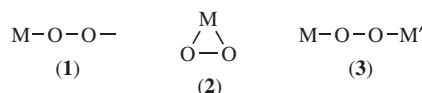


PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES

1. Introduction

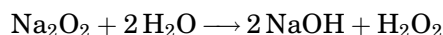
A peroxide or peroxy compound contains at least one pair of oxygen atoms, bound by a single covalent bond, in which each oxygen atom has an oxidation number of -1 . The peroxide group can be attached to a metal M or an inorganic element (eg, S, B, P), through one (1) or two (2) oxygen atoms, or it can bridge two metals (3):



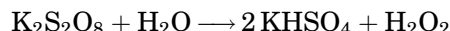
Peroxides in a wider sense also include the hyperoxides (MO_2), H_2O_2 addition compounds (eg, sodium carbonate peroxohydrate), and the inorganic ozonides (M^1O_3). Peroxides should be distinguished from several other types of compounds having similar names. The higher oxides of lead, manganese, and other elements, although sometimes called *peroxides*, are not peroxides as defined herein because these contain no oxygen–oxygen bond. Similarly, compounds such as the perchlorates and permanganates are not peroxides. Rather, in these cases, the prefix *per* denotes the fully oxidized state for the central atom. It is preferable for peroxides to be designated by the prefixes *peroxo* or *peroxy*. In the IUPAC nomenclature, *peroxo* is used for inorganic compounds, *peroxy* for organic compounds. A very large number of peroxy compounds have been described in the literature (1). All the important inorganic peroxy compounds except hydrogen peroxide are described in this article, as are the major commercial processes and applications. Ozonides and superoxides are also included, but not the dioxygen complexes of the transition metals.

In hydrogen peroxide, the oxygen–oxygen bond strength is 209 kJ/mol (50 kcal/mol), which is approximately half of the normal bond strength for a single covalent oxygen bond. The oxidizing power of the peroxides results from this low bond energy as well as the high energies of $\text{O}-\text{M}$, $\text{O}-\text{C}$, and $\text{O}-\text{H}$ bonds.

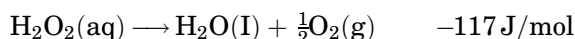
All the simple peroxides form hydrogen peroxide (qv) on contact with water. Some, such as sodium peroxide, hydrolyze almost instantaneously:



Others, eg, the peroxodisulfates, hydrolyze slowly at room temperature:



Many inorganic peroxides tend, as does H_2O_2 , to decompose evolving oxygen:



Whereas decomposition is slow in pure solutions, it is accelerated enormously by alkali and traces of many metal ions. Indeed, hydrolysis to H_2O_2 , followed by its disproportionation, is the main path for decomposition of inorganic peroxides.

1.1. History. In 1811 Gay-Lussac and Thenard first described the peroxides of barium, sodium, and potassium. Hydrogen peroxide was isolated several years later in 1818 by Thenard. Because of the advantages in stability and handling, the solid peroxides were of greater practical use than hydrogen peroxide solutions at this time. Sodium peroxide gained industrial importance as a bleaching agent in the textile industry and was first produced on a commercial scale in 1899. Sodium peroxide lost its importance when hydrogen peroxide could be more cost-effectively manufactured by the anthraquinone process.

Today the most important industrial inorganic peroxo compound is sodium perborate tetrahydrate, which was discovered in 1898 by Tanatar. It has been produced on a commercial scale since 1907 and is still the preferred bleaching agent in powder detergents. Other industrially important inorganic peroxo compounds are the sodium, potassium, and ammonium salts of peroxodisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$), the triple salt of potassium peroxomonosulfate ($2\text{KHSO}_5\text{-KHSO}_4\text{K}_2\text{SO}_4$) and calcium peroxide (CaO_2). From the hydrogen peroxide addition compounds, sodium carbonate peroxohydrate finds increasing use in laundry detergents and dishwashing formulations, since products with good shelf life properties can be manufactured economically using new coating technologies. Urea peroxide is produced on a several-hundred tonnes scale only and has limited applications in pharmaceutical products.

1.2. Group I (1A) Peroxides. Peroxides of all the alkali metals having the formula M_2O_2 are known. There are several general methods of preparation: reaction of the metal and oxygen, reaction of the metal monoxide and oxygen, thermal decomposition of the superoxide, and reaction of alkaline solutions of the metal and hydrogen peroxide. The last method generally gives peroxohydrates and/or hydrates of the peroxides, from which the hydrogen peroxide or water can be removed by mild heat treatment or vacuum. There is also an organic route to sodium peroxide octahydrate. A general account of all these peroxides is available (1).

Alkali metal peroxides are stable under ambient conditions in the absence of water. They dissolve vigorously in water, forming hydrogen peroxide and the metal hydroxide. They are strong oxidizing agents and can react violently with organic substances. Only lithium peroxide and sodium peroxide have been commercialized.

Lithium Peroxide. Lithium peroxide [12031-80-0], Li_2O_2 , M_r 45.9, ρ 2.36 g/cm³, has an active oxygen content of 34.8%, which is the highest of all metal peroxides. Lithium peroxide is pale yellow solid, stable at ambient temperature, and not hygroscopic. On heating to about 300°C, it loses oxygen and forms lithium monoxide. The commercial product contains about 96% Li_2O_2 . Unlike the other alkali peroxides, the lithium salt cannot be made by direct reaction between the metal and oxygen. It is made commercially by reaction of aqueous lithium hydroxide and hydrogen peroxide, which yields the peroxohydrate trihydrate, and is then dehydrated (1-). Lithium peroxide has not attained industrial importance because of comparatively high cost.

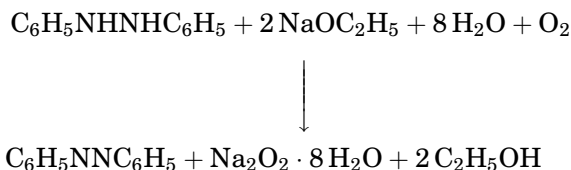
Lithium peroxide is a strong oxidizer and can promote combustion when in contact with combustible materials. It is a powerful irritant to skin, eyes, and mucous membranes (5); protective clothing should be worn when handling lithium peroxide. The LD₅₀ has not been determined, and there is no designated threshold limit value (TLV). However, 5 g of many lithium compounds can be fatal.

Commercial lithium peroxide has been assigned UN No. 1472 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. It is manufactured by Chemetall AG (Germany) and Lithium Corporation of America (United States). The German price in 1997 was DM 121/kg.

Sodium Peroxide. Sodium peroxide [1313-60-6], Na₂O₂, *M_r*, 78.0, ρ 2.6 g/cm³, is a pale yellow solid, stable at ambient temperature, and hygroscopic. On heating, it starts to liberate oxygen at about 300°C and decomposes rapidly above its melting point of 460°C. It dissolves rapidly in water, forming a solution of hydrogen peroxide and sodium hydroxide. The hydrogen peroxide then decomposes, liberating oxygen. The oxygen dissociation pressure is 1.01 kPa (1 atm) (6). When dissolving in water, the peroxide should always be added to the water, not vice versa, because of the large amount of heat evolved. Sodium peroxide forms several peroxohydrates and hydrates: Na₂O₂ · 2 H₂O₂, Na₂O₂ · 2 H₂O₂ · 4 H₂O, NaO₂ · 2 H₂O, and Na₂O₂ · 8 H₂O (7).

The commercial product is a powder containing a minimum of 96% Na₂O₂ and approximately 20% active oxygen. It is made commercially by oxidizing the molten metal with either oxygen or air enriched in oxygen. Early industrial history (1) and manufacturing details (8–10) are available. Sodium peroxide used to be an important industrial chemical. It was used in bleaching wood pulp and linen that require strong alkalinity, as well as for the manufacture of sodium peroxoborates by the acid and duplex processes (11) and of sodium carbonate peroxohydrate. In the 1960s, with the advent of relatively inexpensive hydrogen peroxide from the anthraquinone process, sodium peroxide became uneconomic. As of the mid-1990s, it had only a few special applications, including chemical analysis and the extraction of platinum from its ores by the Leidie process.

The octahydrate of sodium peroxide [12136-94-6], Na₂O₂ · 8 H₂O, was made commercially in Finland in the 1950s (12) by reaction of hydrazobenzene and sodium ethoxide:



The octahydrate, and the other hydrates and peroxohydrates of sodium peroxide that are known, no longer have commercial significance.

Although neither inflammable nor self-igniting, sodium peroxide mixtures with oxidizable substances are highly inflammable. Such mixtures burn violently, even in the absence of air. Sodium peroxocarbonates can be formed under the influence of atmospheric moisture and carbon dioxide. At temperatures

$>50^{\circ}\text{C}$ and when exposed to pressure or friction, these peroxocarbonates can decompose and generate flame.

Sodium peroxide is a powerful irritant to skin, eyes, and mucous membranes (5); protective clothing should be worn when handling. This product has been assigned UN No. 1504 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. Metaux Speciaux (France), Nippon Soda (Japan), and Tosoh Corporation (Japan) manufacture sodium peroxide. Trade names that have been used for this product are Solozone and Flocool 180. The German price in 1997 was DM 60–70/kg.

1.3. Group 2 (11A) Peroxides. All the elements of Group 2 form peroxides, with the exceptions of beryllium and radium. There are two general methods of preparation: (1) reaction of the metal or metal monoxide with oxygen and (2) reaction of the hydroxide with aqueous hydrogen peroxide. These peroxides are more stable in the presence of water than the Group (I) peroxides, primarily because of insolubility in water. Calcium peroxide is used on a larger scale. Magnesium, strontium, barium, and zinc peroxides have small-scale uses, whereas cadmium and mercury peroxides have no commercial uses at all. A general account of these peroxides is available (1).

In spite of the widespread usage of these compounds, the structures of only the calcium, barium, and strontium compounds are reasonably well established. The materials are generally made by triturating the oxides, or hydroxides, with aqueous hydrogen peroxide and drying the solid products. The commercial products are typically mixtures of the peroxides with varying amounts of hydroxides, oxides, carbonates, hydrates, and peroxohydrates.

1.4. Magnesium Peroxide. Magnesium peroxide [14452-57-4], MgO_2 , has not been prepared in the pure state. The hydrates $\text{MgO}_2 \cdot 0.5 \text{H}_2\text{O}$ [77883-47-7] and $\text{MgO}_2 \cdot \text{H}_2\text{O}$ have been postulated. Commercial magnesium peroxide is made by mixing a light grade of magnesium oxide with hydrogen peroxide and drying the slurry. The product is a white powder containing about 25% MgO_2 and 7% active oxygen. The remaining constituents are magnesium oxide, magnesium hydroxide, and magnesium carbonate. This material is sparingly soluble in water but reacts with water slowly, forming hydrogen peroxide and liberating oxygen gas. It is used in bioremediation as an oxygen source and in medicine as a stomach antacid and as an antiseptic (see DISINFECTANTS AND ANTISEPTICS). There are minor uses for magnesium peroxide in household products, veterinary medicine, and metallurgy (qv). Magnesium peroxide is a strong oxidizer and can cause fire when in contact with combustible materials. It is a powerful irritant to skin, eyes, and mucous membranes (5); protective clothing should be worn when handling. It has been assigned UN No. 1516 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. Magnesium peroxide is made by Solvay (Germany, trade name IXPEN 25 M), Regenesis (USA, trade name ORC) and by FMC (USA). The German price of the 24–28% grade in 1997 was DM 11/kg.

1.5. Calcium Peroxide. Pure calcium peroxide [1305-79-9], CaO_2 , M_r 72.1, ρ 2.92 g/cm³ has been prepared, but the commercial product is a mixture made by reaction of calcium hydroxide and hydrogen peroxide. Commercial material contains either 60 or 75% CaO_2 ; the remainder is a poorly defined

mixture of calcium oxide, hydroxide, and carbonate. A well-defined octahydrate [60762-59-6], $\text{CaO}_2 \cdot 8 \text{H}_2\text{O}$, can be crystallized from aqueous systems.

An important application of calcium peroxide is for curing the polysulfide sealants used in double-glazing window units. Calcium peroxide is also used at several gold mines in Australia to increase the recovery of gold and reduce the consumption of cyanide (13,14). Calcium peroxide is made *in situ* by mixing a slurry of calcium hydroxide and aqueous hydrogen peroxide immediately before use (13). Solid calcium peroxide can also be used in the heap leaching of lean gold ores. A proprietary form of calcium peroxide for this purpose is marketed by FMC (United States) under the trademark PermeOx.

PermeOx is also used to improve the bioremediation of soils contaminated with creosote or kerosene (Bioremediation), to deodorize sewage sludge and wastewater (Odor modification), and to dechlorinate wastewater and effluents. A special formulation of calcium peroxide, made by FMC and sold in the United States under the trademark Trapzene, is used for removing metal ions from acidic wastestreams such as coal ash leachate and acid mine drainage (Wastes, industrial).

Calcium peroxide has several horticultural and agricultural applications, particularly in Japan. Usually used in the form of granules, it acts by providing extra oxygen for germinating plants and other organisms. In Japan, it is used in the cultivation of tomatoes, cucumbers, tobacco, and prawns; in Europe, it has been used as a coating on beet seeds. A considerable amount of developmental work has been done on other agricultural application, including composting and the cultivation of rice and trees; however, these applications have not been commercialized.

Calcium peroxide has been used for many years as a dough conditioner in the United States (15), but not in Europe, where this use is not permitted. The application was first mentioned in 1921 (16) and described in 1930 (17). In dough, the calcium peroxide acts primarily by converting the disulfide bonds of gluten into sulfhydryl groups, thereby preserving an open dough structure, which retains more moisture than untreated dough. Other advantages are also provided in bread manufacture. A food grade of calcium peroxide for bakery use is made by FMC in the United States (see BAKERY PROCESSES AND LEAVENING AGENTS; FOOD ADDITIVES). Another industrial application of calcium peroxide is as an oxidizing agent in the production of certain titanium–aluminum alloys. A rather new application for CaO_2 is as a peroxide source in toothpaste (18).

Calcium peroxide is among the safest of the inorganic peroxides, presenting no significant hazard with regard to skin contact or absorption, inhalation, and ingestion; but it may be irritating to the skin under humid conditions. Airborne dust is irritating to the eyes, nose, throat, and lungs, but poses no significant long-term inhalation hazard. It should be handled only in well-ventilated areas and dust-controlled to below the TLV of 5 mg/m^3 ; goggles, dust mask, and gloves should be worn when handling. This product has been assigned UN No. 1457 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances.

Calcium peroxide is made by FMC (USA), Nippon Peroxide (Japan), Shimakyō Chemical (Japan), Solvay (Germany), Solvay Interlox (United Kingdom), and Tomita Seiyaku (Japan). Trade names used for calcium peroxide are Calper,

IXPER 60 C, IXPOR 75 C, PermeOx, and Trapzene. The world market for calcium peroxide in 1997 was about 2000 t. The U.S. prices in 1997 were, for the food-grade (75% CaO_2), \$4/kg; and for the technical grade (60%), \$2.97–3.30/kg.

1.6. Strontium Peroxide. Strontium peroxide [1314-18-7], M_r 119.6, ρ 4.7 g/cm³ is a light-colored solid of good thermal stability. Commercial strontium peroxide contains about 85% SrO_2 and 10% active oxygen. It can be made by heating strontium oxide in the presence of oxygen gas under 20 MPa (200 atm) pressure, or by the reaction of a soluble strontium salt with hydrogen peroxide. The only substantial application for this compound is in pyrotechnics. Strontium peroxide produces a red color in flames.

Strontium peroxide is a strong oxidizer and can cause fire when in contact with combustible materials. It is a powerful irritant to skin, eyes, and mucous membranes (5); protective clothing should be worn during handling. It has been assigned UN No. 1509 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. It is made by Solvay (Germany), which uses the trade name IXPOR 85 S. The price in Germany in 1997 was DM 45/kg (U.S. \$28/kg).

1.7. Barium Peroxide. Barium peroxide [1304-29-6], BaO_2 , M_r 169.4, ρ 5.4 g/cm³ was the first-known peroxy compound. It was used until mid-1900 in the manufacture of oxygen by the Brin process and of hydrogen peroxide by the Thenard reaction (11,19). It is the only Group 2 peroxide that can be prepared at atmospheric pressure by heating the metal monoxide in air. Barium oxide is converted to the peroxide at 500–550°C; further heating to approximately 700°C reverses the reaction. Small concentrations of steam can increase the rate of peroxide production.

The commercial product is a dull yellow powder containing about 90% BaO_2 and about 8.5% active oxygen; the remainder is mainly barium carbonate and barium hydroxide. Today barium peroxide has only limited use in the manufacture of pyrotechnics.

Barium peroxide is a strong oxidizer and can cause fire when in contact with combustible materials. It is powerful irritant to skin, eyes, and mucous membranes (5). Consequently, it is also toxic via the subcutaneous route; protective clothing should be worn during handling. The LD_{50} value (mouse, oral) is 50 mg/kg (5).

This product has been assigned UN No. 1449 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. It is made by Solvay (Germany), who uses the trade name IXPOR 90 B. The U.S. price in 1997 was \$12/kg, the French price was Fr. 55–77/kg depending on grade and quantity.

2. Group 12 (IIB) Peroxides

2.1. Zinc Peroxide. Zinc peroxide [1314-22-3], ZnO_2 , M_r 97.38, is a yellow solid and generally similar in its properties to magnesium peroxide. The commercial product is a pale yellow powder containing about 55% ZnO_2 and 9% active oxygen. It is stable at room temperature, decomposes at $> 150^\circ\text{C}$ to oxygen and zinc oxide, and decomposes explosively at 190–212°C. It is stable

in dry air but loses its oxygen in moist air and on heating. It is insoluble in water but dissolves in dilute acid, liberating hydrogen peroxide. Zinc peroxide is produced commercially by drying a slurry of zinc oxide and hydrogen peroxide. It also can be produced by the reaction of alkaline hydrogen peroxide and a soluble zinc salt (20). It is used as an accelerator in rubber compounding, as a curing agent for synthetic elastomers, and as a deodorant for wounds and skin diseases. Zinc peroxide is a powerful irritant to skin, eyes, and mucous membranes (5); protective clothing should be worn during handling. The systemic toxicity is similar to that of zinc oxide (5), for which the LD_{50} (rat, oral) is 7950 mg/kg (5).

Zinc peroxide is a strong oxidizer and can cause fire when in contact with combustible materials. It has been assigned UN No. 1516 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. It is made by Solvay (Germany), which uses the trade name IXPÉR 55 Z. In 1997, the price in France was Fr. 65–80/kg (\$7–9/kg).

3. Group 13 (IIIB) Peroxides

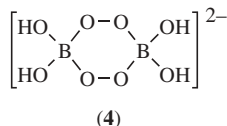
3.1. Boron Compounds. The naming of sodium perborate, one of the most important commercial boron compounds, has long been confused.

The stoichiometry of the most important hydrate is $NaBO_3 \cdot 4 H_2O$, often called *sodium perborate tetrahydrate*. Only one of the oxygen atoms acts as an oxidant. The formula has often been written as $NaBO_2 \cdot H_2O_2 \cdot 3 H_2O$ and the compound referred to as a *trihydrate*. The crystal structure, established in 1961, contains the cyclic diperoxodiborate anion $[B_2(O_2)_2(OH)_4]^{2-}$ and six associated water molecules. The crystallographically derived names are used to avoid confusion (21,22). The prefix *per* usually signifies an element in its highest valence state. Because the boron is always trivalent, the prefix *peroxo*, recommended by IUPAC, is used herein. The commercial name used in the detergent industry is sodium perborate tetrahydrate. Table 1 gives an overview of the common names and molecular structures of the sodium peroxoborates.

3.2. Sodium Perborate Tetrahydrate. The compound sodium perborate tetrahydrate (sodium peroxoborate hexahydrate) [10486-00-7], $Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$, M_r 153.9, ρ 1.731 g/cm³, theoretical active oxygen content 10.38%, melts in its own water of crystallization at 65.5°C. The solubility in water is 0.152 g/L at 20°C and 0.388 mol/L at 40°C. The commercial product is white crystalline solid with a bulk density of 0.65–0.90 kg/L.

The traditional electrochemical process of sodium perborate tetrahydrate is no longer of commercial importance (23). Today it is produced by mixing hydrogen peroxide with an alkaline solution of sodium borate made from a boron mineral, usually technical grade borax pentahydrate or the minerals kernite and tincal (see BORON COMPOUNDS). The mineral is dissolved in aqueous sodium hydroxide and the solution is clarified; hydrogen peroxide and a stabilizer such as magnesium silicate are then added at a temperature <30°C. The product crystallizes when cooled to ambient temperature and is removed by filtration or centrifuge (24–28).

It usually contains several percent of moisture and is dried by warm air at a temperature below 60°C. There are a number of minor variations on this basic process. It is possible to control the crystal morphology or the state of aggregation of the product in order to improve handling characteristics. Because X-ray diffraction (21,22) shows the crystal to contain a dimeric cyclic anion (4), the systematic name is disodium tetrahydroxo-di- μ -*m*-peroxo-diborate (III) hexahydrate [10486-00-7].



In aqueous solution, all the sodium peroxoborates dissociate for the most part into boric acid, or its anion, and hydrogen peroxide. Peroxoborate species are also present in these solutions, depending on the pH and the concentration for the species type. The nature of these species has been extensively examined by conventional physicochemical methods (29), by nmr, and by Raman spectroscopy (30–33). Both monomeric and polymeric species are usually present. There is some evidence (34) suggesting that these peroxoborates are more reactive than hydrogen peroxide alone under similar conditions.

Sodium perborate tetrahydrate has been an important commercial bleaching agent for more than 90 years (at the time of writing) (see BLEACHING AGENTS). It is an important ingredient of many household detergents and cleaning products. These applications account for approximately 90% of the total market. The textile industry generally uses hydrogen peroxide for bleaching, but there are a few areas in which sodium perborate tetrahydrate is preferred.

Organic chemists have been using sodium peroxoborates as oxidants since the 1980s (35). The tetrahydrate and monohydrate generally behave similarly. In the first examples of such oxidations, published in 1983 (36), a solution of the tetrahydrate in glacial acetic acid was found to oxidize aromatic amines to nitroaromatics, and sulfides to sulfoxides or sulfones (37). Since that time, many other such oxidation systems have been studied, although the identity of the oxidants in such systems remains unclear. The oxidant was originally considered to be peroxyacetic acid, but kinetic studies have been inconsistent with this hypothesis. At the conclusion of these reactions in acetic acid, a white solid commonly precipitates; this precipitate is not a peroxygen compound but appears to be a sodium tetraborate having associated acetic acid (35). Other organic solvents, or phase-transfer systems, can be used in place of acetic acid. There have been several mechanistic studies of organic oxidations by peroxoborate in water (39,40).

The toxicity of sodium peroxoborate tetrahydrate in solution is equivalent to those of sodium borate and hydrogen peroxide. The LD₅₀ (mouse, oral) is 1060 mg/kg (5). Local use of high concentrations in the mouth can cause chemical burns and other problems (41). No TLV has been established. An overview and assessment of the available toxicological data is given in Reference 42.

The product is considered nonhazardous for international transport purposes. However, it is an oxidizing agent sensitive to decomposition by water,

direct sources of heat, catalysts, and so on. Decomposition is accompanied by the liberation of oxygen and heat, which can support combustion and cause pressure bursts in confined spaces. Decomposition in the presence of organic material is rapid and highly exothermic.

Sodium peroxoborate tetrahydrate is made commercially by Atochem (France), Belinka (Slovenia), Ausimont (Italy), Caffaro (Italy), Degussa (Germany, United States), Etibank (Turkey), FMC Foret (Spain), Solvay Interlox (Australia, Belgium, France, Germany, Italy, Portugal, Spain, United Kingdom, United States), and Treibacher Chemische Werke (Austria). In 1997, the total world manufacturing capacity for the tetrahydrate was about 700,000 tonnes, about 25% of which were for conversion to sodium perborate monohydrate (sodium peroxoborate). The U.S. price in 1997 was \$0.79–0.86/kg; the German price was DM 0.75–0.90/kg.

3.3. Sodium Perborate Trihydrate. The compound sodium perborate trihydrate (sodium peroxoborate tetrahydrate) [28962-65-4], $\text{Na}_2\text{B}_2(\text{O}_2)_2[(\text{OH})_4] \cdot 4\text{H}_2\text{O}$, M_r 135.9, ρ 1.86 g/cm³, formerly written as $\text{NaBO}_3 \cdot 3\text{H}_2\text{O}$ theoretical active oxygen content 11.8 wt%, melts at 81.7°C. A number of procedures have been published (13) for producing this hydrate; most involve the crystallization from water at 40–50°C. The crystal structure (43) shows the presence of the same cyclic peroxoborate anion (4) as that in the sodium peroxoborate hexahydrate. Stability and vapor pressure determinations indicate that sodium perborate trihydrate is the thermodynamically stable phase above 15°C. It has, however, never been commercialized because of its slow dissolution in water (44).

3.4. Sodium Perborate Monohydrate. Sodium perborate monohydrate [10332-33-9] (sodium peroxoborate), $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4]$, written as $\text{NaBO}_3 \cdot \text{H}_2\text{O}$, M_r 99.8, ρ 2.12 g/cm³, has a theoretical active oxygen content of 16.0 wt%. It has no definite melting point. Sodium perborate monohydrate is known only as a microcrystalline powder made by dehydrating the tetrahydrate. The crystal structure has not been determined, but the vibrational spectrum (45) indicates the presence of the same cyclic peroxodiborate anion (four) as that in the peroxoborate hexahydrate as well as in the peroxoborate trihydrate.

The commercial product has an active oxygen content of at least 15%. This product has replaced the tetrahydrate in some compact household detergents and dishwashing formulations because it dissolves faster and has a greater content of active oxygen per unit volume of granular product. Because of the short washing cycles in North America, sodium perborate monohydrate is the preferred product in this market. Sodium perborate monohydrate is also the preferred product used in denture cleansers.

The toxicity of sodium perborate monohydrate is similar to that of the tetrahydrate. The LD_{50} (rat, oral) is in the range of 890–1300 µg/kg (42,46). Sodium peroxoborate is an eye irritant, but not a skin irritant. Absorption through large areas of abraded or damaged skin can give systemic boron poisoning (5). The maximum eight-hour time-weighted average (TWA) exposure limit is 5 mg/m³ (5). An overview and assessment of the available toxicological data is given in Reference 42. The transport classification of sodium perborate monohydrate has been changed recently to 5.1 (oxidizer) by all major producers due to a change in testing procedures for class 5.1 oxidizer (47). As are all peroxide compounds, it is sensitive to decomposition by water, direct sources of heat, catalysts,

and similar Factors. Decomposition of sodium perborate monohydrate is accompanied by the liberation of oxygen and heat that can support combustion and cause pressure bursts in confined spaces. Decomposition in the presence of organic material is rapid and highly exothermic.

The world market in 1997 was about 150,000 tonnes. Sodium peroxoborate is made commercially by Ausimont (Italy), Degussa (Germany, Belgium), FMC Foret (Spain), Solvay Interlox (Belgium, Italy, Germany, United Kingdom, United States), and Treibacher Chemische Werke (Austria). The U.S. price in 1997 was in the range \$1.30–1.40/kg, the German price was DM 1.35–1.60/kg.

3.5. Anhydrous Sodium Perborate. Anhydrous sodium perborate [7632-04-4], NaBO_3 , M_r 81.8, is an undefined, powdery material, made by heating sodium perborate monohydrate in a current of dry air in a fluidized bed at 150–160°C. Attempts to characterize this material physically have been largely unsuccessful (48,49). Its electron spin resonance spectrum shows several types of free radicals in the powder. It should perhaps be regarded more as an amorphous assemblage of radicals than as a defined compound (50).

Anhydrous sodium perborate effervesces in water. The commercial product contains a minimum of 13% oxygen, which can be released in this way. The content of active oxygen is about 2%. It is used mainly as an ingredient in denture-cleanser tablets to enhance dissolution. The toxicity of oxoborate is considered to be similar to that of the monohydrate (LD_{50} , oral, rat: 890–1300 $\mu\text{g/kg}$). However, no studies could be conducted due to the spontaneous decomposition of the product in the presence of water (qv). Anhydrous sodium perborate is irritating to eyes, skin, and mucous membranes.

This product has been assigned UN No. 3247 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. It is made commercially by Degussa (Germany), and sold under the trade name Oxoborate. The German price was DM 5.60/kg, the U.K. price £1.90/kg.

4. Group 14 (IVB) Peroxides

4.1. Peroxocarbonates. Peroxocarbonates contain the C–O–O–group and should be distinguished from the carbonate peroxohydrates. Although no crystal structures have been determined, the nature of the peroxocarbonates has been deduced from vibrational spectra (51). These compounds can be prepared by three general methods: reaction of carbon dioxide and a solution of the metal hydroxide in hydrogen peroxide, anodic oxidation of normal carbonates at low temperatures, and oxidation of aqueous solutions of carbonates with elemental fluorine. Only the peroxocarbonates of the alkali metals are known. Some are peroxomonocarbonates, containing the CO_4^{2-} anion; others are peroxodicarbonates, containing the $\text{C}_2\text{O}_6^{2-}$ anion. Mixed alkali metal hydrogen salts are also known. Those salts that have been reasonably well characterized include $\text{Li}_2(\text{CO}_4) \cdot \text{H}_2\text{O}$, $\text{Na}_2(\text{C}_2\text{O}_6) \cdot n\text{H}_2\text{O}$, $\text{K}_2(\text{C}_2\text{O}_6)$, $\text{Rb}_2(\text{C}_2\text{O}_6)$, $\text{Cs}_2(\text{C}_2\text{O}_6)$, $\text{NaHCO}_4 \cdot \text{H}_2\text{O}$, KHCO_4 , and RbHCO_4 . These compounds have no commercial importance.

4.2. Peroxosilicates. No solid peroxosilicates are known. There is some indirect evidence based on catalytic studies for the existence of peroxosilicates in

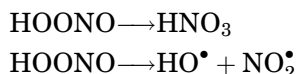
solution (52,53), but nmr spectra of aqueous solutions of silicates mixed with hydrogen peroxide give no evidence for peroxo species (54). A peroxohydrate of sodium silicate, $\text{Na}_3\text{SiO}_3 \cdot 3\text{H}_2\text{O}_2$, is well established (55–57) but has found no application.

4.3. Peroxotin Compounds. Older literature (58) records some tin peroxides or peroxohydrates, but these claims have not been substantiated. In contrast, organometallic peroxotin compounds are well established (59).

5. Group 15 (VB) Peroxides

5.1. Peroxonitrous Acid and Its Salts. Peroxonitrous acid [14691-52-2], HOONO , is an isomer of nitric acid, HNO_3 , to which it rapidly converts. The half-life of peroxonitrous acid at 0°C is 10s; at 27°C , 0.23 s (60,61). It has been known since 1904 (62) that the yellow solution made by mixing nitrous acid and hydrogen peroxide at low temperature contains a stronger oxidant than either ingredient alone, but the chemistry involved was not put on a sound basis until 1994 (63). Additional preparatory methods are also available.

Peroxonitrous acid can decompose by two pathways: isomerization to nitric acid, and dissociation into the hydroxyl radical and nitrogen dioxide.



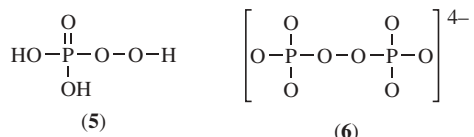
The hydroxyl radical is responsible for some of the oxidation products of organic compounds by peroxonitrous acid.

The peroxonitrite ion, OONO_2^- , an isomer of the nitrate ion, NO_3^- , is fairly stable under certain conditions. It can be made by rapidly neutralizing cold peroxonitrous acid. It can also be made by irradiating sodium nitrate crystals with uv light, X rays, Y rays, neutrons, or electrons. The irradiated crystals are yellow, and in a closed bottle can retain the peroxonitrite for months. When the crystals are dissolved in water at pH 12 that contains a chelating agent to sequester metal impurities, a yellow, fairly stable solution of peroxonitrite results. Acidification of this solution generates the free peroxyacid, which then decomposes with the liberation of hydroxyl radicals. This system has been suggested as a convenient source of aqueous hydroxyl radicals. Peroxonitrite is believed to be present in the crystals of nitric acid trihydrate that form in the stratosphere and in Martian soil (EXTRATERRESTRIAL MATERIALS). Peroxonitrous acid may be present in mammalian blood and other biochemical systems. However, peroxonitric acid, HNO_4 , is not known. Before the chemistry of peroxonitrous acid was understood, these two acids were sometimes confused.

5.2. Peroxophosphoric Acids and Their Salts. The peroxophosphoric acids are structurally similar to the peroxosulfuric acids, and behave similarly. They are hydrolyzed more rapidly, but the oxidation reactions of their anions are kinetically inhibited.

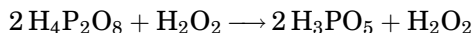
In its usual impure form (H_3PO_4 is the main contaminant), peroxomonophosphoric acid [13598-52-2] (5), is a viscous, colorless liquid. The three ionization

constants for peroxomonophosphoric acid are $pK_1=1.1$, $pK_2=5.5$, and pK_3 (peroxide proton) $=12.8$ (64). Oxidations comparable to those of peroxomonosulfuric acid H_2SO_5 occur in acid solutions of approx. pH 2, but at higher pH values, H_3PO_5 becomes less reactive as an oxidant and more unstable with respect to decomposition (64). The structure of H_3PO_5 (5) is similar to that of H_2SO_5 .

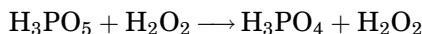


Peroxomonophosphoric acid can be prepared by the hydrolysis of peroxodiphosphates in aqueous acid and by the reaction of hydrogen peroxide with phosphorus pentoxide (65). It is not produced or used commercially, and the salts that have been prepared are unstable and impure. Pure peroxodiphosphoric acid [13825-81-5], $H_4P_2O_8$, can be obtained by anodic oxidation of phosphoric acid. As indicated by ir and Raman spectral data, the $P_2O_8^{4-}$ anion (6) consists of two anionic PO_4 tetrahedrons joined by an $-O-O-$ bond (66).

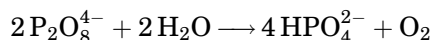
There are four ionizable hydrogen atoms on the corresponding peroxodiphosphoric acid, for which $pK_1=-0.3$, $pK_2=0.5$, $pK_3=5.2$, and $pK_4=7.7$ (67). The rates of hydrolysis of the peroxodiphosphate ion are dependent on both pH and temperature; For instance, as the hydrogen ion concentration increases, the rate increases (68). Peroxodiphosphoric acid hydrolyzes to peroxomonophosphoric acid according to the following equation:



This reaction takes place approximately 50 times more rapidly than the one in which peroxomonophosphoric acid hydrolyzes to hydrogen peroxide:



The rates of hydrolysis for the peroxophosphoric acids are more rapid than the corresponding reactions of the peroxosulfuric acids. The peroxodiphosphate ion is extremely resistant to decomposition by oxidation of water:



However, the peroxomonophosphate ion decomposes relatively rapidly in aqueous solution. A mixture of peroxodiphosphoric and peroxomonophosphoric acids can be produced by treating a cold phosphoric acid solution with elemental fluorine (qv) (69). Peroxodiphosphoric acid is not produced commercially. Ammonium, lithium, sodium, potassium, rubidium, cesium, barium, zinc, lead, and silver salts have all been reported. The crystal structures of the ammonium, lithium, sodium, and potassium compounds, which crystallize with varying numbers of water molecules, have been determined (70).

Tetrapotassium peroxodiphosphate [15593-49-9], $K_4P_2O_8$, is a colorless, crystalline solid, soluble in water to 42.2 wt% at 0°C and 51.2 wt% at 40°C (71). The pH of a 2 wt% aqueous solution is approx. 9.6. It does not melt on heating but decomposes exothermally at 387°C. $\Delta H = 229.6$ kJ/mol (-123.8 kcal/mol). It loses oxygen and forms potassium pyrophosphate. Tetrapotassium peroxodiphosphate is stable in alkaline solutions but hydrolyzes to the peroxomonophosphate in strongly acidic solutions. It is a strong oxidizing agent with an oxidation potential of 2.07 V; however, it is kinetically inhibited and does not readily oxidize many organic materials.

Tetrapotassium peroxodiphosphate is produced by electrolysis of a solution containing dipotassium phosphate and potassium fluoride (72). The electrolytic technique is analogous to that used in the manufacture of peroxodisulfates (73,74). Alkalinity favors the formation of $P_2O_8^{4-}$ anion, whereas the PO_5^{3-} anion is produced in larger yields in acidic solution. It is therefore possible to obtain an 80% yield of $K_4P_2O_8$ by choosing the proper conditions. The tetrapotassium peroxodiphosphate can be crystallized from solution by evaporation of water. The crystals can be separated from the slurry and dried. The material is noncorrosive and cannot be catalytically decomposed by iron ions.

Tetrapotassium peroxodiphosphate has been investigated as desizing agent (75,76) and ingredient in toothpaste as an anticalculus agent and a bactericide (77). However, until today the peroxophosphates have no commercial use mainly because of their higher costs compared to the peroxosulfate salts.

5.3. Arsenic Peroxides. Arsenic peroxides have not been isolated; however, elemental arsenic, and a great variety of arsenic compounds have been found to be effective catalysts in the epoxidation of olefins by aqueous hydrogen peroxide. Transient peroxyarsenic compounds are believed to be involved in these systems. Compounds that act as effective epoxidation catalysts include arsenic trioxide, arsenic pentoxide, arsenous acid, arsenic acid, arsenic trichloride, arsenic oxychloride, triphenyl arsine, phenylarsonic acid, and the arsenates of sodium, ammonium, and bismuth (78). To avoid having to dispose of the toxic residues of these reactions, the arsenic can be immobilized on a polystyrene resin (79).

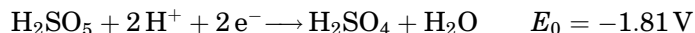
6. Group 16 (VIB) Peroxides

6.1. Peroxosulfuric Acids and Their Salts. Two kinds of peroxosulfuric acid are known: peroxomonosulfuric and peroxodisulfuric acids. Neither is available commercially in the pure state. Both had been important intermediates in the electrochemical production of H_2O_2 (see HYDROGEN PEROXIDE). Peroxodisulfuric acid $H_2S_2O_8$ is not of commercial importance. However, their salts, the peroxodisulfates or also called persulfates, are widely used as oxidizing agents and radical initiators.

Peroxomonosulfuric acid H_2SO_5 in the form of Caro's acid has found industrial applications in the mining industry and pulp bleaching. The term *Caro's acid* is commonly used as a synonym for peroxomonosulfuric acid, but is better reserved for the equilibrium mixture with sulfuric acid and hydrogen peroxide.

From the salts of peroxomonosulfuric acid only the potassium salt in form of the triple salt $2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (80) has gained industrial applications.

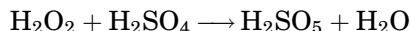
6.2. Peroxomonosulfuric Acid. Peroxomonosulfuric acid [7722-86-3], H_2SO_5 , when pure, forms colorless crystals that melt with decomposition at 45°C . One of its protons is strong, as in sulfuric acid, but its other proton, which is on the peroxide group, is weak ($\text{p}K_{\text{a}}=9.4$). Peroxomonosulfuric acid is a strong oxidizing agent:



The correct value for the oxidation potential of the $\text{HSO}_5\text{--HSO}_4$ couple was established by a thermodynamic method in 1979 (81) and confirmed in 1982 (82). Previously published values have been found inaccurate.

Peroxomonosulfuric acid oxidizes cyanide to cyanate, chloride to chlorine, and sulfide to sulfate (83). It readily oxidizes carboxylic acids, alkenes, ketones, aromatic aldehydes, phenols, and hydroquinone (84). Under neutral and alkaline conditions peroxomonosulfate oxidizes H_2O_2 yielding oxygen gas. Peroxomonosulfuric acid hydrolyzes rapidly in the presence of water to hydrogen peroxide and sulfuric acid. It is usually made and used in the form of Caro's acid. Peroxomonosulfuric acid exhibits significantly better anti-microbial properties than H_2O_2 and has good overall effectiveness against bacteria and viruses (85).

6.3. Caro's Acid. Caro's acid is named after Heinrich Caro (1834–1910), who first described its preparation and oxidizing properties in 1898. Herein Caro's acid is used to designate the equilibrium mixtures that result from mixing hydrogen peroxide and sulfuric acid. These liquids mix instantly, generating a considerable amount of heat. The equilibrium constant for this reaction is 0.1 (86).



The reaction is highly exothermic, requiring removal of the heat of reaction in order to avoid yield losses. There are two manufacturing technologies: the isothermal and the adiabatic process.

In the isothermal process, 70% H_2O_2 is mixed with 93–98% sulfuric acid under efficient heat removal, so that the temperature does not exceed $15\text{--}30^\circ\text{C}$. If stoichiometric quantities of reactants are used, the product contains 42% H_2SO_5 and 10% H_2O_2 . Either increasing the molar amounts of H_2SO_4 or when oleum is employed can significantly improve H_2SO_5 yields. Using a 2:1 ratio of technical sulfuric acid (96%) and 70% H_2O_2 and sufficient cooling yields of over 80% are obtained (87).

In the adiabatic process, the reactants are mixed rapidly in a small-volume, high-throughput static mixer without cooling (88). The hot product is used directly. A 250-mL reactor of this type can produce 8 tonnes/day of peroxomonosulfuric acid. Several patents describe various designs of equipment for adiabatic generation of Caro's acid (89–91). Typical yields for H_2SO_5 vary between 25 and 50% depending on the molar ratio of H_2SO_4 used (92). A process for the

production of stable aqueous sodium peroxomonosulfate solutions has also been described in the patent literature (93).

Peroxomonosulfate (H_2SO_5) can be determined in the presence of H_2O_2 and peroxodisulfate ($\text{H}_2\text{S}_2\text{O}_8$) by redox titration based on the reaction of H_2SO_5 with arsenic acid and subsequent titration of residual H_2O_2 with cerium (IV) sulfate. The peroxodisulfuric acid content is measured by the addition of arsenic acid and JCI, and titration of excess arsenic acid with cerium (IV) sulfate solution (94).

Because of novel and cost-effective on-site generation technologies, Caro's acid is finding increasing application in hydrometallurgy, pulp bleaching, effluent treatment, and electronics. There are several applications of Caro's acid in hydrometallurgy. Caro's acid has been used in Australia as an oxidant in the acid leaching of uranium ores. It acts by oxidizing the iron present in the solution from Fe^{2+} to Fe^{3+} . This Fe^{3+} then oxidizes the uranium. Alternative oxidants that have been used include pyrolusite and chlorate ion. These are both undesirable because their effluents, containing Mn^{3+} or Cl_2 , contaminate water-courses. Another hydrometallurgical use of Caro's acid is for detoxifying residual cyanide in effluents from gold leaching (95–99). Advantages over catalyzed hydrogen peroxide are obtained in the treatment of ore pulp slurries where the total active oxygen consumption is significantly reduced because of the faster oxidation kinetics of H_2SO_5 . Another advantage is that it also destroys thiocyanate ion. This application has been commercialized at several gold mines in North America.

Caro's acid is effective in delignification and bleaching of wood pulp (qv) in (totally chlorine-free (TCF)) bleaching sequences, replacing chlorine and chlorine dioxide. When conditions are carefully controlled, the mechanical properties of the final paper are not impaired. These processes were developed in the 1980s and commercialized in the 1990s (100–106).

A proprietary form of Caro's acid is sold to the electronics industry under the trade name Nanostrip. Used for reclaiming defective silicon wafers, it is manufactured by Cyantech (United States), Micro-Image Technology (UK), and RASA Industries (Japan).

Caro's acid is highly corrosive and a powerful oxidant. Its acidic properties are similar to those of sulfuric acid of equivalent strength. A strong irritant, it is toxic and should always be handled accordingly. No specific toxicological data are available. Depending on the strength of the product, Caro's acid should be transported in accordance with the relevant regulations pertaining to the most appropriate sulfuric acid solution or to those of liquid oxidizers not otherwise specified (NOS).

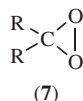
6.4. Peroxomonosulfates. A number of sodium, potassium, ammonium, cesium, lithium, and rubidium salts of peroxomonosulfuric acid have been described in the literature (80,107). Only the potassium salt in form of the triple salt $2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ [3722266-5], M_r 614.8, ρ 2.313 g/cm³, theoretical active oxygen content of 5.2 wt%, is of commercial importance. X-ray structure analyses have shown that it crystallizes in the monoclinic system contrary to earlier reports describing an orthorhombic structure (108,109). The formula should be written in the more general form as $\text{K}_5(\text{HSO}_5)_2(\text{HSO}_4)(\text{SO}_4)$.

The commercial product is a white, finely crystalline powder containing a minimum of 4.7% active oxygen and a bulk density of 1–1.2 kg/L. The solubility

at 20°C is 250 g/L. The pH of a 1% solution is ~2.3. The bactericidal properties of the triple salt are reviewed in Reference 110.

The triple salt is produced by partial neutralization of Caro's acid with aqueous KOH. The water introduced with the raw materials and formed during neutralization reaction is removed by vacuum at ~25°C at 1 kPa (111,112).

Its main use is in denture cleaners that function without mechanical assistance, in which discolorations are bleached and organic deposits are oxidized. In combination with sodium perborate monohydrate it generates effervescent oxygen. It is also used in dishwashing detergents, and hard surface cleaners because of its bleaching and antimicrobial properties (113–116). Furthermore, it is used in the metal-fabricating industry as a mild etchant and pickling agent (117,118) (see METAL SURFACE TREATMENTS), and in the electroplating (qv) industry for detoxifying cyanide solutions. In the latter application, it is mixed with hydrogen peroxide. In water treatment it has found application as a shock treatment agent for swimming-pool water. It quickly oxidizes malodorous chloramines to nitrogen and nitrate (119). Another application is its use in wastepaper recycling for the destruction of wet-strength resins (120). Finally, it is used in the textile industry for rendering wool (qv) shrink-resistant and nonfelting. In general, peroxomonosulfates have fewer uses in organic chemistry than peroxodisulfates. The triple salt is used for oxidizing ketones (qv) to dioxiranes (**7**) (121,122), which in turn are useful oxidants in organic chemistry. Acetone in water is oxidized by triple salt to dimethyldioxirane, which in turn oxidizes alkenes to epoxides, polycyclic aromatic hydrocarbons to oxides and diones, amines to nitro compounds, sulfides to sulfoxides, phosphines to phosphine oxides, and alkanes to alcohols or carbonyl compounds. A review on the use of peroxomonosulfate triple salt in organic synthesis is given in Reference 123.

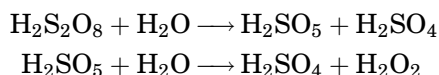


Potassium peroxomonosulfate triple salt is corrosive and irritating to skin, eyes, and mucous membranes (5). Acute toxicity (LC₅₀, oral/rat) is 1204 mg/kg (124). Dermal and inhalation toxicity is >2000 mg/kg and >5000 mg/kg, respectively (125,126). The triple salt is classified by the United Nations not as an oxidizer but as a corrosive, and thus must be transported under the UN No. 1759 for corrosive solids NOS. It should be kept away from combustible material.

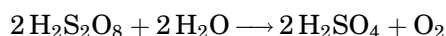
The triple salt is better known by the trademarks Caroat (Degussa), Oxone Monopersulfate Compound (Du Pont), and Curox (Laporte). It is also known as potassium caroate. It has been made on a commercial scale since the 1950s, and the world market in 1997 was ~ 15,000. It is made commercially by Peroxid-Chemie (Germany) and Du Pont (USA). In 1997, the United Kingdom price was £1.80/kg, the US price U.S. \$2.20/kg and the German price DM 4.50/kg.

6.5. Peroxodisulfuric Acid. Also called *persulfuric acid* and *Marshall's acid* (127), peroxodisulfuric acid [13445-49-3], H₂S₂O₈, when pure, forms colorless crystals that melt with decomposition at 65°C. The structure of the S₂O₈²⁻ ion has been established by X-ray analyses of the cesium and ammonium salts

as two anionic SO_4 tetrahedra joined by an O–O linkage (128). Peroxodisulfuric acid is a strong acid but not stable. It is seldom isolated but is synthesized and used in solution. Solutions of peroxodisulfuric acid are reasonably stable when cool but hydrolyze rapidly to hydrogen peroxide and sulfuric acid when heated in strongly acidic solutions (129–132). This hydrolysis proceeds stepwise and involves the intermediate peroxomonosulfuric acid:



A slower decomposition reaction also occurs:



6.6. Peroxodisulfates. The salts of peroxodisulfuric acid are commonly called persulfates, three of which are made on a commercial scale: ammonium peroxodisulfate [7727-54-0], $(\text{NH}_4)_2\text{S}_2\text{O}_8$; potassium peroxodisulfate [7727-21-1], $\text{K}_2\text{S}_2\text{O}_8$; and sodium peroxodisulfate [7775-27-1], $\text{Na}_2\text{S}_2\text{O}_8$. The peroxodisulfates are all colorless, crystalline solids, stable under dry conditions at ambient temperature but unstable above 60°C .

All the peroxodisulfates are made commercially by electrolytic processes (133). The traditional method was developed from the Degussa–Weissenstein process (11) for making hydrogen peroxide, in which a solution containing ammonium sulfate and sulfuric acid was electrolyzed between platinum electrodes. Ammonium peroxodisulfate was crystallized directly from the spent electrolyte, and the other salts were made from this by adding alkali metal hydroxides and volatilizing the ammonia. In the 1970s, an improved electrolytic process was developed (134), giving all three peroxodisulfate salts directly from the corresponding hydrogen sulfate salts; one multipurpose cell could thus produce whichever salt was required. Cells of the old design used diaphragms of asbestos that were troublesome to maintain and would no longer be approved for safety reasons. Cells of the new design operate continuously and do not use a diaphragm.

In addition to cost, several factors influence the choice of salt for a particular application. The ammonium salt is the most soluble in water, but for some applications, the presence of the ammonium ion may be undesirable. The sodium salt (559 g/L) has similar solubility as the ammonium salt (556 g/L) at ambient temperatures and above. The potassium salt is much less soluble (52 g/L).

The peroxodisulfate ion in aqueous solution is one of the strongest oxidizing agents known. The standard oxidation-reduction potential for the following reaction is 2.08 V (135,136). Reactions involving the peroxodisulfate ion are usually slow at about 20°C . The peroxodisulfate ion decomposes into free radicals, which are initiators for numerous polymerization reactions. These radicals act either thermally or by electron transfer with transition-metal ions or reducing agents (137).

Peroxodisulfate is determined by titration with excess of iron (II) sulfate solution and back titration with potassium permanganate (138).

The major use of the peroxodisulfate salts is as initiators (qv) for olefin polymerization in aqueous systems, particularly for the manufacture of polyacrylonitrile and its copolymers (Acrylonitrile polymers). These salts are used in the emulsion polymerization of vinyl chloride, styrene–butadiene, vinyl acetate, neoprene, and acrylic esters (ACRYLIC ESTER POLYMERS; STYRENE; VINYL POLYMERS) (139–141). Etching of printed circuit boards and removal of photoresists are also important applications (see ELECTRONIC MATERIALS; INTEGRATED CIRCUITS) (142). Desizing of woven textiles and finishing of furs are both long-established applications.

Another application in the textile industry is as a bleaching agent in denim finishing (143–146). Sodium persulfate–based formulations are also being sold for shock treatment of swimming-pool water (147,148). Alternatively to potassium peroxomonosulfate, triple salt peroxodisulfates can be employed in waste-paper recycling for the destruction of wet-strength resin (149). Other established applications include curing grouts for soil stabilization (qv), initiating polymerization of graphite filament coatings, for thinning of starch (150), and as the active ingredient in hair bleaching formulations (151,152).

Peroxodisulfates can be employed as oxidants in organic chemistry (153, 154). Heat, light, gamma rays, or transition-metal ions initiate these reaction. The primary oxidizing species is usually the sulfate ion radical $\text{SO}_4^{\cdot -}$, but the peroxodisulfate anion ($\text{S}_2\text{O}_8^{2-}$) and peroxomonosulfuric acid may also be involved. The metal ions commonly used in association with peroxodisulfates are Ag^+ , Cu^+ , Fe^{2+} , Ce^{3+} , Mn^{3+} , and Ti^{3+} . Most organic compounds can be oxidized by these systems, and a great variety of products can be obtained, some in good yield. Phenols yield *p*-hydroquinones, aromatic amines yield *o*-aminophenols, and alkyl aromatic hydrocarbons yield aromatic aldehydes. Many other examples are described in the literature (153,154).

The three peroxodisulfates exhibit moderate toxicity and are irritating to skin, eyes, and mucous membranes. Skin sensitization, irritative and contact dermatitis has also reported. Table 2 (46,155–157) summarizes the available acute toxicity data.

The LD_{50} value for sodium peroxodisulfate using iv administration in rabbits is 178 mg/kg. The U.K. maximum occupational exposure level in air for each of the three salts is 1 mg/kg (158). An 8-h TWA of 0.1 mg/m^3 has been established by ACGIH (159). Persulfate salts should be handled only when wearing suitable protective clothing. The peroxodisulfates assist combustion by releasing oxygen, and must be stored away from combustible materials. Contamination by rust or traces of many metals can cause catalytic decomposition. The peroxodisulfates should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances.

The peroxodisulfates are made commercially by Akkim (Turkey), Degussa (Germany), FMC (USA), Mitsubishi (Japan), Peroxid-Chemie (Germany), ERB Engineering (India), Sangen (Taiwan), and Tokai Denka (Japan). In 1997 the Germany of the sodium salt was DM 3.40/kg, and the ammonium salt DM 2.70/kg. U.S. prices in 1998 are published at \$2.10 for the sodium salt, \$1.85 for the ammonium salt, and \$2.25 for the potassium salt.

7. Other Metal Peroxides

7.1. Transition-Metal Peroxides. A 1964 review paid tribute to the significance of transition-metal peroxide and peroxide chemistry for the catalysis of oxidations and the storage and use of oxygen in biological systems (160). Since that time, many more inorganic peroxo compounds have been isolated and several more transition-metal-catalyzed organic reactions have been commercialized (161–166). However, transition-metal peroxides, as isolated species, have no place in chemical technology because they are too dangerously explosive.

Transition metals can be divided into two groups according to the characteristics of their peroxides. The first group comprises those metals that, in their highest oxidation states, have no *d* electrons; examples are Ti^{4+} and W^{6+} . These metals form peroxides from hydrogen peroxide, the colors of which result from charge transfer between the peroxide group and the metal ion. The peroxo species act as electrophiles.

The other group of transition metals comprises those metals that retain *d* electrons in their normal valence states; examples are Co^{3+} and Pt^{2+} . These metals form peroxides from dioxygen or from hydrogen peroxide. Their colors result from *d*–*d* transitions. These peroxo species act as nucleophiles.

Transition-metal-catalyzed oxidations may or may not proceed via peroxo complexes. Twelve important industrial organic oxidation processes catalyzed by transition metals, many of which probably involve peroxo intermediates, have been tabulated (160). Even when peroxo intermediates can be isolated from such systems, it does not necessarily follow that these are true intermediates in the main reaction.

7.2. Actinide Peroxides. Many peroxo compounds of thorium, protactinium, uranium, neptunium, plutonium, and americium are known (160,167). The crystal structures of a number of these have been determined. Perhaps the best known are uranium peroxide dihydrate [1344-60-1], $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, and, the tetrahydrate [15737-4-5], $\text{UO}_4 \cdot 4\text{H}_2\text{O}$, which are formed when hydrogen peroxide is added to an acid solution of a uranyl salt.

Uranium peroxide has found several applications in the nuclear energy industry. It provides a method for precipitating uranium from solution without introducing any extraneous cations or anions. It has been used in the extraction of uranium from its ores, where ammonia and hydrogen peroxide are used to precipitate uranium from leachate. It is also used in some fuel cycles (168). When the homogeneous aqueous nuclear reactor was being developed (169), there was a concern that uranium peroxide, formed from the autogenous hydrogen peroxide, might precipitate from solution. Under certain conditions this, might have happened, but the project was abandoned for other reasons (see NUCLEAR REACTORS).

8. Peroxohydrates

Peroxohydrates are crystalline adducts containing molecular hydrogen peroxide. These are commonly called *perhydrates*, but this term is better avoided because per historically implied the maximum oxidation state and hydrate implies the

presence of water, neither of which applies to peroxohydrates. They have also been called *hydroperoxidates* (170).

On dissolution in water, peroxohydrates liberate hydrogen peroxide into solution. Some peroxo salts also liberate hydrogen peroxide when dissolved in water, and before the introduction of X-ray crystallography, compounds within these classes were often confused with each other.

Peroxohydrates are usually made by simple crystallization from solutions of salts or other compounds in aqueous hydrogen peroxide. They are fairly stable under ambient conditions, but traces of transition metals catalyze the liberation of oxygen from the hydrogen peroxide. Early work on peroxohydrates has been reviewed (170).

8.1. Sodium Carbonate Peroxohydrate. Known commercially as sodium percarbonate, sodium carbonate peroxohydrate [15630-89-4], M_r 157.0, ρ 2.14 g/cm³ does not contain the C–O–O–C group and is not a peroxocarbonate. Crystallized sodium carbonate peroxohydrate is a white salt with an orthorhombic unit cell (171). Technical sodium percarbonate obtained by a crystallization process consists of coarse, compact grains with a spherulitic crystal form (172). The bulk density of commercial sodium percarbonate can range from 800 to 1200 g/L, depending on the synthesis process and conditions. The solubility in water is 131 g/L at 10°C, 154 g/L at 20°C, and 180 g/L at 30°C (173). The solubility of percarbonate is reduced in the presence of other salts such as Na₂CO₃, Na₂SO₄, and NaCl.

The active oxygen content of technical sodium carbonate peroxohydrate varies between 12.0 and 14.5 wt% (theoretical: 15.28 wt%) depending on the manufacturing process and stabilizing technology. When stored under cool and dry conditions, the rate of active oxygen loss is less than 0.3% (relative) per month (173). However, even in the presence of stabilizers, it is much more sensitive to higher temperatures and moisture than sodium peroxoborate. Uncoated sodium percarbonate loses 82–86% of the active oxygen within 10 days at a relative humidity of 96% and a temperature of 30°C (174), whereas sodium peroxoborate loses <2%. An aqueous solution of sodium carbonate peroxohydrate behaves like an alkaline solution of hydrogen peroxide. The pH of a 1 wt% solution is ~10.5.

The active oxygen content can be determined by titration with potassium permanganate solution in dilute sulfuric acid. The sodium content is obtained by titration with hydrochloric acid with methyl orange as indicator.

Sodium carbonate peroxohydrate was first prepared by in 1899 from hydrogen peroxide and soda ash. The product was isolated by precipitation with ethanol. It was not correctly identified as a hydrogen peroxide addition compound until 1909 when Riesenfeld and Reinhold elucidated its chemical structure (175). There are three basic production processes used for the industrial manufacturing of sodium percarbonate, yielding products with different properties with regard to bulk density, active oxygen content, and stability.

Crystallization Processes. The production of sodium carbonate peroxohydrate is mainly carried out by crystallization from aqueous solution. Sodium carbonate is reacted with hydrogen peroxide at 10–20°C, and crystallized in the presence of stabilizers, such as magnesium silicate, and salting-out agents, preferably sodium chloride. Crystallization aids such as polyphosphates or

polyacrylates are used (172,176–179). The product is obtained as coarse, mechanically stable crystals, which are centrifuged followed by drying, preferably in a fluidized-bed dryer with an air inlet temperature of 75–130°C. The mother liquor from the centrifuge can be further concentrated and mixed with industrial-grade sodium carbonate (sometimes after adding a magnesium salt), filtered to remove iron compounds, and fed back into the crystallizer (180–182). Processes that do not include a salting-out process with sodium chloride are usually less economic because of the lower space–time yield.

An electrolytic process for the production of alkali metal percarbonate solutions in an electrolytic cell consisting of a porous oxygen-diffusion cathode and an anode has been described. The H_2O_2 /alkali mol ratio is <4 . The cell voltage is 0.95 V (183).

Spraying Processes. Several spraying processes for sodium carbonate peroxohydrate are described in the patent literature. These processes avoid the need for filtration and centrifugation of the crystalline product. An aqueous solution or suspension of sodium carbonate and hydrogen peroxide is completely evaporated in a spray dryer (184–186). The product has a very low bulk density (~ 0.35 kg/L) (186). In a variation of this process, solutions of Na_2CO_3 , and H_2O_2 are continuously sprayed onto a bed of sodium carbonate peroxohydrate fluidized with hot air (187,188). The spraying and drying stages can alternatively be carried out in two stages (189). In a further process variation, solutions of sodium carbonate and hydrogen peroxide are sprayed through separate nozzles into a reaction chamber into which a hot mixture of air and carbon dioxide is passed at the same time (190). This process produces a rather porous sodium carbonate peroxohydrate.

A highly attrition resistant product with an active oxygen content of $>14\%$ and high bulk density (>1000 g/L) can be obtained in a continuous spray–granular process using a fluidized-bed reactor (191).

Dry Methods. In these processes, anhydrous or hydrated sodium carbonate (75–90 wt% Na_2CO_3) is reacted with a concentrated solution (50–80 wt%) of hydrogen peroxide, so that only a small amount of water must be removed. This can be achieved in a mixer (192) or fluidized-bed reactor (193) in which gaseous hydrogen peroxide can be used (194). Apart from the long reaction time, these dry processes have the disadvantage that no purification of the sodium carbonate takes place and therefore these sodium carbonate peroxohydrate products have only moderate storage properties. However, this problem can be solved by recrystallizing the sodium carbonate before use and by using sodium carbonate monohydrate (193). Also the use of phosphonic acids as additional stabilizers in the synthesis of sodium percarbonate has been described (195).

Other Methods and Properties. In general, sodium carbonate peroxohydrate is more sensitive to degradation in domestic detergent formulations as sodium peroxoborate hydrates, particular at elevated temperatures. A common detergent ingredient detrimental to the stability of the peroxohydrate is zeolite A, due to its high water content (up to 20%). Formulations based on zeolite P as builder show better compatibility with sodium percarbonate because of its lower moisture content.

A number of patents describe processes for stabilizing the peroxohydrate against decomposition. There are two ways to stabilize percarbonate. One is to

improve the stability of the product (core) during the reaction process by the addition of stabilizers. The second is to stabilize the product by a protective coating in order to prevent moisture and other incompatible materials get into direct contact with the percarbonate, causing enhanced decomposition. As stabilizers for the percarbonate core several compounds such as silicates (196,197), magnesium salts, phosphates, and phosphonic acid (195) have been suggested. A variety of coatings for percarbonate are described in the literature. Most of the coatings consist of inorganic substances such as borates (198,199), perborates (200), sodium silicate (174,201), sodium sulfate (202), and magnesium salts (203). Mitsubishi describes a technology based on a two-layer coating with sodium silicate and magnesium salt forming magnesium silicate on the surface of the percarbonate granules (204). Also organic coatings have been reported in the literature. Examples are chelants (205), fatty acids (206), and organic polymers (207,208).

Sodium percarbonate is used mainly as an alternative for sodium perborates as bleaching agent in laundry powders automatic dishwashing detergents and color-safe bleaches. A formulated product containing sodium carbonate peroxohydrate with a synthetic, lamellar silicate having ion-exchange properties is sold by Clariant (Germany) under the trade name SKS-9/PC. It is intended for incorporation in special washing and cleaning agents as well as for bleaching and disinfecting. Other applications for sodium percarbonate are for industrial textile bleaching, for tripe bleaching, and in denture cleaners. In North America sodium percarbonate is also used in toothpaste for improved cleaning and disinfection.

Small quantities of sodium carbonate peroxohydrate have been used as an oxidizing agent in synthetic organic chemistry (35). In nonaqueous systems it serves as a source of concentrated hydrogen peroxide and thus can be used to make peroxycarboxylic acids from carboxylic anhydrides, chlorides, or imidazolidines. The peroxohydrate does not need high solubility to react (209). A suspension of sodium carbonate peroxohydrate in tetrahydrofuran, or dichloromethane presaturated with water, can be used. These heterogeneous reactions can be accelerated by ultrasonic radiation (see ULTRASONICS) (210).

The LD₅₀ (rat, oral) of sodium carbonate peroxohydrate is 1034 mg/kg (211). The occupational exposure limit is 10 mg/m³ per 40-h week. The compound is a skin and eye irritant; inhalation of dust can cause irritation to the mucous membranes and the respiratory system. It should be handled by using eye protection, rubber gloves, and industrial footwear. It is an oxidizing agent that can be decomposed by water, direct sources of heat, and catalysts. Decomposition is accompanied by liberation of oxygen and heat, which can support combustion and cause pressure bursts in confined spaces. Decomposition in the presence of organic material can be rapid and highly exothermic. Bulk storage of sodium percarbonate peroxohydrate is critical due to its higher sensitivity to decomposition and caking compared to peroxoborates.

Sodium carbonate peroxohydrate had not been classified by DOT as hazardous substance, while sodium peroxocarbonate Na₂(C₂O₆) has been assigned to Class 5.1, oxidizing substances. Because of changes in testing procedures for oxidizing substances (47), all major suppliers have changed to classification for sodium carbonate peroxohydrate to Class 5.1, oxidizing substances.

Sodium carbonate peroxohydrate is made by Degussa (Germany), EKA Chemical (Sweden), Kemira (Sweden), Mitsubishi Gas Chemical (Japan), Oriental Chemical (Korea), Solvay Interlox (Germany, Italy, United Kingdom, United States), Tokai Denka (Japan), and Treibacher Chemische Werke (Austria). Trade names in use are OXYPER, FB Sodium Percarbonate (Solvay), ECOX-C (Kemira), CARBODOX (EKA) and Percarbonate Q30 (Degussa). World production in 1997 was about 100,000 t; the U.S. price was \$1.41/kg, the German price was DM 1.60/kg.

8.2. Other Peroxohydrates. Potassium, rubidium, and cesium carbonates all form peroxohydrates having the general formula $M_2CO_3 \cdot 3H_2O$. Crystal structures have not been established; Raman spectra (51) confirm the presence of molecular hydrogen peroxide in the crystal. These compounds are unstable and have no commercial application.

$(NH_4)_2CO_3 \cdot H_2O_2$, first reported in 1980 (51), is crystallized from a solution of ammonium hydrogen carbonate in aqueous hydrogen peroxide. The vibrational spectrum confirms the presence of molecular hydrogen peroxide. The compound is unstable and unlikely to find commercial application.

Urea peroxohydrate [12443-6], $CO(NH_2)_2 \cdot H_2O_2$, M_r 94.1, ρ 1.4 g/cm³ is a white crystalline substance that melts with decomposition at 80–90°C. The solubility in water is 510 g/L at 20°C. The solution decomposes above 55°C. Urea peroxohydrate also exhibits good solubility in organic solvents such as methanol (260 g/L), ethanol (120 g/L), glycerol (440 g/L), and various glycols. The bulk density is ~600 g/L. The hydrogen peroxide content of the commercial product is ≥ 35 wt%.

Urea peroxohydrate was first synthesized by Tanatar in 1908, mixing 30% H_2O_2 with an aqueous solution of urea. After concentrating the reaction mixture the product was precipitated by cooling and separated by filtration.

The modern industrial process is based on the same principal. Powdered urea is dissolved in 35% H_2O_2 in the presence of stabilizers, and the product is crystallized by cooling and concentration (212). The precipitated solid material is separated from the mother liquor and dried at 30–40°C. The mother liquor is further concentrated under vacuum and recycled. Alternatively, hydrogen peroxide can be sprayed onto urea in a fluidized bed. Excess moisture is removed by drying under vacuum at 30–40°C (213).

Urea peroxohydrate tends to decompose at elevated temperatures. The shelflife of the product can be improved by adding stabilizers such as NaH_2PO_4 , $Na_2H_2P_2O_7$, or $ZnSO_4$ (214).

The product is supplied commercially in 25-kg packaging sizes as powder or as tablets. Suitable packaging materials are polyethylene bags or polyethylene lined containers.

Urea peroxohydrate is mainly used in the cosmetics and pharmaceutical industry as a disinfecting and bleaching agent. It has been employed as the active ingredient in toothwhiteners and dentifrice formulations (215–218), which are sold in the United States as over-the-counter drugs. It is used as a topical disinfectant and mouthwashes, as earwax remover and as a hairdresser's bleach. In the 1990s the compound has been studied as a laboratory oxidant in organic chemistry (219,220).

Urea peroxohydrate is an irritant to skin, eyes, and mucous membranes (5). LD₅₀ (rat) is 1270 mg/kg. The U.S. Food and Drug Administration approves it as an over-the-counter drug. It is slightly hygroscopic and sensitive to decomposition by catalytic materials such as heavy metals and their salts; it is also a flammable solid with oxidizing properties. Mixtures with combustible materials are easily ignited by friction or impact and burn vigorously. It has been assigned UN No. 1511 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances.

Urea peroxohydrate is made commercially by Peroxid Chemie (Germany) and Filofarma/Qwarz (Poland). It is known commercially as urea peroxide, hydrogen peroxide carbamide, Exterol, Hydroperit, Hydroperit, Hyperol, Oritzon, Percarbamid, Percarbamide, Perhydrit, Perhydrol-Urea, Thenardol, and UHP. In 1997 the U.K. price was £7–8/kg, the German price was DM 16/kg, and the U.S. price was \$12/kg. World production in 1997 was several hundred metric tons.

A related compound, the peroxohydrate of melamine, C₃H₆N₆, was made by Peroxid-Chemie but discontinued in the 1980s. In addition, a diperoxohydrate of the organic base DABCO is recognized and has been used as an oxidant in organic chemistry, but such a system has been known to explode (221).

Sodium pyrophosphate peroxohydrate, Na₄P₂O₇ · 2H₂O₂, was made commercially by FMC in the 1960s but was discontinued. It is less stable than sodium peroxoborate and sodium carbonate peroxohydrate in the solid state, but more stable than these in solution are. Many other phosphate peroxohydrates of the Group I and Group II metals are known but have found no uses.

Sodium sulfate peroxohydrate hydrate [29381-14-4], 2Na₂SO₄ · H₂O₂ · 2H₂O, had been studied as a possible ingredient for domestic detergents because it conveniently combines two common detergent ingredients. A related compound containing sodium chloride, 4Na₂SO₄ · 2H₂O₂ · NaCl, is more stable but the chloride ion is undesirable in detergents. Neither of these has been commercialized.

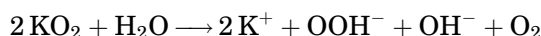
9. Peroxopolymetallates

Polyoxometallates derived from both isopoly acids and heteropoly acids, are important homogeneous oxidation catalysts (222,223). The metals involved are vanadium, niobium, tantalum, molybdenum, and tungsten. The reactions involved are the oxidation of a wide range of organic compounds by hydrogen peroxide or organic hydroperoxide. The tungsten systems, first studied in the 1980s by Venturello (224) and Ishii (225), have come to be known as the Venturello–Ishii systems (226). Crystalline peroxometallates have been isolated from some of these systems. A typical example is tris[tetra-*n*-hexylammonium] peroxophosphotungstate, [N(C₆H₁₃)₄][PO₄[W(O)(O₂)₂]₄]. Whether such peroxopolymetallates are in fact intermediates in the reactions from which they have been isolated is a matter for research in each case. Solutions of peroxometallates, made by acidifying molybdate and tungstate solutions in the presence of hydrogen peroxide, have been studied by ir and Raman spectroscopy, and a large number of peroxo species have been detected (227,228).

10. Superoxides

The superoxides are ionic solids containing the superoxide O_2^- anion. A comprehensive review of the superoxides was published in 1963 (229); they are also described in Reference 1. Superoxides of all the alkali metals have been prepared. Alkaline-earth metals, cadmium, and zinc form superoxides, but these have been observed only in mixtures with the corresponding peroxides (230). The tendency to form superoxides in the alkali metal series increases with increasing size of the metal ion.

Metal superoxides are yellow-to-orange solids. They are strong oxidizing agents, reacting vigorously with most organic materials and reducing agents, and oxidize many metals to their highest oxidation states. One of the most prominent properties is the evolution of oxygen and hydroperoxide ion by reaction with water:



Sodium superoxide [12034-12-7], NaO_2 , is a yellow solid, thermochemically unstable at ambient conditions with respect to the following reaction:



This compound has been prepared in reasonably high purity by the reaction of oxygen with sodium peroxide at 490°C and 298 atm (231). No applications are known.

Potassium superoxide [12030-8-5], KO_2 , M_r 71.1, ρ 2.14 g/cm^3 , is a yellow solid that melts at $450\text{--}500^\circ\text{C}$ when pure. It is paramagnetic and has a magnetic moment of $1.9 \times 10^{-23}\text{ J/T}$. Its heat of formation is $\sim 285\text{ kJ/mol}$ (68 kcal/mol), and the specific heat is $\sim 79.5\text{ J/(mol}\cdot\text{K)}$. The oxygen-dissociation pressures of KO_2 at various temperatures are as follow (to convert kPa to mm Hg, multiply by 7.5) (232):

Temperature, $^\circ\text{C}$	198	279	461	539	589
O_2 pressure, kPa	4.0	14.8	43.1	58.8	73.3

Potassium superoxide, a strong oxidizing agent, is similar to the Group 1 metal peroxides. This superoxide reacts vigorously with water yielding oxygen as well as an alkaline peroxide solution that is susceptible to further decomposition. The mechanism of the reaction with water is not well understood. Potassium superoxide reacts with moist CO_2 below 10°C , yielding oxygen and potassium peroxocarbonate. Above 50°C , the peroxocarbonate decomposes to additional oxygen, potassium carbonate, and potassium hydrogen carbonate.

Potassium superoxide is produced commercially by spraying molten potassium into an air stream, which may be enriched with oxygen. Excess air is used to dissipate the heat of reaction and to maintain the temperature at $\sim 300^\circ\text{C}$. It

can also be prepared in a highly pure state by oxidizing potassium metal that is dissolved in liquid ammonia at 250°C.

Mine Safety Appliances Co. (MSA) manufactures potassium superoxide in the United States for use in self-contained breathing equipment (see OXYGEN GENERATION SYSTEMS). In this equipment, the exhaled air is held within the device where it contacts a bed of KO_2 . Moisture in the exhaled air leads to complete decomposition of the KO_2 , and CO_2 is absorbed by the resulting KOH . This type of equipment is used for rescue and firefighting purposes as well as for space and undersea exploration. There are several published uses for potassium superoxide in organic chemistry, such as for oxidizing aromatic compounds (233, 234) and for initiating anionic polymerization (235).

On contact with skin and mucous membranes, potassium superoxide is converted to potassium hydroxide, which is corrosive and irritating. Protective clothing should be worn when handling it. The reaction with moisture is exothermic and may induce further decomposition with the production of oxygen. This product has been assigned UN No. 2466 and should be transported in accordance with international transport regulations pertaining to Class 5.1, oxidizing substances. MSA manufactures potassium superoxide for use in its own engineering systems. In 1994 the price in France was Fr. 300/kg (\$34/kg).

Rubidium superoxide [12137-25-6], RbO_2 , and cesium superoxide [1201861-0], CsO_2 , are formed by direct reaction of the elements, but are most readily prepared by oxidation of solutions of the metals in liquid ammonia. They are not produced commercially.

Calcium superoxide [12133-35-6], $\text{Ca}(\text{O}_2)_2$; strontium superoxide [12169-210], $\text{Sr}(\text{O}_2)_2$; and barium superoxide [55837-89-3], $\text{Ba}(\text{O}_2)_2$, have all been obtained in low yield and purity by treating the corresponding peroxides with hydrogen peroxide and heating (236). Heating the metal peroxides or their peroxohydrates often yields products containing some superoxides. These superoxides are not produced commercially.

11. Ozonides

The ozonides are characterized by the presence of the ozonide ion, O_3^- . They are generally produced by the reaction of the inorganic oxide and ozone. Two reviews of ozonide chemistry are available (1,237). Sodium ozonide [1205854-7], NaO_3 ; potassium ozonide [12030-89-6], KO_3 ; rubidium ozonide [12060-047], RbO_3 ; and cesium ozonide [12053-67-7], CsO_3 , have all been reported (1). Ammonium ozonide [12161-20-5], NH_4O_3 , and tetramethylammonium ozonide [78657-29-1], $\text{N}(\text{CH}_3)_4 \cdot \text{O}_3$, have been prepared at low temperatures (238).

The potassium salt is the best characterized. It is an orange-red paramagnetic solid having a magnetic moment of 1.6×10^{-23} J/T. It reacts with water, yielding oxygen gas and potassium hydroxide. It decomposes to the superoxide, KO_2 , on standing at room temperature. Potassium ozonide is prepared by ozonation of dry potassium hydroxide. It can be purified by extraction and recrystallization from liquid ammonia. Whereas the inorganic ozonides are of potential importance as solid-oxygen carriers in breathing apparatus, they are not produced commercially.

12. Economic Aspects

All the large-tonnage peroxo compounds, such as sodium peroxoborate tetrahydrate, sodium perborate monohydrate, and sodium carbonate peroxohydrate, are made predominately by hydrogen peroxide producers. The world demand for active oxygen provided by these products is fairly stable, rising with the gross national product in the industrial countries. Higher growth rates are obtained in regions with increasing living standard as South America, the Middle East, and certain Asian countries. Additional demand for perborate and percarbonate is also seen in the automatic-dishwashing market, where trends to less aggressive and environmentally more benign formulations favor the use of persalts as an alternative to chlorine-based products.

In 1997, the world capacity for sodium peroxoborate tetrahydrate was about 700,000 tonnes, about 25% of which as converted to the dehydrated compounds (monohydrate, oxoborate). At the then prevailing prices, the total value of this business was about \$450–500 million. The world capacity for sodium percarbonate (sodium carbonate peroxohydrate) was about 100,000 metric tonnes, valued at about U.S. \$100 million.

Because the peroxodisulfate salts are all made electrochemically, the electrical energy cost is a significant part of their manufacturing cost. The 1997 world capacity for peroxodisulfate salts was about 85,000 metric tonnes, valued in the U.S. at about \$180–230 million. The principal applications are in polymerization catalysis, and the market broadly tracks the polymer and plastics business. The Caro acid business is difficult to quantify because the product itself is not commercialized but made on site from purchased hydrogen peroxide. The 1997 capacity for the potassium peroxomonosulfate triple salt was estimated at 12,000 metric tonnes, valued at about U.S. \$20–25 million.

Of the binary peroxides made from hydrogen peroxide, calcium peroxide is the most important. World production is about 2000 tonnes/yr, which is dominated by the dough-conditioning market in the United States. The markets for the other binary peroxides, such as those of zinc, magnesium, and strontium, total only a few hundred metric tonnes. Sodium peroxide and potassium superoxide is made from the alkali metals, and their total markets are in the hundreds of tonnes.

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Table 1. Overview of Common Names, CAS Number,^a and IUPAC Names of Peroxoborates

Common Name	CAS no.	Historical formula	IUPAC name
sodium peroxoborate hexahydrate	[10486-00-7] ^a	NaBO ₃ ·H ₂ O ₂ ·3 H ₂ O	disodium-di-μ-peroxobis (dihydroxoborate)
sodium perborate tetrahydrate	[13517-20-9]	NaBO ₃ ·4 H ₂ O	hexahydrate
sodium peroxoborate tetrahydrate	[28962-65-4] ^a	NaBO ₃ ·H ₂ O ₂ ·2 H ₂ O	disodium-di-μ-peroxobis bis(dihydroxoborate)
sodium perborate trihydrate	[28108-09-0]	NaBO ₂ ·3 H ₂ O	tetrahydrate
sodium peroxoborate	[10332-33-9] ^a	NaBO ₂ ·H ₂ O ₂	disodium-di-μ-peroxobis bis(dihydroxoborate)
sodium perborate monohydrate	[15120-21-5]	NaBO ₃ ·H ₂ O	
anhydrous sodium peroxoborate	[7632-04-4] ^a	NaBO ₃	no well-defined compound sodium borate–boron oxygen radical

^aCAS No. listed in Material Safety Data Sheet.

Table 2. Acute Toxicity Data of Peroxodisulfate Salts

	Animal	Application	LD ₅₀ , mg/kg	Reference
(NH ₄) ₂ S ₂ O ₈	rat	oral	495–689	46, 155
K ₂ S ₂ O ₈	rat	oral	802	46
Na ₂ S ₂ O ₈	mouse	oral	226	46
	rat	oral	895–920	156,157