ACETIC ANHYDRIDE

1. Introduction

Acetic anhydride [108-24-7], $(CH_3CO)_2O$, is a mobile, colorless liquid that has an acrid odor and is a more piercing lacrimator than acetic acid [64-19-7]. It is the largest commercially produced carboxylic acid anhydride: U.S. production capacity is over 1×10^6 t yearly. Its chief industrial application is for acetylation reactions; it is also used in many other applications in organic synthesis, and it has some utility as a solvent in chemical analysis.

First prepared by C. F. Gerhardt from benzoyl chloride and carefully dried potassium acetate (1), acetic anhydride is a symmetrical intermolecular anhydride of acetic acid; the intramolecular anhydride is ketene [463-51-4]. Benzoic acetic anhydride [2819-08-1]undergoes exchange upon distillation to yield benzoic anhydride [93-97-0] and acetic anhydride.

2. Physical and Chemical Properties

No dimerization of acetic anhydride has been observed in either the liquid or solid state. Decomposition, accelerated by heat and catalysts such as mineral acids, leads slowly to acetic acid (2). Acetic anhydride is soluble in many common solvents, including cold water. As much as 10.7 wt% of anhydride will dissolve in water. The unbuffered hydrolysis rate constant k at 20°C is 0.107 min^{-1} and at 40°C is 0.248 min^{-1}. The corresponding activation energy is $\sim$31.8 kJ/mol (7.6 kcal/mol) (3). Although aqueous solutions are initially neutral to litmus, they show acid properties once hydrolysis appreciably progresses. Acetic anhydride ionizes to acetylium, CH_3CO^+, and acetate, $CH_3CO_2^-$, ions in the presence of salts or acids (4). Acetate ions promote anhydride hydrolysis. A summary of acetic anhydride's physical properties is given in Table 1.

Acetic anhydride acetylates free hydroxyl groups without a catalyst, but esterification is smoother and more complete in the presence of acids. For example, in the presence of p-toluenesulfonic acid [104-15-4], the heat of reaction for

Table 1. **Physical Properties of Acetic Anhydride**

Property	Value	Reference
freezing point, °C	−73.13	5
boiling point, °C at 101.3 kPa[a]	139.5	5
density, d_4^{20}, g/cm^3	1.0820	5
refractive index, n_D^{20}	1.39038	6
vapor pressure (Antoine equation), P in kPa[a] and T in K	$\ln(P) = \frac{14.6497 - 3467.76}{T - 67.0}$	7
heat of vaporization, ΔH_v, at bp, J/g[b]	406.6	5
specific heat, J/kg[c] at 20°C	1817	8
surface tension, mN/m (= dyn/cm)		
25°C	32.16	9
40°C	30.20	9
viscosity, mPa·s (= cP)		
15°C	0.971	10
30°C	0.783	10
heat conductivity, mW/(m·K)[d] at 30°C	136	11
electric conductivity, S/cm	2.3×10^{-8}	12

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J/g to Btu/lb, multiply by 0.4302.

[c] To convert J to cal divide by 4.184.

[d] To convert mW/(m·K) to (Btu·ft)/(h·ft^2·°F), multiply by 578.

ethanol and acetic anhydride is −60.17 kJ/mol (−14.38 kcal/mol) (13):

$$ROH + (CH_3CO)_2O \longrightarrow CH_3COOR + CH_3COOH$$

Amines undergo an analogous reaction to yield acetamides, the more basic amines having the greater activity:

$$RNH_2 + (CH_3CO)_2O \longrightarrow CH_3CONHR + CH_3COOH$$

Potassium acetate, rubidium acetate, and cesium acetate are very soluble in anhydride in contrast to the only slightly soluble sodium salt. Barium forms the only soluble alkaline earth acetate. Heavy metal acetates are poorly soluble.

Triacetylboron [4887-24-5], $C_6H_9BO_6$, is generated when boric acid is added to acetic anhydride and warmed. Although explosions have resulted from carrying out this reaction, slowly adding the boric acid to a zinc chloride solution in acetic anhydride, and maintaining a temperature <60°C, gives a good yield (14). Acetic acid is also formed

$$H_3BO_3 + 3\ (CH_3CO)_2O \longrightarrow (CH_3CO)_3BO_3 + 3\ CH_3COOH$$

Heating triacetylboron at temperatures above its melting point, 123°C, causes a rearrangement to $B_2O(OCCH_3)_4$ (15). An explosive hazard is also generated by dissolving BF_3 in anhydride (see BORON COMPOUNDS).

Hydrogen peroxide undergoes two reactions with anhydride:

$$(CH_3CO)_2O + H_2O_2 \longrightarrow CH_3COOOH + CH_3COOH + H_2O$$

$$(CH_3CO)_2O + 2\ H_2O_2 \longrightarrow 2\ CH_3COOOH + H_2O$$

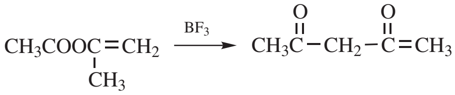
Peroxyacetic acid [79-21-0] is used in many epoxidations (16) where ion-exchange resins, eg, Amberlite IR-1180M, serve as catalysts. Pinene is epoxidized to sobrerol [498-71-5],$C_{10}H_{18}O_2$, using peroxyacetic acid at −5 to −10°C (17). Care must be taken, however, to avoid formation of the highly explosive diacetyl peroxide [110-22-5]:

$$(CH_3CO)_2O + CH_3COOOH \longrightarrow CH_3CO—OO—COCH_3 + CH_3COOH$$

Acetic anhydride can be used to synthesize methyl ketones in Friedel-Crafts reactions. For example, benzene [71-43-2] can be acetylated to furnish acetophenone [98-86-2]. Ketones can be converted to their enol acetates and aldehydes to their alkylidene diacetates. Acetaldehyde reacts with acetic anhydride to yield ethylidene diacetate [542-10-9] (18):

$$CH_3CHO + (CH_3CO)_2O \longrightarrow CH_3CH(O_2CCH_3)_2$$

Isopropenyl acetate [108-22-5], which forms upon reaction of acetone [67-64-1] with anhydride, rearranges to acetylacetone [123-54-6] in the presence of BF_3 (19):



$$CH_3COO\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{BF_3} CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{=}CH_3$$

Unsaturated aldehydes undergo a similar reaction in the presence of strongly acid ion-exchange resins to produce alkenylidene diacetates. Thus acrolein [107-02-8] or methacrolein [78-85-3] react with equimolar amounts of anhydride at −10°C to give high yields of the *gem*-diacetates from acetic anhydride, useful for soap fragrances.

Acids react with acetic anhydride to furnish higher anhydrides (20). An acid that has a higher boiling point than acetic acid is refluxed with acetic anhydride until an equilibrium is established. The low boiling acetic acid is distilled off and the anhydride of the higher acid is left. Adipic polyanhydride is obtained in this manner (21).

3. Manufacture

3.1. The Acetic Acid Process.

Prior to the energy crisis of the 1970s, acetic anhydride was manufactured by thermal decomposition of acetic acid at pressures of 15–20 kPa (2.2–2.9 psi) (22), beginning with the first step:

$$CH_3COOH \longrightarrow CH_2{=}C{=}O + H_2O$$

The heat of reaction is approximately 147 kJ/mol (35.1 kcal/mol) (23). Optimum yields of ketene [463-51-4] require a temperature of ~730–750°C. Low pressure increases the yield, but not the efficiency of the process. Competitive reactions are

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad \text{(endothermic)}$$

$$CH_3COOH \longrightarrow 2\ CO + 2\ H_2 \quad \text{(exothermic)}$$

$$2\ CH_2{=}C{=}O \longrightarrow CH_4 + C + 2\ CO \quad \text{(exothermic)}$$

$$2\ CH_2{=}C{=}O \longrightarrow CH_2{=}CH_2 + 2\ CO \quad \text{(exothermic)}$$

The second step is the liquid-phase ketene and acetic acid reaction

$$CH_2{=}C{=}O + CH_3COOH \longrightarrow (CH_3CO)_2O \quad \text{(exothermic)}$$

Triethyl phosphate is commonly used as dehydration catalyst for the water formed in the first step. It is neutralized in the exit gases with ammonia. Aqueous 30% ammonia is employed as solvent in the second step because water facilitates the reaction, and the small amount of water introduced is not significant overall. Compression of ketene using the liquid-ring pump substantially improves the formation of anhydride. Nickel-free alloys, eg, ferrochrome alloy, chrome–aluminum steel, are needed for the acetic acid pyrolysis tubes, because nickel promotes the formation of soot and coke, and reacts with carbon monoxide yielding a highly toxic metal carbonyl. Coke formation is a serious efficiency loss. Conventional operating conditions furnish 85–88% conversion, selectivity to ketene 90–95 mol%. High petroleum energy costs make these routes only marginally economic.

Acetone cracks to ketene, and may then be converted to anhydride by reaction with acetic acid. This process consumes somewhat less energy and is a popular subject for chemical engineering problems (24,25). The cost of acetone works against widespread application of this process, however.

3.2. The Acetaldehyde Oxidation Process. Liquid-phase catalytic oxidation of acetaldehyde (qv) can be directed by appropriate catalysts, such as transition metal salts of cobalt or manganese, to produce anhydride (26). Either ethyl acetate or acetic acid may be used as reaction solvent. The reaction proceeds according to the sequence

$$CH_3CHO + O_2 \longrightarrow CH_3COOOH$$

$$CH_3COOOH + CH_3CHO \longrightarrow CH_3COOOCH(OH)CH_3$$

$$CH_3COOOCH(OH)CH_3 \longrightarrow (CH_3CO)_2O + H_2O$$

$$CH_3COOOCH(OH)CH_3 \longrightarrow CH_3COOH + CH_3COOH$$

Acetaldehyde oxidation generates peroxyacetic acid, which then reacts with more acetaldehyde to yield acetaldehyde monoperoxyacetate [7416-48-0], the Loesch ester (26). Subsequently, parallel reactions lead to formation of acetic acid and anhydride plus water.

Under sufficient pressure to permit a liquid phase at 55–56°C, the acetaldehyde monoperoxyacetate decomposes nearly quantitatively into anhydride and water in the presence of copper. Anhydride hydrolysis is unavoidable, however, because of the presence of water. When the product is removed as a vapor, an equilibrium concentration of anhydride higher than that of acetic acid remains in the reactor. Water is normally quite low. Air entrains the acetic anhydride and water as soon as they form.

High purity acetaldehyde is desirable for oxidation. The aldehyde is diluted with solvent to moderate oxidation and to permit safer operation. In the liquid take-off process, acetaldehyde is maintained at 30–40 wt% and when a vapor product is taken, no > 6 wt% aldehyde is in the reactor solvent. A considerable recycle stream is returned to the oxidation reactor to increase selectivity. Recycle air, chiefly nitrogen, is added to the air introducted to the reactor at 4000–4500 times the reactor volume per hour. The customary catalyst is a mixture of three parts copper acetate to one part cobalt acetate by weight. Either salt alone is less effective than the mixture. Copper acetate may be as high as 2 wt% in the reaction solvent, but cobalt acetate ought not rise >0.5 wt%. The reaction is carried out at 45–60°C under 100–300 kPa (15–44 psi). The reaction solvent is far above the boiling point of acetaldehyde, but the reaction is so fast that little escapes unoxidized. This temperature helps oxygen absorption, reduces acetaldehyde losses, and inhibits anhydride hydrolysis.

Product refining is quite facile, following the same general pattern for acetic acid (qv) recovery from acetaldehyde liquid-phase oxidation. Low boilers are stripped off using ethyl acetate or acetic acid, then anhydride is distilled. Residues, largely ethylidene diacetate and certain higher condensation products with the catalyst salts, can be recycled (27).

3.3. Methyl Acetate Carbonylation. Anhydride can be made by carbonylation of methyl acetate [79-20-9] (28) in a manner analogous to methanol carbonylation to acetic acid. Methanol acetylation is an essential first step in anhydride manufacture by carbonylation. (see Fig. 1). The reactions are

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O \qquad -4.89\ \text{kJ/mol}\ (-1.2\ \text{kcal/mol})$$

$$CH_3COOCH_3 + CO \longrightarrow (CH_3CO)_2O \qquad -94.8\ \text{kJ/mol}\ (-22.7\ \text{kcal/mol})$$

Surprisingly, there is limited nonproprietary experimental data on methanol esterification with acetic acid (29). Studies have been confined to liquid-phase systems distant from equilibrium (30), in regions where hydrolysis is unimportant. A physical study of the ternary methanol–methyl acetate–water system is useful for design work (31). Methyl acetate and methanol form an azeotrope that boils at 53.8°C and contains 18.7% alcohol. An apparent methanol–water azeotrope exists, boiling at 64.4°C and containing ~2.9% water. These azeotropes seriously complicate methyl acetate recovery. Methyl acetate is quite soluble in water, and very soluble in water–methanol mixtures, hence two liquid phases suitable for decanting are seldom found.

The reaction mechanism and rates of methyl acetate carbonylation are not fully understood. In the nickel-catalyzed reaction, rate constants for formation of methyl acetate from methanol, formation of dimethyl ether, and carbonylation of dimethyl ether have been reported, as well as their sensitivity to partial pressure of the reactants (32). For the rhodium chloride [10049-07-7] catalyzed reaction, methyl acetate carbonylation is considered to go through formation of ethylidene diacetate (33):

$$2\ CH_3COOCH_3 + 2\ CO \longrightarrow 2\ (CH_3CO)_2O$$

$$2\ (CH_3CO)_2O + H_2 \longrightarrow CH_3CH(OOCCH_3)_2 + CH_3COOH$$

The role of iodides, especially methyl iodide, is not known. The reaction occurs scarcely at all without iodides. Impurities and coproducts are poorly reported in the patent literature on the process.

The catalyst system for the modern methyl acetate carbonylation process involves rhodium chloride trihydrate [13569-65-8], methyl iodide [74-88-4], chromium metal powder, and an alumina support or a nickel carbonyl complex with triphenylphosphine, methyl iodide, and chromium hexacarbonyl (34). The use of nitrogen-heterocyclic complexes and rhodium chloride is disclosed in one European patent (35). In another, the alumina catalyst support is treated with an organosilicon compound having either a terminal organophosphine or similar ligands and rhodium or a similar noble metal (36). Such a catalyst enabled methyl acetate carbonylation at 200°C under ~20 MPa (2900 psi) carbon

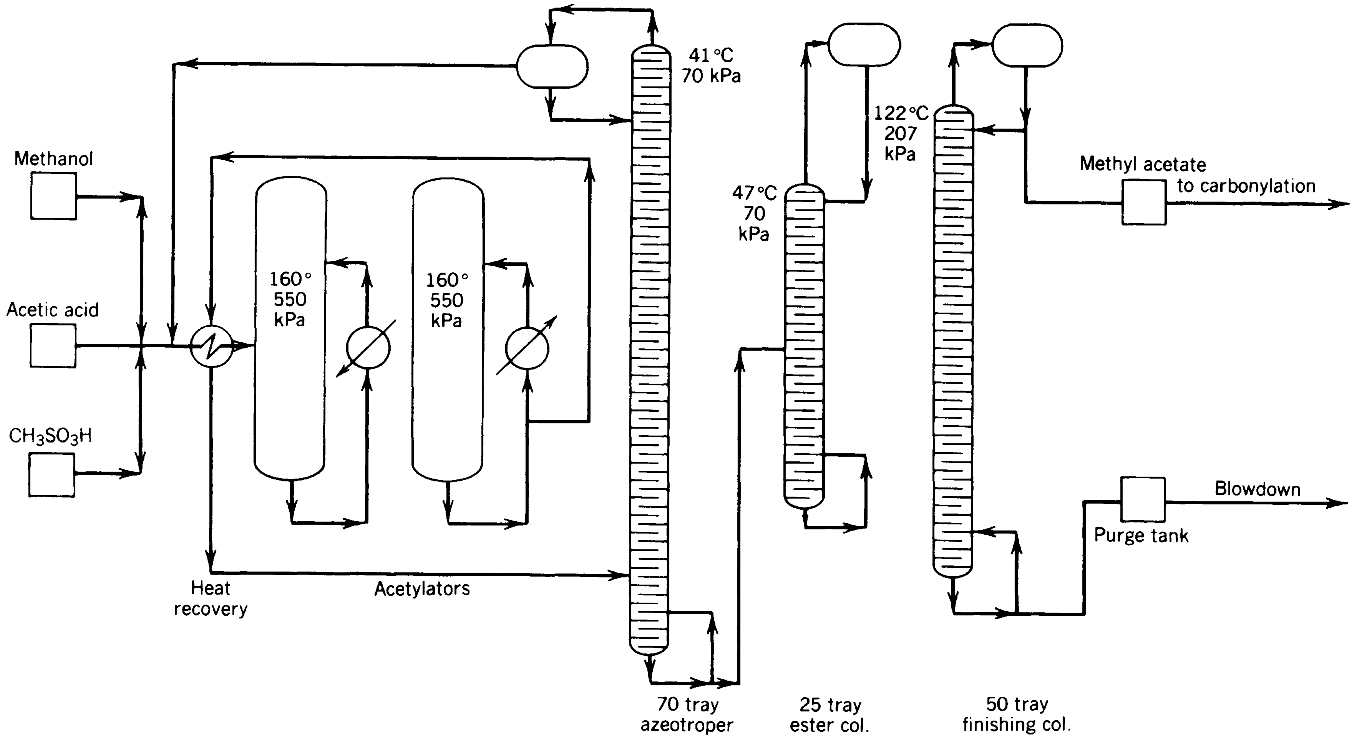


Fig. 1. Flow sheet for methyl acetate manufacture. To convert kPa to psi multiply by 0.145.

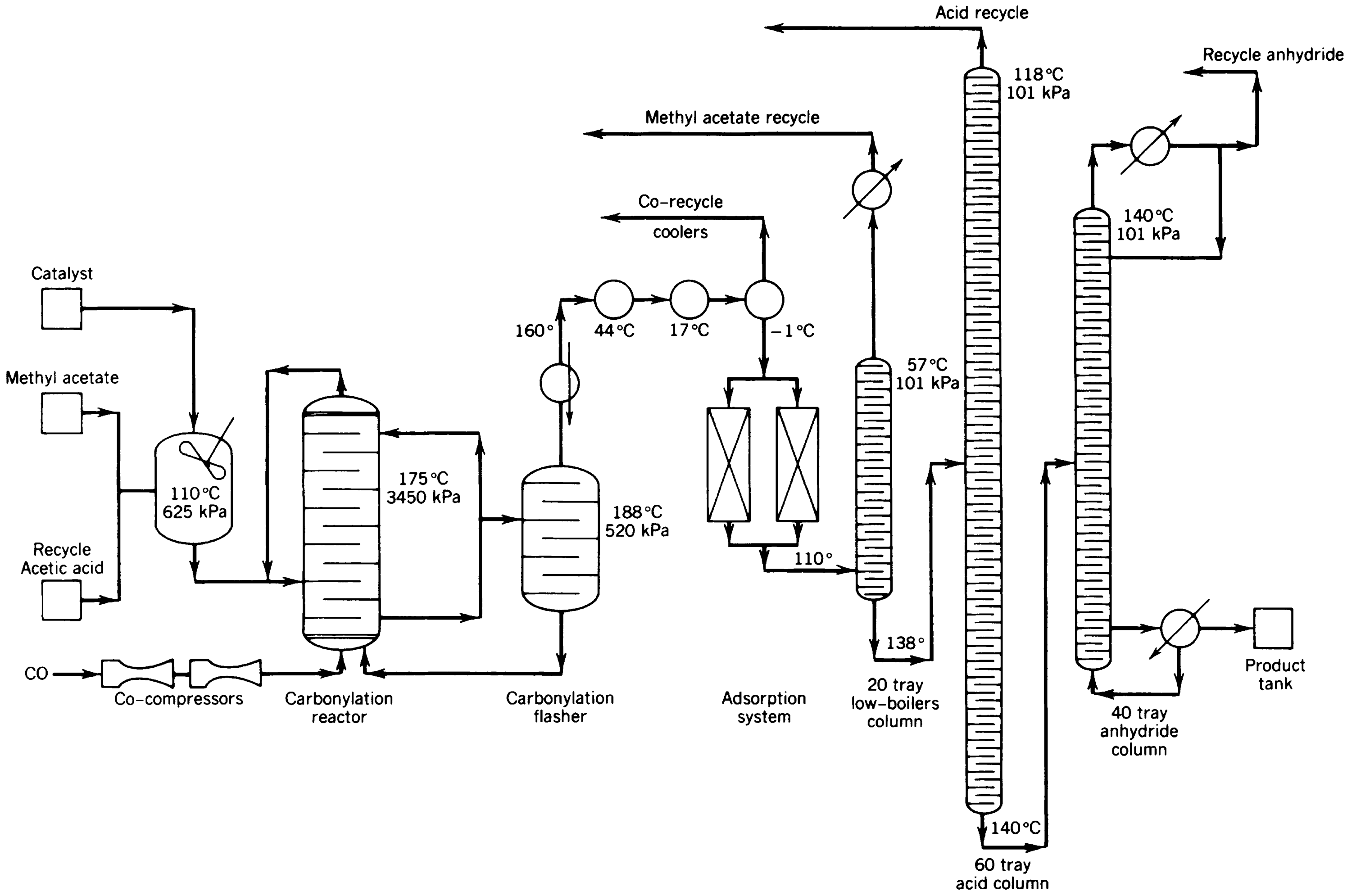


Fig. 2. Flow sheet for methyl acetate carbonylation to anhydride. To convert kPa to psi multiply by 0.145.

monoxide, with a space–time yield of 140 g anhydride per g rhodium per hour. Conversion was 42.8% with 97.5% selectivity. A homogeneous catalyst system for methyl acetate carbonylation has also been disclosed (37). A description of another synthesis is given where anhydride conversion is ~30%, with 95% selectivity. The reaction occurs at 445 K under 11 MPa partial pressure of carbon monoxide (37). A process based on a montmorillonite support with nickel chloride coordinated with imidazole has been developed (38). Other related processes for carbonylation to yield anhydride are also available (39,40).

The first anhydride plant in actual operation using methyl acetate carbonylation was at Kingsport, Tennessee (41). Infrared spectroscopy has been used to follow the apparent reaction mechanism (42).

The unit has virtually the same flow sheet (see Fig. 2) as that of methanol carbonylation to acetic acid (qv). Any water present in the methyl acetate feed is destroyed by recycle anhydride. Water impairs the catalyst. Carbonylation occurs in a sparged reactor, fitted with baffles to diminish entrainment of the catalyst-rich liquid. Carbon monoxide is introduced at ~15–18 MPa from centrifugal, multistage compressors. Gaseous dimethyl ether from the reactor is recycled with the CO and occasional injections of methyl iodide and methyl acetate may be introduced. Near the end of the life of a catalyst charge, additional rhodium chloride, with or without a ligand, can be put into the system to increase anhydride production based on net noble metal introduced. The reaction is exothermic, thus no heat need be added and surplus heat can be recovered as low pressure steam.

Catalyst recovery is a major operational problem because rhodium is a costly noble metal and every trace must be recovered for an economic process. Several methods have been patented (43–45). The catalyst is often reactivated by heating in the presence of an alcohol. In another technique, water is added to the homogeneous catalyst solution so that the rhodium compounds precipitate. Another way to separate rhodium involves a two-phase liquid such as the immiscible mixture of octane or cyclohexane and aliphatic alcohols having 4–8 carbon atoms. In a typical instance, the carbonylation reactor is operated so the desired products and other low boiling materials are flash-distilled. The reacting mixture itself may be boiled, or a sidestream can be distilled, returning the heavy ends to the reactor. In either case, the heavier materials tend to accumulate. A part of these materials is separated, then concentrated to leave only the heaviest residues, and treated with the immiscible liquid pair. The rhodium precipitates and is taken up in anhydride for recycling.

By-products remain unmentioned in most patents. Possibly there are none other than methyl acetate, acetic acid, and ethylidene diacetate, which are all precursors of anhydride.

In anhydride purification, iodide removal is of considerable significance; potassium acetate has been suggested for this procedure (46). A method for removing iodine from crude acetic anhydride has been patented (47). Because of the presence of iodide in the reaction system, titanium is the most suitable material of construction. Conventional stainless steel, SS-316, can be used for the acetylation of methanol, but it is unsuited for any part of the plant where halogen is likely to be present. Although such materials of construction add substantially to the capital cost of the plant, savings in energy consumed are expected to compensate. No authentic data on process efficiency has been published, but a rough estimate suggests a steam consumption of 1.9–2.0 kg/kg product anhydride.

3.4. Prospective Routes to Acetic Anhydride. Methyl acetate–dimethyl ether carbonylation seems to be the leading new route to acetic anhydride production (48). The high energy costs of older routes proceeding through ketene preclude their reintroduction. Thermolysis of acetone, methyl acetate, and ethylidene diacetate suffers from the same costly energy consumption. Acetic acid cracking, under vacuum and at atmospheric pressure, continues to be used for anhydride manufacture in spite of the clear obsolescence of the processes. The plants have high capital investment, and dismantling them demands a large economic advantage from any supplanting process.

Acetaldehyde oxidation to anhydride does not consume great amounts of energy. The strongly exothermic reaction actually furnishes energy and the process is widely used in Europe. Acetaldehyde must be prepared from either acetylene or ethylene. Unfortunately, use of these raw materials cancels the other advantages of this route. Further development of more efficient acetaldehyde oxidation as well as less expensive materials of construction would make that process more favorable.

Copper acetate, ferrous acetate, silver acetate [563-63-3], basic aluminum acetate,nickel acetate [373-02-4],cobalt acetate, and other acetate salts have been reported to furnish anhydride when heated. In principle, these acetates could be obtained from low concentration acetic acid. Complications of solids processing and the scarcity of knowledge about these thermolyses make industrial development of this process expensive. In the early 1930s, Soviet investigators discovered the reaction of dinitrogen tetroxide [10544-72-6] and sodium acetate [127-09-3] to form anhydride:

$$2\,\mathrm{NaOOCCH_3} + 2\,\mathrm{N_2O_4} \longrightarrow (\mathrm{CH_3CO})_2\mathrm{O} + 2\,\mathrm{NaNO_3} + \mathrm{N_2O_3}$$

Yields on the order of 85% were secured in the dry reaction (49). (Propionic anhydride and butyric anhydride can be obtained similarly from their sodium salts.) In as much as dinitrogen tetroxide can be regenerated, the economic prospects of this novel way of making anhydride are feasible.

Sodium acetate reacts with carbon dioxide in aqueous solution to produce acetic anhydride and sodium bicarbonate (50). Under suitable conditions, the sodium bicarbonate precipitates and can be removed by centrifugal separation. Presumably, the cold water solution can be extracted with an organic solvent, eg, chloroform or ethyl acetate, to furnish acetic anhydride. The half-life of aqueous acetic anhydride at 19°C is said to be no >1 h (2) and some other data suggests a 6 min half-life at 20°C (51). The free energy of acetic anhydride hydrolysis is given as -65.7 kJ/mol (-15.7 kcal/mol) (51) in water. In wet chloroform, an extractant for anhydride, the free energy of hydrolysis is strangely much lower, -50.0 kJ/mol (-12.0 kcal/mol) (52). Half-life of anhydride in moist chloroform may be as much as 120 min. Ethyl acetate, chloroform, isooctane, and *n*-octane may have promise for extraction of acetic anhydride. Benzene extracts acetic anhydride from acetic acid–water solutions (53).

Table 2. **North American Producers of Acetic Anhydride and Their Capacities**[a]

Producer	Capacity[a], $\times 10^3$ t ($\times 10^6$ lb)
Celanese, Narrows, Va.	118 (260)
Celanese, Pampa, Tex.	113 (250)
Celanese, Rock Hill, S.C.	113 (250)
Eastman, Kingsport, Tenn.	816 (1,800)
U.S. Total	*1,160 (2,560)*
Celanese, Cangrejera, Mexico	41 (90)
Celanese, Edmonton, Alberta	25 (55)
Other N. American Total	*66 (145)*
Total	*1,226 (2,705)*

[a] From Ref. 56, as of Feb. 19, 2001.

Ketene can be obtained by reaction of carbon oxides with ethylene (54). Because ketene combines readily with acetic acid, forming anhydride, this route may have practical applications.

4. Economic Aspects

Acetic anhydride is a mature commodity chemical in the United States. Exports are strong and have grown at the rate of 4.2% annually in recent years. Estimated demand for 2003 is 1.964×10^9 lb. Table 2 lists North American producers of acetic anhydride and their capacities. Prices for the period 1994–1999 were a high of 49.5 ¢/lb and a low of 47.5 ¢/lb. The price in February of 2001 was 49.5 ¢/lb. All prices quoted are per pound, tanks, delivered, East (55).

5. Analysis and Specifications

Analytical and control methods for acetic anhydride are fully discussed in reference 56. Performance tests are customarily used where the quality of the product is crucial, as in food or pharmaceutical products. Typical specifications are:

assay	99.0 wt% as anhydride
specific gravity$^{20}{}_{20}$	1.080–1.085
color, Pt–Co	10 max
$KMnO_4$ time	5 min needed to reduce 2 mL having no more than 0.1 mL of 0.1 *N* $KMnO_4$.
trace ions	> 1 ppm Al, Cl, PO_4^{3-}, SO_4^{2-}, and Fe.
heavy metals	none
nitrates	none

A technical quality anhydride, assay ~97% maximum, often contains color bodies, heavy metals, phosphorus, and sulfur compounds. Anhydride manufactured by acetic acid pyrolysis sometimes contains ketene polymers, eg, acetylacetone, diketene, dehydroacetic acid, and particulate carbon, or soot, is occasionally encountered. Polymers of allene, or its equilibrium mixture, methylacetylene–allene, are reactive and refractory impurities, which if exposed to air, slowly autoxidize to dangerous peroxidic compounds.

Anhydride has been used for the illegal manufacture of heroin [561-27-3] (acetylmorphine) and certain other addictive drugs. Regulations on acetic anhydride commerce have long been a feature of European practice. After passage in 1988 of the Chemical Diversion and Trafficking Act, there is also U.S. control. Orders for as much as 1023-kg acetic anhydride, for either domestic sale or export, require a report to the Department of Justice, Drug Enforcement Administration (57).

6. Health and Safety Aspects

Acetic anhydride penetrates the skin quickly and painfully forming burns and blisters that are slow to heal. Anhydride is especially dangerous to the delicate tissues of the eyes, ears, nose, and mouth. The odor threshold is 0.49 mg/m^3, but the eyes are affected by as little as 0.36 mg/m^3 and electroencephalogram patterns are altered by only 0.18 mg/m^3. When handling acetic anhydride, rubber gloves that are free of pinholes are recommended for the hands, as well as plastic goggles for the eyes, and face-masks to cover the face and ears.

Acetic anhydride is dangerous in combination with various oxidizing substances and strong acids. Chromium trioxide [1333-82-0]and anhydride react violently to burn (58); mixtures containing nitric acid [7692-37-2] are said to be more sensitive than nitroglycerin (59). Thermal decomposition of nitric acid in acetic acid solutions is accelerated by the presence of anhydride (60). The critical detonation diameter for a nitric acid–acetic anhydride mixture has been subject to much study in the Soviet Union (61). The greatest explosion involving anhydride took place when a mixture of 568 L perchloric acid [7601-90-3] were admixed with 227 L of acetic anhydride. The mixture detonated, killing 17 people and destroying 116 buildings over several city blocks (62). The plant was an illegal metal-treating facility where the mixture was used to finish aluminum surfaces. Acetyl perchlorate is probably present in such solutions. These perchloric acid solutions are useful in metal finishing, but the risks in using them must be recognized. Such solutions are used commonly in metallography.

U.S. exposure standards for acetic anhydride are as follows: Primary bases, Current OSHA PEL, 5 ppm TWA; 1989 OSHA proposed PEL, and NIOSH REL; both 5 pp ceiling (63).

7. Uses

The biggest use of acetic anhydride is in the preparation of cellulose acetates (86%). Acetates produced include cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose acetate propionate, and cellulose butyrate. The remaining 14% is consumed in miscellaneous uses including coatings, pesticides, aspirin, and acetaminophen (55).

Acetic anhydride is used in acetylation processes. There has been some diversification of anhydride usage in recent years. Acetylation of salicylic acid

[69-72-7] using anhydride to furnish acetylsalicyclic acid [50-78-2] (aspirin) is a mature process, although *N*-acetyl-*p*-aminophenol (acetaminophen) is currently making inroads on the aspirin market. Acetic anhydride is used to acetylate various fragrance alcohols to transform them into esters having much higher unit value and vitamins are metabolically enhanced by acetylation. Anhydride is also extensively employed in metallography, etching, and polishing of metals, and in semiconductor manufacture. Starch acetylation furnishes textile sizing agents.

Acetic anhydride is a useful solvent in certain nitrations, acetylation of amines and organosulfur compounds for rubber processing, and in pesticides. Though acetic acid is unexceptional as a fungicide, small percentages of anhydride in acetic acid, or in cold water solutions are powerful fungicides and bactericides. There are no reports of this application in commerce. It is possible that anhydride may replace formaldehyde for certain mycocidal applications.

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