapidly protonates forming the HO_3 radical, pK_a $(HO_3) = 8.2$, that decomposes to HO radicals (36–38).

$$O_3^- + H^+ \rightleftarrows HO_3 \quad k_f = 5.2 \times 10^{10}; \quad k_r = 3.3 \times 10^2$$
$$HO_3 \longrightarrow HO + O_2 \quad k = 1.1 \times 10^5\ s^{-1}$$

However, the data regarding formation of the intermediate HO_3 has been challenged (34). Ozonide ion can react with hydroxyl radicals, eg,: $O_3^- + HO \rightarrow O_2^- + HO_2$ and $O_3^- + HO \rightarrow O_3 + HO^-$ (31–33). Above pH ~8, the proposed HO_3 radicals exist primarily as ozonide ions, which can dissociate to a small extent forming monoxide radical ions (O^-) that react with water forming hydroxyl radicals (31–33).

$$O_3^- \rightleftarrows O^- + O_2 \quad K_{eq} = \sim 10^{-6}$$
$$O^- + H_2O \rightleftarrows HO^- + HO \quad k = 10^8\ s^{-1}; \quad pK_a(HO) = 11.9$$

The monoxide radical ion also is involved in other reactions, eg,: $O_3^- + O^- \rightarrow 2\ O_2^-$; $O^- + O_2^- + H_2O \rightarrow O_2 + 2\ HO^-$; and $O^- + HO_2^- \rightarrow O_2^- + HO^-$ (31–33).

Hydroxyl radicals react with ozone forming hydroperoxyl radicals, which form equilibrium concentrations of the superoxide radical anion (as indicated above) that reenters the ozone chain decomposition.

$$O_3 + HO \longrightarrow O_2 + HO_2 \quad k = 1.1 \times 10^8 (31 - 33); 2 \times 10^8 (35)$$

The formation of the intermediate HO_4 from $O_3 + HO$ ($k = 2 \times 10^9$) that deomposes to HO_2 and O_2 ($k = 2.8 \times 10^4\ s^{-1}$) has been proposed, but not confirmed (36–38).

Termination. Radical chains in the decomposition of pure aqueous ozone are terminated by reactions that consume HO or HO_2/O_2^-, eg, $HO + HO \rightarrow H_2O_2$; $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$; $HO + HO_2 \rightarrow H_2O + O_2$; $HO + O_2^- \rightarrow HO^- + O_2$; $HO + O_3^- \rightarrow HO^- + O_3$; $O_3^- + O^- + H_2O \rightarrow O_2 + 2\,HO^-$, etc.

Computer Simulation. At 25°C and pH 10, calculated concentrations at 50% decomposition of ozone vary as follows: $H_2O_2 > O_3^- > HO_2^- > HO > O_2^- > O^-$ (34).

Promoters. In water containing certain organic matter (eg, primary and secondary alcohols, aryl groups, and formic, glyoxylic, and humic acids), HO radicals can form superoxide radicals that can promote the chain reaction and thereby act as chain carriers (36–38): $H_2R + HO \rightarrow HR + H_2O$; $HR + O_2 \rightarrow HRO_2 \rightarrow R + HO_2$.

Inhibitors. In natural water, the alkalinity (ie, bicarbonate and carbonate ions) also can act as HO radical scavengers forming less reactive intermediate radicals (HCO_3 and CO_3^-) that do not regenerate HO_2/O_2^-, thereby inhibiting the decomposition of ozone (36–38).

$$HO + HCO_3^- \rightarrow HO^- + HCO_3 \quad k = \sim 10^7$$

$$HO + CO_3^{2-} \rightarrow HO^- + CO_3^- \quad k = \sim 10^8$$

In the presence of excess radical scavengers (ie, 10 mM $HCO_3^- + CO_3^{2-}$) the pseudo-first-order rate constant at 20°C for the initiation step is: $k = 175 \times 10^{pH-14}\,s^{-1}$ (36–38). This yields an ozone half-life of 66 min at pH 8. By contrast, phosphate (HPO_4^{2-}) reacts much slower with HO than bicarbonate ($k = \sim 10^5$) and consequently the half-life of ozone in distilled water even containing as much as 50 mM phosphate at pH 8 and 20°C is significantly lower, ie, 7 min. In natural water, the half-lives fall between these extremes, eg, the half-life in Lake Zürich water (20°C, pH 8, 1.5 mM HCO_3^-) is 10 min.

Although some organic compounds promote radical chain deomposition of ozone, certain compounds (eg, *tert*-butanol) can inhibit the decomposition by rapidly consuming HO radicals forming less reactive organic radicals that do not regenerate the superoxide anion: $(CH_3)_3COH + HO \rightarrow (CH_3)_2C(CH_2)OH + H_2O$ $k = \sim 10^9$.

Decomposition in Acidic Solution. The proposed mechanism for decompositon of ozone in acidic solution involves a surface initiation reaction by oxygen atoms (formed by thermal decompostion: $O_3 \rightleftharpoons O + O_2$) or by excited ozone molecules ($O + O_2 \rightleftharpoons O_3^*$) with water molecules producing H_2O_2 that reacts slowly with O_3 forming hydroxyl radicals, which along with HO_2/O_2^- propagate the chain decomposition (39).

Advanced Oxidation Processes (AOPs). Ozone-based AOPs include O_3/H_2O_2, O_3/uv, and O_3/catalyst. The O_3/uv process is discussed under photochemical decomposition. Hydrogen peroxide greatly accelerates the decomposition of ozone in alkaline solutions because of formation of HO_2^-, which reacts rapidly with ozone as discussed above. When the concentration of H_2O_2 exceeds 10^{-7} M, the decomposition of ozone is initiated faster by HO_2^- than by HO^- for pH <11.6 (36–38).

4. Photochemical Decomposition

4.1. Gas Phase.

Gaseous ozone is decomposed to oxygen atoms and molecules by absorbing radiation in the visible and uv spectrum: $O_3 + h\nu \rightarrow O_2 + O$.

Effect of Light Wavelength. When visible light is > 400 nm, only ground-state oxygen molecules ($^3\Sigma_g{}^-$) and oxygen atoms (^3P) are formed (26). The initiation step is followed by ozone formation and destruction reactions, $O + O_2 + M \rightarrow O_3 + M$ and $O_3 + O \rightarrow 2\,O_2$. At ~600 nm, the maximum quantum yield, Φ, is 2.0 mol $h\nu^{-1}$. With 334-nm uv radiation, the decomposition mechanism is similar to that with red light, except that the maximum quantum yield is four (in the absence of O_2) due to the formation of singlet delta oxygen ($^1\Delta_g$), which decomposes ozone (40).

At 313 and 254 nm, a chain decomposition occurs with a maximum Φ of 6 (41,42). The primary step involves photodissociation of ozone to produce an excited oxygen atom (^1D) and a singlet delta oxygen molecule ($^1\Delta_g$). Reaction of ^1D oxygen atoms with molecular oxygen produces singlet sigma oxygen molecules ($^1\Sigma_g{}^+$) as well as ground-state (^3P) oxygen atoms. The energetic, electronically excited singlet oxygen molecules can decompose ozone: $O_2(^1\Delta_g$ and $^1\Sigma_g{}^+) + O_3 \rightarrow 2\ O_2 + O$ (43). Reaction of ^1D oxygen atoms with ozone produces vibrationally excited ground-state oxygen molecules $O_2(^3\Sigma_g{}^-)$, which also can decompose ozone (44). Highly vibrationally excited oxygen molecules ($X^3\Sigma_g{}^-$) formed at 226 nm also can form ozone by reaction with normal oxygen molecules (45). Vibrationally excited ozone molecules (O_3^*) are formed by collisional transfer between vibrationally excited oxygen molecules and ozone, and reaction of $O(^3P)$ with oxygen molecules. Although O_3^* molecules react faster than ground-state O_3 with O atoms, they are largely collisionally quenched by O and O_2 (43), and are reportedly unimportant in the decomposition mechanism (42). The rate of ozone decomposition is much greater in the uv than in the visible region because of the greater energy and absorptivity of uv photons.

Effect of Water Vapor. In the presence of water vapor, ^1D oxygen atoms formed by uv radiation react to form hydroxyl radicals, which can destroy ozone catalytically: $O(^1D) + H_2O \rightarrow 2\ HO$ $k^{25^\circ C} = 6.6 \times\ 10^{10}$ (46).

4.2. Aqueous Phase. In contrast to photolysis of ozone in moist air, uv photolysis in the aqueous phase can produce hydrogen peroxide initially because the hydroxyl radicals do not escape the solvent cage in which they are formed $O(^1D) + H_2O \rightarrow H_2O_2$ (47). Hydrogen peroxide is photolyzed slowly to hydroxyl radicals: $H_2O_2 + h\nu \rightarrow 2\ HO$. In pure water, HO radicals can decompose ozone, while in natural or polluted water, the HO radicals can oxidize undesirable solutes. The photolysis also forms $O(^3P)$ atoms, which can oxidize organic compounds. This is the basis of the O_3/uv process, one of the advanced oxidation processes (AOPs).

5. Chemistry of Ozone

The inorganic chemistry of ozone is extensive, encompassing virtually every element except most noble metals, fluorine (qv), and the inert gases. Reported second-order rate constants ($M^{-1}\,s^{-1}$) refer to 20–25°C and to disappearance of ozone unless stated otherwise.

5.1. Inorganic Reactions. *Radical Reactions.* Ozone reacts rapidly in the gas and/or aqueous phases with various radicals and radical ions, eg, O, O^-, O_2^-, H, HO, HO_2, N, NO, Cl, and Br. Some of these radicals (HO, NO, Cl, and Br) can catalyze decomposition of gaseous ozone.

Singlet Oxygen Formation. Singlet oxygen $O_2(^1\Delta_g)$ is formed in varying amounts when aqueous ozone reacts via O-atom transfer with ions, eg, Br^-, I^-, CN^-, S^{2-} (48).

Protonated Ozone. Gaseous ozone can be protonated with strong Brønsted acids, AH^+, eg, H_3^+, KrH^+, XeH^+, and CH_5^+, according to the reaction

$AH^+ + O_3 \rightleftarrows A + O_3H^+$. Protonated ozone reacts exothermically with methane: $O_3H^+ + CH_4 \rightarrow CH_3^+ + H_2O + O_2$, followed by $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$ (49).

HO$_3$ Radical. The HOOO radical has been structurally characterized in the gas phase via spectroscopic measurements, showing that it has a trans planar structure with a fairly long central bond length of 0.1688 nm (50). It is thought to form in the atmosphere by reaction of HO with O_2 and also is a proposed intermediate in the decompositon of aqueous ozone via the reaction: $O_3^- + H^+ \rightleftarrows HO_3$.

Halogen Compounds. Fluorine is unreactive toward ozone at ordinary temperatures. Chlorine is oxidized to Cl_2O_6 and Cl_2O_7, bromine to Br_3O_8, and iodine to I_2O_3 and I_4O_9. Oxidation of halide ions by ozone increases with the atomic number of halide. Fluoride is unreactive; chloride reacts slowly (51), but bromide is readily oxidized to hypobromite.

$$Br^- + O_3 \rightarrow BrO^- + O_2 \quad k = 160\ (52); 258\ (53)$$

The reaction initially forms $BrOOO^-$, which decomposes to HOBr/BrO^- and O_2 (53). Oxidation of iodide is extremely rapid, initially yielding hypoiodite; $k = 1.2 \times 10^9$ (53). Hypohalite ions are oxidized to halites; hypobromite reacts faster than hypochlorite.

$$XO^- + 2\,O_3 \rightarrow XO_3^- + 2\,O_2 \ k(ClO^-) = 30\ (54);\ k(BrO^-) = 100\ (52)$$

Formation of halide is a competing reaction.

$$XO^- + O_3 \rightarrow X^- + 2\,O_2 \quad k(ClO^-) = 120\ (54);\ k(BrO^-) = 330\ (52)$$

In contrast to reaction of ozone with nucleophilic halide and hypohalite ions, reaction of ozone with electrophilic hypohalous acids is very slow (51).

$$HOX + O_3 \rightarrow H^+ + X^- + 2\,O_2 \quad k(HOCl) = < 0.002;\ k(HOBr) = < 0.01$$

Reaction of ozone with chlorite ion is rapid, involves O_3^-, HO_3, and HO radicals, and forms chlorine dioxide when ClO_2^- is in large excess via the overall reaction (55).

$$2\ ClO_2^- + O_3 + 2\,H^+ \rightarrow 2\,ClO_2 + O_2 + 2\,H_2O \quad k = 8.2 \times 10^6$$

At smaller excesses of ClO_2^-, chlorine dioxide can react competively with chlorite ion forming chlorate, resulting in the following overall stoichiometry:

$$ClO_2^- + O_3 \rightarrow ClO_3^- + O_2$$

The rate constant for the direct reaction of ozone with chlorine dioxide (forming chlorate) is $k = 1.1 \times 10^3$ (51).

The reaction mechanism for oxidation of bromite to bromate by ozone is similar to that for chlorite except for the instability of the intermediate BrO_2, which results in disproportionation to bromite and bromate (55).

$$2\ BrO_2^- + O_3 + 2\ H^+ \rightarrow 2\ BrO_2 + O_2 + H_2O \quad k = 8.9 \times 10^4$$

$$2\ BrO_2 \rightarrow Br_2O_4 \quad k = 1.4 \times 10^9$$

$$Br_2O_4 + H_2O \rightarrow BrO_2^- + BrO_3^- + 2\,H^+ \quad k = 2.2 \times 10^3\ s^{-1}$$

Chlorate, bromate, and iodate ions do not react with ozone (51).

Nitrogen Compounds. Ammonium ion is not oxidized because, like ozone, it is an electrophilic reagent. Raising the pH to the 7–9 range shifts the equilibrium toward free ammonia where slow rates of oxidation are observed (56).

$$NH_3 + 4\,O_3 \rightarrow H^+ + NO_3^- + H_2O + 4\,O_2 \quad k = 20$$

Above pH 9, decomposition of ozone to the reactive intermediate, HO, determines the kinetics of ammonia oxidation. Catalysts, eg, WO_3, Pt, Pd, Ir, and Rh, promote the oxidation of dilute aqueous solutions of ammonia (57). The oxidation of ammonia by ozone depends not only on the pH of the system but also on the presence of other oxidizable species (56). Because the ozonation rate of organic materials in wastewater is much faster than that of ammonia, oxidation of ammonia does not occur in the presence of ozone-reactive organics.

The monochloro derivative of ammonia (ie, monochloramine) is oxidized slightly faster than ammonia.

$$NH_2Cl + 3\,O_3 \rightarrow 2\,H^+ + NO_3^- + Cl^- + 3\,O_2 \quad k = 26$$

Monobromamine reacts much faster, $k = 160$ (51), whereas, dichloramine and dibromamine both react slower than the monohalamine with k values of 1.3 and 40, respectively. By contrast, unprotonated hydroxylamine is oxidized rapidly by ozone, $k = 2.1 \times 10^4$ (51).

The reaction of gaseous ozone with the lower oxides of nitrogen (NO and NO_2) is also rapid and quantitative; the end product is nitrogen pentoxide, which can catalytically decompose ozone. Nitrous oxide, however, reacts slowly, $k < 10^{-3}$ (51).

Nitrogen-containing anions, eg, nitrite and cyanide, also are readily oxidized by ozone (51). Nitrite is oxidized to nitrate [$k = 3.7 \times 10^5$ (51); 5.8×10^5 (53)] and cyanide is oxidized rapidly to cyanate [$k = 2.6 \times 10^3$ (58); 10^3–10^5 (51)]. Cyanate, however, is oxidized slowly.

$$CNO^- + 2\,O_3 \rightarrow CO_2 + NO_3^- + O_2 \quad k < 10^{-2}\ (51)$$

Cyanic acid (HOCN) reacts slowly, whereas undissociated HCN and HNO_2 do not react at all (51).

Oxygen Compounds. Although hydrogen peroxide is unreactive toward ozone at low pH, rapid reaction occurs at higher pH due to formation of hydroperoxyl ions as discussed under decomposition of aqueous ozone. The O_3/H_2O_2 sysytem generates reactive hydroxyl radicals and is one of the advanced oxidation processes (AOPs) used in water treatment for oxidation of micropollutants.

Sulfur Compounds. Aqueous sulfide and H_2S, an odiferous compound in some waters, are oxidized rapidly (initially to sulfite and sulfurous acid); the rate constants are 3×10^9 and $\sim 3 \times 10^4$, respectively (51). Sulfite is oxidized rapidly [($k = 1 \times 10^9$ (51); $k = 1.3 \times 10^9$ (53)] to sulfate by ozone. Bisulfite ion and sulfurous acid also are oxidized rapidly (to bisulfate and sulfuric acid) with k values of 3.2×10^5 and 2×10^4, respectively (51). Thiocyanate is oxidized by ozone to cyanide and sulfate via the intermediate formation of sulfite (59).

$$CNS^- + 2\,O_3 + 2HO^- \rightarrow CN^- + SO_4^{2-} + 2\,O_2 + H_2O$$

Metals and Metallic Ions. Under appropriate conditions, ozone oxidizes most metals with the exception of gold and the platinum group. When oxidized by ozone, heavy metal ions, such as Fe^{2+} and Mn^{2+}, precipitate as insoluble hydroxides or oxides upon hydrolysis. Excess ozone oxidizes ferric hydroxide in alkaline media to FeO_4^{2-}, and MnO_2 to MnO_4^-.

$$2\,Fe^{2+} + O_3 + 5\,H_2O \rightarrow 2\,Fe(OH)_3 + O_2 + 4\,H^+$$
$$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2\,H^+$$

Formation of Ozonides. Although the parent compound, HO_3, is too unstable to be isolated, metal and nonmetal ozonides have been prepared. All ozonides are paramagnetic and are colored due to absorption at 400–600 nm. Alkali metal ozonides are crystalline ionic solids soluble in ammonia, amines, and amides. The preferred method for preparing potassium ozonide (KO_3) [12030-89-6] is the low temperature reaction of KO_2 with ozone: $KO_2 + O_3 \rightarrow KO_3 + O_2$. Lithium and sodium ozonides cannot be prepared by direct ozonation of their peroxides. They only can be isolated from solution in ammonia or an amine by ion exchange (60). Ozonides are thermally unstable, decomposing spontaneously to superoxides slightly above room temperaure (35°C for KO_3 and 37°C for NaO_3): $2\ MO_3 \rightarrow 2\ MO_2 + O_2$. The stability of the alkali metal ozonides increases from Li to Cs. Reaction of metal ozonides with water proceeds through the intermediate formation of hydroxyl radicals: $4\,KO_3 + 2\,H_2O \rightarrow 4\,KOH + 5\,O_2$. Although, pure alkaline-earth ozonides have not been isolated, a binary ozonide, $Cs_2Ba(O_3)_4 \cdot 2\,NH_3$, has been prepared via partial cation exchange of CsO_3 in liquid ammonia (61).

Although ammonium ozonide (NH_4O_3) [12161-20-5] is too unstable to be isolated in pure form, tetramethylammonium ozonide [78657-29-1] has been prepared in near quantitaive yield via an exchange reaction, eg, $KO_3 + N(CH_3)_4\ O_2 \rightarrow N(CH_3)_4O_3 + KO_2$ (62). The insolubility of KO_2 drives the reaction. Organo phosphorus ozonides also have been prepared, eg, $[((C_6H_5)_3P)_2N]O_3$ and $[(((CH_3)_2N)_3PN)_4P]O_3$ (63).

Formation of Hydrogen Trioxide. Formation of hydrogen trioxide, HOOOH, has been observed as a transient intermediate in the ozonation of various organic molecules. For example, ozonation of 2-ethylanthrahydroquinone at

−78°C produces an organic hydrotrioxide and hydrogen trioxide in ~40% yield (64). Hydrogen trioxide decomposes by first-order kinetics beginning at about −40°C, forming water and singlet delta oxygen; in its reactions, hydrogen trioxide is even more electrophilic than ozone. Hydrogen trioxide also has been observed in ozonation of substituted hydrazines at −78°C. A half-life of 16 min was determined at 20°C (65).

Formation of Hydrogen Tetroxide. The reaction of hydrogen atoms with liquid ozone at −196°C proceeds through the intermediate formation of hydroperoxyl radicals forming hydrogen tetroxide, H_2O_4, which decomposes on warming to produce equimolar amounts of H_2O_2 and O_2 (66,67).

5.2. Organic Reactions. A compilation of nonaqueous reactions of ozone with organic compounds is given in Ref. 68. The strong electrophilicity of ozone is manifested in its reaction with a wide variety of organic and organometallic functional groups, eg, olefins, acetylenes, aromatics (carbocyclic and heterocyclic), activated C−H bonds (acetals, alcohols, aldehydes, ethers, and glycosides), unactivated C−H bonds (alkanes, cycloalkanes, and alkyl aromatics), deactivated C−H bonds (carboxylic acids and ketones), C=N and N=N bonds, Si−H and Si−C bonds, organometallic bonds (eg, Grignard reagents), and nucleophiles (eg, ammonia, amines, amino acids, arsines, disulfides, hydroxylamines, nitriles, phosphites, selenides, sulfides, and thioethers). Ozone also acts as a nucleophile, eg, in its reaction with carbocations. Numerous synthetic applications of ozone have been described (7). Rate constants listed in the following sections are second order constants generally at 20–25°C in units of $M^{-1}\,s^{-1}$ unless stated otherwise.

Kinetics and Mechanism of Ozone Reactions. Molecular ozone is an electrophile and attacks nucleophilic centers, ie, points of high electron density, in organic substrates. Reactivity of potential reaction sites is enhanced by the presence of electron-donating groups such as CH_3, and decreased by nonreactive bulky substituents and electron-withdrawing groups, eg, C=O, COOH, Cl, and NO_2. Reaction products depend on solvent type (reactive or nonreactive) and ozonation conditions (eg, pH). Ozone does not totally mineralize (ie, convert to CO_2, water, and relavant inorganic ions, eg, Cl^-, NO_3^-, SO_4^{2-}) most organic compounds during water treatment. Except in rare cases, eg, the oxidation of formate, only partial oxidation is achieved due to the low reactivity of common intermediate oxidation products, eg, acetic and oxalic acids. Although ozone has a high thermodynamic oxidation potential, its effectiveness in water treatment depends on the kinetics of its reactions, which can vary widely; indeed, rate constants can vary over 14 orders of magnitude, from $\sim 10^{-5}$ for acetic acid to $\sim 10^{9}$ for phenolate ion (69).

At low pH and normal temperature, ozone reacts selectively, ie, directly, with organic compounds. Second-order rate constants vary in the range $1–10^3$. By contrast, at higher pH values, eg, at alkaline pH common in natural waters, ozone also reacts nonselectively or indirectly through HO radicals formed by hydroxyl ion-catalyzed decomposition of ozone (see Aqueous Ozone Decomposition Mechanism). Hydroxyl radicals are nonselective oxidants that react rapidly, by radical addition, hydrogen abstraction, and electron transfer, with functional groups (eg, alkyl) that normally are resistant to ozone. Rate constants generally vary over the narrow range of $10^7–10^{10}$. However, the availability of hydroxyl radicals for oxidation of organics is decreased by radical scavengers, eg, bicarbonate and carbonate ions. The yields of HO radicals and O_2^- radical ions in aqueous ozone reactions with organic compounds have been measured (70).

The rate of aqueous ozonation reactions is affected by various factors such as the pH, temperature, and concentrations of ozone, substrate, promoters, and radical scavengers. Kinetic measurements have been carried out in dilute aqueous solution on a large number of organic compounds from different classes (69). A brief review of anhydrous–aqueous ozonation of various organic compounds is given in Refs. 71,72. The chemistry of aqueous ozone and oxidation kinetics and product formation in ozonation of drinking water have been reviewed (73–75). Some of the chemistry discussed in the following sections occurs more readily at high ozone and high substrate concentrations.

Singlet Oxygen Formation. High yields of singlet oxygen $O_2(^1\Delta_g)$ are formed when ozone reacts via oxygen-atom transfer with compounds, eg, methionine, methane sulfinic acid, and trimethylamine; other organic compounds produce significantly lower yields (48).

Activation of Ozone Reactions. As discussed above, the reactivity of ozone can be increased by raising the pH. Since this is not always practical in water treatment, other methods have been investigated and employed. The most studied and frequently used methods for enhancing the reactivity of ozone are uv and H_2O_2 (76) and to a lesser extent TiO_2. These so-called advanced oxidation processes (AOPs) increase the decomposition of ozone generating highly reactive species such as hydroxyl radicals (see discussions under photochemical decomposition of ozone and reaction of ozone with H_2O_2/HO_2^-). The O_3–uv system, initially investigated in 1975, was shown to be effective in the oxidation of complexed cyanides, chlorinated compounds, and pesticides; total mineralization being achieved in most cases (77). The main parameters affecting the efficiency of O_3–uv are ozonation rate, uv intensity, pH, alkalinity, and the type of compound. The O_3–uv system is similar to the O_3–H_2O_2 system except for substrates that absorb uv. The effectiveness of the ozonation of organic compounds is also physically enhanced by ultrasound (Sonozone). In simulated natural water containing fulvic acid, protein, and a disaccharide, the order of effectiveness in reducing the levels of TOC is $O_3{-}TiO_2 > O_3{-}H_2O_2 > O_3$ (78). Other methods also have been under investigation including: homogeneous catalysis via metal ions (79–81) and heterogeneous catalysis via granular activated carbon (82) and alumina (79,83).

Alkanes. Although ozone shows little tendency to react with saturated hydrocarbons under water treatment conditions, it can react via radical and ionic mechanisms with neat hydrocarbons containing secondary or tertiary hydrogen atoms. Isobutane yields mainly *tert*-butyl alcohol (major) and acetone (minor). Similarly, cyclohexane gives cyclohexanol and cyclohexanone as the primary oxidation products.

Nitrogen Compounds. Alkyl, cycloalkyl, and alkaryl primary amines are oxidized to nitro compounds in good yield with dry ozone at −78°C (84). The proposed mechanism involves stepwise oxidation forming intermediate hydroxylamine and nitroso derivatives. Tertiary amines are oxidized to amine oxides.

$$RNH_2 \xrightarrow{+O_3,\ -O_2} RNHOH \xrightarrow{+O_3,\ -O_2,\ -H_2O} RNO \xrightarrow{+O_3,\ -O_2} RNO_2$$

By contrast, the products formed on aqueous ozonation of aliphatic amines result from oxidation of N or C, rupture of the C−N bond, and condensation reactions. Thus, ozonation of primary amines proceeds via formation of hydroxylamine, oxime, and amide intermediates to yield aldehydes, carboxylic acids, esters, acylamines, and nitrate (85).

Low temperature, nonaqueous ozonation converts nitro compounds (where R′ is hydrogen or alkyl) to aldehydes and ketones in high yield (86).

$$\mathrm{RCH(NO_2)R'} \xrightarrow[\text{2. } \mathrm{O_3}, \text{ 3. } \mathrm{(CH_3)_2S}]{\text{1. } \mathrm{CH_3OH, CH_3O^-}} \mathrm{RC(O)R'}$$

Carbon−nitrogen double bonds in imines, hydrazones, oximes, nitrones, azines, and substituted diazomethanes can be cleaved, yielding mainly ketones, aldehydes, and/or carboxylic acids (87).

Alkyl amino acids in protonated form exhibit very low reactivity to ozone because the nucleophilicity of the amino nitrogen is neutralized (69,88). However, sulfur-containing protonated alkyl amino acids (cystine, cysteine, and methionine) can react rapidly due to the easily oxidizable sulfhydryl group, which initially gives sulfoxides and disulfides (89,90). Similarly, presence of aromatic groups (eg, histidine) enhances reactivity of protaonated amino acids. By contrast, unprotonated alkyl amino acids are readily ozonated (69,88). The products depend on whether reaction conditions favor attack by molecular ozone or HO radicals (91).

With a substituted amino acid such as serine [$\mathrm{HOCH_2CH(NH_2)COOH}$)], ozonation at pH 8.5 in the presence of *tert*-butanol as HO scavenger, results in deamination forming nitrate (92). The main organic by-product is hydroxyacetaldehyde (HAA), which is formed via decarboxylation. The HAA is oxidized further to glycolic acid, which also can form by carbon−carbon cleavage along with formic acid. Minor amounts of glyoxal also are formed. By contrast, ozonation under radical producing conditions (pH 8.5, $\mathrm{O_3/H_2O_2}$) results in deamination forming ammonia. Formic acid is the major by-product. Glycolic acid is formed in significant amounts and is oxidized to oxalic acid. Small amounts of glyoxylic acid, glyoxal, ketomalonic acid, and formaldehyde also were formed.

Oxygen Compounds. Saturated oxygen containing compounds react slowly with ozone with k values typically below ~3 (69). The β-diketone, dimedone (5,5-dimethyl-1,3-cyclohexanedione) being an extreme exception with $k = >4 \times 10^5$. The reactivity generally varies as follows: aldehydes > alcohols > ethers > ketones ≅ esters ≫ carboxylic acids. Ozonation of alcohols forms aldehydes or ketones, carboxylic acids, esters, peresters, and H_2O_2 (93). *tert*-Butanol reacts very slowly with molecular ozone but is rapidly oxidized by O_3−uv forming acetone, hydroxyisobutyraldehyde, and formaldehyde as primary intermediates, which are oxidized further to formic, acetic, oxalic, and pyruvic acids (94). Aldehydes are oxidized to carboxylic acids, whereas ketones are cleaved by ozone, eg, methyl ethyl ketone yields 2 mol of acetic acid. Acetals are converted to esters in high yield by low temperature ozonation in inert solvent (95,96).

With the exception of formic and malonic acids, saturated mono- and dicarboxylic acids are relatively unreactive toward ozone. Glyoxylic and malonic acids react at moderate rates and are observed as intermediate products of ozonation of many organics. Acetic and oxalic acids are relatively stable to ozone and often are the end products of ozonation in water treatment. Although acetic and oxalic acids are relatively stable to ozone, they are more readily oxidized by ozone to CO_2 in the presence of uv or H_2O_2; acetic acid is oxidized stepwise, at pH 7, to glycolate, oxalate, and then to CO_2 (77).

Isolated methylene groups are oxidized to carbonyl. For example, ozonation of malonic acid yields oxalic and hydroxymalonic acids; the latter is oxidized further to ketomalonic acid and H_2O_2.

Ethers react slowly with aqueous ozone resulting in C–O bond cleavage yielding alcohols, aldehydes, ketones, and esters. Methyl-*tert*-butyl ether (MTBE), a fuel additive that is becoming an increasingly common groundwater pollutant, is oxidized very slowly by molecular ozone in aqueous media ($k = 0.14$). By contrast, MTBE is readily oxidized by O_3–H_2O_2, yielding *tert*-butyl alcohol, acetone, aldehydes, formic acid, and esters as the major reaction products (97,98).

Sulfur Compounds. Mercaptans, sulfides, and disulfides are readily oxidized by ozone. Mecaptans are oxidized to sulfonic acids.

$$CH_3CH_2SH + 3\,O_3 \rightarrow CH_3CH_2SO_3H + 3\,O_2$$

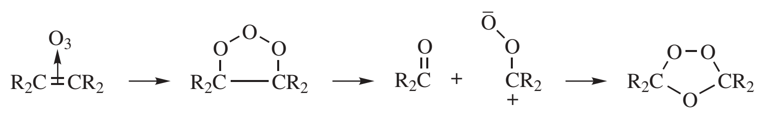
The rate constant for aqueous ozonation of ethyl mercaptan and dipropyl sulfide is $>2 \times 10^5$ (69). Sulfides are oxidized stepwise to sulfoxides and sulfones. Ozonation of disulfides yields a dialkylsulfonic acid anhydride that hydrolyzes to an alkyl sulfonic acid.

$$RSR + O_3 \longrightarrow R_2SO + O_2 \xrightarrow{O_3} R_2SO_2 + 2\,O_2$$

$$RSSR + 3\,O_3 \xrightarrow{-2O_2} RSO_2OSO_2R \xrightarrow{H_2O} 2\,RSO_3H$$

Halogen Compounds. Ozone reacts very slowly with halogenated hydrocarbons, eg, methylene chloride, chlorform, bromoform, and carbon tetrachloride with k values of ≤ 0.1 (69). Although degradation of halogenated aliphatics, eg, chloroform, trichloroethylene, tetrachlorethylene, and CCl_4 is too slow to be practical with ozone alone, it is greatly accelerated by using uv radiation (99–101) or H_2O_2 (102–105).

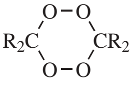
Alkenes. The rate of reaction with olefinic double bonds depends on the type of substituents and varies over eight orders of magnitude. The most common ozone reaction involves the cleavage of olefinic carbon–carbon double bonds. Electrophilic attack by ozone on carbon–carbon double bonds is concerted and stereospecific (65,106). The modified three-step Criegee mechanism involves a 1,3-dipolar cycloaddition of ozone to an olefinic double bond via a transitory π-complex **3** to form an initial unstable ozonide, a 1,2,3-trioxolane or molozonide **4**, where R is hydrogen or alkyl. The molozonide rearranges via a 1,3-cycloreversion to a carbonyl fragment **5** and a peroxidic dipolar ion or zwitterion **6**.



(3) (4) (5) (6) (7)

The dipolar ion **6** and its alternative resonance form $R_2C{=}O^+{-}O^-$, exist in both syn- and anti configurations that are formed in different amounts.

The dipolar ion can react in several ways according to the solvent and the structure of the olefin. In inert solvents, if the carbonyl compound is highly reactive (eg, an aldehyde), the dipolar ion can be added to the carbonyl fragment to give the normal ozonide or 1,2,4-trioxolane **7**; eg, 1,1- and 1,2-dialkylethylenes react in this manner. Tri- or tetraalkyl-substituted olefins produce a small, if any, yield of an ozonide when the ozonolysis is performed in nonreactive solvents (107). However, the ozonide can be prepared indirectly; eg, ozonation of acetone *O*-methyloxime in acetone gives 3,3,5,5-tetramethyl-1,2,4-trioxolane, which is the normal ozonide of tetramethylethylene (108). The same approach is used to prepare ozonides corresponding to those of vinyl ethers and derivatives of acrylonitrile. If the carbonyl fragment **5** is less reactive (eg, in a ketone), the dipolar ion **6** can dimerize to a cyclic bisperoxide **8** or polymerize to a linear peroxide **9**. The undesirable reaction intermediates **8** and **9** can be avoided by performing the reaction in reactive solvents, eg, methanol, followed by hydrolysis (109).



(**8**)

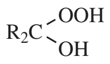
$$\left(\mathrm{CR_2{-}O{-}O}\right)_x$$

(**9**)

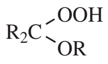
Steric hindrance can cause polymerization to predominate even if **5** is an aldehyde. With increasing bulk of substituents on one side of a double bond, epoxidation can compete with ozonolysis.

Commercially, pure ozonides generally are not isolated or handled because of the explosive nature of lower molecular weight species. Ozonides can be hydrolyzed or reduced (eg, by Zn/CH_3COOH) to aldehydes and/or ketones. Hydrolysis of the cyclic bisperoxide **8** gives similar products. Catalytic (Pt/excess H_2) or hydride (eg, $LiAlH_4$) reduction of **7** provides alcohols. Oxidation (O_2, H_2O_2, peracids) leads to ketones and/or carboxylic acids. Ozonides also can be catalytically converted to amines by NH_3 and H_2. Reaction with an alcohol and anhydrous HCl gives carboxylic esters.

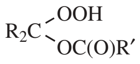
The diploar ion **6** can react with protic solvents to produce a variety of products. Reaction with water yields a transient hydroperoxy alcohol that can dehydrate to a carboxylic acid or split out H_2O_2 to form a carbonyl compound (aldehyde or ketone, R_2CO). In alcoholic media, the product is an isolable hydroperoxy ether **11** that can be hydrolyzed or reduced [with $(CH_3O)_3P$ or $(CH_3)_2S$] to a carbonyl compound. Reductive amination of **11** over Raney nickel produces amides and amines (110). Reaction of the dipolar ion with a carboxylic acid to form a hydroperoxy ester **12** is commercially important because it can be oxidized to other acids, RCOOH and R′COOH. Reaction of the the dipolar ion with HCN produces α-hydroxy nitriles that can be hydrolyzed to α-hydroxy carboxylic acids. Carboxylates are obtained with H_2O_2/HO^- (111). The dipolar ion can be reduced during the course of the reaction by tetracyanoethylene to produce its epoxide (112).


$R_2C(OOH)(OH)$

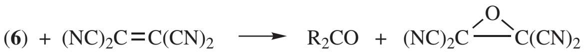
(10)


$R_2C(OOH)(OR)$

(11)


$R_2C(OOH)(OC(O)R')$

(12)



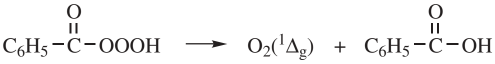
Alkynes. Triple bonds are attacked much more slowly by ozone than double bonds. Acetylene gives primarily glyoxal. With substituted compounds, carboxylic acids and dicarbonyl compounds are obtained; for instance, stearolic acid yields mainly azelaic acid, and a small amount of 9,10-diketostearic acid (113).

Aromatics. Aromatic ring unsaturation is attacked much slower than olefinic double bonds, but behaves as if the double bonds in the classical Kekule structures really do exist. Thus, anhydrous benzene initially yields a triozonide that hydrolyzes forming three mols of glyoxal, which can be oxidized further to glyoxylic acid and then to oxalic acid (71,72). Increasing the number of aromatic rings increases the reactivity, thus, naphthalene and phenanthrene react 1500 and 10^4 times (69,114) faster than benzene. The reactivity of substituted benzenes toward ozone in water at low pH vary widely, with k values ranging from 0.09 for nitrobenzene to 1.4×10^9 for phenolate ion (69). Substituted aromatics give mixtures of aliphatic acids. Ring substituents such as amino, nitro, and sulfonate are cleaved during ozonation forming nitrate and sulfate. Partial oxidation of aqueous phenol with ozone forms catechol, hydroquinone, 1,4-benzoquinone, and *cis,cis*-muconic acid and H_2O_2 (115,116). The product distribution varied with pH and whether HO radical scavegers were employed. Low yields of singlet oxygen $[O_2(^1\Delta_g)\}$ were observed at pH 7 and 10. Further oxidation produces glyoxal and glyoxylic, oxalic, and formic acids, and CO_2. Substituted phenols are oxidized more rapidly by O_3/uv than by O_3 alone, the TOC removal increasing with pH (117). Chlorobenzene reacts more slowly with ozone than does phenol, but gives the same ring-opening products (71,72). Intermediate oxidation products include *o*-, *m-,* and *p*-chlorophenols, as well as chlorotartaric acid. Chlorocresols and thiophenols also give similar ozonation products as does phenol. Aqueous ozonation of naphthalene at pH 5.9 forms *o*-phthalicdicarbaldehyde, phthalaldehydic acid, phthalic acid, oxalic and formic acid, and hydrogen peroxide (118). Aqueous ozonation of *p*-toluenesulfonic acid yields methyl glyoxal, formic, acetic, pyruvic, oxalic, and sulfuric acids and H_2O_2, whereas, I-naphthalene sulfonic acid produced maleic, fumaric, oxalic, and formic acids and sulfate (119,120).

Heterocyclics. Ozone reacts slowly with heterocyclic compounds. Cyanuric acid is resistant to oxidation by ozone. Creatinine is oxidized slowly, even at high ozone and substrate concentrations (69,121). Reaction of ozone (or HO) with atrazine (2-chloro-4ethylamino-6-isopropylamine-*s*-triazine) involves oxidation of the alkyl groups; the C−Cl and C−N bonds being unaffected (122). 3,4-Dimethylpyridine yields glyoxal, biacetal, ammonia, as well as formic, acetic, pyruvic, oxalic, and glyoxylic acids.

Ozone Adducts. At low (−78°C) temperatures ozone forms stable adducts with electron-rich compounds, eg, phosphites (123), phosphines, tertiary amines, sulfides, and sulfoxides. The adduct is a cyclic, four-membered, trioxygencontaining ring that can be regarded as a moloxide. On warming, it decomposes and yields an oxidized form of the substrate, eg, triphenylphosphite gives triphenylphosphate, and singlet oxygen, $O_2(^1\Delta_g)$. Decomposition of adducts, eg, triphenyl phosphite–ozone provides a convenient method for accomplishing chemical oxidations involving singlet oxygen and making it a useful oxygenating agent for synthetic and mechanistic applications.

Formation of Hydrotrioxides. Hydrotrioxides are intermediates in the ozonation of various organic substrates, including hydrocarbons (with reactive secondary or tertiary hydrogen atoms), ethers, alcohols, aldehydes, ketones, acetals, hydroquinones, amines, diazo compounds, and silanes. Hydrotrioxides formed by low (−78°C) temperature ozonation have been isolated and characterized; they can be formed by a 1,3-dipolar insertion mechanism and decompose by radical and ionic pathways in the temperature range of −45 to −10°C, releasing singlet oxygen. For example, ozone inserted into the C−H bond of the carbonyl group of benzaldehyde at −78°C can produce the organic hydrotrioxide **13**, which on decomposition yields singlet O_2 and benzoic acid (124). Ozonation of 2-ethylanthrahydroquinone at −78°C produces 2-ethylanthraquinone, an organic hydrotrioxide, and hydrogen trioxide (H_2O_3) in ~40% yield (64).



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OOOH \longrightarrow O_2(^1\Delta_g) + C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(**13**)

6. Stratospheric Ozone

Kinetic data and chemistry of the stratosphere and troposphere are reviewed in Refs. 10,125, and 126–128.

6.1. The Stratosphere.

The stratosphere extends from ~15 to 50 km. Ozone is a minor, but important constituent of the stratosphere. Its maximum concentration of about 10 ppmv occurs at ~35 km. The temperature ranges from ~215 K at 15 km to ~270 K at 50 km. Light absorption by the atmosphere is responsible for shielding the Earth's surface from solar radiation below ~300 nm. Oxygen is the main absorber at ~200 nm, whereas ozone is the main absorber in the 230–320 nm range. The warm layer at 45–55 km is due to absorption of solar radiation by ozone and heat liberated in ozone formation and destruction, which helps to maintain thermal equilibrium on earth.

Ozone Formation. Ozone is formed rapidly in the stratosphere (15–50 km) by the action of short-wave uv solar radiation (<240 nm) on molecular oxygen, $O_2 + h\nu \rightarrow 2\ O$. At wavelengths > 175 nm, only ground-state (^3P) atoms are formed; whereas at wavelengths < 175 nm, one ground-state and one excited (^1D) atom are formed. Ground-state atoms also can form by the predissociation of electronically excited O_2. The oxygen atoms can react with molecular oxygen to yield ozone: $O + O_2 + M \rightarrow O_3 + M$. Ozone also can form from vibrationally excited O_2: $O_2(X^3\Sigma_g^-) + O_2 \rightarrow O_3 + O$ (45).

Ozone Destruction. Ozone can be destroyed photochemically: $O_3 + h\nu \rightarrow O + O_2$. In addition, ozone can be destroyed by reaction with oxygen atoms ($O + O_3 \rightarrow 2\ O_2$) as well as with excited O_2 molecules ($^1\Delta_g$, $^1\Sigma_g^+$) and $^3\Sigma_g^-$

and other free radicals (10–12). Since the early 1960s, it has been recognized that radicals, eg, NO, HO, Cl, and Br, affect the abundance and distribution of ozone in the stratosphere (43). The so-called ozone deficit problem has arisen because earlier studies simulating stratospheric chemistry concluded that ozone formation is significantly less than its destruction (45,129).

Ozone Concentration. Most ozone is formed near the equator, where solar radiation is greatest, and transported toward the poles by normal circulation patterns in the stratosphere. Consequently, the concentration is minimum at the equator and maximum for most of the year at the north pole and $\sim 60^\circ$S latitude. The equilibrium ozone concentration also varies with altitude; the maximum occurs at ~ 25 km at the equator and 15–20 km at or near the poles. It also varies seasonally, daily, as well as interannually.

6.2. Effect of Nitric Oxide on Ozone Depletion. Nitrous oxide is injected into the atmosphere primarily by bacterial denitrification of nitrogen compounds (augmented by nitrogen fertilizers) in the soil. While this process mainly forms N_2, $\sim 7\%$ results in formation of N_2O. While N_2O is stable in the troposphere, it is degraded in the stratosphere (into which it is transported via Brewer–Dobson Circulation) where most is photolyzed to nitrogen ($N_2O + h\nu \rightarrow N_2 + O$), but $\sim 3\%$ is converted to nitric oxide [$N_2O + O(^1D) \rightarrow 2\ NO$], which in turn can catalyze the destruction of ozone. The two main cycles are 1 and 2.

$$\begin{aligned}
\text{Cycle 1}: \quad & NO + O_3 \rightarrow NO_2 + O_2 \\
& NO_2 + O \rightarrow NO + O_2 \\
\text{Net} \quad & O_3 + O \rightarrow 2\,O_2 \\
\text{Cycle 2}: \quad & NO + O_3 \rightarrow NO_2 + O_2 \\
& NO_2 + O_3 \rightarrow NO_3 + O_2 \\
& NO_3 + h\nu \rightarrow NO + O_2 \\
\text{Net} \quad & 2\ O_3 + h\nu \rightarrow 3\ O_2
\end{aligned}$$

The aircraft campaign via The Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) investigated the photochemistry of the atmosphere up to 21 km between 15 and 60° N latitude in the spring of 1993. It showed that cycles 1 and 2 account for $< 20\%$ of the total ozone loss observed during spring in the lower stratosphere at mid-north latitudes (130). Data from sattelite measurements (the Halogen Occultation Experiment, HALOE, aboard the Upper Atmosphere Research Satellite, UARS) for 1993 show that NO_x (ie, $NO + NO_2$) catalyzed ozone destruction becomes more important at higher altitudes and latitudes (131).

During nighttime, NO_2 and NO_3 reform equilibrium amounts of N_2O_5. Nitrogen pentoxide can react on the surface of sulfuric acid aerosols releasing gaseous nitric acid. Reaction of NO_2 with HO radicals also forms HNO_3. Nitric acid and N_2O_5 photolyze slowly in the gas phase and regenerate NO_2 radicals. Nitric acid is slowly transported from the lower stratosphere into the troposphere where it is removed in rain.

6.3. Effect of Hydroxyl Radicals on Ozone Depletion.

Hydroxyl radicals, formed by reaction of (^1D) oxygen atoms with water vapor or CH_4 are involved in several catalytic cycles, which result from whether HO and the intermediate HO_2 react with O atoms or ozone. Above 40 km, reaction of HO with O atoms is favored, whereas below 40 km, reaction with ozone is favored. Above 30 km the intermediate HO_2 reacts with O atoms, whereas < 30 km reaction with ozone is favored. Below 30 km, where the O atom concentration is low, both HO and HO_2 react with ozone as shown in the following catalytic cycle (10–12,43)

$$\begin{aligned} \text{Cycle 3}: \quad & HO + O_3 \rightarrow HO_2 + O_2 \\ & HO_2 + O_3 \rightarrow HO + 2\ O_2 \\ \text{Net} \quad & 2\ O_3 \rightarrow 3\ O_2 \end{aligned}$$

This cycle accounts for 30–50% of the total photochemical ozone loss observed during spring in the lower stratosphere at mid-north latitudes based on observed HO_2 concentrations (130).

6.4. Effect of Halogen Radicals on Ozone Depletion.

Halogen radicals capable of destroying ozone are formed by photolysis of chemical compounds from anthropogenic and natural sources.

Sources of Halogen Radicals. The release of chlorofluorocarbons (CFCs) from industrial production of aerosol sprays, coolants for refrigerators and air conditioners, blowing agents for foams, cleaners for electronic parts, and Halons (bromofluorocarbons) from fire extinguishing agents, has created conditions for the depletion of O_3 in the stratosphere (132–135). In addition to the main CFCs, $CFCl_3$ (CFC-11), and CF_2Cl_2 (CFC-12), other sources of chlorine are $CHFCl_2$ (CFC-22), $C_2F_3Cl_3$ (CFC-113), CCl_4, CH_3CCl_3, and CH_3Cl released from the oceans and from the burning of biomass. The main Halons are CF_3Br (H 1301) and CF_2ClBr (H 1211). Methyl bromide is another important source of bromine, released into the atmosphere by marine plankton, through the burning of biomass, or by its use as a soil fumigant.

Activation of Halogen Sources. Although inert in the lower atmosphere (troposphere), the fully halogenated CFCs and Halons diffuse into the upper stratosphere where they are photodissociated by the intense ultraviolet radiation.

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

$$CF_3Br + h\nu \rightarrow CF_3 + Br$$

The C−F bonds also are cleaved, resulting ultimately in the formation of HF, a stable fluorine reservoir. Hydrogen-containing molecules are degraded by HO radicals in the troposphere, limiting the fraction that reaches the stratosphere. The small natural source of active chlorine comes from photolysis of methyl chloride ($CH_3Cl + h\nu \rightarrow CH_3 + Cl$) and via HO radical initiated degradation. Small amounts of chlorinated hydrocarbons (eg, CCl_4) also diffuse into the stratosphere from anthrpogenic sources and are photolyzed to Cl radicals. Methyl bromide, from natural and anthropogenic sources, undergoes photodissociation like methyl chloride forming Br atoms.

Ozone Destruction by Halogen Radicals. The Cl (or Br) atoms formed by photodecomposition of CFCs can convert ozone to oxygen catalytically; indeed, one chlorine atom is capable of destroying thousands of ozone molecules. Although much less abundant in the stratosphere than chlorine, bromine is considerably more reactive in some reactions, thus accounting for a significant fraction of ozone destruction in certain catalytic cycles. Satellite and airborne observations have shown significant decreases in total column ozone since 1978, ranging from zero near the equator to 6–8% at high latitudes (136). The most dramatic ozone decrease occurs every year in spring at the Antarctic ozone hole. In 1992 and 1993, the ozone levels were ∼50% less than in 1979.

Catalytic Cycles Involving Halogen Radicals. Halogen radicals account for about one-third of photochemical ozone loss observed in the spring in the lower stratosphere (< 21 km) at 15–60°N latitude (130). The following three cycles (*4–6*) are the most important.

$$\begin{aligned} \text{Cycle 4}: \quad & Cl + O_3 \rightarrow ClO + O_2 \\ & ClO + O \rightarrow Cl + O_2 \\ \text{Net} \quad & O_3 + O \rightarrow 2\ O_2 \end{aligned}$$

This cycle is terminated by the reaction of chlorine atoms with methane: $Cl + CH_4 \rightarrow HCl + CH_3$. The importance of this cycle depends on the availability of oxygen atoms and varies with altitude as well as the time of year; it accounts for only 5% of the halogen-controlled loss at 15 km, but increases to 25% at 21 km.

The following mechanisms are more important for explaining ozone destruction at lower altitudes, where the availability of oxygen atoms is limited; $X = Cl$ and Br:

$$\begin{aligned} \text{Cycle 5}: \quad & HO_2 + XO \rightarrow HOX + O_2 \\ & HOX + h\nu \rightarrow HO + X \\ & X + O_3 \rightarrow XO + O_2 \\ & HO + O_3 \rightarrow HO_2 + O_2 \\ \text{Net} \quad & 2\ O_3 \rightarrow 3\ O_2 \end{aligned}$$

Cycle 5 accounts for ∼30% and 20–30% of the halogen-controlled loss for chlorine and bromine, respectively.

$$\begin{aligned} \text{Cycle 6}: \quad & BrO + ClO \rightarrow Br + ClOO \\ & Br + O_3 \rightarrow BrO + O_2 \\ & ClOO + M \rightarrow Cl + O_2 + M \\ & Cl + O_3 \rightarrow ClO + O_2 \\ \text{Net} \quad & 2\ O_3 \rightarrow 3\ O_2 \end{aligned}$$

Cycle 6 accounts for 20–25% of the halogen-controlled loss (M is a third body molecule for energy absorption). The possible contribution of naturally occurring iodine compounds to ozone destruction (via I and IO radicals) is being investigated (137,138).

Other cycles are possible in the lower startosphere such as the following (127).

$$\begin{aligned}
\text{Cycle 7: } \quad Cl + O_3 &\rightarrow ClO + O_2 \\
NO + O_3 &\rightarrow NO_2 + O_2 \\
ClO + NO_2 + M &\rightarrow ClONO_2 + M \\
ClONO_2 + h\nu &\rightarrow Cl + NO_3 \\
NO_3 + h\nu &\rightarrow NO + O_2 \\
\text{Net} \quad 2\ O_3 &\rightarrow 3\ O_2
\end{aligned}$$

Formation of Chlorine Reservoirs. Other reactions, eg, $ClO + NO_2 + M \rightarrow ClONO_2 + M$, $Cl + CH_4 \rightarrow HCl + CH_3$, and $ClO + HO_2 \rightarrow HOCl + O_2$ also are important and result in formation of temporary inert chlorine reservoirs and retard ozone depletion. Hydrogen chloride is the longest lived with a lifetime of weeks, whereas HOCl is the shortest with a lifetime of hours because it is quickly photolyzed in sunlight. The relative abundance varies as follows: $ClONO_2 > HCl > HOCl$. They are the most abundant chlorine species at lower latitudes before winter. The HCl is slowly transported from the lower stratosphere into the troposphere where it is removed in rain.

Formation of Bromine Reservoirs. By contrast with chlorine, bromine does not form significant reservoirs because $BrONO_2$ and HOBr are readily photolyzed and HBr formation is not favorable.

Denoxification. The slow photolysis of $ClONO_2$ ($ClONO_2 + h\nu \rightarrow Cl + NO_3$) yields chlorine atoms capable of decomposing ozone and accounts for 10–15% of halogen-controlled losses (130). Nitrogen trioxide can photolyze to O_2 and NO, which can react with ozone forming NO_2. It also can react with NO_2 forming N_2O_5, which can hydrolyze on sulfate aerosols forming HNO_3, reducing the availability of NO_2. This allows higher free ClO concentrations, shifting ozone catalytic decomposition from NO_x to ClO_x and HO_x (139). With the exception of NO_2, all radicals are produced photolytically each day and their concentrations fall to zero during the night.

Effect of Antarctic Polar Stratospheric Clouds. Although relatively unreactive in the gas phase, chlorine nitrate and HCl can react on the surface of frozen particles in polar stratospheric clouds (PSCs), which form at altitudes of 10–25 km when air trapped within the polar vortex (a circular wind pattern) that circles the Antarctic in winter is cooled to low temperatures during the polar night, thus preventing replenishment by fresh ozone (140). Type I PSCs form at 193 K and type II (ice) at 187 K. Type I PSCs, originally thought to consist of nitric acid trihydrate, are now thought to consist of nitric and sulfuric acids and water (126–128,141). The main heterogeneous reactions are as follows (126–128).

$$ClONO_{2(g)} + HCl_{(s)} \rightarrow Cl_{2(g)} + HNO_{3(s)}$$

$$ClONO_{2(g)} + H_2O_{(s)} \rightarrow HOCl_{(g)} + HNO_{3(s)}$$

$$HOCl_{(g)} + HCl_{(s)} \rightarrow Cl_{2(g)} + H_2O_{(s)}$$

$$N_2O_{5(g)} + H_2O_{(s)} \rightarrow 2\,HNO_{3(s)}$$

$$N_2O_{5(g)} + HCl_{(s)} \rightarrow ClNO_{2(g)} + HNO_{3(s)}$$

Were the subscripts g and s denote the gas and solid phases. Since the nitric acid formed remains with the cloud particle, PSC chemistry produces an atmosphere rich in reactive chlorine species but depleted in NO_2. These reactions are the key to the formation of the Antarctic hole, and continue until the break-up of the polar vortex and warming of the stratosphere in the spring. Type II PSC particles can grow sufficiently large to sediment out of the stratosphere. This denitrification process removes HNO_3 as a source of NO_2 (142). The volatilized gaseous chlorine and HOCl are photolyzed to chlorine atoms when sunlight returns in the spring: $Cl_2 + h\nu \rightarrow 2\ Cl$ and $HOCl + h\nu \rightarrow HO + Cl$. The chlorine atoms reenter ozone catalytic destruction cycles including cycle 6 and the following (143).

$$\begin{aligned}\text{Cycle 8}: \quad 2\,Cl + 2\,O_3 &\longrightarrow 2\,ClO + 2\,O_2\\ 2\,ClO \xrightarrow{+M} (ClO)_2 &\xrightarrow{h\nu} Cl + ClOO\\ ClOO &\xrightarrow{+M} Cl + O_2\\ \text{Net} \quad 2\,O_3 &\longrightarrow 3\,O_2\end{aligned}$$

The ClO dimer (ClOOCl) has been observed in the stratosphere by direct measurement via a NASA ER-2 aircraft during the joint SOLVE/THESEO-2000 mission over the Arctic in the winter of 1999–2000 (144).

Effect of Sulfate Clouds. Similar heterogeneous reactions also can occur, but somewhat less efficiently, in the lower stratosphere on global sulfate clouds (ie, aerosols of sulfuric acid), which are formed by oxidation of SO_2 and COS from volcanic and biological activity, respectively (139). The effect is most pronounced in the colder regions of the stratosphere at high latitudes. Indeed, the sulfate aerosols resulting from eruptions of El Chicon in 1982 and Mt. Pinatubo in 1991 have been implicated in subsequent reduced ozone concentrations (145).

Effect of Arctic Polar Stratospheric Clouds. Arctic polar stratospheric clouds (mostly type I) form sporadically because only rarely are temperatures sufficiently low. Nevertheless, the northern polar vortex contains enhanced ClO levels, similar to the Antarctic, that contribute to significant ozone loss in late winter (146). This may indicate that crucial heterogeneous chemistry on sulfate aerosols is occurring, although no hole has been observed. This is attributed to the relatively short period of significant loss and to the fact that the warmer, less stable Arctic vortex dissipates by late winter. In addition, there is a lack of denitrification, ie, removal of nitric acid via sedimentation of PSCs, observed in the Antarctic (142). Thus, the presence of HNO_3 throughout the arctic winter moderates ozone destruction by providing a source of NO_2 to quench ClO. Nevertheless, record-low ozone levels, up to 40% below normal and approaching those in the recurring Antarctic ozone hole, were observed in the winter of 1995 due to exceptionally low temperatures in the Arctic vortex (147).

7. Tropospheric Ozone

7.1. The Troposphere. The troposphere (the region of the atmosphere <15 km) contains organic and inorganic compounds that are introduced into the atmosphere via biogenic and anthropogenic sources. The troposphere also contains small amounts of ozone that is formed by photochemical oxidation of CO and hydrocarbons catalyzed by HO_x ($HO + HO_2$) and NO_x ($NO + NO_2$). Efforts are underway to determine how much stratospheric ozone drifts down to the upper troposphere (148,149). Although only ~10% of the atmospheric ozone is present in the troposphere, this small fraction plays a fundamental role in atmospheric chemistry because it is an initiator (via formation of hydroxyl radicals), a reactant, and a product in tropospheric oxidation chemistry. Generally, the concentation of pollutants is prevented from building-up to excessive levels due to their oxidation by the small concentration of hydroxyl radicals. However, in urban areas the concentrations of pollutants and ozone are appreciably higher than in remote areas due to contributions from fossil fuel burning and exhaust from internal combustion engines, which can result in so-called photochemical smog. The chemistry of the troposphere is reviewed in Refs. 125–128.

Photochemical Smog. Although the naturally occurring concentration of ozone at the earth's surface is very low, this distribution has been altered by the emission of anthropogenic pollutants which increase the production of ozone. Photochemical smog, an aerosol irritant gas mixture, occurs in urban industrialized areas where heavy motor vehicle traffic is common, especially those areas where temperature inversions are common (eg, Denver, Los Angeles, Washington, D.C., and Mexico City). It forms at low altitudes by photolytic reactions involving nonmethane hydrocarbons, NO, and CO, resulting in low but potentially harmful concentrations of ozone and other irritating substances, eg, aldehydes, ketones, acids, organo peroxides and nitrates, and H_2O_2.

Factors Affecting Background Ozone. The ambient ozone concentration depends on cloud cover, time of day and year, and geographical location. Although the background concentration of ozone in surface air is ~0.01–0.03 ppm, during severe smog days in the Los Angeles area, eg, it has often reached 0.5 ppm, and a maximum of 1 ppm in 1957. The main automobile exhaust pollutants (CO, NO, and hydrocarbons) peak at ~7 a.m. in Los Angeles, coinciding with the morning rush hour traffic (125); the concentrations of nitrogen dioxide and ozone reach a maximum ~3 and 5 h later, respectively. While NO is largely oxidized in 4–5 h, NO_2 and O_3 persist over longer time spans. The initial buildup of CO and hydrocarbons is followed by a slow decline as they are oxidized. Maximum concentrations of organic oxidation products (eg, aldehydes, organo nitrates) tend to roughly coincide with the ozone maximum. The evening rush hour traffic does not produce much smog primarily because the inversion layer has undergone considerable thermal expansion and the sunlight intensity is weaker and soon disappears. By sundown, the concentration of ozone has fallen to very low levels. Nights are normally free of smog. In the early morning hours, NO is removed slowly by the oxygen atom chain, which is initiated by the photolysis of NO_2 and subsequently by the photolysis of ozone. Later in the day when the light intensity is higher, the hydroxyl chain causes the NO conversion to accelerate.

Daytime Oxidation Chemistry. The primary source of hydroxyl radicals in the troposphere is reaction of electronically excited O atoms formed by photolysis of ozone with water vapor.

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad O(^1D) + H_2O \rightarrow 2\ HO$$

Hydroxyl radicals are widely dispersed throughout the troposphere because of the widespread presence of ozone and water vapor. Most of the $O(^1D)$ atoms formed on photolysis of ozone are quenched back to the ground state by collisions with N_2 and O_2 molecules and can react with oxygen to reform ozone: $O(^3P) + O_2 + M \rightarrow O_3 + M$. However, some of the $O(^3P)$ atoms also can react with reactive hydrocarbons, eg, ethylene, generating reactive radicals: $O(^3P) + C_2H_4 \rightarrow HCO + CH_3$. Minor amounts of HO are formed by reaction of $O(^1D)$ with methane $[O(^1D) + CH_4 \rightarrow HO + CH_3]$. Under urban conditions, hydroxyl radicals also are formed directly from secondary sources, eg, photolysis of HONO and to a lesser extent H_2O_2. In addition, hydroxyl radicals also are formed indirectly via HO_2 and RO_2 (both of which form HO by reaction with NO) formed during oxidation of CO and hydrocarbons and by photolysis of aldehydes and ketones. In addition to its photodecomposition, ozone also reacts with radicals, eg, HO, NO, HO_2, and NO_2; relative rate constants for these reactions vary in the order: 4:1:0.1:0.002.

In unpolluted atmosphere, HO radicals react primarily with naturally occurring CO and to a lesser extent methane, resulting in a net increase in ozone concentration (43,125–128,150–152); In polluted air, the radical-dominated chemistry of the troposphere is more complex involving intertwining cycles of gas- , condensed- , and multiple-phase reactions. Only the more important reactions are shown below where R is hydrogen or an alkyl group. Reactions involving unsaturated hydrocarbons, eg, alkenes and aromatics, are more complex than for saturated hydrocarbons.

Hydroxyl radicals react with CO and hydrocarbons as follows:

$$\begin{array}{ll} CO + HO \rightarrow CO_2 + H & H + O_2 + M \rightarrow HO_2 + M \\ RCH_3 + HO \rightarrow RCH_2 + H_2O & RCH_2 + O_2 + M \rightarrow RCH_2O_2 + M \end{array}$$

When NO_x concentrations are low as in remote areas, HO_2 radicals can react with ozone and result in net ozone destruction rather than formation via a chain reaction.

$$HO_2 + O_3 \rightarrow HO + 2\,O_2 \qquad HO + O_3 \rightarrow HO_2 + O_2$$

Recombination of HO_2 radicals or reaction with an organic peroxo radical also are possible, forming hydrogen peroxide and an organic hydroperoxide, respectively.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad RCH_2O_2 + HO_2 \rightarrow RCH_2O_2H + O_2$$

At higher NO_x, NO is oxidized by HO_2 to NO_2, which on photolysis leads to regeneration of NO and subsequent ozone formation.

$$HO_2 + NO \rightarrow HO + NO_2 \qquad NO_2 + h\nu \rightarrow NO + O(^3P)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

Some of the $O(^3P)$ atoms also can react with reactive hydrocarbons as discussed above. The HO radicals formed in the above sequence can form more peroxy radicals as shown above. Oxidation of NO by ozone results in a null cycle because photolysis of the NO_2 formed leads to regeneration of both NO and O_3. Nitric oxide also is rapidly oxidized to NO_2 by organic peroxo radicals resulting in formation of an aldehyde and HO_2.

$$RCH_2O_2 + NO \rightarrow RCH_2O + NO_2 \qquad RCH_2O + O_2 \rightarrow RCHO + HO_2$$

Photolysis of aldehydes and ketones forms radicals that react further forming HO_x. For example, formaldehyde (formed in oxidation of methane) and acetone (formed by oxidation of propane) are photolyzed as follows:

$$HCHO + h\nu \rightarrow H + HCO \qquad CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO$$

Aldehydes also undergo further reactions forming organic nitrates, eg, peroxyacetyl nitrate ($CH_3COO_2NO_2$ or PAN). This is an important side reaction in hydrocarbon oxidation because PAN is one of the noxious compounds present in photochemical smog.

$$RCHO + HO \rightarrow RCO + H_2O \qquad RCO + O_2 \rightarrow RC(O)O_2$$
$$RC(O)O_2 + NO \rightarrow R + CO_2 + NO_2 \quad \text{(major route)}$$
$$RC(O)O_2 + NO_2 \rightarrow RC(O)O_2NO_2 \quad \text{(minor route)}$$

Reaction of NO_2 with HO eliminates HO_x and NO_x by formation of nitric acid ($HO + NO_2 \rightarrow HNO_3$), which is removed from the atmosphere dissolved in raindrops and adsorbed on particulates. This process is irreversible and represents the principle pathway for removal of NO_x from the troposphere.

Nightime Oxidation Chemistry. Despite the absence of sunlight, oxidation chemistry still occurs. Although oxidation of NO by O_2 is very slow, ozone rapidly converts NO to NO_2, which is slowly oxidized to nitrate radicals by ozone: $NO_2 + O_3 \rightarrow NO_3 + O_2$. Reaction of NO_2 and NO_3 forms equilibrium concentrations of nitrogen pentoxide: $NO_2 + NO_3 + M \rightleftarrows N_2O_5 + M$. Although N_2O_5 does not react with water in the gas phase, it readily reacts with water droplets to form nitric acid ($N_2O_5 + H_2O \rightarrow 2\ HNO_3$) that is removed from the atmosphere as discussed previously. Nitrate radicals can initiate oxidation of organic compounds and also act as a chain propagator. Although reaction by H abstraction is slow with unsubstituted alkanes, aldehydes yield acyl radicals that react with O_2 forming acylperoxy radicals, potential sources of peroxyacyl nitrates. Reaction of NO_3 with alkenes is complex forming nitro-oxy radicals that decompose or form stable organo nitrates. For example, reaction of NO_3 with propylene in the presence of O_2 and NO_x yields HCHO, CH_3CHO, 1,2-dinitropropane, nitroperoxypropyl nitrate, and α-nitro-oxyacetone. In daylight, the nitrate radical is rapidly photolyzed and ultimately converted to NO_2.

$$NO_2 + O(^3P) \leftarrow NO_3 + h\nu \rightarrow NO + O_2$$

$$NO_3 + NO \rightarrow 2\,NO_2$$

Effect of Halogen Chemistry. Inorganic chlorine and bromine radicals and compounds similar to those in the stratosphere are present in the troposphere and are formed by oxidation of halocarbons (eg, CH_3Cl and CH_3Br), however, their chemistry is relatively unimportant. By contrast, significant ozone depletions in high northern latitudes observed during the spring have been attributed to enhanced levels of chlorine and bromine formed in the gas phase in heterogeneous reactions involving seasalt aerosols.

8. Ozone Generation by Electric Discharge

Ozone can be generated by a variety of methods, the most common of which involves the dissociation of molecular oxygen electrically or photochemically (uv). The short-lived oxygen atoms (lifetime $\sim 10^{-5}$ s) react rapidly with oxygen molecules to form ozone. The widely employed technique of electric discharge produces much higher concentrations than the uv technique and is more practical and efficient for production of large quantities. A less common method of ozone formation is electrochemical generation (see Other Methods of Ozone Generation).

Commercial production and utilization of ozone by electric discharge (also called corona or silent discharge) consists of five basic unit operations: gas preparation, electrical power supply, ozone generation, contacting (ie, ozone dissolution in water), and destruction of ozone in contactor off-gases (Fig. 1).

8.1. Discharge Characteristics. The energy for chemical reaction is transferred to oxygen molecules by energetic electrons producing atoms, excited molecules, and ions. In an ozone generator, the feed gas (oxygen or air) passes between two closely spaced electrodes (one of which is coated with a dielectric) under an applied nominal potential of ~10 kV. A corona or dielectric barrier discharge occurs when the gas becomes partially ionized, resulting in a characteristic violet glow in air. Corona discharge consists of numerous randomly distributed, low current (but high current density) microdischarge pulses (153–156). The approximately columnar streamers or filaments (100–200 μm diameter) emanating from the metal electrode discharge at the dielectric and extinguish within 10 ns.

Because ozone formation occurs only within these microdischarge channels, ozone-production efficiency for the most part depends on the strength of the microdischarges, which is influenced by a number of factors, eg, the gap width, pressure, properties of the dielectric and metal electrode, power supply, and moisture. In weak discharges, a significant fraction of the energy is consumed

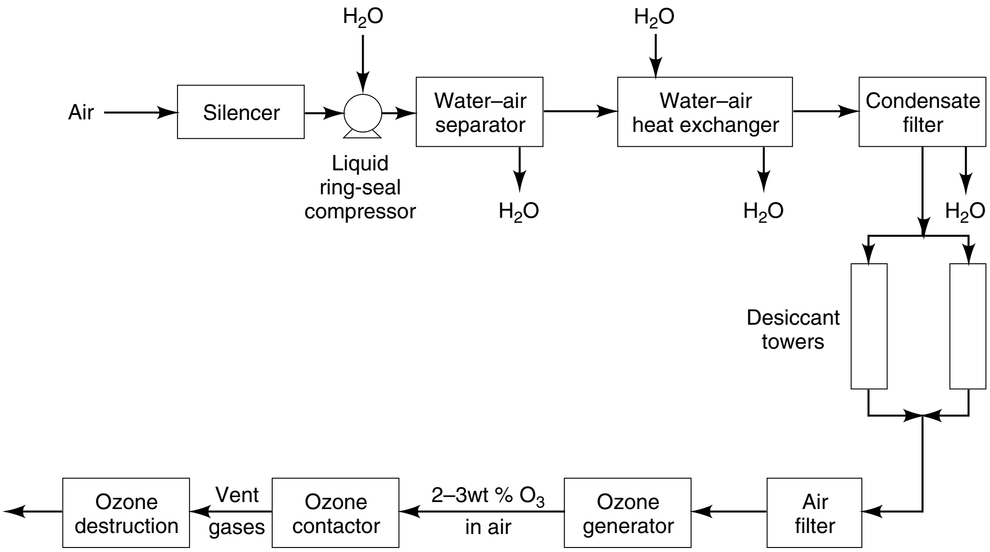


Fig. 1. Typical ozonation flow diagram.

by ions, whereas in stronger discharges, almost all of the discharge energy is transferred to electrons responsible for the formation of ozone. The optimum is a compromise that avoids energy losses to ions but at the same time obtains a reasonable conversion efficiency of oxygen atoms to ozone.

8.2. Ozone Generation from Oxygen. Use of oxygen for ozone generation is advantagious because of its purity and absence of by-products.

Ozone Formation. Oxygen is dissociated into atoms by inelastic collisions with energetic electrons (6–7 eV): $O + e^- \rightarrow 2\,O(^3P \text{ and } ^1D) + e^-$ (153,154). Whereas oxygen atoms are formed in nanoseconds, their subsequent reactions occur on a microsecond time scale. The highly reactive oxygen atoms can recombine in the gas phase and on the wall. For the gas phase, the reaction is $2\,O + M \rightarrow O_2 + M + 498.3\,\text{kJ}$, where $M = O_2$ and $k^{25^\circ C} = {\sim}1 \times 10^{11}\,M^{-2}\,s^{-1}$ (157). Recombination of oxygen atoms is unimportant until $O/O_2 > 0.01$. The main reaction is with oxygen molecules in the presence of a third body, M, forming ozone: $O + O_2 + M \rightarrow O_3 + M + 106.5\,\text{kJ}$. The lower the relative oxygen atom concentration, O/O_2, the greater the fraction of oxygen atoms forming ozone.

Ozone Destruction. Ozone formed in the above reaction is initially in a vibrationally excited state (O_3*). Although most is quenched by collision with other molecules, a small fraction can react faster with oxygen atoms than ground-state ozone. Vibrationally excited ozone also can be formed by collision with (^1D) oxygen atoms and with vibrationally excited oxygen molecules. Vibrationally excited singlet oxygen molecules ($^1\Delta_g$ and $^1\Sigma_g{}^+$) can be formed by electron impact or by recombination of oxygen atoms.

Ozone can be destroyed thermally, by electron impact, by reaction with oxygen atoms, and by reaction with electronically and vibrationally excited oxygen molecules (154). Rate constants for these reactions are given in References 10–12 and

157. Processes involving ions, eg, O_2^-, O_2^+, O^-, O^+, and O_3^-, are of minor importance. The reaction $O_3 + O(^3P) \rightarrow 2\ O_2$, is exothermic and can contribute significantly to heat evolution. Efficiently cooled ozone generators with typical short residence times (seconds) can operate near ambient temperature where thermal decomposition is small.

Ozone Concentration. Experimental studies show that the ozone concentration increases with specific energy (eV/O_2) before reaching a steady state. The steady-state ozone concentration varies inversely with temperature but directly with pressure, reaching a maximum at about 101.3 kPa (1 atm). Above atmospheric pressure the steady-state ozone concentration decreases with pressure, apparently due to the pressure dependence of the rate constant ratio $k(O_2)/k(O_3)$ for the reactions of O_2 and O_3 with energetic electrons. The preparation of ozone from oxygen presents fewer operational problems than that from air because significant amounts of moisture and large concentrations of nitrogen are absent. However, small amounts of nitrogen (~4%) actually increase the ozone concentration.

8.3. Ozone Generation from Air.

Although the use of air for ozone generation has the advantage that air, unlike oxygen, is readily available, the concentration of ozone produced with air is lower than that produced with oxygen. In addition, the presence of moisture in air interferes with discharge formation and reaction kinetics and creates potential for corrosion that can adversely affect the performance of the ozone generator and increase the need for maintenance.

Chemistry of Ozone Formation. The basic chemistry of ozone generation from oxygen is more complex when air is employed because of formation of nitrogen atoms, vibrationally excited nitrogen molecules, and nitrogen oxides (153,158). Nitrogen atoms are formed by the dissociation of nitrogen molecules by electron impact; they can generate oxygen atoms via the following reactions: $N + O_2 \rightarrow NO + O$ and $N + NO \rightarrow N_2 + O$. Oxygen atoms also can be formed by the dissociation of molecular oxygen by vibrationally excited nitrogen molecules. Thus, atomic nitrogen and excited nitrogen molecules enhance the formation of ozone by increasing the atomic oxygen concentration.

Nitric oxide can initiate catalytic decomposition of ozone, as previously discussed, by the reactions $NO + O_3 \rightarrow NO_2 + O_2$ and $NO_2 + O \rightarrow NO + O_2$. Nitrogen dioxide also can destroy ozone: $NO_2 + O_3 \rightarrow NO_3 + O_2$. NO_3 reacts with NO to form NO_2 as indicated by $NO_3 + NO \rightarrow 2\ NO_2$. Nitrogen dioxide and trioxide are in equilibrium with nitrogen pentoxide: $NO_2 + NO_3 \rightleftarrows N_2O_5$. Decreasing the temperature and increasing the pressure shifts the equilibrium to the right, reducing the effect of lower oxides on the decomposition of ozone. Nitrogen pentoxide can react with oxygen atoms to form nitrogen dioxide. Only N_2O_5 and N_2O are present in the gases exiting the discharge. The nitrous oxide (N_2O) that is formed is inert toward ozone. Of less importance is the destruction of ozone by nitrogen atoms, $N + O_3 \rightarrow NO + O_2$, which is much slower than that by oxygen atoms.

Ozone Concentration. Because of the formation of nitrogen oxides, a steady-state ozone concentration cannot be obtained; instead, due to the buildup of nitrogen oxides, an increase in residence time in the discharge results in a decrease in ozone concentration beyond the maximum value. Thus, there is an optimum residence time for maximum ozone production.

Suppression of Nitrogen Oxides. The concentration of nitrogen oxides during preparation of ozone from air increases linearly with the energy density in the discharge, causing a decrease in the formation rate of ozone. Most commercial ozone generators produce 0.5 kg of nitrogen oxides for every 100 kg of ozone generated. The formation of nitrogen oxides at a given energy density is minimized by decreasing the residence time and temperature, increasing the pressure, and reducing the dew point of air.

8.4. Feed Gas Preparation.

Air and oxygen are the two gas sources for preparation of ozone.

Oxygen Feed. The use of oxygen for industrial ozone generation is significant and increasing. Oxygen provides a higher ozone concentration and more efficient ozone dissolution than air, and does not add nitrogen oxides to the water. It is prepared from dry, filtered air by liquefaction and fractional distillation. Liquid oxygen (LOX) can be prepared on-site or purchased from vendors. Oxygen is sometimes used to enrich air-fed systems. Although oxygen-rich offgases from ozone contactors can be recycled, more often they are discarded to avoid redrying costs.

Air Feed. Air is widely used as the feed gas for commercial ozone generators. The air feed gas to the ozone generator should be dry and free of foreign matter. Filtered ambient air is drawn into the plant by vacuum, blower, or compressor. The pressure of the treated air can vary from subatmospheric to >400 kPa (4 atm). Since compression heats the air, cooling is necessary. The air is filtered again to remove oil droplets that can foul the desiccant dryers and interfere with ozone generation. Any hydrocarbons in the air can be removed with activated carbon. Moisture is removed by desiccant-drying or a combination of refrigerant- and desiccant-drying. Desiccant-drying is accomplished by using molecular sieves (qv), silica gel, or activated alumina, all of which are capable of regeneration. Liquid water droplets in refrigerant-dried air should be removed by filtration prior to contacting the desiccant dryers. A final filtration is necessary to remove desiccant dust particles down to 1 μm. The efficiency of ozone generation decreases with increasing moisture content in the air (159–161). At high dew points, nitrous and nitric acids are deposited within the ozone generator, decreasing performance and substantially increasing the maintenance frequency. The air feed to the ozone generator should have a dew point of at least −60°C, corresponding to a moisture content of ≤20 ppmv; some systems, however, operate at a dew point of −80°C. A sensor should be placed in the air stream entering the generator that can shut the system off and sound an alarm if the dew point increases above the desired level. In high pressure systems, the pressure of the compressed air prior to entering the ozone generator is reduced by means of a pressure-reducing valve. The pressure employed depends on the ozone generator type and can vary from 100 to 240 kPa (0–20 psig). The pressure of the ozone generator feed should be maintained at a constant level to avoid affecting power draw and applied voltage.

8.5. Cooling Requirements.

Since the majority of the electrical energy input to the electric discharge is dissipated as heat, cooling is necessary to minimize decomposition of ozone and extend dielectric life. Double-sided cooling is more effective than single-sided cooling in removing heat from the ozone generator. The gas exiting an efficiently cooled ozone generator normally is near ambient temperatures where the rate of decomposition is low.

8.6. Electrical Characteristics. The basic features of an electric discharge cell are depicted in Fig. 2.

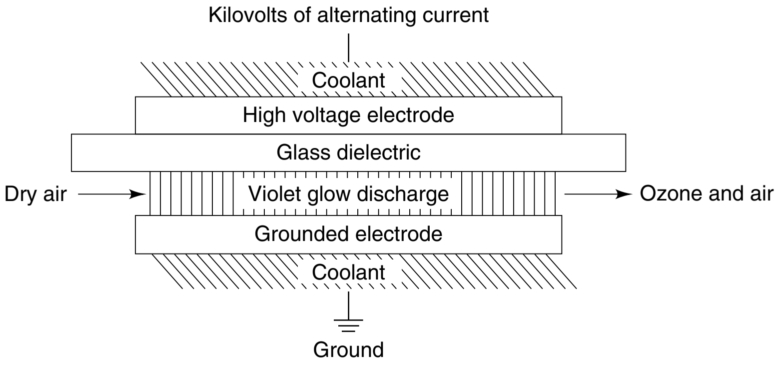


Fig. 2. Basic configuration of ozone generators.

Electrical energy to the ozone generator is provided by a power supply, a frequency converter, and a transformer. Ozone formation is directly proportional to the power consumed in the discharge at constant O_3 concentration, temperature, and pressure. The average discharge power consumption P (W) is given by $P = 4C_d\nu_s f\,[\nu_o - \nu_s(C_d + C_g)/C_d]$; where C_d and C_g are the dielectric and gap capacitances (F), ν_s is the peak gap sparking potential (V), ν_o is the peak driving potential (V), and f is the frequency (Hz) (161). The sparking potential is given by $\nu_s(O_2) = 26.55pt_g + 1480$ and $\nu_s(\text{air}) = 29.64pt_g + 1350$, where p is the absolute pressure (kPa) and t_g is the gap thickness (mm). For a given geometry, gap, and pressure, the power consumed by the discharge can be increased by operating at higher driving voltages and frequencies, and employing thinner dielectrics having higher dielectric constants.

The potential and frequency employed in commercial ozone generators varies with the type of design and can range from 5 to 20 kV and 50 to 3000 Hz, respectively. Typically, high frequency ozone generators operate at lower voltages, where the expected lifetime of the high voltage electrode is virtually unlimited. Although lower voltage decreases the ozone production rate, when combined with high frequency it can produce more ozone per unit electrode area. Modern ozone generators operating at 10 kV rms and 600–1000 Hz employ power densities of 3–4 kW m^{-2}, resulting in production densities of 0.2–0.25 kg hm^{-2} in air and 0.35–0.45 kg hm^{-2} in oxygen (162).

8.7. Ozone Concentration and Yield. The output of an ozone generator can be increased by raising the power input at constant temperature and feed gas flow rate, but the increase in output is less than proportional unless the gas flow is increased to maintain a constant ozone concentration. Raising the flow rate at constant power input decreases the ozone concentration, but increases the ozone and energy yields. At low flow rates, although the ozone concentration is high, the yield is low because the specific energy is high. At higher flow rates, the ozone concentration decreases; the yield approaches a limiting value because the specific energy does not change much at low ozone concentrations.

Commercial ozone generators are available with a wide range of production rates. One manufacturer markets ozonators with production rates from oxygen as high as 247, 202, and 171 kg h^{-1} at 7, 10, and 12 wt% O_3 and as high as 134 and 103 kg h^{-1} from air at 2.1 and 3.5 wt% O_3. Higher production rates are obtained by combining multiple units. Lower capacity units also are available with production rates as low 50 g h^{-1}. The required ozone concentration depends on the application; concentrations as high as 16 wt% have been produced commercially from oxygen. Lab-scale ozonators also are manufactured with production rates of $\sim$10 g h^{-1}.

8.8. Energy Requirements and Efficiency. The thermodynamics of ozone synthesis require the expenditure of 142.7 kJ mol^{-1}; thus the formation of 1 kg of ozone requires 2.97 MJ or 0.85 kWh kg^{-1} at 100% efficiency. The more concentrated the ozone, the higher the specific energy (kWh kg^{-1}) and the lower the efficiency. The specific energy for ozone production from dry oxygen varies from 7 to 14 kWh kg^{-1} over the 1–6 wt% range. For dry air, the specific energy (15–22 kWh kg^{-1} for 0.5–3.0 wt% ozone) is lower than expected due to the contribution of atomic nitrogen to ozone formation. The higher than theoretical specific energy requirements are due to the fact that most of the supplied energy is converted to heat resulting from ozone formation and decomposition reactions. These specific energy requirements correspond to ozone synthesis efficiencies from oxygen and air of 6–12% and 4–6%, respectively. Thus, the portion of the input synthesis energy dissipated as heat is 88–94% for oxygen and 94–96% for air. In addition to the power requirements for the ozone generator, the air-preparation unit requires 4.4–7.7 kWh kg^{-1} ozone, and the oxygen recycle unit an additional 2–7 kWh kg^{-1} ozone.

8.9. Ozone Generator Design. A better understanding of discharge physics and the chemistry of ozone formation has led to improvements in power density, efficiency, and ozone concentration, initiating a trend toward downsizing.

The basic configuration of an electric discharge cell consists of two closely spaced electrodes (one of which is coated with a dielectric), supplied with high voltage alternating current (ac) and filled with a flowing oxygen-containing gas. The gap width varies from 1 to 3 mm, depending on whether oxygen or air is employed. The purpose of the dielectric, usually made of glass or ceramic, is to limit current flow, resulting in the formation of a relatively cold plasma. A thin dielectric with a high dielectric constant facilitates heat removal and improves ozone-generating efficiency. The higher the applied voltage, the thicker the electrode should be to prevent failure by electrical arcing. The dielectric must be strong enough to withstand mechanical shock and prevent puncturing by the applied voltage. High peak voltages induce dielectric failure, as do high power densities, the latter on account of its dielectric heating.

The electric discharge ozone generator is equivalent to a gas-phase reactor having internal heat generation; its design also bears some similarity to heat exchangers such as shell and tube. The gap width influences both the voltage requirement and the back pressure and should be uniform to avoid hot spots. Small gap widths typically are employed to facilitate heat removal; the smaller the discharge gap, the greater the power efficiency.

8.10. Types of Ozone Generators.

Since 1906, a number of different ozone generators have been developed, including the plate-type (water- or air-cooled), the horizontal tube (water-cooled), and the vertical tube (water- or oil- and water-cooled) generators (159–161). Originally introduced in 1906, plate-type ozone generators have experienced operational problems and have been discontinued for use in some countries, even though many installations remain operational and the technology is still being promoted by some manufacturers.

Horizontal Tube Generators. The horizontal tube-type ozone generator (Fig. 3**a**) was a significant improvement over the plate-type ozone generators. A single unit consists of two concentric tubes, an outer stainless steel tube that serves as the ground electrode, and an inner glass tube sealed at one end, which functions as the dielectric, with an inner conductive coating that acts as the high voltage electrode. Discharge occurs in the annular space between the two tubes through which the feed gas flows. A group of tubular units (eg, up to 1000) is arranged in parallel and enclosed in a cylindrical housing so that the ends protrude out of the cooling water jacket, which cools the outside stainless steel tube. Manifolds distribute the feed gas to the annular discharge spaces of the tubes at one end and collect the ozone-containing gas at the other. The tubular electrodes are supplied with low frequency power (~60 Hz). When higher production rates ($>10\,\mathrm{kg\,h^{-1}}$) are required, the use of solid-state variable medium frequency (600–1000 Hz) power supplies may be cost-effective.

Vertical Tube Generators. The vertical tube (water-cooled) generator consists of two concentric tubes; the outer of which is cooled with water and acts as the ground electrode. Feed gas is introduced into the top of the inner stainless steel tube, which serves as the high voltage electrode, exits at the bottom of the outer tube, flows upward through the annular space (which contains the electric discharge), and emerges at the top of the outer tube into a product gas manifold.

Developed in the late 1960s, the double-fluid-cooled, high frequency (1000–3000 Hz) vertical tube generator (Fig. 3**b**) has a more complex design (three tubes) that advantageously cools both electrodes: the high voltage with a noncon-

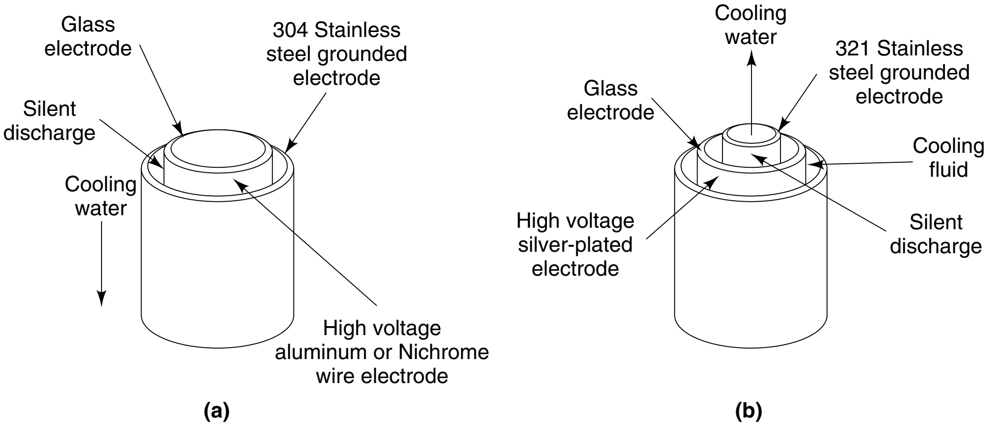


Fig. 3. Comparison of ozone-generator construction: (**a**) single-fluid-cooled; (**b**) double-fluid-cooled generator.

ducting oil (cooled with a heat exchanger) and the ground with water. It has higher production rates at higher ozone concentrations than other types of generators.

8.11. Production Costs and Capital Requirements. The production cost for 1.5 wt% O_3 from air, assuming 100% on-stream time, varies from ~\$8.25 to ~\$2.40 kg^{-1} for production rates of 1–500 $kg\,h^{-1}$ (163). The assumptions are power, 6.5¢ kWh^{-1}; interest, 12.5% $year^{-1}$; depreciation time, 10 year; on-stream time, 8760 h $year^{-1}$; and labor and maintenance, 1% of capital investment per year. The production cost strongly depends on the size of the installation as well as the extent of instrumentation and controls, and varies inversely with on-stream time and ozone concentration. Production costs for manufacturing 5 wt% ozone from oxygen can vary from ~\$10.45 to ~2.50 kg^{-1} for the same on-stream time and production rates. The cost of liquid oxygen is the main contributor to the total production cost. For large production rates, there is little difference between production costs for air and for oxygen; capital costs for the above examples are in the ranges of ~\$5.70 to ~\$0.50 kg^{-1} for air and ~\$2.85 to ~\$0.22 kg^{-1} for oxygen.

9. Other Methods of Ozone Generation

9.1. Ultraviolet Light. *Use of Short Wavelength Light.* The mechanism of the practical photochemical production of ozone is similar to that in the stratosphere; ie, oxygen atoms, formed by the photodissociation of oxygen by short-wavelength uv radiation ($\leq$240 nm), react with oxygen molecules to form ozone. At low conversions, the limiting quantum yield is ~2 (25). The steady-state ozone concentration (~3.5 mol% max) depends on temperature, pressure, and whether oxygen or air is employed; the time-to-steady-state depends on the light intensity. Efficiencies as high as 9% can be obtained, at low ozone concentration, by using narrow-band uv radiation produced by a xenon excimer laser operating at 172 nm (see LASERS) (164).

Use of Short and Long Wavelength Light. In practice, ozone concentrations obtained by commercial uv devices are low. This is because the low intensity, low pressure mercury lamps employed produce not only the 185-nm radiation responsible for ozone formation, but also the 254-nm radiation that destroys ozone, resulting in a quantum yield of ~0.5 compared to the theoretical yield of 2.0. Furthermore, the low efficiency (~1%) of these lamps results in a low ozone production rate of ~2 $g\,kWh^{-1}$ (165,166).

Typical output of a commercial 40-Wt uv lamp using air is ~0.5 $g\,h^{-1}$ of ozone and a maximum concentration of 0.25 wt%. However, these maximum ozone yields and concentrations cannot be obtained simultaneously by the uv method. The low concentrations of ozone available from uv generators preclude their use for water treatment because the transfer efficiencies of ozone from air into water is low and large volumes of carrier gas must be handled. More than 44 kWh are required to generate one kg of ozone from dry air by uv radiation under high gas flow rates and low concentrations.

9.2. Electrolysis. High current density electrolysis of aqueous phosphate solutions at room temperature produces ozone and oxygen in the anodic gas. Electrolysis of 68 wt% sulfuric acid can produce 18–25 wt% ozone in oxygen when a well-cooled cell is used. Although electrolysis of water can produce high concentrations of ozone, the output is low, and the cost is several times more than that of electric discharge processes (167,168).

9.3. Radiochemical. Ozone can be prepared radiochemically by irradiation of gaseous or liquid oxygen with β- and γ-rays from radioactive isotopes or a nuclear reactor (169). Although its energy efficiency is greater than that of ozone produced by electric discharge, this complex process has never been commercialized due to problems associated with recovery of ozone and separation of by-products and radioactive material.

9.4. Miscellaneous. In the laboratory, pure liquid ozone can be produced quantitatively by cooling a stream of atomic oxygen in oxygen at liquid nitrogen temperatures (−196°C): $O + O_2 + M \rightarrow O_3 + M$, where M is the cold reactor wall (170). Pure stable gaseous ozone also can be prepared quantitatively by elctric discharge (using a Tesla coil) through oxygen cooled with liquid nitrogen followed by warming to room temperature (22).

10. Transfer of Ozone into Water

The physical mass-transfer rate of ozone into water is affected by the gaseous ozone concentration, temperature, pressure, composition of the solution (ie, pH, ionic strength, and the presence of reactive substances), gas dispersion, turbulence, mixing, which depends on the type of contactor. Mass transfer of ozone into water in a bubble column as a function of pH has been measured (5).

10.1. Ozone Mass Transfer Rate. Mass transfer of gaseous ozone into water is a diffusion process through the interface of gas and liquid films. Since ozone is only slightly soluble, Henry's law constant (K_H, defined earlier) is large. This means that the resistance in the gas film is negligible compared to that in the liquid film, and diffusion through the liquid film controls the process. The instantaneous rate ($\text{mol m}^{-3}\,\text{s}^{-1}$) of O_3 mass transfer as a function of the concentration gradient ($C_L - C$) is given by the following diferential equation:

$$dC/dt = (D/L)a(C_L - C) - r = k_L a(C_L - C) - r = k_L a(P/K_H - C) - r$$

where D is the diffusion coefficient of ozone ($\text{m}^2\,\text{s}^{-1}$), L is the thickness of the liquid film (m), $k_L a$ is the experimentally determined liquid-phase volumetric mass-transfer coefficient (s^{-1}) that varies with the apparatus, k_L is the liquid-phase mass-transfer coefficient (m s^{-1}), a is the effective interfacial mass-transfer area per unit volume of liquid phase (m^{-1}), C_L and C are the aqueous ozone concentrations in the liquid film and bulk solution (mol m^{-3}), and r is the rate of ozone decomposition and chemical reaction ($\text{mol m}^{-3}\,\text{s}^{-1}$).

10.2. Ozone Contactors and Dispersion Devices. Efficient transfer of ozone into solution requires the dispersion of gaseous ozone into small bubbles. This is accomplished in various types of ozone contactors, eg, porous diffuser bubble columns (co- or countercurrent flow), mechanically agitated vessels, turbine mixers, tubular reactors, in-line static mixers, as well as negative pressure (venturi) and positive pressure injectors (159–161). In turbines and injectors, ozone and water are forced or drawn cocurrently through a small opening. Under intense mixing, bubbles are sheared and mixed thoroughly, decreasing the liquid film thickness but increasing both interfacial area and contact time. Plate and packed columns and spray towers also can be employed to increase the gas–liquid contact. In plate and packed columns, ozone and water can flow co- or countercurrently. Single or multiple contact chambers (up to 5) can be used. Contact time varies from 2–20 min, depending on the application. Faster ozone-transfer rates result in faster disinfection rates. Because ozone is a strong oxidant, corrosion-resistant materials of construction such as stainless steel, glass, and Teflon, should be employed.

10.3. Ozone Dosage. The applied ozone dosage (D_a) in $\mathrm{mg\,L^{-1}}$, is $D_a = Y_i V_g / V_{aq}$, where Y_i *is* the ozone concentration (mg L^{-1}) in the inlet gas and V_g and V_{aq} are the gas and aqueous flow rates (L min^{-1}). The applied dose can be varied by changing Y_i or the V_g/V_{aq} ratio. The transferred ozone dose (D_t) in $\mathrm{mg\,L^{-1}}$ is $D_t = (Y_i - Y_o)V_g/V_{aq}$, where Y_o is the concentration of ozone in the vent gas.

10.4. Ozone Transfer Efficiency and Demand. The transfer efficiency is $\mathrm{TE} = 100(D_t/D_a) = 100(Y_i - Y_o)/Y_i$. The ozone demand of the water is equal to the difference between D_t and the aqueous phase ozone residual. Due to reaction kinetics, the ozone demand will vary with contact time.

10.5. Off-Gas Treatment. Ozone-transfer efficiencies vary with the number of stages and are typically $> 90\%$. However, since even a 95% ozone absorption efficiency can result in a contactor off-gas containing as much as 740-ppmw ozone (based on a 1.5 wt% O_3 feed gas), treatment is required to reduce the ozone concentration to an acceptable maximum level of $0.2\,\mathrm{mg\,m^{-3}}$. Ozone in the vent gases from water-treatment ozone contact chambers is destroyed mainly by thermal (300–350°C for ≤ 5 s) and/or catalytic means, and sometimes by wet granular-activated carbon (GAC). Another option is recycling the off-gas to points in the water-treatment system having a high ozone demand. Dilution of ozone vent gases with air has been employed whenever practical. When oxygen is used as the feed gas, it can be recycled to the ozone-generation step; however, once-through operation is common in order to avoid redrying costs.

11. Uses

The primary use of ozone is in water treatment. State of the art reviews on use of ozone in water treatment in the United States, Europe, and Japan appear in Ref. 171. Operational data from > 100 water treatment plants in Europe show that ozone is used in concentrations ranging from 0.2 to 5 ppm for oxidation of organic and inorganic compounds affecting water quality, particle removal, and disinfection (71). Ozone also has other uses, eg, in pulp bleaching, organic synthesis, and medical applications.

11.1. Ozone Treatment of Drinking Water. Ozonation and treatment strategy depends on the quality of the source water. Ozone is typically applied at the head of the treatment plant (ie, preozonation) and after sedimentation. Ozone is often applied as a predisinfectant for the control of algae and inactivation of bacteria and viruses in direct filtration processes, and as a pre- and/or intermediate oxidant. Ozone is also frequently applied at an intermediate point in conventional treatment processes as an oxidant and for primary disinfection of viruses and cysts. Ozonation of drinking water is reviewed in Refs. 73–74.

Benefits of Ozonation. Ozone oxidizes inorganic pollutants including iron, manganese, and sulfides. It also oxidizes organic micropollutants including taste and odor compounds, phenolics, and some pesticides. In addition, ozone oxidizes organic macropollutants resulting in color removal, increased biodegradability, improved disinfection by-product precursor control, and reduction of chlorine demand. Precipitated trace metals, microflocculated organics, and destabilized colloidal particles enhance coagulation and filtration.

Biologically Active Carbon. Ozone also can be used in conjunction with biological filtration through sand, mixed media, or GAC, for removing biodegradable organics produced during ozonation, especially aldehydes, ketones, acids, etc, which can be precursors to THMs, haloacetic acids (HAAs), and other halogenated by-products. For example, ozonation (1.5–4 ppm) followed by GAC filtration produces biological activated carbon (BAC). Partial oxidation of organic matter by ozone can increase biodegradability, although decreasing adsorption efficiency. Oxygen in the carrier gas assists bacteria in oxididation of ammonia and in mineralization of adsorbed organics, providing an efficient process for removing low concentrations of dissolved organic compounds. Ozone plus BAC extends the life of the GAC by reducing the adsorptive load. Ozone can be used again to disinfect the resultant biologically stabilized water prior to chlorination and/or chloramination and distribution.

Advanced Oxidation Processes. Advanced oxidation processes may be necessary in some cases for the destruction of ozone-refractory compounds such as pescticides, aromatics, and chlorinated solvents. These processes employ $O_3 + \text{uv}$ radiation and $O_3 + H_2O_2$ to cause ozone to react by free-radical mechanisms in order to increase the rate and efficiency of oxidation of organic matter. A significant number of the > 300 drinking water plants in the United States using ozone employ advanced oxidation processes for treating a variety of organic pollutants (171,172). Many French and U.K. plants use O_3–H_2O_2 to meet European Economic Community (EEC) pesticide standards.

Disinfection. Ozone is a more effective broad-spectrum disinfectant than chlorine-based compounds (159,173). Ozone is very effective against bacteria because even concentrations as low as 0.01 ppm are toxic to bacteria. The mode of inactivation of microorganisms by ozone is discussed in Ref. 174. The disinfection rate depends on the type of organism and is affected by ozone concentration, temperature (175), pH, turbidity, clumping of organisms, oxidizable substances, and the type of contactor employed (176). The presence of readily oxidizable substances in ordinary water can retard disinfection until the initial ozone demand is satisfied, at which point rapid disinfection is observed.

Ozone only can be used as a primary disinfectant since it cannot maintain a residual in the distribution system because of its short lifetime. The presence of low molecular weight, oxygenated, and biodegradable organics that ozone produces can promote biological growth, unless removed from the treatment plant. Thus, ozone disinfection needs to be coupled with a secondary disinfectant, eg, chlorine or monchloramine.

Drinking Water Microbial Control Regulations. There are a number of existing and proposed National Primary Drinking Water Regulations controlling disease-causing pathogens in public drinking water: the Total Coliform Rule (TCR) (177), the Information Collection Rule (ICR) (178), the Surface Water Treatment Rule (SWTR) (179) and the Enhanced Surface Water Treatment Rule (ESWTR) (180), and its modifications.

The SWTR of 1989 established treatment techniques (disinfection and filtration) in lieu of MCLs (maximum contaminant levels) for reducing Giardia cysts, viruses, coliforms, heterotrophic bacteria, Legionella, and turbidity in surface and ground water under the influence of surface water. It also established removal efficiencies in filtered and unfiltered surface water systems. For example, the SWTR requires that filtration and disinfection must be provided for most surface waters to ensure that the total treatment of the system achieve at least 3-log (99.9%) and 4-log (99.99%) removal–inactivation of *Giardia lamblia* cysts and enteric viruses, respectively. Disinfection and filtration of most surface waters is required. The required log reductions can be achieved by a combination of filtration (ie, removal) and disinfection (ie, inactivation). Environmental Protection Agency (EPA) data shows that the log removal depends on the filtration method and ranges from 2.0 to 2.5 for *G. lamblia* cysts and 1.0–2.0 for viruses (181).

The EPA has identified conditions for inactivation of Giardia cysts and viruses for various disinfectants via Ct values, which are the product of the residual disinfectant concentration (ppm) and the effective contact time (min). For a given organism, Ct values vary with disinfectant, pH, and temperature. The EPA proposes the following minimum Ct values for a 3-log inactivation of Giardia cysts at pH 6–9 and 10°C: 1.43 for ozone, 23 for ClO_2, 104 for chlorine (at pH 7.0 and chlorine residual of $\leq 0.4\,\text{ppm}$), and 1850 for NH_2Cl (181). Ct values for a 4-log inactivation of viruses at pH 6–9 and 10°C are 1.0 for ozone, 8 for chlorine, 25.1 for ClO_2, and 1491 for NH_2Cl. Because the Ct values for NH_2Cl are large, it is not recommended for primary disinfection.

The interim ESWTR (IESWTR) (182) adds the following requirements for control of cryptosporidium: maximum contaminant level goal of zero, a 2-log physical removal for systems that filter, and a watershed control program for unfiltered systems. It also sets turbidity performance standards: <0.3 NTU in at least 95% of monthly measurements and a maximum turbidity level of 1 NTU. The IESWTR applies to systems serving >10,000 people and has been expanded via the Long Term 1 ESWTR (183), which covers systems serving <10,000 people. The proposed Long Term 2 ESWTR will incorporate the ICR data and may include site-specific treatment requirements (184). The proposed future Ground Water Treatment Rule (GWR) will apply to the approximately 180,000 public water systems using ground water (185).

The EPA provides guidance for systems with poorer quality water to evaluate the need for additional treatment. For example, it provides information on alternate disinfectants and oxidants other than chlorine (ozone, chlorine dioxide, potassium permanganate, chloramines, ozone/hydrogen peroxide, and uv light) so that systems can evaluate their options for controlling water quality problems.

Tastes and Odors. The origin of most tastes and odors in water supplies is synthetic organic compounds (eg, phenols) as well as naturally occurring inorganic (eg, Fe^{2+}, Mn^{2+}, and H_2S) and organic materials (biologically and chemically altered). The action of algae and actinomycetes on humic materials can produce distasteful water-soluble compounds such as geosmin and 2-methylisoborneol. Regrowth in the distribution system also can impart taste. Additionally, oxidation during water treatment can generate other odorous compounds (eg, aldehydes). Although many taste and odorous compounds are readily oxidized by ozone (typically 1.5–2.5 ppm), some compounds are more resistant and may require biofiltration or advanced oxidation processes. A pilot-scale study showed that the Peroxone process (O_3–H_2O_2) was more effective in removing taste and odor compounds than ozone alone (186).

Color. Surface waters generally are colored by naturally occurring organic matter, eg, humic, fulvic, and tannic acids. These compounds result from the decay of vegetative materials and usually are related to condensation products of phenol-like compounds. Such color-causing compounds contain multiple conjugated double bonds, some of which are readily split by ozone. Cleavage of only one double bond generally destroys the chromophoric properties of the molecule. However, with insufficient oxidant, the color can return during storage or distribution. Ozone dosage levels for lake water decolorization usually are 2–4 ppm.

Turbidity. Turbidity in water is removed by ozonation (0.5–2 ppm) through a combination of chemical oxidation and charge neutralization. Colloidal particles that cause turbidity are maintained in suspension by negatively charged particles that are neutralized by ozone. Ozone further alters the surface properties of colloidal materials by oxidizing the organic materials that occur on the surface of the colloidal spherical particles.

Iron and Manganese Removal. Soluble ferrous and manganous ions are oxidized by ozone (typically 2.5 ppm) to less soluble higher oxidation states, which can hydrolyze to $Fe(OH)_3$ and MnO_2 and be removed by settling, filtration, or both. Iron(II) is oxidized faster than manganese(II). The presence of organic matter retards the oxidation by consuming ozone and/or metal complex formation (187,188). Alkalinity (HCO_3^- and CO_3^{2-}) reduces the ozone dosage required for metal ion oxidation by scavenging hydroxyl radicals, which are formed by chain decomposition of ozone initiated by HO^- and organic matter (189). Excess ozone oxidizes manganese dioxide to permanganate, which can be reduced by organic matter to form MnO_2 scale in the distribution lines. As a result, permanganate must be avoided or allowed to dissipate or reduced by filtration through GAC prior to distribution.

Degradation of Readily Oxidizable Organics. Organic contaminants in water supplies consist of not only natural organic matter from various sources but also synthetic organic chemicals. More than 700 organic compounds have been identified in drinking water. Not all of these materials are oxidized by ozone at the same rate; some halogenated hydrocarbons are not oxidized at all. Materials that are oxidized readily by ozone include certain phenolics, detergents, pesticides, herbicides (qv), chemical-manufacturing wastes, humic acids, aromatic compounds, proteins, and most amino acids.

Although little or no reduction in total organic carbon occurs during ozonation, partially oxidized polar compounds (containing, COOH, and OH groups) are formed, which are all readily biodegradable. Some of these can chelate with polyvalent cations, yielding insoluble material that can be removed by coagulation with Al or Fe salts, polyelectrolytes, etc. This microflocculation phenomenon is responsible for the removal of humic substances (eg, humic and fulvic acids) having molecular weights of ~200 to several million, which account for the bulk of the dissolved organic carbon (DOC) in natural waters. Partial oxidation with ozone produces lower molecular weight by-products whose structures depend on the level of ozonation. Lower molecular weight, partially oxidized organics that are not removed by microflocculation or coagulation can be removed by biofiltration.

Removal of Refractory Organics. Ozone reacts slowly or insignificantly with certain micropollutants, eg, carbon tetrachloride, trichlorethylene (TCE), and perchlorethylene (PCE), present in some source waters. In addition, ozone reacts slowly with trihalomethanes (THMs, eg, chloroform and bromoform) and haloacetic acids (HAAs, eg, trichloroacetic acid) present in chlorinated waters. Some removal of these compounds occurs in the ozone contactor as a result of volatilization (190). Air stripping in a packed column is effective for removing some THMs, but not $CHBr_3$. THMs can be adsorbed on GAC but the adsorption efficiency is low.

Advanced oxidation processes can reduce the concentration of refractory organics and are partially effective in destroying TCE and PCE (172,191–193). The O_3–H_2O_2 process is used for removing TCE and PCE from groundwater (11×10^6 L day^{-1}) in a plant operated by the city of Los Angeles. Similar technology is being employed in France and the United Kingdom for treatment of waters contaminated with herbicides and pesticides. The O_3-uv process has been installed for TCE and PCE removal (5×10^6 L day^{-1}) in a plant in South Gate, California.

THM and HAA Formation Potential. Trace concentrations of organic materials, eg, humic, tannic, and fulvic acids, and synthetic organic chemicals, in treated water react with HOCl and ClO^- to produce THMs and HAAs. In bromide-containing waters, both chlorinated and brominated THMs and HAAs are formed. Ozone-treated waters generally have lower THM and HAA levels as a result of lower THM- and HAA-formation potentials (THMFP and HAAFP). Because some of these compounds are carcinogenic, the United States. The EPA has set maximum levels for total THMs and HAAs (see discussion below).

The main strategy for controlling THMs and HAAs is to lower the THMFP and HAAFP by reducing THM and HAA precursors. In preozonation, ozone is added in low dosage levels at the front of the plant to aid the coagulation and partial removal of THM and HAA precursors. Ozone also can be added as an intermediate (prefiltration) unit process to oxidize many remaining THM and HAA precursors; however, caution must be exercised when high concentrations of organics remain in the water. Partial oxidation of high concentrations of organics may alter their structure so that, if biofiltration is not practiced, they produce more THMs and HAAs on subsequent chlorination. In these isolated cases, THM and HAA formation can be controlled by lowering the ozone dosage level, although primary disinfection requirements may not be met. Low pH and high alkalinity enhance the oxidation of THM and HAA precursors by molecular ozone, whereas high pH and low alkalinity enhance precursor oxidation by HO radicals.

Some THM and HAA precursors also can be removed by biological filtration. The resulting biological stability of the effluent can reduce the residual disinfectant requirement, consequently reducing the formation of THMs and HAAs. More organics or THM and HAA precursors are removed in this manner than by using ozone or GAC alone. Formation of THMs and HAAs during disinfection also can be reduced by adding chlorine at the end of the treatment process or by following chlorination with ammoniation, which produces monochloramine, but not halogenated by-products.

Drinking Water Disinfection By-Product Regulations. Disinfection by-products are formed when disinfectants used in water treatment react with natural organic matter and/or bromide present in source water. The type and amount of by-products vary with the disinfectant used. The original Disinfectant/Disinfection Byproducts Rule (D/DBPR) proposed in 1979 set the maximum contaminant level (MCL) for total THMs (TTHMs) at 0.10 ppm (194). Current proposed regulations cover the following by-products that have been identified in drinking water: trihalomethanes, haloacetic acids, bromate, and chlorite.

The original intent of the EPA regulations was to have a two-stage lowering of the MCLs on TTHMs and HAAs to 80 and 40 ppb (Stage 1, 1997) and 40 and 30 ppb (Stage 2, 2002). However, the EPA currently proposes maintaining the Stage 1 MCLs while compliance will be based on modifications relative to monitoring and calculating annual average levels of TTHMs and HAAs (195).

In 1998, the EPA published the Stage 1 D/DBPR (196) that requires water systems to use treatment methods to reduce the formation of disinfection by-products and to meet the following standards: total trihalomethanes (chloroform, bromoform, bromochloromethane, and dibromochloromethane) at 80 ppb, haloacetic acids (mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids) at 60 ppb, bromate at 10 ppb, and chlorite at 1.0 ppm. Efforts to finalize the Stage 2 D/DBPR are continuing (197).

Achieving lower limits may require either advanced oxidation processes or may be met by ozonation, biofiltration, and chloramination (198,199). Ozonation and biodegradation, which have shown promise in controlling TTHMs and THAAs in high bromide-containing water, do not result in excessive bromate formation (200). Natural organic matter, alkalinity, bromide content, and the presence of ammonia significantly affect bromate production during ozonation (201). Prechlorination followed by ammonia addition prior to ozonation in combination with reduced pH significantly reduces bromate formation (202). Bromate can be chemically reduced with SO_3^{2-} or Fe^{2+} (203). Aldehydes, which have been placed on the EPAs Drinking Water Priority List as candidates for future regulation, as well as other organic ozonation by-products, can be mineralized by biofiltration.

The Information Collection Rule (ICR), which became effective in 1997, provides for collection of water quality and treatment data (including THMs and HAAs) within water treatments plants and in distributions systems.

11.2. High Purity Water Systems. The requirements of a high purity water are absence of odors, tastes, and microorganisms.

Bottling and Canning Plants. Breweries ozonate the brewing water to remove any residual taste and odor and to ensure the absence of microorganisms. The soft drink industry removes the ozone residual by vacuum-stripping in a degassing chamber before bottling (see CARBONATED BEVERAGES). The bottled water industry requires that an ozone residual be included with the water in the bottle. The ozone residual disinfects the inside of the bottle where contact is made with the water; some ozone, however, escapes into the gas phase where it also disinfects the inside of the cap and the container, which is not in contact with water. Finally, the ozone residual disappears as it decomposes to oxygen. In similar applications, the inside of bottles and cans is sprayed with water containing an ozone residual for disinfection prior to the introduction of food.

Pharmaceutical Industry. In the pharmaceutical industry, sterility of deionized water systems is maintained by using an ozone residual. The ozone residual concentration is maintained at $>0.3\,\mathrm{ppm}$ in the water recirculation loop. Prior to product compounding, the ozone residual is removed by contact with uv irradiaton for $<1\,\mathrm{s}$. Ozone also is used to oxidize pyrogens from distilled water destined for intravenous solutions.

Electronics Industry. Organic materials on the surface of electronic components are oxidized by immersion in deionized water that contains 0.5–2 ppm ozone residual. In some cases, gaseous ozone is employed to oxidize organic films on the surface of electronic components. In this treatment process, 5–6 wt% ozone, made in an oxygen-fed generator, is required.

11.3. Industrial Wastewater Pollution Control.

Nonbiodegradable industrial waste can be made degradable by treatment with ozone (204). The nonbiodegradable molecules are made biodegradable by the introduction of an oxygenated organic functional group at which site the metabolic process can begin.

In a similar manner, oxygenated functional groups also are formed on the surface of furnace carbon black. Carbon black is suspended in a gas stream and is treated with ozone at 50–150°C. This process produces a long flow, high color ink containing good dispersive properties.

One of the first industrial ozone wastewater applications involved the oxidation of phenol and cyanide in a solution that was used to strip paint from airplanes. Destruction of phenol and cyanide, together with the treatment of textile-dye wastewater, remain the three largest applications of ozone to industrial wastes.

Phenols. The first stable ozone oxidation product of phenol in water is *cis*,*cis*-muconic acid, which requires ~2 mol O_3 per mol phenol. In practice, larger dosage levels of ozone are required because other ozone-reactive substances are present in most wastes. Ozone oxidation of phenolic effluents is employed in paper mills, coke mills, oil refineries, and thermoplastic resin manufacture, producing effluents that are safe to freshwater biota (205,206).

Cyanide Wastes. Ozone is employed to oxidize cyanide-bearing wastes to yield the nontoxic cyanate ion, which can be further oxidized by ozone to carbon dioxide and nitrate ion (58,207). Ozone has been applied to cyanide- bearing plating wastes, photographic wastes, mining wastes, and textile dyeing plant wastewater; a concurrent reduction of heavy-metal concentrations occurs in these processes (208). The photographic industry treats their effluent with ozone to remove the chemical oxygen demand (COD), heavy metal ions, chelating agents (qv), and cyanide ion. A combination of ozone and uv irradiation is used to destroy iron–cyanide complexes and other ozone refractory compounds, eg, glycine, palmitic acid, glycerol, ethanol, and acetic acid (209).

Color Bodies. Effluents possessing either natural color bodies, eg, tannins and lignins from pulp and paper operations, or synthetic color bodies, eg, organic dyes, can be decolorized by ozone (210,211). Ozone cleavage of the carbon–carbon double bonds in the chromophoric molecules shifts the absorption spectrum from the visible to the uv region.

11.4. Wastewater Disinfection. Ozone is used in disinfection of secondary or biologically treated wastewater and in situations where a high quality effluent is required, eg, when the effluent flows into a reservoir or when game fish are in the receiving stream. After ozone is used to disinfect a secondary municipal effluent, it is difficult visually to distinguish it from potable water (212). Ozone-disinfected water is saturated with oxygen and safe to the receiving stream, whereas chlorinated water is toxic to trout and other forms of aquatic life. In addition, ozone is a more effective disinfectant than chlorine since it inactivates all viruses. Concurrent with the disinfection process, ozone lowers the color, chemical oxygen demand, and turbidity. Ozone also removes suspended solids by an ozone-induced flotation process; this process is initiated by precipitating naturally occurring residual ferrous ion as ferric hydroxide, which functions as a coagulant (213) (see FLOTATION).

11.5. Odor Control. The largest number of ozone generators in the United States are employed for sewage odor control (see WATER, SEWAGE). More than 1000 ozone generators are used in wastewater treatment plants and in wastewater pumping stations. Ozone, applied at 2–10 ppm, oxidizes odor-forming compounds in the gas or aqueous phase. Odor properties usually are associated with functional groups of high electron density, eg, sulfides, amines, and olefins. Some industrial odors oxidized by ozone include those from dairy processing plants, composting operations, fish processing, rubber compounding, rendering plants, commercial kitchens, paper mills, chemical plants, food processing, pharmaceutical fermentation, and phenols (214).

11.6. Process Water. Ozone is employed to a limited extent in the treatment of process water, such as cooling tower water, where ozone functions primarily as a biocide (215,216). In 1994, there were an estimated 300 installations employing ozone. Ozone has no direct effect on corrosion or scaling, since these are dependent on water chemistry and water quality. Of the various possible applications, including HVAC (heat, ventilation, and air conditioning), light manufacturing, oil refineries, chemical plants, utilities, and steel mills, only the first two areas, which involve moderate temperatures, have good applicability. In addition, use of ozone and bromide ion shows promise in industrial cooling towers.

11.7. Treatment of Swimming Pools and Spas. Ozone generated by corona discharge is employed primarily as an oxidant in treating swimming pool and spa water, mainly in Europe and to a small extent in North America. The largest application is in large municipal pools and spas, where chlorine typically is used as the disinfectant. In Europe, ozone is sometimes used in combination with NaBr for the generation of $HOBr/BrO^-$ for treating whirlpools and spas. The uv ozone generators marketed in the United States are inadequate for treatment of pools and spas or hot tubs because of the very low ozone concentrations introduced into the water (217) (see WATER, TREATMENT OF SWIMMING POOLS, SPAS, AND HOT TUBS).

11.8. Pulp Bleaching. Ozone is finding increasing use in pulp delignification and bleaching because of environmental concerns with conventional techniques. Lignin (qv), a high molecular weight phenolic material, is readily degraded by ozone. Because cellulose (a β-glycoside) is susceptible to attack by ozone, use of cellulose protectors is being evaluated (218). Research efforts are being directed toward the development of elemental chlorine-free, totally chlorine-free, and totally effluent-free technologies (219). There are numerous mills worldwide (several in the United States) that use ozone bleaching on a commercial scale, and others are in the planning stage (171,220). Various bleaching sequences are employed, depending on the type of pulp and applications. Ozone typically is employed in concentrations of 6–15%. Ozone has been used in conjunction with chlorine dioxide, which forms significantly less adsorbable organic halogen (AOX) than chlorine (221). For example, a plant producing 1000 t/day of a high consistency kraft pulp employs an OZED sequence, where O is oxygen, Z ozone, E caustic, and D chlorine dioxide. A totally chlorine-free process for medium consistency sulfite pulp in Säffle, Sweden uses a ZEP sequence, where P is hydrogen peroxide. Ozone also is used to treat effluents from pulp bleaching plants (222). Development of OZP bleaching has the potential to eliminate effluents (see BLEACHING AGENTS, PULP, AND PAPER).

11.9. Organic Synthesis. Ozone is employed as a selective oxidant in laboratory-scale synthesis (7) and in commercial-scale production of specialty organic chemicals and intermediates, e.g., fragrances, perfumes (qv), flavors, antibiotics (qv), hormones (qv), and vitamins (qv).

Flavors/Fragrances/Perfumes. Vanillin acetate is prepared in 98% yield by ozonation of isoeugenol acetate. *p*-Anisaldehyde is prepared in 93% yield by ozonation of anethole. Piperonal [120-57-0] (3,4-methylenedioxybenzaldehyde) is prepared in 94% yield via ozonolysis and reduction of isosafrole [93-16-3] (223). Anisaldehyde is used in perfumery and in toilet soaps. Piperonal (heliotropine) also is used in perfumery.

Polymer Intermediates. Ozonation of oleic acid [112-80-1], $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, from tall oil (qv) produces pelargonic acid ($C_8H_{17}CO_2H$) and azelaic acid [$HO_2C(CH_2)_7CO_2H$] (224). Oleic acid can be ozonated to azelaic half-aldehyde that can be reduced with hydrogen and ammonia to ω-aminononanoic acid. Polymerization of the latter acid yields nyon-9 or Azelon (225) (see POLYAMIDES). Ozonation of cyclohexene followed by oxidation yields adipic acid, a nylon-6 intermediate.

Polymerization Initiators. Low temperature ozonolysis of compounds such as perfluoro-4-methyl-1,2-pentene in the absence of solvents and oxygen forms perfluoro ozonides useful as initiators of low temperature polymerization and copolymerization (226).

Polymer Treatment. Undesirable residual double bonds in cross-linked elastomeric polymers can be eliminated by ozonation to produce soluble elastomeric polymer latexes (227).

Peracids. Ozone accelerates the autoxidation of acetaldehyde to peracetic acid $< 15°C$. Acetaldehyde hemiacetal peracetate, an intermediate product, is decomposed by heating to peracetic acid. Reaction of peracids with olefins produces epoxides that are hydrolyzed to diols useful in automotive antifreeze mixtures (see ANTIFREEZES AND DEICING FLUIDS).

Pharmaceuticals. The pharmaceutical industry employs ozone in organic reactions to produce peroxides as germicides in skin lotions, for the oxidation of intermediates for bacteriostats, and in the synthesis of steroids (qv) such as cortisone. Ozonation of trimethylhydroquinone is one step in the synthesis of vitamin E.

11.10. Medical Applications. Among other uses, ozone therapy, employing O_3–O_2, is increasingly being employed and studied in dentistry, veterinary and sports medicine, and proctology; in the treatment of dermatoses, osteoporosis, tumors (228), ulcers, human immunodeficiency virus (HIV) and hepatitus B viruses, and sickle cell anemia; and for the healing of wounds and diseases of the extremities, eg, diabetic leg ulcers (229). It also has been used to treat certain cancers, to eliminate arterial blood clots and cholesterol deposits, and during brain surgery.

11.11. Miscellaneous Uses. Many European landfills treat leachates with O_3–uv for the destruction of COD. Ozone is used as an aquatic oxidant and disinfectant in zoos, large aquariums, as well as fish and shrimp hatcheries. Ozone also is used for food preservation, in cold storage rooms, brewery cellars, in exhaust air purification, in hotel and hospital air ducts, and air conditioning systems. Ozone has also been used in textile bleaching and in the bleaching of esters, oils, fats, waxes (qv), starch, flour, ivory, etc. A new use for ozone is in commercial laundries to reduce energy costs and replace chemicals. Oxidation of Ag^+ by ozone is employed commercially to produce high purity AgO. The use of ozone as a chemical agent decontaminant has been patented (230).

12. Analytical and Test Methods

Ozone can be analyzed by titrimetry, direct and colorimetric spectrometry, amperometry, oxidation–reduction potential (ORP), chemiluminescence, calorimetry, thermal conductivity, gas-phase titration with NO, and isothermal pressure change on decomposition. The last four methods are not frequently employed. Proper measurement of ozone in water requires an awareness of its reactivity, instability, volatility, and the potential effect of interfering substances. To eliminate interferences, ozone sometimes is sparged out of solution by using an inert gas for analysis in the gas phase or on reabsorption in a clean solution.

12.1. Iodometric Methods. Historically, the most common analytical procedure has been the iodometric method in which gaseous ozone exiting an ozone generator is absorbed by aqueous KI (dynamic method). Alternatively, a preformed ozone solution can be treated with aqueous KI: $2\ I^- + O_3 + H_2O \rightarrow I_2 + O_2 + 2\ HO^-$. The liberated iodine is measured spectrometrically or titrated with standard sodium thiosulfate solution ($I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$) following acidification with sulfuric acid; buffers are sometimes employed. The method dynamic method requires measurement of the total gas volume used in the dynamic procedure. The presence of other oxidants, such as H_2O_2 and NO_x, can interfere with the analysis. The analysis is also technique-sensitive, since it can be affected by a number of variables, including temperature, time, pH, iodide concentration, sampling techniques, etc (231). A detailed procedure is given in Ref. 232.

12.2. Direct Spectrometry. Ozone in the gas phase can be determined by direct uv spectrometry via its strong absorption at 254 nm. The accuracy of this method depends on the molar absorptivity, which is known to ±1%; interference by CO, hydrocarbons, NO_x, or H_2O vapor is not significant. The method also can be employed to measure ozone in preformed aqueous solution, but is subject to interference from turbidity as well as dissolved inorganics and organics. To eliminate interferences, ozone sometimes is sparged into the gas phase for measurement.

12.3. Colorimetric Spectrometry. Various colorimetric methods have been employed for measuring ozone residuals, however, most are susceptible to significant interferences by secondary oxidants (233). The indigo trisulfonate method (234) has been approved by the Standard Methods Committee of the American Public Health Association for ozone residual measurement (232).

12.4. Electrochemical Methods. Electrochemical methods can involve the amperometric titration of liberated iodine with phenylarsine oxide, using a rotating Au/Cu electrode or excess phenylarsine oxide, and measuring the excess by direct pulse polarography (235). Ozone also can be measured directly by reduction to O_2 on a rotating Au/Cu electrode or a Ni/Ag–AgCl electrode pair (236). To eliminate interferences, membrane cells have been developed that consist of a semipermeable membrane such as Teflon or dimethyl silicone and a suitable sensor (237). Ozone diffuses into the cell through the porous membrane and is measured polarographically by employing electrode combinations such as gold–calomel or Au/Ag–AgCl. ORP cells consist of an indicating and a reference electrode combination, which generates a potential proportional to the ozone concentration. They are typically employed as a monitor or controller in water treatment applications.

12.5. Chemiluminescent Methods. Chemiluminescent analyzers are based on the light (chemiluminescence) emitted in the gas-phase reaction of ozone with ethylene, which is measured with a photomultiplier tube. The resulting current is proportional to the ozone concentration. Aqueous solutions of ozone can be analyzed based on light emitted on reaction with various dyes, including bezoflavin, acridine yellow, indigotrisulfate, fluorescein, etc (238).

12.6. Ozone Analyzers. Laboratory, portable, and rugged industrial ozone meters employing uv, amperometry, or chemiluminescence are available for continuous or semicontinuous analysis of either gaseous or aqueous ozone.

13. Health and Safety Factors

13.1. Depletion of the Ozone Layer. As a constituent of the atmosphere, ozone forms a protective screen by absorbing radiation of wavelengths between 200 and 300 nm, which can damage DNA and be harmful to life. Consequently, a decrease in the stratospheric ozone concentration results in an increase in the uv radiation reaching the earth's surfaces, thus adversely affecting the climate as well as plant and animal life. For example, the incidence of skin cancer is related to the amount of exposure to uv radiation.

Laboratory Studies. Research in 1974 (132–135) indicated that chlorine radicals from photodegradation of CFCs (chlorofluorocarbons) can destroy ozone. Because of these studies and the fact that the two main varieties CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) can persist in the atmosphere for 75–100 years, the United States in 1978 banned their use in aerosols, eg, hair sprays and certain deodorants. However, pressure to eliminate CFCs slackened until 1985, when the Antarctic ozone hole was discovered (239).

The Ozone Hole. The ozone hole is a dramatic seasonal thinning of the normal ozone concentration over the continent of Antarctica, attributed to catalytic decomposition of ozone by halogen free radicals (Cl and Br), which are formed by photodecomposition of CFCs and Halons (bromofluorocarbons). A similar but less severe reduction in ozone levels in the Arctic also has been observed. Reduced ozone levels extend to the lower latitudes and can pose a threat to human, animal, marine, and plant life as a result of increased energetic uv–B radiation (280–320 nm) reaching the surface of the earth. Data from Antarctica show that uv radiation soars under the ozone hole, where fully half of the atmospheric ozone is destroyed each spring. The global drop in amphibian population, eg, frogs, toads, and salamanders has been ascribed to increased uv radiation from ozone thinning (240).

Montreal Protocol. Confirmation of the destruction of ozone by reactive chlorine and bromine from halofluorocarbons has led to international efforts (through the United Nations Environment Program) to reduce emissions of ozone-destroying CFCs and other ozone destroying substances into the atmosphere. The 1987 Montreal Protocol on Substances That Deplete the Ozone Layer (241) and its various revisions established schedules for phasing out production and use of various CFCs and other ozone depleting substances based on their "ozone depletion potential (ODP)". The schedules were based on comparing the projected ozone loss for a given release of a CFC compared to that for CFC-11. Substances with an ODP close to that of CFC-11 were scheduled for rapid phase out, whereas those with lower ODPs were scheduled for slower phase out. Replacement substances, eg, HCFCs (hydrochlorofluorocarbons) were scheduled for later phase out in favor of substances with lower ODPs. The recommendations of the Montreal Protocol have been incorporated into the U. S. EPA's Clean Air Act.

The current schedule for phasing out production and use of ozone depleting chemicals by developed countries is phase out Halons in 1994; phase out CFCs, CCl_4, CH_3CCl_3, and HBFCs by 1996; reduce CH_3Br by 25% by 1999, 50% by 2001, 70% by 2003, and 100% phase out by 2005; reduce HCFCs by 35% by 2004, 65% by 2010, 90% by 2015, 99.5% by 2020, and 0.5% permitted for maintenance purposes only until 2030; phase out bromochloromethane, a new substance that some companies sought to introduce in 1998, has been targetted for immediate phase out to prevent its use (242). Developing countries have until 2010 to complete their transition from CFCs, Halons, and CCl_4 to more ozone friendly substances.

Although production of CH_3Br was due to ease in 2005, farmers and fumagators have been given additional time to develop substitutes. At a meeting of the UN in Montreal (March 2004), some countries were granted exemptions for using the compound based on 35% of 1991 baseline levels (243).

By 1993, worldwide production of CFCs was reduced to 50% of 1986 levels (244). Global consumption of CFCs decreased from 1.1 Mt year^{-1} in 1986 to 160 kt year^{-1} in 1996, the latter due primarily to developing countries (245).

In order to meet the established goals, the industry has accelerated efforts to find alternatives to CFCs (246). In 1988, the first International CFC & Halon Alternatives Conference was held for the purpose of sharing technology. The U.S. industry is switching to hydrofluorocarbons (HFCs), which do not contain chlorine or bromine that can decompose ozone, for use in compressors of home refrigerators and almost all new car and truck air-conditioning systems, and to hydrochlorofluorocarbons (HCFCs) for industrial refrigeration units and in foam-blowing applications. The Montreal Protocol classifies HCFCs as transitional, setting a limit on their production in 1996 and gradually phasing them out, because like CFCs and HCFCs they are absorbers of infrared radiation and can contribute to global warming. Under the stratospheric ozone protection provision of the Clean Air Act, the EPA has issued its final rule regarding the evaluation and regulation of ozone-depleting substitutes (247).

Other Factors Affecting Ozone Depletion. A smaller factor in ozone depletion is the rising levels of N_2O in the atmosphere from combustion and the use of nitrogen-rich fertilizers, since they are the sources of NO in the stratosphere that can destroy ozone catalytically. Another concern is the effect of subsonic and supersonic aircraft that inject additional nitrogen oxides, SO_2, and H_2O into the stratosphere via their exhaust gases (248).

13.2. Environmental Impact of Ambient Ozone. Ozone can be toxic to plants, animals, and fish. The lethal dose, LD_{50}, for albino mice is 3.8 ppmv for a 4-h exposure (249); the 96-h LC_{50} for striped bass, channel catfish, and rainbow trout is 80, 30, and 9.3 ppb, respectively. Although ozone is toxic to humans, it is even more toxic to plants, eg, exposure to 0.1 ppmv results in a reduction in the photosynthesis rate by a factor of 2. Small, natural, and anthropogenic atmospheric ozone concentrations can increase the weathering and aging of materials, eg, plastics, paint, textiles, and rubber. For example, rubber is degraded by reaction of ozone with carbon–carbon double bonds of the rubber polymer, requiring the addition of aromatic amines as ozone scavengers (see ANTIOXIDANTS; ANTIOZONANTS). An ozone decomposing polymer (noXon) has been developed that destroys ozone in air or water (250).

13.3. Urban Air Quality. Although the naturally occurring concentration of ozone at the earth's surface is low, the distribution has been altered by the emission of pollutants, primarily by automobiles but also from industrial sources which lead to the formation of ozone. The strategy for controlling ambient ozone concentrations arising from automobile exhaust emissions is based on the control of hydrocarbons, CO, and NO via catalytic converters. As a result, peak ozone levels in Los Angeles, for instance, have decreased from 0.58 ppm in 1970 to 0.33 ppm in 1990, despite a 66% increase in the number of vehicles.

The EPA is reviewing and revising the Air Quality and Other Photochemical Oxidants (Criteria Document) and reevaluating the national ambient air quality standards (251). The EPA is also proposing that manufacturers ($\geq$ 10,000 lb O_3 year^{-1}) and users ($\geq$25,000 lb O_3 year^{-1}) submit data annually to the EPA on estimated ozone releases (252).

Under the Clean Air Act, the EPA regulates organic chemicals that evaporate quickly into the atmosphere and help form ozone. Many of these volatile organic compounds (VOCs) are key ingredients in solvents, paints, coatings, inks, and other commercial products. To determine whether a VOC has negligible reactivity, and therefore exempt from some regulations, the EPA compares a compound's reactivity with hydroxyl radicals to that of ethane.

13.4. Human Exposure to Ozone.

The toxicity of ozone is largely related to its powerful oxidizing properties. The odor threshold of ozone varies among individuals but most people can detect 0.01 ppm in air, which is well below the limit for general comfort.

EPA Ambient Air Ozone Limits. The Clean Air Act requires the EPA to set National Ambient Air Quality Standards for pollutants considered harmful to public health and the environment. The primary standards are as follows: 0.08 ppm (6-h exposure) and 0.12 ppm (1-h exposure).

OSHA Ozone Exposure Limits. OSHA has established a time-weighted average permissible exposure level for workers for an 8-h day of 0.10 ppmv (0.2 mg m^{-3}) and a short-term exposure limit of 0.30 ppmv (0.6 mg m^{-3}) for an exposure < 15 min (253). The latter is based on observations showing that significant declines in pulmonary function can result from repeated intermittent exposures or from a single short-term exposure to ozone.

Ozone Toxicity. The toxicity of gaseous ozone varies with concentration and exposure time (254). Respiratory impairment results from breathing air containing >0.1 ppmv of ozone, especially by persons suffering from repiratory complaints such as asthma and emphysema. The symptoms experienced on exposure to 0.1–1 ppm ozone are headache, throat dryness, irritation of the respiratory passages, and burning of the eyes caused by the formation of aldehydes and peroxyacyl nitrates. Exposure to 1–100 ppm ozone can cause asthma-like symptoms such as tiredness and lack of appetite. Short-term exposure to higher concentrations can cause throat irritations, hemorrhaging, and pulmonary edema. Additional toxicity data is given in Ref. 255.

The presence of naturally occurring ozone in the lower stratosphere creates a potential hazard for passengers and crew members of high flying aircraft (256,257). Ozone in the inlet air to the aircraft cabin, which can reach 1.2 ppm, is destroyed catalytically. Studies show that ozone has a role in arterial disease (258).

13.5. Ozone Disinfection By-Products.

Ozonation of drinking water produces various by-products, eg, aldehydes, ketones, carboxylic acids, organic peroxides, epoxides, nitrosamines, *N*-oxy compounds, quinones, hydroxylated aromatic compounds, brominated organics, and bromate ion. Although some of these compounds are potentially toxic or carcinogenic, most bioassay-screening studies have shown that ozonated water induces substantially less mutagenicity than chlorinated water (72,259,260). However, further work is necessary to identify and screen (Ames test) ozonation by-products formed under typical water treatment conditions (261). Ozonation by-products are on the Drinking Water Priority List as candidates for future regulation (262). The Disinfection and Disinfection By-Products Rule proposed by the EPA will set limits for both disinfectants (excluding ozone) and disinfection by-products (eg, bromate) and require biofiltration following ozone use (195).

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