Hydrogen Sulfide

Hydrogen sulfide (H_2S) is a colorless, flammable gas formed during the reaction of mineral acids with sulfides of heavy metals, as well as during the decomposition of protein (sewer gas contains up to 10% H_2S). Considerable amounts of H_2S are also formed during the papermaking process. In addition, H_2S accumulates in cellars, canals, and containers. The warning sign—an offensive smell of rotten eggs (sensitivity threshold ~0.025 mL/m^3)—diminishes as the result of rapid habituation. First aid helpers attempting to rescue victims from poisoned areas are therefore prone to accidents.

Effect (A). Concentrations of more than 10–50 mL/m^3 cause irritation, possibly pulmonary edema, and intracellular hypoxia; the mechanisms are unknown. Concentrations of more than 500 mL/m^3 cause unconsciousness and quick development of central respiratory paralysis. H_2S is rapidly oxidized in the body and eliminated as sulfate.

After chronic exposure (e.g., of workers in synthetic fiber manufacturing facilities), corneal damage, increased airway resistance, pulmonary edema, pneumonia, and myocardial degeneration have been observed.

Therapy. Nonspecific measures (keeping the airways free, correction of acidosis).

Fumigants

Some gaseous compounds are used as fumigants for controlling insects, rodents, and other pests in areas that cannot be reached otherwise. Fumigants are very dangerous poisons, and in many industrialized countries their sale is restricted and their use requires a permit (**B**). Details of how to carry out fumigation procedures are described in national legislation and regulations. For example, ships in transit may be fumigated only with phosphine, containers in transit may be treated only with phosphine or methyl bromide, and ethylene oxide may be used only in fumigation chambers.

In industrialized countries, widely used fumigants include the following (**C**):

Methyl bromide (bromomethane). In the 1960s, the use of this insecticide (a colorless, nonflammable gas; boiling point 4.5 °C; density 3 kg/L) caused more lethal accidents in California than the use of organophosphates (see p. 200). The extremely poisonous methyl bromide is commonly mixed with chloropicrin, a potent irritant that serves as a warning agent. The target organ of the systemic effects of methyl bromide is the central nervous system. A likely mechanism of action for poisoning of the central nervous system is the reaction with endogenous sulfhydryl groups. Dithiol compounds (e.g., dimercaptopropanol, dimercaptosuccinic acid [DMSA]) are being considered as possible agents for treatment.

Hydrogen cyanide and formaldehyde. For details, see p. 140 and pp. 94, 136, respectively.

Ethylene oxide (Oxirane). This is a colorless gas (boiling point 11 °C; density 1.5 kg/L) with a high olfactory threshold (at ~700 mL/m^3). It is a strong irritant, and it forms explosive mixtures with air. Ethylene oxide is mutagenic and carcinogenic.

Phosphorus hydrides: hydrogen phosphide (PH_3), phosphines, and phosphine-producing pesticides. Phosphine is the common name for hydrogen phosphide (a colorless, heavy gas; formerly called phosphorus [tri]hydride). In the presence of traces of water, the gas is slowly released from aluminum phosphide tablets. It is a metabolic poison and neurotoxin that is more toxic than methyl bromide but considered safer to handle.

The following fumigants are also used: vinyl cyanide (acrylonitrile, CH_2CHCN), carbon disulfide (CS_2), tetrachloromethane (carbon tetrachloride, CCl_4, see p. 104), trichloronitromethane (CCl_3NO_2), and ethylene dibromide (1,2-dibromoethane, $CH_2BrCH_2Br_2$), and dibromochloropropane ($ClCH_2CHBrCH_2Br$).

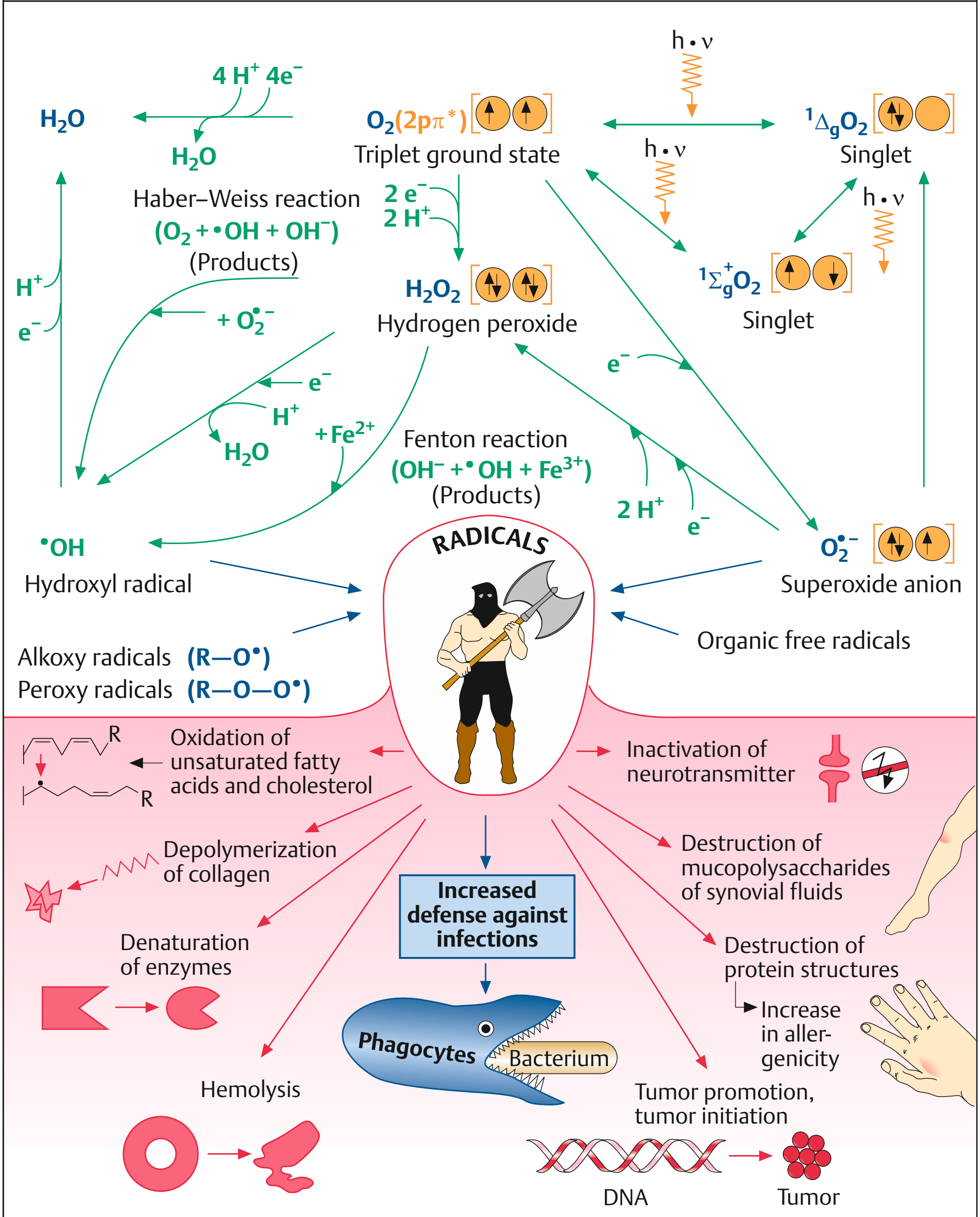
Detection. The gaseous compounds mentioned above can be determined quantitatively by means of gas chromatography or infrared spectroscopy, and semiquantitatively using colorimetric indicator tubes (Draeger tubes).

$R{-}X \longrightarrow R{-}X^{\bullet +} + e^-$ Radical cation

$R{-}X + e^- \longrightarrow R{-}X^{\bullet -}$ Radical anion

$R{-}XH \xrightarrow{\text{Energy}} R{-}X^{\bullet} + H^{\bullet}$ Uncharged radical

A. Formation of radicals



B. Formation of radicals and their effects