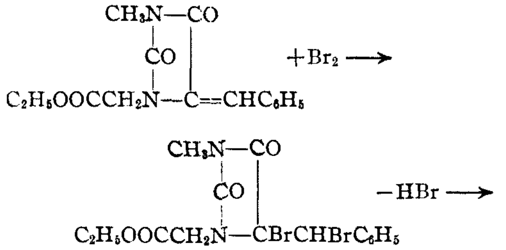
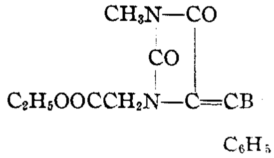
warmed with dilute aqueous sodium hydroxide it slowly hydrolyzes to form a salt. While the complete elucidation of the chemistry of this substance depends upon a more detailed investigation of its derivatives, it seems probable that its formation takes place in the following way.[17]





Summary

The existence of geometrical isomerism in the hydantoin series has again been demonstrated. The substances described together with their various derivatives may all be transformed under the action of various reagents into β-phenylalanine-acetic acid.

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[17] Compare Limpricht, *Ann.*, **165**, 265 (1873); Rupe, *Ann*, **256**, 18 (1890).

SOUTH HADLEY, MASS. RECEIVED OCTOBER 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Quantitative Study of the Reaction between Some Primary Aliphatic Alcohols and Sulfuric Acid

BY C. M. SUTER AND ELMER OBERG[1]

It has been shown by other investigators that the reaction between sulfuric acid and a primary aliphatic alcohol at ordinary temperatures gives only the mono-alkyl ester regardless of whether the acid[2] or the alcohol[3] is present in excess. Quantitative studies of the equilibrium involved in this reaction have, however, been limited to ethyl alcohol.[4] It therefore seemed desirable to compare the extent of ester formation in the reaction of several common aliphatic alcohols with sulfuric acid of various concentrations and to determine the optimum conditions for preparing the corresponding alkyl hydrogen sulfates. The salts of the latter are of value in some alkylation reactions such as the preparation of mercaptans and sulfides[5] and the higher members of the series have become commercially valuable as detergents.

The alcohols studied include the primary straight chain alcohols through *n*-hexyl, ethylenechlorohydrin and *i*-butyl alcohol. Isopropyl alcohol gave a mixture of products apparently containing *i*-propyl ether under the conditions employed, and benzyl alcohol undergoes a condensation[6] reaction when treated with sulfuric acid, so equilibrium measurements could not be completed with these compounds. Four concentrations of sulfuric acid were used. These were 96.70% sulfuric acid, and 5.20, 22.61 and 31.98% sulfur trioxide in sulfuric acid. The use of acid containing sulfur trioxide (or pyrosulfuric acid) results in the formation of the alkyl hydrogen sulfates by the irreversible reaction

$$RCH_2OH + SO_3 = RCH_2OSO_3H$$

in which no water is produced, as well as by the normal esterification reaction. This makes possible the preparation of reaction mixtures containing a smaller concentration of water than would otherwise be obtained. This is useful in the preparation of the alkyl hydrogen sulfates particularly since the value for K in the expression

$$K = [RHSO_4][H_2O]/[H_2SO_4][ROH]$$

increases considerably in most cases as the concentration of the water decreases. In general the acids containing the two higher percentages of sulfur trioxide could not be used with alcohols above *n*-butyl because colored by-products were formed in appreciable quantities accompanied in some cases by the evolution of a trace of sulfur dioxide.

The reaction mixtures were kept in a thermo-

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[1] Eastman Kodak Company Fellow, 1931–1932.

[2] Oddo and Scandola, *Gazz. chim. ital.*, **39**, II, 1 (1909); *Chem. Abs.*, **5**, 879 (1911).

[3] Popelier, *Bull. soc chim. Belg.*, **35**, 264 (1926).

[4] (a) Zaitschek, *Z. physik. Chem.*, **24**, 1 (1879); (b) Kailan, *Monatsh.*, **30**, 1 (1909); (c) Kremann, *ibid.*, **31**, 245, 1031 (1910); (d) Evans and Albertson, THIS JOURNAL, **39**, 456 (1917); (e) Dunnicliff and Butler, *J. Chem. Soc.*, **119**, 1384 (1921).

[5] Gray and Gutekunst, THIS JOURNAL, **42**, 856 (1920).

[6] Cannizzaro, *Ann.*, **92**, 114 (1854); Senderens, *Compt. rend.*, **182**, 612 (1920).

stat at 25° until equilibrium was attained. It has been noted by other investigators[4d] that the per cent. of ester formation with ethyl alcohol increases but slightly with rise in temperature. This was verified in the present work.

In several instances the amount of alkyl hydrogen sulfate present was verified by isolation of the calcium or lead salt. The results obtained by this method were in good agreement with those obtained by titration. This is also in agreement with previous work.[4c, 4d]

Experimental

Materials.—The sulfuric acids used were C. P. quality commercial products. Acid II was made by mixing I and III. The concentrations were determined by diluting weighed samples in a volumetric flask and titrating aliquot portions with standard alkali. The essential data for the acids used are given in Table I.

Table I

Acid	Equiv./g.	SO_3, %	H_2O, %
I	0.01972	...	3.30
II	.02063	5.20	..
III	.02143	22.61	..
IV	.02186	31.98	..

The alcohols were for the most part the best obtainable commercial products which were then dried and fractionated until their physical constants were in satisfactory agreement with the best literature values. The *n*-amyl alcohol was purified through the acid phthalate[7] before a pure product resulted. The *n*-hexyl alcohol had been prepared by the Grignard reaction.[8] The data for the alcohols are given in Table II. The boiling points are uncorrected, the boiling range and density indicating the purity of the sample.

Table II

Alcohol	B. p., °C. (mm.)	d_4^{25}
Methyl	64.0– 64.1 (746)	0.7875
Ethyl	77.4– 77.5 (741)	.7853
n-Propyl	96.3– 96.6 (743)	.7996
n-Butyl	116.2–116.5 (739)	.8059
n-Amyl	135.8–136.8 (735)	.8111
n-Hexyl	154.0–156.0 (747)	.8149
i-Butyl	107.3–107.9 (752)	.7976
β-Chloroethyl	127.9–128.1 (741)	1.1972

Procedure

This was practically the same in all the experiments. Approximately 0.2 mole of the alcohol was weighed out in a small flask equipped with a stirrer, thermometer and an opening just large enough for 10-ml. pipet. The flask was placed in a freezing mixture, the stirrer started and the sulfuric acid added dropwise from the pipet at such a rate that the temperature did not rise above 5°. The flask was then weighed and placed in a thermostat at 25 ± 0.05° until equilibrium had been established, care being taken to prevent the access of moisture from the air. The time required for equilibrium conditions to be attained varied somewhat with the concentration of acid used, the acid highest in percentage of sulfur trioxide reacting most rapidly. To determine the extent of ester formation 1-ml. portions of the reaction mixture were withdrawn, weighed, diluted to 100 ml. with water and aliquot portions titrated with standard alkali. This was repeated until successive determinations several hours apart showed no change in acidity greater than the experimental error of titration. The average of the titration values for the last two samples was used in the calculations. Although the reactions were usually practically complete in two to six hours, the final readings were taken about twenty-four hours after the reaction mixtures were placed in the thermostat. It has been shown by other investigators[4d,9] that the alkyl hydrogen sulfates hydrolyze so slowly in water or acid solution at room temperature that titration results are not measurably different even after the diluted solutions have stood for a day. The results are summarized in Table III.

Calculations.—Since the weights of sulfuric acid and of alcohol present in a given reaction mixture are known, the amount of acid which would be present in 1 g. of reaction mixture, had no reaction occurred, can be calculated. The difference between this value and the one determined experimentally by titration indicates the amount of alkyl hydrogen sulfate formed. Complete formation of the monoalkyl ester for a molar ratio of one would mean the disappearance of half of the acid originally present. The amounts of alcohol and sulfuric acid present are obtained by subtracting the number of moles of alkyl hydrogen sulfate formed from the moles of alcohol and sulfuric acid (including the sulfur trioxide) originally present. The amount of water present at equilibrium when the 96.70% acid was used includes that formed in the reaction and that added with the acid. In the other cases the moles of water present is the moles of alkyl hydrogen sulfate less the number of moles of sulfur trioxide in the acid added.

In order to obtain more comparable results for the percentage of esterification of the various alcohols the experimental values of K obtained with molar ratios of acid and alcohol not exactly unity were used to calculate the extent of esterifi-

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(7) Ashdown and Monier, Organic Division, Atlanta Meeting of the American Chemical Society, April, 1930.

(8) Gilman, "Organic Syntheses," Coll., Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 299.

(9) For hydrolysis rates at higher temperatures see Bauer and Poethke, *J. prakt. Chem.*, 126, 296 (1930).

cation for a molar ratio of one using the formula: $K = x(x + a)/(1 - x)^2$. Here a corresponds to the variation in the moles of water due to the acids used, being positive for acid I and negative for the others, while x is the moles of alkyl hydrogen sulfate produced.

In Table III the results for methyl alcohol are given in detail to indicate the agreement between duplicate experiments.

TABLE III

Acid and concn.	$\frac{\text{Moles Acid}}{\text{Moles ROH}}$	$\frac{(RHSO_4)(H_2O)}{(H_2SO_4)(ROH)} = K$	K, av.	$RHSO_4$, %
96.70%	1.034	3.30	3.30	61.2
H_2SO_4	1.033	3.29		
5.20%	1.029	3.43	3.42	66.0
SO_3	1.025	3.40		
22.61%	1.018	3.61	3.62	70.5
SO_3	1.027	3.62		
31.98%	1.032	3.69	73.2	3.67
SO_3	1.031	3.65		

In Table IV are summarized the results of all the experiments at 25° in which a molar ratio of approximately one was employed.

TABLE IV

REACTION OF ALCOHOLS WITH SULFURIC ACID AT 25°

	96.7% H_2SO_4		5.20% SO_3		22.6% SO_3		31.98% SO_3	
Alcohol	K	$RHSO_4$, %	K	$RHSO_4$, %	K	$RHSO_4$, %	K	$RHSO_4$, %
Methyl	3.30	61.2	3.42	66.0	3.62	70.5	3.67	73.2
Ethyl	1.76	52.6	2.02	59.8	2.08	65.1	1.98	67.7
β-Chloroethyl	2.00	55.0	2.00	59.8	2.44	66.7	2.55	70.0
n-Propyl	2.30	56.8	2.38	61.9	2.59	67.3	2.76	70.6
n-Butyl	2.69	58.8	2.83	63.9	2.82	68.1	3.04	71.5
i-Butyl	3.14	60.8	3.32	65.7	..	..	..	..
n-Amyl	2.78	59.2	2.98	64.4	..	..	..	..
n-Hexyl	2.57	58.3	2.70	63.3	..	..	..	..

The value of K obtained for ethyl alcohol and 96.70% acid at 35° was 1.84.

Discussion of Results

The only comparison that can be made with the results obtained by previous investigators is in the case of ethyl alcohol. Kremann[4c] obtained a value of 1.74 for the equilibrium constant using concentrated sulfuric acid, which is in substantial agreement with our results. Evans and Albertson[4a] reported 58% esterification at 20° and 59.9% at 30° when 99.9% alcohol and 95% sulfuric acid were mixed in molar ratio. These results are much higher than the figures reported here. On the other hand, Dunnicliff and Butler[10] report a value of K of 1.77 for a molar ratio of acid to alcohol of 0.91 with absolute alcohol and 100% sulfuric acid.

In the tables it is noticeable that in general the value of K is higher the lower the concentration of water in the reaction mixtures. Methyl alcohol gives the highest value of K while ethyl alcohol gives the lowest. Branching of the chain as in *i*-butyl alcohol causes an appreciable rise in K over *n*-butyl alcohol, while the substitution of chlorine in ethyl alcohol has little effect.

It is evident from the tables that in the preparation of alkyl hydrogen sulfates the use of sulfuric acid containing 30% sulfur trioxide increases the yields from 10 to 15% over those obtainable from the concentrated acid when the molar ratio of the reactants is unity.

Summary

The extent of ester formation at equilibrium in the reaction between a number of alcohols and sulfuric acid has been determined for a temperature of 25°. The value of the equilibrium constant in general increases with a decrease in the concentration of water in the reaction mixture. Methyl alcohol gives the highest equilibrium constant while that for ethyl alcohol is the lowest. The most satisfactory conditions for the preparation of alkyl hydrogen sulfates are indicated.

EVANSTON, ILL. RECEIVED NOVEMBER 6, 1933

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[10] Dunnicliff and Butler, *J. Chem. Soc.*, **119**, 1384 (1921).