

Isoprene

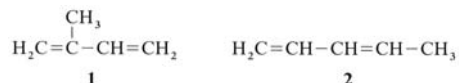
HANS MARTIN WEITZ, (Retired), BASF Aktiengesellschaft, Ludwigshafen, Federal Republic of Germany

ECKHARD LOSER, Bayer AG, Wuppertal, Federal Republic of Germany

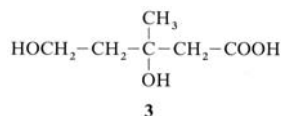
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1. Introduction

Isoprene [78-79-5] (1), C₅H₈, M_r 68.118, is named according to IUPAC rules as 2-methyl-1,3-butadiene. Its isomers include the commercially less important compounds *cis*- and *trans*-1,3-pentadiene (2) [504-60-9] (piperylene).



Free isoprene has been observed in nature only in very low concentration [1], [2]. The compound is present in roasted coffee and in the gas phase of tobacco smoke [3], and can be regarded as a precursor of polycyclic aromatics [4]. Isoprene is the structural unit of countless natural products (the terpenes, which include natural rubber and camphor) as well as biologically important substances such as vitamin A and the steroid sex hormones (cf. the "isoprene rule" of O. WALLACH and L. RUZICKA [5]). It is now known, however, that the biosynthesis of rubber and other natural products containing the isoprene skeleton proceeds not via isoprene itself, but rather via mevalonic acid [150-97-0] (3), 3,5-dihydroxy-3-methylpentanoic acid [6].



Isoprene was first synthesized in 1860 by C. E. WILLIAMS by the pyrolysis of natural rubber [7]. The reverse reaction – polymerization of isoprene to poly(*cis*-1,4-isoprene), with a structure corresponding to that of natural rubber – was long the subject of intensive effort [8]. The first successful attempts were reported in 1954 and 1955 by the Goodrich Gulf (Al – Ti Ziegler catalyst [9]) and Firestone companies (alkyl lithium catalyst [10]).

Isoprene was commonly prepared on a laboratory scale by thermolysis of turpentine oil (the so-called isoprene lamp of C. HARRIES [11]). Pyrolysis of dipentene [5989-27-5], limonene, was even used in the United States early in the Second World War as a commercial source of isoprene (Bibb process [12]). The reverse of this reaction – synthesis of terpenes from isoprene – has been discussed in a vast number of scientific publications, but has so far achieved little commercial significance.

Isoprene itself was commercially unimportant until after the Second World War because it could not be offered at a price that was sufficient-

ly attractive for its principal potential market, the manufacture of synthetic rubber. This situation changed with the development of improved methods for obtaining isoprene from petrochemical sources, as well as of polymerization techniques for the generation of poly(*cis*-1,4-isoprene), a synthetic rubber whose valuable material characteristics have been widely confirmed.

2. Properties

Physical Properties. Under normal conditions, isoprene is a colorless, volatile liquid. Important properties of isoprene are (see also [15]):

<i>mp</i> (101.3 kPa)	−145.95 °C
<i>bp</i> (101.3 kPa)	34.059 °C
Critical data [13]	
Temperature	483.3 K
Pressure	3.74 MPa
Volume	266 cm ³ /mol
Density (293 K)	0.68095 g/cm ³
Viscosity (293 K)	0.216 mPa · s
Surface tension (293 K)	18.22 mN/m
Refractive index n_D^{20}	1.42194
Vapor pressure [14] at − 20 °C	9.8 kPa
0 °C	26.4 kPa
20 °C	60.7 kPa
34.059 °C	101.3 kPa
40 °C	123.8 kPa
60 °C	229.1 kPa
80 °C	392.1 kPa
100 °C	629.5 kPa
Specific heat	
Vapor (298 K)	102.69 J mol ^{−1} K ^{−1}
Liquid (298 K)	151.07 J mol ^{−1} K ^{−1}
Heat of formation	
Vapor (298 K)	75.75 kJ/mol
Liquid (298 K)	49.36 kJ/mol
Free energy of formation	
Vapor (298 K)	146.23 kJ/mol
Liquid (298 K)	145.57 kJ/mol
Entropy of formation	
Vapor (298 K)	314.56 J mol ^{−1} K ^{−1}
Liquid (298 K)	228.3 J mol ^{−1} K ^{−1}
Heat of combustion (298 K)	−3186.58 kJ/mol
Heat of hydrogenation (298 K)	−230.20 kJ/mol
Heat of fusion (− 145.95 °C)	4.88 kJ/mol
Heat of vaporization (at 25 °C)	26.39 kJ/mol
at 34.059 °C	25.87 kJ/mol
Heat of polymerization (298 K)	− 75 kJ/mol
Entropy of polymerization (298 K)	− 101 J mol ^{−1} K ^{−1}
Constants for the Antoine equation	
log $p = A - B/(t + C)$, p in	
hPa, t in °C [14]	A 6.05329
	B 1092.997
	C 236.002
Flash point	−48 °C
Ignition temperature	220 °C

Explosive limits in air (total pressure	
13 kPa, 25 °C)	
Upper limit	7 – 9.7 vol%
	200 – 275 g/m ³
Lower limit	1 – 1.5 vol%
	28 – 40 g/m ³
Maximal explosion pressure	0.66 MPa

Spectra are to be found in the literature: IR [16], UV [17], NMR [18], Raman [19].

The *solubility* of isoprene in water at 20 °C is 0.029 mol%. It is miscible in all proportions with organic solvents such as ethanol, diethyl ether, acetone, and benzene. Regarding solubility in high-boiling, polar solvents, see Chap. 4. The Bunsen absorption coefficient α for oxygen in isoprene is 0.4065 m³ m^{−3} mbar^{−1} at 0 °C and 0.4557 at 20 °C.

Binary *azeotropic mixtures* of isoprene are listed in Table 1. The azeotrope of isoprene with *n*-pentane has acquired commercial significance in the isolation of pure isoprene. For information regarding ternary azeotropes of isoprene see [19].

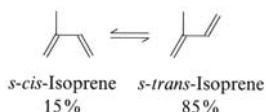
Data for vapor – liquid equilibria of binary and ternary mixtures of isoprene and other organic compounds are provided in [20] and [21]. Liquid – liquid equilibrium data for binary and multicomponent systems containing isoprene are listed in [22]. Activity coefficients at infinite dilution are given in [23]. Curves describing the temperature dependence of various physical quantities may be found in [24] and [25].

Chemical Properties. Spectroscopic analysis has revealed that most isoprene molecules in

Table 1. Binary azeotropes of isoprene [19]

Component	<i>bp</i> , °C	Isoprene content, wt%
Methanol	29.57	94.8
<i>n</i> -Pentane	33.6	72.5
Carbon disulfide	<34.15	<93
Methyl formate	22.5	50
Bromoethane	32	>65
Ethanol	32.65	97
Dimethyl sulfide	32.5	65
Acetone	30.5	80
Propylene oxide	31.6	40
Ethyl formate	<32.5	>76
Isopropyl nitrite	33.5	72
Methylal	32.8	70
Diethyl ether	33.2	52
Perfluorotriethylamine	30.2	82
Acetonitrile	33.5 – 33.6	97.5
Isopropylamine		>72.4

the ground state at 50 °C are in the *s-trans* conformation. Only 15% of the material has the *s-cis* form, which is higher in energy by 6.3 kJ/mol.



Equilibrium concentrations for the isomer system isoprene – pentadiene (a total of seven isomers) are presented graphically in [26] for temperatures between 200 and 1600 K. Reaction enthalpies for the corresponding isomerizations are provided in [27].

Isoprene exhibits the typical characteristics of a conjugated diene. Its methyl group makes the compound react more readily than butadiene with electrophiles and Diels – Alder dienophiles. Moreover, the reactivity of isoprene is more varied than that of butadiene, which only possesses two types of hydrogen atoms in contrast to the four of isoprene. Isoprene can participate in a wide range of reactions (including substitution, addition, ring formation, complexation, and telomerization reactions). For a summary of the general reactivity of isoprene see [19].

The only chemical reaction of isoprene of practical importance is its conversion to terpenes.

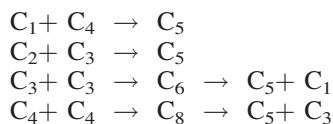
Isoprene is mainly used for polymer synthesis (Chap. 6).

3. Production

3.1. Synthetic Methods

Laboratory methods for the synthesis of isoprene from a wide variety of starting materials are summarized in [19].

Industrial syntheses of isoprene utilize the following four principles in creating the C₅ skeleton:



$\text{C}_1 + \text{C}_4 \rightarrow \text{C}_5$. *Isobutene* [115-11-7] is the C₄ building block in several syntheses of this type (Fig. 1). The C₁ component may be formaldehyde [50-00-0] (reactions 1, 2, and 3 in Fig. 1), one of its derivatives, or methanol [67-56-1] [28]. The C₁ molecule carbon monoxide also plays a role in synthesis; this route (4 in Fig. 1) involves hydroformylation of isobutene to 3-methylbutanal [30].

The most frequently used synthetic procedure is the acid-catalyzed addition of formaldehyde to

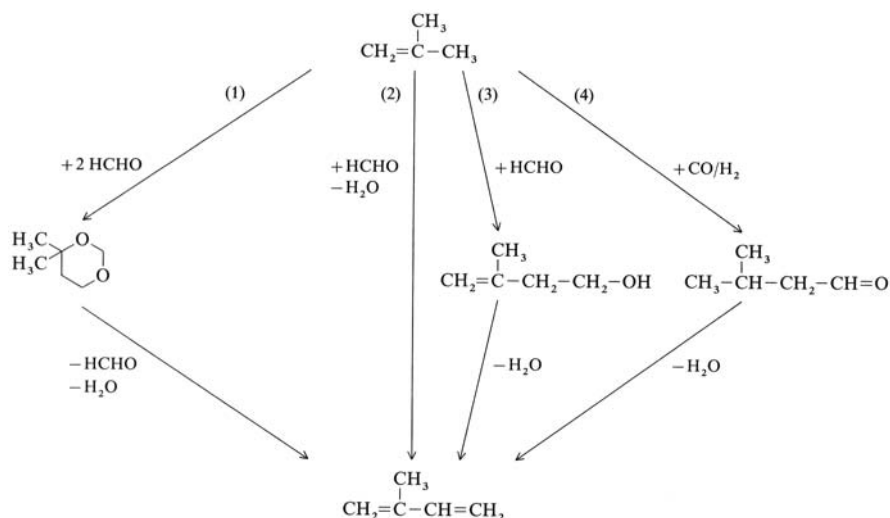
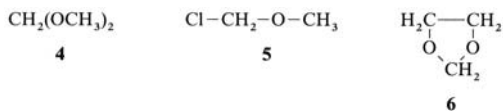


Figure 1. Synthesis of isoprene from isobutene

isobutene (Prins reaction, route 1 in Fig. 1). This produces a 1,3-dioxane, which is then cleaved in the gas phase (at 200 – 300 °C) over an acid catalyst (e.g., H₃PO₄ on a suitable carrier) to give isoprene, with recovery of half of the reacted formaldehyde. This reaction was first suggested for the synthesis of isoprene in 1938 [31], and it became widely known through the work of the Institut Français Pétrol [32], [33]. The method became the subject of further development at several locations as a result of the ready availability of the starting materials [34–36]. Individual procedures differ primarily in terms of catalysts employed and engineering details. Production facilities of this type are currently in operation in Japan (cf. Chap. 7).

The ultimate goal of developmental efforts in the synthesis of isoprene from isobutene and formaldehyde has been simplification and increased competitiveness. Takeda Chemical in Japan has proposed a one-step gas-phase procedure (cf. Fig. 1, route 2), in which isobutene and formaldehyde are passed over oxide catalysts at 300 °C [36]. Much preliminary work toward this approach was contributed by British Hydrocarbon Chemicals.

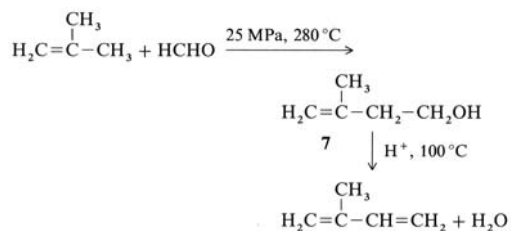
An important aspect of the above syntheses with respect to their economic viability is the problem of byproduct formation from formaldehyde. Efforts have therefore been made to use formaldehyde derivatives as a way of suppressing resin buildup. For example, both Idemitsu and Sun Oil have suggested the use of methylal [109-87-5] (**4**), dimethoxymethane [37], [38]. Marathon Oil has proposed a two-step process based on monochlorodimethyl ether [107-30-2] (**5**) [39], [40], while Sumitomo has discussed the use of dioxolane [646-06-0] (**6**), 1,3-dioxacyclopentane [41].



Consideration has also been given to integrating formaldehyde production directly into the process, i.e., by mixing methanol and oxygen directly with isobutene [42]; a modification of this approach is the use of methyl *tert*-butyl ether (MTBE) and oxygen [43].

Japanese patent applications from Kuraray, Nippon Zeon, and Sumitomo Chemical use *tert*-butyl alcohol [75-65-0] as a C₄ building block in isoprene synthesis, while a number of former Soviet publications describe a variety of methods based on cleavage of 1,3-dioxane. Probably the greatest disadvantage of the one-step gas-phase process is the low space – time yield of the catalysts, together with their rapid deactivation under the prevailing reaction conditions [44–46]. It is not known whether any of the above-described variants have been carried to production scale.

In addition to the Prins reaction with all its modifications, there is one other economically interesting route to the synthesis of isoprene from isobutene and formaldehyde via 2-methyl-1-buten-4-ol (**7**) (Fig. 1, reaction 3) [47]:



One advantage here is that the synthesis (ene reaction) of the intermediate **7** is a purely thermal process occurring in the liquid phase, which permits use of an aqueous formaldehyde solution [48]. Dehydration of **7** is conducted in aqueous NaCl/HCl solution [49] that can be easily regenerated (low catalyst cost).

2-Butene [107-01-7] is the C₄ building block for an entirely different synthesis of isoprene based on the C₁ + C₄ → C₅ principle via the intermediate 2-methylbutanal [96-17-3] (Fig. 2). 2-Methylbutanal is readily prepared by rhodium-catalyzed hydroformylation of 2-butene [30], [50], [51]. An alternative route to this C₅ aldehyde is the catalytic hydrogenation of 2-ethylacrolein which is easily prepared from *n*-butylaldehyde and formaldehyde [52], [62].

Catalytic dehydration of 2-methylbutanal to isoprene has been the subject of numerous studies [53]. A patent issued to Erdölchemie [54] describes the use of a β-phosphate catalyst, which is also discussed in most of the subsequent pub-

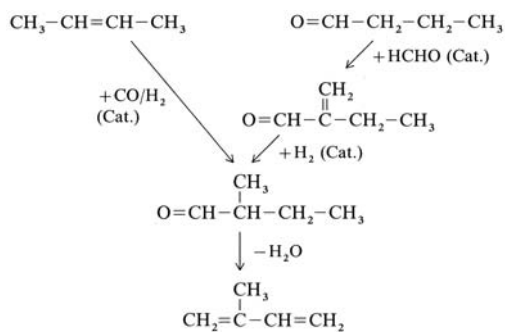


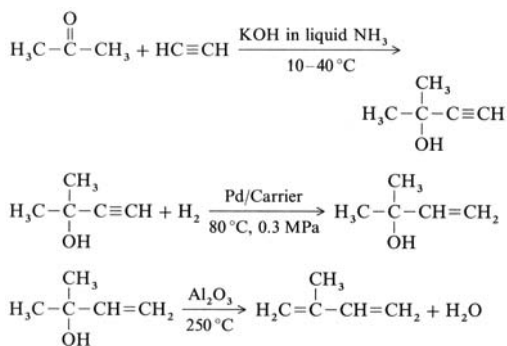
Figure 2. Synthesis of isoprene via 2-methylbutanal.

lications dealing with this reaction [30], [50], [55–57]. Other patents for the dehydration of 2-methylbutanal describe the use of magnesium ammonium phosphate [58], molecular sieve [59], as well as zeolite catalysts [60]. Nevertheless, all the catalysts cited are subject to rapid loss of activity [30], or else display low activity from the outset. Zeolites that have been silanized or doped with small amounts of cesium display longer lifetimes. For example, a zeolite containing 0.4% cesium showed no decrease in yield (51%) or isoprene selectivity (88%) after 120 h of use [61].

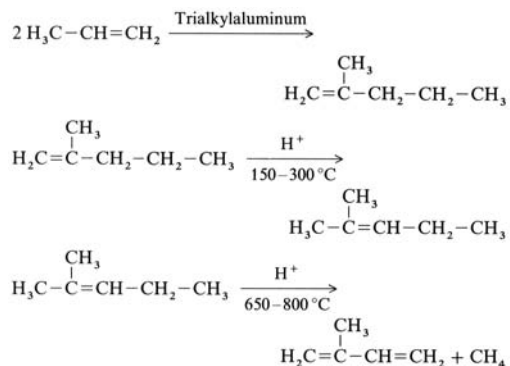
Cleavage of 3-methylbutanal over a boron phosphate catalyst (Fig. 1, route 4) gave poorer results than were observed with the 2-isomer [30], [62]. At the present time there are still no industrial facilities for the synthesis of isoprene from *n*-butenes or butanal via 2-methylbutanal.

$\text{C}_2 + \text{C}_3 \rightarrow \text{C}_5$. Codimerization of ethylene and propene in the presence of triethylaluminum leads to 2-methyl-1-butene, which can be dehydrogenated to isoprene. However, this method has not been carried beyond the experimental stage [63], [64].

By contrast, another isoprene synthesis based on C_2 and C_3 starting materials (acetylene and acetone) was carried to production scale by SNAM in Italy, whose manufacturing facilities in Ravenna had been in operation for several years [65–68]; the plant is, however, not currently in operation. A plant based on this principle has been built in the Republic of South Africa (see Chap. 7). The isoprene produced by this method is extremely pure but the process is relatively expensive.

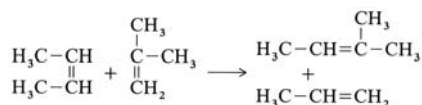


$\text{C}_3 + \text{C}_3 \rightarrow \text{C}_6 \rightarrow \text{C}_5 + \text{C}_1$. The first step of the familiar Goodyear – Scientific Design isoprene synthesis consists of the dimerization of propene to 2-methyl-1-pentene. This is then isomerized to 2-methyl-2-pentene, which is subsequently cracked with loss of methane to give isoprene [64], [69], [70].



The first commercial synthesis of isoprene was based upon this principle (Beaumont, Texas). Production was discontinued after a fire in 1975 because it was no longer competitive due to sharp increases in the price of propene.

$\text{C}_4 + \text{C}_4 \rightarrow \text{C}_8 \rightarrow \text{C}_5 + \text{C}_3$. Olefin metathesis represents a very interesting approach to isoprene manufacture from readily available petrochemicals. Thus, a butene fraction containing 2-butene and isobutene yields 2-methyl-2-butene and propene:



2-Methyl-2-butene can then be dehydrogenated to isoprene by standard methods (cf. Section 3.2) [71–75]. However, one disadvantage of the metathesis reaction is that all of the olefins in the reactor can react with one another yielding a broad spectrum of byproducts. This is especially true if the starting material is a technical-grade butene mixture containing 1-butene, which represents the only economically feasible starting material [76].

3.2. Dehydrogenation Procedures

The production of isoprene by dehydrogenation of isopentane or the isopentenenes (methylbutenes) has been the subject of many investigations [77], [78]. Such reactions closely resemble the analogous dehydrogenations of *n*-butane and the *n*-butenes to butadiene (\rightarrow Butadiene).

One-step dehydrogenation of isopentane to isoprene can be carried out according to the Houdry – Catadiene procedure ($\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst, ca. 600 °C, and ca. 7 kPa) with a yield of 52 % [79–81]. Isoprene is prepared commercially in this way in the former Soviet Union [82]. A two-step process for the dehydrogenation of isopentane is described in [83].

Isoprene production plants based on the dehydrogenation of methylbutenes exist in the United States and the Netherlands but are not currently in operation. The requisite starting material comes largely from cat-cracker off-gases [84], [85]. Methylbutenes are extracted in the form of semesters from the appropriate distillation fraction of these off-gases by dissolution in sulfuric acid, followed by back extraction with paraffinic hydrocarbons (Sinclair procedure). As far as is known, dehydrogenation is effected with a Shell catalyst ($\text{Fe}_2\text{O}_3\text{--K}_2\text{CO}_3\text{--Cr}_2\text{O}_3$) at 600 °C and dilution of the methylbutenes with steam; the yield is 85 % [86]. A Sr – Ni – phosphate catalyst (Dow Type S catalyst, a modification of the well-known Dow Type B catalyst) has also been reported to be suitable for this reaction [87].

Oxidative dehydrogenation of isopentane [88–90] and the methylbutenes [91–95] has also been widely investigated. The behavior of oxide catalysts in the oxidative dehydrogenation of the methylbutenes is described in [45]. The yield and selectivity for isoprene are reported to be 60 % and 95 %, respectively.

Although many publications and patents discuss the preparation of isoprene by dehydrogenation, little significant progress is apparent. Two former Soviet reports will be mentioned as examples. The oxidative dehydrogenation of methylbutenes to isoprene with aluminum phosphate catalysts is described in [96]; the reactivity of the olefins decreases in the order 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene. Oxidative dehydrogenation of methylbutenes to isoprene can also be achieved with a silicate catalyst doped with alkaline-earth oxides or the oxides of nickel, iron, or cobalt [97].

Conversion of isopentane and methylbutenes to isoprene by co-oxidation is claimed in [98].

3.3. Recovery from C_5 Cracking Fractions

The C_5 cracking fractions obtained as a byproduct in the pyrolysis of hydrocarbons to ethylene (\rightarrow Ethylene) have come to play a major role in isoprene manufacture [99]. Workup of the cracking products from naphtha cleavage yields so-called “crack gasoline”, which contains only low concentrations of isoprene and other C_5 hydrocarbons, the major constituents being $\text{C}_6\text{--C}_8$ aromatics. Nevertheless, this material may still be distilled into C_5 and aromatic fractions.

The yield of isoprene is typically 2 – 5 wt % based on ethylene, although it may be increased by starting with a heavier raw material such as gas oil. Table 2 demonstrates the influence of the nature of the cracker feed on the C_5 product distribution. Figure 3 shows that the yield of isoprene decreases with increasing crack severity (temperature and residence time). Nevertheless, this overall decrease is accompanied by an increase in isoprene concentration in the C_5 crack fraction (cf. Table 3). Table 3 also provides the product distribution in a typical methylbutene dehydrogenation fraction. Based on energy consumption, recovery of isoprene from crack fractions is considerably more efficient than synthesizing the compound chemically [101].

Increasingly heavier raw materials will be used in Europe and the United States for ethylene production in crackers [100]. The quantity of the isoprene byproduct will therefore also increase. In some crackers only an aromatic fraction is recovered from crack gasoline. The residue (i.e.,

Table 2. Composition (in weight percent) of the C₅ fraction from the pyrolysis of hydrocarbons [100] and boiling points of the individual components

Component	<i>bp</i> at 101.3 kPa, °C	Starting material					
		1	2	3	4	5	6
Isopentane	27.85	1.99	11.02	0.99	24.1	7.8	0.8
<i>n</i> -Pentane	36.07	0.6	2.54	2.72	26.1	14.3	20.8
2-Methyl-1-butene	31.16	4.95	5.21	3.80	11.8	2.9	0.8
2-Methyl-2-butene	38.57	2.61	2.13	3.01	11.8	2.4	0.8
1-Pentene	29.97	24.10	3.84	4.08	4.2	2.9	3.1
<i>trans</i> -2-Pentene	36.35	4.74	2.14	2.57	4.2	5.8	
<i>cis</i> -2-Pentene	36.94	3.47	1.54	1.36	4.2	5.8	1.6
<i>trans</i> -1,3-Pentadiene	42.03	14.32	4.95	6.84	8.8	7.3	10.2
<i>cis</i> -1,3-Pentadiene	44.07	8.00	22.13	3.65	8.8	4.7	5.5
Isoprene	34.06	6.71	6.65	4.34	13.7	16.1	13.3
Cyclopentadiene	42.50	16.46	2.40	17.77	7.5	20.4	37.0
Cyclopentene	44.24	12.50	5.76	6.16	1.6	5.9	5.5

¹ Paraffin wax (*mp* 43.5 °C).

² Low octane gasoline (high severity cracking).

³ Sulfur-containing petroleum (high severity cracking).

⁴ Naphtha.

⁵ Romaskino straight-run gasoline (boiling range ≈ 40 – 160/180 °C).

⁶ Synthetic gasoline from Fischer – Tropsch synthesis (boiling range ≈ 40 – 150 °C).

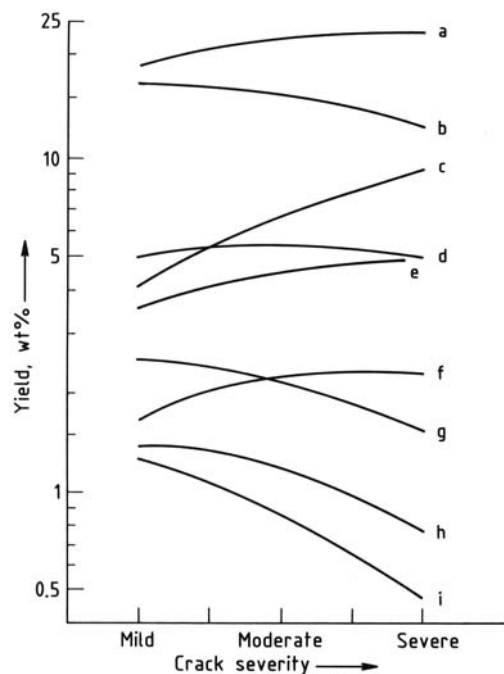


Figure 3. Influence of cracking severity on the product distribution [102] a) Ethylene; b) Propene; c) Benzene; d) Butadiene; e) Toluene; f) Cyclopentadiene; g) Isobutene; h) Isoprene; i) Piperilyenes

the C₅ hydrocarbons) is often combined with the C₄ fraction and recycled with the cracker feed.

Pure isoprene cannot be isolated from the C₅ crack fraction simply by distillation, because the numerous components of the mixture differ only slightly in boiling point (cf. Table 2), and isoprene forms an azeotropic mixture with *n*-pentane (cf. Table 1). For the separation of cyclopentadiene from the C₅ crack fraction by

Table 3. Typical composition (in weight percent) of C₅ crack fractions as a function of cracking severity

Component	Crack severity			Methylbutene dehydrogenation fractions
	Mild	Normal	Severe	
Pentanes	26.70	34.36	14.12	65 – 75
<i>n</i> -Pentenes	5.15	6.60	4.21	65 – 75
Methylbutenes	6.95	9.17	5.76	65 – 75
Pentadienes	10.90	9.40	19.46	traces
Isoprene	14.20	18.00	23.25	25 – 35
Cyclopentane and cyclopentene	4.40	3.30	5.76	traces
Cyclopentadiene (including dimer)	16.70	15.97	24.91	traces
2-Butyne	0.40	0.4	1.03	traces
Other hydrocarbons	balance	balance	balance	

dimerization, see \rightarrow Cyclopentadiene and Cyclopentene.

Distillative enrichment of isoprene in C_5 fractions to a concentration of 25 – 50 % is of some commercial interest because it reduces the transportation and separation costs associated with the isolation of pure isoprene. Examples of special isoprene enrichment processes are described in [103].

Goodyear has developed a process for separating isoprene from C_5 crack fractions in the form of its azeotrope with *n*-pentane [104], [105]. This procedure was carried to production scale in France, although that facility is no longer in operation. The resulting mixture is free of components that might adversely affect the polymerization of isoprene, and is thus suitable for polymerization processes that employ a solution of isoprene in an inert hydrocarbon.

“Chemical” isolation procedures involving copper(I) compounds have also been considered for the recovery of isoprene from C_5 hydrocarbon mixtures [106]. In contrast to the situation with butadiene (\rightarrow Butadiene) this process has never been adopted commercially for isoprene.

Selective organic solvents are used in “physical” processes for separating isoprene by extractive distillation with or without liquid – liquid

extraction. The principles involved are similar to those developed for separation of butadiene from C_4 crack fractions (\rightarrow Butadiene). The most appropriate solvents for production-scale separation of isoprene from other hydrocarbons include *N*-methylpyrrolidone [107], [108], dimethylformamide [109], [110], and acetonitrile [111]. The relative volatilities of the hydrocarbons in various polar solvents (i.e., the selectivities of the solvents for the isolation of isoprene from C_5 hydrocarbon mixtures) are listed in Table 4. Figure 4 shows the relationship between the overall concentration and the relative volatilities of 2-methyl-2-butene – isoprene mixtures in various solvents; these data are of considerable importance for estimating the size of a proposed production facility. 2-Methyl-2-butene is the key low-boiling component under the conditions prevailing in this extractive distillation procedure. Additional data relevant to selective solvents for separation of isoprene are presented in [113]. Isolation of isoprene concentrates from C_5 hydrocarbon mixtures by extraction with selective organic solvents is discussed in [114].

Figure 5 is a flow diagram for the isolation of isoprene from a C_5 cracking fraction. The first step in the separation is a combination of a liquid – liquid extraction with an extractive dis-

Table 4. Relative volatilities* of hydrocarbons to be separated from isoprene in various solvents, based on [112]

Hydrocarbon	<i>bp</i> , °C	Isoprene solvent**						
		ACN	DMF	NMP	MOPN	DMAC	DMSO	γ -BL
Isopentane	27.9	2.92	3.02	3.00	2.62	2.77	2.72	2.79
<i>n</i> -Pentane	36.1	2.37	2.39	2.40	2.27	2.20	2.07	2.13
3-Methyl-1-butene	20.1	2.58	2.63	2.65	2.49	2.53	2.51	2.56
1-Pentene	30.0	1.89	1.90	1.88	1.78	1.82	1.73	1.75
2-Methyl-1-butene	31.2	1.71	1.73	1.75	1.62	1.67	1.62	1.61
<i>trans</i> -2-Pentene	36.3	1.56	1.55	1.56	1.46	1.50	1.45	1.45
<i>cis</i> -2-Pentene	36.9	1.49	1.54	1.53	1.35	1.47	1.41	1.40
2-Methyl-2-butene	38.1	1.38	1.39	1.40	1.32	1.34	1.29	1.28
Isoprene	34.1	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
<i>trans</i> -1,3-Pentadiene	42.0	0.77	0.76	0.78	0.77	0.77	0.77	0.77
<i>cis</i> -1,3-Pentadiene	44.2	0.70	0.70	0.71	0.70	0.72	0.70	0.70
Cyclopentadiene	41.3	0.62	0.62	0.62	0.63	0.63	0.62	0.63
2-Butyne	26.7	0.96	0.90	0.997	0.97	0.99	1.08	1.08
3-Methyl-1-butyne	26.3	1.04	0.89	0.95	1.10	0.93	0.95	0.94
2-Methyl-1-buten-3-yne	32.5	0.62	0.49	0.48	0.67	0.51	0.55	0.53
1-Pentyne	40.2	0.58	0.55	0.54	0.64	0.54	0.55	0.56
2-Pentyne	56.1	0.42	0.44	0.67	0.43	0.46	0.40	0.41

*The figures indicate the ratio of the volatility of the specified hydrocarbon to that of isoprene measured at 50 °C in a mixture containing 12.5 wt % of the hydrocarbon, 12.5 wt % of isoprene, and 75 wt % of solvent.

**ACN = acetonitrile; DMF = dimethylformamide; NMP = *N*-methylpyrrolidone; MOPN = β -methoxypropionitrile; DMAC = dimethylacetamide; DMSO = dimethyl sulfoxide; γ -BL = γ -butyrolactone

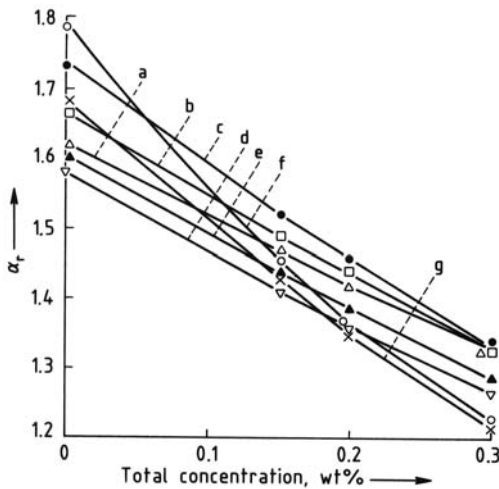


Figure 4. Relationship between the total concentration and the relative volatilities α_r of 2-methyl-2-butene – isoprene mixtures in various solvents [112] a) Acetonitrile; b) Dimethylformamide; c) *N*-Methylpyrrolidone; d) β -Methoxypropionitrile; e) Dimethylacetamide; f) Dimethyl sulfoxide; g) γ -Butyrolactone

tillation, an approach particularly suited to C_5 fractions with a low isoprene concentration. Pre-concentration of isoprene occurs in extractor (a). Crude isoprene is removed as a sidestream from the extractive distillation column (b), after which it is freed from piperylenes and cyclopentadiene in a second extractive distillation step incorpo-

rating columns (c) and (d). Final purification of isoprene to polymerization grade occurs in distillation columns (e) and (f) [115]. C_5 fractions that contain cyclopentadiene can be used in this process because the cyclopentadiene is removed together with the piperylenes.

Incorporation of relevant equipment in this process allows the isolation of cyclopentadiene or the commercially valuable cyclopentene (\rightarrow Cyclopentadiene and Cyclopentene). Introduction of a supplementary column permits recovery of pure piperylenes.

The high quality specifications that are required for isoprene used in the preparation of poly(*cis*-1,4-isoprene) are met with the aid of modern separation facilities. It should be noted, however, that suggestions have also been made for the chemical removal of specific impurities (e.g., cyclopentadiene, acetylene) [116].

Economic comparison of the various techniques for separating isoprene from C_5 cracking fractions is difficult because a large number of criteria must be considered and each must be assigned a proper weighting which depends on the location of the plant. Various selective solvents are compared in [112] with respect to their suitability for isoprene separation. Energy consumption data are analyzed in [117]. A detailed cost analysis for one specific solvent is provided in [118].

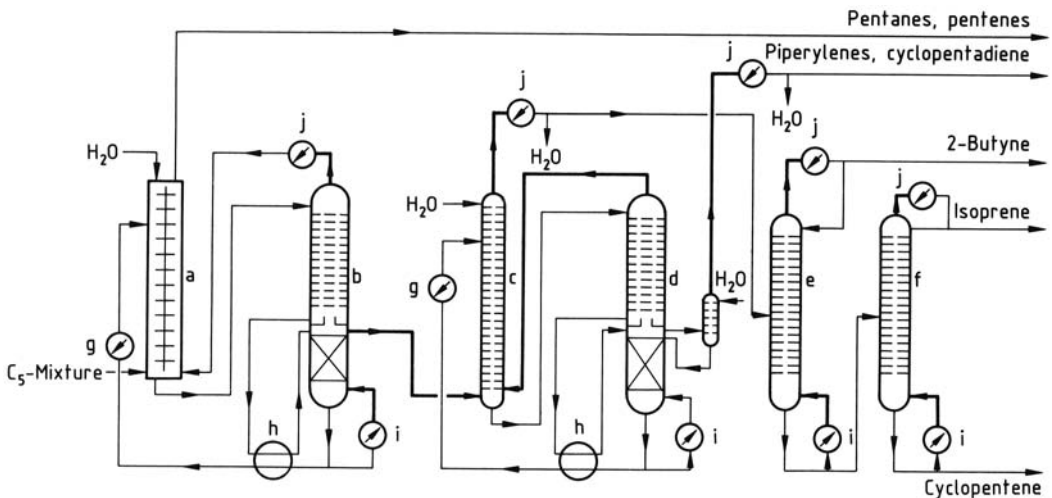


Figure 5. Recovery of isoprene from C_5 hydrocarbon mixtures by a combination of extraction and extractive distillation [107] a) Liquid – liquid extraction column; b) – d) Columns for extractive distillation; e) Butyne column; f) Isoprene column; g) Cooler; h) Heat exchanger; i) Reboiler; j) Condenser
 ——— Vapor phase; ——— Liquid phase

4. Quality Specifications

Isoprene is used primarily for the synthesis of polymers, including poly(*cis*-1,4-isoprene) and block polymers containing styrene (SIS polymers, see Chap. 6) [119].

Table 5 provides typical specifications for isoprene used as a monomer for the production of poly(*cis*-1,4-isoprene). Purity specifications for polymerization with Ziegler catalysts are less rigorous than for polymerization with alkyl lithium catalysts. The latter are also used for preparing SIS polymers.

Isoprene for use as a monomer in the manufacture of butyl rubber (isobutene – isoprene rubber, IIR) may contain higher levels of the common impurities, as indicated in Table 6. Table 6 also contains information about technical-grade isoprene.

In most polymerization processes, isoprene is used in dilution with other inert hydrocarbons. In the production of IR and SIS polymers, it may therefore be more economical to use an isoprene product (isoprene concentrate) in which isoprene of the required purity (content of cyclopentadiene, acetylene, etc.) is diluted with hydrocarbons that do not interfere with polymerization. Thus, in the synthesis of isoprene rubber a starting material containing 60 – 85 % isoprene is sufficient, whereas an isoprene content of 80 – 90 % is required for SIS polymers. For the synthesis of butyl rubber, however, the isoprene cannot be diluted with other hydrocarbons.

The purity of isoprene is normally verified by gas chromatography. Data for sulfur, peroxides, carbonyls, distillation residues, and inhibitors are determined by the usual standard analytical methods, preferably those based on ASTM or ISO/DIN recommendations.

Table 5. Monomer specifications for isoprene used in the production of poly(*cis*-1,4-isoprene) [120]

Component	Alkyl lithium catalyst	Ziegler catalyst (Al/Ti)
Isoprene, wt %	99.5	99.5
Monoolefins, wt %	0.4	0.5
1,3-Pentadiene, ppm	<80	<200
Cyclopentadiene, ppm	< 1	< 1
Acetylene, ppm	< 3	< 50
Allene, ppm	< 5	< 50
Carbonyl compounds, ppm	< 5	< 10
Sulfur (as H ₂ S), ppm	< 5	< 5
Water, ppm	< 5	< 5

Table 6. Specifications for technical-grade isoprene [121] and isoprene intended for use in the production of butyl rubber (IIR) [122]

Component	Technical-grade isoprene	Isoprene for IIR
Isoprene, wt %	99	>92
Diolefins (total), wt %		>95
C ₃ olefins, wt %	1	
Cyclopentadiene, wt %	0.05	<1
α-Acetylene, wt %		<0.35
Peroxides (as H ₂ O ₂), ppm	100	<10
Carbonyl compounds (as acetone), ppm	150	<500
Sulfur (as H ₂ S), ppm	5	<100
Distillation residue, wt %		<1.5

5. Storage and Transportation

Appropriate regulations must be observed during construction and operation of tank storage facilities for isoprene (e.g., the VbF rules in the Federal Republic of Germany). Reference [123] should be consulted regarding special problems, such as prevention of the formation of peroxides (→ Butadiene, Chap. 5). Other conditions being equal, the rate of reaction of oxygen with isoprene is significantly greater than that with butadiene. Data regarding the rate of thermal dimerization of isoprene are given in Table 7; this reaction cannot be suppressed by inhibitors. Thermal dimerization at low temperature is a Diels – Alder reaction, producing only cyclohexene derivatives, while at higher temperatures cyclooctadienes are also formed [124]. Transport regulations are summarized in Table 8 [125].

6. Uses

6.1. Polymer Synthesis

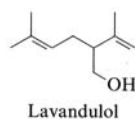
Most of the isoprene that is produced is utilized for the synthesis of poly(*cis*-1,4-isoprene) (isoprene rubber, IR), a material (particularly the

Table 7. Dimerization of isoprene as a function of temperature [123]

Temperature, °C	Dimerized isoprene, wt %/h
20	0.00017
40	0.00019
60	0.0021
80	0.023
100	0.25

chloride which is then converted to dehydrolinalool in two steps [7], [130]. Rhodia used the dehydrolinalool as a starting compound for the industrial synthesis of most of the compounds shown in Figure 6, but the plant was decommissioned. Kuraray in Japan, however, produces the compounds shown in Figure 6, squalane, and other substances from isoprene [131].

C₅+ C₅ Routes. Rhodia has also used a *Grignard synthesis* to produce the C₁₀ terpene alcohol lavandulol [1845-51-8] from two molecules of isoprene [132].

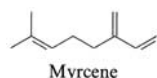


Isoprene can react in a variety of ways to form terpenes via oligomerization or telomerization (\rightarrow Terpenes) [133–137]. The syntheses of myrcene and *N,N*-diethylnerylamine (C₁₀ terpenes) are described below as examples of scientifically and industrially important linear oligomerization and telomerization reactions, respectively.

All naturally occurring terpenes are composed of isoprene units arranged in a “head-to-tail” fashion [133–137]. Terpenes synthesized from isoprene must also possess this structure and their double bonds must be correctly positioned [138], [139]. On account of this problem C₁₀ terpenes and their derivatives are not generally synthesized from isoprene but by other routes [47], [138].

Variation of the quantitative composition of a Pd-complex catalyst can influence the structure of dimethyloctadienes synthesized from isoprene [140].

Myrcene [123-35-3] has been synthesized by *oligomerization* of isoprene with a sodium/dialkylamine catalyst by TAKABE et al. [141] (see also [142–144]).



Nissan Chemical Industries have developed a route for the industrial production of myrcene and have announced that it will be implemented industrially [145].

Telomerization of isoprene proceeds with a variety of compounds, e.g., ammonia or amines [146] (see also [135], [136]). Interestingly, reactions occur in which the regioselectivity can be highly modified by varying the amount and concentration of Brønsted and Lewis acids added to the catalyst [147], [148].

Isoprene can react with diethylamine to form *N,N*-diethylnerylamine [40137-00-6] [149]; this telomerization reaction is catalyzed by butyl lithium. *N,N*-Diethylnerylamine can be further reacted to give linalool, geraniol, nerol, hydroxycitronellal, citronellal, and menthol (Fig. 7) [149–152].

The Takasago Perfumery Company in Japan has developed an industrial synthesis for enantiomerically pure L-menthol [2216-51-5] from optically active citronellal. The reaction involves the asymmetric allylamine – enamine isomerization of *N,N*-diethylgeranylamine or *N,N*-diethylnerylamine with a Rh – BINAP [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] catalyst [153–156]. Geranylamine is obtained by addition of diethylamine to myrcene [22]. The synthesis of nerylamine is described above [149]. Takasago produces 1500 t/a of L-menthol by this route.

7. Economic Aspects

Isoprene is used mainly as a starting material for the manufacture of synthetic rubber, the market for the compound therefore depends heavily upon the widely varying price of natural rubber (cf. [157] and corresponding publications from previous years). As noted in Section 3.3, extraction from C₅ crack fractions is the most economical route to isoprene [101]. Nevertheless, a key factor in the calculation is the location of the separation facility, since separation is only profitable if C₅ fractions (possibly enriched in isoprene) from several cracking plants can be transported economically to a separator of sufficient capacity [158]. Utilization of the large quantities of residual C₅ hydrocarbons is also a major consideration.

The total production of C₅ diolefins in Western Europe in 1987 was 83 000 t [159]. It is of some interest that more (dimeric) cyclopentadiene was produced (44 000 t) than isoprene (23 000 t). The remainder (15 000 t) was

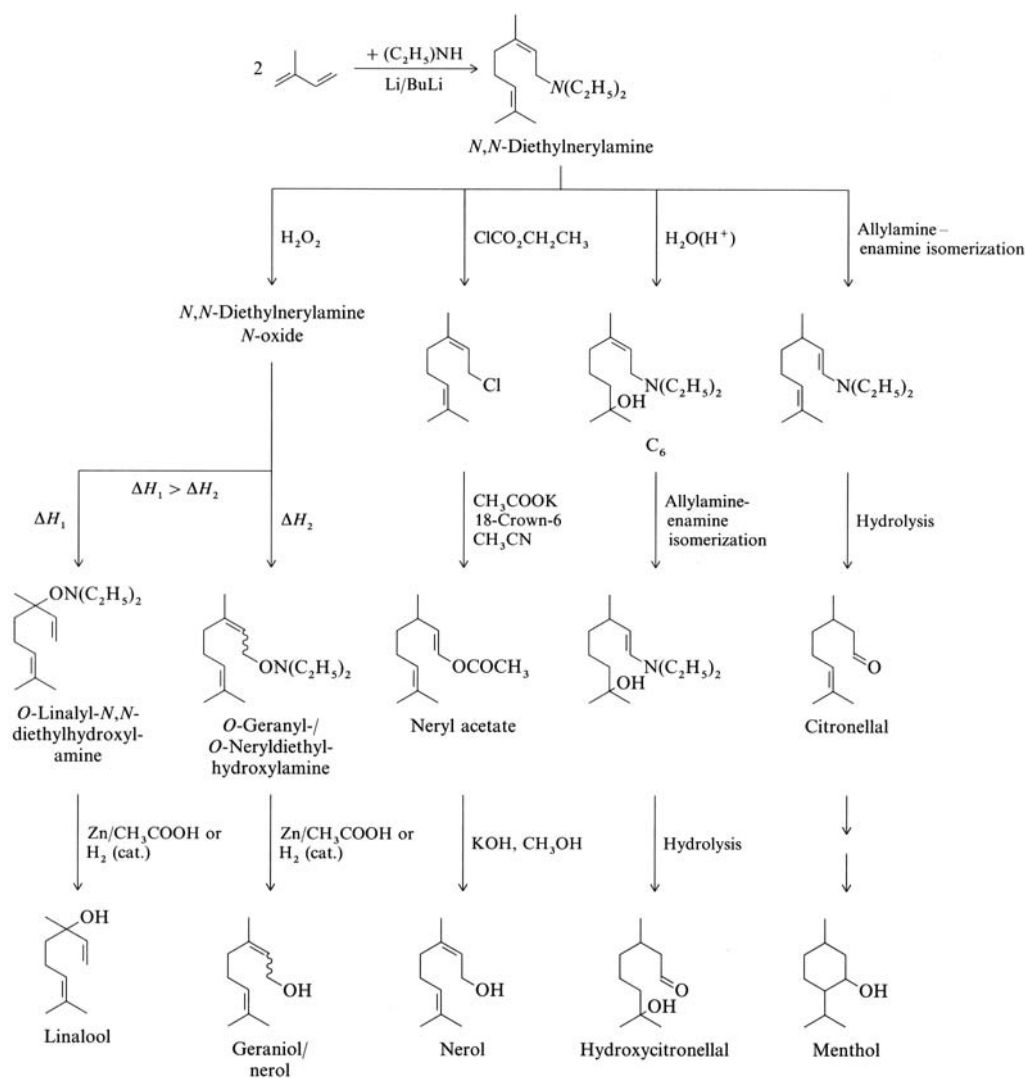


Figure 7. Synthesis of terpenes from isoprene via nerylamine

accounted for by piperylenes. As shown in Figure 8, an increasing demand for cyclopentadiene relative to isoprene is also anticipated in the United States in the coming years. The growing interest in cyclopentadiene may be attributed to the latest developments in the field of metathetic polymerization of the compound [161]. Combining this technology with the reaction injection molding method opens the way to very economical injection castings with good mechanical properties.

Table 9 provides an overview of the known production facilities for pure isoprene and iso-

prene concentrates. The isoprene concentrates are used either directly or, if necessary, after additional purification. Table 10 summarizes production capacities and actual production of polyisoprene (IR), butyl rubber (IIR), and synthetic rubber for the years 1987 and 1989, subdivided according to country. Corresponding totals for the period 1979 – 1989 are given in Table 11. The obvious decrease in the production of polyisoprene is largely a result of declines in the United States. Consumption data for isoprene used in the manufacture of SIS copolymers in 1986 follow [119]:

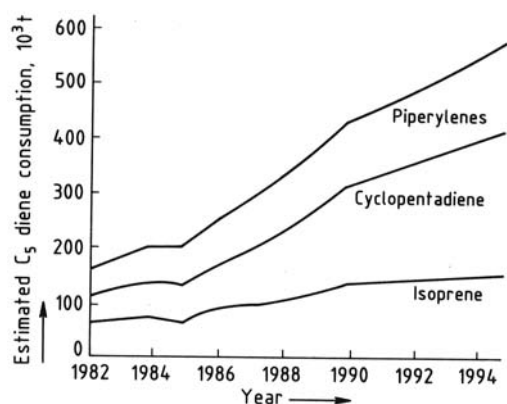


Figure 8. Estimated demand for C₅ dienes in the United States [160]

United States	25 000 t
Western Europe18	000 t
Japan	250 t

8. Toxicity and Occupational Health

Acute Toxicity. At high levels of exposure isoprene is an anesthetic in animals, finally resulting in paralysis and death. Single 2-h inhalation exposures of mice to 56 000 mg isoprene per cubic meter of air did not produce toxic effects. Levels of 98 000 – 126 000 mg/m³ resulted in deep narcosis; death occurred after 2 h of exposure to 140 000 mg/m³. The LC₅₀ for a 2-h exposure was 180 000 mg/m³ in the rat. The

Table 9. Production facilities for isoprene

Country	Company	Location	Capacity as 100 wt % isoprene, t/a ^a	Product ^b	Process ^c
United States	Goodyear	Beaumont, Texas	84 000	P	refining of isoprene concentrate (extractive distillation?)
	Arco Lyondell	Channelview, Texas	36 000	C	extractive distillation (ACN) of C ₅ fractions
	Chevron	Cedar Bayou, Texas	9 000	C	extractive distillation (?)
	Dow	Freeport, Texas	16 000	C	extractive distillation (?)
	Exxon	Baton Rouge, Louisiana	16 000	C	extractive distillation (?)
			14 000	C	extractive distillation (ACN) of C ₅ fractions
		Baytown, Texas	14 000	C	extractive distillation (ACN) of C ₅ fractions
	Shell	Dear Park, Texas	40 000	C	extractive distillation (ACN) of C ₅ fractions
Netherlands	Shell	Pernis	25 000	C	extractive distillation (ACN) of C ₅ fractions
Republic of South Africa	Sentrachem (Karbochem)	New Castle/ Natal	45 000	P	synthesis from acetone and acetylene, plant not yet on line
Japan	Nippon Zeon	Mizushima	45 000	P	extractive distillation (DMF) of C ₅ fractions
	Japan Synthetic Rubber	Kashima	30 000	P	extractive distillation (ACN) of C ₅ fractions
	Kuraray	Kashima	30 000	P	synthesis from isobutene and formaldehyde
former Soviet Union		several locations	ca. 800 000	C	dehydrogenation of isopentane extractive distillation of C ₅ fractions synthesis from isobutene + formaldehyde
<i>Standby Capacities</i>					
United States	Shell	Port Neches, Texas	45 000	P	dehydrogenation of isopentene (plant bought from BF Goodrich in 1982 and modified for production of pure isoprene)
Netherlands	Shell	Pernis	50 000	C	dehydrogenation of isopentene
Italy	Enichem (ANIC)	Ravenna	30 000	P	synthesis from acetone and acetylene

^a Capacities in 1987.

^b C = concentrate; P = pure isoprene.

^c ACN = acetonitrile; DMF = dimethylformamide.

Table 10. Production capacities (in 10^3 t/a) for polyisoprene (IR), butyl rubber (IIR), and total synthetic rubber [162]*

Country	IR		IIR		Synthetic rubber	
	1987	1989	1987	1989	1987	1989
Belgium			85	85	150	150
Germany (FRG)					591	592
France			48	48	719	719
Great Britain			60	60	485	485
Netherlands	40	40			719	719
<i>Western Europe</i>	40	40	193	193	2970	3044
Canada			120	120	284	284
USA	68	68	219	219	2 733	2 796
<i>North America</i>	68	68	339	339	3 017	3 080
Brazil		13			350	427
<i>Latin America</i>		13			594	689
Japan	67	67	75	75	1 587	1 627
Republic of South Africa	45	45			136	136
Countries with market economics	220	233	607	607	8 844	9 195
Countries with centrally planned economics	1 045	1 045	120	210	3 579	3 860
World Total	1 265	1 278	727	817	12 423	13 055

* Year-end data, 1989 being based on available projections.

threshold concentration for irritative effects in cats is reported as 800 mg/m^3 . An oral LD_{50} of 2100 mg liquid isoprene per kilogram of body weight and an intraperitoneal LD_{50} of 1400 mg/kg in the male rat have been determined. A single dermal exposure of rats to a 1-mL dose of liquid isoprene per kilogram body weight did not cause adverse symptoms or mortality [164], [165].

Toxicity after Repeated Exposure.

Fischer 344 rats and B6C3F1 mice were exposed by inhalation for two weeks to atmospheric isoprene concentrations of 0, 438, 875, 1750, 3500, and 7000 ppm. The rats did not show any exposure-related changes (survival, clinical symptoms, body weight, biochemistry, hematology, macro- and micropathology). Mice at the 7000 ppm level only showed lower body weight gain, but the mice in all groups suffered from anemia, testicular atrophy, olfactory epithelial

degeneration, and epithelial hyperplastic changes in the stomach. As in the case of 1,3-butadiene, mice therefore seem to be more susceptible than rats [166].

Repeated dermal exposure (2 applications of 500 μL on each of 5 consecutive days) to the ear of the rabbit caused only limited, reversible irritation [165]. No data on long-term inhalation exposure are available.

Mutagenicity. Isoprene and its monoepoxides do not induce point mutations in the Ames test. The dioxide of isoprene (2-methyl-1,2,3,4-diepoxybutane) was found to be mutagenic in this test system [167–170]. Due to some similarities with 1,3-butadiene in the formation of mutagenic metabolites the possible carcinogenic effects of isoprene need further evaluation.

Inhalative exposure of B6C3F1 mice to isoprene levels from 438 to 7000 ppm in air for

Table 11. Production and production capacity (in 10^3 t) for polyisoprene (IR), butyl rubber (IIR), and total synthetic rubber [163]*

		1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989
IR	capacity	281	289	289	297	397	289	285	255	225	220	213
IR	production	242	219	168	129	120	146	110	132	113		
IIR	capacity	493	498	446	533	539	583	580	583	585	607	615
IIR	production	457	395	426	370	372						
Synthetic rubber	capacity	7975	8144	8379	8878	8944	8710	8639	8772	8730	8844	9108
Synthetic rubber	production	5830	6167	5347	5281	4623	4854	5397	5211	5486		

* Excluding countries with centrally planned economies.

6 h/d on 12 days resulted in elevated frequencies of sister chromatid exchange indicating cytogenetic effects [171].

Reproduction. No data on reproductive or teratogenic effects are available.

Metabolism. Rodent mitochondrial fractions transformed isoprene to its monoepoxides 3,4-epoxy-3-methyl-1-butene and 3,4-epoxy-2-methyl-1-butene, leading finally to the corresponding diols. Minor oxidation of the more stable metabolite (3,4-epoxy-2-methyl-1-butene) to a diepoxide has been described [172], [173]. Isoprene is metabolized significantly in the respiratory tract. Up to atmospheric isoprene concentrations of about 300 ppm, metabolism is directly proportional to the exposure concentration [174], [175]; a saturation effect occurs at levels above 300 – 500 ppm. Mice metabolize isoprene at a higher rate than rats [174].

Isoprene is synthesized endogenously. The synthesis rate in unexposed mice and rats has been calculated to be $0.4 \mu\text{mol h}^{-1} \text{kg}^{-1}$ and $1.9 \mu\text{mol h}^{-1} \text{kg}^{-1}$, respectively [174].

Effects in Humans. Isoprene is narcotic in humans at very high exposure levels. It may also cause irritation of the skin, eye, mucous membranes, and respiratory tract.

Hygienic Standards. No TLV or MAK values have been established for isoprene. A threshold of 40 mg/m^3 has been set in the former Soviet Union.

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