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QUALITATIVE ESTIMATION OF THE COMPOSITION OF BUTENE MIXTURES BY DISTILLATION METHODS¹

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Introduction

This paper describes some of the preliminary work done in studying methods for the analysis of the normal butenes, as follows: separation of dibromobutanes by fractional distillation at 50 mm.; separation of butenes by fractional distillation at atmospheric pressure; the reaction of 1-butene with hydrogen bromide.

Preparation of Dibromobutanes

Materials.—Eastman's 1-butanol No. 50, b. p. 116–118°, was slowly distilled through a 75 × 3 cm. fractionating column of cut-glass rings. The reflux ratio was ten to one. The fraction between 117.2 and 117.4° at 746.6 mm., which constituted about 85% of the whole, was collected. The 2-butanol⁴ was similarly distilled and the fraction distilling at 98.8–99.0° at 745.3 mm. was used. This had a refractive index n_D^{20} 1.3976, in satisfactory agreement with 1.397.⁵ Merck's bromine was shaken with a solution of potassium bromide and distilled from concentrated sulfuric acid.

The aluminum oxide catalyst was prepared by precipitating aluminum hydroxide from a 5% solution of aluminum nitrate by the addition of dilute ammonium hydroxide. The precipitate was filtered off with suction, the solid was thoroughly agitated with a volume of water half that of the original solution and filtered again. The process was repeated. The final product was dried at 110–115° and broken into small pieces, the maximum dimensions being about 5 mm. This material was placed in the reaction tube and heated to 320–360° for four hours while air was drawn through. Some water was given off. The catalyst was now ready for use.

Decomposition of the Alcohols.—The alcohols were decomposed in the apparatus shown in Fig. 1. The alcohol, as it dropped from the graduated container into the heated tube, was volatilized and passed into a pyrex tube, 2.5 × 80 cm. The first half served as a preheater and the second half contained the aluminum oxide catalyst packed for a length of 25 cm. As the gas entered the reaction zone from the preheater the temperature was 205° for the 1-butanol and 250° for the 2-butanol, while the catalyst was maintained at 330–340° for the first, and 310–320° for the second alcohol. The average rates

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⁴ We have been aided in this research by the Stanco Distributors, Inc., New York, who through the courtesy of Mr. C. L. Bowman have kindly supplied us with pure 2-butanol.

⁵ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I.

of flow were 35 g. and 25 g. per hour, respectively. The butene was cooled first in the condenser, then in the ice trap in order to condense water and unchanged alcohol, and then, after bubbling through 23% perchloric acid and drying with calcium chloride, passed into the all-glass reaction flask maintained at -15 to -20° and so arranged that it could be easily shaken. Except at the beginning and at the very end of the experiment butene was always in excess, the bromine being added slowly and at intervals. The possibility of substitution taking place with the production of tribromobutanes and

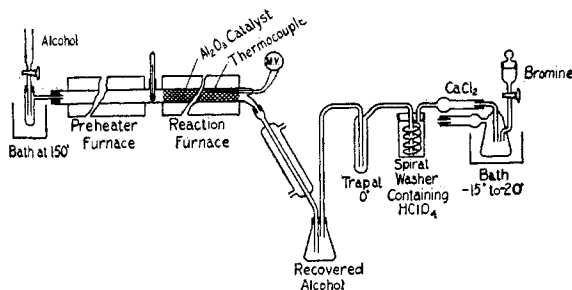


Fig. 1.—Apparatus used in the decomposition of the butanols over aluminum oxide.

monobromobutane was small. The resulting dibromobutane was shaken once each with cold water and dilute sodium sulfite solution, then twice with water and dried over calcium chloride. The yield was 85% on the alcohol reacted (corrected for that recovered) and 99% on the bromine.

Fractional Distillation of the Dibromobutanes.—The dibromobutane mixtures were fractionally distilled at 50-mm. pressure in the apparatus shown in Fig. 2. The material was placed in the flask B and when heated by the electric heater A boiled in a satisfactory manner without much bumping. (Pieces of scrap platinum or of anhydrous

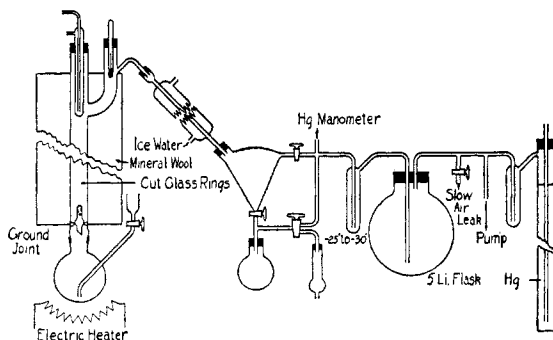


Fig. 2.—Apparatus used for fractionally distilling dibromobutanes at 50 mm. pressure.

calcium chloride were found to be an aid.) The flask was attached by means of a ground-glass joint to the fractionating tube, 2×95 cm., containing a 70-cm. column of cut-glass rings and provided with a reflux condenser at the top. In lieu of a vacuum jacket, the tube was surrounded for a length of 70 cm. with a 5-cm. layer of mineral wool⁶ packed in

⁶ Supplied by the Mineral Wool Products Co., Torrance, Calif. This material has a lower heat conductivity than 85% magnesia, ground cork or pure wool, and gave satisfactory insulation.

a stove pipe. The cuts were made in the usual manner and the fractions were introduced into the distilling flask at the proper time through the side arm. The pressure was maintained at 50 mm. by a regulating device similar to that used by Schofield,⁷ except that the greater part of the entering air came through a slowly leaking stopcock instead of through the mercury regulator. This gave a more uniform pressure. Fifty mm. was selected as the working pressure in order to have a satisfactory distilling temperature and one where decomposition and isomeric change would be negligible, since in the distillation at atmospheric pressure, hydrogen bromide is often evolved while on heating to higher temperatures isomeric change has been noted.⁸

Of the dibromides, 400 g. from 1-butanol and 480 g. from 2-butanol were systematically fractionated by six distillations. A comparison of the properties of the fractions with those of the pure dibromides, which were distilled in the same apparatus, and a consideration of the distribution of material in the various fractions shows that the separation was not complete. The densities, d_4^{20} , of the 80.5–81.0° fraction in the first experiment and of the 79.0–80.2° fraction in the second were both 1.7938, whereas that of pure 1,2-dibromobutane, b. p. 80.5–80.7° at 50.0 mm., is 1.7951. The incompleteness of the separation was also proved by the analysis of the largest (5th) fraction in the second experiment by the method subsequently developed,⁹ which instead of pure higher boiling 2,3-dibromobutane showed 2.0% of 1,2-dibromobutane, 74.7% of higher boiling and 23.2% of lower boiling 2,3-dibromobutane. The separation, however, appears to be as good as or better than that obtained by Lépingle after ten distillations of a similar product.¹⁰ These materials were used for preliminary work on reaction rates.

Butene from 2-Bromobutane

Preparation.—Butene was obtained in 85% yield from the action of 400 g. of potassium hydroxide in 600 g. of 95% ethanol upon 305 g. (2.23 moles) of 2-bromobutane, b. p., 89.8–89.9°, prepared from 2-butanol and 48% hydrobromic acid. The butene was generated in a suitable flask heated in an oil-bath at 128°, washed with 30% methanol and pure water in two scrubbing towers, passed through one tower of soda lime and three towers of anhydrous calcium chloride and collected in tubes immersed in ice–hydrochloric acid mixture. The tubes were sealed off.

Distillation of the Butene Mixture.—The mixed butenes resulting from the decomposition were fractionally distilled through a 60-cm. column of cut-glass rings kept cold by the circulation of ice–hydrochloric mixture at –10 to –15° through an outer jacket and provided at the top with a reflux condenser cooled with brine at –14 to –18° for the purpose of insuring a rapid run-back of liquid, Fig. 3. This is the same

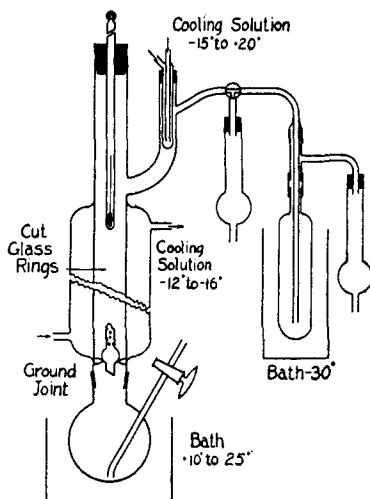


Fig. 3.—Apparatus used for fractionally distilling butenes at atmospheric pressure.

⁷ Schofield, *Ind. Eng. Chem.*, **18**, 717 (1926).

⁸ Favorsky, *Ann.*, **354**, 370 (1907).

⁹ Dillon, Young and Lucas, *THIS JOURNAL*, **52**, 1953 (1930).

¹⁰ Lépingle, *Bull. soc. chim.*, **39**, 741 (1926).

apparatus as that used in the final distillation of the isomeric 2-butenes.¹¹ Cuts were made at intervals of 0.5 and 1.0°, the latter where the temperature increased the more rapidly, for example between -5.5 and +0.5°. The butene was sealed off in the tubes in which it was collected and when needed was transferred to the distilling flask through the side arm, usually without material loss. Occasionally a part or all of the butene was lost. After four distillations the 1-butene, b. p. -6.7 to -6.5°, was fairly well separated, and apparently constituted 15 to 20% of the total. However, there was very little separation of the isomeric 2-butenes, b. p. 0.3 and 3.0°, respectively, the temperature rising gradually from 0 to 2°. The separation of any considerable quantity of a pure 2-butene from its stereoisomer by fractional distillation would appear to be impractical. Coffin and Maass¹² collected a fraction of 2-butene, free from 1-butene, over the temperature range of 1.5-1.7° for their physical measurement work. It is evident that their product was a mixture of the stereoisomeric forms.

Hydrogen Bromide and 1-Butene

Materials.—The 1-butene was synthesized from allyl bromide and methyl magnesium iodide,¹³ the fraction used distilling at -6.6 to -6.4° in the apparatus described above (yield was 68%). The 1-bromobutane and 2-bromobutane, on which densities and refractive indices were taken, were prepared in amounts of 215 g. and 180 g. by the action of 48% hydrobromic acid upon pure specimens of the respective alcohols. After careful washing and drying, the bromides on distillation gave fractions of 170 g. and 160 g., respectively, at constant temperatures of 101.5 and 89.8°.

Procedure.—22.4 g. (0.40 mole) of 1-butene was distilled into a solution of 41.0 g. (0.51 mole) of hydrogen bromide in 50 g. of glacial acetic acid at -18 to -20°. The tube containing the mixture was sealed off and left in the ice box at 5° for three days. The tube was opened, the contents poured into ice water, the bromide layer separated and washed in succession with dilute sodium bisulfite, water, cold concentrated sulfuric acid, water, dilute sodium bicarbonate and water. The yield was 63%. The product, after drying over anhydrous potassium carbonate, was distilled, 80% coming over at 90.0-90.2° and 95% up to 90.4°. By taking refractive indices on different fractions it was shown that the 3% fraction, 90.4-91.0°, was practically identical with the rest. A comparison of the refractive indices and densities of pure 1-bromobutane, pure 2-bromobutane and of the reaction product, Table I, shows the latter to be 2-bromobutane containing not more than 3% of 1-bromobutane. The reaction of 1-butene with hydrogen bromide is therefore of no use as a means of analyzing a mixture of 1- and 2-butene since they both yield the same product.

TABLE I
PHYSICAL PROPERTIES OF BROMOBUTANES

	B. p., °C. (corr.)	Pressure mm.	Density <i>in vacuo</i>		Refractive index n_D^{20}
			d_4^{20}	d_4^{25}	
1-Bromobutane	101.5	744	1.2756	1.2686	1.4403
2-Bromobutane	89.8	744	1.2607	1.2534	1.4374
Reaction product	90.0-90.2	...	1.2609	1.4374

The densities were taken in a 10-ml. pycnometer and are corrected to vacuum.¹⁴ The refractive indices were taken with an Abbé refractometer, standardized at the time.

¹¹ Young, Dillon and Lucas, *THIS JOURNAL*, 51, 2528 (1929).

¹² Coffin and Maass, *ibid.*, 50, 1427 (1928).

¹³ Lucas and Dillon, *ibid.*, 50, 1460 (1928).

¹⁴ Reilly, Rae and Wheeler, "Physical-Chemical Methods," D. Van Nostrand Co., New York, 1925, p. 322.

Summary

The dehydration of 1-butanol and 2-butanol over aluminum oxide at 300–350° gave butenes which were converted to the bromides. By means of fractional distillation at 50 mm. the three component dibromobutanes were separated from one another but not in a pure state. The approximate compositions of the butene mixtures were 68% 1-butene, 12% 2-butene, b. p. 0.3° and 20% 2-butene, b. p. 3.0° from 1-butanol and 26, 26 and 48%, respectively, from 2-butanol.

The butene mixture obtained from 2-bromobutane was partially separated by fractional distillation. It contained 15–20% of 1-butene, the balance consisting of a mixture of the isomeric 2-butenes.

When hydrogen bromide in glacial acetic acid reacted with 1-butene, the product was practically pure 2-bromobutane.

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THE REACTION RATES OF POTASSIUM IODIDE WITH 1,2- AND 2,3-DIBROMOBUTANE. THE ANALYSIS OF MIXTURES OF THE NORMAL BUTENES¹

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The butenes are the simplest unsaturated hydrocarbons which exist in isomeric as well as stereoisomeric forms, *viz.*, 1-butene, *cis*-2-butene, *trans*-2-butene and isobutene. The variety of isomeric changes which they might conceivably undergo in passing from one form to another would include: (1) stereoisomeric change, for example, *cis*- to *trans*-2-butene, or *vice versa*; (2) shifting of the double bond, 1-butene or 2-butene, or *vice versa*; and (3) shifting of a methyl group, isobutene to 1- or 2-butene, or *vice versa*. A study of the transformations of these comparatively simple olefins would presumably be of value in the study of the higher olefins.

Before undertaking an investigation on the effect of subjecting the isomeric butenes to different treatments, it was first necessary to develop a satisfactory method of analyzing mixtures containing any combination of these four hydrocarbons. For this purpose the analysis of mixtures of the three normal butenes, *viz.*, 1-butene, *cis*-2-butene and *trans*-2-butene

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