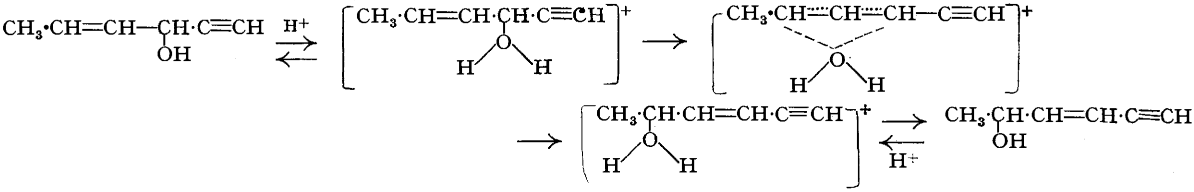
119. *The Kinetics of Anionotropic Rearrangement. Part II. Medium Effects in the Oxotropy of Propenylethynylcarbinol. The Determination of Isodielectric Energies of Activation.*

By Ernest A. Braude.

Further evidence is adduced for the reaction mechanism proposed in Part I from a study of the effect of varying the alcohol content of the reaction medium on the rate of reaction and energy of activation. The rearrangement of the oxonium ion ROH_2^+, not the preceding proton-transfer reaction, appears to be the rate-determining step. A method is outlined for the calculation of isodielectric energies of activation, the values obtained being 4 to 10 kg.-cals. higher than the experimental energies of activation and practically independent of the composition of the aqueous-alcoholic solvent.

In Part I (Braude and Jones, preceding paper) the mechanism



was proposed for the rearrangement of propenylethynylcarbinol, as the result of an investigation of the kinetics of the reaction in aqueous solution containing 20% by volume of ethyl alcohol. It appeared worth while to extend the investigation to other ethyl alcohol–water mixtures, both for the intrinsic interest of the dependence of reaction rate on medium composition and the additional evidence it would provide concerning the reaction 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 rate constants for any one catalyst in different media at constant temperature can be accurately represented by the relation

$$\log k = mD + n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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

TABLE I.

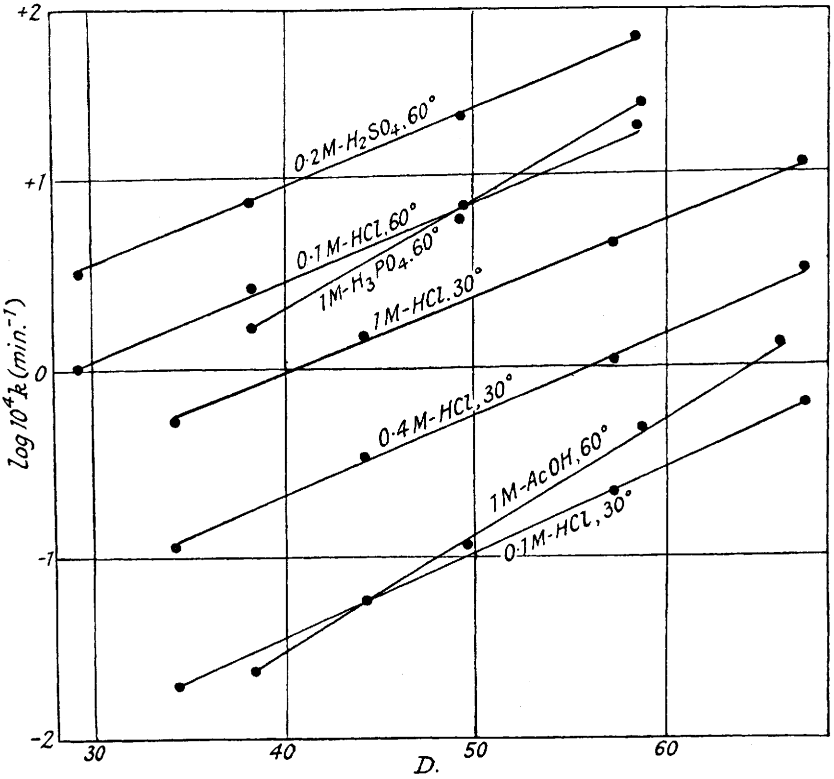
k = first-order rate constant (in min.$^{-1}$); D = dielectric constant of solvent; $\log k = mD + n$. Concentration of carbinol = 0·0729 mol./l. throughout.

Catalyst.	Solvent (vol.-% EtOH).	*D*.	10^4k.		Catalyst.	Solvent (vol.-% EtOH).	*D*.	10^4k.	
					t = 30·0°.				
0·1M-HCl	20	67·7	6·25		0·4M-HCl	20	67·7	32·8	
	40	57·6	2·09	$m = 0{\cdot}0469$		40	57·6	10·5	$m = 0{\cdot}0439$
	60	46·3	0·583	$n = -2{\cdot}39$		60	46·3	3·25	$n = -1{\cdot}49$
	80	34·6	0·210			80	34·6	1·12	
1M-HCl	20	67·7	111		4M-HCl	20	67·7	3700	
	40	57·6	43·1	$m = 0{\cdot}0385$		30	62·7	2600	
	60	46·3	15·3	$n = -0{\cdot}581$		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°.				
0·1M-HCl	20	64·4	21·0		1M-HCl	20	64·4	415	
	40	54·6	7·70	$m = 0{\cdot}0468$		40	54·4	164	$m = 0{\cdot}0419$
	60	43·9	2·22	$n = -1{\cdot}569$		60	43·9	49·7	$n = -0{\cdot}095$
	80	32·6	0·851			80	32·6	21·8	
0·4M-HCl	20	64·4	122			90	27·2	21·8	
	40	54·6	33·8	$m = 0{\cdot}0444$		100	22·0	156	
	60	43·9	13·6	$n = -0{\cdot}795$					
	80	32·6	4·57						
					t = 50·0°.				
0·1M-HCl	20	61·5	64·4		0·4M-HCl	20	61·5	330	
	40	52·1	22·0	$m = 0{\cdot}0420$		40	52·1	149	$m = 0{\cdot}0393$
	60	41·4	8·10	$n = -0{\cdot}823$		60	41·4	42·9	$n = -0{\cdot}075$
	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	$m = 0{\cdot}0400$
	95	23·1	2·98			60	41·4	172	$n = 0{\cdot}612$
	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°.				
0·1M-HCl	20	59·2	220		1M-H_3PO_4	20	59·2	225	$m = 0{\cdot}0528$
	40	49·7	56·8	$m = 0{\cdot}0393$		40	49·7	66·8	$n = -0{\cdot}802$
	60	38·3	28·1	$n = -0{\cdot}119$		60	38·3	15·8	
	80	29·3	10·0			80	29·3	2·72	
0·2M-H_2SO_4	20	59·2	550		1M-AcOH	0	68·7	14·3	
	40	49·7	201	$m = 0{\cdot}0374$		20	59·2	4·49	$m = 0{\cdot}0621$
	60	38·3	74·5	$n = 0{\cdot}432$		40	49·7	0·995	$n = -2{\cdot}98$
	80	29·3	32·3			60	38·3	0·25	
						80	29·3	0·020	
						100	19·0	0·014	

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.

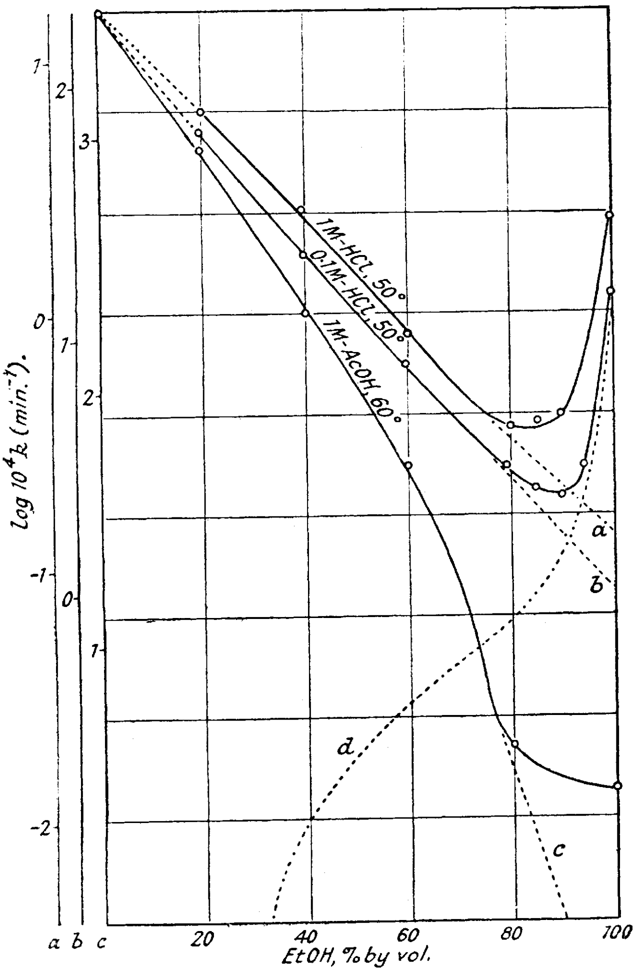
Moreover, on increasing the alcohol content of the medium beyond 80%, the rate constants in hydrochloric acid are found to pass through a minimum at *ca.* 90% alcohol content and then to increase again, while in acetic acid the log k–D curve becomes almost parallel to the x axis (Fig. 2). The exact location 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" (r) as the equilibrium constant of the reaction

$$\mathrm{EtOH} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{EtOH_2^+} + \mathrm{H_2O}$$

multiplied by the alcohol concentration, and r 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 ($[\mathrm{EtOH_2^+}]/[\mathrm{H_3O^+}] < 0{\cdot}01$) 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 $\mathrm{EtOH_2^+}$ is a far more effective catalyst than $\mathrm{H_3O^+}$. 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.

FIG. 2.



We have to consider the following set of reactions:

(a) $\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}$

(b) $\mathrm{HA} + \mathrm{EtOH} \rightleftharpoons \mathrm{EtOH_2^+} + \mathrm{A^-}$

(c) $\mathrm{HA} + \mathrm{ROH} \rightleftharpoons \mathrm{R{\cdot}OH_2^+} + \mathrm{A^-}$

(f) $\mathrm{R{\cdot}OH_2^+} \xrightarrow{k_f} \mathrm{R'{\cdot}OH_2^+}$

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

(d) $\mathrm{R{\cdot}OH} + \mathrm{H_3O^+} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \mathrm{R{\cdot}OH_2^+} + \mathrm{H_2O}$

(e) $\mathrm{R{\cdot}OH} + \mathrm{EtOH_2^+} \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \mathrm{R{\cdot}OH_2^+} + \mathrm{EtOH}$

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

$$v = k_f[\mathrm{R{\cdot}OH_2^+}]f_{\mathrm{R\cdot OH_2^+}}/f_{\mathrm{X}_f} \quad \ldots\ldots\ldots\ldots \quad (2)$$

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

$$k = v/[\mathrm{R{\cdot}OH}] = k_f[\mathrm{R{\cdot}OH_2^+}]f_{\mathrm{R\cdot OH_2^+}}/[\mathrm{R{\cdot}OH}]f_{\mathrm{X}_f} \quad \ldots\ldots\ldots \quad (3)$$

This reduces to

$$k = \alpha k_f[\mathrm{R{\cdot}OH_2^+}]/[\mathrm{R{\cdot}OH}] \quad \ldots\ldots\ldots\ldots \quad (3a)$$

where $f_{\mathrm{R\cdot OH_2^+}} = \alpha f_{\mathrm{X}_f}$, if $f_{\mathrm{R\cdot OH_2^+}}$ varies in the same way as f_{X_f} with environment, or to

$$k = k_f[\mathrm{R{\cdot}OH_2^+}]/[\mathrm{R{\cdot}OH}] \quad \ldots\ldots\ldots\ldots \quad (3b)$$

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 $[\mathrm{R{\cdot}OH_2^+}]/[\mathrm{R{\cdot}OH}]$. Now the logarithm of this ratio is proportional to Hammett's acidity function which is defined by

$$H_0 = -\log a_{\mathrm{H}^+} f_{\mathrm{B}}/f_{\mathrm{BH}^+} = \mathrm{p}K_a^{\mathrm{B}} - \log (c_{\mathrm{BH}^+}/c_{\mathrm{B}}) \tag{4}$$

where a_{H^+} represents the activity of the hydrogen ion and K_a^{B} is a constant (the equilibrium constant of the reaction $\mathrm{B + H^+ \rightleftharpoons BH^+}$) 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

$$k = \frac{k_d k_f a_{\mathrm{H_3O^+}}}{k_f/f_{\mathrm{X}_d} + k_{-d} a_{\mathrm{H_2O}}} + \frac{k_e k_f a_{\mathrm{EtOH_2^+}}}{k_f/f_{\mathrm{X}_e} + k_{-e} a_{\mathrm{EtOH}}} \tag{5}$$

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

$$k = k_d a_{\mathrm{H_3O^+}}/f_{\mathrm{X}_d} + k_e a_{\mathrm{EtOH_2^+}}/f_{\mathrm{X}_e} \tag{5a}$$

This reduces further to

$$k = k_d a_{\mathrm{H_2O^+}}/f_{\mathrm{X}_d} = k_d[\mathrm{H_3O^+}] \times \frac{f_{\mathrm{H_3O}}{}^{+}}{f_{\mathrm{X}_d}} = \beta k_a[\mathrm{H_3O^+}] \tag{5b}$$

for a constant medium of low alcohol content where $[\mathrm{EtOH_2^+}] \ll [\mathrm{H_3O^+}]$ 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 $[\mathrm{H_3O^+}]$, *i.e.*, the stoicheiometric acid concentration. It has already been shown (Part I) that in the present reaction log k is not proportional to log c_{A} above $c_{\mathrm{A}} = 0{\cdot}1$ 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, $a_{\mathrm{H_3O^+}}/f_{\mathrm{X}_d}$ is not proportional to H_0 (the latter differing from the former by the factor $f_{\mathrm{B}} f_{\mathrm{X}_d}/f_{\mathrm{BH}^+}$ which is not a constant) and a reaction obeying (3b) is therefore unlikely to obey (5b).

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. Brönsted 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 $[\mathrm{R{\cdot}OH_2^+}]/[\mathrm{R{\cdot}OH}]$ or of the acidity function, with medium composition, the log k–[EtOH] curve being identical with the log $[\mathrm{R{\cdot}OH_2^+}]/[\mathrm{R{\cdot}OH}])$–[EtOH] curve according to equations (3a) and (3b). 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 Litmanovitsch, *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 $\mathrm{EtOH_2^+}$ as compared with $\mathrm{H_3O^+}$ ions becomes appreciable and as $\mathrm{EtOH_2^+}$ gives up its extra proton much more readily than $\mathrm{H_3O^+}$ (the equilibrium constant of the reaction $\mathrm{EtOH_2^+ + H_2O \rightleftharpoons EtOH + H_3O^+}$ is about 100) the ratio $[\mathrm{R{\cdot}OH_2^+}]/[\mathrm{R{\cdot}OH}]$ 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 $[\mathrm{EtOH_2^+}]/[\mathrm{H_3O^+}]$. 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 h been studied under comparable conditions, appears to be the hydrochloric acid catalysed inversion of sucro (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 erroneous attributed to the formation of $EtOH_2^+$ ions, which would, if anything, tend to increase the rate. Actual the concentration of $EtOH_2^+$ ions at the alcohol concentrations used is negligible (cf. Goldschmidt, *loc. ci* and it is probable that the reaction mechanism is much more complicated than $S + H^+ \rightleftharpoons SH^+ \longrightarrow$ produc (cf. Leininger and Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **59**, 2891).

(B) *The Variation of Energy of Activation with Medium Composition. The Calculation of Isodielect Energies of Activation.*—The data relating to rate constants at different temperatures are collected in Tables and III, where $E_{\text{exp.}}$ represents the experimental energy of activation calculated from the Arrhenius equatic It will be seen that $E_{\text{exp.}}$ varies with medium composition and catalyst in an irregular fashion to the extent 6 kg.-cals. (the estimated maximum error in $E_{\text{exp.}}$ is $\pm 0{\cdot}3$ kg.-cal.).

It was pointed out in Part I that $E_{\text{exp.}}$ calculated from the overall temperature coefficient includes the temp ature 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 $HOAc \rightleftharpoons H^+ + OAc^-$, and the dependence of that equilibrium on the dielectric constant of the medium which, in turn, varies considerat with temperature. The latter effect, together with the dependence, if any, of the reaction itself on the dielect constant, will make up the larger part of the " untrue " portion of the experimental energy of activatic We can write this

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

TABLE II.

k = first-order rate constant (in min.$^{-1}$) ; $k_{[D]}$ = isodielectric rate constant (in min.$^{-1}$) ; $E_{\text{exp.}}$ = experimental energy activation (in kg.-cals.) ; $E_{[D]}$ = isodielectric energy of activation (in kg.-cals.). Catalyst = 0·1M-HCl.

Temp.	10^4k.	$E_{\text{exp.}}$.	$10^4k_{[D]}$.	$E_{[D]}$ by (8).	m.	b.	$E_{[D]}$ 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).	$E_{[D]}$ 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_2SO_4	20	23·8 *	0·037	0·365	6·2	30·0
1M-H_3PO_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.

where $E_{[D]}$ represents the *isodielectric energy of activation, i.e.*, for a medium of constant dielectric constant. Actually, since D decreases with increasing temperature, $E_{\text{exp.}}$ will generally be smaller than $E_{[D]}$ for reactions exhibiting mainly specific ion catalysis, *i.e.*, ΔE_D will be positive.

The correction for ΔE_D can be applied by combining Wyman's data (*J. Amer. Chem. Soc.*, 1931, **53**, 3292) for the dielectric constants of ethyl alcohol–water mixtures at different temperatures with the data on the variation of the reaction rate with the dielectric constant referred to above. Wyman's data can be expressed with sufficient accuracy by

$$D = a - b(t - 20) \qquad \qquad (7)$$

where a and b are constants for any one reaction medium and t is the temperature. By combining (1) and (7), the correction takes the simple form

$$k_{[D]} = k \text{ antilog } [(t_2 - t_1)mb] \qquad \qquad (8)$$

where $k_{[D]}$ represents the rate constant at the temperature t_2 for a medium having the same dielectric constant as at t_1 and will be subsequently referred to as *isodielectric rate constant.* Values of a and b are tabulated by Wyman, and values of m can be taken directly from Table I. The large magnitude of the correction is evident from the $k_{[D]}$ values given in Table II. $E_{[D]}$ is then obtained by applying the Arrhenius equation to the $k_{[D]}$ values.

There is a more direct way of obtaining $E_{[D]}$ in the present case, in view of the simple form of the relation between D and t. Since

$$E_{[D]} = 2{\cdot}3\boldsymbol{R}[T_1T_2/(T_2 - T_1)] \log k_{[D]2}/k_1$$

and, by (8)

$$\log k_{[D]2} = \log k_2 mb(T_2 - T_1)$$

hence

$$E_{[D]} = E_{\text{exp.}} + 2{\cdot}3\boldsymbol{R}T_1T_2mb \qquad \qquad (9)$$

Table II shows the close agreement between values of $E_{[D]}$ obtained by (8) and by (9), an agreement which demonstrates the linearity of the $k_{[D]}$–$1/T$ plot. Equation (9) is, of course, the less accurate, but much more convenient to use. T_1 and T_2 are taken as the limits of the temperature range for which $E_{\text{exp.}}$ has been measured.

The objection may be raised that the dielectric constant of the actual solution and not that of the solvent should be used. This objection is answered if it is remembered that we are concerned with the variation in D and not its absolute value, and if the not unreasonable assumption may be made that variations in D of the solution are proportional to the variations in D of the solvent.

The method outlined above for determining isodielectric energies of activation is identical in principle with that employed by Svirbely and by Amis (*J. Amer. Chem. Soc.*, 1935, **57**, 1883; 1938, **60**, 330, 1613; 1941, **63**, 1606, 2231, 2621, 2833; *J. Physical Chem.*, 1943, **47**, 338). Both methods depend on the assumption that, within the range of medium composition considered, the chief influence of the change of solvent on the rate of reaction is exerted through the change in dielectric constant. This assumption appears to be strongly supported by the fact that while the values of $E_{\text{exp.}}$ vary in an irregular fashion with alcohol content and acid concentration over a range of 6 kg.-cals., the values of $E_{[D]}$ are constant to ± 1 kg.-cal. (Table III), a variation which does not greatly exceed the experimental error ($\pm 0{\cdot}3$ kg.-cal.) and would not in any case be unexpected, because, although the variation of D with temperature is assumed to be the chief factor responsible for the difference between the true and the experimental energy of activation, it is probably not the only factor. Variations of solvation and activities of the reactants with solvent composition have, of course, generally to be considered, but their influence in reactions of the present type is likely to be small, because the rate equation (3) involves the ratio of the activities of the actual reactant ($R{\cdot}OH_2^+$) and the very similar transition state.

The constancy of $E_{[D]}$ for media of different dielectric constants lends additional support to the reaction mechanism proposed in Part I and excludes a bi-ionic mechanism of the type $R{\cdot}OH \overset{\text{slow}}{\rightleftarrows} R^+ + OH^- \xrightarrow{\text{fast}} R'{\cdot}OH$, the energy of activation of which should vary with the medium to an extent which can be calculated theoretically from electrostatic considerations (Moelwyn-Hughes and Sherman, *loc. cit.*; Amis, *loc. cit.*; Waters, J., 1942, 153).

The experimental procedure was as described in Part I. Solutions of hydrochloric acid in absolute alcohol were prepared by the method of Hickling and Salt (*Trans. Faraday Soc.*, 1941, **37**, 224).

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