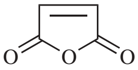
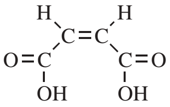
MALEIC ANHYDRIDE, MALEIC ACID, AND FUMARIC ACID

1. Introduction

Maleic anhydride [108-31-6] (**1**), maleic acid [110-16-7] (**2**), and fumaric acid [110-17-8] (**3**) are multifunctional chemical intermediates that find applications in nearly every field of industrial chemistry. Each molecule contains two acid carbonyl groups and a double bond in the α, β-position.



(**1**)



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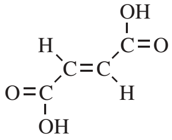


(**3**)

Maleic anhydride and maleic acid are important raw materials used in the manufacture of phthalic-type alkyd and polyester resins, surface coatings, lubricant additives, plasticizers (qv), copolymers (qv), and agricultural chemicals (see Alkyd resins; Polyesters, unsaturated; Lubrication and lubricants). Both chemicals derive their common names from naturally occurring malic acid [6915-15-7]. Other names for maleic anhydride are 2,5-furandione, dihydro-2,5-dioxofuran, toxilic anhydride, and *cis*-butenedioic anhydride. Maleic acid is also called (*Z*)-2-butenedioic acid, toxilic acid, malenic acid, or *cis*-1,2-ethylenedicarboxylic acid.

Fumaric acid occurs naturally in many plants and is named after *Fumaria officinalis*, a climbing annual plant, from which it was first isolated. It is also known as (*E*)-2-butenedioic acid, allomaleic acid, boletic acid, lichenic acid, or *trans*-1,2-ethylenedicarboxylic acid. It is used as a food acidulant and as a raw material in the manufacture of unsaturated polyester resins, quick-setting inks, furniture lacquers, paper sizing chemicals, and aspartic acid [56-84-8].

Maleic anhydride and the two diacid isomers were first prepared in the 1830s (1) but commercial manufacture did not begin until a century later. In 1933, the National Aniline and Chemical Co., Inc., installed a process for maleic anhydride based on benzene oxidation using a vanadium oxide catalyst (2). Maleic acid was available commercially in 1928 and fumaric acid production began in 1932 by acid-catalyzed isomerization of maleic acid.

2. Physical Properties

Physical constants (3–25) for maleic anhydride, maleic acid, and fumaric acid including solid and solution properties are given in Tables 1–3. From single-crystal X-ray diffraction data (10, maleic anhydride is a nearly planar molecule with the ring oxygen atom lying 0.003 nm out of the molecular plane. A twofold rotation axis bisects the double bond and passes through the ring oxygen atom. Figure 1 summarizes the bond distance for maleic anhydride (10). Similar bond distances and angles for maleic anhydride were obtained using electron diffraction (11) and double-resonance modulation microwave spectroscopic (12) techniques. Values of the Raman polarizability were reported for single crystals of maleic anhydride (13). Density functional theory has been applied to maleic anhydride to give optimized geometry, harmonic vibrational frequencies, and electron affinity (14).

Maleic and fumaric acids have physical properties that differ owing to the cis and trans configurations about the double bond. Aqueous dissociation constants and solubilities of the two acids show variations attributable to geometric isomer effects. X-ray diffraction results for maleic acid (15) reveal an intramolecular hydrogen bond that accounts for both the ease of removal of the first carboxyl proton and the smaller dissociation constant for maleic acid compared to fumaric acid. Crystals of maleic acid usually form as twins owing to the presence of lattice pseudosymmetries (16). Two crystal forms are known for fumaric acid with the monoclinic form (often also twinned) obtained by evaporation from solution (17). The triclinic form, β-fumaric acid, is formed through sublimation at 130°C under reduced pressure (18). Both maleic and fumaric acids are planar molecules with packing within the lattice into extended chains in which carboxyl groups interlink by $O{-}H\cdots O$ bonds into cyclic pairs (19). Maleic acid isomerizes to fumaric acid with a derived heat of isomerization of −22.7 kJ/mol (−5.43 kcal/mol) (21). The activation energy for the conversion of maleic to fumaric acid is 66.1 kJ/mol (15.8 kcal/mol) (22).

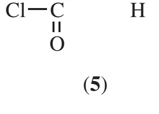
3. Chemical Properties

The *General References* and two other reviews (20,26) provide extensive descriptions of the chemistry of maleic anhydride and its derivatives. The broad industrial applications for this chemistry derive from the reactivity of the double bond in conjugation with the two carbonyl oxygens.

3.1. Acid Chloride Formation.

Monoacid chlorides of maleic and fumaric acid are not known. Treatment of maleic anhydride or maleic acid with various reagents such as phosgene [75-44-5] (qv), phthaloyl chloride [88-95-9], phosphorus pentachloride [10026-13-8], or thionyl chloride [7719-09-7] gives 5,5-dichloro-2(5*H*)furanone [133565-92-1] (**4**) (27). Similar conditions convert fumaric acid to fumaryl chloride [627-63-4] (**5**) (27,28). Noncyclic maleyl chloride [22542-53-6] (**6**) forms in 11% yield at 220°C in the reaction of 1 mol of maleic anhydride with 6 mol of carbon tetrachloride [56-23-5] over an activated carbon [7440-44-4] catalyst (29).


(**4**)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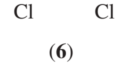
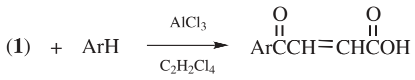

(**6**)

3.2. Acylation.

In chlorinated solvents, maleic anhydride reacts with aromatic hydrocarbons (ArH) in the presence of aluminum chloride [7446-70-0],

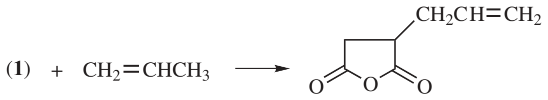
$AlCl_3$, to form β-aroylacrylic acids (30).



$$(\mathbf{1}) + \mathrm{ArH} \xrightarrow[\mathrm{C_2H_2Cl_4}]{\mathrm{AlCl_3}} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH}$$

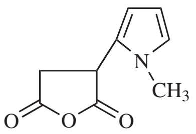
Under Friedel–Crafts conditions, *trans*-1,2-dibenzoylethylene [959-28-4] is synthesized by the reaction of 1 mol of fumaryl chloride with 2 mol of benzene (31) (see FRIEDEL–CRAFTS REACTIONS).

3.3. Alkylation. Maleic anhydride reacts with alkene and aromatic substrates having a C–H bond activated by α,β-unsaturation or an adjacent aromatic resonance (32,33) to produce the following succinic anhydride derivatives:



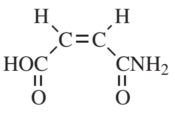
Typical reaction conditions are 150–300°C and up to 2-MPa pressure. Polyalkenyl succinic anhydrides are prepared under these conditions by the reaction of polyalkenes in a nonaqueous dispersion of maleic anhydride, mineral oil, and surfactant (34).

N-Alkylpyrroles react with maleic anhydride to give the electrophilic substitution product (**7**) and not the Diels–Alder addition product found for furan and thiophene compounds (35). However, the course of this reaction can be altered by coordination of the pyrrole compound to a metal center.



(**7**)

3.4. Amidation. Reaction of maleic anhydride or its isomeric acids with ammonia [7664-41-7] (qv), primary amines (qv), and secondary amines produces mono- or diamides and is called amidation. The monoamide derivative from the reaction of ammonia and maleic anhydride is called maleamic acid [557-24-4] (**8**). Another monoamide derivative formed from the reaction of aniline [62-53-3] and maleic anhydride is maleanilic acid [555-59-9] (**9**).



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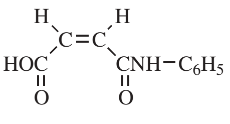
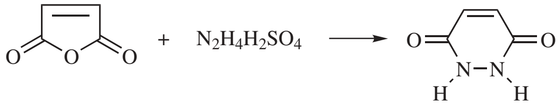


(**9**)

The reactions of primary amines and maleic anhydride yield amic acids that can be dehydrated to imides, polyimides (qv) or isoimides depending on the reaction conditions (36–38). However, these products require multistep processes.

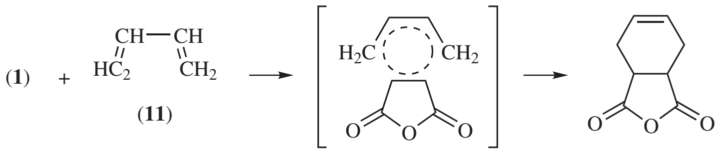
Pathways with favorable economics are difficult to achieve. Amines and pyridines decompose maleic anhydride, often in a violent reaction. Carbon dioxide [124-38-9] is a typical end product for this exothermic reaction (39).

Maleic hydrazide [123-33-1] (**10**) is one of a number of commercial agricultural chemicals derived from maleic anhydride. Maleic hydrazide was first prepared in 1895 (40) but ~60 years elapsed before the intermediate products were elucidated (41).



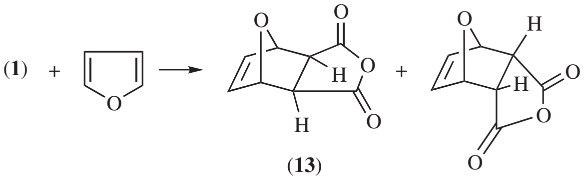
(**10**)

3.5. Concerted Nonpolar Reactions. Maleic anhydride exemplifies the model dienophile for cycloaddition with dienes such as 1,3-butadiene [106-99-0] (**11**) (42). Tetrahydrophthalic anhydride [85-43-8] (**12**) or its derivatives are produced in this Diels–Alder reaction.



(**12**)

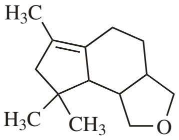
The success of the cycloaddition reaction of maleic anhydride varies greatly depending on which heterocyclic diene is used. The cycloaddition of maleic anhydride to furan [110-00-9] occurs in a few seconds under ambient conditions (43,44). Although the endo adduct (**14**) is favored kinetically, the exo adduct (**13**) is isolated.



(**13**) (**14**)

Endo adducts are usually favored by interactions between the double bonds of the diene and the carbonyl groups of the dienophile. As mentioned in the section on alkylation, the reaction of pyrrole compounds and maleic anhydride results in a substitution at the 2-position of the pyrrole ring (35,45). Thiophene [110-02-1] forms a cycloaddition adduct with maleic anhydride but only under severe pressures and ~100°C (46). Addition of electron-withdrawing substituents about the double bond of maleic anhydride increases rates of cycloaddition. Both α-(carbomethoxy) maleic anhydride [69327-00-0] and α-(phenylsulfonyl) maleic anhydride [120789-76-6] react with 1,3-dienes, styrenes, and vinyl ethers much faster than tetracyanoethylene [670-54-2] (47).

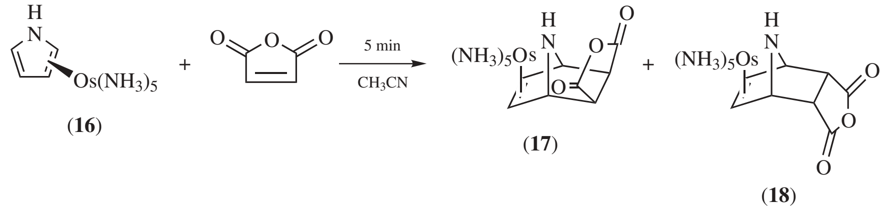
Other Diels–Alder Reactions. Since maleic anhydride, its two isomeric acids, and the alkyl- or aryl-substituted acid derivations readily form Diels–Alder adducts, vegetable oil lipids such as soybean oil react in Diels–Alder fashion with these maleic or fumaric compounds to form an important class of emollients used in human skin and hair preparations (48). The preferred adduct in this class is maleated soybean oil. It is used for both cleansing and lathering properties as well as mildness and skin conditioning (49–52). Generally, dienophiles such as maleic and fumaric compounds react readily in Diels–Alder type reactions, but in 1999 use of solid Lewis acid catalysts was disclosed (53) for reaction of maleic acid and fumaric dienophiles with dienes such as cyclopentadiene, acrolein, furan, 4-methoxyisoxazole, and related compounds. Perfumes having a "woody odor" form from the Diels–Alder reaction of maleic anhydride with pure isomers of trimethylvinyl cyclopentenes (54). Two further reactions of the Diels–Alder adduct involving adduct reduction to the diol followed by dehydrating cyclization of the diol form the 11-oxa-tricyclo[7.3.0.0^{2,6}]dodecene derivative (**15**). Compound (**15**) and four double-bond isomers represent a class of woody fragrance compounds in which the tetrahydrofuran (thf) ring adopts a trans configuration. Studies on regio- and stereochemical structural assignments of Diels–Alder adducts with maleic anhydride continue to be reported (55).



(**15**)

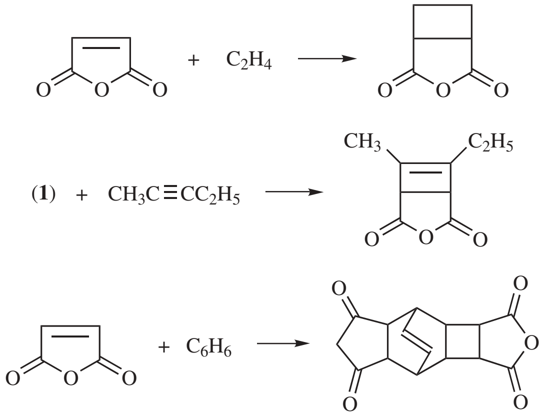
The reaction between coal and maleic anhydride has been known for over 20 years (56), but the identity of the reactive functional groups in coal has remained a mystery. Recently, convincing evidence has been presented that suggests diene groups in coal react by way of Diels–Alder reactions to form maleic anhydride adducts. Solid-state ^{13}C nmr data on the maleic anhdyride–coal adduct support the Diels–Alder reaction, although elemental analysis shows higher maleic anhydride content in the adduct than can be accounted for solely by diene groups in the coal. Nevertheless, all other possible reactions of maleic anhydride with coal were excluded, including the ene reaction, polymerizations, ester formation from maleic anhydride, radical addition, Michael addition, election-transfer interaction (charge-transfer complex), and physical entrapment. While this study (57) appears to solve the mystery behind the maleic anhydride–coal reaction, it challenges current coal structures and invites further work.

Metal-Induced Cycloadditions. The effect of coordination on the metal-induced cycloadditions of maleic anhydride and the isostructural heterocycles furan, pyrrole, and thiophene has been investigated (58). Each heterocycle is bound to an Os(II) center in the complex $[(NH_3)_5Os(2,3\text{-}\eta^2\text{-L})]^{2+}$, where L =furan, pyrrole, and thiophene. Although neither the furan nor thiophene complexes react with maleic anhydride over a period of 10 days, the pyrrole complex (**16**) reacts rapidly at room temperature and 101.3 kPa to form a mixture of endo (**18**) and exo (**17**) complexes. An azomethine ylide intermediate was postulated as the key intermediate through which maleic anhydride added to the 2- and 5-positions of the coordinated pyrrole ring.

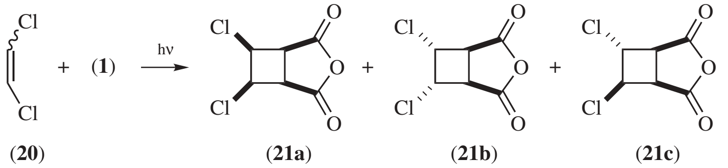


2 + 2 Cycloadditions. Cyclobutene adducts are formed from the reaction of acetylenic derivatives and maleic anhydride through a 2 + 2 cycloaddition (59). The reaction is photochemically catalyzed (see PHOTOCHEMICAL TECHNOLOGY, SURVEY).

Cyclobutane derivatives are formed after exposing a mixture of alkenes and maleic anhydride to light. Photoadducts are formed by reaction of maleic anhydride with ethylene [74-85-1] (60) and benzene (61).

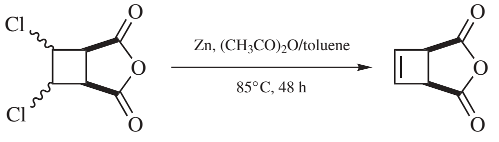


A new two-step route to *cis*-cyclobut-3-ene-1,2-dicarboxylic anhydride (**19**) has been described that uses [2 + 2] photochemical cycloaddition between (*E*)-1,2-dichloroethene (**20**) and maleic anhydride (62).



Compound (**21**) is a mixture of these dichloro isomers [**21a**=(1*R**, 2*S**, 3*R**, 4*S**); **21b**=(1*R**, 2*S**, 3*S**, 4*R**); **21c**=(1*R**, 2*S**, 3*R**, 4*R**)] that in ethyl acetate solvent are produced in 85% yield in the amounts of 18% (**21a**), 44% (**21b**), and 38%

(**21c**). Reductive chlorine elimination of **21** with activated zinc in acetic anhydride/toluene solution gives (**19**) in 80% yield.



(**21a**–c) (**19**)

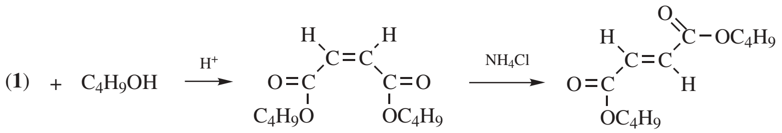
Ene Reaction. Maleic anhydride and maleate and fumarate esters participate in thermal ene reactions (63) with alkenes having an allylic hydrogen. An ene reaction is the thermal reaction of an alkene having an allylic hydrogen (an ene) with a compound containing a double or triple bond to form a new bond with migration of the ene double bond and 1,5-hydrogen shift. Alkenylsuccinic anhydrides are produced. ^{13}C nmr spectroscopy has been used to determine regioselectivity, selectivity for endo and exo, and selectivity for cis and trans in the reaction (200°C, 16 h) of maleic anhydride with the nine linear decene isomers (64). The results show a slight preference for maleic anhydride addition to the least hindered end of the decene isomer. Similar reaction conditions were used to form ene adducts with mono- and disubstituted oligoisobutylenes (65,66).

3.6. Decomposition and Decarboxylation. Maleic anhydride undergoes anaerobic thermal decomposition in the gas phase in a homogeneous unimolecular reaction to give carbon monoxide, carbon dioxide, and acetylene [74-86-2] in equimolar amounts. The endothermic [$\Delta H = +142$ kJ/mol (33.9 kcal/mol)] decomposition was studied in a quartz tube with and without quartz packing in the temperature range of ~370–490°C (67). The same linear Arrhenius plot was obtained for packed and unpacked reaction vessels. The same decomposition products were found during photolysis between 220 and 350 nm (67). Catalysts alter the decomposition profile for maleic anhydride. The decomposition of maleic acid in an aqueous solution over a bed of Y zeolite which contains copper and sodium at ~200°C, occurs with 95% conversion. The selectivity of the zeolite catalyst to acrylic acid [79-10-7] is 91%.

Maleic anhydride is decomposed in the liquid phase by various nitrogen bases. Treatment of maleic anhydride in refluxing acetic acid with 2-aminopyridine [504-29-0] gives, after work up in 4 N H_2SO_4 at 100°C, the decarboxylative dimerization product, 2,3-dimethylmaleic anhydride [766-39-2] (75% yield), and CO_2 (68). Homopolymers of maleic anhydride form in the liquid phase upon addition of pyridine [110-86-1] (69,70). At a maleic anhydride/pyridine ratio of 1.64 in acetone solution at 25°C, reproducible oligomers having molecular weights of 400–700 are formed (70). Exothermic decomposition of maleic anhydride can occur with amines and alkali (39,69). Explosions can result from this reaction (39).

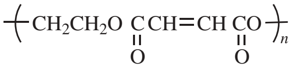
3.7. Electrophilic Addition. Electrophilic reagents attack the electron-deficient bond of maleic anhydride (26). Typical addition reagents include halogens, hydrohalic acids, and water.

3.8. Esterification. Both mono- and dialkyl maleates and fumarates are obtained on treatment of maleic anhydride or its isomeric acids with alcohols or alkoxides (26). An extensive review is available (71). Alkyl fumarates (22) often are made from isomerization of the corresponding maleate (**23**) (72).



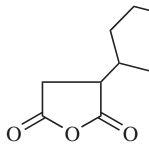
(**23**) (**22**)

Glycols and epoxides react with maleic anhydride to give linear unsaturated polyesters (73,74). Ethylene glycol and maleic anhydride combine to form the following repeating unit. This reaction is the first step in industrially important polyester resin production (see POLYESTERS, UNSATURATED).



$$\left(\mathrm{CH_2CH_2O}\,\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH{=}CH}\,\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{O}\right)_n$$

3.9. Free-Radical Reactions. Free-radical reactions of maleic anhydride are important in polymerizations and monomer synthesis. Nucleophilic radicals such as the one from cyclohexane [110-82-7] serve as hydrogen donors that add to maleic anhydride at the double bond to form cyclohexylsuccinic anhydride [5962-96-9] (**24**) (75).



(**24**)

Free-radical reaction rates of maleic anhydride and its derivatives depend on polar and steric factors. Substituents added to maleic anhydride that decrease planarity of the transition state decrease the reaction rate. The reactivity decreases in the order maleic anhydride > fumarate ester > maleate ester.

3.10. Grignard-Type Reactions. Grignard reagents provide nucleophilic addition to the maleyl carbonyl groups, but yields are often poor (26). Phenyl addition to dimethyl maleate has been demonstrated with a palladium-based catalyst system (75). A solution of dimethyl maleate, iodobenzene [591-50-4], triethylamine [121-44-8], and palladium diacetate [19807-27-3] (1 mol%) in acetonitrile [75-05-8] after reflux for 5 h gives 39% (*Z*)-dimethyl phenylmaleate [29576-99-6] and 54% (*E*)-dimethyl phenylmaleate [29394-47-6] without loss of unsaturation.

3.11. Halogenation. Halogens add directly to the double bond of maleic anhydride to give dihalosuccinic acids. However, different procedures are used for dihalomaleic anhydride derivatives. Fluorinated C_4 substrates offer access to difluoromaleic anhydride [669-78-3] (76,77). Hexafluoro-2,5-dihydrofuran [24849-02-3] is distilled into sulfur trioxide [7446-11-9] at 25°C. Addition of trimethyl borate [121-43-7] initiates a reaction that upon heating and distillation leads to a 53% yield of difluoromaleic anhydride. The molecular structure of difluoromaleic anhydride has been determined by both gas-phase electron diffraction and microwave spectroscopy (78). Structural and theoretical data within the dihalomaleic anhydride series (X=xF, Cl, or Br) indicate an interplay between steric and electronic effects such that neither effect accounts for the observed bond distances and angles (78). Dichloromaleic anhydride [1122-17-4] can be prepared with 92% selectivity by oxidation of hexachloro-1,3-butadiene [87-68-3] with SO_3 in the presence of iodine-containing molecules (79). Passing vaporized hexachlorobutadiene over a vanadium–phosphorus oxide catalyst also gives dichloromaleic anhydride (80). A benzene solution of tetrabromofuran [32460-09-6] can be photooxidized to dibromomaleic anhydride [1122-12-9] in 85% yield with ultraviolet (uv) light (81). Radical chain mechanisms are suggested.

3.12. Hydration and Dehydration. Maleic anhydride is hydrolyzed to maleic acid with water at room temperature (82). A process has been reported for continuous hydration of maleic anhydride at a constant temperature near 65°C in a continuous stirred tank reactor (83). By limiting the aqueous maleic anhydride acid concentration to 40% and the temperature to <85°C, fumaric acid will not form in >0.1% be weight of the reaction mixture. Catalysts enhance formation of fumaric acid from maleic anhydride hydrolysis through maleic acid isomerization.

Hydration of fumaric acid proceeds at high temperatures and pressures to give DL-malic acid [6915-15-7], $HOOCCH_2CHOHCOOH$ (26).

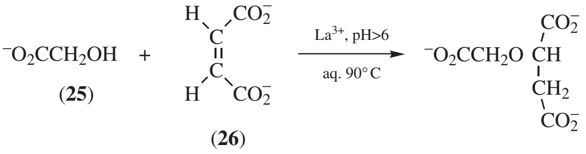
Maleic acid can be thermally dehydrated to maleic anhydride (84), dehydrated from aqueous solution (85–87), or dehydrated through azeotropic distillation. Solvents such as xylenes (88) or dibutyl phthalate [84-74-2] (89) are preferred, but conditions must be carefully adjusted to avoid isomerization to fumaric acid.

3.13. Hydroformylation. Esters of maleate and fumarate are treated with carbon monoxide and hydrogen in the presence of appropriate catalysts to give formyl derivatives. Dimethyl fumarate [624-49-7] is hydroformylated in 1:1 CO/H_2 at 100°C and 11.6-MPa pressure with a cobalt [7440-48-4] catalyst to give an 83% yield of dimethyl formylsuccinate [58026-12-3] product (90).

3.14. Isomerization. Production of maleic anhydride readily gives maleic acid by controlled hydrolysis. To avoid isomerization of maleic acid to fumaric acid, maleic acid processing must avoid conditions favorable for fumaric acid formation. Maleic acid is isomerized to fumaric acid by both thermal treatment and a variety of catalytic species. An historical account of geometric isomerism of maleic and fumaric acids is given by Ihde (91). Isomerization of maleic acid occurs above the 130–140°C melting point range but below ~230°C, at which point fumaric acid is dehydrated to maleic anhydride. Derivatives of maleic acid such as acid esters can also be isomerized. Kinetic data are available for the isomerization of the cis-to-trans diacids in the absence of a catalyst (92,93), in the presence of thiourea catalyst (94,95), and in the presence of both thiourea catalyst and ultrasound (95). The data suggest that neither carbonium ion nor succinate intermediates are involved in the isomerization. Rather, conjugate addition to the double bond imparts sufficient single bond character to afford rotation about the central C−C bond of the diacid (96). Highly polar solvents such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) facilitate cis-to-trans isomerization in the presence of 4,4′-bipyridine (97). No isomerization of maleic acid occurs in DMF or DMSO in the absence of 4,4′-bypyridine.

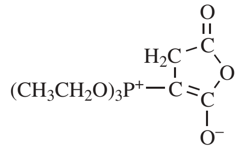
3.15. Ligation-to-Metal Atoms. Maleic anhydride and its diacid isomers coordinate to metal atoms through either the double bond or the carboxylate oxygen atoms when the diacid is deprotonated. Generally, low valent (soft) metals prefer coordination to the double bond, while high valent (hard) metals coordinate through the carboxylate oxygen atoms of the deprotonated diacids (98). Examples of double-bond coordination in maleic anhydride, maleic acid, and fumaric acid include molybdenum bis(maleic anhydride) carbonyl complex, $Mo(CO)_2(2,3\text{-}\eta^2\text{-}C_4H_2O_3)_2(CH_3CN)_2$ (99), the *endo*- and *exo*- (*R*,*R*) palladium(L) $(2,3\text{-}\eta^2\text{-}C_4H_2O_3)$ complexes of maleic anhydride where L is 1-diphenylphosphino-2,1′-(1-dimethylaminopropanediyl)ferrocene (100); the singly deprotonated maleic acid complex of Cu(I), $Cu(2,3\text{-}\eta^2\text{-}C_4H_4O_4)\cdot H_2O$ (101); *cis*-tetracarbonyl (2-3-η^2-maleic acid) iron complex, $Fe(2,3\text{-}\eta^2\text{-}C_4H_4O_4)(CO)_4$ (102), and *trans*-tetracarbonyl (2-3-η^2-fumaric acid) iron complex, $Fe(2,3\text{-}\eta^2\text{-}C_4H_4O_4)(CO)_4$ (102). These structures were determined by single-crystal X-ray diffraction data. In the case of the Mo(0) complex, the trans-coordinated maleic anhydride molecules are almost mutually orthogonal (85.2°) to one another. 2,3-η^2-Maleic anhydride coordinated to Mo(0) has a central C−C bond length of 0.1420 nm (99) vs a C−C double-bond length of 0.1303 nm for maleic anhydride (10–12). This increase in the central C−C bond length suggests significant π-backbonding interaction (98). The 2,3-η^2-maleic acid in the Cu(I) hydrogen maleate complex (101) shows the same trend with a central C−C bond length of 0.1405 nm (10). Singly deprotonated maleic acid coordinates through symmetrical carboxylate oxygens to Zn(II) in the structure of the zinc maleic acid complex, $Zn(O_2CCH{=}CHCO_2H)_2\cdot 4H_2O$ (103); through both symmetrical carboxylate oxygen atoms and the C=C bond to Cu(I) in Cu $(\eta^2\text{-}C_4H_4O_4)\cdot H_2O$ (101); through bridging carboxylate oxygen atoms (O−C−O) in the Ag(I) complex, $Ag(O_2CCH{=}CO_2H)$ (104); and through only one carboxylate oxygen atom in the Sb(V) complex $(H_5C_6)_4Sb{-}[OC(O)CH{=}CHCO_2H]$ (105). Hydrogen bonding in crystals of maleic and fumaric acid is remarkably similar in the organometallic complexes of $(2,3\text{-}\eta^2\text{-}C_4H_4O_4)Fe(CO)_4$ (106), where $C_4H_4O_4$ is either maleic or fumaric acid (102). The maleate dianion coordinates to a single metal center in the Be(II) complex, $K_2[Be(C_4H_4O_4)_2]\cdot H_2O$ (107). In contrast, the coordinatively saturated $Sb(C_6H_5)_4^+$ species affords maleate bonding through only a single carboxylate oxygen atom resulting in a bridging maleate dianion between two Sb(V) centers in the compound bis(tetraphenylantimonium) maleate (105).

3.16. Nucleophilic Addition. Nucleophilic reagents attack the β-carbon position in the conjugated maleic and fumaric frameworks. Basic reaction conditions favor these condensations for the addition of glycolate (**25**) to maleate [142-44-9] (**26**):



This Michael-type addition is catalyzed by lanthanum (III) [16096-89-2] (108). Ethylene glycol [107-21-1] reacts with maleate under similar conditions (109). A wide range of nucleophilic reagents add to the maleate and fumarate frameworks including alcohols, ammonia, amines, sulfinic acids, thioureas, Grignard reagents, Michael reagents, and alkali cyanides (**26**).

Thiols and phosphines add to maleic anhydride to give α-thiosuccinic anhydrides (110) and phosphoranylidene–maleic anhydride adducts (111). Triethyl phosphite [122-52-1] reacts with maleic anhydride to give the ylide structure (**27**) (112). Hydrolysis of this adduct (**27**) leads to succinic acid [110-15-6], maleic acid, triethyl phosphate [78-40-0], and diethyl phosphite [762-04-9].



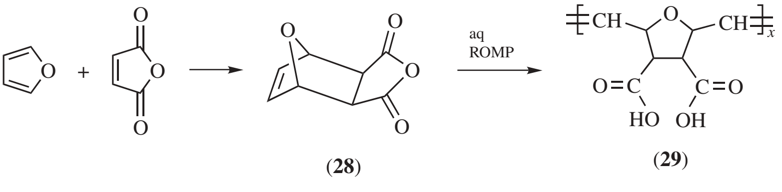
(**27**)

3.17. Oxidation. Maleic and fumaric acids are oxidized in aqueous solution by ozone [10028-15-6] (qv) (113). Products of the reaction include glyoxylic acid [298-12-4], oxalic acid [144-62-7], and formic acid [64-18-6]. Catalytic oxidation of aqueous maleic acid occurs with hydrogen peroxide [7722-84-1] in the presence of sodium tungstate(VI) [13472-45-2] (114) and sodium molybdate(VI) [7631-95-0] (115). Both catalyst systems avoid formation of tartaric acid [133-37-9] and produce *cis*-epoxysuccinic acid [16533-72-5] at pH values >5. The reaction of maleic anhydride and hydrogen peroxide in an inert solvent (methylene chloride [75-09-2]) gives permaleic acid [4565-24-6], HOOC–CH=CH–CO_3H (116) which is useful in Baeyer–Villiger reactions. Both maleate and fumarate [142-42-7] are hydroxylated to tartaric acid using an osmium tetroxide [20816-12-0]/iodate [15454-31-6] catalyst system (117).

3.18. Polymerization. Maleic anhydride, which contains a double bond and an anhydride group, is used in both addition and condensation polymerization schemes. Research since the early 1960s has shown that homopolymerization occurs using γ and uv radiation, free-radical initiators, pyridine bases, and electrochemical initiation. Although the polymerization mechanism is unknown, in 1997 poly(maleic acid) was shown by means of ^{13}C nmr spectroscopy (118) to arise from poly(maleic anhydride) in which racemic (maleic anhydride groups oriented in a cis configuration across the backbone carbon chains) propagation is preferred by about a factor of two over mesomeric propagation. Melt functionalization of polypropylene has shown homopolymerization of maleic anhydride occurs up to 190°C, ~30°C higher than had been thought possible (119).

Copolymers of maleic anhydride and its isomeric acids (or ester derivatives) are formed with a wide variety of monomers. Suitable monomers for copolymerization with maleic anhydride include styrene [100-42-5], (120–125), vinyl chloride [75-01-4], vinyl esters and related vinyl compounds (126,127), acrylonitrile [107-13-1], acrylic acid [79-10-7], acrylic and methacrylic esters, acrylamide [79-06-1], acrolein [107-02-8], vinylsulfonic acid [1184-84-5], allyl acetate [591-87-7], and related allyl compounds (128), and alkenes (129–131) such as ethylene, vinyl ketones, 3,4-epoxy-1-butene [930-22-3] (132), and carbon monoxide. Among the growing number of nitrogen-containing monomers that copolymerize with maleic anhydride are 2,6-diisopropyl-*N*-methylenaniline (133), *N*-(2-hydroxyethyl) ethyleneimine (134), various maleimide derivatives (135,136), and maleic acid or its cyclic imide repeat units (137,138). Step-growth polymerization of maleic anhydride with 1,2-propylene glycol has been studied (139), and formation of the resulting polyester is complex. Copolymers may be assembled, in random or alternating additions, by grafting maleic anhydride onto existing polymers or by condensations. Maleic anhydride grafting onto polyethylene (140–142) and polypropylene (143–149) has been extensively studied. Grafting of maleic anhydride onto other polymers (142), including polyorganophosphazenes (150), has also been investigated. Polymer mixtures of maleated polypropylene, ethylene–propylene rubber, and a polyetheramine (151) or related mixtures (152) have yielded thermoplastic polyolefins (TPDs) that are directly paintable. An enormous amount of literature on these polymers exists and representative references are given here (see, eg, *General References*).

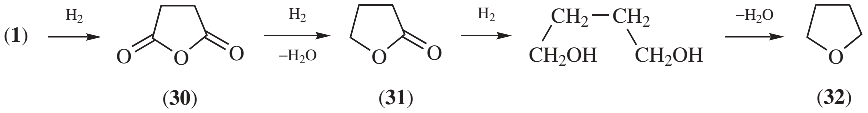
Aqueous ring-opening metathesis polymerization (ROMP), first described in 1989 (153), has been applied to maleic anhydride (154). Furan [110-00-9] reacts in a Diels–Alder reaction with maleic anhydride to give exo-7-oxabicyclo[2.2.1]-hept-5-ene-2,3–dicarboxylate anhydride [6118-51-0] (**28**). The condensed product is treated with a soluble ruthenium(III) [7440-18-8] catalyst in water to give upon acidification the polymer (**29**). Several applications for this new copolymer have been suggested (154).



Unsaturated polyester resins prepared by condensation polymerization constitute the largest industrial use for maleic anhydride. Typically, maleic anhydride is esterified with ethylene glycol [107-21-1], and a vinyl monomer or styrene is added along with an initiator such as a peroxide to produce a three-dimensional macromolecule with rigidity, insolubility, and mechanical strength.

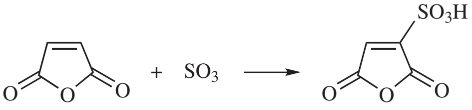
3.19. Reduction. Heterogeneous catalytic reduction processes provide effective routes for the production of maleic anhydride derivatives such as succinic anhydride [108-30-5] (**30**), succinates, γ-butyrolactone [96-48-0] (**31**), THF

[109-99-9] (**32**), and 1,4-butanediol [110-63-4] (**33**). The technology for production of 1,4-butanediol from maleic anhydride has been reviewed (155–159).



Several companies have developed hydrogenation technology for conversion of maleic anhydride, maleic acid, or dialkyl maleates to 1,4-butanediol or its hydrogenatable precursors γ-butyrolactone and THF (160–169). These processes use maleic anhydride (166) or dialkyl maleate (160–162) in the vapor phase over heterogeneous copper catalysts in fixed-bed reactors, aqueous maleic acid over multimetallic (Pd, Ag, Re) extrudates in trickle-bed reactors (163–165), or aqueous maleic acid with slurries of bimetallic (Ru, Re) carbon catalysts in slurry reactors (169). Routes to partially reduced products from maleic anhydride have been reported for succinic anhydride using a samarium(II) iodide complex with hexamethylphosphoric triamide (170) or homogeneous rhodium–phosphine catalyst (171) and succinic acid using an electrochemical route (172). γ-Butyrolactone is obtained directly over a heterogeneous copper-containing catalysts (173) by hydrogenation of maleic anhydride in the gas phase.

3.20. Sulfonation. Maleic anhydride is sulfonated to α-sulfomaleic anhydride [40336-85-4] (**34**) with sulfur trioxide [7446-11-9] (174,175). Uses for this monomer have not been published.



(**34**)

4. Manufacture

4.1. Process Technology Evolution. Maleic anhydride was first commercially produced in the early 1930s by the vapor-phase oxidation of benzene [71-43-2]. The use of benzene as a feedstock for the production of maleic anhydride was dominant in the world market well into the 1980s. Several processes have been used for the production of maleic anhydride from benzene, with the most common one being that of Scientific Design. Small amounts of maleic acid are produced as a by-product in production of phthalic anhydride [85-44-9]. This compound can be converted to either maleic anhydride or fumaric acid. Benzene, although easily oxidized to maleic anhydride with high selectivity, is an inherently inefficient feedstock because two excess carbon atoms are present in the raw material. Various C_4 compounds have been evaluated as raw material substitutes for benzene in production of maleic anhydride. Fixed- and fluid-bed processes for production of maleic anhydride from the butenes present in mixed C_4

streams have been practiced commercially. None of these processes is currently in operation.

Rapid increases in the price of benzene and the recognition of benzene as a hazardous material intensified the search for alternative process technology in the United States. These factors led to the first commercial production of maleic anhydride from butane [106-97-8] at Monsanto's J. F. Queeny plant in 1974. By the early 1980s the conversion of the U.S. maleic anhydride manufacturing capacity from benzene to butane feedstock was well under way, using catalysts developed by Monsanto, Denka, and Halcon. One factor that inhibited the conversion of the installed benzene-based capacity was that early butane-based catalysts were not active and selective enough to allow the conversion of benzene-based plant without significant loss of nameplate capacity. In 1983 Monsanto started up the world's first butane-to-maleic anhydride plant, incorporating an energy-efficient, solvent-based product collection and refining system. This plant was the world's largest maleic anhydride production facility in 1983 at 59,000 t/yr capacity, and through rapid advances in catalyst technology remains the world's largest facility with a capacity of 105,000 t/yr (1999). Advances in catalyst technology, increased regulatory pressures, and continuing cost advantages of butane over benzene have led to a rapid conversion of benzene-to-butane-based plants. By the mid-1980s in the United States, 100% of maleic anhydride production used butane as the feedstock.

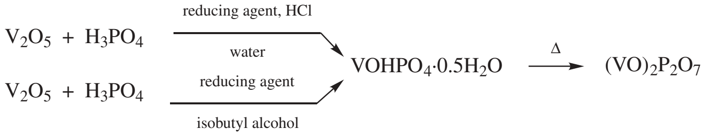
Coincident with the rapid development of the butane-based fixed-bed process, several companies have developed fluidized-bed processes. Badger and Denka, collaborated on an early fluid-bed reaction system that was developed through the pilot-plant stage but was never commercialized. Three fluid-bed butane-based technologies were commercialized during the latter half of the 1980s by Mitsubishi Kasei, Sohio (British Petroleum), and Alusuisse. A second fluidized-bed technology for the oxidation of butane to maleic anhydride, known as transport bed, has been developed by Du Pont (176). A world-scale plant in Spain for the production of THF by the hydrogenation of maleic acid started up in late 1996 (177).

Europe has largely converted from benzene- to-butane-based maleic anhydride technology with the construction of several new butane-based facilities by CONDEA-Huntsman, Pantochim, and Lonza. Growth in the worldwide maleic anhydride industry is predominantly in the butane-to-maleic anhydride route, often at the expense of benzene-based production. Table 4 shows 1993 and 2000 worldwide maleic production capacity broken down in categories of fixed-bed benzene, fixed-bed butane, fluidized-bed butane, and phthalic anhydride coproduct. As the table indicates, both fixed- and fluidized-bed butane routes have grown dramatically, with the fixed-bed route adding 336,000-t/yr capacity vs 90,000 t/yr for the fluid-bed process. Only a few newer benzene-based fixed-bed processes have been built since the early 1980s, and these were built where the availability of butane was limited. The fluidized-bed butane-based process is experiencing some growth, but based on growth rates from Table 4 (178,179), it does not appear destined to challenge fixed-bed technology. The announcement from Huntsman Specialty Chemicals Corp., formerly Monsanto, and DWE (180), that they intend to cooperate in the development of catalyst and reactor technology to permit operation at 50% higher productivity than the standard nonflammable fixed-bed butane process indicates that the largest companies in fixed-bed technology are confident that further advances are possible. Three fixed-bed processes, from Huntsman (181), Pantochim (182), and Scientific Design (183), and two fluidized-bed processes, from Alusuisse-Lummus (ALMA) (184) and BP Chemicals (185), are currently offered for license.

4.2. Butane-Based Catalyst Technology. The increased importance of the butane-to-maleic anhydride conversion route has resulted in efforts being made to understand and improve this process. Since 1980, over 225 U.S. patents have been issued relating to maleic anhydride technology. The predominant area of research concerns the catalyst because it is at the heart of this process. The reasons for this statement are twofold. First, there is the complexity of this reaction: for maleic anhydride to be produced from butane, eight hydrogen atoms must be abstracted, three oxygen atoms inserted, and a ring closure performed. This 14-electron oxidation occurs exclusively on the surface of the catalyst. The second reason for the emphasis placed on the catalyst is that all the commercial processes use the same catalyst. This catalyst is the only commercially viable system that selectively produces maleic anhydride from butane.

The catalyst used in the production of maleic anhydride from butane is vanadium–phosphorus oxide (VPO). Several routes may be used to prepare the catalyst (186–188), but the route favored by industry involves the reaction of vanadium(V) oxide [1314-62-1] and phosphoric acid [7664-38-2] to form vanadyl hydrogen phosphate, $VOHPO_4{\cdot}0.5\ H_2O$. This material is then heated to eliminate water from the structure and irreversibly form vanadyl pyrophosphate, $(VO)_2P_2O_7$ (186,189). Vanadyl pyrophosphate is believed to be the catalytically active phase required for the conversion of butane to maleic anhydride (190,191).

The reaction of V_2O_5 with H_3PO_4 to form $VOHPO_4{\cdot}0.5\ H_2O$ can be carried out in either an aqueous or organic medium such as isobutyl alcohol [78-83-1] (88,186). Two possible routes are as follows.



The use of an organic medium yields an increase in the surface area of the $VOHPO_4{\cdot}0.5\ H_2O$ (88,191). This increase in surface area is carried over to the resulting vanadyl pyrophosphate phase (186) and is desirable because a concurrent increase in activity toward butane oxidation is observed (88,192). Alternatively, some patented technologies purport precursors as intercalation compounds with the formula $VOHPO_4{\cdot}0.5\ H_2O\{[C_nH_{(2n}+1)]X\}_z$, where $1.5<z<1.9$, $0<n<20$, and X=oxygen-, nitrogen-, or sulfur-containing functional groups that form hydrogen bonds with the $VOHPO_4$ layers (193,194). The use of vanadyl phosphite as a precursor is also claimed (195,196). Other routes to effective precursors have focused on cosolvents, cluster compounds, or heteropolyacids as starting materials (193,197–201).

An additional effect of the use of an organic medium in the catalyst preparation is creation of more defects in the crystalline lattice in comparison to a catalyst made by the aqueous route (186). These defects persist in the active phase and are thought to result in creation of strong Lewis acid sites on the surface of the catalysts (186,202). These sites are viewed as being responsible for the activation of butane on the catalyst surface by means of abstraction of a hydrogen atom, as supported by a recent detailed fourier transform ir spectroscopic investigation (203).

There are two types of patented technology for the transformation of $VOHPO_4{\cdot}0.5\ H_2O$ into $(VO)_2P_2O_7$ (88). In the first procedure, the vanadyl hydrogen phosphate is transformed through heating to 415°C in a controlled environment with combinations of nitrogen, air, and steam (204). The second procedure is an *in situ* process that transforms the vanadyl hydrogen phosphate into the active phase while the catalyst is placed in the maleic reactor (205). This procedure entails slow heating of the catalyst in air with gradual introduction of butane to the gas stream. The use of the *in situ* activation method requires little capital investment. However, the possibility exists of inhomogenities in the activated catalyst due to nonuniformities in reactor flow distribution. On the other hand, the controlled environment procedure reduces plant downtime and increases the homogeneity of the catalyst in the reactor.

Promoters are sometimes added to the VPO catalyst during synthesis (205–211) to increase its overall activity and/or selectivity. Promoters may be added during formation of the catalyst precursor ($VOHPO_4{\cdot}0.5\ H_2O$), or impregnated onto the surface of the precursor before transformation into its activated phase. They are thought to play a twofold structural role in the catalyst (206). First, promoters facilitate transformation of the catalyst precursor into the desired vanadium–phosphorus oxide active phase, while decreasing the amount of nonselective VPO phases in the catalyst. For example, a molybdenum-containing VPO catalyst tends to decrease the amount of certain undesirable by-products including acrylic acid (212,213). The second role of promoters is to participate in formation of a solid solution which controls the activity of the catalyst.

The bulk structure of the catalytically active phase is not completely known and is under debate in the literature (190,214–216). The central point of controversy is whether $(VO)_2P_2O_7$ alone or in combination with other phases is the most catalytically active for the conversion of butane to maleic anhydride. The heart of this issue concerns the role of structural disorder in the bulk and how it arises in the catalyst (190,217,218). Most researchers agree that the catalysts with the highest activity and selectivity are composed mainly of $(VO)_2P_2O_7$, which exhibits a clustered or distorted platelet morphology (190). It is also generally acknowledged that during operation of the catalyst, the bulk oxidation state of the vanadium in the catalyst remains very close to the $+4$ valence state (190).

Only the surface layers of the catalyst solid are generally thought to participate in the reaction (190,216). This implies that while the bulk of the catalyst may have an oxidation state of $4+$ under reactor conditions, the oxidation state of the surface vanadium may be very different. It has been postulated that both V^{4+} and V^{5+} oxidation states exist on the surface of the catalyst, the latter arising from oxygen chemisorption (216). Phosphorus enrichment is also observed at the surface of the catalyst (190,191). The exact role of this excess surface phosphorus is not well understood, but it may play a role in active site isolation and consequently, the oxidation state of the surface vanadium.

VPO-based catalysts are unstable in that they tend to lose phosphorus over time at reaction temperatures. Hot spots in fixed-bed reactors tend to accelerate this loss of phosphorus. This loss of phosphorus also produces a decrease in selectivity (88,219). Many steps have been taken, however, to alleviate these problems and to create an environment in which the catalyst can operate at lower temperatures. For example, volatile organophosphorus compounds are fed to the reactor to mitigate the problem of phosphorus loss by the catalyst (220). The phosphorus feed also has the effect of controlling catalyst activity and thus improving catalyst selectivity in the reactor. The catalyst pack in the reactor may be stratified with an inert material (221–223). Stratification has the effect of reducing the extent of reaction per unit volume and thus reducing the observed hot spots in catalyst temperature (223). Aluminizing the reactor wall that is in contact with the catalyst also minimizes undesirable side reactions (224). These measures have minimized concerns of heat removal in the reactor and improved catalyst performance.

Fluidized-bed reactor systems put other unique stresses on the VPO catalyst system. The mixing action inside the reactor creates an environment that is too harsh for the mechanical strength of a VPO catalyst and thus requires that the catalyst be attrition resistant (184,225–229). To achieve this goal, VPO is usually spray-dried with colloidal silica [7631-86-9] or polysilicic acid [1343-98-2]. VPO catalysts made with colloidal silica are reported to have a loss of selectivity, while no loss in selectivity is reported for catalysts spray-dried with polysilicic acid (225). Even with the increased mechanical properties, the continuous operation of a fluidized-bed or recirculating solids reactor subjects the catalyst to conditions so harsh that even the strongest catalyst is eventually reduced to extremely fine material, which is lost from the reactor. The catalyst inventory therefore diminishes and needs to be replenished. To maintain maleic anhydride production levels, fresh catalyst needs to be constantly added to the system (230) or some means to regenerate the catalyst must be employed (231–233). While a supported VPO catalyst is not yet operated commercially, there are efforts to develop such a catalyst (234–236).

4.3. Benzene-Based Catalyst Technology. The catalyst used for the conversion of benzene to maleic anhydride consists of supported vanadium oxide [11099-11-9]. The support is an inert oxide such as kieselguhr, alumina [1344-28-1], or silica and is of low surface area (237). Supports with higher surface area adversely affect conversion of benzene to maleic anhydride. The conversion of benzene to maleic anhydride is a less complex oxidation than the conversion of butane, so higher catalyst selectivities are obtained. The vanadium oxide on the surface of the support is often modified with molybdenum oxides. There is $\sim$70% vanadium oxide and 30% molybdenum oxide [11098-99-0] in the active phase for these fixed-bed catalysts (238). The molybdenum oxide is thought to form either a solid solution or compound oxide with the vanadium oxide and result in a more active catalyst (237).

4.4. Butane-Based Fixed-Bed Process Technology. Maleic anhydride is produced by reaction of butane with oxygen, using the vanadium–phosphorus oxide heterogeneous catalyst discussed earlier. The butane oxidation reaction to produce maleic anhydride is very exothermic. The main reaction by-products are carbon monoxide and carbon dioxide. Stoichiometries and heats of reaction for the three principal reactions are as follows:

$$C_4H_{10} + 3.5\ O_2 \longrightarrow C_4H_2O_3 + 4\ H_2O \qquad \Delta H = -1236\ \text{kJ/mol}\ (-295.4\ \text{kcal/mol})$$

$$C_4H_{10} + 6.5\ O_2 \longrightarrow 4\ CO_2 + 5\ H_2O \qquad \Delta H = -2656\ \text{kJ/mol}\ (-634.8\ \text{kcal/mol})$$

$$C_4H_{10} + 6.5\ O_2 \longrightarrow 4\ CO + 5\ H_2O \qquad \Delta H = -1521\ \text{kJ/mol}\ (-363.5\ \text{kcal/mol})$$

Air is compressed to modest pressures, typically 100–200 kPa (∼15 – 30 psig) with either a centrifugal or radial compressor, and mixed with superheated vaporized butane. Static mixers are normally employed to ensure good mixing. Butane concentrations are often limited to <1.7 mol% to stay below the lower flammable limit of butane (239). Operation of the reactor at butane concentrations below the flammable limit does not eliminate the requirement for combustion venting, and consequently most processes use rupture disks on both the inlet and exit reactor heads. A flow diagram of the Huntsman fixed-bed maleic anhydride process is shown in Figure 2.

The highly exothermic nature of the butane-to-maleic anhydride reaction and the principal by-product reactions require substantial heat removal from the reactor. Thus the reaction is carried out in what is effectively a large multitubular heat exchanger that circulates a mixture of 53% potassium nitrate [7757-79-1], KNO_3; 40% sodium nitrite [7632-00-0], $NaNO_2$; and 7% sodium nitrate [7631-99-4], $NaNO_3$. Reaction tube diameters are kept at a minimum 25–30 mm in outside diameter to facilitate heat removal. Reactor tube lengths are between 3 and 6 m. The exothermic heat of reaction is removed from the salt mixture by the production of steam in an external salt cooler. Reactor temperatures are in the range of 390–430°C. Despite the rapid circulation of salt on the shell side of the reactor, catalyst temperatures can be 40–60°C higher than the salt temperature. The butane-to-maleic anhydride reaction typically reaches its maximum efficiency (maximum yield) at ∼85% butane conversion. Reported molar yields are typically 50–60%.

Efficient utilization of waste heat from a maleic anhydride plant is critical to the economic viability of the plant. Often site selection is dictated by the presence of an economic use for by-product steam. The steam can also be used to drive an air compressor, generate electricity, or both. Alternatively, an energy consuming process, such as a butanediol plant, can be closely coupled with the maleic anhydride plant. Several such plants have been announced (240). Design and integration of the heat recovery systems for a maleic anhydride plant are very site specific. Heat is removed from the reaction gas through primary and sometimes secondary heat exchangers. In addition to the heat recovered from the reactor and process gas heat exchangers, additional heat can be recovered from the destruction of unreacted butane, the carbon monoxide by-product, and other by-products that cannot be vented directly to the atmosphere.

This destruction is done typically in a specially designed thermal oxidizer or a modified boiler.

Reactor operation at 80–85% butane conversion to produce maximum yields provides an opportunity for recycle processes to recover the unreacted butane in the stream that is sent to the oxidation reactor. Patents have been issued on recycle processes (241) both with and without added oxygen. Pantochim has announced the commercialization of a partial recycle process (182). Mitsubishi Chemical Corporation has announced plans to add butane recovery from the off-gas of their fluid-bed process through the use of PETROX, BOC Gases's proprietary selective hydrocarbon separation system (242). This technology is particularly well suited to use in fluid-bed processes where the hydrocarbon-to-air ratio is relatively high and in world areas where butane has a high value relative to its energy content. Operation of the butane-to-maleic anhydride process in a total recycle configuration can produce molar yields that approach the reaction selectivity which is typically 65–75%, significantly higher than the 50–60% molar yields from a single-pass, high conversion process. The Du Pont transport-bed process achieves its high reported yields at least partially through implementation of recycle technology. Recovery of the fuel value of the butane in the off-gas from a single pass configuration plant reduces the economic attractiveness of recycle operation.

4.5. Butane-Based Fluidized-Bed Process Technology. Fluidized-bed processes offer the advantage of excellent control of hot spots by rapid catalyst mixing, simplification of safety issues when operating above the flammable limit, and a simplified reactor heat-transfer system. Some disadvantages include the effect of backmixing on the kinetics in the reactor, product destruction and by-product reactions in the space above the fluidized bed, and vulnerability to large-scale catalyst releases from explosion venting.

A schematic flow diagram for the ALMA fluidized-bed process is shown in Figure 3 (184). Compressed air and butane are typically introduced separately into the bottom of the fluidized-bed reactor. Heat from the exothermic reaction is removed from the fluidized bed through steam coils in direct contact with the bed of fluidized solids. Fluidized-bed reactors exploit the extremely high heat-transfer coefficient between the bed of fluidized solids and the steam coils. This high heat-transfer coefficient allows a relatively small heat-transfer area in the fluid-bed process for the removal of the heat of reaction in comparison to the fixed-bed process. Gas flow patterns in a commercial-scale fluid-bed reactor are generally backmixed, which can lead to maleic anhydride destruction. Patents have been issued for mechanical modifications to the reactor internals which claim to control backmixing (243). Other methods to reduce backmixing include introduction of catalyst fines (small particles of catalyst) to decrease bubble size and operation of the reactor in the turbulent, fast fluidization regime in an attempt to minimize bubbling (225). Fluidized-bed reactors require a significant amount of space above the catalyst level to allow the solids to separate from the gases. This exposure of the product to high temperatures at relatively long residence times can lead to side reactions and product destruction. Fluidized-bed processes are operated at high butane concentrations (184) but at longer gas residence times than fixed-bed processes.

The product stream contains gases and solids. The solids are removed by using either cyclones, filters, or both in combination. Cyclones are devices used to separate solids from fluids using vortex flow. The product gas stream must be cooled before being sent to the collection and refining system. The ALMA process uses cyclones as a primary separation technique with filters employed as a final separation step after the off-gas has been cooled and before it is sent to the collection and refining system (243). As in the fixed-bed process, the reactor off-gas must be incinerated to destroy unreacted butane and by-products before being vented to the atmosphere.

Fluidized-bed reaction systems are not normally shut down for changing catalyst. Fresh catalyst is periodically added to manage catalyst activity and particle size distribution. The ALMA process includes facilities for adding back both catalyst fines and fresh catalyst to the reactor.

4.6. Butane-Based Transport-Bed Process Technology. Du Pont announced the commercialization of a moving-bed, recycle-based technology for the oxidation of butane to maleic anhydride (176,244). Athough maleic anhydride is produced in the reaction section of the process and could be recovered, it is not a direct product of the process. Maleic anhydride is recovered as aqueous maleic acid for hydrogenation to THF [109-99-9].

The reaction technology known as transport bed is a circulating solids technology in which the oxygen required in the oxidation of butane to maleic anhydride is provided by the VPO catalyst and the catalyst is reoxidized in a separate step. The exclusion of gas-phase oxygen from the reaction step is claimed to enhance selectivity (225,245,246). Separation of butane oxidation from catalyst reoxidation allows both steps to be independently optimized. The circulating solids system is similar to catalytic cracking as can be seen from an examination of Figure 4.

Fresh butane mixed with recycled gas encounters freshly oxidized catalyst at the bottom of the transport-bed reactor and is oxidized to maleic anhydride and CO_x during its passage up the reactor. Catalyst densities ($80-160$ kg/m^3) in the transport-bed reactor are substantially lower than the catalyst density in a typical fluidized-bed reactor ($480-640$ kg/m^3) (176). The gas flow pattern in the riser is nearly plug flow, which avoids the negative effect of backmixing on reaction selectivity. Reduced catalyst is separated from the reaction products by cyclones and is further stripped of products and reactants in a separate stripping vessel. The reduced catalyst is reoxidized in a separate fluidized-bed oxidizer, where the exothermic heat of reaction is removed by steam coils. The rate of reoxidation of the VPO catalyst is slower than the rate of oxidation of butane, and consequently residence times are longer in the oxidizer than in the transport-bed reactor.

Maleic anhydride in the product stream is removed and converted to a maleic acid solution in a water scrubbing system. The maleic acid is sent to the hydrogenation reactor to produce THF, while the reactor off-gas after scrubbing is sent to the recycle compressor. A small purge stream is sent to incineration.

4.7. Benzene-Based Fixed-Bed Process Technology. The benzene fixed-bed process is very similar to the butane fixed-bed process and, in fact, the Scientific Design butane process has evolved directly from its benzene process. Benzene-based processes are easily converted to butane-based processes.

Typically, only a catalyst change, installation of butane handling equipment, and minor modifications to the recovery process are required. The benzene reaction is a vapor-phase partial oxidation reaction using a fixed-bed catalyst of mixed vanadium and molybdenum oxides. The reactors used are the same multitubular reactors cooled by circulating a molten mixture of KNO_3–$NaNO_2$–$NaNO_3$ salts described in the section on the butane process. The benzene concentrations used are ~1.5 mol% or just below the lower flammable limit of benzene in air. Unlike the butane reaction, the reactor normally operates at conversions >95% and molar yields >70%. The benzene oxidation reaction runs a little cooler than the butane oxidation reaction, with typical reactor temperatures in the 350–400°C range.

The reactor off-gas is cooled by one or more heat exchangers and sent to the collection and refining section of the plant. Unreacted benzene and by-products are incinerated.

4.8. Recovery and Purification. All processes for the recovery and refining of maleic anhydride must deal with the efficient separation of maleic anhydride from the large amount of water produced in the reaction process. Recovery systems can be separated into two general categories: aqueous- and nonaqueous-based absorption systems. Solvent-based systems have a higher recovery of maleic anhydride and are more energy efficient than water-based systems.

The Huntsman solvent-based collection and refining system will be used as a generic model for solvent-based recovery systems (see Fig. 2). The reactor exit gas is cooled in two heat exchangers for energy recovery. The cooled gas product stream is passed to a solvent absorber, where a proprietary solvent is used to absorb, almost completely, the maleic anhydride contained in the product stream. The solvent stream, coming from the bottom of the absorber with a high concentration of maleic anhydride, known as rich oil, is sent to a stripper, where the rich oil is heated and maleic anhydride is vacuum-stripped from the solvent. The vacuum-stripped maleic anhydride, typically >99.8% in purity, is sent to the purification section of the plant, where it is batch distilled to produce extremely pure maleic anhydride. A small slipstream of the solvent from which the maleic anhydride was removed by stripping is sent to the solvent purification section of the plant, where impurities are removed.

The Scientific Design water-based collection and refining system is in broad use throughout the world in butane- and benzene-based plants (183,247). The reactor off-gas is cooled from reaction temperatures in a gas cooler with generation of steam. The off-gas is then sent to a tempered water-fed aftercooler, where it is cooled below the dew point of maleic anhydride. The liquid droplets of maleic anhydride are separated from the off-gas by a separator. The condensed crude is pumped to a crude tank for storage. The maleic anhydride remaining in the gas stream after partial condensation is removed in a water scrubber by conversion to maleic acid, which accumulates in the acid storage section at the bottom of the scrubber. The acid solution is converted to crude maleic anhydride in a dual-purpose dehydrator/refiner. Xylene [1330-20-1] is used as an azeotropic agent for the conversion of maleic acid to maleic anhydride. Water from the dehydration step is recycled to the scrubber. When the conversion of the acid solution to crude maleic anhydride is complete, condensed crude maleic anhydride is added to the still pot and a batch distillation refining step is conducted.

The UCB collection and refining technology [owned by BP Chemicals (185,248–250)] also depends on partial condensation of maleic anhydride and scrubbing with water to recover the maleic anhydride present in the reaction off-gas. The UCB process departs significantly from the Scientific Design process when the maleic acid is dehydrated to maleic anhydride. In the UCB process, the water in the maleic acid solution is evaporated to concentrate the acid solution. The concentrated acid solution and condensed crude maleic anhydride is converted to maleic anhydride by a thermal process in a specially designed reactor. The resulting crude maleic anhydride is then purified by distillation.

4.9. Fumaric Acid. Fumaric acid for commerce is derived from maleic acid through catalytic isomerization. Purified maleic anhydride is the main source of maleic acid. In addition, crude maleic acid may be used as recovered in benzene oxidation or phthalic anhydride manufacture (23). Numerous catalysts exist for maleic acid isomerization (92–94), but three types are widely used: mineral acids (251), peroxycompounds with bromides (252) and bromates (253), and sulfur-containing compounds such as thiourea [62-56-6] (94) and its derivatives (254). Little change in process technology has occurred since the 1970s. Processing is simplest with purified maleic anhydride as the raw material. High purity fumaric acid is produced through crystallization of the aqueous mixture, washing, and drying (255). A process for recovery of fumaric acid from molten maleic anhydride refining has been described (256). Decolorizing and crystallization techniques are used to treat impure maleic solutions (257).

5. Shipment

Molten maleic anhydride is shipped in tank rail cars, tank trucks, and isotanks (for overseas shipments). Tank rail cars are typically constructed of lined carbon steel and are insulated and equipped with steam coils. Tank rail cars of up 20,000 gal are used. Tank trucks are typically constructed of stainless steel [12597-68-1], insulated, and equipped with steam coils. Tank trucks of up to 4500 gal are used. Isotanks are typically constructed of stainless steel and are insulated and equipped with steam coils. Isotanks of up to 4500 gal are used.

Solid-form maleic anhydride is produced from molten maleic anhydride as briquettes or pastilles weighing 0.5–20 g. Flaked maleic anhydride is used in some areas of the world but is not generally accepted in the United States because of the high dust content. Briquettes or pastilles are packed in 50-lb (25-kg) bags and supersacks of up to 2500 lb (1136 kg). Outside the United States, the standard bag weight is 25 kg. Typical bag construction is either polyethylene or multi-ply paper with at least one polyethylene layer. Solid-form maleic anhydride can be stored in bags for several months in a cool, dry location.

Fumaric acid is shipped in solid form, the particle size varying based on the specification. The standard shipping containers are 50-lb bags (25-kg bags outside the United States), supersacks containing up to 2500 lb, and occasionally bulk hopper truck.

6. Economic Aspects

Data for the production and sales of maleic anhydride and fumaric acid in the United States between 1986 and 2000 are shown in Table 5 (258,259). Production of maleic anhydride during this time period grew ~3% on average per annum, with production downturns reaching a minimum in 1991. Production of fumaric acid in the United States has declined during the same period as producers in the United States have rationalized and customers have switched to the less costly maleic anhydride in all applications where that is possible. Table 6 presents the producers of maleic anhydride in the United States as of 2000 (258). All production of maleic anhydride in the United States in 1992 was butane-based, and fixed-bed reactor technology was used. Only one producer of fumaric acid remained in the United States in 2000. Bartek in Canada does represent a significant factor in the supply of fumaric acid to the United States. The Bartek facility has a capacity of 17.3 kt/yr, out of which fumaric acid production is tolled for Huntsman.

Capacities of maleic anhydride facilities worldwide are presented in Table 7. The switch of feedstock from benzene to butane was completed in the United States in 1985, driven by the lower unit cost and lower usage of butane in addition to the environmental pressures on the use of benzene. Worldwide, the switch from benzene to butane is continuing.

Between 1992 and 2000, maleic anhydride capacity increases have been pronounced in Asia. This increase has resulted in a significant oversupply situation in that world area. Western Europe has also experienced a pronounced increase in capacity. North America has experienced a relatively modest increase in capacity, which resulted from the construction of a new plant, debottlenecks of existing plants, and one rationalization.

7. Specifications

The general sales specification under which maleic anhydride is sold in the United States cites a white fused mass or briquettes of 99.5% minimum assay and 52.5°C minimum crystallization point. The melt color specification is 20 APHA maximum, with a maximum APHA color of 40 after 2 h of heating at 140°C. The solution of 4 g of maleic anhydride in 10 mL of water is to be complete and the solution colorless. The acidity as maleic acid is a maximum of 0.2%.

Fumaric acid is sold as resin grade and food grade. The general sales specification under which resin-grade fumaric acid is sold in the United States calls for white, crystalline granules with a minimum assay of 99.6% and maximum ash content of 0.05%. The moisture specification is 0.3% maximum with <10 ppm heavy metals. The color of a 5% solution in methanol is to be <10 APHA. Food-grade fumaric acid must have somewhat lower impurity levels. Particle size and particle size distribution are important in many applications.

8. Analytical and Test Methods

The test methods used by industry to determine whether a sample of maleic anhydride is within specifications (260) are ASTM methods D 2930, D 1493, and D 3366. These methods describe procedures for the determination of maleic acid content, the crystallization point, and the color properties of the maleic anhydride sample, respectively. By quantitative determination of these properties, a calculation of the overall purity of the maleic anhydride sample can be made.

The free maleic acid content in maleic anhydride is determined by direct potentiometric titration (261). The procedure involves the use of a tertiary amine, *N*-ethylpiperidine [766-09-6], as a titrant. A tertiary amine is chosen as a titrant because it is nonreactive with anhydrides (261,262). The titration is conducted in an anhydrous solvent system. Only one of the carboxylic acid groups is titrated by this procedure. The second hydrogen's dissociation constant is too weak to titrate (261). This test method is used not only to determine the latent acid content in refined maleic acid, but also as a measure of the sample exposure to moisture during shipping.

The other two methods used by industry to examine the purity of maleic anhydride are the crystallization point (263) and color determination of the sample (264). These tests determine the temperature at the point of solidification of the molten sample and the initial color properties of the melt. Furthermore, the color test determines the color of the sample after a 2-h heat treatment at 140°C. The purpose of these tests is to determine the deviation in properties of the sample from those of pure maleic anhydride. This deviation is taken as an indication of the amount of contaminants in the maleic anhydride sample. Six published international test standards relating to maleic anhydride (265) are for crystallization point determination, color of molten maleic anhydride, free acidity using the potentiometric method, maleic anhydride content using a titrimetric method, ash determination, and determination of iron content in maleic anhydride.

Other analytical techniques are also available for the determination of maleic anhydride sample purity. For example, maleic anhydride content can be determined by reacting it with a known excess of aniline [62-53-3] in an alcohol mixture (266). The solution is then titrated with an acid to determine the amount of unconsumed aniline. This number is then used to calculate the amount of maleic anhydride reacted and thus its concentration. Another method of a similar type has also been reported (267).

Finally, the techniques of nuclear magnetic resource (nmr), infrared (ir) spectroscopy, and thin-layer chromatography (tlc) also can be used to assay maleic anhydride (268). Maleic anhydride has been analyzed by gas chromatography (gc) (269,270) and a detailed review of this analysis focusing on the products formed during butane oxidation has appeared (271). The isomeric acids can be determined by polarography (272), thermal analysis (273), paper and thin-layer chromatographies (274), and nonaqueous titrations with an alkali (275), ion-exclusion chromatography (276), isotachophoresis (277), and high performance liquid chromatography (hplc) (278,279). Maleic and fumaric acids may be separated by both gel filtration (280) and ion-exchange techniques (281).

9. Health and Safety Factors

9.1. Maleic Anhydride. The American Conference of Governmental Industrial Hygienists' (ACGIH) threshold limit value in air for maleic anhydride is 0.25 ppm and the Occupational Safety and Health administration (OSHA) permissible exposure level (PEL) is also 0.25 ppm (282). Maleic anhydride is a corrosive irritant to eyes, skin, and mucous membranes. Pulmonary edema (collection of fluid in the lungs) can result from airborne exposure. Skin contact should be avoided by the use of rubber gloves. Dust respirators should be used when maleic anhydride dust is present. Maleic anhydride is combustible when exposed to heat or flame and can react vigorously on contact with oxidizers. The material reacts exothermically with water or steam. Violent decompositions of maleic anhydride can be catalyzed at high temperature by strong bases (sodium hydroxide, potassium hydroxide, calcium hydroxide, alkali metals, and amines, etc). Precaution should be taken during the manufacture and use of maleic anhydride to minimize the presence of basic materials in maleic anhydride.

9.2. Maleic Acid. Maleic acid is produced by the hydration of maleic anhydride. The hazards of its use are analogous to those of maleic anhydride. It is a skin and severe eye irritant. It is combustible when exposed to heat or flame. As discussed, contamination with bases should be avoided where the material is to be handled at high temperature and high concentration because of the potential decomposition hazard.

9.3. Fumaric Acid. Fumaric acid is used as a beverage acidulant for human consumption as well as in many industrial applications. Its acidic properties can cause skin and eye irritation. It will combust when exposed to heat or flame and can react vigorously with oxidizing agents. Table 8 lists toxicological data (282).

10. Uses

Maleic anhydride is truly a remarkable molecule in that its possesses two types of chemical functionality, making it uniquely useful in chemical synthesis and applications. Maleic anhydride itself has few, if any, consumer uses but in derivatized form is extremely versatile in the consumer uses in which it is found. The chemical structure of each maleic anhydride derivative of significant commercial interest can be found in a more detailed reference (237).

The distribution of end uses for maleic anhydride is presented in Table 9 for the year 2000 (258). The majority of the maleic anhydride produced is used in unsaturated polyester resin (see POLYESTERS, UNSATURATED). Unsaturated polyester resin is then used both in glass-reinforced applications and in unreinforced applications. The distribution of end uses for unsaturated polyester resin is shown in Table 10 for the year 2000 (283).

There are many unsaturated polyester resin formulations. A typical unsaturated polyester resin formulation consists of an aromatic dibasic acid (or anhydride) such as phthalic anhydride, an unsaturated dibasic acid (or anhydride) such as maleic anhydride, and a glycol such a propylene glycol. The polyester chains are then cross linked through the double bond with vinyl cross-linking agents such as styrene. Reinforcement in the form of glass fibers or other reinforcement fibers may be added to provide the strength requirements of the end product. The exact unsaturated polyester formulation, its cross-linking agent, and the reinforcement fiber, if any, are selected to optimize the performance of the end product.

Fumaric acid and malic acid [6915-15-7] are produced from maleic anhydride. The primary use for fumaric acid is in the manufacture of paper sizing products (see PAPERMAKING ADDITIVES). Fumaric acid is also used as a food acidulant, as is malic acid. Malic acid is a particularly desirable acidulant in certain beverage selections, specifically those sweetened with the artificial sweetener aspartame [22839-47-0].

Lube oil additives represent another important market segment for maleic anhydride derivatives, the molecular structure of importance being adducts of polyalkenyl succinic anhydrides (see LUBRICATION AND LUBRICANTS). These materials act as dispersants and corrosion inhibitors (see DISPERSANTS; CORROSION AND CORROSION CONTROL). One particularly important polyalkenyl succinic anhydride molecule in this market is polyisobutylene succinic anhydride (PIBSA) where the polyisobutylene group has a molecular weight of 900−1500. Other polyalkenes are also used. Poly(alkenyl succinic anhydride) is further derivatized with various amines to produce both dispersants and corrosion inhibitors. Another type of dispersant is a polyester produced from a poly(alkenyl succinic anhydride) and pentaerythritol [115-77-5].

Maleic anhydride is used in a multitude of applications in which a vinyl copolymer is produced by the copolymerization of maleic anhydride with other molecules having a vinyl functionality. Typical copolymers (and their end uses) are styrene−maleic (engineering thermoplastic, paper treatment chemical, floor polishes, emulsifiers, protective colloids, antisoil agents, dispersants, stabilizing agent, adhesives, detergents, cosmetics, and toiletries), diisobutylene−maleic (dispersing agent), acrylic acid−maleic (detergent ingredient), butadiene−maleic (sizing agent), and C_{18} α-olefin−maleic (emulsification agent and paper coating).

The use of maleic anhydride in the manufacture of agricultural chemicals has declined in the United States over the last decade. Malathion [121-75-2] [*S*-(1,2-dicarbethoxyethyl)*O*,*O*-dimethyldithiophosphate] and Difolatan [2425-06-1] [*cis*-*N*-(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarboximide] are no longer produced in the United States, and Alar [1596-84-5] (*N*-dimethylaminosuccinamic acid) volumes have been significantly reduced by intense environmental scrutiny. Maleic hydrazide, Captan [133-06-2] [*cis*-*N*-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide], Endothall [145-73-3], (7-oxabicyclo[2,2,1]-heptane-2,3-dicarboxylic acid, disodium salt), and several other maleic derivatives continue use in a number of agricultural functions: plant growth regulation, fungicides, insecticides, and herbicides (see FUNGICIDES, AGRICULTURAL; INSECT CONTROL TECHNOLOGY; HERBICIDES).

There are numerous further applications for which maleic anhydride serves as a raw material. These applications prove the versatility of this molecule. The popular artificial sweetener aspartame [22839-47-0] is a dipeptide with one amino acid (L-aspartic acid [56-84-8]), which is produced from maleic anhydride as the starting material. Processes have been reported for production of poly(aspartic acid) [26063-13-8] (284–286) with applications for this biodegradable polymer aimed at detergent builders, water treatment, and poly(acrylic acid) [9003-01-4] replacement (284,287,288) (see DETERGENCY). Alkenylsuccinic anhydrides made from several linear α-olefins are used in paper sizing, detergents, and other uses. Sulfosuccinic acid esters serve as surface active agents. Alkyd resins (qv) are used as surface coatings. Chlorendric anhydride [115-27-5] is used as a flame-resistant component (see FLAME RETARDANTS). Tetrahydrophthalic acid [88-98-2] and hexahydrophthalic anhydride [85-42-7] have specialty resin applications. Gas barrier films made by grafting maleic anhydride to polypropylene [25085-53-4] film are used in food packaging (qv). Poly(maleic anhydride) [24937-72-2] is used as a scale preventer and corrosion inhibitor (see CORROSION AND CORROSION CONTROL). Maleic anhydride forms copolymers with mono-*O*-methyl-oligoethylene glycol vinyl ethers that are partially esterified for biomedical and pharmaceutical uses (289) (see PHARMACEUTICALS).

An important developing use for maleic anhydride is the production of products in the 1,4-butanediol–γ-butyrolactone–THF family. Kvaerner Process Technology licenses a process (155) for producing 1,4-butanediol from maleic anhydride. This technology can be used to produce the product mix of the three molecules as needed by the producer. Two plants using the Kvaerner technology were in operation in 1998, with a combined capacity of 50 kt/yr 1,4-butanediol. Several other plants using the Kvaerner technology are under construction or have been announced. SISAS produces 1,4-butanediol from maleic anhydride in their facility in Feluy, Belgium. Du Pont produces THF in Spain from maleic anhydride. The Du Pont technology oxidizes butane to maleic anhydride, which is recovered as maleic acid and then reduced to tetrahydrofuran. BP Amoco announced a facility in Lima, Ohio., to produce 1,4-butanediol from maleic anhydride using their own technology.

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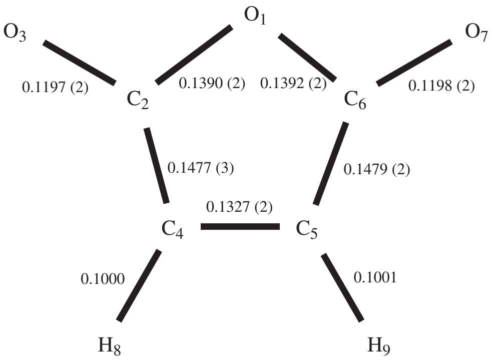

Fig. 1. Bond distances in nanometers (estimated standard deviations in parentheses) for the structure of maleic anhydride determined by single-crystal X-ray diffraction methods at 110 K (10). The maleic anhydride molecule is nearly planar. The plane containing the O1, C4, and C5 atoms has no other atomic nuclei in the molecule deviating from the plane by >0.0036 nm.

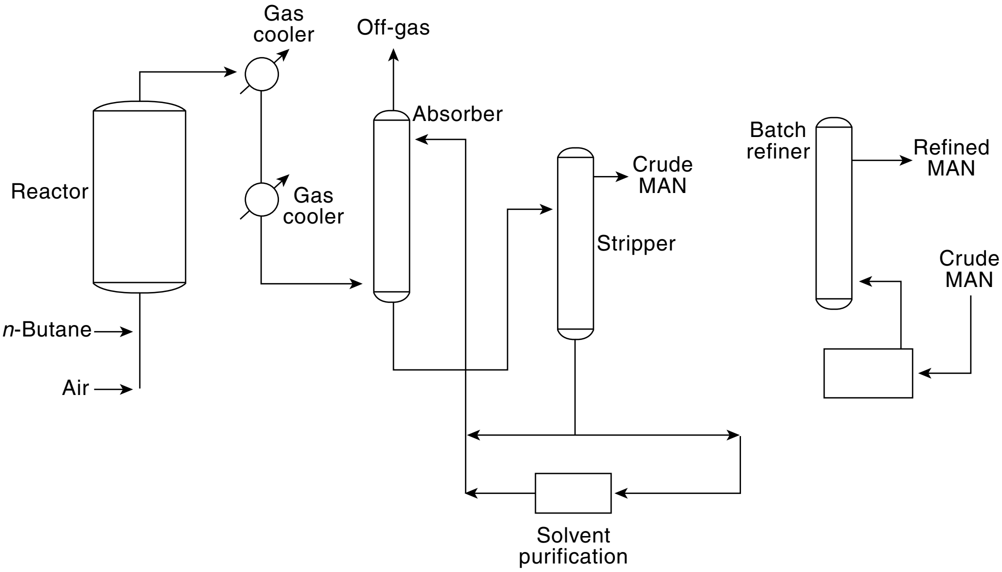

Fig. 2. Schematic flow diagram of the Huntsman fixed-bed maleic anhydride process. MAN = maleic anhydride.

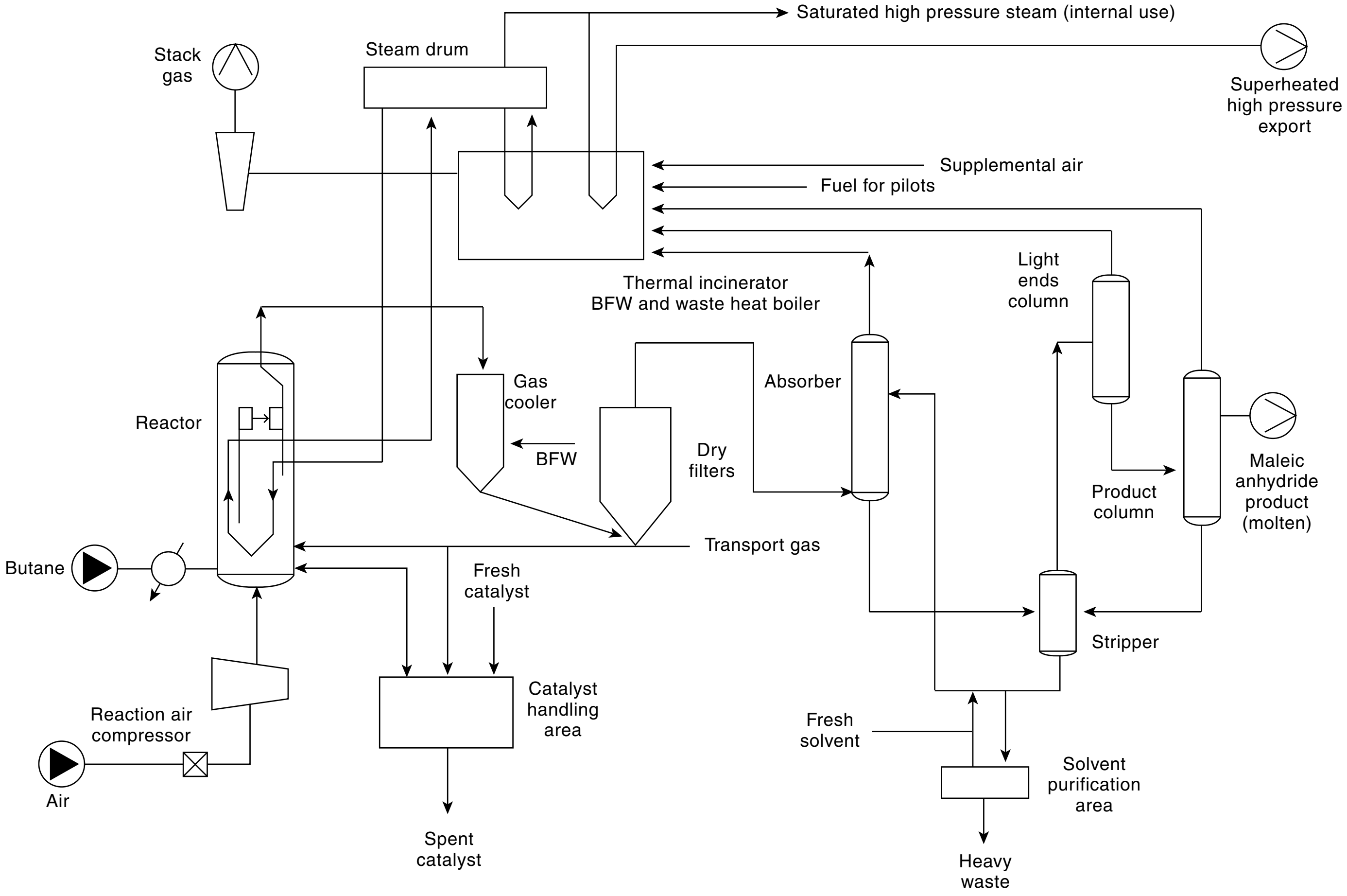

Fig. 3. Schematic flow diagram of the ALMA fluidized-bed process (184). BFW = boiler feed water.

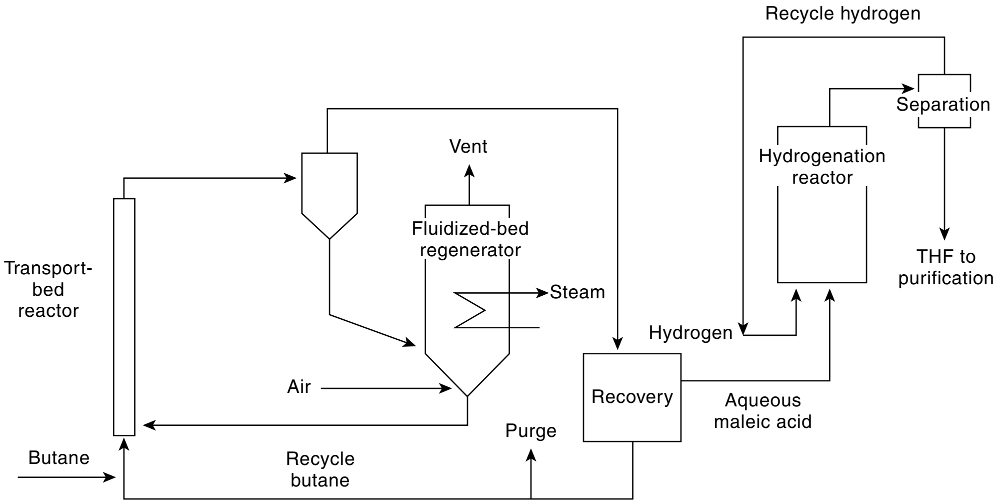

Fig. 4. Du Pont transport-bed process for making THF from butane (176).

Table 1. **Physical Properties of Maleic Anhydride, Maleic Acid, and Fumaric Acid**

Property	Maleic anhydride	Maleic acid	Fumaric acid		Reference
formula	$C_4H_2O_3$	$C_4H_4O_4$	$C_4H_4O_4$		
formula weight	98.06	116.07	116.07		
mp, °C	52.85	138–139[a]	287		3,4
		130–130.5[b]			
		144 (air)	282 (air)		5
bp, °C	202	~138 (dec)	290		4
sp gr, at 20/20°C, solid	1.48[c]	1.590	1.635		4
molar volume		81	79		7
heat of formation, kJ/mol[d]	−470.41	−790.57	−811.03		8
free energy of formation, kJ/mol[d]		−625.09	−655.63		
heat of combustion, kJ/mol[d]	−1389.5	−1355.2	−1334.7		8
heat of hydrogenation, kJ/mol[d]		−153.2	−130.3		8
heat capacity, kJ/(K mol)[d]					
solid	0.1199	0.1356	0.1418		8
liquid	0.164				
heat of sublimation, kJ/mol[d]	71.5	105.4	123.6		8
heat of vaporization, kJ/mol[d]	54.8				8
heat of fusion, kJ/mol[d]	13.55				8
heat of hydrolysis, kJ/mol[d]	−34.9				8
dipole moment, 10^{-30}C·m[e]	13.2	10.6	8.17		9
crystalline form	orthorhombic	monoclinic	monoclinic prismatic, needles, or leaflets		10,15,17,18
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P1$	10,15,17,18
a, nm	0.5322	0.7473	0.7619	0.5264	
b, nm	0.7009	1.0098	1.5014	0.7618	
c, nm	1.0987	0.7627	0.6686	0.4487	
α, deg	90	90	90	106.85	
β, deg	90	123.59	112.0	86.33	
γ, deg	90	90	90	134.94	
dissociation constant at 25°C					20
K_1		1.14×10^{-2}	9.57×10^{-4}		
K_2		5.95×10^{-7}	4.13×10^{-5}		
heat of neutralization, KJ/mol[d]	126.9				6

[a] Crystallized from water.

[b] Crystallized from alcohol; sublimes at 165°C at 0.23 kPa.

[c] Specific gravity at 70/70°C, molten = 1.3 (6).

[d] To convert kJ to kcal, divide by 4.184.

[e] In dioxane at 25°C. To convert coulomb-meters to debye, divide by 3.336×10^{-30}.

Table 2. **Solubility[a] of Maleic Anhydride, Maleic Acid, and Fumaric Acid, g/100 g Solution**

Solvent	Maleic anhydride (g/100 g solvent)	Maleic acid[b]	Fumaric acid
water at[c]			
25°C		44.1	0.70
40°C		52.9	1.05
60°C		58.9	2.34
97.5°C		79.7	
100°C			8.93
acetone at			
20°C		38.6	
25°C	227		
29.7°C		26.3	1.69
benzene at 25°C	50	0.024	0.003
toluene at 25°C	23.4		
o-xylene, at 25°C	19.4		
kerosene (bp 190–210°C) at 25°C	0.25		
methanol at 22.5°C		41.0	
ethanol at			
0°C		30.2	
22.5°C		34.4	
95% ethanol at 29.7°C		41.1	5.44
1-propanol at			
0°C		20.0	
22.5°C		24.3	
chloroform at 25°C	52.5	0.11	0.02
carbon tetrachloride at 25°C	0.6	0.002	0.027
diethyl ether at 25°C		7.57	0.71
2-butenenitrile at 50°C		4.38	0.034
ethyl acetate at 25°C	112		

[a] Refs. 9 and 20; g/100 g solution unless otherwise noted.

[b] Heat of solution = 18.6 kJ/mol (4.45 kcal/mol) (6).

[c] At all temperatures given maleic anhydride hydrolyzes slowly.

Table 3. **Other Properties of Maleic Anhydride**

Property	Value	Property	Value
flash point, °C[a]		vapor pressure,[b] kPA[c]	
open cup	110	at 44.0°C	0.13
closed cup	102	63.4°C	0.67
flammable limits, vol%[a,d]		78.7°C	1.3
lower	1.4–3.4	95.0°C	2.7
upper	7.1	111.8°C	5.3
autoignition temperature, °C[a]	477	122.0°C	8.0
vapor density (air = 1)[a]	3.38	135.8°C	13.3
viscosity, mPa s (=cP)[e]		155.9°C	26.7
60°C	0.61	179.5°C	53.3
90°C	1.07	202.0°C	100
150°C	0.6		
pH of water solutions[f]			
$1 \times 10^{-2}\,M$	2.42		
$5 \times 10^{-3}\,M$	2.62		
$1 \times 10^{-4}\,M$	3.10		
polarographic half-wave potential,[d] V			

[a] Ref. 23.

[b] Ref. 9.

[c] To convert kilopascals (kPa) to millimeters of mercury (mmHg) multiply by 7.5.

[d] Ref. 24.

[e] Ref. 20.

[f] Ref. 25.

Table 4. **World Maleic Anhydride Capacity by Reactor Type**

	1993 Actual[a]		2000 Actual[b]	
Reactor (feed)	kt/yr	%	kt/yr	%
fixed bed (butane)	369	43.0	704	51.8
fixed bed (benzene)	325	37.9	388	28.5
fluid bed (butane)	127	14.8	217	16.0
fixed bed (phthalic anhydride coproduct)	37	4.3	50	3.7
Total	*858*	*100.0*	*1359*	*100.0*

[a] Ref. 178.

[b] Industry sources.

Table 5. **Production and Sales in the United States**

	Maleic anhydride[a]		Fumaric acid[b]
Year	Production, kt	Sales, kt	Production, kt
1986	163.0	137.1	14.5
1987	173.4	141.7	15.4
1988	194.4	162.3	15.9
1989	199.5	169.9	15.4
1990	192.3	160.2	15.4
1991	183.7	142.9	12.2
1992	197.7	159.7	13.2
1993	199.6	151.9	13.2
1994	219.4	175.9	6.4
1995	238.1	205	4.5
1996	247.2	212	4.5
1997	242.7	220	4.5
1998	256.3	223	4.5
1999	256[c]	228[c]	4.5[c]
2000	250[c]	223[c]	4.5[c]

[a] Ref. 258.

[b] Ref. 259.

[c] Industry sources.

Table 6. **Maleic Anhydride[a] and Fumaric Acid[b] Producers in the United States, 2000**

Producer	Location	Capacity, kt/year
Ashland[a]	Neal, W. Va	43.1[c]
Ashland[a]	Neville Island, Penn.	20.4[c]
Bayer[a]	Baytown, Tex.	54.4[c]
BP Amoco[a]	Joliet, Ill.	45.4[c]
Huntsman[a]	Pensacola, Fla.	105.0[c]
Tate and Lyle[b]	Duluth, Minn.	5.5[c]
	Total	*273.8*

[a] Ref. 258.

[b] Ref. 259.

[c] Industry sources.

Table 7. **World Maleic Anhydride Nameplate Capacities**[a]

	Capacity, kt/yr 1992	2000
North America	235	311
South and Central America	44	41
Western Europe	168	456
Central and eastern Europe	64	58
Asia	315	483
Africa	10	10
Total	*836*	*1359*

[a] Industry sources.

Table 8. **Toxicological Data for Maleic Anhydride, Maleic Acid, and Fumaric Acid**[a]

	Maleic anhydride	Maleic acid	Fumaric acid
oral, rat, LD_{50}, mg/kg	400	708	10,700
oral, mouse, LD_{50}, mg/kg	465	2400	
skin, rabbit, LD_{50}, mg/kg	2620	1560	20,000
intraperitoneal, rat,LD_{50}, mg/kg	97		
LD_{Lo}, mg/kg			587
subcutaneous, rat, TD_{Lo}, mg/kg	1220		

[a] Ref. 282.

Table 9. **Uses for Maleic Anhydride in the United States, 2000**[a]

Product	% of Demand
unsaturated polyester resins	63
fumaric and malic acid	5
lube oil additives	11
maleic copolymers	8
agricultural chemicals	2
others	11
Total	*100*

[a] Ref. 258 and industry sources.

Table 10. **Uses for Unsaturated Polyester in the United States, 2000**[a]

Product	Demand
marine	16.2
construction	34.2
corrosion	10.4
transportation	15.0
electrical	1.9
other	22.3
Total	*100.0*

[a] Ref. 283 and industry sources.