# Butadiene

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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## 1. Introduction

The name butadiene generally refers to 1,3-butadiene [*106-99-0*], $C_4H_6$, $M_r$ 54.09. The thermodynamically less stable 1,2-butadiene [*590-19-2*], which has two cumulated double bonds, has only minor industrial importance. The 1,3 isomer is economically the most important unsaturated $C_4$ hydrocarbon.

$CH_2 = CH{-}CH = CH_2$ 1, 3−Butadiene

$CH_2 = C = CH{-}CH_3$ 1, 2−Butadiene

Caventou was the first to isolate butadiene, by the pyrolysis of amyl alcohol. Berthelot produced it by passing a mixture of acetylene and ethylene through a red-hot iron tube. In 1895 the structure of butadiene was elucidated by Ciamician and Magnaghi. In 1886, Armstrong and Miller discovered butadiene in the products obtained on cracking petroleum.

Practical interest in butadiene and its derivatives began with the discovery by Lebedew in 1910 that butadiene forms rubberlike polymers. Butadiene was produced on a large scale in Germany prior to World War II and in the United States during the war. Simultaneously, methods were developed for the manufacture of useful butadiene polymers [1]. After the war, the work of Ziegler and Natta, among others, on polymerization with organometallic catalysts led to higher quality rubber.

## 2. Physical Properties

Butadiene is a colorless gas under normal conditions. Some physical properties are summarized in the following [3, 4]:

| | |
|---|---|
| *bp* at 101.3 kPa | − 4.4 °C |
| *mp* at 1013. kPa | − 108.9 °C |
| Critical temperature | 425 K |
| Critical pressure | 4.32 MPa |
| Critical molar volume | 221 $cm^3$/mol |
| Density, liquid | |
| at 0 °C | 0.646 $g/cm^3$ |
| at 25 °C | 0.616 $g/cm^3$ |
| at 50 °C | 0.582 $g/cm^3$ |
| Gas density (air = 1) | 1.87 |
| Vapor pressure | |
| at − 4.4 °C | 101.3 kPa |
| at 0 °C | 120.0 kPa |
| at 25 °C | 273.6 kPa |
| at 50 °C | 537.9 kPa |
| at 75 °C | 986.7 kPa |
| at 100 °C | 1733 kPa |
| Viscosity, liquid | |
| at 0 °C | 0.25 mPa · s |
| at 50 °C | 0.20 mPa · s |
| Enthalpy of vaporization | |
| at 25 °C | 20.86 kJ/mol |
| at − 4.4 °C | 22.47 kJ/mol |
| Enthalpy of formation, gaseous, at 298 K, 101.3 kPa | 110.0 kJ/mol |

(*Continued*)

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| | |
|---|---|
| Free enthalpy of formation, gaseous, at 298 K, 101.3 kPa | 151.5 kJ/mol |
| Enthalpy of combustion, gaseous, at 298 K, 101.3 kPa | 2541.5 kJ/mol |
| Enthalpy of hydrogenation to butane, gaseous, at 298 K, 101.3 kPa | 235.7 kJ/mol |
| Entropy of formation, liquid, at 298 K, 101.3 kPa | 199.0 J mol$^{-1}$ K$^{-1}$ |
| Enthalpy of melting at 164.2 K, 101.3 kPa | 7.988 kJ/mol |

The technical data [2] important for reasons of safety are, above all, the flash point, − 85 °C, the ignition temperature, 415 °C, and the explosion limits when mixed with air and oxygen (Table 1). Unstabilized or insufficiently stabilized butadiene forms explosive peroxides with atmospheric oxygen.

Table 2 lists azeotropic mixtures relevant to the distillation of butadiene-containing hydrocarbons.

Butadiene is sparingly soluble in water, see Table 3, soluble in methanol and ethanol, and very soluble in higher-boiling polar solvents, e.g., methylpyrrolidone.

**Table 1.** Explosion limits of butadiene in air (concentrations of butadiene stated) [5]

| | At 101.3 kPa, 20 °C | | At 490.4 kPa, 30 °C | |
|---|---|---|---|---|
| | vol % | g/m$^3$ | vol % | g/m$^3$ |
| Lower limit | 1.4 | 31 | 1.4 | 150 |
| Upper limit | 16.3 | 365 | ca. 22 | ca. 2400 |

**Table 2.** Binary azeotropic mixtures of 1,3-butadiene and of other $C_4$-hydrocarbons [6]

| Mixture | *bp*, °C* | Composition |
|---|---|---|
| Butane/butadiene | min. | |
| *trans*-2-Butene/1-butyne | | 25.5 wt % 1-butyne |
| *cis*-2-Butene/vinylacetylene | min. | |
| Butadiene/2-butene | − 5.53 | 24.5 wt % 2-butene |
| Methylamine/vinylacetylene | − 6.8 | 2.5 wt % vinylacetylene |
| Ammonia/butadiene | − 37 | 45 wt % butadiene |
| Ammonia/1-butene | − 37.5 | 55 wt % 1-butene |
| Ammonia/isobutene | − 38.5 | 55 wt % isobutene |
| Ammonia/*n*-butane | − 37.1 | 55 wt % *n*-butane |
| Ammonia/isobutane | − 38.4 | 65 wt % isobutane |
| Methylamine/butadiene | − 9.5 | 58.6 wt % butadiene |
| Acetaldehyde/butadiene | 5.0 | 94.8 wt % butadiene |

* At 101.3 kPa.

**Table 3.** Solubility $\alpha$ of butadiene in water at 101.3 kPa (Bunsen's solubility coefficient) and solubility $L$ of water in liquid butadiene

| $t$, °C | α, m$^3$/m$^3$ | $L$, g $H_2O$/kg butadiene |
|---|---|---|
| 10 | 0.29 | 0.53 |
| 20 | 0.23 | 0.66 |
| 30 | 0.19 | 0.82 |
| 40 | 0.16 | |

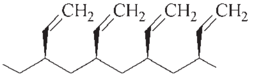
## 3. Chemical Properties

Butadiene has two conjugated double bonds and therefore can take part in numerous reactions, which include 1,2- and 1,4-additions with itself (polymerization) and other reagents, linear dimerization and trimerization, and ring formation.

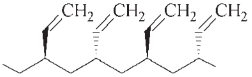
**Polymerization.** Polymerization by 1,2- and 1,4-addition is the most important reaction of butadiene [7].

***cis*-1,4-addition**

***trans*-1,4-addition**



**isotactic 1,2-addition**

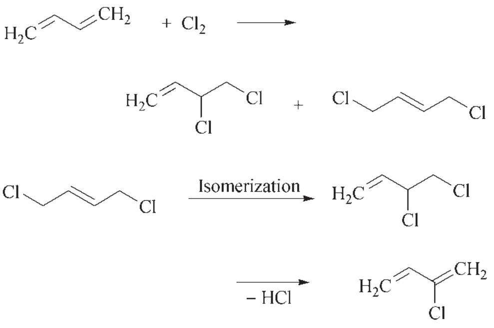


**syndiotactic 1,2-addition**

The nature of these polymers depends greatly on the way in which they are prepared and on the catalyst system employed (→ Rubber, 5. Solution Rubbers, Chap. 2.).

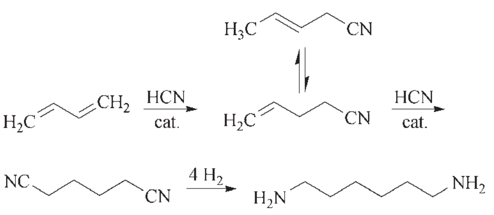
**Other Addition Reactions.** Butadiene undergoes 1,2- or 1,4-addition with many reagents. The relative proportions of the 1,4- and 1,2-addition products depend on the reaction conditions such as temperature, solvent, reaction time. The addition products are important intermediates in the manufacture of, for example, chloroprene and hexamethylenediamine. A typical example of an electrophilic addition to butadiene is the reaction with hydrogen chloride.

*Chloroprene* [*126-99-8*] (**1**) is produced by the chlorination of butadiene followed by isomerization of the 1,4-isomers and alkaline dehydrochlorination (→ Chloropropanes, Chlorobutanes, and Chlorobutenes, Chap. 3.):



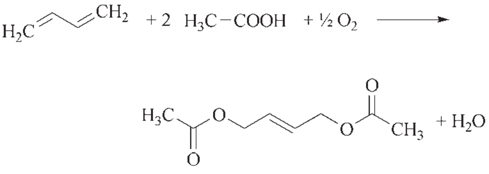
**1**

In the production of *adiponitrile* [*111-69-3*] (**2**) and *hexamethylenediamine* [*124-09-4*] (**3**), [8, 9] hydrogen cyanide reacts with butadiene in two steps, and the adiponitrile thus obtained is hydrogenated to give the diamine. Typical catalysts are $Ni^0$ phosphine and phosphite complexes with Al/Zn promotors. Typical reaction conditions are 90 – 150 °C and ambient pressure in THF.



**2** **3**

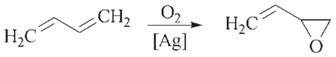
Several processes have been developed for the production of *1,4-butanediol* [*110-63-4*] from butadiene. In the three-step Mitsubishi process [10, 11], butadiene catalytically reacts with acetic acid to give 1,4-diacetoxy-2-butene (**4**), which in turn is hydrogenated to 1,4-diacetoxybutane and hydrolyzed to 1,4-butanediol. A similar process was reported by BASF [12].



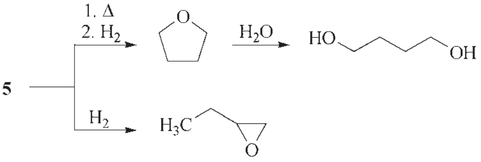
**4**

The Toyo Soda process [13] for the preparation of 1,4-butanediol involves the reaction of the butadiene chlorine addition products 1,4-dichloro-2-butene and 1,2-dichloro-3-butene with sodium acetate or formate to give 1,4-diacetoxy-2-butene or 1,4-diformyl-2-butene, which are then hydrolyzed and hydrogenated to 1,4-butanediol.

The direct oxidation of butadiene with air or oxygen, a method introduced by Eastman Chemical [14], is an economic process for the production of several $C_4$ derivatives. In the oxidation 3,4-epoxy-1-butene (**5**) is formed with high selectivity. Thermal rearrangement of **5** followed by hydrogenation affords tetrahydrofuran, which can be hydrolytically ring opened to give 1,4-butanediol. Hydrogenation of **5** affords ethyloxirane (**6**).

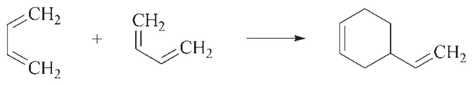


**5**



**6**

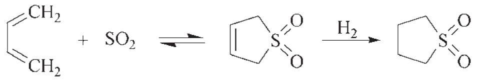
The *Diels – Alder reaction* is one of the best known reactions of butadiene [15]. The dienophile is usually an olefin with an activated double bond, which reacts with butadiene to give a cyclohexene ring. This addition reaction, which is exclusively a 1,4-addition, can also take place with a second molecule of butadieneto give 4-vinylcyclohexene [*100-40-3*] (**7**) [16]. The reaction can take place with or without a catalyst [17–19]. Vinylcyclohexene can be dehydrogenated or oxidized to give styrene [*100-42-5*] [20].



**7**

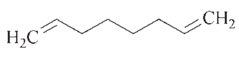
Two molecules of butadiene can cyclodimerize to form 1,5-cyclooctadiene [*111-78-4*] and three molecules of butadiene can cyclotrimerize to 1,5,9-cyclododecatriene [*4904-61-4*] [21]. Typical catalysts are $Ni^0$ complexes with phosphine or phosphite ligands. 1,5-Cyclooctadiene and 1,5,9-cyclododecatriene are important intermediates in the production of higher polyamides. 1,5-Cyclooctadiene can also be used to produce polyoctenamers via hydrogenation to cyclooctene and metathesis reaction.

Butadiene readily undergoes a reversible 1,4-addition with sulfur dioxide to form the cyclic sulfone 2,5-dihydrothiophene 1,1-dioxide [*1708-32-3*] (**8**) [22, 23], which is converted into sulfolan [*126-33-0*] (**9**), a heat-stable and highly polar solvent, by catalytic hydrogenation.

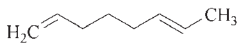


**8** **9**

**Linear Dimerization and Trimerization; Telomerization.** Butadiene forms linear dimers or trimers in the presence of Ni, Co, Pd, or Fe catalysts [24]. Since the linear oligomers of butadiene differ from each other by a chain length of four carbon atoms, their separation is easier than that of ethylene oligomers. Dimerization results in the formation of 1,3,7-octatriene [*1002-35-3*] and 1,3,6-octatriene [25, 26], which are, however, industrially uninteresting. The aromatic hydrocarbons xylene and ethylbenzene [27] can be made by the dehydrocyclization of 1,3,7-octatriene. If the dimerization is carried out under hydrogenation conditions, 1,7-octadiene and 1,6-octadiene are formed [28, 29]. 1,7-Octadiene is converted into a $C_{10}$ diol by hydroformylation and into a $C_{10}$ diamine by hydrocyanation and subsequent hydrogenation.

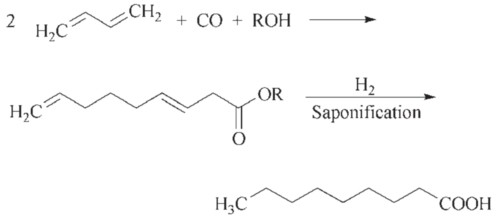


**1,7-Octadiene**

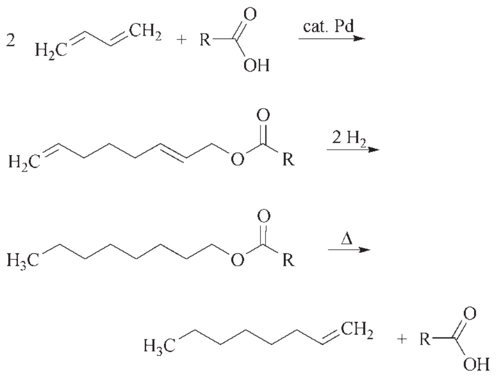


**1,6-Octadiene**

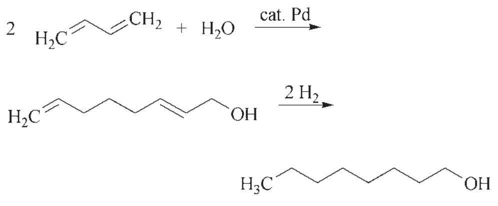
Dimerization of butadiene and simultaneous reaction with carbon monoxide and alcohol, followed by hydrogenation and saponification leads to pelargonic acid (*n*-nonanoic acid) [30], a starting material in the production of heat-resistant lubricants.



The telomerization of butadiene with a carboxylic acid [31] eventually results in 1-octene [*111-66-0*].

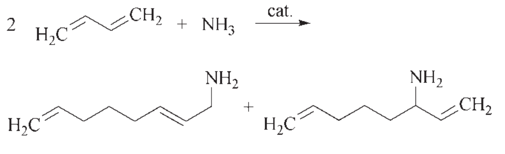


The telomerization of butadiene with water, a Kuraray process [32], and subsequent hydrogenation eventually results in *n*-octanol [*111-87-5*] with a selectivityof greater than 90 %.



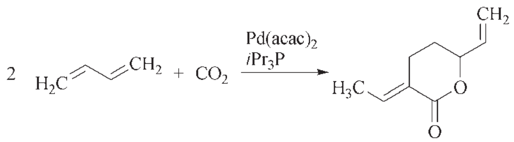
The telomerization of butadiene with ammonia [*7664-41-7*] in biphasic liquid – liquid systems with palladium acetate and trisodium

3,3′,3″-phosphanetriylbenzenesulfonate as catalyst yields in high selectivity the primary octadienylamines 2,7-octadienylamine (**10**) and 3-amino-1,7-octadiene (**11**) [33]. In biphasic systems the consecutive reactions to give the secondary and tertiary amines are dramatically suppressed in comparison to monophasic systems. The industrially important *n*-octylamine (starting material for softeners, corrosion inhibitors, flotation agents) is obtained by hydrogenation of 2,7-octadienylamine.



**10** **11**

The telomerization of butadiene with carbon dioxide yields different products. Products, yields and selectivities depend on the catalyst type [34]. If $[Pd(acac)_2]/iPr_3P$ (acac = acetylacetonoate) is used as the catalyst system, the δ-lactone **12** is formed in high yield and with high selectivity. This lactone could be of interest as a starting material for the synthesis of unsaturated and functionalized long-chain carboxylic acids.



**12**

Selective hydrogenation of butadiene to butene and complete hydrogenation to butane are possible. Industrially, these reactions are carried out with mixed $C_4$ fractions in cases of butadiene oversupply. The hydrogenated $C_4$ fractions are recycled to the steam cracker.

**Formation of Complexes.** Butadiene reacts with numerous metal compounds to form complexes, e.g., with Cu(I) salts, which were formerly used in the extraction of butadiene from $C_4$ hydrocarbon mixtures. This method has been replaced by modern extractive distillation techniques (Section 4.2). Complexes with other transition metals like Fe, Ni, Co, Pd, and Pt are also well known.

## 4. Production

A series of articles was published in 1942 describing all the methods used to produce butadiene [35]. Historically butadiene was industrially produced from acetylene by two processes (Fig. 1)

These methods are no longer used as the production of acetylene requires much energy and is expensive. Only the first steps of the Reppe process leading to 1,4-butanediol and tetrahydrofuran are commercially employed today. The production from ethanol [36, 37], was first developed by Ipatjew and Ostromislensky and was modified by Lebedew into a commercial process.

$$2\,CH_3CH_2OH \rightarrow CH_2 = CHCH = CH_2 + 2\,H_2O + H_2$$

This process, which operates at 370 – 390 °C on $MgO - SiO_2$ or $SiO_2 - Al_2O_3$ catalysts with a selectivity of up to 70 % can be of interest for countries with cheap ethanol or a large surplus of agricultural alcohol. Nowadays butadiene is preferentially isolated from $C_4$ fractions obtained by cracking naphtha and gas oil to ethylene (→ Ethylene). The dehydrogenation of *n*-butane or *n*-butenes plays a minor role and is only operated on a campaign basis when there is a large enough differential between feedstock and butadiene prices.

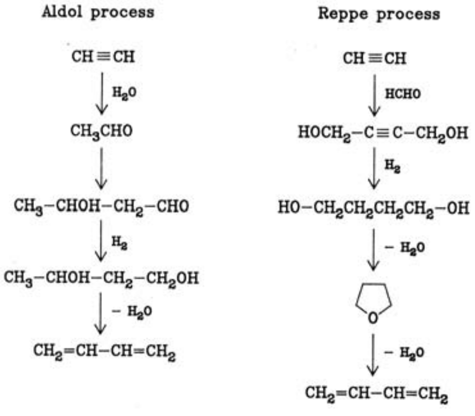


**Figure 1.** Production of butadiene from acetylene

## 4.1. Dehydrogenation of Butane and Butenes

The dehydrogenation reactions are endothermic, the following values being valid at 430 °C:

$$\text{Butane} \rightarrow \text{1-Butene} + H_2$$

$$\Delta H = 131\ \text{kJ/mol}$$

$$\text{Butane} \rightarrow \textit{cis}\text{-2}-\text{Butene} + H_2$$

$$\Delta H = 118\ \text{kJ/mol}$$

$$\textit{cis}\text{-2-Butene} \rightarrow \text{Butadiene} + H_2$$

$$\Delta H = 126\ \text{kJ/mol}$$

According to the Le Chatelier's principle, the yield is increased by decreasing the partial pressure of the reaction products. Practically, the dehydrogenation can be improved by conducting the reaction under vacuum or by addition of steam. The latter has the following advantages:

1. It reduces coking of the dehydrogenation catalyst
2. It provides the heat required for the endothermic dehydrogenation process
3. Steam can be easily separated from the reaction products by condensation

A further increase in yield is achieved by raising the reaction temperature.

Undesirable side reactions are cracking, isomerization, and polymerization. Compounds which tend to undergo these reactions are removed before the dehydrogenation process. As the dehydrogenation process does not proceed to completion, the reaction products must be separated, and the starting materials must be recovered and recycled into the dehydrogenation process.

**Dehydrogenation of *n*-Butane.** The best known one-step dehydrogenation is the Houdry Catadiene process (Fig. 2), which has been in operation on a commercial scale since 1943 [38–41]. In this adiabatic process, several packed-bed reactors, arranged parallel to each other, are operated alternatingly. Aluminum oxide mixed with approximately 20 % chromium oxide is the catalyst. *n*-Butane is subjected to dehydrogenation as such or in a mixture of *n*-butenes at 600 – 700 °C and 10 – 25 kPa. The use of high temperatures results in byproducts like $C_1$ – $C_3$ hydrocarbons, hydrogen, and carbon deposits on the catalyst. After 5 – 15 min of running time, the reactor is switched to regeneration. The heat generated by burning the coke residue during the regeneration phase is stored in the catalyst and in the added inert material and is then reused in the next reaction phase.

The concentration of butadiene at the outlet of the reactor is 15 – 18 %. During the recovery process, which includes absorption of the $C_3$ and $C_4$ hydrocarbons, compression, stripping, and separation from unconverted *n*-butane and *n*-butenes, the concentration of butadiene is increased to 30 – 50 %. Approximately 550 t of butadiene is obtained from 1000 t of *n*-butane.

Phillips Petroleum has developed a two-step dehydrogenation process [42, 43]:

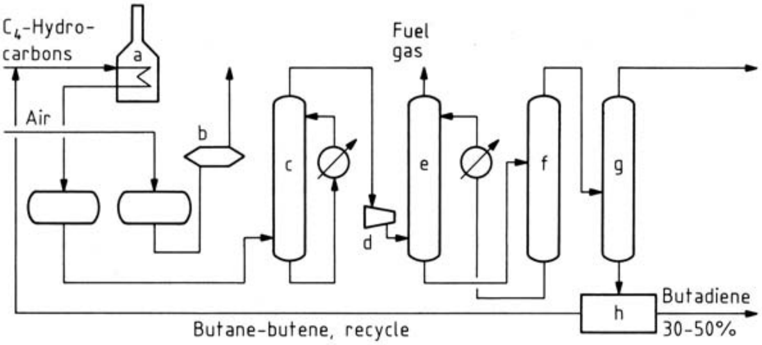


**Figure 2.** Houdry Catadiene process
a) Reactor; b) Waste-heat boiler; c) Quench column; d) Compressor; e) Absorber; f) Stripper; g) $C_3$ Column; h) $C_4$ Separation

1. *n*-Butane is catalytically dehydrogenated to butene at 600 °C and 1 bar on $Cr_2O_3$ – $Na_2O$ – $Al_2O_3$.
2. The *n*-butenes are separated by extractive distillation with auxiliaries such as acetone, acetonitrile, and furfural.
3. The *n*-butenes are dehydrogenated to butadiene in an isothermic tubular reactor, heated with flue gas to 600 °C, at a pressure of 1 bar, with addition of superheated steam on a $Fe_2O_3$ – $K_2O$ – $Al_2O_3$ catalyst.
4. Butadiene is recovered by extractive distillation with the above-mentioned auxiliaries and purified.

The advantages of this method are the longer running times without catalyst regeneration and higher butadiene yields (65 % based on butane).

**Dehydrogenation of *n*-Butenes.** *n*-Butenes are formed in the production of standard gasoline by catalytic cracking, in the production of olefins by thermal cracking, and in the dehydrogenation of LPG. Normally, butenes are a part of a $C_4$ hydrocarbon mixture. The $C_4$ paraffins can be separated from the $C_4$ olefins by extractive distillation, as routinely employed in the recovery of butadiene [42]. The boiling points of isobutene and *n*-butene are so close together that they can only be separated by special methods. The gas-phase BASF process employs 40 – 45 % $H_2SO_4$ to selectively convert isobutene into *tert*-butanol [48]. Today, separation is carried out by conversion to methyl *tert*-butyl ether or to isobutene oligomers [49–52]. Table 4 lists catalysts for the dehydrogenation of *n*-butenes to butadiene.

**Oxidative Dehydrogenation of *n*-Butenes.** [53, 54]. The conversion and the selectivity of the dehydrogenation of *n*-butenes to butadiene can be significantly improved by removing the hydrogen from the equilibrium. The addition of oxygen causes the oxidation of hydrogen to water:

$$2\,C_4H_8 + O_2 \rightarrow 2\,C_4H_6 + 2\,H_2O$$

The exothermic oxidation of hydrogen partially covers the heat requirements of the endothermic dehydrogenation reaction and, in addition, the oxygen, together with steam added during the reaction, leads to decreased catalyst coking. Especially productive methods are the Oxo-D process of Petro-Tex [55] and the O-X-D process of Phillips [56, 57].

The Oxo-D process was first applied on a large scale in 1965. The advantages of this method are the low consumption of steam and heating energy, high conversion and selectivity per reactor cycle, longer life span of the catalyst, and no necessity for catalyst regeneration. Petro-Tex achieved a 65 % conversion and a butadiene selectivity of 93 % by using a molar steam/butene ratio of 12/1.

Phillips has operated a plant in Borger (Texas) since 1970 based on the O-X-D process, producing 125 000 t/a of butadiene. Phillips also obtains a high conversion and a 88 – 92 % selectivity of butadiene.

The addition of oxygen to the dehydrogenation of butanes is not meaningful because at the high temperatures required, oxygen reacts with the reaction products to give undesired byproducts.

**Oxidative Dehydrogenation of Butane with Iodine.** [58, 59]. Shell has developed a one-step dehydrogenation of butane to butadiene with iodine as the hydrogen acceptor. The addition of iodine enables a high conversion and yield of butadiene but causes serious corrosion problems in the plant.

**Table 4.** Catalytic dehydrogenation of butenes [44–47]

| Catalyst | Phillips 1490 | Shell 205 | Dow Type B |
|---|---|---|---|
| Composition | $Fe_2O_3$– Bauxite | $Fe_2O_3$ –$Cr_2O_3$ | Ca/Na phosphate – $Cr_2O_3$ |
| Mole ratio $H_2O$/butene | 9 – 12/1 | 8/1 | 18 – 20/1 |
| Conversion per pass, % | 26 – 28 | 27 – 33 | $\leqq 45$ |
| Selectivity, % | 76 | 70 | 90 |
| Regeneration after |  | 24 h | 30 min |
| Duration of regeneration |  | 1 h | 15 min |

## 4.2. Isolation of Butadiene from $C_4$ Steam Cracker Fractions

Today, the isolation of butadiene is based worldwide predominantly on butadiene-containing $C_4$ fractions from the steam cracking of ethane, LPG, naphtha, gas oil, and other higher boiling hydrocarbon fractions to form ethylene and homologous compounds. In Western Europe, naphtha is primarily used as raw material. In the United States, however, liquefied petroleum gas (LPG) and natural gas liquids account for more than 70 % of the starting materials (→ Ethylene, Chap. 4.) [60].

Table 5 shows typical cracking yields and their relationship to the starting materials [61–63]. The influence of the cracking severity (temperature and duration) on the butadiene yield is minor compared to the influence exerted by the starting materials. However, the composition of the $C_4$ fraction itself is greatly dependent on cracking severity (Table 6).

Butadiene cannot be separated from this $C_4$ hydrocarbon mixture by simple distillation, because 1,3-butadiene and butane form an azeotrope (see Table 2). Hence, butadiene is isolated by liquid – liquid extraction or extractive distillation.

**CAA Liquid – Liquid Extraction** [42]. The cuprous ammonium acetate (CAA) process, introduced by ESSO, is based on the ability of butadiene to form a complex with $Cu^I$ compounds. Butadiene is separated from the $C_4$ hydrocarbon mixture by countercurrent extraction with $Cu^I$ acetate in aqueous ammonia solution. This method is advantageous in the processing of $C_4$ fractions with a low butadiene and $C_4$ acetylene content, which is the case in dehydrogenation fractions [66]. A higher content of $\alpha$-acetylenes (e.g., ca. 100 ppm of vinylacetylenes) strongly interferes with this process as a result of foam formation. Acetylenes, especially the unstable vinylacetylene, can be removed by selective hydrogenation before the isolation of butadiene [67–69].

**Extractive Distillation.** The method of choice for the isolation of butadiene from $C_4$ fractions is extractive distillation with selective

**Table 5.** Feedstocks and steam cracking yields (in wt %)

| | Light hydrocarbons | | | Naphthas and heavier | | |
|---|---|---|---|---|---|---|
| | Ethane | Propane | *n*-Butane | Medium range naphthas | Atm. gas oil | Light vacuum gas oil |
| **Feedstocks** | | | | | | |
| Methane | 0.6 | | | | | |
| Ethane | 95.2 | | | | | |
| Propane | 4.2 | 100 | | | | |
| *n*-Butane | | | 100 | | | |
| Paraffins | | | | 79.9 | | |
| Olefins | | | | – | | |
| Naphthenes | | | | 17.4 | | |
| Aromatics | | | | 2.7 | | |
| Total | 100 | 100 | 100 | 100 | | |
| TBP cut range, °C | | | | | 204 – 343 | 343 – 454 |
| ASTM boiling range, °C | | | | 47 – 148 | | |
| Rel. density | | | | 0.692 | 0.844 | 0.901 |
| **Cracking yields** | | | | | | |
| Hydrogen and methane | 15.1 | 29.7 | 23.8 | 17.7 | 12.1 | 9.5 |
| Ethylene | 77.7 | 42.0 | 40.0 | 34.0 | 25.9 | 20.5 |
| Propylene | 2.8 | 16.8 | 17.2 | 15.7 | 16.2 | 14.1 |
| Butenes and butanes | 0.8 | 1.3 | 6.7 | 4.3 | 4.8 | 6.3 |
| Butadiene | 1.9 | 3.0 | 3.5 | 4.7 | 4.6 | 5.4 |
| Pyrolysis gasoline | 1.7 | 6.6 | 7.1 | 18.8 | 18.4 | 19.3 |
| Pyrolysis fuel oil | – | 0.6 | 1.7 | 4.8 | 18.0 | 25.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

**Table 6.** Typical analyses of $C_4$-fractions (in vol %) [64, 65]

| | Cracking intensity | | | | Dehydro- |
|---|---|---|---|---|---|
| | moderate | medium | high | very high | genates |
| $C_3$-Hydrocarbons | 0.3 | 0.3 | 0.3 | 0.16 | * |
| Butane | 4.2 | 5.2 | 2.8 | 0.54 | * |
| Isobutane | 2.1 | 1.3 | 0.6 | 0.53 | * |
| 1-Butene | 20.0 | 16.0 | 13.6 | 9.18 | * |
| *cis*-2-Butene | 7.3 | 5.3 | 4.8 | 1.61 | * |
| *trans*-2-Butene | 6.6 | 6.5 | 5.8 | 3.63 | * |
| Isobutene | 32.4 | 27.2 | 22.1 | 10.13 | * |
| 1,3-Butadiene | 26.1 | 37.0 | 47.4 | 70.10 | 15 – 45 |
| 1,2-Butadiene | 0.12 | 0.15 | 0.2 | 0.40 | ** |
| Methylacetylene | 0.06 | 0.07 | 0.08 | 0.10 | ** |
| Vinylacetylene | 0.15 | 0.3 | 1.6 | 2.99 | ** |
| Ethylacetylene | 0.04 | 0.1 | 0.2 | 0.53 | ** |
| $C_5$-Hydrocarbons | 0.5 | 0.5 | 0.5 | 0.1 | ** |

[*] sum of fractions = 85 – 55 vol%

[**] sum of fractions = 0.03 – 0.2 vol%

organic solvents. The affinity of hydrocarbons to polar solvents depends directly upon their degree of unsaturation. A highly unsaturated hydrocarbon is not only more soluble in a polar solvent, but the solvent is also more effective in decreasing the volatility of the hydrocarbon (see Table 7).

The first plants using furfural as solvent were built in the United States during World War II (the process was developed by Phillips Petroleum) [42, 71]. The method introduced by Shell in the early 1950s uses acetonitrile as solvent. It was developed from a one-step procedure involving separate removal of acetylene into a two-step process [42]. Union Carbide has described a process based on dimethylacetamide [72]. Modern plants employ the BASF procedure [66, 73–76] with *N*-methylpyrrolidone or the DMF method [77, 78] of Nippon Zeon.

A flowsheet of the BASF process is shown in Figure 3. *N*-Methylpyrrolidone (*bp* 203 °C at 101.3 kPa), containing 5 – 10 % water to increase the selectivity, is used as solvent. In the main washer (a), the more unsaturated hydrocarbons, such as acetylenes and diolefins, are dissolved in NMP, and the butenes/butanes are removed from the top of the washer. In a second extractive distillation step, in tower (c) and in the lower part of tower (b), the $C_4$ acetylenes and part of the 1,2-butadiene, which are more soluble in NMP than butadiene, are removed from the bottom of (c). The butadiene, which corresponds to specifications as far as alkanes, alkenes, and $C_4$ acetylenes are concerned, is removed from the top of tower (c) and is separated from the more volatile propyne in tower (h) and from the less volatile 1,2-butadiene and $C_5$ hydrocarbons in tower (i). The loaded solvent is led from the sump of tower (b) into tower (e) for complete degassing. Here the $C_4$ acetylenes are removed as a sidestream and, after selective hydrogenation, returned to tower (a). Recoveries of 99 – 100 %, based on the butadiene content of the $C_4$ feed, are achieved with selective hydrogenation of vinylacetylenes to butadiene [79]. An additional advantage of hydrogenation is the safe removal of the unstable $C_4$ acetylenes. Improper handling of $C_4$ acetylenes led to a severe explosion and complete destruction of a U.S. plant working with dimethylacetamide [80, 81]. Other efficient solvents for the extractive distillation of butadiene are given in [82]; e.g., methoxypropionitrile is used in some plants [85, 86].

In newer developments, $C_4$ acetylenes are removed by selective hydrogenation of the crude $C_4$ feedstock. UOP offers the KLP process, in which the crude $C_4$ stream is mixed with

**Table 7.** Relative volatility of $C_3$- and $C_4$-hydrocarbons in comparison to butadiene (50°C, infinite dilution) [70]

| | Without solvent | NMP* | DMF* | Acetonitrile | DMAC* | Furfural |
|---|---|---|---|---|---|---|
| Butane | 1.17 | 3.66 | 3.43 | 3.13 | 3.13 | 2.89 |
| 1-Butene | 1.08 | 2.38 | 2.17 | 1.92 | 2.07 | 1.78 |
| *trans*-2-Butene | 1.23 | 1.90 | 1.76 | 1.59 | 1.71 | 1.20 |
| *cis*-2-Butene | 1.37 | 1.63 | 1.56 | 1.45 | 1.52 | 1.26 |
| 1,3-Butadiene | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 1,2-Butadiene | 1.79 | 0.74 | 0.72 | 0.73 | 0.71 | 0.65 |
| Methylacetylene | 2.16 | 0.81 | 0.72 | 1.00 | 0.73 | 1.04 |
| Ethylacetylene | 1.62 | 0.42 | 0.42 | 0.48 | 0.44 | 0.52 |
| Vinylacetylene | 1.44 | 0.21 | 0.23 | 0.39 | 0.23 | 0.41 |

[*] NMP *N*-Methylpyrrolidone; DMF Dimethylformamide; DMAC Dimethylacetamide

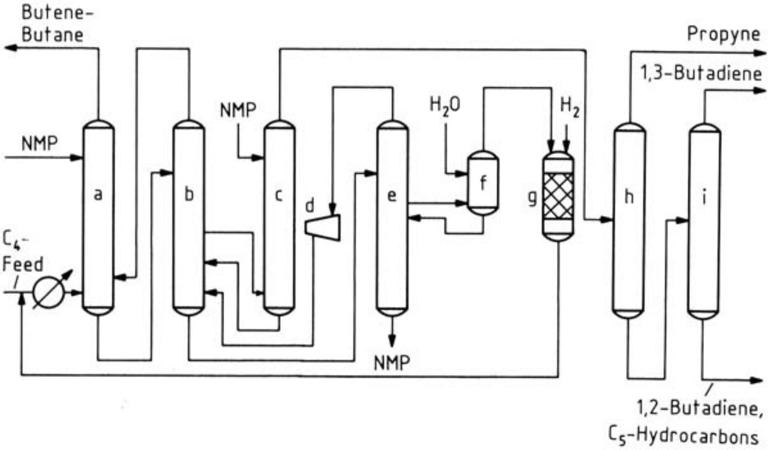


**Figure 3.** BASF Extractive distillation process with NMP
a) Main washer; b) Rectifier; c) After washer; d) Centrifugal compressor; e) Degassing tower; f) Water washer; g) Hydrogenation reactor; h) First distillation; i) Second distillation

a stoichiometric amount of hydrogen and fed to a fixed-bed reactor containing a selective hydrogenation catalyst [83]. Temperatures are not allowed to exceed 85 °C. The reactor pressure is set to maintain the reaction mixture in the liquid phase. Because of catalyst fouling caused by polymeric materials that are produced during operation, catalyst regeneration by carbon combustion with air followed by catalyst reduction with hydrogen, is necessary every two months. The butadiene yield in comparison with a conventional two-stage extraction is increased from 95.5 to 99.5 %.

CDTECH offers the CDHYDRO process for acetylenes conversion in the crude $C_4$ feedstock [84]. The CDHYDRO process involves placing catalyst in the steam cracker debutaniser, adding hydrogen to the feed, and venting off any gases from the reflux receiver. Two modes of operation are available. In the first, the acetylenes concentration can be reduced to levels low enough to allow a single extraction system for butadiene purification, but with a loss of 3 – 4 % butadiene by hydrogenation. The second mode is only applicable with a double extraction unit. The acetylenes conversion is lower so that there is nearly no loss of butadiene. Unconverted acetylenes are extracted in the second stage and recycled to the debutanizer feed. Conversion of butadiene to butenes is less than 1 %.

## 5. Specifications of Butadiene

A typical butadiene specification to meet market requirements is listed in Table 8. The purity requirements have been intensified because the Ziegler-type catalysts employed in the stereospecific synthesis of rubbers are sensitive to, for example, allenes and acetylenes. The purity requirements are less stringent for butadiene

**Table 8.** Typical specifications of butadiene

| Compound | Specification | Test method |
|---|---|---|
| 1,3-Butadiene | $\geqq$ 99.6 % | ASTM-D 2593-86 |
| Propyne | max. 5 ppm | ASTM-D 2593-86 |
| Propadiene | max. 2 ppm | ASTM-D 2593-86 |
| Vinylacetylene | max. 5 ppm | ASTM-D 2593-86 |
| Ethylacetylene | max. 2 ppm | ASTM-D 2593-86 |
| Σ Acetylenes (calculated as vinylacetylene) | max. 20 ppm | ASTM-D 1020-76 |
| Dimerics | max. 250 ppm* | ISO 7381 |
| 1,2-Butadiene | max. 30 ppm | ASTM-D 2593-86 |
| Carbonyls (calculated as $CH_3CHO$) | max. 25 ppm | ASTM-D 4423-91 |
| Sulfur | max. 1 ppm | ASTM-D 3246-76 |
| Peroxides (calculated as $H_2O_2$) | max. 1 ppm | ASTM-D 1022-76 |
| Methanol | max. 10 ppm | ISO 8174 |
| $H_2O$ | max. 5 ppm | ISO 6191 |
| Residue | max. 10 ppm | ASTM-D 2593-86 |
| Inhibitor TBC** | 75 – 125 ppm | ASTM-D 2593-86 |
| Oxygen in the gas phase | max. 0.1 vol % | ASTM-D 2593-86 |

*Maximum set by battery producers;
**TBC = *tert*-butylpyrocatechol

used in emulsion polymerization, such as in the synthesis of styrene – butadiene rubber and latex [85].

## 6. Stabilization, Storage, and Transportation

Stabilization [78] involves protection against the action of oxygen and against polymerization. Butadiene forms dangerous polymeric peroxides [86, 87] with oxygen, which are viscous liquids sparingly soluble in liquid butadiene. They are deposited at the bottom of butadiene containers. Hence, the handling of butadiene requires complete exclusion of oxygen. In addition, inhibitors such as *p-tert*-butylcatechol (TBC) and 2,6-di-*tert*-butyl-*p*-cresol (TBK), are added because they are especially effective at scavenging radicals. They also prevent spontaneous polymerization of butadiene and can easily be removed by washing with aqueous sodium hydroxide. Aqueous sodium nitrite solution is also used as an antioxidant in the production of butadiene.

Butadiene can polymerize during production, storage, and transportion in three ways. Dimerization to vinylcyclohexene [88] is dependent on time and temperature and can be stopped by adding potassium cyanide solution to butadiene [89]. Second, butadiene can polymerize under the influence of oxygen and high temperatures, especially during manufacture, to give rubberlike polymers (fouling). Antioxidants such as TBC, exclusion of oxygen, low temperatures, and short exposures to higher temperatures reduce this polymerization [90]. Third, butadiene can polymerize, initiated by oxygen, high temperatures, and rust, to give a glassy, granular, opalescent, and very hard polymer (so-called popcorn) [90, 91]. It forms preferentially in off-stream tubes. Its growth is favored when popcorn seeds are present in the plant. The formation of popcorn in closed areas can lead to pressures of $>$ 1000 bar, causing the bursting of off-stream tubes or containers. It can be prevented by the addition of TBC and by the careful elimination of all popcorn seeds. Popcorn is spontaneously inflammable in air and hence must be kept moist during its removal.

Liquified butadiene is stored at normal temperatures in liquid-gas containers or, preferably, for safety reasons at a temperature of 4 °C in almost pressureless containers. It is transported at normal temperatures and raised pressures in tankers, railroad tank wagons, and in ships. Especially in ships, temperatures of 4 °C and pressureless containers are required [92–94].

The following regulations must be followed when labeling and transporting butadiene:

- By road: Germany: GGVS, Class 2, no. 2F; Europe: ADR; USA: DOT regulations.
- By rail: Germany: GGVE, Class 2, no. 2F; Europe: RID; USA: DOT regulations.
- By inland shipping: GGVS/GGVE, Class 2, no. 2F; Europe: ADR.
- By sea freight: Germany: GGVSee: Class 2, no. 2F; International: IMDG Code.
- By air freight: International: IATA, Class 2, no. 2.1.

Butadiene is safely transported today in amonts greater than 100 000 t/a from, for example, Western Europe to Japan and to the United States.

## 7. Uses and Economic Importance

The majority of the butadiene produced worldwide is used as a monomer or co-monomer in the manufacture of synthetic rubber (→ Rubber, 3. Synthetic Rubbers, Introduction and Overview), above all for styrene – butadiene rubber and latex (SBR), polybutadiene rubber (BR), acrylonitrile – butadiene rubber and latex (NBR), and for chloroprene rubber (CR). Important plastics containing butadiene as a monomer component are impact-resistant polystyrene, a two-phase system consisting of polystyrene and polybutadiene; ABS polymers, consisting of acrylonitrile, butadiene, and styrene; and a copolymer of methyl methacrylate, butadiene, and styrene (MBS), which is used as a modifier for poly(vinyl chloride) (→ Polystyrene and Styrene Copolymers, Section 5.12.2.). In addition, butadiene is an intermediate in the synthesis of several important chemicals (Chap. 3).

The worldwide production capacity, production, and consumption of butadiene are summarized in Table 9. Butadiene-containing $C_4$ steam cracker fractions are the starting material for more than 95 % of production. In Western

**Table 9.** Butadiene production, capacities, and consumption 1998 (in $10^3$ t/a) [95]

| | Production | Capacities | Consumption |
|---|---|---|---|
| USA/Canada | 2020 | 2105 | 2218 |
| Latin America | 312 | 333 | 398 |
| Western Europe | 2000 | 2345 | 1752 |
| Eastern Europe * | 430 | 1080 | 452 |
| Asia and Pacific | 142 | 203 | 269 |
| Middle East | 160 | 267 | 33 |
| Japan | 1010 | 955 | 928 |
| East Asia | 1223 | 1430 | 1294 |
| Africa | | | 44 |
| Total | 7297** | 8718*** | 7388 |

*Including the former Soviet Union.

**Production by extraction 7097 × $10^3$ t/a, production by dehydrogenation 200 × $10^3$ t/a.

***Extraction capacity 8213 × $10^3$ t/a, dehydrogenation capacity 505 × $10^3$ t/a.

Europe, naphtha is the principal raw material for steam cracking. High yields of butadiene are obtainied by this method, which explains the absence of dehydrogenation capacities. In the United States more than 90 % of the butadiene production is based on steam cracking. The available dehydrogenation plants are only used at times of butadiene shortage.

In the United States, Japan, and Western Europe, most of the butadiene rubber is required by the automobile industry. Table 10 shows the worldwide butadiene usage according to products [95]. In 1986 a strong price drop of butadiene occurred.

In the early 1990s an oversupply of butadiene caused by increased cracking capacities led to a further price drop. This resulted, for example, in the hydrogenation of butadiene surplusses and use as cracker feedstock. Co-cracking of butadiene-containing $C_4$ streams was also used.

**Table 10.** Butadiene usage in 1998 [95]

| Application | Consumption | |
|---|---|---|
| | $10^3$ t/a | % |
| Styrene – butadiene rubber/latex | 3440 | 46.5 |
| Polybutadiene rubber | 1986 | 27 |
| Nitrile – butadiene rubber/latex | 289 | 4 |
| Polychloroprene rubber | 189 | 2.5 |
| Acrylonitrile – butadiene – styrene polymer | 737 | 10 |
| Adiponitrile | 427 | 6 |
| Others | 320 | 4 |
| Total | 7388 | 100 |

Since the late 1990s growing demand for rubber products and other polymers in Asia have increased butadiene rubber demand exponentially. In 2008 global butadiene demand dropped about 5.1% from the 2007 value due to the economic recession. Global production and consumption of butadiene in 2009 were ca. $9.2\times10^6$ t, respectively [96].

## 8. Toxicology

Workers usually are exposed to butadiene by inhalation. Contact of liquid butadiene with skin may exceptionally occur.

### 8.1. Experimental Toxicity Data

**Acute Toxicity.** Butadiene is of low acute toxicity. Lethal concentrations are: $LC_{50}$ 12.5 vol % (rat, inhal., 2 h) and 11.5 – 12 vol % (mouse, inhal., 2 h) [97, 98]. Like some other hydrocarbons butadiene causes narcotic effects after inhalation of high concentrations, sometimes preceded by excitation and hyperventilation [99].

**Repeated Short-Term Exposure.** Rats, guinea pigs, rabbits, and one dog were exposed to butadiene at concentrations of 0, 600, 2300, and 6700 ppm for 7.5 h per day, 6 days a week during 8 months with no significant progressive injury occurring; only the highest concentration slightly retarded the growth and caused light cloudy swelling of liver in some cases. The data on fertility, hematology, body weights, blood biochemistry, urinalysis, and histopathology did not reveal any adverse effect to the animals [99].

In a similar study on Sprague-Dawley rats no clinical sign of toxicity was observed with the exception of moderately increased salivation, particularly at higher concentrations (4000, 8000 ppm). No adverse effects on growth rate, food consumption, neuromuscular function, hematological and biochemical parameters were recorded in the second, sixth, or thirteenth week of the test. Histopathologic investigations of the rats also did not demonstrate any change [100].

Mice were exposed to butadiene at levels of 0, 625 – 8000 ppm during 15 days or 14 weeks with no effect on survival or pathology during

15 days. Only the body weight decreased slightly at the 8000 ppm level. Exposure for 14 weeks resulted in dose dependent lower body weights and markedly increased mortality. No other effect has been reported [101].

**Long-term Exposure.** Groups of Sprague-Dawley CD rats were exposed to butadiene in air (0, 1000, 8000 ppm) on 6 h/day, 5 days/week for up to 105 (females) or 111 (males) weeks. The effects were: transient nasal secretion, slight ataxia, early increased mortality (at 8000 ppm concentration), suggestive higher frequency of spontaneous nephropathy in males (8000 ppm), higher liver weight, and a slightly increased incidence of metaplasia in the lung (males at 8000 ppm). Various tumors were identified with higher incidence in the exposed groups, others appeared earlier than in controls [102].

The authors concluded that butadiene was a “weak oncogen” under the conditions of this experiment. It is, however, questionable whether the small increase in mostly benign tumors and tumors with high background incidence like mammary tumors are biologically significant at these extremely high exposure levels.

Groups of B6C3F$_1$ mice were exposed to butadiene in air (0, 625, 1250 ppm) on 6 h/day, 5 days/week. Following week 60 for males and week 61 for females the study was terminated because of excessive mortality. Toxic and proliferative lesions of the nasal cavity occurred at increased incidence in the 1250-ppm group, but no neoplastic lesions were observed in the nasal cavity. Butadiene was also associated with liver necrosis as well as ovarial and testicular atrophy.

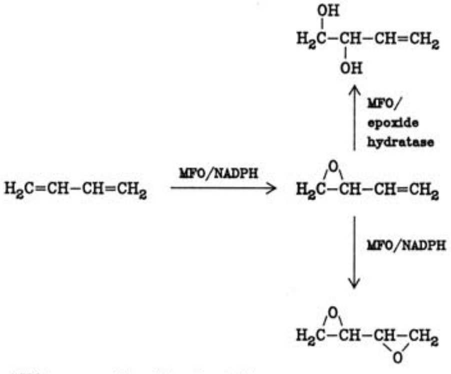
There was an early onset and a high incidence of several tumors including malign ones in the exposed mice. The authors concluded that there was clear evidence of carcinogenicity for butadiene. Mice obviously are much more sensitive to butadiene than rats are with respect to toxicity and carcinogenicity [101].

**Mutagenicity.** Gaseous butadiene was mutagenic in the Ames test only in the presence of liver microsomal enzyme preparations. This suggests the formation of a mutagenic intermediate (see Section 8.2) [103, 104].

**Embryotoxicity and Teratogenicity.** Groups of rats were exposed from day 6 through day 15 of gestation to various concentrations of butadiene [105]. There was an effect on body weight of the dams. The fetuses showed reduction of fetal weight at 8000 ppm (highest concentration) and an increased incidence of normally occurring variations, especially in wavy ribs, indicating retarded development, most prominent in the high-level animals. Major malformations occurred in two pups of one litter of the 8000-ppm group only. The 1000-ppm group did not exhibit higher incidences of malformed fetuses [105].

## 8.2. Metabolism

**In vitro** 1,2-Epoxy-3-butene is formed when butadiene is incubated with liver microsomes and NADPH. Further metabolism involving epoxide hydratase yields 3-butene-1,2-diol [106–110]. The diepoxybutane and epoxybutanediol as well as conjugation products are postulated as further intermediates:



MFO = monofunctional oxidase

The formation of 1,2-epoxy-3-butene is significantly more pronounced in mouse liver tissue than in liver cells from rats, rhesus monkeys, and humans [110]. The experiments using lung tissues of the same species demonstrated the very rapid formation of 1,2-epoxy-3-butene in mice. However, rat lung preparations were capable of producing only one tenth of the amount seen in mouse lung preparations, whereas the epoxide could not be detected using monkey or human lung tissue. The formation of diepoxybutane could not be detected in any experiment [110].

**In vivo** When rats were exposed to butadiene in a closed system, 1,2-epoxy-3-butene also was detected in the exhaled air [109, 110]. Mice in a similar experiment exhaled more of the monoepoxide than rats.

## 8.3. Human Data

Adverse effects after occupational exposure to butadiene are not reported in the literature. Volunteers exposed to a very high level of 8000 ppm of butadiene in air complained of eye irritation, blurring of vision, coughing, nasal congestion, and drowsiness. Subsequent repeated exposures did not suggest any cumulative effect [99, 111].

A hematology survey of workers at a styrene – butadiene rubber plant showed no pronounced evidence of hematological abnormalities in the peripheral blood. Exposure to butadiene was up to an average of 20 ppm in the tank farm area; in other departments less than 2 ppm occurred [112].

A retrospective study was conducted at two styrene – butadiene rubber plants involving 2756 male workers with an average duration of employment of approx. 10 years. No significant excess of total or cause-specific mortality has been found [112, 113]. Another mortality study covered a period of 36 years and reviewed a population of approx. 14 000 workers from styrene – butadiene rubber production facilities [114]. The study indicated that the overall mortality was lower as compared to general population (Healthy Worker Effect). There were no statistically significant differences in tumor mortality in total or for any specific cause of death.

**Hygiene Standards** [115, 116]. As a result mainly from the long-term mice study, butadiene is listed as an A 2 carcinogen with a TLV of 10 ppm by the ACGIH (1984/1985). The German MAK value of butadiene is 5 ppm (TRK). A 2 of the 1984 MAK list; a TRK value (lowest technically feasible level) will be established as a consequence.

The in vitro studies on the formation of critical intermediates in tissues from different species (mice, rat, monkey, man), however, suggest that the data from the long-term rat and especially from the mice study may not considered appropriate for direct use in risk evaluation for man.

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