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The Infrared Spectrum of 1,2-Butylene Oxide

An Azeotropic System (1,2-Butylene Oxide/Chloroform) with a Maximum Boiling Point

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Pure 1,2-butylene oxide has been obtained by fractional distillation of a mixture rich in isomeric butylene oxides. The infrared spectrum of the pure substance is recorded. 1,2-butylene oxide forms with chloroform an azeotrope with a maximum boiling point of 69.0° C at atmospheric pressure. The azeotrope contains 39.4 % by weight of the oxide.

In connection with an investigation of impurities in raw technical ethylene chloride obtained as a by-product during the manufacture of ethylene oxide by the ethylene chlorohydrin process, it was found that 1,2-butylene oxide forms with chloroform an azeotropic system with a maximum boiling point. This azeotrope does not seem to have been described in literature before.

EXPERIMENTAL

Distillation apparatus. A Podbielniak Hyper-Cal apparatus, Cat. No. HC-701-A, Series "D", has been used for all distillations. Butylene oxide or mixtures of this and other substances have been fractionated in a 25 mm I. D. × 72″ long Heli-Grid packed column. The chloroform was distilled in the same kind of column which in this case was only 36″ long. The distillation temperature was measured with an iron-constantan thermocouple which was calibrated against a standardized thermometer.

Analysis. Butylene oxides were analysed by a method given by Swern *et al.*[1] using the reaction of epoxides with hydrochloric acid in absolute ethyl ether.

1,2-Butylene oxide. In order to obtain this substance in a pure form, a fraction was used which had been enriched in butylene oxides during a technical distillation of raw ethylene chloride which contained butylene oxides as impurities. The mixture was fractionated in the above mentioned apparatus with a reflux ratio of 100:1. When the distillation temperature reached the boiling point of ethylene chloride, the distillation was stopped. The distillate was redistilled with a reflux ratio of 200:1. Three main fractions were obtained in the second distillation.

The first one had a boiling point of 54° C at atmospheric pressure, which is close to the value 53.5° C that Winstein and Lucas [2] found for *trans*-2,3-butylene oxide. The identi-

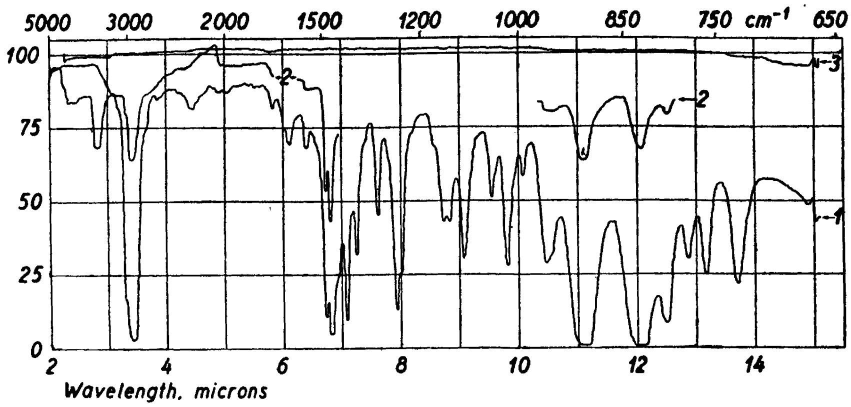

Fig. 1. Infrared spectrum of 1,2-butylene oxide. Phase: Liquid. Thickness: 1 = 0.05 mm; 2 = cap. Prism: NaCl. Resolution: 895. Response: 1. Gain: 6. Speed 2. Suppression: 1; 3 = Example of compensation with the same adjustments. Ordinate: Transmittance (% Transmission).

fication was confirmed by recording the infrared spectrum of the fraction and comparing this with the spectrum of *trans*-2,3-butylene oxide published by Patterson [3].

The second fraction boiled at 58—60° C, indicating that it consists of *cis*-2,3-butylene oxide since, according to Winstein and Lucas [2], the boiling point of this compound is 59.7 ° C. The identification was also in this case confirmed when the infrared spectrum was found to be identical with the one published by Patterson [3].

The third main fraction boiled at 65° C and ought to consist of 1,2-butylene oxide. Analysis of this fraction gave 99.8 (99.6, 99.8, 100.1) % butylene oxide. Its infrared spectrum (Fig. 1) shows that it does not contain any *cis*- or *trans*-2,3-butylene-oxide.

In order to confirm that it really was 1,2-butylene oxide, this substance was synthetized from ethyl bromide and monochloro acetaldehyde by a method used by Andersson [4]:

$$C_2H_5MgBr + OHC \cdot CH_2Cl \rightarrow C_2H_5CH(OH)CH_2CL \xrightarrow{OH^-} C_2H_5\underset{\diagdown O \diagup}{CH \cdot CH_2}$$

The yield in our synthesis was poor but enough product was obtained to record its infrared spectrum. Although the oxide obtained contained some impurities it was obvious that it was identical with the fraction boiling at 65° C. Therefore the third fraction with the boiling point 65° C was used as pure 1,2-butylene oxide in the experiments with the azeotrope.

Chloroform. Pure chloroform was obtained by distilling a pharmaceutical product in the Podbielniak apparatus with a reflux ratio of 200:1.

THE AZEOTROPE

A mixture of 41 % pure 1,2-butylene oxide and 59 % pure chloroform was distilled in the above mentioned distillation apparatus with a reflux ratio of 200 : 1. The distilling temperature soon reached 69° and remained constant at this point during the distillation. A sample was taken in the middle of the fraction for analysis and exact boiling point determination.

The azeotrope contained 39.4 (39.4, 39.4) % by weight of 1,2-butylene oxide.

The boiling point was determined by boiling the azeotrope slowly under reflux in a Claisen flask and the temperature was read on a standardized thermometer graduated to 0.1° C. At 769 mm Hg the boiling point was 69.0° C.

In the same way the boiling points of the pure 1,2-butylene oxide and chloroform was found to be 63.2 and 61.2° C, respectively, at 763 mm Hg. The boiling point of chloroform at atmospheric pressure is given [5] as 61.2° C and that of 1,2-butylene oxide [6] as 63.7° C at 767 mm Hg.

The infrared spectrum of the pure 1,2-butylene oxide was recorded on a Perkin-Elmer Model 21 Double Beam Infrared Spectrometer at Uppsala University *. The positions of the strongest absorption maxima are 3.39, 6.72, 6.80, 7.07, 7.93, 11.08, 12.06 μ. The wave lengths of the absorption maxima were determined by calibration against the spectrum of polystyrene [7].

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