CXLII.—*Ethyl Hydrogen Sulphate.   Part II.*

By M. Abdul Hamid, Kirpal Singh, and Horace Barratt Dunnicliff.

Several subjects not investigated by Dunnicliff and Butler (J., 1921, **119**, 1384) have been studied.

Preparation of Ethyl Hydrogen Sulphate.—Attempts to prepare the pure ester have been made by the following methods :

1. By the action of hydrogen sulphide on lead ethyl sulphate (*a*) dry, (*b*) in alcoholic solution, and (*c*) suspended in ether. No action took place in the absence of water.

2. Passing ethylene into (*a*) sulphuric acid, (*b*) an ethereal solution of sulphuric acid, and (*c*) alcoholic sulphuric acid. Only very impure products were obtained.

3. Extraction of such sulphates as Ag_2SO_4,H_2SO_4, $BaSO_4,H_2SO_4$, and Li_2SO_4,H_2SO_4 gave a mixture of sulphuric acid and ethyl hydrogen sulphate in ether.

4. Barium ethyl sulphate, $Ba(C_2H_5 \cdot SO_4)_2, 2H_2O$, was prepared in the ordinary way. On treatment with dry alcohol, the anhydrous salt, $Ba(C_2H_5 \cdot SO_4)_2$, was formed. In order to start with an alcoholic sulphuric acid in which the free sulphuric acid was a minimum, 20% alcoholic sulphuric acid was taken after standing for a month. The percentage esterification of the sulphuric acid was 85. The free sulphuric acid was estimated. Barium ethyl sulphate in excess of the calculated amount required to react with the free sulphuric acid present was added to a weighed quantity of the alcoholic sulphuric acid and well shaken. The mixture was filtered and the filtrate heated with excess of barium ethyl sulphate under reduced pressure on a water-bath. When no more distillate was obtained, the residue in the flask was (*a*) filtered off or (*b*) extracted with dry ether in an apparatus of the Soxhlet type specially arranged for the extraction of liquids. It was hoped that the filtrate from (*a*) and the residue after driving off the ether from (*b*) would be free from sulphuric acid and probably from water and alcohol.

Among a large number of determinations of the equivalent weight of the ester so prepared, nine samples gave values which were within experimental error of the theoretical value, 126. The others were either high or low. The ester darkened on standing and the equivalent weight fell owing to the formation of free sulphuric acid. After some months, some preparations became black and free carbon was among the products of decomposition.

Attempts were made to determine the composition of several of the samples by combining the results of analyses by combustion.

estimation of sulphate by the barium sulphate method, and determination of esterification by the volumetric method. The greatest degree of purity obtained showed a yield of 84.5% of ester. A typical analysis was : Equivalent weight, 126. $C_2H_5 \cdot HSO_4$, 64.9; H_2SO_4, 13.7; $C_2H_5 \cdot OH$, 10.0; H_2O, 11.8; total, 100.4%.

5. By the action of dry hydrogen chloride on anhydrous barium ethyl sulphate (a) dry, (b) in anhydrous alcoholic solution, and (c) in ethereal solution. In the dry state no appreciable action was observed. In alcoholic and ethereal solution the hydrogen chloride reacted with the salt, giving insoluble barium chloride and ethyl hydrogen sulphate in solution. At first sulphuric acid was absent but, on concentration either by evaporation on the water-bath or at the ordinary temperature in a desiccator, the ester decomposed. The solution, at first colourless, slowly turned yellow with increasing concentration and, long before the solvent was driven off, a strong test for sulphuric acid was obtained. This decomposition was not due to the presence of hydrochloric acid, because the same result was obtained in the presence of excess of barium ethyl sulphate. The potassium salt behaves in a similar manner.

All attempts to prepare pure ethyl hydrogen sulphate have failed. The ester appears to become more unstable with increasing concentration.

Solubility of Ethyl Hydrogen Sulphate in Ether.—Most books of reference state that ethyl hydrogen sulphate is insoluble in ether. Since pure ethyl hydrogen sulphate has not been prepared, it is difficult to say if this is so, as all ethereal solutions of the ester in ether contain some sulphuric acid. Determinations of the solubility of the ester at 30° in presence of a small percentage of sulphuric acid show that the concentration of the ethyl hydrogen sulphate diminishes as the concentration of free sulphuric acid rises. Extrapolation of the results indicates that the solubility of pure ethyl hydrogen sulphate in pure ether should be about 1.27 g. of ester per 100 g. of dry ether at 30°.

TABLE I.

Solubility of Ethyl Hydrogen Sulphate in Ether containing free Sulphuric Acid at 30°.

Free H_2SO_4 %	0.092	0.152	0.186	0.314	0.372	0.516	0.533
$C_2H_5 \cdot HSO_4$ %	1.125	1.061	0.999	0.818	0.722	0.509	0.470

These points lie practically on a straight line, but as the concentration of the sulphuric acid increases, the relationship is not so simple, *e.g.*, when the concentration of sulphuric acid is 4.06%,

the concentration of the ester is 0·242%. If the solution were kept for some time, the concentration of the ester would increase on account of the interaction between ether and sulphuric acid. At the very low concentrations given in the table, the rate of esterification would be very slow and the total esterification very small. As the solutions were estimated immediately after they were formed, the line obtained by plotting the above points may be correctly described as a solubility graph. The fact that ethyl hydrogen sulphate is soluble in ether may be demonstrated by extracting silver hydrogen sulphate in a Soxhlet apparatus. The liquid which syphons over eventually separates into two layers, a lower one rich in ethyl hydrogen sulphate and an upper one poor in the ester. If the upper one be separated and allowed to evaporate, the ether first becomes cloudy and then a heavy layer of impure ethyl hydrogen sulphate separates.

The Order of the Reaction between Ethyl Alcohol and Sulphuric Acid at High Concentrations of Acid.—In the previous work, the velocity of the reaction at concentrations of sulphuric acid above 13·18% was not studied. The order of the reaction at concentrations of sulphuric acid between 60 and 75% has now been investigated. The practical difficulties encountered in this work were very considerable. At 18°, the reaction is very violent, so the experiments were carried out at 0°. In order to mix the interacting substances, alcohol which had been cooled to $-5°$ was added slowly to super-cooled sulphuric acid. At the highest concentration, the acid was cooled to $-10°$ and great care had to be exercised to prevent it from crystallising out. After the alcohol had been added there was no fear of this. The ingredients were thoroughly mixed, the flask being always immersed in the freezing mixture. When all the alcohol had been added, the reaction vessel was transferred to a bowl containing clean crushed ice. As soon as the temperature of the reaction mixture rose to 0°, the first portion of the reaction mixture was withdrawn in an ice-cold 1 c.c. pipette and run into a known quantity of standard caustic soda more than sufficient to neutralise it, and its weight was determined. The proportions in which the sulphuric acid and alcohol had been mixed in the reaction mixture were estimated after the experiment. The esterification was measured and the value of z, the time to be added to the observed time to compensate for the disturbed period, was calculated as previously described (*loc. cit.*, p. 1390).

The object was to obtain :

1. A minimal esterification during the disturbed period.

2. As large a difference as possible between the actual time of observation, t, and the correction, z, to be added.

3. A final total esterification several multiples of the esterification during the disturbed period.

The results in Tables II to IV show conclusively that, as in the case of low concentrations of sulphuric acid, the reaction is of the first order even when 1·44 molecules of sulphuric acid are mixed with one of alcohol, forming an alcoholic sulphuric acid containing 74·45% of sulphuric acid.

x = quantity of ethyl hydrogen sulphate expressed as g.-mol. per 100 g. of mixture, and t = the actual time.
$$k = \{1/(t + z)\} \log \{a/(a - x)\}.$$

TABLE II.

Sulphuric acid = 60·00% = 0·612 g.-mol. = a.
Ethyl alcohol = 40·00% = 0·869 g.-mol. z = 2·4 hrs.

x.	t (hrs.).	$t + z$.	$k \times 10^3$.	x.	t (hrs.).	$t + z$.	$k \times 10^3$.
0·054	—	2·40	16·7	0·112	2·90	5·30	17·2
0·087	1·35	3·75	17·2	0·122	3·78	6·18	15·6
0·099	2·20	4·60	16·7	0·134	4·45	6·85	15·7
						Mean	16·5

TABLE III.

Sulphuric acid = 68·14% = 0·695 g.-mol. = a.
Ethyl alcohol = 31·86% = 0·693 g.-mol. z = 87·6 mins.

x.	t (mins.).	$t + z$.	$k \times 10^3$.	x.	t (mins.).	$t + z$.	$k \times 10^3$.
0·136	—	87·6	1·08	0·292	137·5	225·1	1·05
0·201	45·8	133·4	1·11	0·330	193·2	280·8	1·00
0·267	105·5	193·1	1·09	0·349	210·0	297·6	1·02
						Mean	1·06

TABLE IV.

Sulphuric acid = 75·45% = 0·770 g.-mol. = a.
Ethyl alcohol = 24·55% = 0·534 g.-mol. z = 85 mins.

x.	t (mins.).	$t + z$.	$k \times 10^3$.	x.	t (mins.).	$t + z$.	$k \times 10^3$.
0·187	—	85·0	1·42	0·313	77·5	162·5	1·45
0·245	31·0	116·0	1·43	0·332	103·5	188·5	1·30
0·284	52·0	137·0	1·46			Mean	1·41

The mass-action coefficient obtained after 1 molecule of sulphuric acid had been allowed to interact with 1·05 molecules of alcohol at laboratory temperature for 25 days was 0·5650, and the ethyl hydrogen sulphate formed corresponded with 0·5787 g.-mol. These values are in agreement with (a) the " calculated " esterification (loc. cit., p. 1387), which was 0·5595 g.-mol., (b) the variation in the value of the mass-action coefficient as explained in equation (3) (loc. cit.) and the general proposition that the ratio

$$\frac{\text{actual esterification obtained}}{\text{maximum possible esterification}} = 0.5787 \text{ (observed)}$$

is a minimum when equimolecular proportions of the reacting

compounds are employed.   Clæsson (*J. pr. Chem.*, 1879, **19**, 246) obtained the value 0·5710.

In some preliminary experiments it appeared that the final maximum esterification in an alcoholic sulphuric acid made by treating sodium hydrogen sulphate with dry alcohol was less than that found in an alcoholic sulphuric acid of the same strength made by mixing the constituents directly and that this was due to the presence of some sulphate of sodium in the first case.   This has now been shown to be erroneous as instanced by the examples given below :

H_2SO_4 % in the alcoholic sulphuric acid containing sodium sulphate.	$C_2H_5 \cdot HSO_4$% found.	Theoretical % of $C_2H_5 \cdot HSO_4$ for alcoholic H_2SO_4.
9·46	10·16	10·08
12·86	13·87	14·06
43·50	44·16	44·36

Summary.

All attempts to prepare pure ethyl hydrogen sulphate have been unsuccessful.

From determinations at 0° of the velocity coefficients of the reaction between sulphuric acid and alcohol in which the concentration of sulphuric acid is from 60 to 75%, it is shown that the reaction is of the first order.

The solubility of ethyl hydrogen sulphate in ether containing small quantities of sulphuric acid has been determined at 30°.

GOVERNMENT COLLEGE, PANJAB UNIVERSITY,
          LAHORE, INDIA.