bumping. The precipitated sulfur was removed by filtration and washed with small portions of ethanol. Small pieces of ice were added to the alcohol solutions until crystals separated. After the slow addition of water (400 cc.) the mixture was chilled overnight. The solid formed was dissolved in concentrated hydrochloric acid (130 cc.) and then filtered. Slow addition of alkali gave an amine; 5.5 g. (54%); m. p. 59–59.5°.

3-Nitro-4-propylphenol.—3-Nitro-4-propylaniline (16.5 g.) was dissolved in 26 cc. of concentrated sulfuric acid and 125 cc. of water by warming on a steam cone. The hot solution was added with good stirring to a mixture of 250 cc. of water and 270 g. of ice. At 0° sodium nitrite (6.0 g. in 51 cc. of water) was added. The amine salt dissolved and the excess nitrous acid was decomposed with urea. This solution was added dropwise to a boiling solution of 152 cc. of concentrated sulfuric acid and 1500 cc. of water. The tar was removed by filtration through sand. The cooled filtrate was extracted with ether. Basic extraction of the ether layer followed by acidification and another ether extraction gave a solution which on evaporation and distillation yield the nitrophenol; 2.7 g.; m. p. 46.5–47.5°.

Anal. Calcd. for $C_9H_{11}O_3N$: C, 59.70; H, 6.13. Found: C, 59.48; H, 6.43.

3-Amino-4-propylphenol.—3-Nitro-4-propylphenol (4.0 g.) was dissolved in ethanol (50 cc.) and reduced with platinum at room temperature. Careful removal of the solvent followed by recrystallization from toluene-petroleum ether and finally hot water gave a white solid; m. p. 152–153°. Attempts to acetylate this material gave oils.

Anal. Calcd. for $C_9H_{13}ON$: C, 71.52; H, 8.67. Found: C, 71.30; H, 8.94.

Summary

1. It has been shown that m-acetamidophenyl allyl ether on thermal rearrangement gives 2-allyl-5-acetamidophenol.

2. 2-Allyl-5-acetamidophenol has been converted to 2-propyl-5-aminophenol which is identical with the product formed from propylresorcinol by direct amination.

MINNEAPOLIS, MINNESOTA   RECEIVED JANUARY 19, 1942

The Action of Hydrogen Fluoride, Sulfuric Acid and Phosphoric Acid on Optically Active 2-Butanol

BY ROBERT L. BURWELL, JR.

In the absence of suitable catalysts, alcohols are strongly resistant to configurational change. Thus, those fractions of d-active amyl alcohol[1] and l-2-butanol[2] which escape decomposition at elevated temperatures are unchanged in rotation.

Catalytic racemizations of alcohols have been little studied. Frankland and Price[3] investigated the racemization of the d-active amyl alcohol by sodium alcoholate in a sealed tube at 200°. Burwell[2] investigated the heterogeneous catalytic racemization of l-2-butanol in the presence of zinc chromite, chromium oxide and copper.

In this paper the racemizing action of hydrogen fluoride, sulfuric acid and phosphoric acid on optically active 2-butanol is reported. This reaction gains interest from its interrelations with the dehydrating and alkylating reactions which are known to be effected by the same catalysts.

Experimental

Materials and Technique.—Compositions of sulfuric acid solutions were determined by density measurements. Density *vs.* composition tables of the "International Critical Tables" were employed. The composition of the concentrated sulfuric acid was determined in this way by a weight dilution.

100% phosphoric acid was prepared by heating Baker and Adamson 85% phosphoric acid to constant weight at 160°. The liquid anhydrous hydrogen fluoride was supplied by the Harshaw Chemical Company.

2-Butanol was resolved by the method of Viditz.[4] The product of the first crystallization was employed in this research without further resolution: l-2-butanol, $\alpha^{20}D$ −4.14°; d-2-butanol, $\alpha^{22}D$ +5.80°.

The active alcohol after a preliminary treatment with anhydrous potassium carbonate was dried by distillation in a small bore vacuum-jacketed column with a double internal nichrome spiral 50 cm. in length. A 50-cc. still pot was heated internally with a coil of no. 30 B. and S. gage nichrome wire. The column gave twenty-five theoretical plates as determined by the methylcyclohexane–n-heptane method.[5]

It was not found possible to fractionate commercial 2-butanol to such purity that solutions could be prepared with concentrated sulfuric acid which would remain colorless for several hours. This could readily be done, however, with the active 2-butanols (which, of course, had undergone further purification during their resolution).

The activity of the alcohol was measured in a 1-dm. semimicro polarimeter tube. The rotation of the alcohol is

(1) Von Weber, *Z. physik. Chem.*, **179A**, 295 (1937).

(2) Burwell, THIS JOURNAL, **59**, 1609 (1937).

(3) Frankland and Price, *J. Chem. Soc.*, **71**, 255 (1897).

(4) Viditz, *Biochem. Z.*, **259**, 294 (1933).

(5) Beatty and Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934).

very sensitive to traces of water. To avoid the intensive drying of small samples, rotations were ordinarily measured of an alcohol equilibrated with a saturated solution of dihydrated potassium carbonate plus excess solid at 25°. This method gave consistent results.

In a 10-cc. pycnometer a sample of 2-butanol so treated gave d^{20}_4 0.8132. From the data of Clough and Johns[6] this corresponds to a composition of 96.7% alcohol by weight, n^{20}D 1.3961. Rotations of such a solution will be recorded as β. α will be reserved for pure substances. $\beta/\alpha = 0.927$ (20-24°). β_0 will refer to the rotation of the original alcohol equilibrated with the saturated solution of potassium carbonate.

Experiments with Sulfuric Acid

2-Butanol was recovered from sulfuric acid solutions by dilution with water to yield an acid concentration of 25% or less. This solution was heated on a steam-bath for an hour in a flask to which was fused a small condenser. During this period most of the alcohol distilled over as the water–alcohol azeotrope. The remaining portions were brought over by passage of steam through the flask. If steam distillation was attempted immediately, recovery was somewhat less, presumably because of the rather slow hydrolysis of s-butylsulfuric acid. The distillate was treated with potassium carbonate and the upper layer placed in a thermostat at 25° over a saturated solution of the carbonate.

Refractive indices of the recovered alcohol (over saturated potassium carbonate solution) were always determined. Since the value was always n^{20}D 1.3961 within 0.0002, they will not be separately listed save for one exception.

The data presented in Table I were obtained by heating the indicated mixtures in a tube connected with a gas buret. The evolved gas was found to be absorbed in 87% sulfuric acid and was presumed to be butylene. Because of the considerable solubility of butylene in these mixtures, only qualitative significance attaches to quantities of butylene reported as evolved.

Table I

Mixtures of Sulfuric Acid and *l*-2-Butanol[a] Heated at 100°

Moles of $C_4H_{10}O$	Moles of H_2SO_4	Moles of H_2O	Time, min.	Moles of C_4H_8	β/β_0
0.0366	0.0010[b]	0.00025	10	None	1.00
.0293	.0031[b]	.0007	30	0.0002	0.966
.0285	.0187[b]	.0045	1	.002	
.0284	.0344[c]	.0566	5	.0018	.010

[a] β^{22}D −3.79°. [b] Corresponds to 95.8% acid. [c] Corresponds to 76.8% acid.

(6) Clough and Johns, *Ind. Eng. Chem.*, **15**, 1030 (1923).

Mixtures of 95.8% acid and alcohol in which the molar ratio was greater than about 1.6 gave polymers. By adding the acid to the alcohol cooled in ice, slowly and with good stirring, colorless solutions were prepared. These solutions, however, reacted as the following experiments indicate.

0.0250 mole of *dl*-2-butanol, 0.0435 mole of sulfuric acid, 0.0104 mole of water.—On standing at 25° for two days about 0.3 cc. of upper layer had appeared. There was no further change in two weeks.

0.0254 mole of 2-butanol (α^{22}D −4.14°), 0.0819 mole of sulfuric acid, 0.0195 mole of water.—The mixture was removed from ice upon completion of mixing. It became turbid in six minutes. The formation of the upper layer was complete in thirty minutes; yield, 1.1 g., n^{20}D 1.4509; α^{21}D 0.

In a similar mixture kept at 0°, turbidity appeared in forty minutes. The reaction required ten hours for completion. Otherwise the results were similar.

A similar mixture was prepared in six minutes from an alcohol of β^{22}D −3.79. After standing at 0° for one minute more, the mixture was diluted and the alcohol was recovered with an 87% yield; β/β_0 0.968.

A study was made of the reaction of approximately equimolar acid–alcohol mixtures.

Table II

Mixtures of Sulfuric Acid with *l*-2-Butanol[a] at 25°

Moles of $C_4H_{10}O$	Moles of H_2SO_4	Moles of H_2O	Time, days	β/β_0
0.0276	0.0325[b]	0.0539	1	0.943
.0276	.0325[b]	.0539	14	.305
.101	.105[c]	.025	2	.011[d]

[a] β^{22}D −3.79. [b] Corresponds to 76.8% acid. [c] Corresponds to 95.8% acid. [d] The mixture was yellow after one day, brown in two. Recovery 60%, n^{20}D 1.3971 (high).

The rates of racemization of *l*-2-butanol (β^{22}D −3.79) in approximately equimolar mixtures of 95.8% and 86.6% sulfuric acid were investigated at 0, 25 and 40°. With the 95.8% acid the mixture contained 19.07 g. of alcohol and 27.18 g. of acid; with the 86.6% acid, 16.69 g. and 26.12 g. If the moles of alcohol be taken as 1.000, then in the more concentrated acid the molar composition was: alcohol, 1.000, acid 1.031 and water 0.246; with the 86.6% acid 1.000, 1.023 and 0.862, respectively.

The samples were prepared in a freezing mixture at −10°. They were placed in the thermostat and shaken for one minute. The end of this minute was taken as zero time. Samples were periodically removed from the reaction flask and run into water. The successive treatment has been described. The samples corresponded about to an original 2.5 cc. of *l*-2-butanol. The volume of the recovered alcohol was measured in a graduated pipet to within an accuracy of about 0.05 cc. The volume was corrected for density and water content in calculating recoveries.

Just before inserting the reaction mixture in the thermostat a sample was removed. The rotation of this sample was taken as β_0. Its value was around 1% less than that of the initial alcohol. To allow for mechanical losses, the recovery of this sample was assumed 100% in calculating percentage recoveries. The actual measured recovery of

the standard sample was about 4% below theoretical or about 0.1 cc.

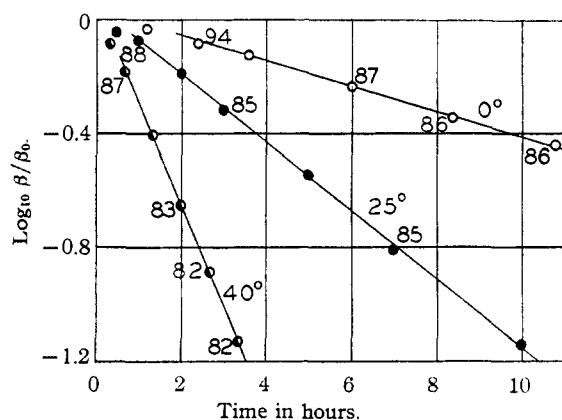The results of these runs are given in Figs. 1 and 2.

Fig. 1.—Racemization of optically active 2-butanol by 95.8% sulfuric acid. The figures adjacent to the experimental points give the measured recoveries in %. The recoveries at the first point at 0, 25 and 40° were 96, 96 and 89%, respectively. To allow plotting in the same graph, the values of the time in the results at 0° have been multiplied by 0.1 and those at 40° by 2.

As a check on the purity of the recovered alcohol in addition to that provided by the determination of the refractive index, a sample of dl-2-butanol and 95.8% sulfuric acid of the same composition as that employed in the rate experiments was diluted after two hours at 25°. The recovered alcohol was fractionated in the small 25-plate column without evidence of anything save 2-butanol. The residue from the steam distillation was extracted with chloroform. Nothing additional could be found in the chloroform layer.

As a further check on the procedure, samples of partially racemized l-alcohol prepared by concentrated sulfuric acid of values of β/β_0 0.266, 0.620 and 0.950 were converted into the 3,5-dinitrobenzoyl ester,[2] and the specific rotations of the esters determined: $[\alpha]/[\alpha]_0$ 0.255, 0.610 and 0.956.

The cause of the decline in recovery was investigated. A mixture identical with that in the rate experiments with 95.8% acid was prepared with inactive alcohol. After three and one-half hours at 25° the weight of the reaction flask was unchanged within a centigram. However, a distinct odor of butylene could be detected. This was always true in similar experiments. The mixture was poured into 56 cc. of water and heated on a steam-bath in the flask with the sealed-on condenser. An additional outlet at the end of the condenser led to a gas buret. After 1.4 hours on the steam-bath, steam was passed through the apparatus. The recovery of the alcohol amounted to 85.5%; the yield of butylene was 10.5%. One-half of this was obtained upon boiling the condensate so that it is not practical to state just when the butylene was formed. However, about one-fourth seems to be liberated rapidly, the remainder slowly.

The experiment was repeated save that the acid was diluted with the 56 cc. of water before the alcohol was

added. Recovery amounted to 95% but about 1.8% of olefin was liberated.

An attempt to determine directly the quantity of butylene actually present as such by the bromate–bromide method[7] was unsuccessful because of large blanks. However, an upper limit of 1% was indicated.
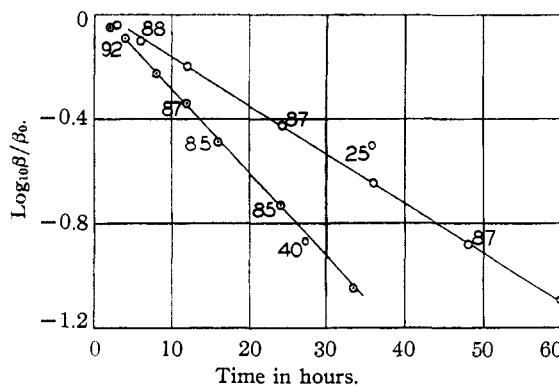

Fig. 2.—Racemization of optically active 2-butanol by 86.6% sulfuric acid. The figures adjacent to the experimental points give the measured recoveries in %. The recoveries at the first point at 25 and 40° were 92 and 94%, respectively. The values of the time in the results at 40° have been multiplied by 4.

Action of Hydrogen Fluoride

In the investigation of the effect of hydrogen fluoride upon 2-butanol, liquid anhydrous hydrogen fluoride was poured into the alcohol contained in a copper beaker cooled with ice. The beaker was covered with a copper plate for the reaction period. The contents of the beaker were then poured on ice, neutralized with potassium hydroxide and saturated with potassium carbonate. The alcohol layer was steam-distilled and treated as previously described.

TABLE III

ACTION OF HYDROGEN FLUORIDE ON 2-BUTANOL

Moles of $C_4H_{10}O$	Molar ratio $HF/C_4H_{10}O$	Temp., °C.	Time, hours	Re-covery, %	β/β_0
0.466^d	1.57	8	4	91	
.400^d	2.50	15	8	87	
.162^e	3.89	16	5^a	69	0.982
.162^f	4.63	15	3^b	49^c	.770

[a] At the end of the reaction period the beaker and contents weighed 4.3 g. less than initially.   [b] Loss as above, 3.5 g.   [c] This sample was fractionated in the small 25-plate column. The rotation was unchanged.   [d] Inactive alcohol.   [e] β^{26}_0 +5.29°.   [f] β^{23}_0 −2.22°.

With 0.40 mole of inactive 2-butanol and 2.0 moles of hydrogen fluoride, a little upper layer appeared in forty-five minutes. The total reaction time was six hours at 15°. The unchanged alcohol and polymer were separated by treatment with 33% sulfuric acid. The recovered alcohol amounted to 35%; the polymer to 12% by weight of the initial alcohol.

With 0.40 mole of dl-alcohol and 4.4 moles of hydrogen fluoride, vigorous boiling occurred twenty seconds after

(7) Francis, Ind. Eng. Chem., 18, 821 (1926).

mixing and considerable upper layer appeared. Some material was lost by overflow. After eight hours at 15° the mixture was neutralized with potassium hydroxide and the upper layer thrice washed with water. The yield was 52% by weight, $n^{20}D$ 1.4469. An attempt was made to distill the polymer. The material started to boil at about 140°. At 170° the material turned dark brown and copious clouds of hydrogen fluoride were evolved.

A repetition of the above experiment in which the alcohol was kept in ice throughout the addition of the hydrogen fluoride produced but 50% yield of polymer. There was no boiling and no loss.

Action of Phosphoric Acid

The procedure with phosphoric acid followed that with sulfuric acid. The results are tabulated in Table IV.

TABLE IV

ACTION OF PHOSPHORIC ACID ON l-2-BUTANOl.[a]

Moles of $C_4H_{10}O$	Moles of H_3PO_4	Moles of H_2O	Temp., °C.	Time	Moles of C_4H_8	Recovery, %	β/β_0
0.024	0.035	0.033[b]	100	20 min.	0.0009	95	0.983
.0265	.0364	.00	100	20 min.	.0014	89	1.002
.0253	.070	.067[b]	25	43 hrs.	....	97	1.002
.0254	.0842	.00	25	3 days	....	45	.937
.0245	.0958	.00	25	6 days	....	0	

[a] $\beta^{20}D$ −3.83. [b] Corresponds to 85% phosphoric acid.

A mixture of 0.0272 mole of dl-2-butanol and 0.224 mole of 100% phosphoric acid was prepared. After about five days an upper layer began to appear which amounted to 0.2 cc. in about ten days, 0.4 cc. in three weeks and 1.0 cc. in two months.

Discussion

In their general action with 2-butanol, sulfuric acid and hydrogen fluoride resemble one another. The divergences exhibited by phosphoric acid must result at least in part from its lower activity.

Sulfuric Acid.—Variation in temperature and concentration can lead to several different reactions in mixtures of sulfuric acid and 2-butanol: (1) racemization; (2) evolution of butylene; (3) polymerization; (4) ether formation; (5) formation of s-butylsulfuric acid; and in the presence of aromatic hydrocarbons, (6) alkylation.

No ether formation was observed under the conditions employed in this research, but Drake and Veitch[8] found the ether to be formed with 75% acid under pressure at 80° along with the dipolymer of butylene.

Butylene *evolution* was not observed in any mixture of sulfuric acid and 2-butanol at 40° or less. However, at 100°, butylene is evolved from mixtures in which the acid–alcohol molar ratio much exceeds 0.1 with concentrated acid or a somewhat larger value when more water is present.

An excess of concentrated sulfuric acid acting upon alcohols above ethanol leads to the production of polymers.[9] An upper layer is formed which consists very largely of saturated hydrocarbons. The lower layer contains highly unsaturated substances. The number of carbon atoms in the hydrocarbons in the upper layer has been found not to be confined to integral multiples of the number of carbon atoms in the alcohol.

In our research the critical molar ratio (with concentrated acid) for the production of polymers was found to be about 1.5. With a ratio of 1.74, polymer formation stops when the quantity of polymer reaches one-fifth that obtained with larger ratios. The cessation is undoubtedly due to dilution of the acid with water formed in the dehydration. With a ratio of 3.5 the production of polymer is complete. An optically inactive product results from an optically active 2-butanol. However, if the acid–alcohol mixture is diluted shortly after it is prepared and before polymer formation starts, the recovered alcohol has nearly its original rotation.

The alkylation of benzene[10] by 2-butanol and sulfuric acid proceeds with an acid–alcohol ratio of 1.1 at 53°, conditions distinctly less drastic than those for dehydration–polymerization and at a temperature lower than that at which butylene is evolved. With an optically-active alcohol the resulting s-butylbenzene is nearly but not quite racemic. The fractional retention of configuration is 0.0034.

Racemization is more rapid than dehydration, polymerization or alkylation. Like the other reactions its rate is increased by an increase in temperature and by an increase in the acid–alcohol ratio and is decreased by the addition of water. It is of interest to note that Meth[11] in the course of resolving 2-butanol via the brucine salt of s-butylsulfuric acid, observed the inactivity of the barium salt of s-butylsulfuric acid recovered after one day's standing at room temperatures from a solution of a sample of 2-butanol of slight activity in sulfuric acid.

As Figs. 1 and 2 exhibit, the racemization of alcohol in approximately equimolar acid–alcohol mixtures is first-order with respect to the optically active alcohol. There is, however, a short initial

(8) Drake and Veitch, THIS JOURNAL, **57**, 2623 (1935).

(9) Oddo and Scandola, *Gazz. chim. ital.*, **39**, 11, 44 (1911); *C. A.*, **5**, 879 (1911); Ormandy and Craven, *J. Soc. Chem. Ind.*, **47**, 317–320T (1928).

(10) Burwell and Archer, THIS JOURNAL, **64**, 1032 (1942).

(11) Meth, *Ber.*, **40**, 695 (1907).

period in which the reaction appears slower. This initial lag, while small, occurs in all of the rate studies and is too large to be accounted for as an erroneous assumption of zero time.

From the straight sections of the plots in Figs. 1 and 2 the results in Table V have been calculated. The reaction constants are expressed in moles/liter/sec., the calculated activation energies in kilocalories.

TABLE V

RATE CONSTANTS AND CALCULATED ACTIVATION ENERGIES FOR THE RACEMIZATION OF 2-BUTANOL BY SULFURIC ACID

	95.6% acid		86.6% acid	
t, °C.	k	E, kcal.	k	E, kcal.
0	2.84×10^{-6}	21.3		
25	7.65×10^{-5}	22.1	1.20×10^{-5}	23.8
40	4.54×10^{-4}		8.20×10^{-5}	

The recoveries as exhibited by Figs. 1 and 2 decrease with time and reach a value stationary to within the experimental error at a point where the ratio β/β_0 is about 0.5. The recovery appears to decline slightly with increasing temperature and with decreasing concentration of water.

The material lost as alcohol appears during the recovery process as butylene. But even if the acid is diluted before the alcohol is added a small quantity of butylene is formed. Since the rate of hydrolysis of alkylsulfuric acids is slow in acid solution, probably the appearance of butylene is to be ascribed to the competitive reactions of hydrolysis and decomposition of the acid sulfate. If this is true, the equilibrium

$$CH_3CHOHC_2H_5 + H_2SO_4 \rightleftarrows C_4H_9OSO_3H + H_2O$$
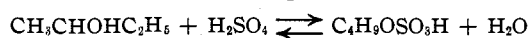
is attained about the time the alcohol is half racemized.

Robey[12] has shown that mixtures of appropriate quantities of 2-butanol, water and sulfuric acid become indistinguishable from those prepared from butylene, water and sulfuric acid. With a mixture representable as 1.00 mole of alcohol, 1.42 moles of acid and 0.94 mole of water, no alcohol is extractable by immiscible solvents. At equilibrium, which is substantially attained in five to ten hours, but 30–35% of the alcohol is present as butylsulfuric acid; the remainder is presumed present in the ion $C_4H_9OH_2^+$.
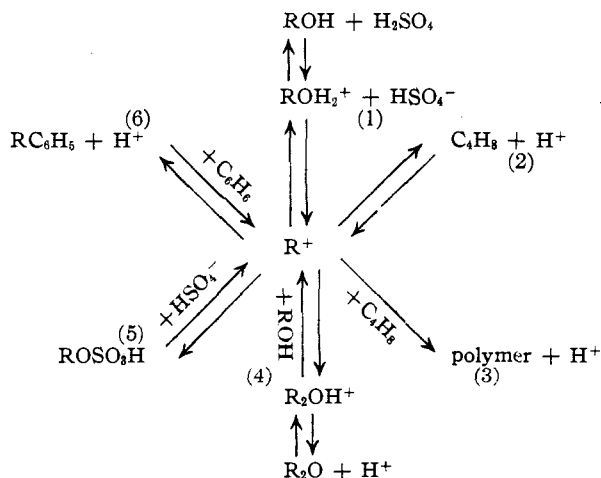
In the reaction

$$CH_3CHOHC_2H_5 \rightleftarrows CH_3—CH=CH—CH_3 + H_2O$$
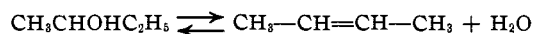
the position of equilibrium at 100° in the presence of concentrated sulfuric acid corresponds to a

concentration of butylene high enough to permit its rapid evolution. Therefore, even at 0° its concentration at equilibrium cannot be wholly inappreciable. Its odor was evident in all equimolar mixtures of concentrated acid–alcohol which had stood awhile. In the experiments investigating the loss in recovery an initial quantity was evolved almost immediately. The concentration of butylene at equilibrium cannot be greater than 1% as shown by the bromate–bromide titration. The dynamic establishment of equilibrium in this reaction necessitates the ultimate racemization of the alcohol.

As the data in Table I show, with 76.8% acid in five minutes, 6.3% of the alcohol was dehydrated, 99% racemized. No definite decision can be reached from these data as to whether the gross rates of dehydration and rehydration can so far exceed the rate of butylene evolution that such extensive racemization can accompany such slight net dehydration. However, the rate of racemization is so much faster that another mechanism would appear likely. If butylene were the intermediate in the racemization, then deuterosulfuric acid should introduce a deuterium atom on the 3-carbon atom as fast as it racemizes the alcohol. Such an investigation is projected.

The concept of a positive ion intermediate which was introduced by Whitmore[13] as a mechanism for polymerization reactions has been employed in other related reactions.[14] It would appear possible to explain all of the reactions occurring in mixtures of sulfuric acid and optically active 2-butanol on such a basis.

(12) Robey, Ind. Eng. Chem., 33, 1076 (1941).

(13) Whitmore, ibid., 26, 94 (1934).

(14) A general discussion is given by Hammett, "Physical Organic Chemistry." McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter X.

In these proposed reactions, (1) allows race-mization, (2) evolution of butylene, (3) polymeri-zation, (4) ether formation, (5) formation of s-butylsulfuric acid, and (6) alkylation. The hydrogen ions set free must immediately react or be solvated. Alternatively the reactions may involve reaction with a proton acceptor (HSO_4^-).

In reaction (1) it is assumed of course that the free R^+ is incapable of maintaining configuration. Thus racemization follows from the establishment of the indicated equilibria.

Reaction (3) is much more complex than indi-cated. The indicated reaction would presumably be the first step in the "cojunct polymerization."

In reaction (6) the problem of activation of benzene has been ignored.

The fact that equilibrium seems to obtain in the formation of s-butylsulfuric acid by the time the alcohol is but half racemized indicates that the ion R^+ reacts with HSO_4^- so soon after its forma-tion that there is but partial racemization in the formation of the alkylsulfuric acid. It is, there-fore, dubious whether one should think of the ion R^+ as having any real, independent existence. One could replace all of the reactions written above as involving the carbonium ion intermedi-ate with bimolecular reactions with ROH_2^+. As the average life of R^+ decreases it becomes diffi-cult to distinguish between the reactions

$$ROH_2^+ + HSO_4^- \longrightarrow RSO_4H + H_2O$$
$$ROH_2^+ \longrightarrow R^+ + H_2O$$
$$R^+ + HSO_4^- \longrightarrow RSO_4H$$
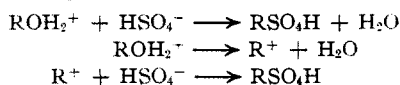
In a bimolecular reaction pattern racemization would presumably enter by Walden inversions of the type

$$HSO_4^- + RSO_4H \longrightarrow HSO_4R + SO_4H^-$$
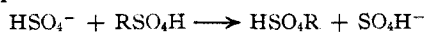
In a mixture of 2-butanol and sulfuric acid, at equilibrium with respect to the formation of s-butylsulfuric acid, one can readily understand that the racemization would proceed as a first order reaction with respect to the concentration of the optically active alcohol. However, if the composition of the solution is changing with time—as the recoveries demonstrate—until β/β_0 is about 0.5, why should the reaction be first order from the point where β/β_0 equals about 0.85? This is intelligible if, as is likely, the s-butylsul-furic acid is as effective a proton donor as sulfuric acid, and if 2-butanol allows the production of HSO_4^- to about the same degree as water. In other words, the reaction

$$ROH_2^+ + H_2SO_4 \longrightarrow ROSO_3H + H_2O$$
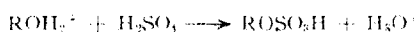
changes the nature of the reaction medium in-sufficiently to affect the rate of formation and reaction of R^+. The small initial lag in the reac-tion rate probably results from the fact that this statement is not quite true.

Hydrogen Fluoride.—The general action of anhydrous hydrogen fluoride is similar to that of sulfuric acid save that the effective molar ratio of catalyst to alcohol must be increased from about 1 to 5. The range of concentration in which racemization occurs but polymerization does not is much more restricted than with sulfuric acid. The polymer contains certain quantities of fluo-ride. It was not found whether the polymer is simple or whether it contains hydrocarbons, the numbers of carbon atoms in which may be other than simple multiples of four.

Because of the technique necessitated by the corrosive nature of anhydrous hydrogen fluoride, the extent of recovery could not be determined with high precision. However, as Table III ex-hibits, recoveries steadily declined with increasing concentrations of hydrogen fluoride. The reac-tions were run in copper beakers covered loosely with a copper plate. The loss in weight during the reaction period is quite incapable of account-ing for the low recoveries. The loss in weight must largely have consisted of hydrogen fluoride in any case.

An accounting of such large losses at 16° as butylene formation would appear unreasonable. The formation of s-butyl fluoride would, however, appear likely. Fredenhagen[15] has shown that no measurable quantities of alkyl fluoride are formed under similar conditions from methyl or ethyl alco-hols but that water under such conditions converts the alkyl fluoride to alcohol. However, with a secondary alcohol the position of equilibrium would be much more likely to favor the fluoride (which would be lost in the recovery of the alcohol).

The general set of reactions in the presence of hydrogen fluoride may be explained by a mech-anism similar to that employed with sulfuric acid. A slight concentration of butylene at equilibrium must be assumed to allow polymerization. The close analogy with sulfuric acid would support this assumption. The formation of R^+ proceeds as with sulfuric acid

$$ROH + HF \rightleftharpoons ROH_2^+ + F^-$$
$$ROH_2^+ \rightleftharpoons R^+ + H_2O \; (+ HF \longrightarrow H_3O^+ + F^-)$$
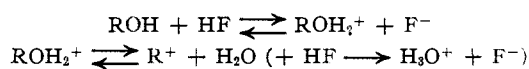
(15) Fredenhagen, Cadenbach and Klatt, Z. physik. Chem., **A164**, 188 (1933).

This process allows racemization. The ion R$^+$ could form butylene by a proton loss, polymer by reacting with butylene, s-butyl fluoride by reaction with F$^-$ or s-butylbenzene by reaction with benzene.

There is one important failure of the analogy with sulfuric acid: the ester, which in the case of sulfuric acid is as strong a proton donor as the free acid, is in this case a neutral substance. Therefore, the effective molar ratio of hydrogen fluoride to alcohol must be much larger than the acid–alcohol ratio in the case of sulfuric acid. Similar increase in the molar ratio necessary for alkylation is reported.[10]

Phosphoric Acid.—The behavior of phosphoric acid was not studied extensively but the data presented here show that it diverges considerably from that of sulfuric acid. At 100° with sulfuric acid, butylene is evolved from mixtures of phosphoric acid—2-butanol in which the molar ratio is of the order of 1; but, as an examination of Tables I and IV exhibits, with equal degrees of dehydration the recovered alcohol in the case of phosphoric acid is wholly unracemized whereas with sulfuric acid it was 99% racemized.

At 25° with an acid–alcohol ratio of about 4, the recovered alcohol after three days is but slightly racemized. The recovery is but 45%. After six days the recovery falls to zero.

Ormandy and Craven[16] reported that upper layers appeared upon heating mixtures of higher alcohols and phosphoric acid. These[16] are largely olefinic in character, are simple polymers of the corresponding olefins and are produced under conditions under which the free olefin is not polymerized.

In the present communication it is shown that the polymer can be formed at room temperature but that the reaction required weeks for completion.

(16) Ormandy and Craven, *J. Soc. Chem. Ind.*, **48**, 291T (1929).

These divergences from the behavior of sulfuric acid result apparently from two causes: the weaker acidity of phosphoric acid and the very slow formation and hydrolysis[17] of the ester. The latter point explains the declining recoveries, since the ester would not be hydrolyzed under the conditions of the recovery. The latter point also implies that the monoalkylphosphate has much less tendency to ionize

$$ROPO_3H_2 \rightleftharpoons R^+ + OPO_3H_2^-$$
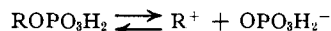
than has the monoalkyl sulfate.

Summary

Sulfuric acid racemizes optically active 2-butanol under conditions less drastic than those which promote alkylation, polymerization, or butylene evolution.

The racemization is first order in respect to the optically active alcohol and decreases with increasing concentration of water. The calculated activation energies are about 22,000 calories.

By means of the carbonium ion hypothesis the racemization has been correlated with the other reactions which may occur in mixtures of 2-butanol and sulfuric acid: butylene evolution, dehydration-polymerization, ether formation, alkylation, and formation of s-butylsulfuric acid.

Large molar ratios of hydrogen fluoride or phosphoric acid to 2-butanol lead to the formation of polymers.

The behavior of mixtures of optically active 2-butanol and hydrogen fluoride resembles those with sulfuric acid and is similarly interpretable. However, much larger ratios of acid–alcohol are required with hydrogen fluoride.

Racemization produced by phosphoric acid under any condition studied is slight.

(17) Cavalier, *Ann. chim. phys.*, [7] **18**, 485 (1899); Plimmer, *Biochem. J.*, **7**, 75 (1913).