Isoprene

HANS MARTIN WEITZ, (Retired), BASF Aktiengesellschaft, Ludwigshafen, Federal Republic of Germany
ECKHARD LOSER, Bayer AG, Wuppertal, Federal Republic of Germany

1. Introduction

Isoprene \([78-79-5]\) \((1), \text{C}_5\text{H}_8, M_r 68.118\), 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).

\[
\begin{align*}
1 & : \text{CH}_3 \\
2 & : \text{H}_2\text{C} = \text{C} - \text{CH} = \text{CH}_2 \\
& \quad \text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2
\end{align*}
\]

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. RŮZICKA \([5]\)). 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]):

- \( mp \) (101.3 kPa) = -145.95 °C
- \( bp \) (101.3 kPa) = 34.059 °C
- Critical data [13]:
  - Temperature: 483.3 K
  - Pressure: 3.74 MPa
  - Volume: 266 cm³/mol
  - Density (293 K): 0.68095 g/cm³
  - Viscosity (293 K): 18.22 mN/s
  - Surface tension (293 K): 18.22 mN/m
  - Refractive index: \( n_D \) = 1.42194
  - Vapor pressure [14] at:
    - 20 °C: 9.8 kPa
    - 34.059 °C: 60.7 kPa
    - 40 °C: 101.3 kPa
    - 60 °C: 229.1 kPa
    - 80 °C: 392.1 kPa
    - 100 °C: 629.3 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
  - Bunsen absorption coefficient \( a \) for oxygen in isoprene:
    - 0 °C: 0.4065 m³ m⁻³ mbar⁻¹
    - 20 °C: 0.4557 m³ m⁻³ mbar⁻¹
  - Flash point:
    - Vapor (298 K): 48 °C
    - Liquid (298 K): 220 °C

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].

Table 1. Binary azeotropes of isoprene [19]

<table>
<thead>
<tr>
<th>Component</th>
<th>( bp, ^\circ C )</th>
<th>Isoprene content, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>29.57</td>
<td>94.8</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>33.6</td>
<td>72.5</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>&lt;34.15</td>
<td>&lt;93</td>
</tr>
<tr>
<td>Methyl formate</td>
<td>22.5</td>
<td>50</td>
</tr>
<tr>
<td>Bromoethane</td>
<td>32</td>
<td>&gt;65</td>
</tr>
<tr>
<td>Ethanol</td>
<td>32.65</td>
<td>97</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>32.5</td>
<td>65</td>
</tr>
<tr>
<td>Acetone</td>
<td>30.5</td>
<td>80</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>31.6</td>
<td>40</td>
</tr>
<tr>
<td>Ethyl formate</td>
<td>&lt;32.5</td>
<td>&gt;76</td>
</tr>
<tr>
<td>Isopropyl nitrite</td>
<td>33.5</td>
<td>72</td>
</tr>
<tr>
<td>Methylal</td>
<td>32.8</td>
<td>70</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>33.2</td>
<td>52</td>
</tr>
<tr>
<td>Perfluorotritylmethane</td>
<td>30.2</td>
<td>82</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>33.5 – 33.6</td>
<td>97.5</td>
</tr>
<tr>
<td>Isopropylamine</td>
<td>&gt;72.4</td>
<td></td>
</tr>
</tbody>
</table>

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 \( a \) 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].

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 \( a \) 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].
the ground state at 50 °C are in the \textit{s-trans} conformation. Only 15\% of the material has the \textit{s-cis} form, which is higher in energy by 6.3 kJ/mol.

\begin{center}
\begin{tabular}{c c c c c}
\textit{s-cis}-Isoprene & & \textit{s-trans}-Isoprene & & \\
15\% & & 85\% & & \\
\end{tabular}
\end{center}

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 C\textsubscript{5} skeleton:

\begin{align*}
\text{C}_1 + \text{C}_4 & \rightarrow \text{C}_5 \\
\text{C}_2 + \text{C}_3 & \rightarrow \text{C}_5 \\
\text{C}_3 + \text{C}_3 & \rightarrow \text{C}_6 \rightarrow \text{C}_5 + \text{C}_1 \\
\text{C}_4 + \text{C}_4 & \rightarrow \text{C}_8 \rightarrow \text{C}_5 + \text{C}_3 \\
\text{C}_1 + \text{C}_4 & \rightarrow \text{C}_5.
\end{align*}

Isobutene [115-11-7] is the C\textsubscript{4} building block in several syntheses of this type (Fig. 1). The C\textsubscript{1} 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 C\textsubscript{1} 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](image-url)
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 Pétrôle [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-butyralcohol [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-butene-4-ol (7) (Fig. 1, reaction 3) [47]:

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_2\text{C}=\text{C}--\text{CH}_3 + \text{HCHO} \quad 25 \text{MPa}, 280 \text{°C} \\
& \quad \text{H}_2\text{C}=\text{C}--\text{CH}_2--\text{CH}_2\text{OH} \\
& \quad \quad \downarrow \quad \text{H}^+, 100 \text{°C} \\
& \quad \text{CH}_3 \\
& \quad \text{H}_2\text{C}=\text{C}--\text{CH}--\text{CH}_2 + \text{H}_2\text{O}
\end{align*}
\]

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-buten [30], [50], [51]. An alternative route to this C₅ aldehyde is the catalytic hydrogenation of 2-ethylacrolein which is easily prepared from n-butyraldehyde and formaldehyde [52], [62]. Catalytic dehydration of 2-methylbutanal to isoprene has been the subject of numerous studies [53]. A patent issued to Erdolchemie [54] describes the use of a β-phosphate catalyst, which is also discussed in most of the subsequent pub-
Applications 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.

C$_2$ + C$_3$ → 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.

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.

C$_4$ + C$_4$ → C$_8$ → C$_5$ + 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 isopentenes (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 (Cr\(_2\)O\(_3\)/Al\(_2\)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 semicesters 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 (Fe\(_2\)O\(_3\)–K\(_2\)CO\(_3\)–Cr\(_2\)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 C\(_6\)--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.,
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>
<thead>
<tr>
<th>Component</th>
<th>bp at 101.3 kPa, °C</th>
<th>Starting material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Isopentane</td>
<td>27.85</td>
<td>1.99</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>36.07</td>
<td>0.6</td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>31.16</td>
<td>4.95</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>38.57</td>
<td>2.61</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>29.97</td>
<td>24.10</td>
</tr>
<tr>
<td>trans-2-Pentene</td>
<td>36.35</td>
<td>4.74</td>
</tr>
<tr>
<td>cis-2-Pentene</td>
<td>36.94</td>
<td>3.47</td>
</tr>
<tr>
<td>trans-1,3-Pentadiene</td>
<td>42.03</td>
<td>14.32</td>
</tr>
<tr>
<td>cis-1,3-Pentadiene</td>
<td>44.07</td>
<td>8.00</td>
</tr>
<tr>
<td>Isoprene</td>
<td>34.06</td>
<td>6.71</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>42.50</td>
<td>16.46</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>44.24</td>
<td>12.50</td>
</tr>
</tbody>
</table>

Table 2. Composition (in weight percent) of the C₄ fraction from the pyrolysis of hydrocarbons [100] and boiling points of the individual components.

1 Paraffin wax (mp 43.5 °C).
2 Low octave 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) Piperylenes

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Crack severity</th>
<th>Methylbutene dehydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mild</td>
<td>Normal</td>
</tr>
<tr>
<td>Pentanes</td>
<td>26.70</td>
<td>34.36</td>
</tr>
<tr>
<td>n-Pentenes</td>
<td>5.15</td>
<td>6.60</td>
</tr>
<tr>
<td>Methylbutenes</td>
<td>6.95</td>
<td>9.17</td>
</tr>
<tr>
<td>Pentadienes</td>
<td>10.90</td>
<td>9.40</td>
</tr>
<tr>
<td>Isoprene</td>
<td>14.20</td>
<td>18.00</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>4.40</td>
<td>3.30</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(including dimer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other hydrocarbons</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Vol. 20  Isoprene  89
dimerization, see → Cyclopentadiene and Cyclopentene.

Distillative enrichment of isoprene in C₅ 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 C₅ 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 C₅ hydrocarbon mixtures [106]. In contrast to the situation with butadiene (→ 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 C₄ crack fractions (→ 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 C₅ hydrocarbon mixtures) are listed in Table 4. Figure 4 shows the relationship between the overall concentration and the relative volatilities of 2-methyl-2-buten – isoprene mixtures in various solvents; these data are of considerable importance for estimating the size of a proposed production facility. 2-Methyl-2-buten 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 C₅ 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 C₅ cracking fraction. The first step in the separation is a combination of a liquid – liquid extraction with an extractive distillation procedure. The relative volatilities of the hydrocarbons to be separated from isoprene in various solvents, based on [112]

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>bp, °C</th>
<th>Isoprene solvent**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ACN</td>
</tr>
<tr>
<td>Isopentane</td>
<td>27.9</td>
<td>2.92</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>36.1</td>
<td>2.37</td>
</tr>
<tr>
<td>3-Methyl-1-butene</td>
<td>20.1</td>
<td>2.58</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>30.0</td>
<td>1.89</td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>31.2</td>
<td>1.71</td>
</tr>
<tr>
<td>trans-2-Pentene</td>
<td>36.3</td>
<td>1.56</td>
</tr>
<tr>
<td>cis-2-Pentene</td>
<td>36.9</td>
<td>1.49</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>38.1</td>
<td>1.38</td>
</tr>
<tr>
<td>Isoprene</td>
<td>34.1</td>
<td>(1.00)</td>
</tr>
<tr>
<td>trans-1,3-Pentadiene</td>
<td>42.0</td>
<td>0.77</td>
</tr>
<tr>
<td>cis-1,3-Pentadiene</td>
<td>44.2</td>
<td>0.70</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>41.3</td>
<td>0.62</td>
</tr>
<tr>
<td>2-Butyne</td>
<td>26.7</td>
<td>0.96</td>
</tr>
<tr>
<td>3-Methyl-1-butyne</td>
<td>26.3</td>
<td>1.04</td>
</tr>
<tr>
<td>2-Methyl-1-butene-3-yne</td>
<td>32.5</td>
<td>0.62</td>
</tr>
<tr>
<td>1-Pentyne</td>
<td>40.2</td>
<td>0.58</td>
</tr>
<tr>
<td>2-Pentyne</td>
<td>56.1</td>
<td>0.42</td>
</tr>
</tbody>
</table>

1The 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.
2ACN = acetonitrile; DMF = dimethylformamide; NMP = N-methylpyrrolidone; MOPN = β-methoxypropionitrile; DMAC = dimethylacetamide; DMSO = dimethyl sulfoxide; γ-BL = γ-butyrolactone
tillation, an approach particularly suited to C5 fractions with a low isoprene concentration. Preconcentration 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 incorporating columns (c) and (d). Final purification of isoprene to polymerization grade occurs in distillation columns (e) and (f) [115]. C5 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 (→ 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 C5 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 4](image1.png)

**Figure 4.** Relationship between the total concentration and the relative volatilities $a_r$ 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

![Figure 5](image2.png)

**Figure 5.** Recovery of isoprene from C5 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

---

<table>
<thead>
<tr>
<th>Vapor phase</th>
<th>Liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentanes, pentenes</td>
<td>Piperylenes, cyclopentadiene</td>
</tr>
<tr>
<td>C5-Mixture</td>
<td>2-Butyne</td>
</tr>
<tr>
<td>H2O</td>
<td>H2O</td>
</tr>
<tr>
<td>j</td>
<td>j</td>
</tr>
<tr>
<td>a</td>
<td>j</td>
</tr>
<tr>
<td>j</td>
<td>j</td>
</tr>
<tr>
<td>b</td>
<td>j</td>
</tr>
<tr>
<td>c</td>
<td>j</td>
</tr>
<tr>
<td>d</td>
<td>j</td>
</tr>
<tr>
<td>e</td>
<td>j</td>
</tr>
<tr>
<td>f</td>
<td>j</td>
</tr>
<tr>
<td>g</td>
<td>j</td>
</tr>
<tr>
<td>h</td>
<td>j</td>
</tr>
<tr>
<td>i</td>
<td>j</td>
</tr>
<tr>
<td>j</td>
<td>j</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Cyclopentene</td>
</tr>
</tbody>
</table>
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]

<table>
<thead>
<tr>
<th>Component</th>
<th>Technical-grade isoprene</th>
<th>Isoprene for IIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene, wt %</td>
<td>99</td>
<td>&gt;92</td>
</tr>
<tr>
<td>Monoolefins, wt %</td>
<td>1</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Cyclopentadiene, ppm</td>
<td>0.05</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Peroxides (as H2O2), ppm</td>
<td>100</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Carbonyl compounds (as acetone), ppm</td>
<td>150</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Sulfur (as H2S), ppm</td>
<td>5</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Distillation residue, wt %</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
</tr>
</tbody>
</table>

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
titanium type) that closely resembles natural rubber in both structure and properties (→ Rubber, 5. Solution Rubbers). This IR is largely used for the production of vehicle tires (→ Tires). By contrast, poly(trans-1,4-isoprene) has the properties of guttapercha or balata, and has found no major commercial application. Most of the trans polymer is limited to the manufacture of cable insulation and golf balls [124, p. 499], [126].

The second largest market for isoprene is the manufacture of styrene – isoprene – styrene (SIS) block copolymers (→ Thermoplastic Elastomers) [119], [120, p. 837], [124, p. 532], [127]; 0.79 – 0.88 t of isoprene are required per tonne of polymer. These products are especially useful as thermoplastic rubbers and as pressure-sensitive or thermosetting adhesives.

Smaller amounts of isoprene are used in the production of butyl rubber (isobutene – isoprene rubber, IIR), a copolymerize with isobutene (→ Rubber, 5. Solution Rubbers) [128]. The isoprene content of butyl rubber is 0.5 – 3.0 mol%. The distinctive features of IIR include its low gas permeability, leading to its use in the construction of hoses and as a liner in tubeless tires.

Finally, mention should also be made of the hydrocarbon resins (petroleum resins), which result from the copolymerization of isoprene from cyclopentadiene-free C₅ crack fractions with other unsaturated C₅ compounds (→ Resins, Synthetic) [129].

6.2. Terpene Synthesis

The chemical reactions of isoprene are very varied [19], but they have limited industrial significance. Only terpene synthesis is important and is the subject of intensive investigation.

C₅ + C₃ + C₂ Routes. In 1972, Rhodia Incorporated (United States) began to develop a route for the industrial synthesis of C₁₀ terpenes and their derivatives from isoprene (C₅), acetone (C₃), and acetylene (C₂) (Fig. 6). The isoprene is first reacted with hydrochloric acid to give prenylv
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 (→ 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-diethylnerlamine [40137-00-6] [149]; this telomerization reaction is catalyzed by butyl lithium. N,N-Diethylnerlamine 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-diethylnerlamine 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
accounted for by piperlenes. 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 isoprene 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 7. Synthesis of terpenes from isoprene via nerylamine
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

<table>
<thead>
<tr>
<th>Country</th>
<th>Company</th>
<th>Location</th>
<th>Capacity as 100 wt % isoprene, t/a</th>
<th>Product</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>Goodyear</td>
<td>Beaumont, Texas</td>
<td>84 000</td>
<td>P</td>
<td>refining of isoprene concentrate (extractive distillation?)</td>
</tr>
<tr>
<td>Arco Lyondell</td>
<td>Channelview, Texas</td>
<td>36 000</td>
<td>C</td>
<td></td>
<td>extractive distillation (ACN) of C₅ fractions</td>
</tr>
<tr>
<td>Chevron</td>
<td>Cedar Bayou, Texas</td>
<td>9 000</td>
<td>C</td>
<td></td>
<td>extractive distillation (?)</td>
</tr>
<tr>
<td>Dow</td>
<td>Freeport, Texas</td>
<td>16 000</td>
<td>C</td>
<td></td>
<td>extractive distillation (?)</td>
</tr>
<tr>
<td>Exxon</td>
<td>Baton Rouge, Louisiana</td>
<td>14 000</td>
<td>C</td>
<td></td>
<td>extractive distillation (ACN) of C₅ fractions</td>
</tr>
<tr>
<td>Baytown, Texas</td>
<td>14 000</td>
<td>C</td>
<td>extractive distillation (ACN) of C₅ fractions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell</td>
<td>Dear Park, Texas</td>
<td>40 000</td>
<td>C</td>
<td></td>
<td>extractive distillation (ACN) of C₅ fractions</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Shell</td>
<td>Pernis</td>
<td>25 000</td>
<td>C</td>
<td>extractive distillation (ACN) of C₅ fractions</td>
</tr>
<tr>
<td>Republic of South Africa</td>
<td>Sentruchem</td>
<td>New Castle/ Natal</td>
<td>45 000</td>
<td>P</td>
<td>synthesis from acetone and acetylene, plant not yet on line</td>
</tr>
<tr>
<td>Japan</td>
<td>Nippon Zeon</td>
<td>Mizushima</td>
<td>45 000</td>
<td>P</td>
<td>extractive distillation (DMF) of C₅ fractions</td>
</tr>
<tr>
<td>Japan Synthetic Rubber</td>
<td>Kashima</td>
<td>30 000</td>
<td>P</td>
<td></td>
<td>extractive distillation (ACN) of C₅ fractions</td>
</tr>
<tr>
<td>Kuraray</td>
<td>Kashima</td>
<td>30 000</td>
<td>P</td>
<td></td>
<td>synthesis from isobutene and formaldehyde</td>
</tr>
<tr>
<td>former Soviet Union</td>
<td>several locations</td>
<td>ca. 800 000</td>
<td>C</td>
<td></td>
<td>dehydrogenation of isopentane extractive distillation of C₅ fractions synthesis from isobutene + formaldehyde</td>
</tr>
<tr>
<td>Standby Capacities</td>
<td>Shell</td>
<td>Port Neches, Texas</td>
<td>45 000</td>
<td>P</td>
<td>dehydrogenation of isopentene (plant bought from BF Goodrich in 1982 and modified for production of pure isoprene)</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Shell</td>
<td>Pernis</td>
<td>50 000</td>
<td>C</td>
<td>dehydrogenation of isopentene synthesis from acetone and acetylene</td>
</tr>
<tr>
<td>Italy</td>
<td>Enichem (ANIC)</td>
<td>Ravena</td>
<td>30 000</td>
<td>P</td>
<td>dehydrogenation of isopentene synthesis from acetone and acetylene</td>
</tr>
</tbody>
</table>

* Capacities in 1987.
* C = concentrate; P = pure isoprene.
* ACN = acetonitrile; DMF = dimethylformamide.
threshold concentration for irritative effects in cats is reported as 800 mg/m³. An oral LD₅₀ of 2100 mg liquid isoprene per kilogram of body weight and an intraperitoneal LD₅₀ 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, hematol-ogy, 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 monoepox-ides 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>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IR capacity</td>
<td>281</td>
<td>289</td>
<td>289</td>
<td>397</td>
<td>289</td>
<td>285</td>
<td>255</td>
<td>225</td>
<td>220</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>IR production</td>
<td>242</td>
<td>219</td>
<td>168</td>
<td>129</td>
<td>120</td>
<td>146</td>
<td>110</td>
<td>132</td>
<td>113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR capacity</td>
<td>493</td>
<td>498</td>
<td>446</td>
<td>533</td>
<td>539</td>
<td>583</td>
<td>580</td>
<td>583</td>
<td>585</td>
<td>607</td>
<td>615</td>
</tr>
<tr>
<td>IR production</td>
<td>457</td>
<td>395</td>
<td>426</td>
<td>370</td>
<td>372</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic rubber capacity</td>
<td>7975</td>
<td>8114</td>
<td>8379</td>
<td>8878</td>
<td>8944</td>
<td>8710</td>
<td>8639</td>
<td>8772</td>
<td>8730</td>
<td>8844</td>
<td>9108</td>
</tr>
<tr>
<td>Synthetic rubber production</td>
<td>5830</td>
<td>6167</td>
<td>5347</td>
<td>5281</td>
<td>4623</td>
<td>4854</td>
<td>5397</td>
<td>5211</td>
<td>5486</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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 μmol h⁻¹ kg⁻¹ and 1.9 μmol h⁻¹ 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/m³ has been set in the former Soviet Union.

References
5 L. Ruzicka, Experientia 9 (1953) 357.
8 F. Hofmann, Chem. Ztg. 60 (1936) 693.
10 Firestone Tire and Rubber Comp., US 3 208 988, 1955 (L. E. Forman et al.).
18 Sadler Research Laboratories: Nuclear Magnetic Resonance Spectra, Spectrum no. 3434 M.
21 Landolt – Börnstein, NS IV/3, 1975, 367.
30 D. Forster, J. P. Sluka, A. Vavere, CHEMTECH 16 (1986) no. 12, 746.
31 I.G. Farbenind., DE 741 152, 1938 (W. Friedrichsen).
42 Sumitomo Chem., DE-OS 1 816 739, 1968 (Y. Watanabe et al.).
43 Sumitomo Chem., DE-OS 1 941 949, 1969 (Y. Watanabe et al.).
66 Bayer, DE 246 241, 1910.
72 *Oil Gas J.* **69** (1971) no. 16, 17.
86 *Hydrocarbon Process.* **52** (1973) no. 11, 140.
98 Halcon, DE-AS 1 568 746, 1966 (J. Kollar).


142 Nissan Chem. Ind., DE-OS 2 542 798, 1974 (K. Takabe et al.).


150 Nissan Chem. Ind., DE-OS 2 634 309, 1975 (J. Tanaka et al.).

151 Nissan Chem. Ind., DE-OS 2 720 839, 1976 (A. Murata et al.).


Vol. 20

Further Reading
