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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Hydrolysis of Optically Active Secondary Butyl Hydrogen Sulfate¹

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At 100° (+)sodium *s*-butyl sulfate hydrolyzes slowly in basic solutions to give an alcohol of inverted configuration. Since the rate is nearly independent of the hydroxide ion concentration, a rearward displacement of sulfate ion by a water molecule seems to be involved. In acidic solution, a much more rapid hydrolysis leads to a partially racemized alcohol of retained configuration. The degree of racemization of the 2-butanol is influenced by the acid employed as catalyst and by other conditions. The fraction of the alkyl sulfate diverted to butylene varies similarly.

Hydrolysis of dextrorotatory salts of *s*-butyl hydrogen sulfate yields (+)2-butanol² in acid solution, but (–)2-butanol in basic solution.³ Such an apparent change in mechanism is rare, particularly for singly substituted alkyl derivatives, and therefore the stereochemistry of the hydrolysis as a function of the acidity of the solution has been

studied in detail. Interpretation of results has been facilitated by the recent demonstration⁴ that (+)2-butanol is most probably configurationally related to (+)sodium *s*-butyl sulfate.

Experimental

(+)Sodium *s*-butyl sulfate was prepared from partially resolved (+)2-butanol.⁴ Recovered alcohol was equilibrated with a saturated solution of potassium carbonate dihydrate⁵ before polarimetry. Configurations were correlated by equating optically pure (+)2-butanol, $[\alpha]_D^{25} +10.97^\circ$, to optically pure (+)sodium *s*-butyl sulfate, $[\alpha]_D^{25} +10.7^\circ$ (aqueous solution, *c* 26).⁴

Hydrolysis Apparatus.—Hydrolyses were run in the apparatus shown in Fig. 1. Reactants were added through B. Flask A was either heated directly by a micro-burner or immersed in a steam-bath and the riser tube C-D heated by a winding of Nichrome ribbon, in each case to such a degree that a mixture approximating the alcohol-water azeotrope could just distill out. The volume of the distillate

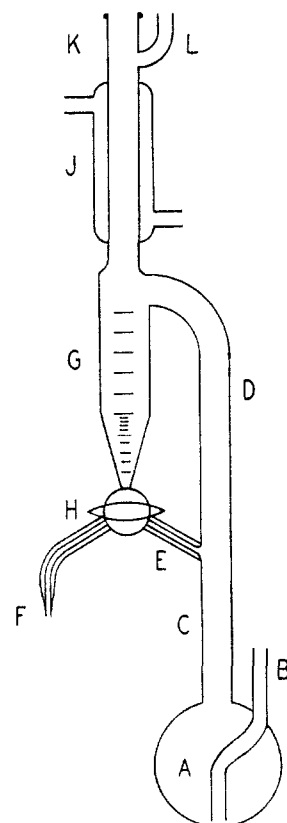


Fig. 1.—Hydrolysis apparatus.

(commonly two phase with the alcohol rich phase in greater proportion) was measured in the receiver G prepared from a graduated 12-cc. centrifuge tube. Outlet L was connected to a gas buret.

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September 21, 1949.

(2) R. L. Burwell, Jr., *THIS JOURNAL*, **67**, 220 (1945).

(3) R. L. Burwell, Jr., and H. Holmquist, *ibid.*, **70**, 878 (1948).

(4) R. L. Burwell, Jr., *ibid.*, **71**, 1769 (1949).

(5) R. L. Burwell, Jr., *ibid.*, **64**, 1025 (1942).

For slow reactions ($t_{1/2} > 1$ day), heating on a steam-bath was satisfactory but for more rapid reactions the rate of alcohol collection fell behind. Where the solution in A was kept refluxing, however, it was possible to keep the alcohol and butylene contents of the reaction flask at very low values even for reactions whose time of half reaction was as little as five minutes. Rates of reaction, crude but nevertheless useful, could, thus, be obtained in addition to the primary stereochemical data.

Experimental Results.—Results of hydrolysis runs are presented in Table I. The amount of sodium *s*-butyl sulfate employed varied between 0.023 and 0.037 mole. All of the runs in acid solutions were at the former figure. Precision in alcohol yield is about 4 percentage points; in butylene yield, about 2; and in optical purity, 0.5% or better.

The ethanesulfonic acid which was employed was obtained from the Indoil Chemical Company. In computations it was assumed pure but it was reported to contain 1% sulfuric acid.

Run 20.—A solution of 0.156 mole of sodium hydrogen sulfate, 0.078 mole of sodium sulfate, 0.0227 mole of (+)sodium *s*-butyl sulfate and 4.18 moles of water was refluxed 37 minutes and rapidly cooled. 6.3% alcohol and 4.4% butylene were evolved. The reaction mixture was neutralized with sodium hydroxide and extracted with methanol to give 82% of the original alkyl sulfate, optical purity +94.9%. The optical purity of the 2-butanol was –39% as found by weight dilution with inactive material to give enough material to examine. Recovered alkyl sulfate, made up into a solution of the same mole fraction composition as before, was refluxed 234 minutes to give alcohol, 34%, optical purity –31.6%; butylene, 14%; recovered alkyl sulfate, 34%; optical purity +66%. Upon ignition of the recovered alkyl sulfate followed by re-ignition with a drop of sulfuric acid, a weight loss of 56.9% was observed. The theoretical is 59.6%. If the only impurity was sodium chloride, it would, thus, amount to 3.4%. The optical purity of the recovered sodium *s*-butyl sulfate would then be +68%.

Run 21.—A sulfuric acid solution identical to run 9 was refluxed for 12 minutes and processed similarly. Alcohol amounted to 37%, optical purity +15.3%; recovered salt amounted to 26.5%; optical purity +77.3%. Loss on ignition was 57.2%. Chloride (inadvertently introduced during neutralization with sodium hydroxide which contained chloride) was found in the recovered salt. If all impurity was sodium chloride, it would amount to 3.1% and corrected optical purity of recovered alkyl sulfate would be 80%.

Table II presents initial rates of dehydration of 2-butanol by sulfuric acid and by ethanesulfonic acid as measured by the rate of gas evolution with solutions of the indicated composition held at reflux. The initial boiling point is given but this presumably rises as the alcohol concentration declines. Several similar mixtures were prepared from (+)2-butanol. When about 21% of the stoichiometric quantity of butylene had been evolved, a sample of alcohol was rapidly distilled from the mixture by slightly increasing the heating. Its optical purity was then determined as given in the last column of Table II.

Discussion

The hydrolysis of optically active sodium *s*-butyl

TABLE I
 HYDROLYSES OF SODIUM *s*-BUTYL SULFATE

Run no.	Cmpd. A	Molality Cmpd. A	NaC ₄ H ₉ SO ₄	Temp., ^a °C.	Yield alc., mole %	Optical ^b purity, alc.	Yield C ₄ H ₉ S, mole %	Rate t _{1/2}
1	NaOH	5.0	0.91	99	54	-94	7	20 hours
2	K ₂ CO ₃	5.4	.92 ^c	99	58	-97	9	30 hours
3		2.7	.44	B.p.	65	-96	°	14 hours
4	KHCO ₃	5.0	.92	99	69	..	f	26 hours
5	Mg(OH) ₂	1.4 ^d	.74	B.p.	0-25 25-43 43-52	-87 -89 ..	°	24 hours
6	H ₂ SO ₄	0.50	.91 ^h	99	77	+30	13	1 hour
7		0.127	.37	99	0-30 30-55 55-69	+18 +11 -11	7
8		1.05	.30	101	0-35 35-65	+19 +15	13	26 min.
9		2.3	.68	103	0-34 34-56	+15 +4	22	10 min.
10		5.7	1.66	111	46	+11	48	25 min.
11		2.3 ⁱ	0.67	B.p.	0-33 33-54	+7 +1	29	7 min.
12		1.33 NaHSO ₄	2.3	B.p.	0-24 24-60	+41 +18	21	7 min.
12A		2.3	2.3	99	63	+30	16	19 min.
12B ^k		2.3	2.3	99	57	+28	..	18 min.
13	H ₃ PO ₄	4.8	1.59	B.p.	52	..	40	26 min.
14 ^m	C ₂ H ₅ SO ₃ H	2.3	0.68	103	0-30 30-62	+45 +41	11	16 min.
15		5.7	1.67	108	74	+62	15	4 min.
16		5.7	1.67	99	"	+60	15
18	C ₇ H ₇ SO ₃ H	2.3	0.68	B.p.	78	..	9	16 min.
19		5.7	1.67	108	74	+72	13	3.5 min.

^a If 99°, heating by steam-bath was employed; any other entry indicates that the mixture was kept refluxing at atmospheric pressure. Where the temperature of the boiling solution was not measured, "b.p." is entered. ^b The % of maximum rotation is listed, + if of the same configuration, - if of the opposite. If no entry is given, the starting material was racemic. ^c In more protracted runs with inactive alkyl sulfate, yields of 72% resulted. Similar results were obtained by running at reflux. Addition of KI to a molality of 0.3 had no effect on rate. ^d Present as a separate phase. Powdered, freshly precipitated Mg(OH)₂ was kept well suspended by the refluxing. The pH of a suspension at 25° was 7.8. Added sulfuric acid was rapidly neutralized. ^e Not measured. ^f At 100°, KHCO₃ solutions liberate CO₂. The butylene yield was not measured. ^g Not measured but in a similar experiment with inactive material, 7% of butylene resulted. ^h The reaction mixture was prepared from (+)barium *s*-butyl sulfate, the precipitated BaSO₄ being centrifuged out. Thus, this figure gives molality of *s*-C₄H₉SO₄H. ⁱ NaHSO₄ was also present, two moles per mole of NaC₄H₉SO₄. ^j In this experiment, 2-butene (Phillips Petroleum Co., 95%) was fed into inlet tube B of the apparatus of Fig. 1 at 50 cc. (S.T.P.) per minute. Tube L was connected to a mercury blow-off with 17 cm. head. The process proceeded at 17 cm. of mercury, gage. Rates of appearance of alcohol were almost identical with those of run 12A. Following completion of the hydrolysis, no detectable quantities of 2-butanol were collected. ^m A similar experiment in which barium ethane sulfonate was added to precipitate sulfuric acid as rapidly as it was formed gave a similar yield and optical purity of alcohol. ⁿ The reaction mixture was heated on the steam-bath 24 min., diluted and distilled. A 65% yield of alcohol was obtained but no attempt was made to recover it all.

 TABLE II
 DEHYDRATION AND RACEMIZATION OF SECONDARY BUTYL ALCOHOL

Run no.	Acid	Water	Moles Acid	Alcohol	Initial b.p., °C.	Fraction alcohol dehydrated per min.	Optical purity recovered alcohol, %
22	H ₂ SO ₄	1.16	0.092	0.022	97	0.0019	
23 ^a		1.16	.092	.022	97	.0019	42.5
24		1.10	.104	.0220050	
25		1.00	.122	.022	105	.0165	
26 ^b		1.00	.122	.022	105	.0165	59.3
27		0.84	.151	.022	108	.060	
28	C ₂ H ₅ SO ₃ H	0.79	.144	.022	107	.006	
29 ^c		0.79	.144	.022	107	.006	68.8

^a The refluxing was stopped when 21.9% of the alcohol had been dehydrated and the rotation of the recovered alcohol was found. ^b Similarly at 20.8%. ^c Similarly at 20.5%.

sulfate in basic solution leads to *s*-butyl alcohol of

inverted configuration and of almost unchanged optical purity. In acidic solutions, the reaction has the unusual feature of proceeding with retention of configuration accompanied by considerable racemization. Although both processes have unusual features the reaction in acidic solutions seems to be much the more complicated.

Hydrolysis in Basic Solution.⁶—As shown by runs 1-5 in Table I, *s*-butyl alcohol resulting from hydrolysis in basic solution is of inverted configuration and substantially unracemized. Linhart⁷ reported that the hydrolysis of sodium ethyl sulfate in solutions of sodium hydroxide is second order. Ordinarily then, one would assume⁸ that the saponification of sodium *s*-butyl sulfate

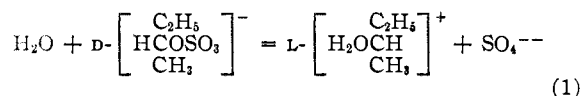
(6) Dr. Howard Holmquist ran certain preliminary experiments in connection with run 1 as reported in his Senior Honors Thesis, 1947.

(7) G. A. Linhart, *Am. J. Sci.*, **185**, 283 (1913); see also G. H. Green and J. Kenyon, *J. Chem. Soc.*, 1389 (1950).

proceeded by a standard bimolecular displacement reaction (SN₂) involving attack of the hydroxide ion on the *s*-butyl sulfate ion and resulting in inversion of configuration.

However, runs 1, 2, 4 and 5 proceeded at nearly the same rate; the half-lives cannot have varied from 24 hours by a factor of more than two or three in spite of change in the concentration of the hydroxide ion by a factor of one million. Unpublished work in this Laboratory⁸ shows that the hydrolysis of sodium isopropyl sulfate is substantially independent of hydroxide ion concentration at 99° in sodium hydroxide solutions of 0.025 to 0.25 molarity.

The probable mechanism of the basic hydrolysis is the following bimolecular displacement mechanism (SN₂)



in which water rather than hydroxide ion is the displacing species. This is interesting as an example of a first order SN₂ reaction. The very large ionization constant of *s*-butyl hydrogen sulfate would seem to eliminate the otherwise kinetically and sterically satisfactory mechanism in which an hydroxide ion attacks *s*-butyl hydrogen sulfate. The hydrolytic behavior of *s*-butyl sulfate anion differs considerably from that of esters of carboxylic acids where the saponification proceeds enormously more rapidly than uncatalyzed water solvolysis. A similar, though less extreme, relatively rapid solvolysis occurs with another non-carboxylic ester, ethyl *p*-toluenesulfonate.⁹

Hydrolysis in Acidic Solutions.—Hydrolysis is much faster in acidic solutions than in basic ones and increases in rate with acid concentration.¹⁰

The alcohol produced is of the original configuration but considerably racemized. The sodium *s*-butyl sulfate is somewhat racemized prior to reaction but, as run 21 exhibits, the degree of this racemization is slight compared to that of the alcohol formed. Since butylene also appears as a reaction product, the racemization might result from some alcohol being formed from butylene as an intermediate. Or, the alcohol might be racemized after its formation. To reduce the possibility of these two means of racemization, hydrolyses were usually run at reflux to remove liberated alcohol and butylene rapidly from the system and to keep their concentrations low.

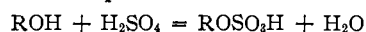
Comparison of runs 12, 12A and 12B (hydrolysis of 2.3 *m* sodium *s*-butyl sulfate in 2.3 *m* sulfuric acid) demonstrates the unlikelihood of butylene being involved as an intermediate to any significant extent. The first two runs differ only in that the first was run at reflux, the other at steam-

bath temperatures. Owing to the absence of boiling, butylene was evolved much more slowly in the second case and, since its average concentration in the solution would have been higher, the fraction hydrated should have been greater. The optical purities of the alcohols were 27 and 30%, respectively. The difference is slight and opposite to that which should occur if hydration of butylene occurs to any extent. Similarly in run 12B, which was like 12A save that butylene was bubbled through the reaction mixture during hydrolysis, the optical purity of the recovered alcohol was nearly the same, 28%. In the later case, the absence of butylene hydration was observed directly since alcohol evolution stopped at customary yields even though passage of butylene through the reaction mixture was continued.

s-Butyl alcohol is racemized in refluxing solutions of sulfuric acid of rather high acidity (runs 23 and 26) but the rate is far too slow to account for the observed racemization of the hydrolytic product of runs 6–12. For example, in run 23 in 4.3 *m* sulfuric acid, racemization of *s*-butyl alcohol present as such amounted to 57.5% in 112 minutes whereas, in the hydrolytic experiments run at reflux, the half-life of the alcohol in the solutions subsequent to its formation could have amounted to no more than 1 minute. Thus, the contribution to the total racemization of racemization of alcohol after it is formed is negligible.

Accordingly, the heavy racemization of the product alcohol cannot be accounted for by preliminary racemization of the reactant, by subsequent racemization of the product nor by any reaction proceeding in large part *via* the optically inactive butylene.

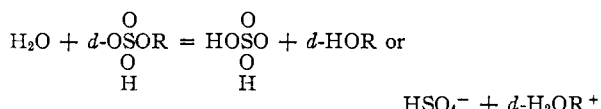
The slow racemization of *s*-butyl alcohol in solutions of sulfuric acid probably results from the establishment of equilibrium in the reaction



Since the reverse of this reaction leads to racemization, the forward one must too.

Mechanism of Acid Hydrolysis.—In singly substituted alkyl derivatives, reactions involving retention of configuration plus racemization are rare. If retention is taken as implying that no bond attached to the optically active carbon atom is broken then at least two simultaneous hydrolytic processes must be involved: one proceeding with retention of configuration and no racemization and at least one leading to the observed partial racemization.

The reaction involving retention must closely resemble



This involves displacement on sulfur. There is no point in considering how or when the hydrogen ion is transferred¹¹ in highly conducting solutions where chain transfer of hydrogen ions may occur.

A reaction closely related to the reverse of re-

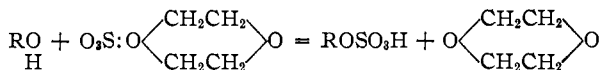
(8) L. Hellberg, Senior Honors Thesis, Northwestern University.

(9) The rate of solvolysis exceeds that of saponification at all concentrations of hydroxide ion below 0.02 *M*: H. R. McCleary and L. P. Hammett, THIS JOURNAL, 63, 2254 (1941).

(10) In 0.2 and 0.4 *M* sulfuric acid, the hydrolysis of isopropyl hydrogen sulfate is very nearly first order in hydrogen ion (Burwell and L. Grotz, unpublished). G. A. Linhart, *Am. J. Sci.*, 134, 289 (1912), reported that rates of hydrolysis of barium methyl, ethyl and propyl sulfates are approximately proportional to hydrochloric acid concentration at 0 to 1.0 *M*.

(11) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, 37, 686 (1941).

action (2) is involved in sulfation of alcohols by several sulfating agents which may be written as Lewis salts of sulfur trioxide and bases, such as dioxane-sulfur trioxide, pyridine-sulfur trioxide and sulfamic acid.⁴ They proceed with retention of configuration and without racemization. With dioxane-sulfuric acid, for example

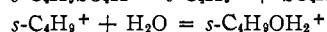
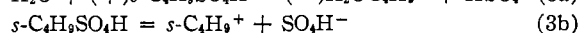
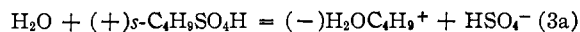


A similar situation prevails initially in sulfation in concentrated sulfuric acid since Deno and Newman¹² have shown that the first quantities of *s*-butyl hydrogen sulfate formed in mixtures of alcohol and sulfuric acid have an optical purity of nearly 100%. As has been suggested, sulfuric acid may conveniently be considered to react as $\text{H}_2\text{O}:\text{SO}_3$ in the same manner as dioxane-sulfur trioxide.⁴

A reaction which bears some resemblance to the over-all acidic hydrolysis is the saponification of the hydrogen phthalate of (+)-methylphenylcarbinol.¹³ This proceeds with retention of configuration and in strong solutions of sodium hydroxide with no racemization. In weak solutions, however, considerable racemization enters. In the second case, apparently, dissociation to methylphenylcarbiny carbonium ion accompanies the conventional saponification reaction. The authors, in fact, suggest similarity with the racemization of *s*-butyl alcohol by sulfuric acid.⁵

In the reaction of Balfe, *et al.*,¹³ the two simultaneous reactions have different orders. In the hydrolysis of *s*-butyl hydrogen sulfate, any two such reactions must be assumed to have approximately the same order since the degree of racemization of product alcohol varies but slightly with considerable variation in acid concentration (runs 8, 9 and 10).

At least in dilute acid solution, the hydrolysis is apparently second order: proportional to hydrogen ion concentration and to alkyl sulfate anion. Reaction (2) which involves retention of configuration is of this type since the concentration of the free alkyl hydrogen sulfate is proportional to these same quantities. Among possible reactions of the same order which could lead to partial racemization one might think first of the bimolecular displacement by water on the free acid, or the dissociation of the free acid to a carbonium ion and bisulfate ion. The first of these would involve inversion without racemization, the second, presumably, inversion and racemization.



To accord with the observed retention of configuration, reaction (2) must be assumed to preponderate over reaction (3). It is a little disturbing that, save for the third fraction in run 7, in very dilute acid where reaction (1) might be involved, no examples of inverted configuration appear in spite of

(12) N. C. Deno and M. S. Newman, *THIS JOURNAL*, **72**, 3852 (1950).

(13) M. P. Balfe, E. A. W. Downer, A. A. Evans, J. Kenyon, R. Poplett, C. E. Searle and A. L. Tátrnoky, *J. Chem. Soc.*, 797 (1946). References to similar reactions are given.

considerable variation in conditions. Reactions of a type not commonly considered may be involved. In these considerations, an activated state involving alkyl sulfate and hydrogen ions would be kinetically equivalent to free hydrogen alkyl sulfate.

The occurrence of the sulfation reaction with racemization in rather concentrated solutions of sulfuric acid at rates about the same as those of alkylation of benzene, butylene formation and conjunct polymerization made the assumption of a common intermediate carbonium ion attractive.⁵ Cryoscopic considerations seemed also to favor this.¹⁴ However, in view of the retention of configuration⁴ and the data of Deno and Newman¹² a carbonium ion reaction cannot be in general the principal reaction path in the sulfation of alcohols or in the acidic hydrolysis of primary or secondary alkyl hydrogen sulfates.

The degree of racemization of the product alcohol increases during a run and varies with acid concentration and ratio of acid to sodium alkyl sulfate. Substitution of ethanesulfonic acid or *p*-toluenesulfonic acid for sulfuric acid (run 14 *vs.* run 9 and runs 15 and 19 *vs.* run 10) results in very considerable decrease in racemization and in much less increase in racemization as the reaction proceeds. The over-all rate of the hydrolysis is, however, little changed. The origin of these effects is obscure but increased racemization in all cases is correlated with an increased proportion of bisulfate ion. The effect of bisulfate ion is particularly striking in the comparison of runs 9 and 11.

While reactions (2) and (3) are of the same kinetic order, the activated complexes differ. Since the rates of (2) and (3) must be assumed not very unequal in dilute solutions, rather minor unsymmetric medium effects could cause a considerable change in the rotation of the product alcohol.

Hydrolysis of aryl hydrogen sulfates is catalyzed by acids but no hydrolysis can be observed in strongly alkaline solutions at 150°. ¹⁵ Since substituents in the ortho-position of the benzene ring exert no steric effect, it is concluded that the sulfur-oxygen bond is broken and the hydrolysis proceeds by a process something like that of reaction (2). Any reactions of the type of reactions (1) and (3) should proceed much slower than in the case of the *s*-butyl sulfate ion because of the difficulty of displacement substitution on a benzenoid carbon atom.

Interrelations with Esters of Other Strong Acids.—An attractive feature of assuming the free acid, the alkyl hydrogen sulfate, to be the intermediate in acidic hydrolysis is the correlation introduced between reactivities of alkyl hydrogen sulfates and those of neutral esters of strong acids such as dialkyl sulfates, trichloroacetates and sulfonic acid esters. Rates of hydrolyses of these esters are independent of hydrogen ion concentration in acidic solutions¹⁶⁻¹⁸ as one might expect from

(14) M. S. Newman, *THIS JOURNAL*, **63**, 2434 (1941).

(15) G. N. Burkhardt and A. Lapworth, *J. Chem. Soc.*, 684 (1926); G. N. Burkhardt, W. G. K. Ford and E. Singleton, *ibid.*, 17 (1936).

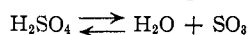
(16) R. Kremann, *Monatsh.*, **28**, 13 (1907); Ch. Boulin and L. J. Simon, *Compt. rend.*, **170**, 392 (1920).

(17) L. Demény, *Rec. trav. chim.*, **50**, 60 (1931).

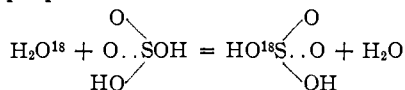
(18) R. Skrabal, *Monatsh.*, **71**, 298 (1938).

the fact that the conjugate acids of these materials should be nearly of the strength of that of the conjugate acid of sulfuric acid itself. Relatively rapid solvolysis is characteristic of these neutral esters. The rates of hydrolysis of alkyl hydrogen sulfates in strongly acidic solutions should be similar to those of dialkyl sulfates since replacement of an alkyl group by hydrogen, with its very similar electronegativity, should have no gross effect on the carbon-oxygen bond. In basic solutions much lower rates should obtain with *s*-butyl sulfate anion since it is an ester of the much weaker acid, the bisulfate ion.

Exchange Reactions.—The sulfate ion does not exchange in protracted periods at 100° with H₂O¹⁸, the bisulfate ion exchanges slowly, sulfuric acid rapidly.^{19,20} Most workers in this field have favored a mechanism involving



However, in the light of the present paper, reaction involving the hydrolysis of sulfuric acid may be proposed



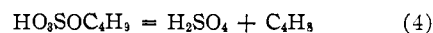
Formation of Butylene.—The fraction of *s*-butyl sulfate ion diverted to butylene during hydrolysis amounts to 0.08 in basic solution. In solutions of

(19) G. A. Mills, *THIS JOURNAL*, **62**, 2833 (1940).

(20) E. R. S. Winter and H. V. A. Briscoe, *J. Chem. Soc.*, 631 (1942).

sulfuric acid, it rises slowly to one-half in about 40% sulfuric acid. The rise in temperature of the refluxing solutions may be in part involved. In solutions of sulfonic acids, the relative rate of the elimination reaction rises much less than with sulfuric acid. There is some correlation between high positive configurations and low butylene yields.

These considerations are consistent with an intramolecular elimination reaction



In dilute acidic solutions, butylene yield changes but slowly with acid concentration. Thus, the elimination reaction probably has the same order as reactions (2) and (3). The relative balance among reactions (2), (3) and (4) would depend upon medium effects and upon the activity of the water molecule. The activated complex of reaction (4) involves a six-membered ring. If the elimination reaction proceeds by reaction (4), then, *under these conditions*, the reverse reaction, sulfation of butylene, must proceed by direct addition of sulfuric acid to butylene. An activated complex of this nature seems first to have been proposed by Hurd and Blunck.²¹

Acknowledgment.—The author is indebted to Dr. Ralph G. Pearson for several valuable discussions.

(21) C. D. Hurd and F. H. Blunck, *THIS JOURNAL*, **60**, 2419 (1938), for the decomposition of esters of acetic acid to acid and olefin. See also Hüchel, Tappe and Legutke, *Ann.*, **543**, 191 (1940), with regard to the decomposition of xanthates.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE SUGAR RESEARCH FOUNDATION, INC., AND THE EASTERN REGIONAL RESEARCH LABORATORY¹]

Acidic Constituents of Lactic Acid-Water Systems

BY REX MONTGOMERY²

A partition chromatographic procedure is described for estimating monomeric lactic acid, lactyllactic acid, lactyllactyllactic acid and higher polymers in solutions of lactic acid and dehydrated lactic acid. The procedure is applied in a study of the composition of lactic acid-water systems.

It is well known that the concentration of a dilute solution of lactic acid results in autoesterification of the monomer to produce lactyllactic acid, lactyllactyllactic acid and higher condensation polymers. The composition of aqueous lactic acid solutions and dehydrated lactic acid has been studied by several workers,³⁻⁵ and their results have been reviewed recently by Filachione and Fisher.⁶ In general, the method of analysis involved determination of free acidity, under conditions which minimized concomitant hydrolysis of the ester linkages, and total acidity after complete hydrolysis. Obviously

this method could not give the relative amounts of all the components, and it was assumed, therefore, that only monomeric lactic acid and lactyllactic acid were present. Bezzi, Riccoboni and Sullam³ greatly extended our knowledge by a study which included determination of the dissociation constants of lactyllactic acid and the polylactic acids, and the kinetics of hydrolysis of these esters and lactide. Their results furnished more accurate data on the composition of lactic acid-water systems: they concluded that lactide was present in trace amounts only. However, the proportion of each component, with the possible exception of the monomer, could not be derived. Even in dilute solutions, polyesters were present, their average degree of polymerization being 2.0 in very dilute solutions. The degree of polymerization increased gradually to 2.6 in 95% solution and then rapidly to 6.5 in 118% total available lactic acid. It is apparent, therefore, that analyses by the general method described above decreases in accuracy as the concentration of the lactic acid increases.

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(2) University of Minnesota, Department of Agricultural Biochemistry, St. Paul 1, Minnesota.

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