265. *Esterification by Sulphuric Acid.*

By (the late) GWYN WILLIAMS and D. J. CLARK.

Velocity and equilibrium constants for the solvolytic esterification of 2 : 4-dinitrobenzyl alcohol have been determined in 64—82% aqueous sulphuric acid at 25°, in 68—93% aqueous sulphuric acid at 0°, and (at 25°) in deutero-sulphuric acid–deuterium oxide solutions containing 69 and 76% of D_2SO_4.

Possible esterification mechanisms are discussed.

IN previous measurements of the rates of the esterification of alcohols by concentrated aqueous sulphuric acid,[1,2,3] which established a number of the kinetic features of the reactions, the method of experiment has been to determine the sulphuric acid concentration in the reaction mixture; and therefore it has been necessary to avoid having the initial sulphuric acid concentration in too large excess over that of the alcohol. When the initial alcohol and sulphuric acid concentrations are not far apart, the acidity of the mixture inevitably changes as esterification proceeds.

---

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

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

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

The experiments which follow, on the sulphuric esterification of 2 : 4-dinitrobenzyl alcohol, differ in that we have always determined the *alcohol* concentration in samples of the reaction mixture by oxidation with potassium dichromate. It has thus been possible to keep the alcohol (and ester formed) at a low concentration in a sulphuric acid–water medium which retains a virtually constant composition throughout the reaction.

The Esterification Equilibrium.—The rate of sulphuric esterification of 0·1M-2 : 4-dinitrobenzyl alcohol is measurable in 64—82% sulphuric acid at 25° and in 68—93% sulphuric acid at 0°. The alcohol concentration falls to an equilibrium value, which remains constant indefinitely in solvents less acid than 82% sulphuric acid, but shows an apparent slow rise from a minimum in more concentrated acids. Simultaneously, in the most concentrated acids, the reaction mixture, normally colourless, becomes yellow and ultimately red. The apparent slow increase of alcohol concentration in the strongest acids, after esterification has reached equilibrium, may be attributed to an unidentified side reaction giving products which reduce the oxidising agent employed to determine the alcohol concentration. The analogous compound, benzyl alcohol, polymerises in concentrated sulphuric acid,[4] and 2 : 4-dinitrobenzyl chloride polymerises under the influence of alkali.[5] Tian [2] observed a formally analogous disturbance of the sulphuric esterification of alcohols $C_nH_{2n+1}\cdot OH$ with $n > 2$, and isolated hydrocarbons from the reaction mixtures.

The equilibrium concentration of ester, and the rates of approach to equilibrium, all fall with increasing water content of the system. The effect of medium composition on the esterification equilibrium is shown in Table 1. The results are expressed in terms of an equilibrium ratio, K, defined by equation (1), in which the suffixes i and e refer, respectively, to initial and equilibrium concentrations :

$$K = ([\mathrm{ROH}]_i - [\mathrm{ROH}]_e)/[\mathrm{ROH}]_e = [\mathrm{RO\cdot SO_3H}]_e/[\mathrm{ROH}]_e \quad . \quad . \quad . \quad (1)$$

Evidently, the calculated value of K is sensitive to error in the measurement of $[\mathrm{ROH}]_e$ if $[\mathrm{ROH}]_e \longrightarrow [\mathrm{ROH}]_i$. The error in K, caused by the unidentified side reaction, is considerable only in acids containing more than 87% of sulphuric acid.

The equilibrium ratio, K, of equation (1) naturally varies with the composition of the sulphuric acid–water reagent; but in a given sulphuric acid–water mixture, K changes only slightly for a four-fold variation of the initial alcohol concentration (Table 2).

Rates and Orders of Reaction.—Rates of esterification were generally measured by separate experiments (duplicated for each medium composition) in which the decrease of alcohol concentration with time was pursued to 80—85% of its equilibrium value. Over this range the quantity $\log (x_e - x)$ is accurately linear with time. The course of reaction may therefore be represented by equation (2*a*) (esterification and hydrolysis of first order with respect to alcohol and ester, respectively), equation (2*b*) (zero-order esterification and first-order hydrolysis), or equation (2*c*) (first-order esterification and zero-order hydrolysis),

$$2{\cdot}303 \log \{x_e/(x_e - x)\} = \begin{cases} (k_{\mathrm{E}} + k_{\mathrm{H}})t & . \quad . \quad . \quad . \quad . \quad (2a) \\ k_{\mathrm{H}}t & . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b) \\ k_{\mathrm{E}}t & . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2c) \end{cases}$$

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.

Of these three equations, (2*a*) is definitely to be preferred, because (2*b*) requires $[\mathrm{RO\cdot SO_3H}]_e$ to be independent of $[\mathrm{ROH}]_i$, and (2*c*) requires the same for $[\mathrm{ROH}]_e$. Neither is true in 76·79% sulphuric acid at 25° (Table 2). Instead, $[\mathrm{ROH}]_e \propto [\mathrm{ROH}]_i$, and $[\mathrm{RO\cdot SO_3H}] \propto [\mathrm{ROH}]_i$, as required by equation (2*a*). Further, the zero-order velocity coefficients calculated from (2*b*) and (2*c*) are proportional to $[\mathrm{ROH}]_i$, whereas the velocity coefficients derived from equation (2*a*) are nearly constant for a four-fold variation of $[\mathrm{ROH}]_i$ in 76·79% sulphuric acid at 25° (Table 2), k_{H} being a little more variable than k_{E}

---

[4] Shriner and Berger, *J. Org. Chem.*, 1941, **6**, 305.

[5] Friedländer and Cohn, *Monatsh.*, 1902, **23**, 546.

TABLE 1. *Variation of acid composition and temperature.*

Medium, H_2SO_4 (%)	Expt. no.	$[\mathrm{ROH}]_t$ (M)	Esterifn. at equilm. (%)	K (mean)	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	10^4k_E, mean (min.$^{-1}$)	10^4k_H, mean (min.$^{-1}$)
(a) *Temperature,* 0° : $[\mathrm{ROH}]_t = 0{\cdot}1014 \pm 0{\cdot}0001$M.								
68·03	115	0·0860	15·2	0·178	—	—	—	—
	114	—	—	—	0·524	2·94	0·521	2·93
	116	—	—	—	0·516	2·90		
	117	—	—	—	0·523	2·94		
72·72	102	0·0747	26·3	0·358	—	—	1·96	5·47
	100	—	—	—	1·97	5·50		
	103	—	—	—	1·95	5·43		
76·79	87	0·0587	42·1	0·727	—	—	7·12	9·81
	86	—	—	—	7·09	9·77		
	88	—	—	—	7·14	9·84		
	89	—	—	—	7·11	9·80		
80·71	112	0·0388	61·8	1·62	—	—	26·2	16·2
	111	—	—	—	26·2	16·2		
	113	—	—	—	26·2	16·2	—	—
82·20	105	0·0310	69·4	2·28	—	—	46·1	20·3
	104	—	—	—	46·0	20·2		
	106	—	—	—	46·1	20·3		
87·08	108	0·0125	87·7	7·12	—	—	268	37·7
	107	—	—	—	268	37·6	—	—
	109	—	—	—	269	37·7		
90·05	96	0·0076	92·5	12·4	—	—	682	55·3
	94	0·0075	92·6	—	692	56·0		
	95	—	—	—	673	54·5		
92·91	98	0·0050	95·1	19·4	—	—	1490	77·1
	97	—	—	—	1500	77·4		
	99	—	—	—	1490	76·8		
(b) *Temperature,* 25° : $[\mathrm{ROH}]_t = 0{\cdot}1014 \pm 0{\cdot}0002$M.								
64·56	78	0·0903	10·8	0·121	—	—	7·48	61·8
	79	—	—	—	7·40	61·2		
	80	—	—	—	7·57	62·5		
	81	—	—	—	7·47	61·7		
69·70	52	0·0820	19·0	0·235	—	—	31·3	133
	53	0·0820	19·0	—	31·1	133		
	51	—	—	—	31·6	134		
72·72	62	0·0745	26·5	0·0360	—	—	71·7	200
	60	0·0744	26·5	—	71·4	199		
	61	—	—	—	72·1	201		
74·64	65	0·0684	32·5	0·481	—	—	122	254
	63	0·0684	32·5	—	123	255		
	64	—	—	—	121	252		
76·79	59	0·0602	40·6	0·684	—	—	236	345
	57	0·0602	40·6	—	234	342		
	58	—	—	—	238	347		
78·56	40	0·0527	48·0	0·924	—	—	390	423
	56	0·0527	48·0	—	—	—		
	54	—	—	—	385	417		
	55	—	—	—	396	428		
82·20	82	0·0355	65·0	1·86	—	—	1260	676
	83	—	—	—	1260	677		
	84	—	—	—	1260	677		
	85	—	—	—	1250	673		
(c) *Temperature,* 35° : $[\mathrm{ROH}]_t = 0{\cdot}1014$—$0{\cdot}1015$M.								
76·79	90	0·0605	40·3	0·680	830	1220	832	1220
	91	0·0603	40·5	—	833	1220		
	92	0·0605	40·4	—	834	1230		

TABLE 2. *Reactions in* 76·79% *sulphuric acid at* 25°.

Expt. no.	$[ROH]_i$ (M)	Salt concn. (M)	$[ROH]_e$ (M)	Esterifn. at equilm. (%)	K (mean)	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	10^4k_E, mean (min.$^{-1}$)	10^4k_H, mean (min.$^{-1}$)
(a) *Variation of initial alcohol concentration.*									
68	0·0507	—	0·0304	40·0	0·667	231	346	233	349
66	0·0507	—	0·0304	40·0	—	234	351	—	—
67	0·0507	—	—	—	—	233	349	—	—
—	0·1014	(Table 1)	0·0602	40·6	0·684	—	—	236	345
71	0·2031	—	0·1196	41·1	0·698	234	336	236	337
69	0·2031	—	0·1198	41·0	—	235	336	—	—
70	0·2030	—	—	—	—	237	339	—	—
(b) *Effects of added salts.*									
—	0·1014	(Table 1)	—	40·6	0·684	—	—	236	345
72	0·1015	KHSO$_4$ 0·500	0·0605	40·4	0·677	229	338	229	338
73	0·1015		0·0605	40·4	—	229	338	—	—
74	0·1015		0·0605	40·4	—	228	336	—	—
75	0·1014	(NH$_4$)$_2$SO$_4$ 0·500	0·0636	37·4	0·599	193	322	193	322
76	0·1014		0·0634	37·5	—	192	321	—	—
77	0·1014		0·0633	37·6	—	193	322	—	—

and accounting mainly for the small corresponding variation of K in Table 1. Of the various constants measured, the values of k_E are the most accurate.

For a given sulphuric acid–water composition, therefore, the rate of reaction is expressed by equation (3).

$$-d[ROH]/dt = k_E[ROH] - k_H[RO{\cdot}SO_3H] \quad . \; . \; . \; . \; . \quad (3)$$

Variations of Rate with Sulphuric Acid–Water Compositions.—The individual velocity coefficients, k_E and k_H, are derived from the graphically computed ($k_E + k_H$) of equation (2*a*) and K of equation (1). The variations of k_E with sulphuric acid–water composition at 25° and 0° are given by equations (4) and (5), in which H_0 is Hammett's acidity function :[6]

$$\log k_E\,(25^\circ) = -0{\cdot}959H_0\,(25^\circ) - 7{\cdot}775 \quad . \; . \; . \; . \; . \quad (4)$$

$$\log k_E\,(0^\circ) = -1{\cdot}084H_0\,(25^\circ) - 10{\cdot}071 \quad . \; . \; . \; . \; . \quad (5)$$

The numerical terms in these equations are calculated by the method of least squares. The accuracy of fit may be judged from Table 5. The values of H_0 are not known at 0°, so equation (5) is significant only if the variation of H_0 with sulphuric acid–water composition at 0° is assumed to be strictly parallel to that at 25°.

Salt Effects.—Added salts may affect the reaction rates by altering activity coefficients which appear in the rate equations and also by changing the acidity of the medium. The effect of 0·5M-potassium hydrogen sulphate is small, but that of 0·5M-ammonium sulphate is more considerable [Table 2(b)]. The SO_4^{2-} ion is a base in 76·79% sulphuric acid, which contains little of this ion.[7] If the added 0·5M-SO_4^{2-} ion undergoes the reaction $SO_4^{2-} + OH_3^+ \longrightarrow HSO_4^- + H_2O$, then, from equation (6) which is due to Deno and Taft,[8] *viz.* :

$$H_0 = -6{\cdot}66 + \log X_{H_2O}/X_{OH_3^+} + 1{\cdot}67 + \log f_{H_2O} \quad . \; . \; . \; . \quad (6)$$

it may be estimated (without allowance for any change in f_{H_2O}) that 0·5M-ammonium sulphate alters H_0 by +0·05, and hence, from equation (4), reduces k_E from 0·0236 to 0·021, the observed fall being to 0·019. The change in H_0 is thus nearly great enough to account for the small retardation of esterification.

The effect of added salts on the rate of esterification is much less than it is on rates of reactions (such as nitration) which run parallel to the J_0 acidity function.[9]

---

[6] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827.

[7] Young, *Rec. Chem. Progr.*, 1951, Spring Issue, p. 81.

[8] Deno and Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244.

[9] *E.g.*, Williams and Simkins, *J.*, 1953, 1386.

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

TABLE 3. *Parameters of equation* $k_1 = Ae^{-E/RT}$.

H_2SO_4 (%)	Temp.	Esterification $10^{-13}A$ (sec.$^{-1}$)	Esterification E (kcal./mole)	Hydrolysis $10^{-13}A$ (sec.$^{-1}$)	Hydrolysis E (kcal./mole)
72·72	0·00—25·05°	1·3	23·23	3·6	23·23
76·79	0·00—35·01	1·8	22·72	4·2	23·01
82·20	0·00—25·05	0·95	21·35	4·4	22·64

Reactions in Deuterosulphuric Acid.—Both esterification and ester hydrolysis are faster in deuterosulphuric acid than in sulphuric acid (Table 4). An analogy to this result for hydrolysis of the sulphuric ester exists in the faster, acid-catalysed hydrolyses of some carboxylic esters in deuterium oxide than in water.[10] Faster reaction by a deuterated reagent is an indication that a rapidly established proton-transfer equilibrium precedes the rate-determining step in the process.[11]

TABLE 4. *Esterification by deuterosulphuric acid at* 25°.

$[ROH]_t$ = 0·1018—0·1019M

Medium: D_2SO_4 (%)	Expt. no.	$[ROH]_e$ (M)	Esterifn. at equilm. (%)	K (mean)	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	k_ED/k_EH	k_HD/k_HH
69·17	122	0·0779	23·5	0·306	83·4	272	—	—
	123	0·0780	23·4	—	84·9	277	—	—
				Mean	84·1	275	1·90	1·74
75·54	120	0·0576	43·5	0·765	451	590	—	—
	121	0·0579	43·2	—	439	574	—	—
				Mean	445	582	1·74	1·63

State of the Reagents.—The 64·5—82·2% sulphuric acid used for the experiments at 25° contains water in initial molecular excess over sulphuric acid, and the concentration of molecular sulphuric acid present is small.[7] The condition of alcohol and ester in this solvent range cannot be certain. Cryoscopy shows that ester may exist to a small extent as $RO{\cdot}SO_3H_2^+$ (or R^+) in anhydrous sulphuric acid,[12] but does not reveal clearly that an alcohol ROH forms ROH_2^+, because of further reactions with sulphuric acid.[13] 2 : 4-Dinitrobenzyl alcohol must be a weaker base than ethyl alcohol, which is considered to be a weaker base than water.[14] In 64·5—82·2% sulphuric acid, the alcohol may be assumed to exist predominantly as ROH, while the ester may be largely [15] present as $RO{\cdot}SO_3^-$.

Reaction Mechanisms.—With alcohol in small initial concentration, both esterification and ester hydrolysis are solvolytic, and the results of Table 1 establish no reaction order with respect to the solvent component. The effective reacting species cannot be identified unequivocally; and multiplicity of mechanisms, or change of mechanism with changing acid composition, cannot be rigidly excluded. Nevertheless, the variation of esterification rate is given, for the whole range of acid compositions investigated, by equation (4) at 25° and equation (5) at 0°. The *simplest* interpretation of equation (4) is that the rate-determining step in esterification is a unimolecular decomposition of the conjugate acid of an initial reagent.[16] A rate-determining step $ROH \longrightarrow R^+$ is improbable, for Deno and Newman have argued convincingly against alkyl–oxygen fission in sulphuric esterification (*a*) that sulphuric acid esterifies (+)-butan-2-ol with retention of configuration, though the

---

[10] Hornel and Butler, *J.*, 1936, 1361.

[11] Bell, " Acid–Base Catalysis," Oxford Univ. Press, 1941, p. 145.

[12] Gillespie, *J.*, 1950, 2542.

[13] Newman, Craig, and Garrett, *J. Amer. Chem. Soc.*, 1949, **71**, 869; 1950, **72**, 163; Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

[14] Braude, *J.*, 1948, 1971; Braude and Stern, *ibid.*, p. 1976.

[15] Cf. Deno and Newman, *J. Amer. Chem. Soc.*, 1951, **73**, 1920.

[16] Zucker and Hammett, *ibid.*, 1939, **61**, 2791; Long and Purchase, *ibid.*, 1950, **72**, 3272; McIntyre and Long, *ibid.*, 1954, **76**, 3240.

ester is then racemised, and (*b*) that *neo*pentyl alcohol forms *neo*pentyl hydrogen sulphate without molecular rearrangement.[17]

A possible reaction sequence for the solvolytic esterification is

$$\mathrm{ROH} + \mathrm{HSO_4^-} \longrightarrow \mathrm{Q}\ \text{fast};\ [\mathrm{Q}] \sim [\mathrm{ROH}]_{\mathrm{st}} \tag{7}$$

$$\mathrm{Q} + \mathrm{H^+} \rightleftharpoons \mathrm{QH^+}\ \text{fast};\ [\mathrm{Q}] \gg [\mathrm{QH^+}] \tag{8}$$

$$\mathrm{QH^+} \longrightarrow \mathrm{RO{\cdot}SO_3^-}\ \text{slow} \tag{9}$$

in which the whole of the alcohol forms a complex, Q, with a component of the acid; a small proportion of Q exists as QH^+; and the rate-determining step is a unimolecular decomposition of QH^+ to form ester. From equations (7)—(9), in which $[ROH]_{st}$ stands for the stoicheiometric concentration of 2 : 4-dinitrobenzyl alcohol, the rate of esterification, r_E, is given by

$$r_E = k_E[\mathrm{ROH}]_{\mathrm{st}} = k_E^{\circ}[\mathrm{QH^+}]f_{\mathrm{QH^+}}/f_{\mathrm{tr}} = k_E^{\circ}K_8[\mathrm{Q}]a_{\mathrm{H^+}}f_{\mathrm{Q}}/f_{\mathrm{tr}} \tag{10}$$

In (10), K_8 is the equilibrium constant of (8) and $k°_E$ is supposed independent of the acid composition. The transition state of (9) is akin to the conjugate acid of Q, so that (10) gives (11):

$$\log k_E + H_0 = \log k_E^{\circ} + \log K_8 \tag{11}$$

in agreement with equation (4).

Although a unimolecular mechanism offers the simplest interpretation of the solvolytic esterification results, bimolecular mechanisms cannot be excluded,[18] since the range of sulphuric acid–water compositions in which k_E can be measured at 25° is not very wide and lies in a region [8] in which individual activity coefficients are not constant and in which concentrations of bisulphate and oxonium ions probably do not vary by more than some 30%, though the concentration of molecular water may change 5-fold and the small concentration of molecular sulphuric acid (which cannot be accurately estimated) may change very markedly. Deno and Newman [1] found that their results with equimolar proportions of alcohol and sulphuric acid were best represented by the equation:

$$d[\mathrm{RO{\cdot}SO_3H}]/dt = k[\mathrm{ROH}][\mathrm{H_2SO_4}]a_{\mathrm{H^+}}$$

Bimolecular esterification could occur between either ROH, or ROH_2^+, and HSO_4^-, H_2SO_4, $H_3SO_4^+$, or HSO_3^+. However, $H_3SO_4^+$ and HSO_3^+ can be excluded because reaction of alcohol with these would require $\log k_E$ to run parallel to $2H_0$ and $(H_0 + J_0)$ respectively, contrary to equation (4). Deno and Newman regarded the pairs $(ROH_2^+ + H_2SO_4)$, $(ROH + H_2SO_4)$, or $(ROH + H_3SO_4^+)$ as being the most probable. The reaction sequence:

$$\mathrm{HSO_4^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2SO_4}\ \text{fast};\ [\mathrm{HSO_4^-}] \gg [\mathrm{H_2SO_4}] \tag{12}$$

$$\mathrm{H_2SO_4} + \mathrm{ROH} \longrightarrow \mathrm{RO{\cdot}SO_3H} + \mathrm{H_2O}\ \text{slow} \tag{13}$$

leads to the equation:

$$\log k_E = \log k_E^{\circ} + \log a_{\mathrm{H_2SO_4}} + \log f_{\mathrm{ROH}}/f_{\mathrm{tr}} \tag{14}$$

in which k_E° is supposed independent of medium and f_{tr} refers to the transition state. If the ratio f_{ROH}/f_{tr} (referring to two neutral species) is supposed independent of medium, then:

$$\log k_E - \log a_{\mathrm{H_2SO_4}} = \text{const.} \tag{15}$$

Alternatively:

$$\log k_E = \log k_E^{\circ} + \log K_{12} + \log [\mathrm{HSO_4^-}] - H_0 + \log (f_{\mathrm{ROH}}f_{\mathrm{H_2SO_4}}/f_{\mathrm{tr}}) \tag{16}$$

[17] Whitmore and Rothrock, *J. Amer. Chem. Soc.*, 1932, **54**, 3432.

[18] Cf. Schubert and Zahler, *ibid.*, 1954, **76**, 1; Schubert, Donohue, and Gardner, *ibid.*, p. 9.

if products of the type $f_{BH^+}f_{HSO_4^-}/f_B f_{H_2SO_4}$ are invariant throughout the medium range. Only if the expression in activity coefficients in (16) is also invariant is equation (17) true:

$$\log k_E - \log [HSO_4^-] + H_0 = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The same expression may be derived from the reaction sequence:

$$ROH + H^+ \rightleftharpoons ROH_2^+ \text{ fast, } [ROH] \gg [ROH_2^+] \quad . \quad . \quad (18)$$

$$ROH_2^+ + HSO_4^- \longrightarrow RO{\cdot}SO_3H + H_2O \text{ slow} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

if the product $f_{ROH_2^+}f_{HSO_4^-}/f_{tr}$ is invariant. Reaction between H_2SO_4, formed as in (12), and ROH_2^+, formed as in (18), requires log k_E to run parallel to a multiple of H_0, contrary to equation (4).

Constancy of the sums on the left-hand side of equations (11) and (17) is tested in Table 5(*a*) and (*c*) respectively, the concentrations of the medium constituents being calculated from mole fractions X_{H_2O} derived by Deno and Taft [8] on the supposition that $X_{OH_3^+}X_{HSO_4^-}/X_{H_2O}X_{H_2SO_4} = 50$ at 25°. Equation (15) is tested in Table 5(*b*) from values of $a_{H_2SO_4}$ at 25°, calculated by Abel.[19]

TABLE 5.

H_2SO_4 (%)	H_0 (25°)	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
64·56	−4·84	−7·97	−8·19	−8·96	−7·77	—
68·03	−5·29	—	—	—	—	−10·02
69·70	−5·50	−8·00	−8·45	−9·06	−7·78	—
72·72	−5·88	−8·03	−8·56	−9·11	−7·78	−10·08
74·64	−6·11	−8·03	−8·63	−9·13	−7·78	—
76·79	−6·40	−8·03	−8·68	−9·15	−7·77	−10·09
78·56	−6·63	−8·04	−8·73	−9·17	−7·77	—
80·71	−6·93	—	—	—	—	−10·09
82·20	−7·17	−8·07	−8·74	−9·20	−7·78	−10·11
87·08	−7·85	—	—	—	—	−10·08
90·05	−8·18	—	—	—	—	−10·03
92·91	−8·50	—	—	—	—	−10·04

(*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°) + $0{\cdot}959H_0$.
(*e*) log k_E (0°) + $1{\cdot}084H_0$.

Equations (15) and (17), referring to bimolecular mechanisms, have no advantage over (11) in reproducing the experimental equation (4); but they cannot be rejected (or accepted) out of hand in view of the possible variations of activity coefficients with changing acid composition. The results at 0° [Table 1(a)] extend to acid compositions made up with sulphuric acid in molecular excess over water; but they cannot be tested satisfactorily, because H_0 has not been measured at 0° and the concentrations of solvent constituents are doubtful.

EXPERIMENTAL

Materials.—2 : 4-Dinitrobenzyl alcohol was prepared [20] from 2 : 4-dinitrobenzyl chloride (either a commercial product, or a sample made by nitration of *p*-nitrobenzyl chloride [21]), by conversion into the acetate and hydrolysis of this with 50% sulphuric acid at 120°. The product was crystallised from water, methanol, and benzene (twice), and had m. p. 115·5—116° (Found: C, 42·7; H, 3·25; N, 14·25. Calc. for $C_7H_6O_5N_2$: C, 42·4; H, 3·05; N, 14·15%). Analysis by dichromate oxidation gave 99·9% alcohol.

The sulphuric acid–water mixtures were analysed by titrating samples from a weight-burette (with methyl-orange–xylene-cyanol indicator) against 0·8N-sodium hydroxide, this being standardised against N-hydrochloric acid, itself standardised against standard potassium iodate and checked occasionally against standard sodium carbonate and also gravimetrically. Six samples of each medium were analysed; *e.g.*, medium S9 gave 64·59, 64·54, 64·55, 64·58,

---

[19] Abel, *J. Phys. Chem.*, 1946, **50**, 260.
[20] Friedländer and Cohn, *Monatsh.*, 1902, **23**, 546; *Ber.*, 1902, **35**, 1266.
[21] Escales, *Ber.*, 1904, **37**, 3599.

64·54, 64·57, mean 64·56% sulphuric acid. The mixtures maintained their composition when stored in glass-stoppered bottles; *e.g.*, medium S11, when prepared, was 72·73, and, after 8 months, was 72·71% sulphuric acid.

Deuterosulphuric acid–deuterium oxide reagents were prepared by distilling sulphur trioxide (itself distilled from oleum) into heavy water (d_4^{20} 1·10513) containing 99·74% of D_2O, in all-glass apparatus.[22] The products were analysed by titration with 0·4N-alkali; *e.g.*, one medium gave 75·49, 75·53, 75·55, 75·55, 75·55, 75·55, mean 75·54% D_2SO_4.

Inorganic salts used were of " AnalaR " quality and were dried at 110° before use, except ammonium sulphate, which was dried at 60—65°.

Reaction Mixtures.—100 c.c. of sulphuric acid reagent, at thermostat temperature, were transferred from a weighed standard flask to the 250 c.c. stoppered reaction flask. After a standard drainage time of 30 sec., the empty standard flask was re-weighed, to determine the exact amount of sulphuric acid used. A weighed amount of the alcohol (2 g.) was introduced from a cone-cap fitting the flask neck. Dissolution of the alcohol (accelerated by shaking) required a time (from <1 min. in 82% H_2SO_4 at 25° to over 4 hr. in 68% H_2SO_4 at 0°) short compared with the whole time of reaction. A small initial timing error was unimportant, since velocity coefficients were computed graphically. When dissolution was complete, the flask was placed under vacuum to remove air bubbles, after which samples (10 c.c.) were extracted by pipette at timed intervals. Volumetric apparatus was calibrated for the liquids used.

For experiments in deuterosulphuric acid, only 25 c.c. of reaction mixture were used and 2 c.c. samples were extracted. The loss in accuracy was small, *e.g.*, in 76·79% H_2SO_4 the standard method gave $K = 0{\cdot}684$, $k_E = 0{\cdot}0236$, and the modified procedure yielded $K = 0{\cdot}666$, $k_E = 0{\cdot}0238$.

Analytical Method.—The sample of reaction mixture was run on to a partly frozen mixture (cooled externally; for crushed ice in the reagent introduced oxidisable impurity) of 25 ml. of 0·32N-potassium dichromate with enough water to bring the final acid concentration to 6N. After 18 hr. the solution was titrated with 0·2M-ferrous ammonium sulphate (made up in 0·8N-sulphuric acid), with three drops of ferroin indicator.

For this adaptation of the dichromate oxidation method to the determination of 2 : 4-dinitrobenzyl alcohol, in presence of its sulphuric ester, 6N-sulphuric acid was found to be the optimum oxidation medium, allowing fast enough oxidation of the alcohol with minimal hydrolysis of the ester. Oxidation of the alcohol was complete after 3 hr. at 15°; but longer oxidation periods were more convenient for routine analyses. Twenty-two analyses, in the absence of ester, on 0·02—0·2 g. samples of 2 : 4-dinitrobenzyl alcohol (corresponding to concn. 0·01—0·1M in a reaction mixture), oxidised in 6N-acid at 13—18° for 16—216 hr., gave results within ±0·3% of the theoretical. To test the effect of ester, 0·1016M-alcohol was allowed to come to the esterification equilibrium (202 min.) in 87·08% sulphuric acid at 0°. Samples were then analysed for alcohol with exposure to the oxidant in 6N-acid, at 13—18°, for different times (Table 6).

TABLE 6.

Oxidation time (hr.)	18·9	19·0	44·4	44·8	68·9	90·8	91·0	215	217
10^2(ROH] (M)	1·28	1·27	1·33	1·33	1·38	1·40	1·41	1·60	1·60
$10^2[RHSO_4]$ (M)	8·88	8·89	8·83	8·83	8·78	8·75	8·75	8·56	8·56

From these figures it may be inferred that 0·5% of the ester present is hydrolysed in 24 hr. at 15°, and that hydrolysis during the oxidation period of 18 hr. can only affect the measured alcohol concentration appreciably when ester is present in great excess over alcohol. When this was so, the temperature was held below 10° during oxidation.

Equilibrium Constants.—The equilibrium concentration of alcohol was usually measured, for each medium, by a special experiment (see Table 1) continued long enough (0·8—33 hr. at 25°; 0·7—427 hr. at 0°) to allow for 4—9 determinations of the steady alcohol concentration. *E.g.*, in expt. 65 seven analyses, after reaction periods ranging from 3½ to 11 hr., returned $[ROH]_e$ = 0·0685, 0·0685, 0·0684, 0·0683, 0·0683, 0·0683, 0·0683, mean 0·0684.

ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.

[*Received, November 28th, 1955.*]

---

[22] Best and Wilson, *J.*, 1946, 239; Bonner, Bowyer, and Williams, *J.*, 1953, 2650.