OXALIC ACID

Oxalic acid [144-62-7], HOOC–COOH, or ethanedioic acid, mol wt 90.04, is the simplest dicarboxylic acid. It is soluble in water, and acts as a strong acid (1). This acid does not exist in anhydrous form in nature and is available commercially as a solid oxalic acid dihydrate [6153-56-6], $C_2H_2O_4 \cdot 2H_2O$, mol wt 126.07. The commercial product is packed in polyethylene-lined paper bags or flexible containers. Anhydrous oxalic acid can be efficiently prepared from the dihydrate by azeotropic distillation in a low boiling solvent that can form a water azeotrope, such as benzene and toluene (2).

Oxalic acid was synthesized for the first time in 1776 by Scheele through the oxidation of sugar with nitric acid. Then, Wöhler synthesized it by the hydrolysis of cyanogen [460-19-5] in 1824.

The potassium or calcium salt form of oxalic acid is distributed widely in the plant kingdom. Its name is derived from the Greek *oxys,* meaning sharp or acidic, referring to the acidity common in the foliage of certain plants (notably *Oxalis* and *Rumex*) from which it was first isolated. Other plants in which oxalic acid is found are spinach, rhubarb, etc. Oxalic acid is a product of metabolism of fungi or bacteria and also occurs in human and animal urine; the calcium salt is a principal constituent of kidney stones.

Oxalic acid is used in various industrial areas, such as textile manufacture and processing, metal surface treatments (qv), leather tanning, cobalt production, and separation and recovery of rare-earth elements. Substantial quantities of oxalic acid are also consumed in the production of agrochemicals, pharmaceuticals, and other chemical derivatives.

1. Physical Properties

The physical and thermochemical constants of anhydrous oxalic acid and oxalic acid dihydrate are summarized in Table 1.

1.1. Anhydrous Oxalic Acid

The anhydrous form of oxalic acid is odorless and colorless. It exists in two crystal forms, ie, the rhombic or α-form and the monoclinic or β-form (3). The rhombic crystal is thermodynamically stable at room temperature, but the monoclinic form is metastable or slightly stable. The main difference between the rhombic and monoclinic forms exists in the melting points which are 189.5 and 182°C, respectively (Table 1).

Anhydrous oxalic acid normally melts and simultaneously decomposes at 187°C. Sublimation starts at slightly below 100°C and proceeds rapidly at 125°C; partial decomposition takes place during sublimation at 157°C. Anhydrous oxalic acid is hygroscopic and thus absorbs moisture in the air to form the dihydrate.

Anhydrous oxalic acid is very soluble in polar solvents. The ionization constant K_1 is comparable with those of many mineral acids and is exceeded only by those of a few organic acids; K_2 is approximately the same as the ionization constant of benzoic acid (see Table 1).

Table 1. Physical and Thermochemical Properties of Oxalic Acid and its Dihydrate

Property	Value
Oxalic acid, anhydrous, $C_2H_2O_4$	
melting point, °C	
α	189.5
β	182
density d^{17}_4, g/mL	
α	1.900
β	1.895
refractive index, β, n^{20}_4	1.540
vapor pressure (solid, 57–107°C), kPa[a]	$\log_{10}P = -(4726.95/T) + 11.3478$
specific heat (solid, −200 to 50°C), J/g	$C_p{}^b = 1.084 + 0.0318\,t$
heat of combustion, ΔE_c (at 25°C), kJ/mol[c]	−245.61
standard heat of formation, ΔH_f (at 25°C), kJ/mol[c]	−826.78
standard free energy of formation, ΔG_f (at 25°C), kJ/mol[c]	−697.91
heat of solution (in water), kJ/mol[c]	−9.58
heat of sublimation, kJ/mol[c]	90.58
heat of decomposition, kJ/mol[c]	826.78
specific entropy, S (at 25°C), J/(mol·K)[c]	120.08
logarithm of equilibrium constant, $\log_{10}K_f$	122.28
thermal conductivity (at 0°C), W/(m·K)[d]	0.9
ionization constant	
K_1	6.5×10^{-2}
K_2	6.0×10^{-5}
coefficient of expansion (at 25°C), nL/(g·K)	178.4
Oxalic acid dihydrate, $C_2H_2O_4 \cdot 2H_2O$	
mp, °C	101.5
density d^{20}_4, g/mL	1.653
refractive index, n^{20}_4	1.475
standard heat of formation, ΔH_f (at 18°C), kJ/mol[c]	−1422
heat of solution (in water), kJ/mol[c]	−35.5
pH (0.1 M soln)	1.3

[a] To convert $\log_{10}P_{kPa}$ to $\log_{10}P_{mmHg}$, add 0.875097 to the constant, $T = K$.
[b] To convert C_p, J/g, to C_p, cal/g, divide both terms of the equation by 4.184.
[c] To convert J to cal, divide by 4.184.
[d] To convert $W/(m·K)$ to $(Btu·in.)/(h·ft^2·°F($, divide by 0.1441.

1.2. Oxalic Acid Dihydrate

Oxalic acid dihydrate is made up of odorless, colorless, monoclinic prisms or granules which contain 71.42 wt % anhydrous oxalic acid and 28.58 wt % water.

When the dihydrate is carefully heated to 100°C it loses its water to give anhydrous oxalic acid. On the other hand, when the dihydrate is heated rapidly or in a sealed tube, it melts at 101.5°C.

The dihydrate is soluble in water. The specific gravities of aqueous oxalic acid solutions are summarized in Table 2. The solubility of the dihydrate in water increases with temperature. Approximate solubility values (S) are given by the following formulas, where $S = g(COOH)_2/100$ g soln and $t = $ °C.

$$0 - 60°C, \quad S = 3.42 + 0.168\,t + 0.0048\,t^2$$

$$50 - 90°C, \quad S = 0.33\,t + 0.003\,t^2$$

Table 2. Specific Gravities of Various Aqueous Solutions of Oxalic Acid Dihydrate

Weight of dihydrate in soln, g/L[a]	Dihydrate, wt %	Sp gr	Baumé,[b] degrees	Twaddell,[c] degrees
10.04	1	1.0035	0.5	0.70
20.14	2	1.0070	1.0	1.40
30.32	3	1.0105	1.5	2.10
40.56	4	1.0140	2.0	2.80
50.88	5	1.0175	2.5	3.50
61.26	6	1.0210	3.0	4.20
71.72	7	1.0245	3.5	4.90
82.24	8	1.0280	4.0	5.60
92.84	9	1.0315	4.4	6.30
103.5	10	1.0350	4.9	7.00
114.2	11	1.0385	5.4	7.70
125.0	12	1.0420	5.8	8.40
135.9	13	1.0455	6.3	9.10

[a] To convert g/L to lb/gal, divide by 119.8. To convert g/L to lb/ft^3, divide by 16.02.
[b] Sp gp $= 145 \div (145 - n)$, where n is Baumé, degrees.
[c] Sp gp $= 1.000 + 0.005\,n$, where n is Twaddell, degrees.

The dihydrate is very soluble in polar solvents, such as methanol, ethanol, acetone, dioxane, and tetrahydrofuran, but insoluble in benzene, chloroform, and petroleum ether. Solubility of the dihydrate in diethyl ether (1.47 g/100 g solvent) is different from that of the anhydrous form (23.6 g/100 g solvent).

2. Reactions

The reactions of oxalic acid, including the formation of normal and acid salts and esters, are typical of the dicarboxylic acids class. Oxalic acid, however, does not form an anhydride.

On rapid heating, oxalic acid decomposes to formic acid, carbon monoxide, carbon dioxide, and water (qv). When it is heated in 96 wt % glycerol solution at 88–121°C, the presence of formic acid in the decomposed product tends to accelerate the decomposition reaction. Formic acid is thus decomposed further to carbon dioxide and water (4). In aqueous solution, it is decomposed by uv, x-ray, or γ-radiation with the liberation of carbon dioxide. Photodecomposition also occurs in the presence of uranyl salts.

Oxalic acid is a mild reducing agent, and is oxidized by potassium permanganate in acid solution to give carbon dioxide and water. This autocatalytic reaction is of great importance in volumetric analysis. Oxalic acid is catalytically reduced by hydrogen in the presence of ruthenium catalyst to ethylene glycol (5), and electronically reduced to glyoxylic acid.

Oxalic acid reacts with various metals to form metal salts, which are quite important as the derivatives of oxalic acid. It also reacts easily with alcohols to give esters. Crystalline dimethyl oxalate is, for example, produced by the reaction of oxalic acid dihydrate and methanol under reflux for a few hours. When oxalic acid is treated with phosphorus pentachloride, oxalyl chloride, ClCOCOCl, is formed (6).

3. Manufacture

Many industrial processes have been employed for the manufacture of oxalic acid since it was first synthesized. The following processes are in use worldwide: oxidation of carbohydrates, the ethylene glycol process, the propylene process, the dialkyl oxalate process, and the sodium formate process.

Nitric acid oxidation is used where carbohydrates, ethylene glycol, and propylene are the starting materials. The dialkyl oxalate process is the newest, where dialkyl oxalate is synthesized from carbon monoxide and alcohol, then hydrolyzed to oxalic acid. This process has been developed by UBE Industries in Japan as a CO coupling technology in the course of exploring C-1 chemistry.
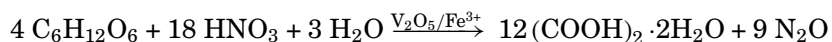
The sodium formate process is comprised of six steps: (*1*) the manufacture of sodium formate from carbon monoxide and sodium hydroxide, (*2*) manufacture of sodium oxalate by thermal dehydrogenation of sodium formate at 360°C, (*3*) manufacture of calcium oxalate (slurry), (*4*) recovery of sodium hydroxide, (*5*) decomposition of calcium oxalate where gypsum is produced as a by-product, and (*6*) purification of crude oxalic acid. This process is no longer economical in the leading industrial countries. UBE Industries (Japan), for instance, once employed this process, but has been operating the newest dialkyl oxalate process since 1978. The sodium formate process is, however, still used in China.

3.1. Oxidation of Carbohydrates

Oxalic acid is prepared by the oxidation of carbohydrates (7–9), such as glucose, sucrose, starch, dextrin, molasses, etc, with nitric acid (qv). The choice of the carbohydrate raw material depends on availability, economics, and process operating characteristics. Among the various raw materials considered, corn starch (or starch in general) and sugar are the most commonly available. For example, tapioka starch is the Brazilian raw material, and sugar is used in India.

The oxidation of carbohydrates is the oldest method for oxalic acid manufacture. The reaction was discovered by Scheele in 1776, but was not successfully developed as a commercial process until the second quarter of the twentieth century. Technical advances in the manufacture of nitric acid, particularly in the recovery of nitrogen oxides in a form suitable for recycle, enabled its successful development. Thus 150 t of oxalic acid per month was produced from sugar by I. G. Farben (Germany) by the end of World War II.

Monosaccharides such as glucose and fructose are the most suitable as starting materials. When starch is used, it is first hydrolyzed with oxalic acid or sulfuric acid into a monosaccharide, mainly glucose. It is then oxidized with nitric acid in an approximately 50% sulfuric acid solution at 63–85°C in the presence of a mixed catalyst of vanadium pentoxide and iron(III) sulfate.

$$C_6H_{12}O_6 + 12\,HNO_3 \xrightarrow{V_2O_5/Fe^{3+}} 3\,(COOH)_2 \cdot 2H_2O + 3\,H_2O + 3\,NO + 9\,NO_2$$

$$4\,C_6H_{12}O_6 + 18\,HNO_3 + 3\,H_2O \xrightarrow{V_2O_5/Fe^{3+}} 12\,(COOH)_2 \cdot 2H_2O + 9\,N_2O$$

The Allied process (Fig. 1) is a typical example of the oxidation of carbohydrates. However, Allied Corporation itself has stopped the production of oxalic acid.

Oxalic acid manufacture via the oxidation of carbohydrates is still actively pursued, especially in China (10–12). In India, processes which produce silica and oxalic acid have been developed (13, 14). The raw materials include agricultural wastes, such as rice husks, nut shell flour, corn cobs, baggase, straw, etc.
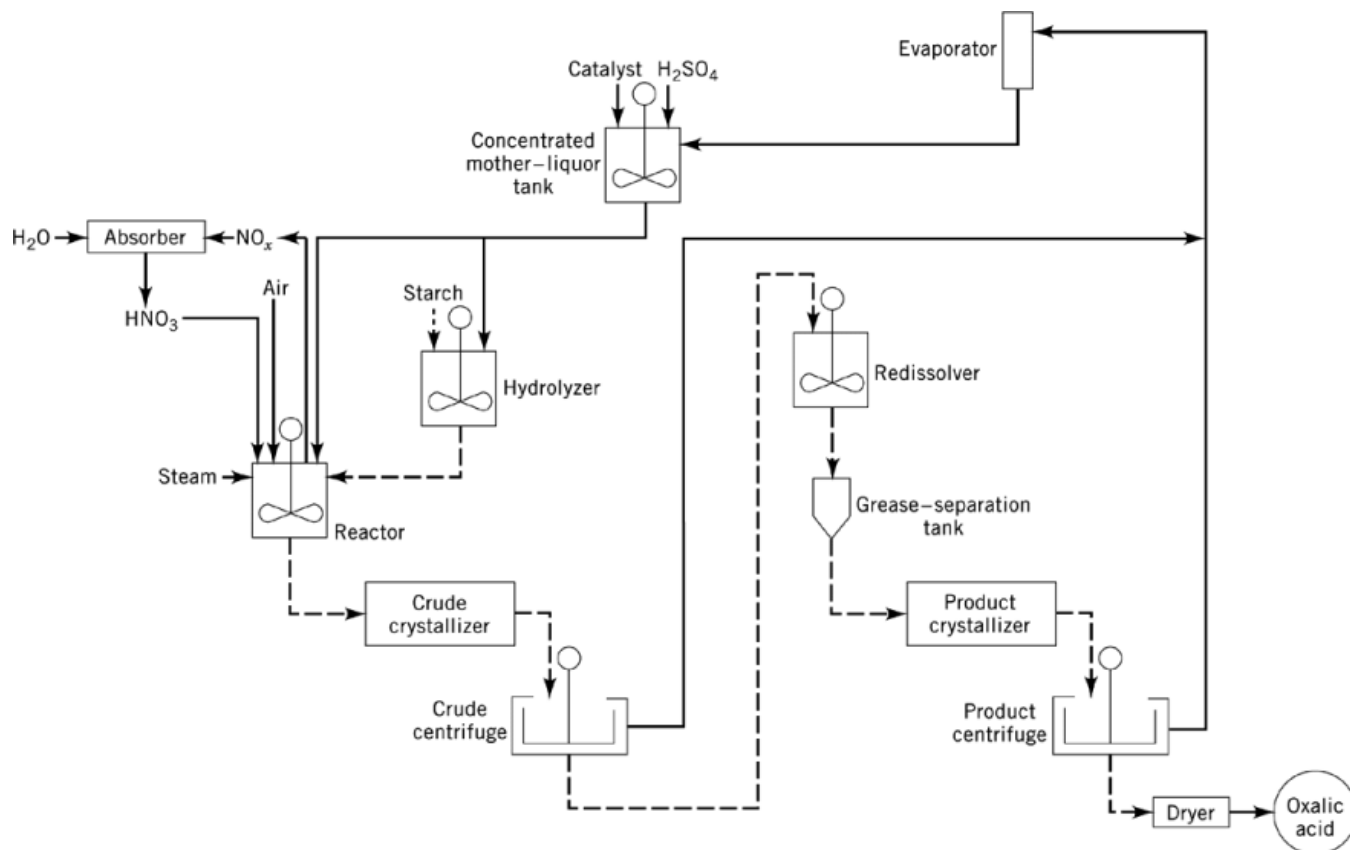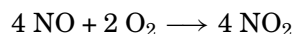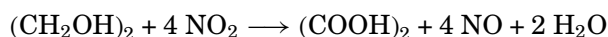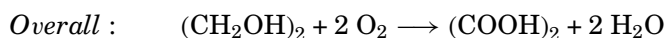
Fig. 1. Manufacture of oxalic acid from starch.

3.2. Ethylene Glycol Process

Oxalic acid is also prepared by the nitric acid oxidation of ethylene glycol (15–21), and the process is basically the same as in the case of carbohydrates except for the absence of the hydrolyzer (see Fig. 1). In this process, ethylene glycol is oxidized in a mixture of 30–40% sulfuric acid and 20–25% nitric acid in the presence of 0.001–0.1% vanadium pentoxide at 50–70°C to give oxalic acid at more than 93% yield.

An improved process has been developed in Japan by Mitsubishi Gas Chemical, who produces 12,000 t/yr of oxalic acid by this process. Ethylene glycol is oxidized in ca 60% nitric acid at 0.3 MPa (43.5 psi), 80°C with oxygen (16, 20). An initiator, such as $NaNO_2$, may be used to help the generation of nitrogen oxides, and a promoter, such as vanadium compounds or sulfuric acid, also may be employed to accelerate the oxidation reaction. The yield of oxalic acid is 90%. The reaction proceeds according to the following equations. Neither nitrogen nor N_2O, that cannot be recovered as nitric acid, is produced in this method.

$$(CH_2OH)_2 + 4\ NO_2 \longrightarrow (COOH)_2 + 4\ NO + 2\ H_2O$$

$$4\ NO + 2\ O_2 \longrightarrow 4\ NO_2$$

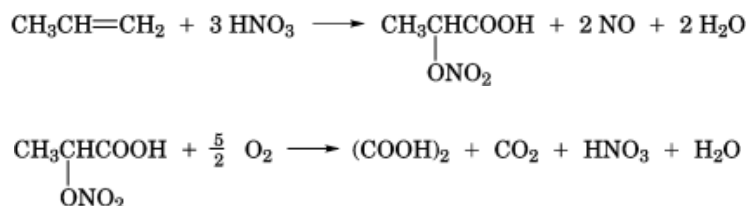$$Overall: \qquad (CH_2OH)_2 + 2\,O_2 \longrightarrow (COOH)_2 + 2\,H_2O$$

3.3. Propylene Process

The oxidation of propylene with nitric acid is a two-step process (22–29). Propylene reacts with liquid NO_2 to produce an intermediate, α-nitratolactic acid, in the first step; the intermediate is then oxidized at higher temperature to form oxalic acid by mixed acid, ie, nitric acid and sulfuric acid. This process does, however, have shortcomings. Because of the use of sulfuric acid, severe equipment corrosion occurs at the oxidation mother liquor recovery step and the concentration step. Nitrogen dioxide is not readily available, and the second oxidation reaction is slow, so that the reactor must be large; during the formation of α-nitratolactic acid, unstable by-products may form which can lead to runaway decomposition or explosion.

Rhône-Poulenc (France) developed a modified version of the process for making either oxalic acid or lactic acid, or both, from propylene. In 1978, 65,000 t/yr of oxalic acid was produced worldwide by this process, although in the 1990s this process is operated only by Rhône-Poulenc. Oxidation reactions of the Rhône-Poulenc process are as follows.

$$CH_3CH{=}CH_2 \;+\; 3\,HNO_3 \;\longrightarrow\; CH_3\underset{\overset{|}{ONO_2}}{CH}COOH \;+\; 2\,NO \;+\; 2\,H_2O$$

$$CH_3\underset{\overset{|}{ONO_2}}{CH}COOH \;+\; \tfrac{5}{2}\,O_2 \;\longrightarrow\; (COOH)_2 \;+\; CO_2 \;+\; HNO_3 \;+\; H_2O$$
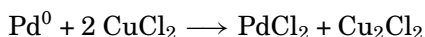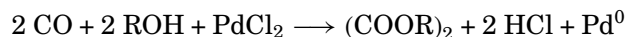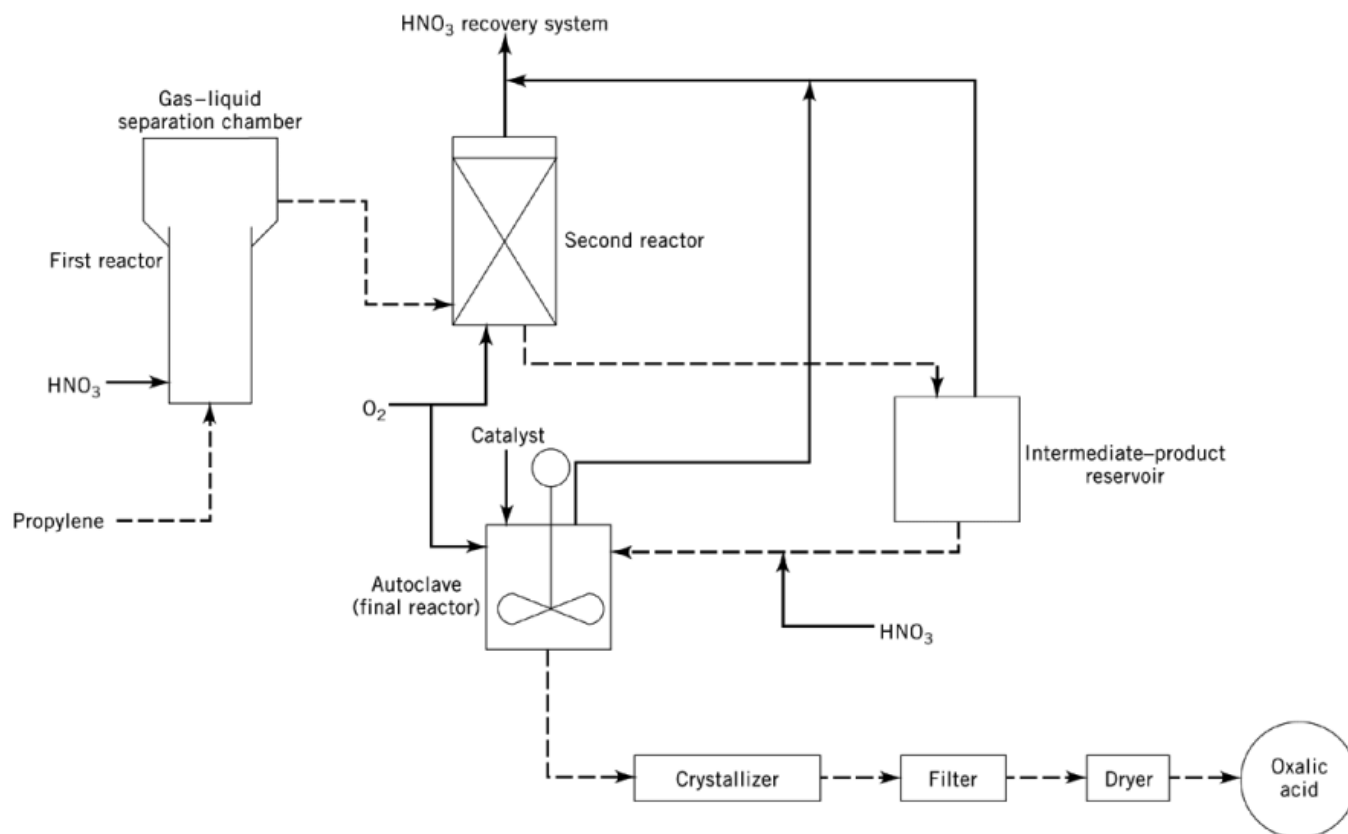
In the first step, propylene is introduced at 10–40°C into nitric acid, the concentration of which is kept at 50–75 wt % and molar ratio to propylene at 0.01–0.5, and converted into α-nitratolactic acid and lactic acid. α-Nitratolactic acid is oxidized by oxygen in the second step in the presence of a catalyst at 45–100°C to produce oxalic acid dihydrate. The overall yield based on propylene is greater than 90% and the conversion of propylene, 77.5%. The outline of the process is shown in Figure 2. The Rhône-Poulenc process can be characterized by the coproduction of lactic acid.
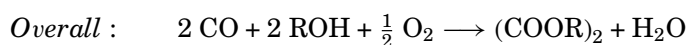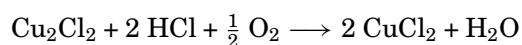
3.4. Dialkyl Oxalate Process

Oxalic acid is prepared by the hydrolysis of diesters of oxalic acid which are prepared by an oxidative CO coupling reaction. UBE Industries (Japan) commercialized this two-step process in 1978. This is the newest manufacturing process of oxalic acid.

Dialkyl oxalates can be prepared by oxidative CO coupling in the presence of alcohols. The first reported example of the synthesis was in a $PdCl_2$–$CuCl_2$ redox system (30, 31).
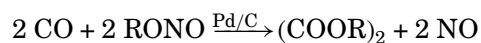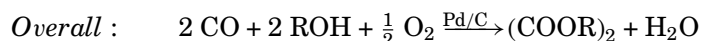
$$2\,CO + 2\,ROH + PdCl_2 \longrightarrow (COOR)_2 + 2\,HCl + Pd^0$$

$$Pd^0 + 2\,CuCl_2 \longrightarrow PdCl_2 + Cu_2Cl_2$$

Fig. 2.   Manufacture of oxalic acid from propylene.

$$Cu_2Cl_2 + 2\,HCl + \tfrac{1}{2}\,O_2 \longrightarrow 2\,CuCl_2 + H_2O$$

$$Overall: \qquad 2\,CO + 2\,ROH + \tfrac{1}{2}\,O_2 \longrightarrow (COOR)_2 + H_2O$$

This method, however, is not industrially practical because a large amount of dehydrating agent, such as ethyl orthoformate, is required to remove water formed in the reaction. Because water is an inhibitor of the reaction, the reaction system has to be kept under substantially anhydrous conditions.

UBE Industries, Ltd. has improved the basic method (32–48). In the UBE process, dialkyl oxalate is prepared by oxidative CO coupling in the presence of alkyl nitrite and a palladium catalyst.

$$2\,CO + 2\,RONO \xrightarrow{\text{Pd/C}} (COOR)_2 + 2\,NO$$

$$2 \, NO + \tfrac{1}{2} \, O_2 + 2 \, ROH \longrightarrow 2 \, RONO + H_2O$$

$$Overall: \quad 2 \, CO + 2 \, ROH + \tfrac{1}{2} \, O_2 \xrightarrow{\text{Pd/C}} (COOR)_2 + H_2O$$
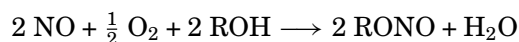
The dialkyl oxalate thus prepared is hydrolyzed to oxalic acid and the corresponding alcohol.

$$(COOR)_2 + 2 \, H_2O \longrightarrow (COOH)_2 + 2 \, ROH$$
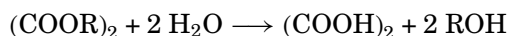
The alkyl nitrites employed industrially are n-butyl nitrite [544-16-1] (BN) and methyl nitrite [624-91-9] (MN). In 1978, UBE Industries constructed the first plant to use this process (6000 t/yr as oxalic acid), using BN, and the plant is still being operated satisfactorily. The advantage of BN as alkyl nitrite is that it works not only as a reaction component but also as a dehydrating agent of water formed. BN forms an azeotropic mixture with water, so that the water formed is removed by distillation from the reaction system. Other features of this process are that the catalyst system is simple and the catalyst can be easily recovered and recycled, the reaction rate is fast and selectivity of dialkyl oxalate is high, even in the presence of some water (CO_2, CH_4, etc) the catalyst activity is high and the catalyst life is long, and inexpensive construction material can be used for the equipment because the catalyst system does not contain chloride.

The liquid-phase process using BN is outlined in Figure 3 (49). The circulating solution containing BN and n-butanol, and the circulating gas containing CO and O_2 are pressurized and fed to a reactor. In the reactor, di-n-butyl oxalate (DBO) is formed while BN is consumed and equimolar NO is generated. BN is regenerated simultaneously from NO. The overall reaction is exothermic.

As for the selectivity of DBO, the higher the reaction pressure and the lower the reaction temperature, the higher the selectivity. As for the reaction rate, the higher the reaction temperature, the larger the rate. Therefore, the industrial operation of the process is conducted at 10–11 MPa (1450–1595 psi) and 90–100°C. In addition, gas circulation is carried out in order to keep the oxygen concentration below the explosion limit during the reaction, and to improve the CO utilization rate and the gas–liquid contact rate.

The reaction solution is flushed under reduced pressure after it is sent out from the column, to remove CO_2 gas formed as a by-product. The water formed is then removed from the reaction solution by azeotropic distillation with BN, and most of the resultant reaction solution is recycled to the reaction column as the circulating solution. Part of the circulating solution is taken out from the reaction system and processed further to obtain DBO. The catalyst is first filtered, then BN, C_4H_9OH, and by-products are removed from the resultant solution. Purified DBO is thus obtained. The catalyst, BN, and C_4H_9OH are recovered and recycled to the circulating solution. After the make-up C_4H_9OH and nitric acid are added, the circulating solution is pressurized and fed back to the reaction column.

Purified DBO is mixed with the mother liquor from the oxalic acid crystallization, and hydrolyzed at about 80°C into oxalic acid and n-butanol. The resultant mixture undergoes phase separation; oxalic acid dihydrate is thus crystallized from the oxalic acid solution, and C_4H_9OH is purified and recycled to the circulating solution.

In addition to the liquid-phase n-butyl nitrite (BN) process, UBE Industries has established an industrial gas-phase process using methyl nitrite (50–52). The outline of the process is described in Figure 4 (52). This gas-phase process is operated under lower reaction pressure (at atmospheric pressure up to 490 kPa = 71 psi) and is more economical than the liquid-phase process because of the following reasons: owing to the low pressure operation, the consumption of electricity is largely reduced (∼60%); dimethyl oxalate (DMO) formation and the methyl nitrite (MN) regeneration reaction are run separately in different reaction vessels so that side-reactions are suppressed and the yield of DMO increases (98%); and methanol is less expensive than n-butanol.
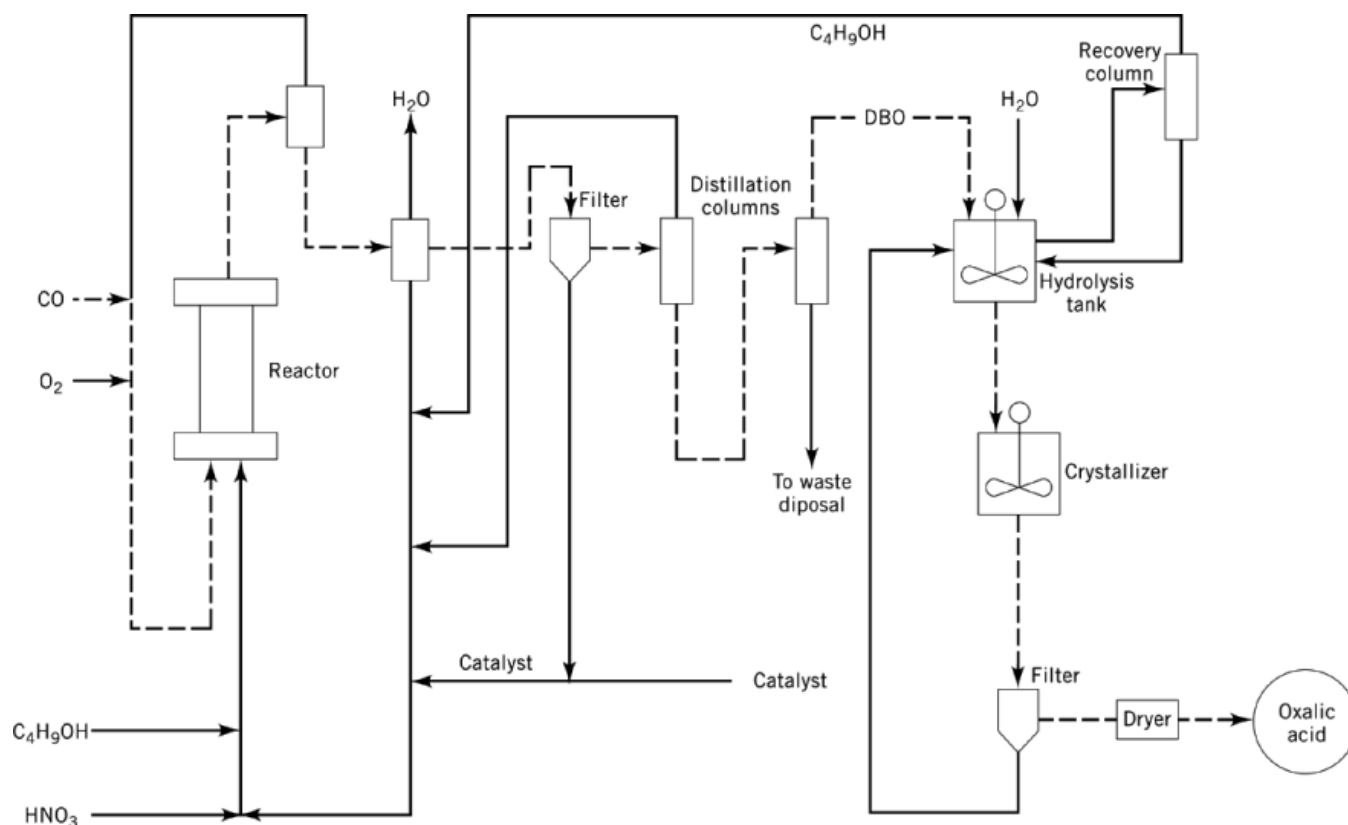
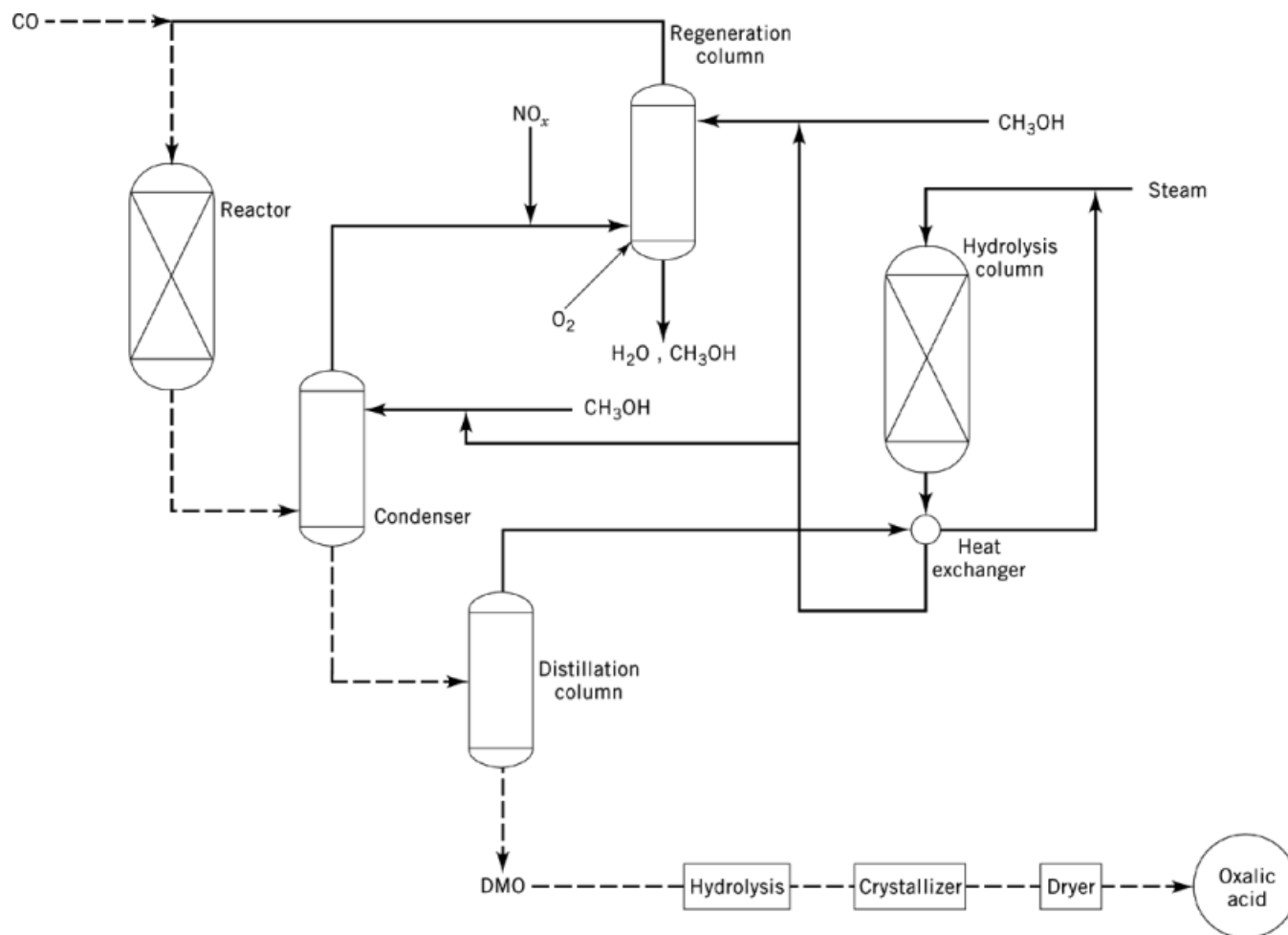**Fig. 3.**   UBE dibutyl oxalate process.

3.5. New Synthesis

Many attempts have been made to synthesize oxalic acid by electrochemical reduction of carbon dioxide in either aqueous or nonaqueous electrolytes (53–57). For instance, oxalic acid is prepared from CO_2 as its Zn salt in an undivided cell with Zn anodes and stainless steel cathodes in acetonitrile containing $(C_4H_9)_4NClO_4$ and current efficiency of $>90\%$ (53). Micropilot experiments and a process design were also made.

4. Economic Aspects

There are five processes employed for the manufacture of oxalic acid as shown in Table 3 (58). Processes are selected depending on geographical conditions.

Supply and demand of oxalic acid in the world market in 1992 are summarized in Table 4 (58). Asia has the largest production capacity, and western Europe the second largest. There is no production of oxalic acid in North America (the United States, Canada, and Mexico) and thus all needs are met by imports. In China, new plants have been constructed and existing plants have been enlarged continuously since 1986. As a consequence, the number of oxalic acid producers exceeds 20, and the total production capacity in China is estimated to be about 100,000 t/yr. China also has the world's largest domestic consumption and export of oxalic acid. India was an importing country until Punjab Chemicals & Pharmaceuticals, a subsidiary of

Fig. 4. UBE dimethyl oxalate process.

Table 3. Manufacturing Processes of Oxalic Acid

Processn	Company	Location
sodium formate		China
dialkyl oxalate	UBE Industries	Japan
propylene	Rhône-Poulenc	France
ethylene glycol	Mitsubishi Gas Chemical	Japan
		Brazil, China, Taiwan, India, Korea, and
oxidation of carbohydrates		Spain

Excel Industries, enlarged its capacity in 1990; now India exports oxalic acid. In Japan, UBE Industries and Mitsubishi Gas Chemical are the only producers. In western Europe, Rhône-Poulenc (France) and DAV (Spain) are significant producers. Although western Europe exports and imports oxalic acid mainly within the region, a fair amount of oxalic acid is also imported from China, India, Brazil, and Taiwan.

Table 4. Supply and Demand of Oxalic Acid in the World Market in 1992, tons

Country	Production Capacity	Produced	Consumption	Exports	Imports
North America					
United States	0	0	8,000	0	8,000
Canada, Mexico	0	0	900	0	900
Total	*0*	*0*	*8,900*	*0*	*8,900*
South America					
Brazil	7,000	2,600	1,000	1,600	0
Venezuela, etc	0	0	100	0	100
Total	*7,000*	*2,600*	*1,100*	*1,600*	*100*
Europe					
France	8,000	5,000	4,000	1,000	0
Spain, etc	14,000	12,200	14,200	4,700	6,700
Total, Western Europe	*22,000*	*17,200*	*18,200*	*5,700*	*6,700*
Eastern Europe	10,000	9,000	9,500	3,500	4,000
Asia					
China	100,000	60,000	50,000	10,000	0
Japan	18,000	8,600	10,300	800	2,500
India	20,000	13,000	11,500	3,000	1,500
Korea, etc	12,000	3,700	4,600	2,600	3,500
Total	*150,000*	*85,300*	*76,400*	*16,400*	*7,500*
World Total	*189,000*	*114,100*	*114,100*	*27,200*	*27,200*

Uses of oxalic acid in each region are summarized in Table 5 (58). The demand for agrochemical/pharmaceutical production and for separation/recovery of rare-earth elements in each region has been increasing. The use for marble polishing in western Europe is unique to the region.

5. Analytical and Test Methods

5.1. Qualitative Analysis

Several qualitative analyses can be employed. For example, in the oxamide method (59), oxalic acid is first heated at approximately 200°C with concentrated aqueous ammonia in a sealed tube. When thiobarbituric acid is added and heated to 140°C, a condensed compound of red color forms. The analysis limit is 1.6 μg. In the diphenylamine blue method (59, 60), oxalic acid is heated with diphenylamine to form a blue color, aniline blue. The analysis limit is 5 μg.

5.2. Quantitative Analysis

Oxalic acid is precipitated as calcium oxalate from a solution containing oxalic acid, and the calcium oxalate obtained is then weighed. If there are no organic substances other than oxalic acid present, oxalic acid can be titrated quantitatively with potassium permanganate.

Table 5. Uses of Oxalic Acid by Region

Use	Amount, %
United States	
separation/recovery of rare-earth elements	20
textile treatment	20
metal treatment	10
bleaching agent	20
leather tanning	10
agrochemical/pharmaceutical production	20
Western Europe	
cobalt production	20
metal treatment	15
agrochemical/pharmaceutical production	15
bleaching agent	15
leather tanning	9
marble polishing	7
separation/recovery of rare-earth elements	5
salts, esters, textile treatment, etc	14
China	
separation/recovery of rare-earth elements	50
agrochemical/pharmaceutical production and metal treatment	50
Japan	
separation/recovery of rare-earth elements	35
agrochemical/pharmaceutical production	20
metal treatment	10
anodic aluminum coatings	4
millet jelly production	6
catalyst	5
salts, esters, and others	20

6. Shipment, Storage, and Handling

Dry oxalic acid is packed and sold in polyethylene-lined, multilayered 25-kg paper bags or in polyethylene-lined 300–600-kg PVC flexible containers. It should be stored in a cool, dry, ventilated place. For storage of its solutions at ordinary temperature, 316 stainless steel is often used as a construction material.

Oxalic acid is not flammable but its decomposition products, both formic acid and carbon monoxide, are toxic and flammable. Its dust and mist are irritating, especially under prolonged contact. Personnel who handle oxalic acid should wear rubber gloves, aprons, protection masks or goggles, etc, to avoid skin contact and inhalation. Adequate ventilation also should be provided in areas in which oxalic acid dust fumes are present.

Because oxalic acid is toxic and corrosive, neither its crystals nor its solutions should be discarded to the environment without proper treatment. The common treatment methods are acidification, neutralization, and incineration. When oxalic acid is heated slightly in sulfuric acid, it is converted to carbon monoxide, carbon dioxide, and water. Reaction with acid potassium permanganate converts it to carbon dioxide. Neutralization with alkalies, such as caustic soda, yields soluble oxalates. Neutralization with lime gives practically insoluble calcium oxalate, which can be safely disposed of, for instance, by incineration.

7. Health and Safety Factors

Oxalic acid is caustic and corrosive to humans. The severity of symptoms associated with oxalic acid poisoning is related to the concentration and quantity ingested. With dilute solutions, burning gastrointestinal pain which is experienced with ingestion of oxalic acid crystals may not occur. Ingestion of a strong solution or oxalic acid crystals is accompanied by burning pain in the mouth, esophagus, and stomach, and may cause severe gastroenteritis with symptoms of vomiting, diarrhea, or melena. Oxalic acid removes calcium in the blood, forming calcium oxalate, and severe damage to the kidney may occur because of the insoluble calcium oxalate (61). The minimal fatal dose, LD_{LO} for humans is 71 mg/kg (62), and the mean lethal dose for an adult is 15–30 g (63).

If ingestion occurs, dilute solutions of calcium compounds (calcium lactate, calcium gluconate, etc) or a large amount of milk followed by magnesium sulfate should be administered (63, 64).

8. Uses

8.1. Separation and Recovery of Rare-Earth Elements

Because rare-earth oxalates have low solubility in acidic solutions, oxalic acid is used for the separation and recovery of rare-earth elements (65). For the decomposition of rare-earth phosphate ores, such as monazite and xenotime, a wet process using sulfuric acid has been widely employed. There is also a calcination process using alkaline-earth compounds as a decomposition aid (66). In either process, rare-earth elements are recovered by the precipitation of oxalates, which are then converted to the corresponding oxides.

8.2. Metal Treatment

The oxalic acid process for anodizing aluminum (67, 68) was developed in Japan. Oxalic acid is used as an electrolyte, and the thin aluminum oxide layer forms on the surface of aluminum. The coatings are hard, abrasion- and corrosion-resistant. In addition to oxalic acid, inorganic oxalate salts are also used in coloring anodic coatings (qv). Oxalic acid is a constituent of cleaners that are used for automotive radiators, boilers, and steel plates before phosphating. Many of its industrial cleaning applications are based on its acidity and reducing power which promote dissolution of rust and formation of oxalate coatings on steel (qv). As a chelating agent, oxalic acid forms water-soluble complexes on metal surfaces during cleaning and rinsing.

8.3. Bleaching Agent

In pulp bleaching (69), oxalic acid serves as a bleaching agent, but is often used together with other bleaching agents (qv) because of its relatively high cost. Oxalic acid is also used for the bleaching of cork, wood (particularly veneered wood), straw, cane, and natural waxes.

8.4. Textile Treatment

Oxalic acid has various uses in fabric cleaning, application of dyestuff, and modifying properties of cellulose fabrics. Rust stains, which form on fabrics during weaving and finishing, are removed by the chelating action of oxalic acid by forming iron oxalate which is readily washed from the fabric. In laundries, oxalic acid neutralizes excess alkalinity. It also dissolves iron and metallic salts, which could discolor fabrics, and kills bacteria (70). In mordant wool dyeing (71), oxalic acid is used as a reducing or fixing agent. Oxalic acid can be used as a catalyst for cross-linking of textile finishing agents to cellulosic fabrics in the manufacture of permanent press fabrics (72). It is also used in flame proofing for cellulosic fabrics (73–75).

8.5. Leather Tanning

Oxalic acid is used as a pH modifier in leather tanning by tannin and basic chromium sulfate. It also functions as a bleaching agent for leather (qv).

8.6. Marble Polishing

Oxalic acid is used for marble polishing especially in Italy. It not only removes iron veins by forming water-soluble iron oxalate, but also serves as a polishing auxiliary.

8.7. Millet Jelly Production

Starch powder is heated together with oxalic acid and hydrolyzed to produce millet jelly. Oxalic acid functions as a hydrolysis catalyst, and is removed from the product as calcium oxalate. This application is carried out in Japan.

8.8. Others

Oxalic acid is used for the production of cobalt, as a raw material of various agrochemicals and pharmaceuticals, for the manufacture of electronic materials (76–83), for the extraction of tungsten from ore (84), for the production of metal catalysts (85, 86), as a polymerization initiator (87–89), and for the manufacture of zirconium (90) and beryllium oxide (91).

9. Derivatives

9.1. SALTS AND COMPLEXES

Oxalic acid forms neutral and acid salts, as well as complex salts.

9.1.1. Ammonium Oxalate

This salt [1113-38-8], $(NH_4)_2C_2O_4$, mol wt 124.10, exists as a monohydrate [6009-70-7] or in anhydrous form. Anhydrous ammonium oxalate is obtained when the monohydrate is dehydrated at $65°C$. The monohydrate is a colorless crystal or white powder, and dissolves in water at $0°C$ up to 2.17 wt %, and $50°C$ up to 9.63 wt %. It is slightly soluble in alcohol and insoluble in ether. It is used for textiles, leather tanning, and precipitation of rare-earth elements.

9.1.2. Ammonium Iron(III) Oxalate

This mixed salt [29696-35-3], $(NH_4)_3[Fe(C_2O_4)_3]$, mol wt 374.04, is produced as an emerald-green crystalline trihydrate [13268-42-3]. It is soluble in water to the extent of 100 g in 100 mL at $25°C$ and is insoluble in both alcohol and ether. It is used in formulations for anodizing aluminum. The compound is not stable to light. On exposure to light, it is reduced from the ferric to the ferrous ion. It was once used extensively in the manufacture of blueprinting papers, where the development of the blue color results from the photochemical reduction of the oxalate salts containing the ferric iron. The ferrous ion thus formed subsequently reacts with the ferricyanide- or ferrocyanide-coated paper to form the blue pigment, Precision Blue. Blueprinting is now obsolete.

Table 6. Solubilities of Alkaline-Earth Oxalates

Formula, solid phase	Anhydrous salt in sat'd soln, %	
	0°C	100°C
$CaC_2O_4 \cdot H_2O$	0.0005	0.0015
$SrC_2O_4 \cdot H_2O$	0.006	0.015
$BaC_2O_4 \cdot \frac{1}{2} H_2O$	0.009	0.021
$MgC_2O_4 \cdot 2H_2O$	0.026	0.041

9.1.3. Potassium Hydrogen Oxalate

Potassium acid oxalate [127-95-7], KHC_2O_4, mol wt 146.15, exists as a monohydrate [6100-03-4]. It is of historical interest because it is the salt of sorrel found in vegetation and the first oxalate isolated.

9.1.4. Potassium Oxalate

The monohydrate [6487-48-5], $K_2C_2O_4 \cdot H_2O$, mol wt 184.24, is produced as a colorless crystalline material or a white powder. The anhydrous salt [583-52-8], mol wt 166.22, is obtained when the monohydrate is dehydrated at 160°C. The monohydrate is preferred as a reagent in analytical chemistry and in miscellaneous uses principally because of its high solubility as compared with other simple neutral oxalates; the saturated solution, at 0°C, contains about 20 wt %, and at 20°C, about 25 wt % $K_2C_2O_4$.

9.1.5. Sodium Oxalate

This salt [62-76-0], $Na_2C_2O_4$, mol wt 134.01, is obtained in such high purity and is so stable that it is used as a titrimetric standard. The salt is not very soluble in water; the saturated solution contains 2.6 wt % and 6.1 wt % $Na_2C_2O_4$ at 0°C and 100°C, respectively.

9.1.6. Calcium Oxalate

The monohydrate [5794-28-5], $CaC_2O_4 \cdot H_2O$, mol wt 128.10, is of importance principally as an intermediate in oxalic acid manufacture and in analytical chemistry; it is the form in which calcium is frequently quantitatively isolated. Its solubility in water is very low, lower than that of the other alkaline-earth oxalates. The approximate solubilities of this and several related salts are indicated in Table 6.

9.1.7. Nickel Oxalate

This salt, NiC_2O_4, mol wt 146.7, is produced as a greenish white crystalline dihydrate [6018-94-6]. It decomposes by heating at 320°C under vacuum into Ni metal and carbon dioxide. Nickel oxalate is used for the production of nickel catalysts and magnetic materials.

9.1.8. Yttrium Oxalate

This compound [126476-37-7], $Y_2(C_2O_4)_3$, mol wt 441.91, exists as a trihydrate, nonahydrate [7100-75-6], or heptadecahydrate. The compound is used for the production of a red fluorescent material for color television.

9.2. ORGANIC DERIVATIVES

9.2.1. Dialkyl Oxalates

Oxalic acid gives various esters. Dialkyl esters, ROOC–COOR, are industrially useful, but monoalkyl esters, ROOC–COOH, are not. The dialkyl esters are characterized by good solvent properties and serve as starting materials in the synthesis of many organic compounds, such as pharmaceuticals, agrochemicals, and fine

Table 7. Physical Properties of Dialkyl Oxalates

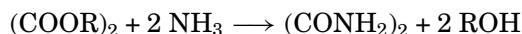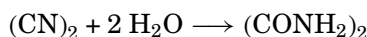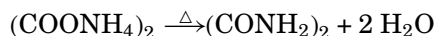| Oxalate	CAS Registry Number	Mol wt	Mp, °C	Bp, °C	d^{20}_4
dimethyl	[553 – 90 – 2]	118.09	54	163.5	1.148^a
diethyl	[95 – 92 – 1]	146.14	−40.6	185.4	1.079
di-n-butyl	[2050 – 60 – 4]	202.25	−29.6	245.5	0.9873

^{a} At 54°C.

chemicals (qv). Among the diesters, dimethyl, diethyl, and di-n-butyl oxalates are industrially important. Their physical properties are given in Table 7.

9.2.2. Oxamide

This diamide [471-46-5], $H_2NCOCONH_2$, mol wt 80.07, is sparingly soluble in water and insoluble in various organic solvents. It melts at about 350°C, with accompanying decomposition. Because of the low solubility in water, the compound is granulated and used as a slow-release nitrogen fertilizer. Conventional nitrogen fertilizers (qv), such as ammonium sulfate, urea, ammonium nitrate, and ammonium phosphate, are soluble in water, and thus are easily lost as run-off when it rains. On the contrary, oxamide stays in the soil longer. Therefore, it is gradually decomposed by microorganisms in the soil and utilized by plants for longer periods.

There are three reactions used for the production of oxamide:

$$(COONH_4)_2 \xrightarrow{\triangle} (CONH_2)_2 + 2\ H_2O$$

$$(CN)_2 + 2\ H_2O \longrightarrow (CONH_2)_2$$

$$(COOR)_2 + 2\ NH_3 \longrightarrow (CONH_2)_2 + 2\ ROH$$

The second and third reactions are economical, but the first is not. The second reaction is used in a process where HCN is oxidized to $(CN)_2$ and hydrolyzed in the presence of a strong acid catalyst to give oxamide. The third reaction is employed in a newly developed process where dialkyl oxalates are converted to oxamide by the ammonolysis reaction. This reaction easily proceeds without catalysts and quantitatively gives oxamide as a powder.

9.2.3. Oxalyl Chloride

This diacid chloride [79-37-8], ClCOCOCl, mol wt 126.9, is produced by the reaction of anhydrous oxalic acid and phosphorus pentachloride. The compound vigorously reacts with water, alcohols, and amines, and is employed for the synthesis of agrochemicals, pharmaceuticals, and fine chemicals.

9.2.4. Reduction Products

Glyoxylic acid [298-12-4], HOOCCHO, mol wt 74.04, is produced as aqueous solution by the electrolytic reduction of oxalic acid. It is used for the manufacture of vanillin.

Glycolic acid [79-14-1], $HOOCCH_2OH$, mol wt 76.05, can be obtained by the electrolytic reduction of oxalic acid or the catalytic reduction of oxalic acid with hydrogen in the presence of a ruthenium catalyst. Because of its acidity it is used as a cleaning agent for metal surface treatments and for boiler cleaning. It also serves as an ingredient in cosmetics (qv).

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Bleaching, survey; Textile finishing