846. *Esterification by Sulphuric Acid. Part II.* Ethyl Alcohol.*

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Velocity and equilibrium constants are reported for the solvolytic esterification of ethyl alcohol in 60—82 wt.-% aqueous sulphuric acid at 25°, and in 70—93 wt.-% aqueous sulphuric acid at 0°.

THE esterification of ethyl alcohol by sulphuric acid has been investigated by Dunnicliff and his collaborators,[1] by Tian,[2] and by Deno and Newman,[3] but under conditions such that the composition of the medium changed considerably during the course of the reaction. In the present investigation the initial concentration of alcohol has been kept low (0·1M) and the progress of esterification has not significantly affected the medium. This has been achieved by analysing it for alcohol instead of for acid.

The Esterification Equilibrium.—Esterification is accompanied by a decrease in the alcohol concentration to an equilibrium value which then remains constant indefinitely in all media. The position of the equilibrium has been recorded in terms of an equilibrium ratio, K, defined by

$$K = ([\mathrm{EtOH}]_i - [\mathrm{EtOH}]_e)/[\mathrm{EtOH}]_e = [\mathrm{EtHSO_4}]_e/[\mathrm{EtOH}]_e \quad . \quad (1)$$

where the subscripts i and e refer to initial and equilibrium concentrations, respectively.

The value of K is affected only slightly by change in the initial concentration of alcohol (Table 2), but markedly by change in the sulphuric acid–water ratio (Table 1).

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* Part I, *J.*, 1956, 1304.

[1] Dunnicliff and Butler, *J.*, 1920, **117**, 649; 1921, **119**, 1384; Hamid, Singh, and Dunnicliff, *J.*, 1926, 1098.

[2] Tian, *Bull. Soc. chim. France*, 1950, 1223.

[3] Deno and Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 3852.

TABLE 1. *Velocity and equilibrium constants.*

H_2SO_4 (wt.-%)	Expt. no.	$[EtOH]_e$ (M)	Esterifn. at equilm. (%)	K	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	10^4k_E, mean (min.$^{-1}$)	10^4k_H, mean (min.$^{-1}$)
(*a*) Temp., 0°: $[EtOH]_i$ = 0·1019 ± 0·0005M								
69·70	144	0·0625	38·7	0·630	0·826	1·30	0·819	1·29
	145	0·0626	38·9	0·636	0·812	1·28		
80·71	141	0·0445	56·3	1·29	22·0	17·1	22·0	17·2
	154	0·0447	56·1	1·28	22·0	17·2		
92·91	142	0·0145	85·8	6·02	459	76·4	459	76·4
(*b*) Temp., 25°: $[EtOH]_i$ = 0·1018 ± 0·0004M								
59·99	149	0·0773	23·8	0·312	1·91	6·11	1·91	6·15
	150	0·0777	23·5	0·308	1·90	6·18		
64·56	136	0·0715	29·8	0·425	—	—	6·41	15·1
	137	0·0714	30·0	0·428	6·41	15·1		
	151	0·0712	29·8	0·425	6·41	15·1		
69·70	132	0·0640	37·2	0·592	—	—	25·9	43·8
	133	—	—	—	26·2	44·2		
	134	0·0635	37·5	0·600	25·7	43·3		
76·79	127	0·0536	47·4	0·899	—	—	189	210
	126	—	—	—	188	210		
	128	—	—	—	190	211		
	146	0·0536	47·5	0·903	188	209		
80·71	140	0·0474	53·5	1·15	543	473	545	477
	147	0·0475	53·2	1·14	547	480		
82·20	129	0·0447	56·1	1·28	—	—	806	636
	138	0·0452	55·7	1·26	811	645		
	139	0·0449	56·0	1·27	811	638		
	152	0·0448	56·1	1·28	797	625		
92·91	143	0·0182	82·1	4·59	—	—	—	—

TABLE 2. *Effect of initial concentration of alcohol.*

In 82·20% H_2SO_4. Temp. 25°.

Expt. no.	$[EtOH]_i$ (M)	$[EtOH]_e$ (M)	Esterifn. at equilm. (%)	K	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	10^4k_E, mean (min.$^{-1}$)	10^4k_H, mean (min.$^{-1}$)
148	0·2038	0·0904	55·7	1·26	786	626	786	626
153	0·2041	0·0905	55·7	1·26	787	626		
138	0·1021	0·0452	55·7	1·26	811	645	806	636
139	0·1019	0·0449	56·0	1·27	811	638		
152	0·1019	0·0448	56·1	1·28	797	625		

Rates and Orders of Reaction.—The decrease in alcohol concentration was followed in each experiment to 85—90% of the equilibrium value, and over this range of reaction log $(x_e - x)$ is accurately linear with time (Figure). This is the behaviour required for a reversible reaction of first order in both directions, the kinetic expression for which is

$$2{\cdot}303 \log\{x_e/(x_e - x)\} = (k_E + k_H)t \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

where x and x_e are, respectively, the ester concentrations at time t and at equilibrium, and k_E and k_H are, respectively, the first-order velocity coefficients for esterification and hydrolysis. The possibility that the reaction is of first order in one direction but of zero order in the reverse direction, which would also yield a linear relation between $\log(x_e - x)$ and t, is excluded by the observation that $[EtOH]_e$ is proportional to $[EtOH]_i$.

For a given sulphuric acid–water medium, therefore, the rate of reaction is expressed by

$$-d[EtOH]/dt = k_E[EtOH] - k_H[EtHSO_4] \qquad . \quad . \quad . \quad . \quad (3)$$

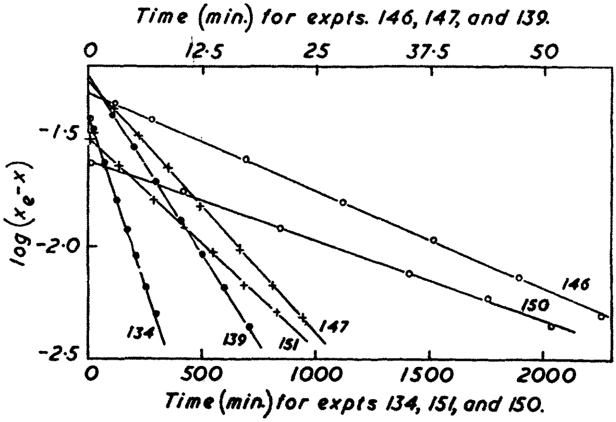
Variation of Rate with Sulphuric Acid–Water Composition.—A plot of log $k_E(25°)$ against Hammett's acidity function H_0 is accurately linear in solutions containing less than 80% sulphuric acid but shows a small curvature at higher acidities. The equation to the best straight line through *all* the points is

$$\log k_{\mathrm{E}} = -0{\cdot}926H_0 - 7{\cdot}690 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

but if points corresponding to solutions more acid than 80% sulphuric acid are omitted the best line becomes

$$\log k_{\mathrm{E}} = -0{\cdot}955\, H_0 - 7{\cdot}832 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the coefficient of H_0 is now almost identical with that found for 2 : 4-dinitrobenzyl alcohol (—0·959; cf. Part I). The numerical terms in eqns. (4) and (5) have been calculated by the method of least squares, and the accuracy with which these expressions represent the experimental results can be judged from Table 4.



With 2 : 4-dinitrobenzyl alcohol the linear relation between log k_{E} and H_0 holds over the whole range of acidities in which k_{E} can be accurately measured and the contrary behaviour of ethyl alcohol, which must be considered a stronger base than 2 : 4-dinitrobenzyl alcohol, can plausibly be attributed to appreciable protonation in solutions containing more than 80% sulphuric acid.

Effect of Temperature.—The Arrhenius parameters, calculated from the results in Table 1, are shown in Table 3.

TABLE 3. *Parameters of equation* $k_1 = A \exp(-E/\boldsymbol{R}T)$.

		Esterification		Hydrolysis	
H_2SO_4 (wt.-%)	Temp.	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)
69·70	0·00—25·05°	0·10	22·3	0·33	22·7
80·71	,,	0·14	20·7	0·43	21·5

Reaction Mechanisms.—The reaction mechanism proposed in Part I, in which the rate of esterification is governed by the unimolecular decomposition of a protonated solvation complex of the alcohol, requires

$$\log k_{\mathrm{E}} + H_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This equation and also eqns. (7) and (8), which refer to a bimolecular reaction between

$$\log k_{\mathrm{E}} - \log a_{\mathrm{H_2SO_4}} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\log k_{\mathrm{E}} - \log\,[\mathrm{HSO_4^-}] + H_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

alcohol and molecular sulphuric acid present in small concentration (Part I; p. 1309), are tested in Table 4. The hypothesis of a unimolecular esterification is in best accord with the experimental observations but the bimolecular mechanism cannot be definitely excluded.

TABLE 4.

H_2SO_4 (%)	H_0 (25°)	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
59·99	−4·32	−8·04	−8·02	−9·00	−7·72	−7·84
64·56	−4·84	−8·03	−8·26	−9·04	−7·67	−7·82
69·70	−5·50	−8·09	−8·53	−9·14	−7·68	−7·84
76·79	−6·40	−8·12	−8·77	−9·24	−7·65	−7·84
80·71	−6·93	−8·19	−8·91	−9·33	−7·68	(−7·88)
82·20	−7·17	−8·26	−8·93	−9·40	−7·73	(−7·94)

(*a*) log k_E(25°) + H_0. (*b*) log k_E(25°) −log $a_{H_2SO_4}$. (*c*) log k_E(25°) − log [HSO_4^-] + H_0. (*d*) log k_E(25°) + 0·926 H_0. (*e*) log k_E(25°) + 0·955 H_0.

EXPERIMENTAL

Materials.—A commercial re-distilled absolute alcohol was used without further treatment. Analysis by dichromate oxidation indicated 99·7% of alcohol.

Kinetic Measurements.—The procedure for preparing the reaction mixtures and for carrying out the kinetic experiments was as described in Part I, p. 1311.

Analytical Method.—A 10-ml. sample of the mixture was run on to a partly frozen mixture of 0·32N-potassium dichromate (25 ml.) and sufficient water to make the final solution 4N with respect to sulphuric acid. After 18 hr. the excess of dichromate was titrated against standard ferrous ammonium sulphate, with ferroin as indicator. An acid concentration of 4N was chosen for the oxidation rather than the 6N used for the analysis of 2 : 4-dinitrobenzyl alcohol because oxidation of ethyl alcohol in 6N acid gave results which were too high (by a few tenths per cent.) in the 18-hr. oxidation period which it was convenient to adopt. In 4N-acid, oxidation of 45 mg. of ethyl alcohol is complete in 10—12 hr. at room temperature and no further dichromate is consumed during more than 72 hr.

Analysis of numerous samples of the redistilled absolute alcohol used in these experiments has invariably returned a value of 99·7 ± 0·2% for a sample size of the order 30—50 mg., but the experimental error increases as the size of the sample is reduced, and with 7 mg. of ethyl alcohol (corresponding to 0·015M-ethyl alcohol in the mixture, the lowest concentration reached in any experiment) the error becomes ±1·0%.

Hydrolysis of ethyl hydrogen sulphate is so slow under the oxidation conditions as to introduce no appreciable error. Table 5 gives the results of an experiment in which 0·1036M-ethyl alcohol in 87·08% sulphuric acid was allowed to attain equilibrium (165 min.) at 25°, samples then being analysed in the usual way but with an acid concentration of 6N and with varying oxidation periods. In 4N-acid hydrolysis will be still slower.

TABLE 5.

Oxidation time (hr.)	2·9	3·1	21·6	22·0	69	69	192	192
10^2[EtOH] (M)	3·47	3·47	3·48	3·48	3·47	3·47	3·54	3·56
10^2[$EtHSO_4$] (M)	6·89	6·89	6·88	6·88	6·89	6·89	6·82	6·80

Equilibrium Constants.—The equilibrium concentration of alcohol was in some cases determined by a separate experiment but more usually the last two samples from the reaction mixture were used for this purpose.

Tian[8] has shown that, for aliphatic alcohols higher than ethyl, esterification is accompanied or followed by a side-reaction so that no stable equilibrium is reached, and the same is true for 2 : 4-dinitrobenzyl alcohol in media containing more than 80% of sulphuric acid. With ethyl alcohol, however, the equilibrium concentration, once established, is maintained indefinitely in all media. For example, in expt. 143 (92·91% H_2SO_4 at 25°) eight samples taken at intervals between 0·2 and 627 hr. gave $[EtOH]_e$ = 0·0182, 0·0182, 0·0182, 0·0182, 0·0182, 0·0182, 0·0183, and 0·0183.

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