Rate measurements with the pure dibromobutanes were made at 59.72°. From the results at the two temperatures the heats of activation, Q, and the temperature coefficients were calculated by means of the Arrhenius equation. The values are given in Table X.

TABLE X

TEMPERATURE COEFFICIENTS AND HEATS OF ACTIVATION

Dibromo-butane	k_2		Heats of activation, cal.	Temp. coeff. for 10°	
	59.72°	74.93°		$\frac{69.72°}{59.72°}$	$\frac{74.93°}{64.93°}$
1,2-	0.0147	0.0765	24,900	3.01	2.91
2,3-meso-	.00896	.0544	27,300	3.33	3.22
2,3-racemic	.00462	.0297	28,100	3.46	3.34

Summary

The specific reaction rates of 1,2-dibromobutane and of racemic and meso-2,3-dibromobutane with potassium iodide in methanol have been measured at 60 and at 75°. They are second-order reactions. The heats of activation and temperature coefficients have been calculated.

The reaction rates of mixtures of these dibromides have likewise been measured at 75°. Calculation of the composition of binary mixtures from the reaction rates and of a ternary mixture from the reaction rate and density gave results in satisfactory agreement with the known compositions. The maximum deviation was 4%.

Mixtures of the three normal butenes may be analyzed by first converting them to the corresponding dibromides and determining for these the reaction rates and densities.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 242]

THE COMPOSITION OF BUTENE MIXTURES RESULTING FROM THE CATALYTIC DECOMPOSITION OF THE NORMAL BUTYL ALCOHOLS

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Introduction

Within recent years considerable interest has been attached to the decomposition of the normal butyl alcohols, partly because of its importance as a source of butenes and partly because of its bearing upon the theory of catalysis. These decompositions would be of particular value if they should yield, under the proper conditions, pure butenes, rather than mixtures of these hydrocarbons.

The catalytic decomposition of 1-butanol was first accomplished by Le

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[1] Du Pont Fellow in Chemistry, 1928–1929.

Bel and Green,[2] who dropped the alcohol upon hot zinc chloride. The alcohol has also been dehydrated by passing the vapor over a variety of catalysts at elevated temperatures.[3] The catalytic dehydration of 2-butanol has likewise been accomplished in different ways.[3n,o,4]

The composition of the butene mixtures obtained in the decompositions of these alcohols depends to a considerable extent upon the catalyst used and in most cases has been reported as being 1-butene, 2-butene, or a mixture of these. The isobutene present in some of these mixtures, as reported by a few investigators,[3a,c,e,4a] probably arose from isobutanol in the alcohol used, as was actually demonstrated in one case.[4a] The methods which have been used for analyzing mixtures of 1- and 2-butene, except those which depend upon a separation of the corresponding dibromobutanes[2,3f,l,o] in general rely upon a difference in the reactivity of 1-butene and 2-butene. Since, however, there are two isomeric 2-butenes, it is evident that any method developed on the assumption that a mixture of the 2-butenes behaves as a pure compound lacks accuracy and consequently the results obtained by it are in error.[3n,5] This criticism, however, does not apply to the ozonide method,[4b,c] which distinguishes between 1-butene and the mixed 2-butenes.

TABLE I

THE CATALYTIC DECOMPOSITION OF THE NORMAL BUTYL ALCOHOLS

No.	Alcohol	Catalyst	Temp., °C.	Duration of run min.	Alcohol Used, g.	Alcohol Recovered, g.
1	1-Butanol	H_2SO_4 60%	140–160	...	74	..
2	2-Butanol	H_2SO_4 60%	115–140	...	74	..
3	2-Butanol	H_3PO_4 85%	95–126	...	148	..
4	1-Butanol	P_2O_5	100–140	...	74	..
5	2-Butanol	P_2O_5	90–130	...	74	..
6	1-Butanol	H_3PO_4 on pumice	390–400	105	80	..
7	2-Butanol	H_3PO_4 on pumice	340–345	78	60	0
8	1-Butanol	$AlPO_4$	440–450	87	72	24
9	2-Butanol	$AlPO_4$	340–350	81	72	18
10	1-Butanol	Al_2O_3	340–370	80	60	5
11	2-Butanol	Al_2O_3	335–345	125	60	3

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[2] Le Bel and Green, *Am. Chem. J.*, **2**, 24 (1881).

[3] (a) Ipatiew, *Ber.*, **36**, 1999 (1905); (b) Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 458 (1905); (c) Senderens, *Compt. rend.*, **144**, 1110 (1907); (d) Sabatier and Mailhe, *Ann. chim. phys.*, [8] **20**, 325 (1910); (e) Senderens, *ibid.*, **25**, 449 (1912); (f) King, *J. Chem. Soc.*, **115**, 1404 (1919); (g) Pease and Yung, THIS JOURNAL, **46**, 402 (1924); (h) Adkins and Nisson, *ibid.*, **46**, 130 (1924); (i) Brown and Reid, *J. Phys. Chem.*, **28**, 1081 (1924); (j) Adkins and Perkins, THIS JOURNAL, **47**, 1163 (1925); (k) Lazier and Adkins, *ibid.*, **47**, 1719 (1925); **48**, 1671 (1926); (l) Lépingle, *Bull. soc. chim.*, **39**, 741 (1926); (m) Coffin and Maass, THIS JOURNAL, **50**, 1427 (1928); (n) Davis, *ibid.*, **50**, 2769 (1928); (o) Lucas, Dillon and Young, *ibid.*, **52**, 1949 (1930).

[4] (a) Ipatiew and Sdzitowecky, *Ber.*, **40**, 1827 (1907); (b) Harries, *Ann.*, **383**, 181 (1911); (c) Harries and Evers, *ibid.*, **390**, 238 (1912).

[5] Michael and Brunel, *Am. Chem. J.*, **41**, 135 (1909).

Table I (*Concluded*)

		Dibromide mixture				% Composition of butene mixtures				
						By density and reaction rate			By density alone	
No.	Yield on alcohol, %	B. p., °C.	Press., mm.	Reaction rate	Density in vacuo d_4^{25}	1-Butene, b. p. −6.7°	2-Butene, b. p. +3.0° *cis*	2-Butene, b. p. +0.3° *trans*	2-Butene, b. p. +3.0° *cis*	2-Butene, b. p. +0.3° *trans*
1	39.0	74.5–75.8	51.0	0.0466	1.7775	0.1	31.5	68.4	31.5	68.5
2	88.1	73.8–75.5	48.5	.0435	1.7784	−1.1	43.1	58.0	41.6	58.4
3	95.0	73.0–75.6	50.0	.0435	1.7782	−2.1	42.2	59.9	39.4	60.6
4	45.0	74.3–76.5	52.0	.0470	1.7774	0.2	30.1	69.7	30.4	69.6
5	77.0	73.0–75.2	49.0	.0429	1.7783	−2.5	44.0	58.5	40.4	59.6
6	..	73.3–75.5	48.0	.0504	1.7880	19.1	33.2	47.7	..	..
7	85.5	72.3–74.5	47.0	.0485	1.7799	15.2	37.4	47.4	..	..
8	86.0	75.2–78.3	47.7	.0631	1.7829	56.0	14.8	29.2	..	..
9	85.5	73.4–77.5	48.0	.0486	1.7806	18.8	40.3	40.9	..	..
10	80.5	74.0–77.4	47.5	.0668	1.7850	72.9	15.0	12.1	..	..
11	97.7	75.2–78.0	50.0	.0446	1.7824	20.6	58.1	21.3	..	..

The method for analyzing mixtures of 1-butene, *cis*-2-butene and *trans*-2-butene by means of the densities and the reaction rates of the corresponding dibromides[6] has been applied to the mixtures resulting from the decomposition of 1-butanol and 2-butanol with different dehydrating agents. The results are given in Table I.

Experimental

Materials.—The 1-butanol and 2-butanol were purified as described for other decompositions.[3c,7]

Merck's bromine was shaken with a solution of potassium iodide and distilled from concentrated sulfuric acid.

Columbian spirits, free from acetone, was refluxed with sirupy phosphoric acid for three hours in order to remove traces of amines, and slowly distilled through the column used for purifying the butanols, the first and last portions being discarded. The main portion of the methanol was then refluxed for three hours with flake caustic soda, slowly distilled and the part distilling at 64.2–64.6° (745 mm.) was diluted with water to a density, d_4^{20}, of 0.7945, the density of 99.0% methanol.

The potassium iodide, P. W. R. analytical, was heated to 120° for four hours and placed in a desiccator until used.

The dehydrating agents for the alcohol decompositions were aluminum oxide,[3c] Baker's c. p. aluminum phosphate previously heated to 400°, Merck's phosphorus pentoxide, P. W. R. "highest purity" 85% phosphoric acid, 60% sulfuric acid, made by diluting Baker's c. p. acid, and pumice impregnated with phosphoric acid.

Apparatus.—The decompositions of 1-butanol and 2-butanol with phosphorus pentoxide, phosphoric acid and sulfuric acid were accomplished in a three-necked three-liter flask. The resulting butene was passed in succession through a reflux condenser, a trap at 0°, a 24% solution of perchloric acid contained in a spiral wash bottle, a calcium chloride drying tube and finally into the brominating flask at −15° provided with an outlet attached to calcium chloride and soda lime tubes. The apparatus used for effecting the decompositions over aluminum oxide, aluminum phosphate and pumice

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[6] Dillon, Young and Lucas, This Journal, 52, 1953 (1930).

[7] The 2-butanol was kindly supplied by the Stanco Distributors, N. Y., through the courtesy of Mr. C. L. Bowman.

impregnated with phosphoric acid and also the set-up employed in the distillation of the dibromides at 50 mm. were the same as those used for other decompositions.[3o]

Decomposition of the Alcohols.—The rate of decomposition of the alcohols was determined as rapidly as consistent with effective handling of the butene by the purifying train. The procedures used varied with the dehydrating agents. In the case of 60% sulfuric acid and 85% phosphoric acid, the alcohols and acid were heated together in the generating flask in the following proportions: 220 g. of 60% sulfuric acid with 74 g. (1.0 mole) of alcohol, 475 g. of 85% phosphoric acid with 148 g. (2 moles) of alcohol.[3n] The decomposition of 2-butanol proceeds the more readily. In the case of phosphoric acid no butene could be obtained from 1-butanol, even with the addition of diatomaceous earth.

The alcohols were dropped onto the phosphorus pentoxide in the following proportions: 74 g. (1.0 mole) of 1-butanol or 118 g. (1.6 moles) of 2-butanol[4b] upon 100 g. of phosphorus pentoxide.

In the case of aluminum oxide, aluminum phosphate and phosphoric acid on pumice the decompositions were effected in the usual manner.[3o] Of the last three catalysts, aluminum oxide was the most effective and the aluminum phosphate was decidedly inferior to the other two. Here also the 2-butanol was the more easily decomposed. The yield was calculated from the amount of alcohol decomposed, obtained by subtracting the amount recovered from that put through the furnace.

Purification of the Dibromobutanes.—The crude dibromides contained small amounts of lower-boiling impurities but no higher-boiling ones, such as tribromobutane. In every case the low-boiling impurity was removed by conducting the first part of the distillation at a very slow rate and removing in the first fraction about 10% of the total weight of the dibromides. The range of this fraction was usually three or four degrees and of this material about 90% came over at the top of its boiling range. The necessity of removing this first fraction was indicated by the analysis of the binary mixture of isomeric 2-butenes obtained in the decomposition of 2-butanol with phosphoric acid. A marked discrepancy was found between the reaction rate and the density of the resulting 2,3-dibromobutanes following one distillation at 50 mm. without fractionation. The separation effected by a subsequent fractional distillation was indicated by the refractive indices of successive cuts, the values being 1.5097, 1.5128, 1.5129, 1.5130 and 1.5132. After discarding the first fraction, the remaining fractions were combined and density and reaction rate measurements were taken. These values were 1.7775 and 0.0435, respectively, whereas the corresponding values for the material before fractionation were 1.7759 and 0.0435. From these figures it is evident that the impurity was material of low density and not isobutene dibromide, the density of which lies close to that of the 2,3-dibromobutanes. The ratio of the dibromides had not been materially altered by the removal of this first fraction since (1) the reaction rate was not affected, (2) the refractive indices of the other four fractions were about the same and (3) previous attempts at fractional distillation of dibromobutanes had not effected a complete separation even after six fractionations.[3o]

Analysis of the Dibromobutane Mixtures.—From the densities and the reaction rate measurements of the dibromobutane mixtures with potassium iodide in methanol, the percentage of 1-butene, *cis*-2-butene, b. p. 3.0°, and *trans*-2-butene, b. p. 0.3°, in the original butene mixture can be calculated according to the respective equations

$$X = \frac{-K_{2b}(d_c - D) + k_{2c}(d_b - D) - K_2(d_b - d_c)}{\Delta}$$

$$Y = \frac{k_{2a}(d_c - D) - k_{2c}(d_a - D) + K_2(d_a - d_c)}{\Delta}$$

$$Z = \frac{-k_{2a}(d_b - D) + k_{2b}(d_a - D) - K_2(d_a - d_b)}{\Delta}$$

in which k_{2a}, k_{2b} and k_{2c} are the specific second-order constants of the corresponding pure dibromobutanes, d_a, d_b, d_c are their densities, K_2 and D are the observed reaction rate and density of the dibromide mixture and $\Delta = k_{2a}(d_a - d_c) - k_{2c}(d_a - d_b) - k_{2a}(d_b - d_c) = 0.0005004$.

Since the results on known mixtures showed an error of 2 to 4%, it seems reasonable to assume that the maximum error in this method is not greater than 5%.[6] When analysis indicated that the decomposition product was a binary mixture, calculation from the density alone gave results in agreement within the limits specified, as shown in the table.

It should be pointed out that in using this method for the analysis of butene mixtures the purity of the solvent must be checked by running a reaction rate with pure 1,2- or 2,3-dibromobutane.

Discussion

Perhaps the most striking features of the decompositions are the presence of the 2-butenes in all of the reaction products and the absence of 1-butene in the reaction product from both 1-butanol and 2-butanol when phosphorus pentoxide, phosphoric acid or sulfuric acid is used at temperatures below 160°. In all these cases the lower-boiling 2-butene is in excess and its amount is largest from 1-butanol. The behavior of 2-butanol with the pentoxide is in agreement with the results of Harries and Evers,[4c] who found that no 1-butene was present although they made no distinction between the isomeric 2-butenes. The decomposition of 2-butanol with phosphoric acid has been carried out by Davis,[3n] who analyzed the butene fraction distilling at 1.5–1.7° by the bromine absorption method and found 84% to be rapidly brominated, therefore 2-butene, and 16% to be slowly brominated, therefore presumably 1-butene. He has misinterpreted his results, having failed to appreciate that the isomeric 2-butenes might absorb bromine at different rates. From our analysis and his bromination experiments it is evident that the lower-boiling (0.3°) isomer has the faster reaction rate with bromine. It is interesting to note that the dibromide of this isomer also has the higher reaction rate with potassium iodide. It is not likely that the composition of the distillate studied by Davis was materially different from that of his original butene mixture since the fraction at 1.5–1.7° is midway between the pure hydrocarbons.[8]

No appreciable quantity of butene was formed when 1-butanol was refluxed with 85% phosphoric acid. The composition of the butene mixtures resulting from the decomposition with 60% sulfuric acid has not been reported previously.

[8] Young, Dillon and Lucas, THIS JOURNAL, **51**, 2528 (1929).

Of the higher temperature decompositions in the gas phase, 1-butene was in excess in only two cases, the largest amount coming from 1-butanol over aluminum oxide. Approximately the same quantity of 1-butene was obtained from 2-butanol irrespective of the catalyst. The higher-boiling 2-butene (*cis*) was in excess over the other two products in only one case, *viz.*, 2-butanol over aluminum oxide; and it was only with this catalyst that the amount of the *cis*-isomer exceeded that of the *trans*.

The decomposition of 1-butanol over phosphoric acid on pumice has been reported previously by King[3f] and by Coffin and Maass.[3m] The former found no isobutene and obtained nearly pure 2,3-dibromobutanes on fractionation of the mixed dibromides. The latter, by distillation of both the olefin and its dibromide, obtained 10–15% of 1-butene, the balance being 2-butene. Their result for 1-butene, although somewhat lower than ours, is in substantial agreement. The fraction distilling at 1.0° and believed by them to be pure 2-butene was undoubtedly a mixture.

The composition of the mixture from the decomposition of 1-butanol over aluminum oxide first reported by Ipatiew[3a] has been studied recently by Davis,[3n] Lépingle,[3l] and by Lucas, Dillon and Young.[3o] Davis claimed 65% 1-butene and 35% 2-butene by his bromine absorption method. His result for 1-butene would agree better with ours if correction could be made for the difference in reactivity of the isomeric 2-butenes. The results obtained by Lépingle for 1-butanol and by Lucas, Dillon and Young for 1- and 2-butanol over aluminum oxide agree fairly well with the analyses given in the table, considering the limitations of the distillation method. Lépingle obtained 78% 1-butene and 22% 2-butene for 1-butanol while Lucas, Dillon and Young report 68% 1-butene, 20% higher- and 12% lower-boiling 2-butene. The latter obtained from 2-butanol 26%, 48% and 26%, respectively.

The decomposition of 1-butanol over aluminum phosphate has been reported by Senderens,[3c] who obtained a mixture of 73% 1-butene and 27% isobutene. Since no evidence has been found for the presence of isobutene in any of the decompositions described in this paper, it seems likely that the presence of isobutene in the product reported by Senderens was due to isobutanol in the alcohol used by him.

From the results listed in the table it is evident that neutral dehydrating agents favor 1-butene, whereas the acidic ones favor 2-butene, the order for both alcohols being aluminum oxide, aluminum phosphate, phosphoric acid on pumice and finally the three acidic reagents, phosphorus pentoxide, phosphoric acid and sulfuric acid. The last three likewise favor the lower-boiling 2-butene.

Removal of Bromine from Dibromobutane.—Since bromine adds across the bond, and not on the same side,[9] a study was made of the re-

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[9] Michael, *J. prakt. Chem.*, **52**, 344 (1893); Chavanne, *Revue Générale des Sciences*,

moval of bromine from 2,3-dibromobutane to determine whether the original or the isomeric 2-butene was produced. It was found that the hydrocarbon formed by the removal of bromine from a mixed 2,3-dibromobutane gave, with bromine, a dibromide identical with the original. The removal of bromine therefore appears to be a *trans* elimination similar to other reactions in which halogens or halogen halides are eliminated.

135.5 g. of 2,3-dibromobutane, obtained from the butene resulting from the decomposition of 2-butanol with phosphorus pentoxide and having a second order reaction rate with potassium iodide, K_2, of 0.0430, was allowed to drop upon 77 g. of 10-mesh granulated zinc, P. W. R. C. P. under 110 ml. of ethanol at 80–95°. The evolved butene, after passage through a reflux condenser, was purified as usual and allowed to react with bromine. The purified dibromide, 122.3 g. (90% yield), gave for K_2 the value of 0.0431. It was thus identical, within experimental error, with the original dibromide.

Summary

Decompositions of 1-butanol and 2-butanol have been effected by dropping the alcohols upon phosphorus pentoxide, by heating the alcohols with 85% phosphoric acid and with 60% sulfuric acid and by passing the vapor of the alcohols at high temperatures over aluminum oxide, over aluminum phosphate and over pumice impregnated with phosphoric acid. The butene mixtures were analyzed by converting them to the dibromides and determining for the latter the densities and the reaction rates with potassium iodide in methanol. Both 1-butanol and 2-butanol gave a mixed 2-butene free from 1-butene when the dehydrating agent was phosphorus pentoxide, phosphoric acid or sulfuric acid and the decomposition was carried out below 160°, except, however, that 1-butanol was not decomposed by phosphoric acid. 2-Butanol with phosphoric acid on pumice, with aluminum phosphate, or with aluminum oxide gave largely 2-butene, the amount of 1-butene increasing slightly in the order named. With 1-butanol the amount of 1-butene obtained when these three catalysts were used increased rapidly in the order named, being 73% with aluminum oxide. In general, the more acidic reagents favor *trans*-2-butene and the less acidic favor 1-butene and *cis*-2-butene.

The removal of bromine with zinc from a mixed 2,3-dibromobutane produced a mixed 2-butene identical in composition with the butene from which the dibromide was prepared.

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35, 229 (1924). The *cis* addition observed by Terry and Eichelberger, THIS JOURNAL, **47,** 1067 (1925), was effected in aqueous solution in the presence of bromide ions.