

mechanism. The effect of change of solvent on a catalysed reaction is, of course, composite in nature, affecting the reaction (a) directly and (b) indirectly through the catalyst, e.g., by altering its acid or base strength. These two types of effect are somewhat analogous to the salt effects encountered in catalysed reactions, and will be referred to as *primary and secondary solvent effects*. This aspect of catalysed reactions has so far received but little attention. The study of solvent effects in two-component media seems particularly important in the case of catalysed reactions, because, as will be shown below, it allows the determination of isodielectric energies of activation, i.e., energies of activation calculated for a reaction medium of temperature-invariant dielectric constant. These are a better estimate of the true energy of activation than the values obtained by the direct application of the Arrhenius equation, and are likely to differ from the latter to a particularly large extent in reactions catalysed by substances themselves subject to a thermodynamic equilibrium.

(A) *The Variation of Rate Constants with Medium Composition.*—The relevant data are collected in Table I. In the range 20–80% by volume alcohol content the rate constants at constant acid concentration decrease rapidly with increasing alcohol concentration and decreasing dielectric constant of the solvent (hex-3-en-5-yn-2-ol remaining the sole reaction product), an increase by 20% of the alcohol content decreasing the rate by a nearly constant factor of ca. 3 when strong, and of ca. 4 when weak acids are employed as catalysts. The

TABLE I.

k = first-order rate constant (in min.⁻¹); D = dielectric constant of solvent; $\log k = mD + n$. Concentration of carbinol = 0.0729 mol./l. throughout.

Catalyst.	Solvent (vol.-% EtOH).	D .	10^4k .		Catalyst.	Solvent (vol.-% EtOH).	D .	10^4k .	
$t = 30.0^\circ$.									
0.1M-HCl	20	67.7	6.25	} $m = 0.0469$ $n = -2.39$	0.4M-HCl	20	67.7	32.8	
	40	57.6	2.09			40	57.6	10.5	
	60	46.3	0.583			60	46.3	3.25	
	80	34.6	0.210			80	34.6	1.12	
1M-HCl	20	67.7	111	} $m = 0.0385$ $n = -0.581$	4M-HCl	20	67.7	3700	
	40	57.6	43.1			30	62.7	2600	
	60	46.3	15.3			40	57.6	1440	
	80	34.6	5.07			60	46.3	1060	
	90	29.0	4.90						
	100	23.5	47.1						
$t = 40.0^\circ$.									
0.1M-HCl	20	64.4	21.0	} $m = 0.0468$ $n = -1.569$	1M-HCl	20	64.4	415	
	40	54.6	7.70			40	54.4	164	
	60	43.9	2.22			60	43.9	49.7	
	80	32.6	0.851			80	32.6	21.8	
0.4M-HCl	20	64.4	122	} $m = 0.0444$ $n = -0.795$	100	22.0	156		
	40	54.6	33.8						
	60	43.9	13.6						
	80	32.6	4.57						
$t = 50.0^\circ$.									
0.1M-HCl	20	61.5	64.4	} $m = 0.0420$ $n = -0.823$	0.4M-HCl	20	61.5	330	
	40	52.1	22.0			40	52.1	149	
	60	41.4	8.10			60	41.4	42.9	
	80	31.0	3.19			80	31.0	20.0	
	85	28.3	2.42			1M-HCl	20	61.5	1230
	90	25.8	2.29				40	52.1	517
95	23.1	2.98	60	41.4	172				
100	20.5	15.6	80	31.0	72.9				
				85	28.3	75.1			
				90	25.8	77.0			
				100	20.0	471			
$t = 60.0^\circ$.									
0.1M-HCl	20	59.2	220	} $m = 0.0393$ $n = -0.119$	1M-H ₃ PO ₄	20	59.2	225	
	40	49.7	56.8			40	49.7	66.8	
	60	38.3	28.1			60	38.3	15.8	
	80	29.3	10.0			80	29.3	2.72	
0.2M-H ₂ SO ₄	20	59.2	550	} $m = 0.0374$ $n = 0.432$	1M-AcOH	0	68.7	14.3	
	40	49.7	201			20	59.2	4.49	
	60	38.3	74.5			40	49.7	0.995	
	80	29.3	32.3			60	38.3	0.25	
						80	29.3	0.020	
				100	19.0	0.014			

rate constants for any one catalyst in different media at constant temperature can be accurately represented by the relation

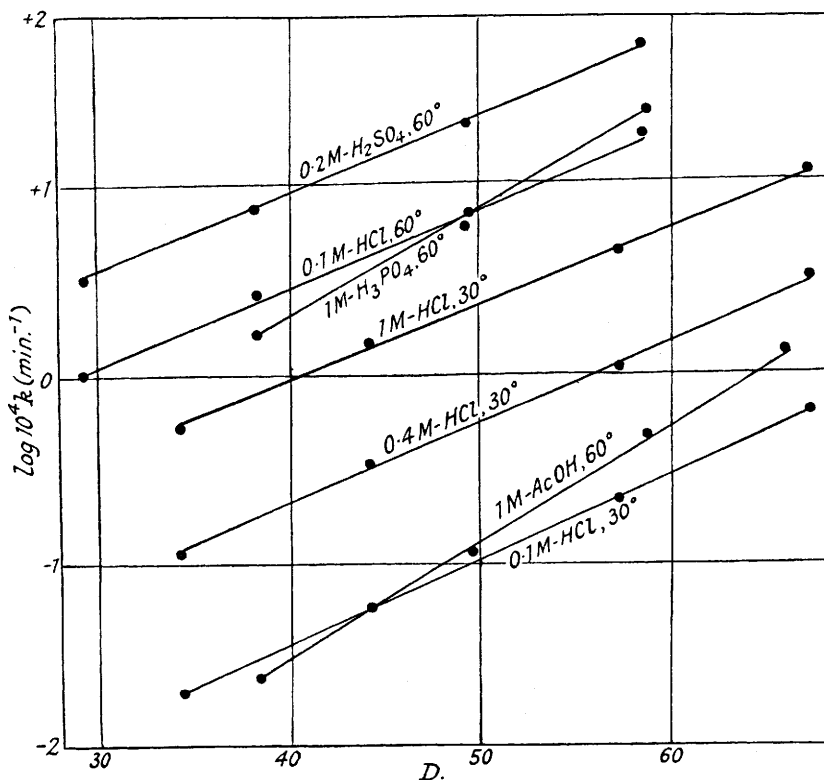
$$\log k = mD + n \dots \dots \dots (1)$$

where D is the dielectric constant of the alcohol-water mixture, and m and n are constants (Fig. 1); m varies

only slightly with acid concentration and temperature. In phosphoric and acetic acid, relation (1) only holds up to 60% alcohol content. In the latter case, the range of media could be extended to 0% alcohol content, propenylethynylcarbinol being sufficiently soluble in aqueous 1M-acetic acid. It may be noted that the $\log k$ - D plot is considerably more nearly linear than the $\log k$ -[EtOH] one (the [EtOH]- D plot being itself not quite linear), but that the variation in k can also be fairly satisfactorily represented by certain monotonic functions of D other than (1), such as $\log k = -p/D + q$, a form preferred by some authors on theoretical grounds. Actually, their results, as our own, are often more accurately represented by (1), and we prefer it for this reason and also because it is the most convenient relation for the calculation of isodielectric constants (see below), but no theoretical conclusions are based on this choice.

When 4M-hydrochloric acid is used as catalyst, intermediate formation of 2-chlorohex-3-en-5-yne and subsequent hydrolysis to the carbinol probably occurs, and relation (1) no longer holds.

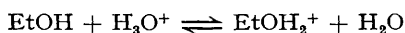
FIG. 1.



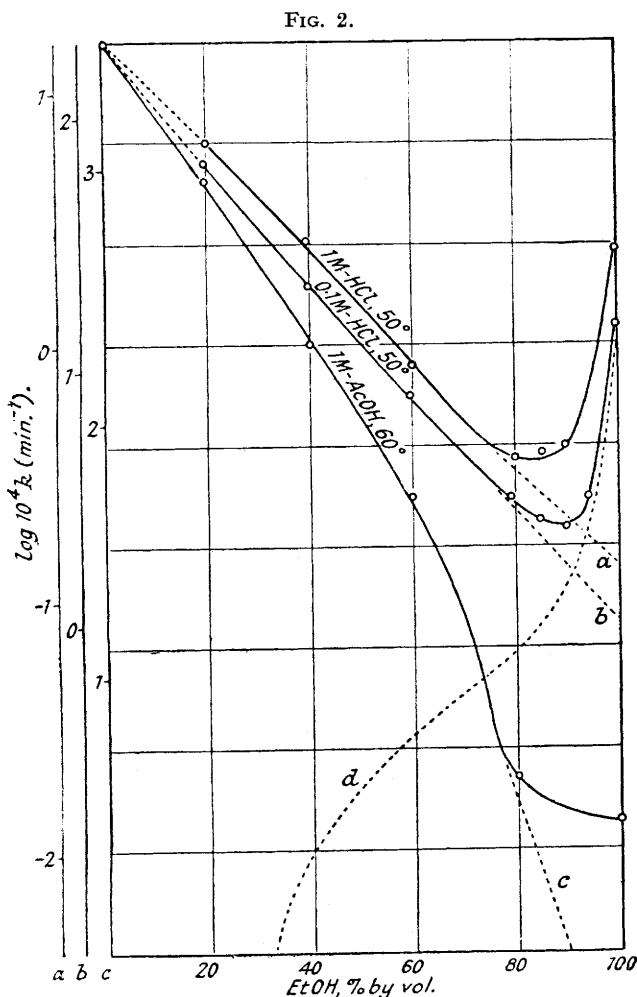
The linear dependence of k upon D according to (1) has been encountered before in first-order reactions such as the isomerisation of camphene hydrochloride and various keto-enol transformations (Meerwein and Emster, *Ber.*, 1920, **53**, 1815; 1922, **55**, 2500; Stobbe, *Annalen*, 1903, **326**, 347; Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933, p. 118). These investigations refer to a series of solvents rather than to change of composition in a two-component medium, but the same behaviour has been found more recently for series of water-alcohol mixtures (Hughes, J., 1935, 255; Price and Westheimer, *J. Chem. Physics*, 1943, **11**, 150) and has been interpreted by Hückel ("Theoretische Grundlagen der Organischen Chemie," Leipzig, 1931, p. 266) in terms of the dependence of the free energy of ionisation of the molecule undergoing a change on the dielectric constant of the medium. Such an interpretation is obviously valid only when the reaction mechanism actually involves a separation of two ions, whereas the present reaction, according to the mechanism proposed in Part I, involves the intramolecular fission of a carbon-oxygen bond into a carbonium ion and a neutral water molecule, the ease of which should be almost independent of the dielectric constant of the solvent.

Moreover, on increasing the alcohol content of the medium beyond 80%, the rate constants in hydrochloric acid are found to pass through a minimum at *ca.* 90% alcohol content and then to increase again, while in acetic acid the $\log k$ - D curve becomes almost parallel to the x axis (Fig. 2). The exact location of the minimum in the former case depends on the acid concentration and moves towards lower alcohol content with increasing acid concentration. The rise in the rate constants in hydrochloric acid between 90% and 100% alcohol content is very steep, the rate constant in 100% alcohol being similar to that in 40% alcohol, and it is probable that still higher values could be obtained in completely anhydrous alcohol (100% alcohol refers to Burnett's "absolute alcohol" which probably contains 0.1-0.3% of water). Some 2-ethoxyhex-3-en-5-yne is formed during the rearrangement in media of high alcohol content.

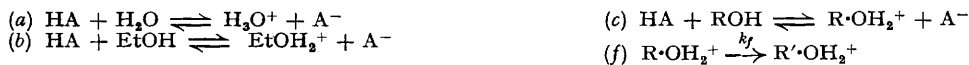
This behaviour is very similar to that exhibited by acid-catalysed esterification, and the acid-catalysed decomposition of diazoacetic ester (Goldschmidt, *Z. physikal. Chem.*, 1907, **60**, 728; *Z. Elektrochem.*, 1914, **20**, 473; Fraenkel, *Z. physikal. Chem.*, 1907, **60**, 202; Kailan, *Monatsh.*, 1907, **28**, 115; Bredig, *Ber.*, 1906, **39**, 1576; Millar, *Z. physikal. Chem.*, 1913, **85**, 129; and later papers) where minima in the rate constants occur for 85–95% alcohol content of the medium, depending on the catalysing acid and its concentration. The investigations of Goldschmidt and Bredig and their collaborators were concerned mainly with the inhibiting effects of small concentrations of water on the rate of reaction in alcohol, *i.e.*, with the range of reaction medium of very high alcohol content, and led to Goldschmidt's theory of ethoxonium-ion formation, adhered to by later workers, in which the strong anti-catalytic effect of adding water to the acid-alcohol medium was explained by the concomitant decrease in the concentration of ethoxonium ions, regarded as effective catalyst. Goldschmidt defined the "hydrolytic constant" (ν) as the equilibrium constant of the reaction



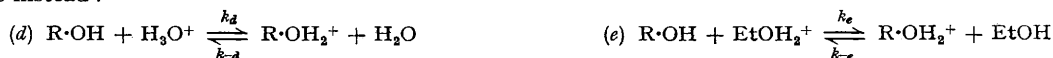
multiplied by the alcohol concentration, and ν was shown to have a value of *ca.* 0.2 for high alcohol concentrations. From this it can be calculated that the concentration of ethoxonium ions will become negligibly small ($[\text{EtOH}_2^+]/[\text{H}_3\text{O}^+] < 0.01$) on increasing the water content beyond *ca.* 20%. Goldschmidt's theory is now well accepted, but it may be noted that it deals only with the right hand part of the log k -alcohol content curve (Fig. 2) and gives no explanation why EtOH_2^+ is a far more effective catalyst than H_3O^+ . It will be shown below that such an explanation is provided by regarding the present case of acid catalysis as a proton-transfer reaction, the increase of rate constant with water content on the left-hand part of the curve being accounted for mainly as a secondary solvent effect, the increase in dielectric constant resulting in an increase in effective catalyst strength.



We have to consider the following set of reactions :



Since in dilute solution the amount of carbinol ($\text{R}\cdot\text{OH}$) is small compared with that of H_2O and EtOH , we can write instead :



The system (d), (e), (f) is amenable to simple analysis. Two possibilities arise; either the proton transfer (d), (e), or the rearrangement of the oxonium ion (f) is rate-determining. In the latter case, the rate of reaction is given by the transition-state theory as

$$v = k_f[\text{R}\cdot\text{OH}_2^+]f_{\text{R}\cdot\text{OH}_2^+}/f_{\text{X}_f} \quad \dots \quad (2)$$

where k 's represent rate constants, f 's represent activity coefficients and X_f refers to the transition state of reaction (f), and the rate constant of the total reaction

$$k = v/[\text{R}\cdot\text{OH}] = k_f[\text{R}\cdot\text{OH}_2^+]f_{\text{R}\cdot\text{OH}_2^+}/[\text{R}\cdot\text{OH}]f_{\text{X}_f} \quad \dots \quad (3)$$

This reduces to

$$k = \alpha k_f[\text{R}\cdot\text{OH}_2^+]/[\text{R}\cdot\text{OH}] \quad \dots \quad (3a)$$

where $f_{\text{R}\cdot\text{OH}_2^+} = \alpha f_{\text{X}_f}$, if $f_{\text{R}\cdot\text{OH}_2^+}$ varies in the same way as f_{X_f} with environment, or to

$$k = k_f[\text{R}\cdot\text{OH}_2^+]/[\text{R}\cdot\text{OH}] \quad \dots \quad (3b)$$

if the activity coefficients of the oxonium ion and the transition state have the same value, as is likely to be the case. We obtain the simple result that the rate constant of the reaction is equal to the rate constant of the actual rearrangement multiplied by the ratio $[R\cdot OH_2^+]/[R\cdot OH]$. Now the logarithm of this ratio is proportional to Hammett's acidity function which is defined by

$$H_0 = -\log a_{H^+} f_B / f_{BH^+} = pK_a^B - \log (c_{BH^+} / c_B) \dots \dots \dots (4)$$

where a_{H^+} represents the activity of the hydrogen ion and K_a^B is a constant (the equilibrium constant of the reaction $B + H^+ \rightleftharpoons BH^+$) and B is any neutral base (Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 827), so that at constant temperature $\log k$ should be simply proportional to H_0 . This has already been shown to be the case for the variation of k with acid concentration in a constant medium (Part I); the relevant values of the acidity functions for media of varying alcohol content are not at present available, but will form the subject of a separate investigation.

If, on the other hand, the oxonium-ion formation (*d*), (*e*) were rate-determining, application of Christiansen's equation (*Z. physikal. Chem.*, 1935, *B*, **28**, 303; Hammett, "Physical Organic Chemistry," McGraw-Hill, 1941, p. 107) yields

$$k = \frac{k_d k_f a_{H_3O^+}}{k_f / f_{x_d} + k_{-d} a_{H_2O}} + \frac{k_e k_f a_{EtOH_2^+}}{k_f / f_{x_e} + k_{-e} a_{EtOH}} \dots \dots \dots (5)$$

and approximately, since $k_f \gg k_d, k_e$ on the present assumption

$$k = k_d a_{H_3O^+} / f_{x_d} + k_e a_{EtOH_2^+} / f_{x_e} \dots \dots \dots (5a)$$

This reduces further to

$$k = k_d a_{H_3O^+} / f_{x_d} = k_d [H_3O^+] \times \frac{f_{H_3O^+}}{f_{x_d}} = \beta k_d [H_3O^+] \dots \dots \dots (5b)$$

for a constant medium of low alcohol content where $[EtOH_2^+] \ll [H_3O^+]$ and β is the ratio of the activity coefficients of the hydroxonium ion and the transition state of reaction (*f*). Since the latter is itself an oxonium ion, β should be inappreciably affected by change in acid concentration, and the rate constants should thus be proportional to $[H_3O^+]$, *i.e.*, the stoichiometric acid concentration. It has already been shown (Part I) that in the present reaction $\log k$ is not proportional to $\log c_A$ above $c_A = 0.1$ or to the pH at constant alcohol concentration, nor is it proportional to the pH at constant acid concentration, as shown by a comparison with the pH values of 0.5M-hydrochloric acid solutions in alcohol-water mixtures (Millet, *Trans. Faraday Soc.*, 1927, **23**, 515). In any case, $a_{H_3O^+} / f_{x_d}$ is not proportional to H_0 (the latter differing from the former by the factor $f_B f_{x_d} / f_{BH^+}$ which is not a constant) and a reaction obeying (3*b*) is therefore unlikely to obey (5*b*).

It therefore appears that the first assumption is the correct one and that the rearrangement (*f*) rather than the proton-transfer (*d*), (*e*) is the rate-determining step. Brønsted originally took the view that the proton-transfer is always rate-determining in acid catalysis, but evidence has since accumulated which shows that the other alternative applies in many instances (Euler, *Z. physikal. Chem.*, 1927, **131**, 107 and earlier papers; Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686) and this reaction is evidently one of them. It is hoped to adduce further evidence for this conclusion from the study of the effect of substituents on the rate of rearrangement. If the distinction between the linear variation of rate with oxonium-ion concentration or acidity function respectively can be further substantiated as a criterion of the rate-determining step, the concept of acidity function becomes one of the first importance in the study of the mechanisms of catalysed reactions.

It remains then to explain the variation of the ratio $[R\cdot OH_2^+]/[R\cdot OH]$ or of the acidity function, with medium composition, the $\log k$ -[EtOH] curve being identical with the $\log [R\cdot OH_2^+]/[R\cdot OH]$ -[EtOH] curve according to equations (3*a*) and (3*b*). The linear decrease of k up to 80% alcohol content is undoubtedly a dielectric-constant effect. In the case of hydrochloric acid, even if complete dissociation takes place in purely aqueous solution, this no longer applies to alcoholic solutions. The existence of ion pairs in solutions of strong electrolytes has been demonstrated by optical as well as conductivity measurements (Falkenhagen, "Elektrolyte," Leipzig, 1932, p. 304; Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1935, **55**, 21; Halban and Litmanovitch, *Helv. Chim. Acta*, 1941, **24**, 41) and dissociation will become more incomplete with increasing alcohol content of the medium, with a corresponding decrease in the ability of the solution to transfer protons to R·OH. In the case of acetic acid the decrease in D runs parallel with a decrease in the extent of ionisation. The primary solvent effect, *i.e.*, the direct influence of the change in dielectric constant on the equilibrium constants of reaction (*d*), (*e*) and on the rate of reaction (*f*), is likely to be small, since all these three reactions are of the dipole-ion type (cf. Moelwyn-Hughes and Sherman, *J.*, 1936, 101). At 85% alcohol content, the proportion of $EtOH_2^+$ as compared with H_3O^+ ions becomes appreciable and as $EtOH_2^+$ gives up its extra proton much more readily than H_3O^+ (the equilibrium constant of the reaction $EtOH_2^+ + H_2O \rightleftharpoons EtOH + H_3O^+$ is about 100) the ratio $[R\cdot OH_2^+]/[R\cdot OH]$ increases. The curve relating k and [EtOH] is therefore really the sum of two broken curves (Fig. 2), one (*a*, *b*, or *c*) representing the decrease in k with decreasing acidity function and dielectric constant, and the other (*d*) the increase in k with the increase in the ratio $[EtOH_2^+]/[H_3O^+]$. When a weak acid such as acetic acid is used as catalyst, the curve is steeper, but flattens out for high values of [EtOH] without a distinct minimum, because the decrease of acid ionisation with increasing alcohol content is very

much faster than the decrease in dissociation of the strong hydrochloric acid, and of the same order magnitude as the rate of increase of ethoxonium-ion concentration even at high alcohol concentrations.

The only reaction for which a mechanism analogous to the present one has been postulated and which has been studied under comparable conditions, appears to be the hydrochloric acid catalysed inversion of sucrose (Amis, *J. Amer. Chem. Soc.*, 1941, **63**, 2231). A decrease in rate with increasing alcohol content (up to 50% of the medium is also found, which is much smaller in magnitude than in the present case and is erroneously attributed to the formation of EtOH_2^+ ions, which would, if anything, tend to increase the rate. Actual concentration of EtOH_2^+ ions at the alcohol concentrations used is negligible (cf. Goldschmidt, *loc. cit.*) and it is probable that the reaction mechanism is much more complicated than $\text{S} + \text{H}^+ \rightleftharpoons \text{SH}^+ \rightarrow \text{product}$ (cf. Leininger and Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **59**, 2891).

(B) *The Variation of Energy of Activation with Medium Composition. The Calculation of Isodielectric Energies of Activation.*—The data relating to rate constants at different temperatures are collected in Tables II and III, where E_{exp} represents the experimental energy of activation calculated from the Arrhenius equation. It will be seen that E_{exp} varies with medium composition and catalyst in an irregular fashion to the extent 6 kg.-cals. (the estimated maximum error in E_{exp} is ± 0.3 kg.-cal.).

It was pointed out in Part I that E_{exp} , calculated from the overall temperature coefficient includes the temperature dependence of the catalyst strength. The latter will be made up mainly of two parts: (i) the pure thermodynamic temperature dependence of the catalyst equilibrium such as $\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-$, and (ii) the dependence of that equilibrium on the dielectric constant of the medium which, in turn, varies considerably with temperature. The latter effect, together with the dependence, if any, of the reaction itself on the dielectric constant, will make up the larger part of the "untrue" portion of the experimental energy of activation. We can write this

$$E_{[\text{D}]} = E_{\text{exp.}} + \Delta E_{\text{D}} \dots \dots \dots (6)$$

TABLE II.

k = first-order rate constant (in min.^{-1}); $k_{[\text{D}]}$ = isodielectric rate constant (in min.^{-1}); $E_{\text{exp.}}$ = experimental energy of activation (in kg.-cals.); $E_{[\text{D}]}$ = isodielectric energy of activation (in kg.-cals.). Catalyst = 0.1M-HCl.

Temp.	$10^4 k$	$E_{\text{exp.}}$	$10^4 k_{[\text{D}]}$	$E_{[\text{D}]}$ by (8).	m .	b .	$E_{[\text{D}]}$ by (9).
Medium: 20% EtOH (by vol.).							
30°	6.25	23.2	6.25	30.9	0.044	0.365	30.5
40	21.0		30.3				
50	64.4		133				
60	220		652				
Medium: 40% EtOH (by vol.).							
30	2.09	22.7	2.09	29.7	0.044	0.342	29.5
40	7.70		10.8				
50	22.0		43.4				
60	56.8		157				
Medium: 60% EtOH (by vol.).							
30	0.583	25.7	0.583	31.4	0.044	0.286	31.4
40	2.22		2.95				
50	8.10		14.3				
60	28.1		65.8				
Medium: 80% EtOH (by vol.).							
30	0.210	25.7	0.210	30.2	0.044	0.225	30.7
40	0.851		1.06				
50	3.19		4.95				
60	10.0		19.5				

TABLE III.

Catalyst.	Solvent (vol.-% EtOH).	$E_{\text{exp.}}$	m .	b .	ΔE_{D} by (9).	$E_{[\text{D}]}$ by (9).
0.1M-HCl	20	23.2	0.044	0.365	7.3	30.5
	40	22.7	0.044	0.342	6.8	29.5
	60	25.7	0.044	0.286	5.0	31.4
	80	25.7	0.044	0.225	4.5	30.2
0.4M-HCl	20	23.5	0.042	0.365	6.8	30.3
	40	25.1	0.042	0.342	6.4	31.5
	60	24.7	0.042	0.286	5.3	30.0
	80	27.5	0.042	0.225	4.2	31.7
1M-HCl	20	24.2	0.040	0.365	6.5	30.7
	40	24.7	0.040	0.342	6.1	30.8
	60	25.8	0.040	0.286	5.1	30.9
	80	26.5	0.040	0.225	4.0	30.5
	90	27.3	—	—	—	—
	100	22.5	—	—	—	—
0.2M-H ₂ SO ₄	20	23.8 *	0.037	0.365	6.2	30.0
1M-H ₃ PO ₄	20	21.6 *	0.053	0.365	8.9	30.5
1M-AcOH	20	22.2 *	0.061	0.365	10.1	32.3

* Values taken from Part I.

