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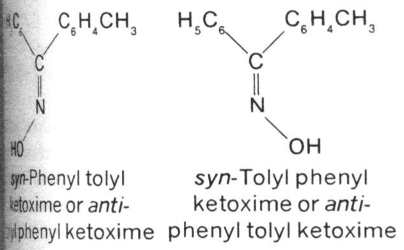
Oxime

One of a group of chemicals derived from aldehydes (RCH═NOH, aldoximes) or ketones (RR′C═NOH, ketoximes) used for isolation and identification of carbonyl compounds. In general, oximes are easily purified and have characteristic melting points. The properties of certain oximes have made them industrially important.

Oximes have received considerable attention because of their stereochemistry and their participation in the Beckmann rearrangement.

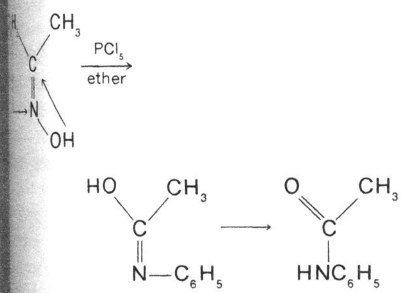
The discovery of geometrical isomers involving the carbon-nitrogen double bond demonstrated the effect of restricted rotation about such a bond in a manner analogous to that obtaining about a carbon-carbon double bond. However, relatively few pairs of geometric isomers of the oximes, which are conventionally termed syn and anti isomers analogous to the more familiar cis and trans terminology used in carbon-carbon systems, have been isolated. This suggests that interconversion of such isomers involves relatively little energy. Thus, *syn*-benzaldehyde oxime (H and OH in a cis arrangement with respect to the double bond) is converted to the anti (trans) form by ethereal hydrogen chloride solution; reversion to the syn form can be accomplished by irradiation of a benzene solution of the anti form. *See* MOLECULAR ISOMERISM.

In ketoximes the prefixes syn and anti refer to the relative positions of the hydroxyl group and the group adjacent to the prefix [notation (1).]



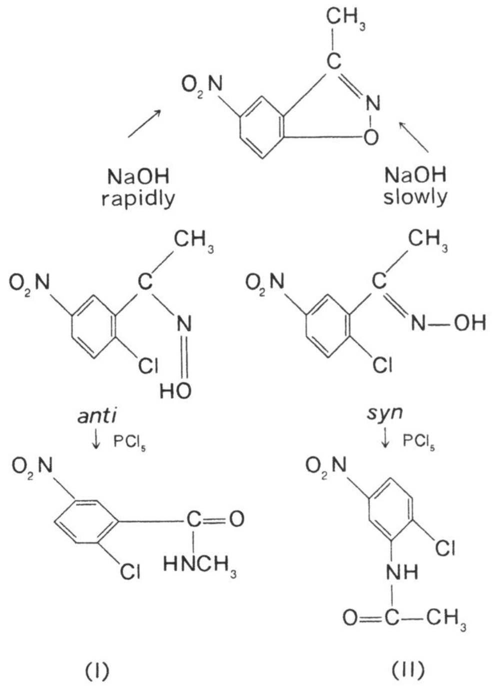
(1)

Ketoximes undergo the Beckmann rearrangement under the influence of acidic reagents. In this rearrangement, the substituent anti to the hydroxyl group changes positions with the hydroxyl group with the formation of the lactim form of an amide which immediately tautomerizes to the more stable lactam form. Thus, the oxime of acetophenone (methyl phenyl ketoxime) yields the lactim form of the stable acetanilide [reaction (2)].



(2)

J. Meisenheimer assigned the presently accepted configurations of the ketoximes largely on the basis of a study of ring-closure reactions involving



(3)

chloro-5-nitrophenyl ketoxime readily undergoes ring closure with elimination of hydrogen chloride under the influence of sodium hydroxide, whereas the other form gives the same product much more slowly. Therefore, it is concluded that the isomer which undergoes facile ring closure is the anti form and that the resistant isomer has the syn configuration. On rearrangement the anti and syn forms gave (I) and (II), respectively, thus providing a basis for the trans migration of the groups concerned and also providing a basis for the assignment of configuration from the nature of the products of the Beckmann rearrangement.

Cyclohexanone oxime rearranges to the lactam of 6-aminohexanoic acid (caprolactam), a precursor of a polyamide of the nylon type (nylon 6) shown in notation (4).

$$—[NH\,(CH_2)_5CO]_n— \qquad (4)$$

Aldoximes are dehydrated to nitriles by the action of acetic anhydride; oximes may be reduced to primary amines. The lower aliphatic aldoximes find use as antiskinning agents in paints. *See* ALDEHYDE; KETONE.

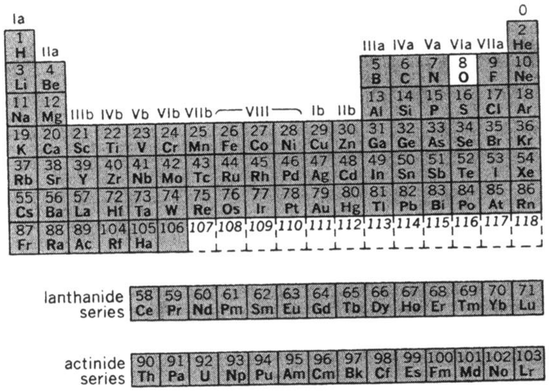
[LEALLYN B. CLAPP]

Oxygen

A gaseous chemical element, O, atomic number 8, and atomic weight 15.9994. Oxygen is of great interest because it is the essential element both in the respiration process in most living cells and in combustion processes. It is the most abundant element in the Earth's crust. About one-fifth (by volume) of the air is oxygen.

DESCRIPTION AND OCCURRENCE

Oxygen is separated from air by liquefaction and fractional distillation. The chief uses of oxygen in order of their importance are (1) smelting, refining, and fabrication of steel and other metals; (2) manu-



Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII	VIII	VIII	Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106	107	108	109	110	111	112	113	114	115	116	117	118

lanthanide series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinide series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

port and medicine; and (5) mining, production, and fabrication of stone and glass products.

Uncombined gaseous oxygen usually exists in the form of diatomic molecules, O_2, but oxygen also exists in a unique triatomic form, O_3, called ozone. *See* OZONE.

In 1774, Joseph Priestley, an English clergyman who later immigrated to the United States and settled in Northumberland, Pa., observed that mercuric oxide, on heating, yielded a gas that vigorously supported the combustion of a candle. Priestley found that the gas would support respiration and called the gas dephlogisticated air. The name oxygen, meaning acid-former, was given the gas by a group of French chemists in 1787 in recognition of the ability of some oxides, such as the oxides of sulfur, to form acids.

USES

Oxygen is widely used in a variety of applications. While the fraction of oxygen present in the atmosphere is sufficient for many purposes, higher concentrations are necessary to improve some processes.

Metallurgical uses. Oxygen is a component which is used in the metallurgical processes of smelting, refining, welding, cutting, and surface conditioning.

Smelting. Smelting of ore in the blast furnace involves the combustion of about 1 ton of oxygen for each ton of metal produced. When air is used, 3½ tons of nitrogen accompany each ton of oxygen and must be compressed, heated, and blown into the furnace. A large amount of heat is lost with the exhaust gases, which also carry powdered ore and coke away as dust and limit the capacity of the furnace. By removing some or all of the nitrogen, the furnace capacity can be increased, less expensive fuels can be used in place of some of the coke, and fuels can be used more efficiently.

Metal refining. In refining copper and in making steel from pig iron various impurities such as carbon, sulfur, and phosphorus must be removed from the metal by oxidation. If air is blown through the molten metal, as in the Bessemer converter, nitrogen is picked up, limiting the product quality. Nitrogen also carries away a great deal of the heat produced by the oxidation process. Better-quality steel and copper can be produced by injecting pure oxygen into the molten metal until the impurities are completely removed. Oxygen injection can be utilized in the open hearth or electric furnaces. However, newer steelmaking equipment has been oxygen. All the heat for the furnace operation is supplied by oxidation of carbon and other impurities. The technique is called the basic oxygen process. The most common form is known as the L-D process, named after the Austrian cities of Linz and Donawitz, where the procedure was first used in 1951.

Welding, cutting, and surface conditioning. The high-temperature flame of the oxyacetylene torch can be used in welding steel, although most welding is now done by the electric arc process.

In cutting, the point of the steel at which the cutting is to start is first heated by an oxygen-acetylene flame. A powerful jet of oxygen is then turned on. The oxygen burns some of the iron in the steel to iron oxide, and the heat of this combustion melts more iron; the molten iron is blown out of the kerf by the force of the jet. By feeding powdered iron into the oxygen stream this cutting process can be extended to alloys, such as stainless steel, which are not readily cut by oxygen alone and to completely noncombustible materials such as concrete.

Steel ingots normally have oxide inclusions and other defects at the outer surface. After preliminary rolling, the steel in slab or billet form has the surface skin removed to eliminate these defects. This can be most easily accomplished by scarfing. Streams of oxygen from many nozzles are played on all sides of the billet at once. The oxygen burns off the surface defects and some of the steel in a spectacular shower of sparks. The billet is then ready for further rolling. Oxygen scarfing, also known as skinning, became a standard practice in most steel mills.

Chemical syntheses. Several syntheses in the chemical industry involve oxygen. These processes are outlined.

Partial oxidation of hydrocarbons. When natural gas or fuel oil is burned, the heat of combustion first cracks the hydrocarbon molecules into fragments. These fragments usually encounter oxygen molecules within a few hundredths of a second and are oxidized to water and carbon dioxide. However, if the supply of oxygen is carefully controlled and the passage of material through the combustion zone is very rapid, it is possible to freeze the reaction at various stages of completion.

In this manner natural gas (mostly methane, CH_4) can be converted to acetylene (C_2H_2), ethylene (C_2H_4), or propylene (C_3H_6). Ethylene (C_2H_4), in turn, can be partially oxidized to ethylene oxide (CH_2CH_2O).

Syngas production. Reaction of carbon or hydrocarbons with oxygen and steam yields a mixture of carbon monoxide (CO) and hydrogen (H_2), that is syngas. By use of suitable catalysts, syngas can be recombined to form various organic compounds such as methanol (CH_3OH), octane (C_8H_{16}), and many others. In the presence of other catalysts carbon monoxide can combine with steam to form more hydrogen and carbon dioxide. After removal of the carbon dioxide, the hydrogen can be used for chemical reactions, such as the manufacture of ammonia (NH_3), hydrogenation of fats, and hydrocracking of petroleum.

Manufacture of pigments. Both titanium dioxide white and carbon black are useful primarily because of the characteristics of their small pa

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les govern the ability of the material to per- properly as a pigment, bulking agent, or ner when blended into other materials. For- on of titanium dioxide or carbon in a flame ess produces very fine, useful particles. Care- controlled addition of oxygen to such burner ations can improve yield and quality of the uct. *See* ORGANIC CHEMICAL SYNTHESIS.

uid fuel rockets. In rocket engines liquid en is used as an oxidizer either with kerosine uid hydrogen fuels. While fluorine could theo- ally provide somewhat improved performance rms of specific impulse, oxygen is very nearly od. is much cheaper and is easier to handle. lid-fueled rockets, based on hydrocarbon poly- that contain sufficient oxidizer to effect self- ustion, dominate the short-range military Liquid-fueled rockets are expected to remain nant in space work until the full development clear propulsion. The Saturn-Apollo launch le has a fully loaded weight of about 3000 tons hich more than 2000 tons are liquid oxygen. of the liquid oxygen consumed by the aero- industry has been used in the development proof testing of rocket engines mounted in test stands. The usage of oxygen in this test- s been in excess of 1000 tons per day.

logical applications. Oxygen is a fundamen- rt of many biological processes. A few are bed below.

ospace and diving. Oxygen is necessary for pport of animals of this planet. Whenever ns desire to live or work in environments low icient in oxygen, it is necessary to carry oxy- ing to supplement or substitute for the avail- atmosphere. High-altitude military aircraft ally provide oxygen for the aviators. Commer- ansports carry oxygen for emergency use in f failure of the cabin pressurizing system. nauts must of course carry their entire hing gas requirements with them, which be- one of the larger load requirements for any led mission. Divers in shallow water are able e air transmitted to them from the surface. ver, for deeper diving the special breathing frequently are carried to the ocean bottom in d diving bells.

dicine. In medical applications oxygen is ied to patients in amounts up to 15 times d. This is usually done to reduce the work f heart and lungs during the course of an ous disease, during or after major surgery, ing recovery from a heart attack.

ste treatment. Tests have shown that addition gen to waste treatment plants can assist the ical treatment process. Oxygen is sometimes d directly into rivers and streams that otherwise be overloaded with contamina- With the assistance of the extra oxygen, the bacteria are able to decompose the waste s.

e, clay, and glass industry. Oxygen has a n these industries as described below.

s manufacture and fabrication. The glass ry uses large quantities of oxygen in the acture and shaping of glass. Oxygen addi- ise the combustion temperature in the fur- ding up and improving control over the shaping, and flame-polishing rough edges.

Mining and quarrying. An oxygen-kerosine burner can be used to heat and shape some types of stone. Granite and similar rocks expand when heated rapidly by such a burner so that the surface cracks loose, or spalls. The hot combustion gases blow the fine chips of rocks away, presenting a fresh surface which is rapidly heated, continuing the process.

In this manner the extremely hard taconite iron ore can be pierced for blast holes more effectively than by conventional drilling methods. Granite for construction and decorative purposes can be quarried by special burners equipped to cut channels through the rock. Slabs of granite can be cut to desired dimension and given an even and pleasing surface using still other burner designs. A rock surface fouled with paint or tarry materials can easily be cleaned by this technique. Artists have used flame shaping to produce statuary.

Cement and kiln operations. In most kiln-type operations, such as manufacture of cement, roasting or sintering ore, and production of refractories, the essential reactions take place at rather high temperatures. When enough heat is provided at the high temperature to carry out the desired reaction, there is more than enough heat to raise the temperature of the fresh feed. Much heat is wasted at lower temperatures where it is not useful to the process. By using oxygen instead of air, the flame temperature is raised and much more heat is available for the high temperature reaction from a given amount of fuel. Extensive tests have shown that large increases in capacity and reductions in fuel consumption are possible. However, certain changes in equipment are needed to achieve all the potential benefits.

Occurrence. About 49.5% by weight of the Earth's crust, including the oceans and atmosphere, is oxygen. Most of this oxygen is combined in the form of silicates, oxides, and water. Water is composed of 88.81% oxygen by weight.

Oxygen also exists outside the atmosphere of the Earth, but since more than 98% of the matter in the visible universe (stars, nebulae, and interstellar space) is composed of hydrogen and helium, the cosmic concentration of oxygen is relatively low.

Dry air contains 20.946% oxygen by volume, and this concentration has been found to be the same at any level between the surface of the Earth and a height of 40 mi. The atoms in atmospheric oxygen consist of three isotopes in the following atomic proportions: 99.759%, oxygen-16; 0.037%, oxygen-17; and 0.204%, oxygen-18. The molecules of oxygen in the air, each of which has two atoms, consist of the statistically expected proportion of the possible combinations of these isotopes, the most abundant molecules being $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{16}O^{17}O$. The isotopic composition of the oxygen in water is slightly different from that in air and varies slightly in samples from different bodies of water (lakes, oceans, and seas).

Even though large quantities of oxygen from the air are continuously being used in respiration, combustion, and other oxidation processes, the concentration of oxygen in the atmosphere remains very nearly constant, chiefly because oxy-

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