BUTADIENE

1. Introduction

Butadiene, C_4H_6, exists in two isomeric forms: 1,3-butadiene [106-99-0], $CH_2{=}CH{-}CH{=}CH_2$, and 1,2-butadiene [590-19-2], $CH_2{=}C{=}CH{-}CH_3$. 1,3-Butadiene is a commodity product of the petrochemical industry with a 2000 U.S. production of 4.4 billion pounds (2.0×10^9 kg) (1). Although this is not very different from the production in 1971, it represents significant rebound from the low production in the mid-1980s. Elastomers consume the bulk of 1,3-butadiene, led by the manufacture of styrene–butadiene rubber (SBR). 1,3-Butadiene is manufactured primarily as a coproduct of steam cracking to produce ethylene in the United States, Western Europe, and Japan. However, in certain parts of the world it is still produced from ethanol. The earlier manufacturing processes of dehydrogenation of *n*-butane and oxydehydrogenation of *n*-butenes have significantly declined in importance and output. Efforts have been made to make butadiene from other feedstocks such as other hydrocarbons, coal (2,3), shale oil (4); and renewable sources like animal and vegetable oil (5), cellulose, hemicellulose, and lignin (6,7), but in the United States none of these have moved beyond the research and development stage.

The other isomer, 1,2-butadiene, a small by-product in 1,3-butadiene production, has no significant current commercial interests. The production of 1,2-butadiene in purities of 85% has been described (8). However, there are a number of publications and patents on its recovery and applications, particularly in the specialty polymer area (9,10) and as a gel inhibitor (11).

2. Properties

1,3-Butadiene is a noncorrosive, colorless, flammable gas at room temperature and atmospheric pressure. It has a mildly aromatic odor. It is sparingly soluble in water, slightly soluble in methanol and ethanol, and soluble in organic solvents like diethyl ether, benzene, and carbon tetrachloride. Its important

Table 1. **Physical Properties of 1,3-Butadiene**[a]

Property	Value
CAS Registry Number	[*106-99-0*]
RTECS accession number	EI9275000
UN number	1010
molecular formula	C_4H_6
molecular weight	54.092
boiling point at 101.325 kPa[b], °C	−4.411
freezing point, °C	−108.902
critical temperature, °C	152.0
critical pressure, MPa[c]	4.32
critical volume, cm^3/mol	221
critical density, g/mL	0.245
density (liquid), g/mL at	
0°C	0.6452
15°C	0.6274
20°C	0.6211
25°C	0.6194
50°C	0.5818
density (gas) (air = 1)	1.9
heat capacity at 25°C, J/(mol · K)[d]	79.538
refractive index, n_D at −25°C	1.4292
solubility in water at 25°C, ppm	735[e]
viscosity (liquid), mPa · s (=cP) at	
−40°C	0.33
0°C	0.25
40°C	0.20
heat of formation, gas, kJ/mol[d]	110.165
heat of formation, liquid, kJ/mol[d]	88.7
free energy of formation, kJ/mol[d]	150.66
heat of vaporization, J/g[d] at	
25°C	389
boiling point	418
flash point, °C	−85
autoignition temperature, °C	417.8
explosion limits in air, vol %	
lower	2.0
upper	11.5
minimum oxygen for combustion (MOC), %v/vO_2	
N_2−air	10
CO_2−air	13
absorption	
λ, cm^{-1}	217
log ε	4.32

[a] Refs. 23–28.

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

[c] To convert MPa to psi, multiply by 145.

[d] To convert J to cal, divide by 4.184.

[e] 245 mol ppm.

Table 2. **Physical Properties of 1,2-Butadiene**[a]

Property	Value
CAS Registry Number	[590-19-2]
molecular formula	C_4H_6
molecular weight	54.092
boiling point at 101.325 kPa,[b] °C	10.85
freezing point, °C	−136.19
density (liquid), g/mL at	
0°C	0.676
20°C	0.652
heat of formation at 25°C (gas), kJ/mol[c]	162.21
heat of vaporization at 25°C, kJ/mol[c]	23.426
refractive index at 1.3°C	1.4205

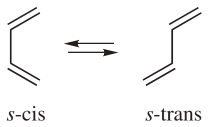
[a] Refs. 24,29.

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

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

physical properties are summarized in Table 1 (see also Ref. 12,13). 1,2-Butadiene is much less studied. It is a flammable gas at ambient conditions. Some of its properties are summarized in Table 2.

1,3-Butadiene, the simplest conjugated diene, has been the subject of intensive theoretical and experimental studies to understand its physical and chemical properties. The conjugation of the double bonds makes it 15 kJ/mol (3.6 kcal/mol) (14) more thermodynamically stable than a molecule with two isolated single bonds. The *s*-trans isomer, often called the trans form, is more stable than the *s*-cis form at room temperature. Although there is a 20 kJ/mol (4.8 kcal/mol) rotational barrier (15,16), rapid equilibrium allows reactions to take place with either the *s*-cis or *s*-trans form (17,18).



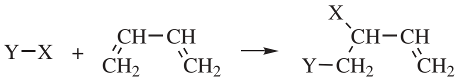
The double-bond length in 1,3-butadiene is 0.134 nm, and the single-bond, 0.148 nm. Since normal carbon–carbon single bonds are 0.154 nm, this indicates the extent of double-bond character in the middle single bond. Upon complexing with metal carbonyl moieties like $Fe(CO)_3$, the two terminal bonds lengthen to 0.141 nm, and the middle bond shortens even more to 0.145 nm (19).

Solubilities of 1,3-butadiene and many other organic compounds in water have been extensively studied to gauge the impact of discharge of these materials into aquatic systems. Estimates have been advanced by using the UNIFAC derived method (20,21). Similarly, a mathematical model has been developed to calculate the vapor–liquid equilibrium (VLE) for 1,3-butadiene in the presence of steam (8).

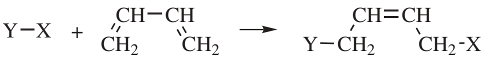
3. Reactions

Since the discovery of 1,3-butadiene in the nineteenth century, it has grown into an extremely versatile and important industrial chemical (30). Its conjugated double bonds allow a large number of unique reactions at both the 1,2- and 1,4-positions. Many of these reactions produce large volumes of important industrial materials.

3.1. Addition Reactions. 1,3-Butadiene reacts readily via 1,2- and 1,4-free radical or electrophilic addition reactions (31) to produce 1-butene or 2-butene substituted products, respectively.

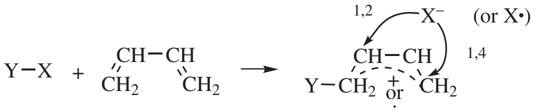


1,2-addition product

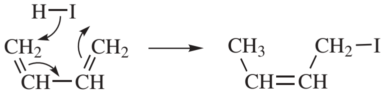


1,4-addition product

The intermediate in these reactions in the case of the addition of YX is consistent with the addition of Y to the 1-position to form an allylic intermediate to which X adds to produce either the 1,2- or 1,4-product.



The addition of HX, where X is a halogen, has been thoroughly investigated (32,33). Whether 1,2- or 1,4-product dominates depends on reaction conditions. For example, although HCl adds to butadiene at low temperatures to produce 75–80% of the 1,2-addition product, the thermodynamically more stable 1,4-isomer is favored at higher temperatures (34). On the other hand, HI has been shown to add to butadiene in the vapor phase by a pericyclic mechanism to produce the 1,4-product (35).



Addition of water (36) or alcohols (37–39) directly to butadiene at 40–100°C produces the corresponding unsaturated alcohols or ethers. Acidic ion exchangers have been used to catalyze these reactions. The yields for these latter reactions are generally very low because of unfavorable thermodynamics. At 50°C addition of acetic acid to butadiene produces the expected butenyl acetate with 60–100% selectivity at butadiene conversions of 50%. The catalysts are ion-exchange resins modified with quaternary ammonium, quaternary phosphonium, and ammonium substituted ferrocenyl ions (40). Addition of amines yields unsaturated alkyl amines. The reaction can be catalyzed by homogeneous catalysts such as $Rh[P(C_6H_5)_3]_3Cl$ (41) or heterogeneous catalysts such as MgO and other solid bases (42).

The manufacture of hexamethylenediamine [124-09-4], a key comonomer in nylon-6,6 production proceeds by a two-step HCN addition reaction to produce adiponitrile [111-69-3], $NCCH_2CH_2CH_2CH_2CN$. The adiponitrile is then hydrogenated to produce the desired diamine. The other half of nylon-6,6, adipic acid (qv), can also be produced from butadiene by means of either of two similar routes involving the addition of CO. Reaction between the diamine and adipic acid [124-04-5] produces nylon-6,6.

The first CO route to make adipic acid is a BASF process employing CO and methanol in a two-step process producing dimethyl adipate [627-93-0], which is then hydrolyzed to the acid (43–46). Cobalt carbonyl catalysts such as $Co_2(CO)_8$ are used. Palladium catalysts can be used to effect the same reactions at lower pressures (47–49).

The other CO route for adipic acid manufacture involves 1,4-addition of CO and O_2 to butadiene to produce an intermediate, which is subsequently hydrogenated and hydrolyzed to adipic acid (50). This is called the oxycarbonylation process. Both the BASF and the oxycarbonylation processes have been intensively investigated.

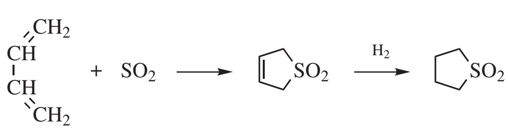
Halogenation of butadiene has also attracted a lot of interest. Both 1,2- and 1,4-isomers are formed. Since the *trans*-1,4-isomer was observed from the 1,4-addition product, researchers postulate that the electrophilic X^+ forms a 1,2-cyclic intermediate and not a 1,4-cyclic intermediate that would form the *cis*-1,4-addition product (51,52).

Fluorination with XeF_2 or $C_6H_5IF_2$ gives both the 1,2- and 1,4-difluoro products. This reaction proceeds via the initial electrophilic addition of F^+ to the diene (53).

Chloroprene (qv), 2-chloro-1,3-butadiene, [126-99-8] is produced commercially from butadiene in a three-step process. Butadiene is first chlorinated at 300°C to a 60:40 mixture of the 1,2- and 1,4-dichlorobutene isomers. This mixture is isomerized to the 3,4-dichloro-1-butene with the aid of a $Cu-Cu_2\,Cl_2$ catalyst followed by dehydrochlorination with base such as NaOH (54).

The 1,4-dichloro-2-butene can also be separated and hydrolyzed with aqueous NaOH to form 1,4-butenediol, which is hydrogenated with Ni catalyst to produce 1,4-butanediol. In 1971, this process was commercialized in Japan (55). The plant is now shut down because of unfavorable economics.

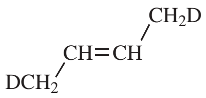
Butadiene also undergoes a 1,4-addition reaction with SO_2 to give sulfolene [77-79-2]. This reaction followed by hydrogenation is commercially used to manufacture sulfolane [126-33-0] (56).



Formaldehyde also reacts with butadiene via the Prins reaction to produce pentenediols or their derivatives. This reaction is catalyzed by a copper-containing catalyst in a carboxylic acid solution (57) or $RuCl_3$ (58). The addition of hydrogen also proceeds via 1,2- and 1,4-addition.

3.2. Hydrogenation Reactions. Butadiene can be hydrogenated to *n*-butanes and *n*-butane using a large number of heterogeneous (59) and homogeneous (60–64) catalysts. Palladium-containing membranes have also been used to allow the use of permeated hydrogen to effect hydrogenation (65–67). Many catalysts have been developed and used commercially to remove small quantities ($\leq 3\%$) of butadiene from 1-butene streams (68–71). Since 2-butene [107-01-7] is more stable thermodynamically than 1-butene [106-98-9] under mild conditions, catalysts that promote 1,2-addition and do not isomerize 1-butene are essential for getting high 1-butene selectivity. Many of the palladium catalysts require the use of CO to improve 1-butene selectivity (72–74).

Selectivities to various isomers are more difficult to predict when metal oxides are used as catalysts. Zinc oxide (ZnO) preferentially produced 79% 1-butene and several percent of *cis*-2-butene [624-64-6] (75). Cadmium oxide (CdO) catalyst produced 55% 1-butene and 45% *cis*-2-butene. It was also reported that while interconversion between 1-butene and *cis*-2-butene was quite facile on CdO, cis–trans isomerization was slow. This finding was attributed to the presence of a π-allyl anion intermediate (76). High *cis*-2-butene selectivities were obtained with molybdenum carbonyl encapsulated in zeolites (77). On the other hand, deuteration using ThO_2 catalyst produced predominantly the 1,4-addition product, *trans*-2-butene-d_2 with no isotope scrambling (78).



Although supported Pd catalysts have been the most extensively studied for butadiene hydrogenation, a number of other catalysts have also been the object of research studies. Some examples are Pd film catalysts, molybdenum sulfide, metal catalysts containing Fe, Co, Ni, Ru, Rh, Os, Ir, Pt, Cu, MgO, $HCo(CN)_5^{3-}$ on supports, and $LaCoC_3$ Perovskite. There are many others (79–85). Studies on the well-characterized Mo(II) monomer and Mo(II) dimer on silica carrier catalysts have shown wide variations not only in catalyst performance, but also of activation energies (86).

Another method to hydrogenate butadiene occurs during an oxidation–reduction reaction in which an alcohol is oxidized and butadiene is reduced. Thus copper–chromia or copper–zinc oxide catalyzes the transfer of hydrogen from 2-butanol or 2-propanol to butadiene at 90–130°C (87,88).

3.3. Oxidation Reactions. Like all reactions between oxygen and hydrocarbons, complete oxidation of butadiene is controlled by limiting the oxygen and operating at specific temperature ranges. Other ways to control selectivity to specific products involve the use of catalysts and/or conducting the reaction in the presence of other reagents. Some of the many oxidized products are depicted in Figure 1.

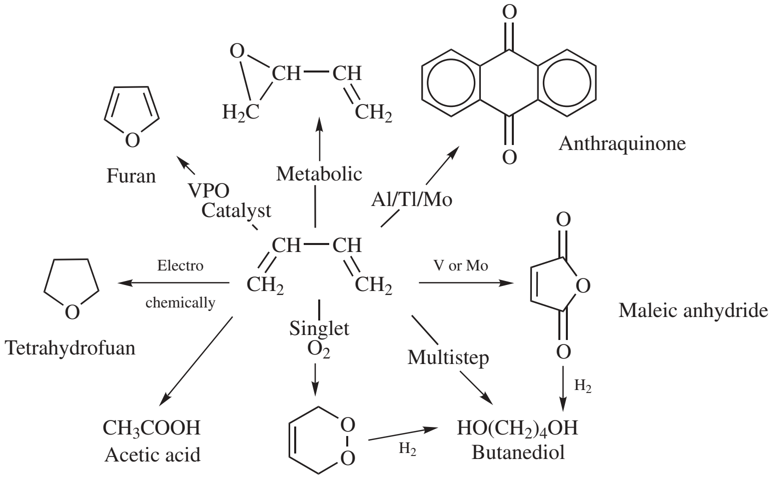


Fig. 1. Oxidative reactions of butadiene.

The vapor-phase oxidation (VPO) of butadiene with air at 200–500°C produces maleic anhydride [108-31-6]. Catalysts used are based on vanadium and molybdenum oxides (89,90). Alternatively, when using a catalyst containing Al, Mo, and Ti, butadiene undergoes a complex series of condensations and oxidations to form anthraquinone at 250°C (91).

Reaction between oxygen and butadiene in the liquid phase produces polymeric peroxides that can be explosive and shock-sensitive when concentrated. Both Ir(I) and Rh(I) complexes have been shown to catalyze this polymerization at 55°C (92). These peroxides, which are formed via 1,2- and 1,4-addition, can be hydrogenated to produce the corresponding 1,2- or 1,4-butanediol [110-63-4] (93). Butadiene can also react with singlet oxygen in a Diels–Alder type reaction to produce a cyclic peroxide that can be hydrogenated to 1,4-butanediol.

Oxygen has also been shown to insert into butadiene over a VPO catalyst, producing furan [110-00-9] (94). Under electrochemical conditions butadiene and oxygen react at 100°C and 0.3 amp and 0.43 V producing tetrahydrofuran (THF) [109-99-9]. The selectivity to THF was 90% at 18% conversion (95) and it can also be made via direct catalytic oxidation of butadiene with oxygen. Active catalysts are based on Pd in conjunction with polyacids (96), Se, Te, and Sb compounds in the presence of Cu_2Cl_2, $LiCl_2$ (97), or Bi–Mo (98).

The oxidation reaction between butadiene and oxygen and water in the presence of CO_2 or SO_2 produces 1,4-butenediol. The catalysts consist of iron acetylacetonate and LiOH (99). The same reaction was also observed at 90°C with groups 8–10 (VIII) transition metals such as Pd in the presence of I_2 or iodides (100). The butenediol can then be hydrogenated to butanediol [110-63-4]. In the presence of copper compounds and at pH 2, hydrogenation leads to furan (101).

Alternatively, butadiene can be oxidized in the presence of acetic acid to produce butenediol diacetate, a precursor to butanediol. The latter process has been commercialized (102–104). This reaction is performed in the liquid phase at 80°C with a Pd–Te–C catalyst. A different catalyst system based on

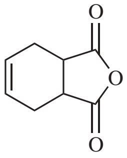
$PdCl_2(NCC_6H_5)_2$ has been reported (105). Copper- (106) and rhodium- (107) based catalysts have also been studied.

$$CH_2{=}CH{-}CH{=}CH_2 + 2\ CH_3COOH + O_2 \longrightarrow CH_3COOCH_2$$
$$CH{=}CHCH_2OOCCH_3 \longrightarrow H_2\ CH_3COOCH_2CH_2CH_2CH_2OOCCH_3\ ^{H_2O}$$
$$HOCH_2CH_2CH_2CH_2OH + 2\ CH_3COOH$$

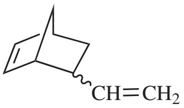
Another butadiene oxidation process to produce butanediol is based on the 1,4-addition of *tert*-butyl hydroperoxide to butadiene (108). Cobalt on silica catalyzes the first step. This is followed by hydrogenation of the resulting olefinic diperoxide to produce butanediol and *tert*-butyl alcohol.

Butadiene can also be readily epoxidized with peracids to the monoepoxide or the diepoxide (109,110). These have been proposed as important intermediates in the metabolic cycle of butadiene in the human body (111).

3.4. Diels–Alder Reactions. The important dimerization between 1,3-dienes and a wide variety of dienophiles to produce cyclohexene derivatives was discovered in 1928 by Otto Diels and Kurt Alder. In 1950, they won the Nobel Prize for their pioneering work. Butadiene has to be in the *s*-cis form in order to participate in these concerted reactions. Typical examples of reaction products from the reaction between butadiene and maleic anhydride (1), or cyclopentadiene (2), or itself (3), are *cis*-1,2,3,6-tetrahydrophthalic anhydride [27813-21-4], 5-vinyl-2-norbornene [3048-64-4], and 4-vinyl-1-cyclohexene [100-40-3], respectively.



(1)



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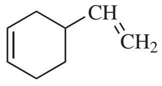


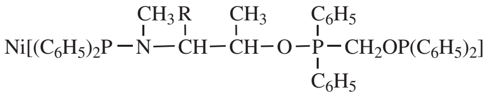
(3)

Diels–Alder reactions with butadiene are generally thermally reversible and can proceed in both gas and liquid phases. The reactions are exothermic and follow second-order kinetics; first-order with respect to each reactant.

The dienophiles for reaction with butadiene can be alkenes, allenes, and alkynes. Simple alkenes like ethylene are poor dienophiles resulting in sluggish reactions. Substituted olefins, $X{-}C{=}C{-}X'$, are more reactive when X and/or X′ are C=C, Ar, COOR, COOH, COH, COR, COCl, CN, halogens, and many other electron-withdrawing substituents (112–116). A compilation of the reaction parameters between butadiene and C2–C4 olefins in the temperature range of 510–750°C has been published (117). Other double-bond or triple-bond compounds, such as $C{=}N{-}$, $-N{=}N{-}$, $O{=}C{-}$, $-C{\equiv}N$, and O_2 can also act as dienophiles to give heterocyclic products. These types of concerted reactions have been the subject of extensive orbital symmetry studies (118,119).

Diels–Alder reactions are thermal reactions requiring no catalysts (120). However, over the years both acid- and metal-based homogeneous or heterogeneous catalysts have been developed (121–127). Some catalysts used in

Diels–Alder catalyzed reactions of butadiene are $Fe(NO)_2Cl–(CH_3CH_2)_2AlCl$, $Pd[P(C_6H_5)_3]_4$, Cu(I) exchanged silica–alumina (128,129), large pore zeolites (130), and carbon molecular sieves. An electrochemical process has also been used to catalyze the self-condensation to vinylcyclohexene (131). When the asymmetric Ni catalyst (**4**) was used, specificity to the enantomeric (*S*)-4-vinylcyclohexene (132,133) was observed (26% enantiomeric excess).

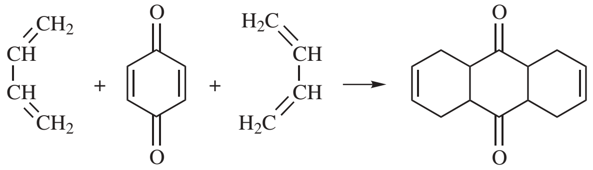


$$Ni[(C_6H_5)_2P-\overset{CH_3}{N}-\overset{R}{C}H-\overset{CH_3}{C}H-O-\underset{C_6H_5}{\overset{C_6H_5}{P}}-CH_2OP(C_6H_5)_2]$$

(**4**)

When the Diels–Alder reaction between butadiene and itself is carried out in the presence of alkali metal hydroxide or carbonate (such as KOH, Na_2CO_3, and K_2CO_3 on alumina or magnesia supports) dehydrogenation of the product, vinylcyclohexene, to ethylbenzene can occur at the same time (134). The same reaction can take place on simple metal oxides like ZrO_2, MgO, CaO, SrO, and BaO (135).

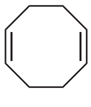
The Diels–Alder reaction between 2 mol of butadiene and 1 mol of quinone [106-51-4] produces tetrahydroanthraquinone [28758-94-3] (136).



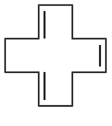
3.5. Dimerization and Oligomerization Reactions.

Besides Diels–Alder type dimerization reactions, butadiene undergoes a number of other dimerization or oligomerization reactions to produce cyclic or linear products. With the proper catalysts these reactions proceed quite selectivity. Noncatalyzed or photocatalyzed dimerizations produce compounds like divinylcyclobutanes and have been studied in detail (137,138).

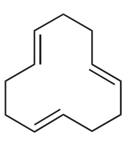
A fascinating series of cyclodimerization or cyclotrimerization reactions was first observed in the labs of Wilke to produce 1,5-cyclooctadiene [111-78-4] (COD) and *cis,trans,trans*-1,5,9-cyclododecatriene [2765-29-9] (CTT), or *trans,-trans, -trans*-1,5,9-cyclododecatriene [676-22-2] (TTT).



COD



CTT



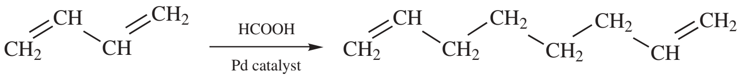
TTT

These cyclodimerization and cyclotrimerization reactions are catalyzed by low valent Ziegler-type Ni catalysts (139–144). Large ligands, such as tris-*o*-biphenylyl phosphite on nickel tend to favor COD formation while smaller ligands favor the linear dimer, 1,3,7-octatriene. The dimer yield at 80°C and 101.3 kPa (1 atm) is 96%. The nickel catalyst can also be placed on a support so that it can be recycled (145). Many other type catalysts have been reported for this reaction (146). The linear 1,3,7-octatriene and its 1,3,6 isomer are also obtained by a Pd catalyzed dimerization (147–151). The kinetics of thermally induced dimerization to cod has also been studied (152).

One of the butadiene dimerization products, cod, is commercially manufactured and used as an intermediate in a process called FEAST to produce linear α,φ-dienes (153). 1,5-cyclooctadiene or cyclooctene [931-87-3], obtained from partial hydrogenation, is metathesized with ethylene to produce 1,5-hexadiene [592-42-7] or 1,9-decadiene [1647-16-1], respectively. Many variations to make other diolefins have been demonstrated. Huls AG also metathesized cyclooctene with itself to produce an elastomer useful in rubber blending (154). The cyclic *cis,-trans,trans*-triene described above can be hydrogenated and oxidized to manufacture dodecanedioic acid [693-23-2]. The product was used in the past for the production of the specialty nylon-6,12, Qiana (155,156).

The trimerization to produce *cis,trans,trans*-1,5,9-cyclododecatriene has also been practiced commercially using a Ziegler–Natta catalyst $TiCl_4$–$Al_2(C_2H_5)_3Cl_3$ (157).

Linear dimerization and oligomerization of butadiene can be achieved by using a number of catalyst systems based on Pd, Ni (158–161), and Fe (162). 1,7-Octadiene can be obtained selectively when the dimerization is carried out in the presence of a reducing agent such as formic acid (163–165) or H_2/CO_2 (166).

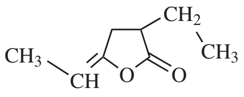


Ziegler-type catalysts based upon Co, Ni, and Fe and in the presence of aluminum alkyls codimerize butadiene with olefins such as ethylene, producing 1,4-hexadiene derivatives. A rhodium-based catalyst can be used to produce all the *trans*-1,4-hexadiene used as the termonomer in the commercial EPDM (155,156) (see ELASTOMERS, SYNTHETIC; ETHYLENE–PROPYLENE RUBBER). In contrast, cobalt and iron catalysts are known to give the cis-isomer.

3.6. Telomerization Reactions. Butadiene can react readily with a number of chain-transfer agents to undergo telomerization reactions. The more often studied reagents are carbon dioxide (167–178), water (179–181), ammonia (182), alcohols (183–185), amines (186), acetic acid (187), water and CO_2 (188), ammonia and CO_2 (189), epoxide and CO_2 (190), mercaptans (191), and other systems (171). These reactions have been widely studied and used in making unsaturated lactones, alcohols, amines, ethers, esters, and many other compounds.

Reaction between butadiene and CO_2 has been extensively studied (171) since the reaction was first demonstrated (167–170). This reaction has been shown to be catalyzed by Pd (172,173), Ni (174), Ru (175), Pt (178), and Rh (172,173) catalysts. Products include gamma (**5**) and delta lactones (**6**), acids (**7**,**8**), and esters (**9**). Mechanistic studies have shown that butadiene initially forms a dimer (Pd, Ru, Ni) or trimer (Rh) intermediate followed by CO_2 insertion

(171). The fate of these intermediates depends on the metal, the ligands, and the reaction conditions.



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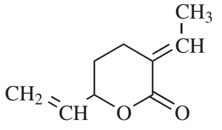

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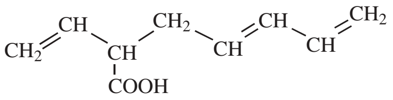

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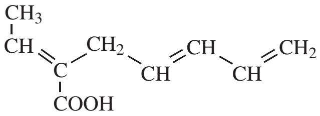

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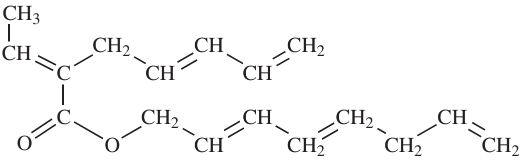


(**9**)

The delta lactone can be obtained in very high yields when triisopropylphosphine or tricyclohexylphosphine is the ligand along with Pd(acac)$_2$ (acac = acetylacetoacetonate) as the metal source (171).

Coupling of butadiene with CO$_2$ under electrochemically reducing conditions produces decadienedioic acid, and pentenoic acid, as well as hexenedioic acid (192). A review article on diene telomerization reactions catalyzed by transition metal catalysts has been published (193).

3.7. Polymerization Reactions. The polymerization of butadiene with itself and with other monomers represents its largest commercial use. The commercially most important polymers are SBR, polybutadiene (BR), styrene–butadiene latex (SBL), acrylonitrile–butadiene–styrene polymer (ABS), and nitrile rubber (NR). The reaction mechanisms are free-radical, anionic, cationic, or coordinate, depending on the nature of the initiators or catalysts (194–196).

Different grades of SBR copolymers are prepared by either free-radical initiated emulsion polymerization or anionic solution polymerization. The technology was developed during World War II to produce a substitute for natural rubber. The properties of these SBRs are so good that natural rubber has never again regained its importance. Today, SBR represents the single largest use of butadiene (see Elastomers, synthetic, polybutadiene; Styrene–butadiene rubber).

The original SBR process is carried out at $\sim$50°C and is referred to as hot polymerization. It accounts for only $\sim$5% of all the rubber produced today. The dominant cold polymerization technology today employs more active initiators to effect polymerization at about 5°C. It accounts for $\sim$ 85% of the products manufactured. Typical emulsion polymerization processes incorporate about 75% butadiene. The initiators are based on persulfate in conjunction with mercaptans (197), or organic hydroperoxide in conjunction with ferrous ion (198). The rest of SBR is produced by anionic solution polymerization. The density of unvulcanized SBR is 0.933 (199). The T_g ranges from -59 to -64°C (199).

Homopolymerization of butadiene can proceed via 1,2- or 1,4-additions. The 1,4-addition produces the geometrically distinguishable trans or cis structures with internal double bonds on the polymer chains. 1,2-Addition, on the other

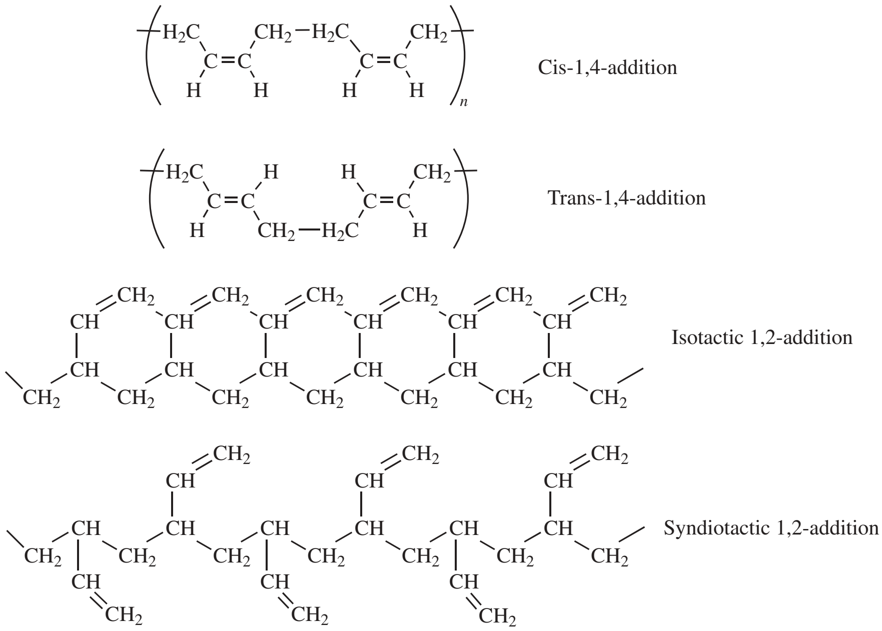


Fig. 2. Modes of addition of butadiene.

hand, yields either atactic, isotactic, or syndiotactic polymer structures with pendent vinyl groups (Fig. 2). Commercial production of these polymers started in 1960 in the United States. Firestone and Goodyear account for >60% of the current production capacity (see Elastomers, synthetic–polybutadiene).

Very high cis-1,4-addition (≥80%) imparts more desirable properties for applications like heavy-duty tires (200). Structural properties of some typical polybutadienes are listed in Table 3 (200–202).

Extensive efforts have been made to develop catalyst systems to control the stereochemistry, addition site, and other properties of the final polymers. Among the most prominant ones are transition metal-based catalysts including Ziegler or Ziegler–Natta type catalysts. The metals most frequently studied are Ti (203,204), Mo (205), Co (206–208), Cr (206–208), Ni (209,210), V (205), Nd (211–215), and other lanthanides (216). Of these, Ti, Co, and Ni complexes

Table 3. **Properties of Polybutadiene**

Type[a]	Unit cell	Density	Melting point, °C	T_g, °C
1,4-*cis*	monoclinic	1.01	2	−106
1,4-*trans*-	hexagonal[b]			−107
modification I		0.97	97	
modification II		0.93	145	
1,2-syndiotactic	rhombic	0.96	154	−28
1,2-isotactic	rhombohedral	0.96	120	

[a] See Figure 2.
[b] Up to 60°C.

have been used commercially. It has long been recognized that by varying the catalyst compositions, the trans/cis ratio for 1,4-additions can be controlled quite selectively (204). Catalysts have also been developed to control the ratio of 1,4- to 1,2-additions within the polymers (203).

In situ preparation of polymer blends of 1,4-polybutadiene with polystyrene, or poly(1-butene) has been achieved by using the heterogeneous Ziegler–Natta type catalyst $(C_2H_5)_2AlCl{-}Ti(OC_4H_9)_4$ in the host polymers (217). Homogeneous catalysts can also be used to catalyze these reactions (218).

Anionic polymerization of butadiene has been intensively investigated over the years. Alkali metals and their alkyl derivatives are most frequently used. The process employing alkyllithium compounds as the initiators was first commercialized in the 1950s. Typical vinyl (1,2-addition) content is ~10–25%, with the balance about evenly divided between cis- and trans-1,4-addition, depending on the alkyllithium catalyst selected (219). The vinyl content can be increased substantially by the addition of polar compounds such as ethers or amines to the reaction mixture (202,220,221). The most common catalyst used commercially appears to be butyllithium. The products are mostly amorphous and provide desirable vulcanized rubber properties (202). By taking advantage of the living polymer nature of the reaction, products containing various end groups, such as —OH, —COOH, —SH, and others, can be prepared by terminating the polymerization with the proper reagent (195).

Another better studied system is the Alfin (alkoxide–olefin) catalyst, which is composed of a sodium salt, sodium alkoxide, and allylsodium (222). Similarly, there are many different modifications of the system to produce polymers with different 1,2- to 1,4-addition ratios as well as other properties (223).

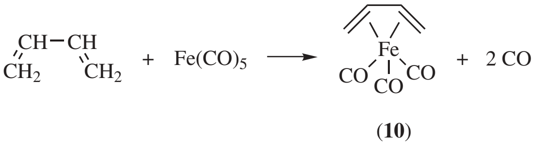
Acrylonitrile–butadiene copolymers (nitrile–butadiene rubber, NBR) are also produced via emulsion polymerization of butadiene with acrylonitrile, $CH_2{=}CH{-}CN$ [107-13-1].

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{-}CH{-}CN \longrightarrow \sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}\sim$$

Acrylonitrile–butadiene–styrene resins are two-phase blends. These are prepared by emulsion polymerization or suspension grafting polymerization. Products from the former process contain 20–22% butadiene; those from the latter, 12–16%.

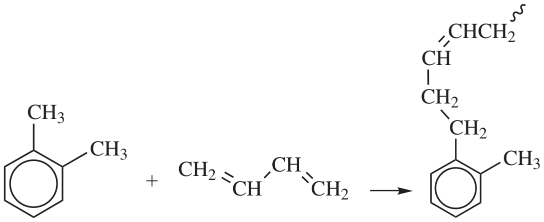
Butadiene can also be copolymerized with a large number of other olefins (224) and SO_2 (225).

3.8. Other Reactions. Due to the highly reactive conjugated double bonds, butadiene can undergo many reactions with transition metals to form organometallic complexes. For example, iron pentacarbonyl reacts with butadiene to produce the tricarbonyl iron complex (**10**) (226). This and many other organometallic complexes have been covered (227).



(**10**)

Side-chain anionic alkylation reactions with aromatic compounds take place when catalyzed with strong basic catalysts, like Na–K (228). The yield is 83% when *o*-xylene reacts with butadiene.



4. Manufacture and Processing

The pattern of commercial production of 1,3-butadiene parallels the overall development of the petrochemical industry. Since its discovery via pyrolysis of various organic materials, butadiene has been manufactured from acetylene as well as ethanol, both via butanediols (1,3- and 1,4-) as intermediates (see ACETYLENE-DERIVED CHEMICALS). On a global basis, the importance of these processes has decreased substantially because of the increasing production of butadiene from petroleum sources. China and India still convert ethanol to butadiene using the two-step process while Poland and the former USSR use a one-step process (229,230). In the past butadiene also was produced by the dehydrogenation of *n*-butane and oxydehydrogenation of *n*-butenes. However, butadiene is now primarily produced as a by-product in the steam cracking of hydrocarbon streams to produce ethylene. Except under market dislocation situations, butadiene is almost exclusively manufactured by this process in the United States, Western Europe, and Japan.

4.1. Steam Cracking. Steam cracking is a complex, highly endothermic pyrolysis reaction. During the reaction a hydrocarbon feedstock is heated to ~800°C and 34 kPa (5 psi) for less than a second during which carbon–carbon and carbon–hydrogen bonds are broken. As a result, a mixture of olefins, aromatics, tar, and gases are formed. These products are cooled and separated into specific boiling range cuts of C_1, C_2, C_3, C_4, etc. The C_4 fraction contains butadiene, isobutylene, 1-butene, 2-butene, and some other minor hydrocarbons. The overall yields of butadiene depend on both process parameters (231) and the composition of feedstocks (Table 4) (232). Generally, heavier steam cracking feedstocks produce greater amounts of butadiene as a by-product. Thus, with heavier feedstocks like light naphtha or virgin gas oil, up to about 5.4 wt% of the total product is butadiene. The processes of separating butadiene from the other C_4 compounds are described later.

4.2. Dehydrogenation of *n*-Butane. Dehydrogenation of *n*-butane [106-97-8] via the Houdry process is carried out under partial vacuum, 35–75 kPa (5–11 psi), at ~535–650°C with a fixed-bed catalyst. The catalyst consists of aluminum oxide and chromium oxide as the principal components. The reaction is endothermic and the cycle life of the catalyst is ~10 min because of coke buildup.

Table 4. **Product Distribution from Steam Cracking Various Feedstocks**[a]

	Product yield, wt %					
Feedstock	Ethylene	Propylene	Butadiene	Butenes	BTX	Fuel products
ethane	77.5	2.8	1.9	0.8		17.0
propane	42.0	16.8	3.0	1.3	3.0	33.9
light naphtha	33.7	15.6	4.5	4.2	9.1	32.9
light VGO[b]	20.4	14.1	5.4	6.3	8.5	45.3

[a] Ref. 232.

[b] VGO = vacuum gas oil.

Several parallel reactors are needed in the plant to allow for continuous operation with catalyst regeneration. Thermodynamics limits the conversion to ~30–40% and the ultimate yield is 60–65 wt% (233).

4.3. Oxydehydrogenation of *n*-Butenes. Normal butenes can be oxidatively dehydrogenated to butadiene in the presence of high concentration of steam with fairly high selectivity (234). The conversion is no longer limited by thermodynamics because of the oxidation of hydrogen to water. Reaction temperature is below ~600°C to minimize over oxidation. Pressure is ~34–103 kPa (5–15 psi).

4.4. Separation and Purification. Separation and purification of butadiene from other components is dominated commercially by the extractive distillation process. The most commonly used solvents are acetonitrile and dimethylformamide. Dimethylacetamide, furfural, and *N*-methyl-2-pyrrolidinone also accomplish the separation. These solvents are aprotic polar compounds that have high complexing affinity toward the more polarizable butadiene than other olefins in the streams. Among the many factors that must be considered in choosing the solvent process are cost, solvency, thermal stability, viscosity, toxicity, corrosivity, heat of vaporization, and fouling. The fact that no single solvent has dominated the process suggests that there are no significant differences in both operation and economics using most of these solvents. 1,3-Butadiene separation from a crude C_4 stream using catalytic extractive distillation has been described (235). There are continuous efforts around the world to search for solvents (236,237) that reduce fouling (238,239) and improve operations (240,241). A typical process schematic is shown in Figure 3. Processes using membranes for butadiene separation have also been patented (242,243). A system for purifying a 1,3-butadiene feedstock by using a separation column has been patented (244).

Another approach to separate butadiene from other hydrocarbons is to use a solution containing cuprous ammonium acetate that forms a weak copper(I) complex with butadiene (245,246). The latter process has been used in a number of plants.

In commercial extraction operations, the C_4 fractions that contain butadiene, isobutene, and 1- and 2-butenes usually first go through a butadiene extraction unit in which the butadiene is removed. This may be followed by isobutylene removal via reaction between isobutylene and methanol to form methyl *tert*-butyl ether [1634-04-4] (MTBE). The butenes are then distilled from the MTBE. 1-Butene may then be separated from 2-butene by distillation.

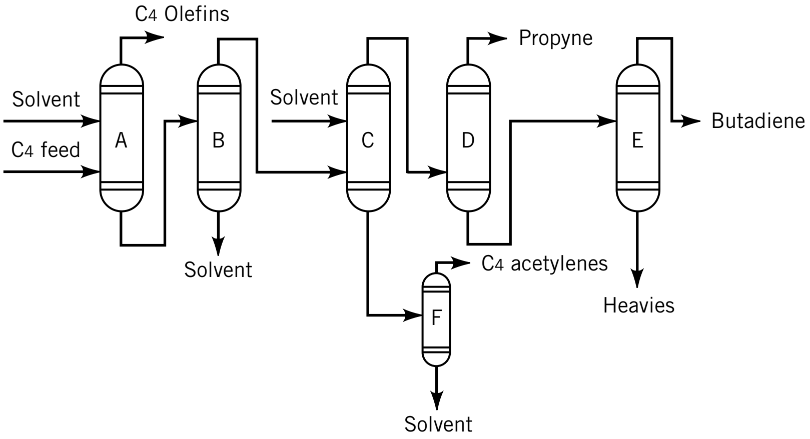


Fig. 3. Separation and purification of butadiene: A, first extraction distillation tower; B, solvent stripper; C, second extraction distillation tower; D, topping tower; E, tailing tower; F, solvent recovery towers.

5. Handling, Storage, and Shipping

Large quantities of butadiene are manufactured, stored, transported, and handled in a safe manner every day. Typical product specifications are listed in Table 5. However, butadiene reacts with a large number of chemicals, has an inherent tendency to dimerize and polymerize, and is toxic. Therefore, specific handling, storage, and shipping procedures must be followed. A review of means to prevent occupational exposure during handling, storage, and shipping has been published (247).

Table 5. **Butadiene Specifications and Test Methods**[a]

Component	Specification	Test method
1,3-butadiene	$\geq$99.5%	ASTM D2593
inhibitor[b], wppm	50–150	ASTM D1157
impurities, wppm, max		
1,2-butadiene	20.0	ASTM D2593
propadiene	10.0	ASTM D2593
acetylenes (methyl, ethyl, vinyl)	20.0	ASTM D2593
dimers	500.0	ASTM D2426
isoprene	10.0	ASTM D2593
C5s	500.0	ASTM D2593 or D2426
sulfur	5.0	ASTM D4045 or D2784
peroxides (calculated as H_2O_2)	5.0	ASTM D1022
ammonia	5.0	water wash and ASTM D1426
water	300.0	Karl Fischer or panametric dew point
carbonyls	10.0	ASTM D4423
nonvolatile residues, wt %	0.05	ASTM D1025
oxygen in gas phase, vol %	0.10	teledyne oxygen analyzer

[a] Courtesy of Exxon Chemical Co.

[b] *tert*-Butylcatechol [27213-78-1] TBC.

Table 6. **Effects of Temperature on Dimerization Rate of Butadiene**

Temperature, °C	Butadiene, % dimerized/h
20	0.00015
40	0.0014
60	0.013
80	0.12
100	1.1

The thermally induced Diels–Alder dimerization reaction producing vinylcyclohexene is very difficult to prevent except by lowering the storage temperature (248). Since the reaction rate increases about ninefold for every 20°C increase in temperature (Table 6), care must be taken to keep butadiene at a low temperature.

Butadiene reacts readily with oxygen to form polymeric peroxides, which are not very soluble in liquid butadiene and tend to settle at the bottom of the container because of their higher density. The peroxides are shock sensitive; therefore it is imperative to exclude any source of oxygen from butadiene. Addition of antioxidants like *t*-butylcatechol (TBC) or butylated hydroxy toluene (BHT) removes free radicals that can cause rapid exothermic polymerizations. Butadiene shipments now routinely contain ~100 ppm TBC. Before use, the inhibitor can easily be removed (249,250). Inert gas, such as nitrogen, can also be used to blanket contained butadiene (251).

Butadiene is also known to form rubbery polymers caused by polymerization initiators like free radicals or oxygen. Addition of antioxidants like TBC and the use of lower storage temperatures can substantially reduce fouling caused by these polymers. Butadiene and other olefins, such as isoprene, styrene, and chloroprene, also form so-called popcorn polymers (252). These popcorn polymers are hard, opaque, and porous. They have been reported to ignite spontaneously on exposure to air and, therefore, are usually kept under water. They grow faster in the presence of seeds, or oxygen and rust. Because popcorn polymers can grow exponentially (253), they can generate tremendous pressure resulting in sudden rupture or plugging of containers, distillation towers, and pipes (254). It is reported that rigorous exclusion of oxygen from the system, metal surface passivation, and removal of popcorn polymer seeds can mitigate most of this problem (253). Addition of antioxidants will also help, but the high boiling points of many of these materials render them effective primarily in the liquid phase. Recently, a comprehensive study of this phenomenon and effective mitigation methods have been investigated, developed, and are available for license (255).

Butadiene is primarily shipped in pressurized containers via railroads or tankers. U.S. shipments of butadiene, which is classified as a flammable compressed gas, are regulated by the Department of Transportation (256). Most other countries have adopted their own regulations (30). Other information on the handling of butadiene is also available (257). As a result of the extensive emphasis on proper and timely responses to chemical spills, a comprehensive handbook from the National Fire Protection Association is available (258).

Table 7. **U.S. Producers of Butadiene and their Capacities**

Producer	Capacity[a] × 10^6 kg (10^6lb)
BP Amoco, Chocolate Bayou, Texas	90.7 (200)
Equistar, Channelview, Texas	281.2 (620)
Equistar, Chocolate Bayou, Texas	68.0 (150)
Equistar, Corpus Christi, Texas	90.7 (200)
Exxon, Baton Rouge, La.	149.7 (330)
Exxon, Baytown, Texas	122.5 (270)
Huntsman, Port Neches, Texas	370.6 (850)
Shell, Deer Park, Texas	136.0 (300)
Shell, Norco, La.	260.8 (575)
Texas Petrochemicals, Houston, Texas	415.0 (915)
Total	*1985 (4,410)*

[a] Per year of finished butadiene capacity.

6. Economic Aspects

World capacity grew at 3.3%/yr in 1994–1999 and reached 10×10^6 t as of January 2000 (259). Most capacity was in Asia, South America, and the Middle East. Asia is the world's leading producer.

United States producers are listed in Table 7 (1). The estimated world demand for 2003 is 5.8 billion lb (2.6 million tons) (1).

During 1994–1999 the price of butadiene was a high of \$0.24/lb and a low of \$0.13/lb tanks fob Gulf (1).

Since the bulk of butadiene is recovered from steam crackers, its economics is very sensitive to the selection of feedstocks, operating conditions, and demand patterns. Butadiene supply and, ultimately, its price are strongly influenced by the demand for ethylene, the primary product from steam cracking. Currently, there is a worldwide surplus of butadiene. Announcements of a number of new ethylene plants will likely result in additional butadiene production, more than enough to meet worldwide demand for polymers and other chemicals (1). When butadiene is in excess supply, ethylene manufacturers can recycle the butadiene as a feedstock for ethylene manufacturer.

7. Health and Safety Aspects

Butadiene has been used widely in producing many important industrial polymers and other products. Thus over the years the effects on plant workers who have been exposed to different levels of butadiene have been under increasing scrutiny from manufacturers, users, health organizations, as well as government agencies. Short-term exposure to high concentrations of butadiene may cause irritation to the eyes, nose, and throat. Dermatitis and frostbite may result from exposure to the liquid and the evaporating gas (247). Long-term physiological reactions to 1,3-butadiene may vary individually.

Exposure studies have been made using mice and rats (260). These experiments have demonstrated species differences in butadiene toxicity and

Table 8. **Exposure Limits of Butadiene in Selected Countries**

Country	Exposure limit[a]
Belgium	10 ppm
France	10 ppm
Germany	carcinogen
Russia	STEL 100 mg/m^3
The Netherlands	21 ppm
United Kingdom	10 ppm
United States	2 ppm (ACGIH) 5 ppm for 15 min (OSHA) 1 ppm 8-h time weighted average (OSHA)

[a] Ref. 263.

carcinogenicity. Butadiene was found to be a potent carcinogen in the mouse, but only a weak carcinogen in the rat. The interpretations have focused on differences in toxification rates and detoxification metabolisms as causative factors (257). The metabolism is believed to proceed through intermediates involving butadiene monoepoxide and butadiene diepoxide (260). A similar mechanism has been proposed for its biodegradation pathway (261).

A retrospective epidemiological study covering a period of 36 years and a population of ~14,000 workers from eight SBR production facilities in the United States and Canada was the largest of several such studies conducted (260–262). The study covered the period between 1943 and 1976 with an update from 1977 to 1985. Despite the difficulty in ascertaining the exposure levels, the authors of that paper suggested there were no statistically significant differences in tumor mortality in total or for any specific cause of death as compared to the general population (260). In several epidemiological studies elevation in mortality were observed for small subgroups and tumor types. See Table 8 for exposure limits in selected countries.

There have been many reviews published on the toxicity of butadiene (264). A summary of environmental health perspectives was presented at the 1988 Symposium on Toxicology, Carcinogenesis, and Human Health Effects of 1,3-Butadiene (265). Detailed comparisons of various personal monitoring devices are available (266), and control of occupational exposure to 1,3-butadiene has been reviewed (267).

8. Uses

Butadiene is used primarily in polymers, including SBR, BR, ABS, SBL, and NR. In 2000 these uses accounted for about 89% of butadiene consumed in the United States (1). Styrene–butadiene rubber, the single largest user of butadiene, consumes 29% of the total. It is followed by polybutadiene rubber at 27%. Consumption for the other polymers, ABS, SBL, polychloroprene, and nitrile rubber are listed in Table 9.

Another significant butadiene use is for manufacturing adiponitrile, $NC(CH_2)_4CN$ [111-69-3], a precursor for nylon-6,6 production. Other miscellaneous chemical uses, such as for ENB (ethylidene norbornene) production, account for 7% combined (Fig. 4) (271).

Table 9. **Pattern of Butadiene Uses in the United States, 2000**[a]

End use	Percentage of total, %
synthetic elastomers	61
styrene–butadiene rubber (SBR)	29
polybutadiene (BR)	27
polychloroprene (Neoprene)	3
nitrile rubber (NR)	2
polymers and resins	18
acrylonitrile–butadiene–styrene (ABS)	6
styrene–butadiene copolymer (latex)	12
chemicals and other uses	21
adiponitrile	14
others	7

[a] Ref. 1

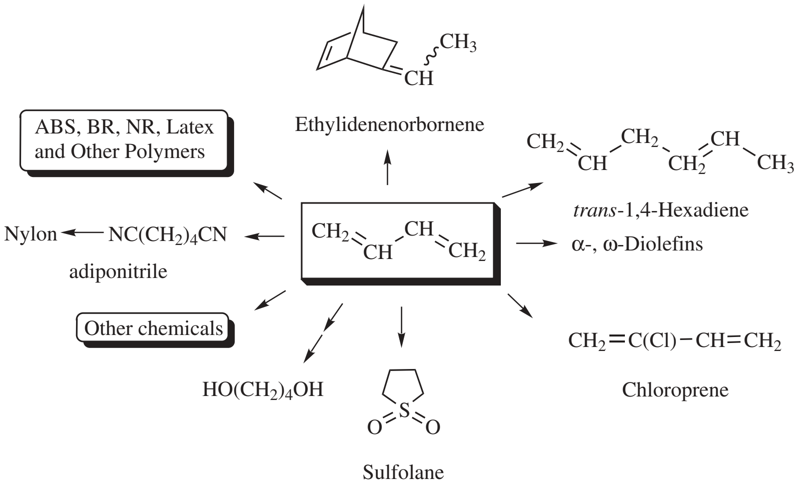


Fig. 4. Commercial uses of butadiene.

New butadiene applications are expected to grow from a small base, particularly liquid hydroxy-terminated homopolymers used in polyurethane for sealants, waterproofing, electrical encapsulation, and adhesive (1). A recent patent describes an epoxy resin composition for semiconductor encapsulation comprising an epoxy resin, phenolic resin, and butadiene rubber particles (268). An invention for improved polybutadiene composition suitable for use in molded golf ball cores has been described (269). A butadiene rubber adhesive composition with specified low syndiotactic butadiene has been patented (270).

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