Dimethyl Ether

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1. Introduction

Dimethyl ether [*115-10-6*], C_2H_6O, is the simplest aliphatic ether.

CH_3 —O —CH_3

For a long time it was obtained on an industrial scale as a byproduct in the high-pressure production of methanol. Recently the high-pressure methanol plants have been almost completely replaced by low-pressure plants; this has led to the erection of special plants for the synthesis of dimethyl ether. The production of dimethyl ether in Western Europe is approx. 50 000 t per year. Dimethyl ether is industrially important as the starting material in the production of the methylating agent dimethyl sulfate and is used as an aerosol propellant.

2. Properties

Dimethyl ether (DME, methoxymethane), M_r 46.07, is a colorless, almost odorless gas at room temperature and atmospheric pressure and has the following physical properties:

M_r	46.07
bp at 0.1 MPa	− 24.8 °C
mp	− 141 °C
Critical pressure	5.28 MPa (52.84 bar) [1]
Critical temperature	400.29 K [1] (127.1 °C)
Critical density	269.9 kg/m^3 [1]
Heat of combustion (gas)	31.75 MJ/kg
Heat of formation	−183 kJ/mol
Specific heat capacity (at −24 °C)	2.26 kJ kg^{-1} K^{-1}
Heat of vaporization (at −20 °C)	410.2 kJ/kg
Autoignition temperature	235 °C [2]
Explosive limits	3.0 – 17 vol % in air
Flash point	− 41 °C
Relative density (gaseous, air = 1)	1.59
Density	
(at 20 °C)	668.3 kg/m^3 [2]
(at 50 °C)	615.0 kg/m^3 [2]
Solubility in water	
(at 20 °C, 1 bar)	5.7 wt % [2]
(at 20 °C, 4.8 bar)	36 wt % [2]
Surface tension (liquid)	0.0125 N/m [2]
Viscosity	
gaseous	0.0091 mPa · s [2]
liquid	0.11 mPa · s

Density of liquid dimethyl ether [2]:

t, °C	10	20	30	40	50	60	70	80
ϱ, kg/m^3	682	666	649	631	612	593	573	552

Vapor pressure [2]:

t, °C	−20	−10	0	10	20	50
p, MPa						
measured	0.124	0.184	0.266	0.375	0.512	1.149
calculated	0.114	0.185	0.267	0.374	0.512	1.152

Dimethyl ether is miscible with most polar and nonpolar organic solvents. It is also partly miscible with water (76 g in 1 L of water at

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18 °C). In addition, numerous polar and nonpolar substances readily dissolve in dimethyl ether.

Chemical Properties. Unlike most other aliphatic ethers, dimethyl ether is not susceptible to autoxidation. This is of considerable importance for industrial applications. Numerous studies have confirmed that dimethyl ether is stable to atmospheric oxygen and does not form peroxides [3].

Dimethyl ether is converted to dimethyl sulfate [*77-78-1*] by sulfur trioxide (→ Dialkyl Sulfates and Alkylsulfuric Acids).

$$SO_3 + CH_3\text{—}O\text{—}CH_3 \rightarrow (CH_3)_2SO_4$$

Addition of boron trifluoride to dimethyl ether results in the formation of $BF_3 \cdot CH_3OCH_3$ [*353-42-4*], *mp* −14 °C, *bp* 127 °C, a distillable liquid which fumes when exposed to moist air. This addition compound is easier to handle than gaseous boron trifluoride.

In the presence of CoI_2, dimethyl ether reacts with carbon monoxide and water to form acetic acid [*64-19-7*] (→ Acetic Acid, Section 4.1.) [4].

$$CH_3\text{—}O\text{—}CH_3 + H_2O + 2\,CO \rightarrow 2\,CH_3COOH$$

The reaction of dimethyl ether with hydrogen sulfide in the presence of a catalyst, e.g., tungsten sulfide (WS_2), gives dimethyl sulfide [*75-18-3*] [5].

$$CH_3\text{—}O\text{—}CH_3 + H_2S \rightarrow CH_3\text{—}S\text{—}CH_3 + H_2O$$

The reaction of dimethyl ether to give unsaturated and saturated hydrocarbons proceeds in the presence of zeolitic catalysts [6].

$$CH_3\text{—}O\text{—}CH_3 \rightarrow H_2C{=}CH_2 + H_2O$$

The catalytic conversion of dimethyl ether to formaldehyde has also been observed [7].

$$CH_3\text{—}O\text{—}CH_3 + O_2 \rightarrow 2\,CH_2O + H_2O$$

3. Production

Until about 1975 dimethyl ether was obtained as a byproduct in the high-pressure production of methanol [8]. In this process up to 3 – 5 wt % dimethyl ether is formed. Dimethyl ether can be recovered in pure form by distillation of crude methanol. The development of the low-pressure methanol synthesis, particularly by Lurgi [9] and ICI [10], has resulted in the almost complete replacement of all high-pressure plants by 1980. The low-pressure processes, which require less severe conditions, produce only very small amounts of dimethyl ether (→ Methanol). As a result, special catalytic processes have been developed for the production of dimethyl ether.

The preparation of dimethyl ether from methanol in the presence of acidic catalysts on a laboratory scale has been known for many years [11]. Numerous methods have been discussed in the patent literature. For instance, aliphatic ethers can be prepared by heating alcohols in the presence of zinc chloride [12]. Other suitable catalysts are iron chloride, copper sulfate, copper chloride, manganese chloride, aluminum chloride, aluminum sulfate, chromium sulfate, alums, thorium compounds, aluminum oxide, titanium oxide, barium oxide, silica gel, and aluminum phosphate [13]. Aluminum oxide and aluminum silicate, with or without doping, are the most important catalysts for industrial use [14]. Figure 1 illustrates the process developed by Union Rheinische Braunkohlen Kraftstoff AG (now DEA Mineraloel AG, Wesseling) for the production of high-purity dimethyl ether (purity > 99.99). This quality is virtually odorless.

The catalytic dehydration of pure, gaseous methanol is carried out in a pipe reactor. The product is cooled in two stages and subsequently distilled to yield pure dimethyl ether. Small amounts of dimethyl ether are recovered from the off-gas in a scrubber and recycled to the reactor. Unreacted methanol is separated from water in a second column and also recycled.

Very pure dimethyl ether which is suitable as an aerosol propellant is obtained by special rectification processes.

Direct synthesis of dimethyl ether from synthesis gas ($CO + H_2$) has also been described [15].

Safety and Environmental Aspects. Dimethyl ether is a flammable gas. Water, foam, carbon dioxide, and dry chemical powders can be employed to control dimethyl ether fires. Fire extinguishers suitable for class C (Europe) or class B (United States) can be used. Endangered vessels must be cooled.

Although dimethyl ether is soluble in water and biologically easily degradable, large

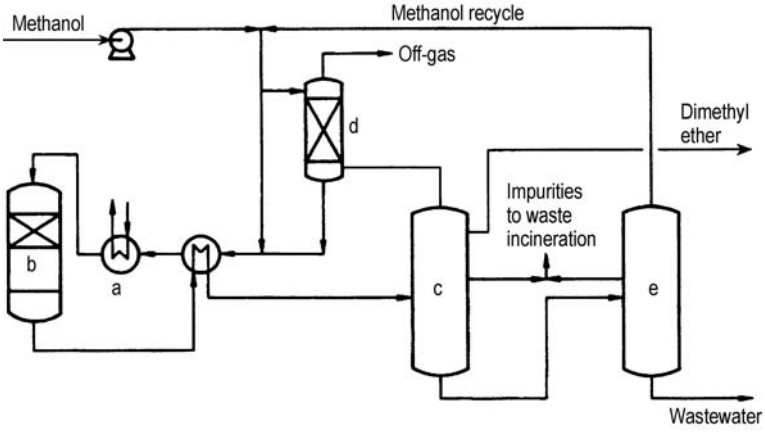

Figure 1. Dimethyl ether production by dehydration of methanol
a) Vaporizer; b) Reactor; c) Dimethyl ether column; d) Scrubber; e) Methanol column

amounts of this compound should not enter the wastewater system because evaporation can cause the formation of explosive mixtures over the surface of the water.

Available data do not indicate a danger for the environment [2].

Quality Specifications and Analysis. Dimethyl ether is available in two commercial qualities:

- Technical grade contains up to 0.05 % methanol and contaminations with a strong odor.
- High-purity dimethyl ether, practically free of sulfur-containing and other substances with an unpleasant odor, can be used in the aerosol industry; the methanol content should not exceed 10 mg/kg for this quality.

The purity of dimethyl ether is determined by GC analysis. Oil and ash content are measured by special methods of evaporation and combustion.

Storage and Transportation. Dimethyl ether is usually stored as a liquid under pressure. It is transported in railway pressure tanks, tank trucks, and other pressure containers. Overseas transport is carried out in ISO tankers (International Shipping Organization).

Transportation is subject to the following regulations: GGVS/ADR GGVE/RID class 2, no. 2 F; ADN/ADNR class 2, no. 2 F; UN no. 1033; IMDG Code (Amendment 20–82), class 2.1, p. 2052.

Suppliers are DEA Mineraloel AG in Germany, Akzo Nobel Chemicals B.V. in the Netherlands, and DuPont & Nemours in Switzerland.

4. Uses

Up to the 1980s, the main industrial use for dimethyl ether was its conversion to dimethyl sulfate by treatment with sulfur trioxide. Dimethyl sulfate is used as a methylating agent. Of the 50 000 t of dimethyl ether produced in Western Europe in 1998, about 15 000 t was used in the production of dimethyl sulfate. The remaining 35 000 t of DME were used in the aerosol industry as a propellant. Owing to its high solubility coefficient, it also acts as a solvent in aerosol formulations. This property is of particular value in aerosol formulations which contain substances that are difficult to dissolve.

The reaction of dimethyl ether with carbon monoxide and water can be used in large-scale production of acetic acid instead of the methanol – carbon monoxide reaction. Future industrial uses of dimethyl ether could include the production of olefins, especially ethylene, propene, and butenes in the presence of zeolitic catalysts.

DME is also considered an alternative fuel for diesel engines (compression ignition) [16]:

- It has a low autoignition temperature
- It is an oxygenated fuel, and as a gas it helps establishing a good air – fuel mixture and consequently prevents soot formation
- It enables NO_x reduction.

5. Toxicology

Pure dimethyl ether is nontoxic. Inhalation experiments conducted on rats using concentrations of up to 20 000 ppm (2 vol % in air) over a period of 8 months did not lead to any deaths [3]. Contact with dimethyl ether is not irritating to the skin.

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