in the algin preparation is decomposed by the bacteria, the lignin-like material is precipitated in the culture in a form similar to natural humus, commonly found in soil and in the sea bottom.

Alginic acid decomposing bacteria attack readily both the acid hydrolyzable and the nonhydrolyzable fractions of the polymannuronic acid, the former to a somewhat greater extent, however.

Alginic acid decomposing bacteria isolated from soil and from sea water produce active enzymes which hydrolyze alginic acid, starch and various other polysaccharides.

The enzyme alginase hydrolyzes the alginic acid largely to simpler groups of mannuronic acid but not to simple units.

The optimum reaction for the action of alginase produced by a marine bacterium was pH 7.0, the optimum temperature 40° and the optimum salt concentration 2% sodium chloride.


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Catalytic Dehydration of Butyl Alcohols

BY V. KOMAREWSKY, W. JOHNSTONE AND P. YODER

The catalytic dehydration of alcohols first studied by Ipatieff[1] is a simple reaction of the first two representatives of this class, ethyl and propyl alcohols. However, in the case of the butyl alcohols, the production of different isomeric butenes has been reported by different investigators.[2] These differences were caused partly by the different catalysts used, but mainly, as shown in the present work, by inaccurate methods of identification of the butenes produced. Usually the butenes obtained were identified by converting them into the corresponding dibromides, but this reaction is not suitable for the identification of the isomeric butenes. When butenes are passed into cold bromine there is some formation of tribromides[3] as well as dibromides, along with simultaneous evolution of hydrogen bromide, which then reacts with butenes to form monobromides. The final product therefore is a mixture of mono-, di- and tribromides. In the distillation of this product there is always a certain amount of hydrogen bromide evolved and the formation of higher boiling residues (tribromides). For this reason it was decided to base the determination and identification of the butenes upon their physical properties. Due to the development of distillation technique in recent years, it was possible to identify the butenes by distilling them in the low temperature apparatus of Podbielniak.[4] The identification of isobutene, whose boiling point (−6.3° at 760 mm.) is very close to that of 1-butene (−5° at 760 mm.), was checked by the formation of the two isomeric monobromides
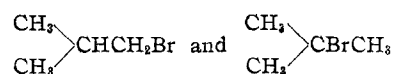
by the action of hydrogen bromide in glacial acetic acid, according to the method of Ipatieff and Ogonowsky,[5] and subsequent hydrolysis of the tertiary monobromide to the corresponding tertiary butyl alcohol.

Using the above methods of determination, the catalytic action of phosphoric acid on the dehydration of normal, secondary and isobutyl alcohols was studied. In order to follow the usual procedure of passing the alcohol vapors at constant speed through a heated tube filled with catalyst, a solid catalyst was prepared by mixing phosphoric acid with pure dried alumina. The experiments of Ipatieff[6] and Pines[7] have proved that pure alumina has no isomerizing action on butenes. The dehydration of butyl alcohols over such a phosphoric acid–alumina catalyst has shown that phosphoric acid has an isomerizing effect on 1-butene, but the yields of 1- and 2-butenes reported by other investigators[8] are not exact. The dehydration of isobutyl alcohol resulted in the formation of pure isobutene and not a mixture of the three isomers as found by Mitchell.[9]

(1) Ipatieff, Ber., 34, 596, 3579 (1901).

(2) Le Bel and Greene, Am. Chem. J., 2, 23 (1880); Nef, Ann., 318, 211 (1901); Harries, ibid., 383, 181 (1911); Senderens, Bull. soc. chim., [4] 1, 693 (1907); Senderens, Ann. chim. phys., [8] 25, 497 (1912).

(3) Faworsky, Dissertation, 1890.

(4) Podbielniak, Oil and Gas Jour., October, 1929.

(5) Ipatieff and Ogonowsky, Ber., 36, 1988 (1903).

(6) Ipatieff, ibid., 36, 2011 (1903).

(7) Pines, THIS JOURNAL, 55, 3892 (1933).

(8) See Reference 10.

(9) Whitmore, THIS JOURNAL, 54, 3278, Footnote 14 (1932).

In order to prove that the dibromide method of analysis leads to erroneous conclusions both as to the amount and the nature of the butenes produced, parallel experiments on the dehydration of butyl alcohols by our phosphoric acid–alumina catalyst were made and the butenes were identified by fractionation of the dibromides. The results were entirely different from those of the distillation analysis, as shown by Table I.

TABLE I

DEHYDRATION OF BUTYL ALCOHOLS OVER PHOSPHORIC ACID–ALUMINA

		Distillation method, %	Dibromide method, %, see exptl. part
n-Butyl alcohol	1-Butene	45	25
	2-Butene	55	63
s-Butyl alcohol	1-Butene	24.1	11
	2-Butene	75.9	89
Isobutyl alcohol	1-Butene		1
	2-Butene		47
	Isobutene	100	10

In order to check the results of other investigators, the experiments of King,[10] and of Young and Lucas[11] were repeated using their catalyst consisting of pumice impregnated with phosphoric acid. From the following table it is evident that

TABLE II

DEHYDRATION OF BUTYL ALCOHOLS OVER PHOSPHORIC ACID–PUMICE

		King, %	Young and Lucas, %	Ours, %
n-Butyl alcohol	1-Butene	Traces	19.1	27.5
	2-Butene	100	80.9 (cis and trans)	72.5
s-Butyl alcohol	1-Butene		15.2	47.5
	2-Butene		84.8 (cis and trans)	52.5

Experimental Part

Materials Used.—Butyl alcohols (Eastman Kodak) were carefully redistilled in a Podbielniak column; n-butyl alcohol, b. p. 116–117°; secondary butyl alcohol, b. p. 99.5–100°; isobutyl alcohol, b. p. 107°. Aluminum oxide was prepared by precipitation from aluminum nitrate solution (Merck) by sodium hydroxide and reprecipitation of the (formed) sodium aluminate by ammonium chloride. The catalyst was washed anion free with distilled water and dried at 240°. The phosphoric acid–alumina catalyst was prepared by mixing 42 g. of alumina with 160 g. of 90% phosphoric acid to a smooth paste. The mixture was dried at 190° for twenty-two hours, ground and screened to produce particles of 8–10 mesh.

The phosphoric acid–pumice catalyst was prepared by treating 8–10-mesh pumice (Sargent Company) with 90% phosphoric acid for twelve hours. The mixture was dried at 190° for twenty-four hours.

The dehydration experiments were made in a glass tube (when checking the King results a copper tube was used) containing 60 g. of catalyst.

The alcohols were introduced by means of the constant speed dropper of Corson,[12] at a rate of 10 drops per minute. The temperature of dehydration was 250° with phosphoric acid–alumina catalyst and 350–400° with phosphoric acid–pumice. The reaction products were first passed through an ice-cooled trap (to remove the traces of unreacted alcohol and water formed) and then through two receivers cooled in dry ice–acetone mixture. A gas holder was placed after the dry ice receivers but no uncondensable gases were obtained. The liquids condensed in the dry ice condensers were fractionated in the Podbielniak column. The check experiments using the dibromide method of identification were made in the same way, except that instead of condensing the reaction products in dry ice-cooled condensers, the reaction products were passed directly into ice-cooled bromine. The excess bromine was subsequently neutralized with ice-cooled sodium hydroxide solution and the separated bromides were washed with water, dried and fractionated through a Vigreux column. The results of the distillation of the bromides are represented in Table III.

TABLE III

DIBROMIDES FROM DECOMPOSITION OF BUTYL ALCOHOLS OVER PHOSPHORIC ACID–ALUMINA CATALYST

Butyl alcohol	Total wt., g.	1 Fraction B. p., °C.	G.	2 Fraction B. p., °C.	G.	3 Fraction B. p., °C.	G.
Normal	25.5	161–162	16.1	165–166	6.4	Higher boiling residue	3.0
Secondary	50.1	154–162	45.2	165–166	4.5		
Iso-	46.0	149–150	5.0	155–162	21.9	163–225	18.0
						+ Bottoms	1.0

In the case of isobutyl alcohol the third fraction (163–225°) contained only 0.5 g. of material boiling at 165–166° which corresponds to about 1% of 1,2-dibromobutane.

the results obtained by King are incorrect. There is also some difference between the results of Young and Lucas and ours, especially with secondary butyl alcohol.

(10) King, J. Chem. Soc., 115, 1404 (1919).
(11) Young and Lucas, THIS JOURNAL, 52, 1964 (1930); Matignon, Moureu and Dodé, Compt. rend., 196, 973 (1933).

Monobromoisobutanes from an Isobutyl Alcohol Dehydration.—The butene formed was passed through two wash bottles filled with an ice-cooled glacial acetic acid solution of hydrogen bromide. The wash bottle contents was decomposed with ice. The layer of monobromides was separated, dried and distilled, the range being b. p.

(12) Corson, Ind. Eng. Chem., Anal. Ed., 6, 297 (1934).

72–92°. The monobromides were then hydrolyzed three times, each time with a fresh quantity of water, for two hours on a steam-bath. The combined water layers were salted out by means of potassium carbonate, resulting in a layer of pure tertiary butyl alcohol of b. p. 83°. The unhydrolyzed product was a pure monobromide

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\Big\rangle CHCH_2Br, \text{ boiling at } 92°$$
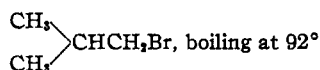
From the butene obtained by dehydration of 37 g. of isobutyl alcohol, 60.5 g. of monobromides was formed, resulting after hydrolysis in 15 g. of unhydrolyzable primary monobromide [Br determination: calcd. for C_4H_9Br: Br, 58.39. Found: Br, 58.01] and 22.1 g. of tertiary butyl alcohol.

The authors acknowledge the grant of the Fellowship to one of us (P. Yoder) by the Universal Oil Products Company, Chicago.

Summary

1. The butene mixtures obtained by the catalytic dehydration of butyl alcohols by phosphoric acid catalysts were analyzed by low temperature distillation in a Podbielniak column.

2. It was found that both 1- and 2-butenes were obtained by the dehydration of normal and secondary butyl alcohols, but that pure isobutene resulted from the dehydration of isobutyl alcohol.

3. The results of King and Mitchell were found to be incorrect due to the inaccuracy of the dibromide method of identifying the butenes.

The Chemistry of Lignin. IX. Lignin from Barley Straw

BY MAX PHILLIPS AND M. J. GOSS

Although the literature on lignin is now rather extensive, comparatively few papers have been published dealing with the chemistry of lignin from annual plants. Most investigators have studied the chemistry of lignin from wood, particularly spruce wood. The present paper is one of a series to be published from this Bureau dealing with the chemistry of lignin from cereal straws.

Among the older investigations may be mentioned those of Cross and Bevan[1] on the lignin from jute. Beckmann, Liesche and Lehmann[2] reported on a lignin fraction isolated from winter rye straw. Powell and Whittaker[3] isolated the lignin from flax shoves by the alkali method, and found that its composition agreed with the formula $C_{45}H_{48}O_{16}$. Several papers[4] dealing with the chemistry of lignin from corncobs and from oat hulls have been published from this Bureau.

The two lignin fractions described in this paper were isolated from barley straw by extracting it successively and exhaustively, first with an alcoholic sodium hydroxide solution at room temperature, and then by refluxing with 4% aqueous sodium hydroxide solution. The composition of the first lignin fraction agreed with the formula $C_{40}H_{48}O_{15}$. On the basis of a compound having a molecular weight represented by this formula, four methoxyl groups and five hydroxyl groups definitely were shown to be present. Three of the five hydroxyl groups could be methylated with diazomethane, thus indicating that these are more acidic, possibly phenolic or enolic in character. The other two hydroxyl groups could be methylated only after repeated treatment with dimethyl sulfate and 40% potassium hydroxide solution.

The analytical results on the residual lignin fraction isolated by means of aqueous sodium hydroxide solution are more in agreement with that represented by the formula $C_{40}H_{42}O_{16}$. In this lignin fraction four hydroxyl and four methoxyl groups were shown to be present.

By means of a method previously described,[4d] the alkoxyl groups in both lignin fractions were shown to be methoxyls. The presence of other alkoxyl groups, such as, for example, ethoxyl groups, was definitely excluded.

When either of the two lignin fractions was distilled with 12% hydrochloric acid, a small quantity of formaldehyde was obtained in the distillate. Freudenberg and Harder[5] distilled

(1) Cross and Bevan, "Cellulose," Longmans, Green and Co., London, 2d ed., 1895, p. 137; Vol. III, 1912, p. 104.

(2) Beckmann, Liesche and Lehmann, Z. angew. Chem., 34, 285 (1921).

(3) Powell and Whittaker, J. Chem. Soc., 125, 357 (1924).

(4) (a) Phillips, THIS JOURNAL, 49, 2037 (1927); (b) 50, 1986 (1928); (c) 51, 2420 (1929); (d) 52, 793 (1930); (e) 53, 768 (1931); (f) Science, 73, 368 (1931); (g) Phillips and Goss, THIS JOURNAL, 54, 1518 (1932); (h) 54, 3374 (1932); (i) Ind. Eng. Chem., 24, 1436 (1932); (j) THIS JOURNAL, 55, 3466 (1933).

(5) Freudenberg and Harder, Ber., 60, 581 (1927).