118. *The Kinetics of Anionotropic Rearrangement. Part I. The Rearrangement of Propenylethynylcarbinol.*

By Ernest A. Braude and E. R. H. Jones.

A kinetic study of the acid-catalysed anionotropic rearrangement :

$$CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}CH \longrightarrow CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{\vdots}CH$$

has been made, the course of the reaction being followed by measuring the changing absorption of ultra-violet light. This accurate and convenient method of determining reaction rates is of wide applicability but has been little employed hitherto. In aqueous solution containing 20% by volume of alcohol the reaction is of the first order, the rate being independent of the initial concentration of the carbinol, strictly proportional to the hydrogen-ion concentration at low, and to Hammett's acidity function at high acidities, and almost identical with the rate of racemisation. The salt effect is positive. The experimental energy of activation varies from 19 to 24 kg.-cals. over a wide range of conditions. The mechanism of the reaction is discussed with reference to current theories of anionotropy, and the oxonium ion (II ; see p. 443) is suggested as the principal intermediate.

Although tautomeric systems of the type $X{-}A{-}B{=}C \rightleftharpoons A{=}B{-}C{-}X$ (where X is an anion) have long been known, and have been recognised as counterparts to prototropic systems during the past twenty years, few quantitative kinetic studies of anionotropy have been made. The work of Burton and Ingold (J., 1928, 904) and of Burton (J., 1928, 1650 *et seq.*) on the rearrangement of arylallylcarbinols was entirely qualitative, and the velocity measurements reported by Kenyon, Partridge, and Phillips (J., 1937, 207) are rather incomplete. Meisenheimer and Beutter (*Annalen*, 1937, **508**, 58) made a quantitative study of the replacement acetylation of cinnamyl chloride, but not primarily from the point of view of the simultaneous partial rearrangement to the phenylallyl derivative. Similarly, the work of Meisenheimer and Link (*Annalen*, 1930, **479**, 211), and of Young and Lane (*J. Amer. Chem. Soc.*, 1938, **60**, 847) on replacement halogenations in the phenylvinylcarbinol and the crotyl alcohol series, was concerned mainly with the analysis of reaction products.

The range of examples of simple anionotropic systems has recently been considerably extended by the discovery (Jones and McCombie, J., 1943, 261 and subsequent papers) of rearrangements such as :

$$CH_3\cdot CH{:}CH\cdot CH(OH)\cdot C{\vdots}CH \xrightarrow{\text{acid}} CH_3\cdot CH(OH)\cdot CH{:}CH\cdot C{\vdots}CH$$

which, in common with the cases cited above, involve the formation of a conjugated system, but have the advantage of being purely aliphatic in nature, thus avoiding complications arising from the presence of a benzenoid ring. A ready means of following the rate of rearrangements of this type is provided by the large difference in ultra-violet light absorption between isolated and conjugated vinylacetylene systems. For work in dilute solution, absorption spectrophotometric assay is far more convenient and accurate than, for instance, the determination of refractive index or chemical analysis, which often involves the isolation of the reaction products at several stages of the reaction. The wide scope and great potentialities of this method of studying reaction kinetics deserve special emphasis. Visible and infra-red light absorption have been utilised for the determination of reaction rates in a limited number of cases, but ultra-violet light absorption, which is more widely applicable to organic systems than the former and more easily accessible experimentally at present than the latter, does not appear to have been used previously in this way except by Batley (*Trans. Faraday Soc.*, 1928, **24**, 438). With photographic spectrophotometry, the accuracy of the rate constants obtained by this method is limited to about 1%, as it is in most other methods commonly employed, but by the introduction of photoelectric spectrophotometry much higher precision could be attained. Actually, the limit to accuracy is generally set by internal factors such as the incomplete exclusion of side reactions.

The present paper deals exclusively with the rearrangement of propenylethynylcarbinol, but the kinetics of other cases of the anionotropic formation of vinylacetylene systems have been examined and will be reported in due course. The investigation will also be extended to embrace anionotropic changes yielding styrene, butadiene, and higher polyene and polyenyne systems.

The heterogeneous conditions of rearrangement used by Jones and McCombie (*loc. cit.*) were obviously unsuitable for kinetic studies, propenylethynylcarbinol and its isomer, hex-3-en-5-yn-2-ol, being only sparingly soluble in water. Although the use of an aqueous medium in the study of reactions involving ionic components has theoretical disadvantages (see Bell, *Trans. Faraday Soc.*, 1938, **34**, 234), the lack of knowledge regarding acid strengths in other solvents made it, nevertheless, desirable, in the first instance, to retain water as the principal component of the reaction medium. An organic solvent was sought which (i) is miscible with water and the carbinols, (ii) has low ultra-violet light absorption, (iii) is unaffected by acids over prolonged periods, and (iv) does not interact with propenylethynylcarbinol, its isomer, or any intermediates in the presence of acids. Alcohol was an obvious choice, after it had been ascertained that no ether formation took place in hydrochloric acid solutions containing up to 80% by volume of alcohol, other solvents such as acetone or dioxan, in which ether formation is impossible, being excluded because of conditions (ii) and (iii).

In a water–alcohol mixture containing 20% by volume of alcohol the reaction is strictly of the first order (see Experimental) and the rate constant is independent of the initial concentration of carbinol between $c = 0{\cdot}02$ and 0·15 mol./l. At higher concentrations, when the carbinol becomes an appreciable constituent of the reaction medium, a slight decrease in the rate constant occurs (Table I), similar in magnitude to that produced by increasing the alcohol concentration (unpublished observation). In the range of conditions investigated, the reaction product is always hex-3-en-5-yn-2-ol and the reaction goes to > 98% completion, as indicated by the final

TABLE I.

Reaction medium, 20% aqueous EtOH; * $t = 30{\cdot}0°$; k = first-order rate constant; c = concentration of carbinol.

c (g./100 ml.).	c (mols./l.).	$k \times 10^4$ (min.$^{-1}$).	c (g./100 ml.).	c (mols./l.).	$k \times 10^4$ (min.$^{-1}$).	c (g./100 ml.).	c (mols./l.).	$k \times 10^4$ (min.$^{-1}$).
Catalyst, 0·4M-HCl.						Catalyst, 2M-HCl.		
0·210	0·0219	32·7	1·50	0·156	32·6	0·350	0·0364	542
0·700	0·0729	32·8	2·00	0·208	30·8	0·700	0·0729	544
0·790	0·0822	32·9	3·86	0·402	29·2			

* 20% Aqueous EtOH in this and subsequent tables refers to an aqueous solution containing 20% by volume of ethyl alcohol.

TABLE II.

Reaction medium, 20% aqueous EtOH; k = first-order rate constant; $c = 0{\cdot}0729$ mol./l.; c_A = acid concentration in mols./l.; H_0 = Hammett's acidity function for aqueous solution.

$t = 30{\cdot}0°$.

Catalyst.	pH.	$k \times 10^4$ (min.$^{-1}$).	$10^4k/c_A$.	Catalyst.	pH.	$k \times 10^4$ (min.$^{-1}$).	$10^4k/c_A$.
0·012M-HCl + 0·04M-KCl	1·81	0·770	64	0·2M-HCl + 0·04M-KCl	1·41	14·0	70
0·032 ,, ,,	1·70	2·06	64	0·4 ,, ,,	1·35	32·9	82
0·08 ,, ,,	1·54	5·13	64				

Catalyst.	H_0.	$k \times 10^4$ (min.$^{-1}$).	$10^4k/c_A$.	$1{\cdot}09H_0 +$ log 10^4k.	Catalyst.	H_0.	$k \times 10^4$ (min.$^{-1}$).	$10^4k/c_A$.	$1{\cdot}09H_0 +$ log 10^4k.
0·02M-HCl	+1·80	1·19	60	2·04	0·02M-H_2SO_4	+1·85	1·50	75	2·19
0·1 ,,	1·05	6·25	63	1·87	0·1 ,,	1·15	7·20	72	2·11
0·2 ,,	0·69	13·4	67	1·87	0·2 ,,	0·90	15·2	76	2·16
0·4 ,,	0·38	32·8	82	1·94	0·8 ,,	0·20	85·0	110	2·15
0·6 ,,	0·23	58·0	97	2·02	1 ,,	0·10	152	150	2·09
1 ,,	−0·05	111	110	1·99	2 ,,	−0·60	635	320	2·15
2 ,,	−0·60	544	170	2·09					
3 ,,	−0·95	1350	450	2·09					
4 ,,	−1·20	3700	930	2·26					

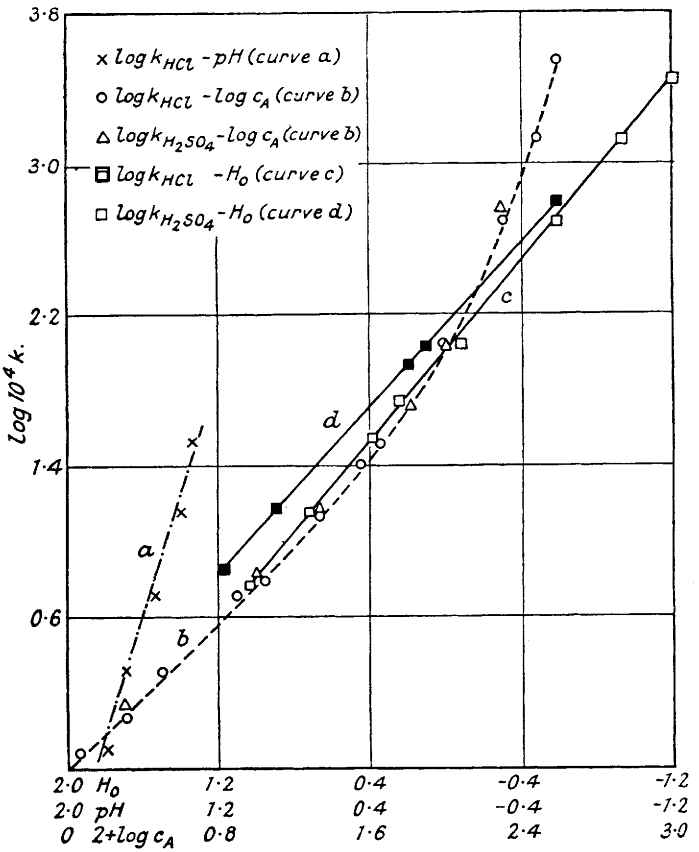
$t = 60{\cdot}0°$.

Catalyst.	$k \times 10^4$ (min.$^{-1}$).	Catalyst.	$k \times 10^4$ (min.$^{-1}$).	Catalyst.	$k \times 10^4$ (min.$^{-1}$).
0·1M-AcOH + 0·1M-AcONa + 1·5M-LiCl	0·080	0·1M-AcOH	1·3	0·1M-H_3PO_4	32·0
0·4M-AcOH + 0·4M-AcONa + 1·2M-LiCl	0·073	0·4M- ,,	3·9	0·4M- ,,	69·9
1M-AcOH + 1M-AcONa + 0·6M-LiCl	0·078	1M- ,,	4·5	1M- ,,	225

intensity of light absorption of the reaction mixture compared with that of the pure rearrangement product. In hydrochloric acid media where the acid concentration exceeds 1M, it appears that the corresponding chloride is actually the first reaction product, but is rapidly hydrolysed to the carbinol (forthcoming paper).

Analysis of the preliminary data given by Jones and McCombie (*loc. cit.*) seemed to indicate a proportionality between log k (where k is the first-order velocity constant of the reaction) and the pH value of the solution. It was desirable, as a first step, to establish whether this was indeed the case or whether k was proportional to c_A (where c_A is the stoicheiometric concentration of acid), which is the more common type of behaviour in acid-catalysed reactions (see Bell, " Acid–Base Catalysis," Oxford Univ. Press, 1942). Table II and Fig. 1, where log k is plotted against both log c_A and the electrometrically determined pH for a series of hydrochloric acid–potassium chloride mixtures in which the pH varies much more slowly than log c_A, show that k is strictly proportional to c_A up to c_A = 0·1M (*i.e.*, the plot of log k against log c_A has unit slope) and not to the thermodynamic hydrogen-ion activity measured by the pH. The primary salt effect is thus smaller than the experimental erorr (*i.e.*, $< 1\%$) for 0·04M-potassium chloride, and only amounts to 10% for 0·4M-potassium chloride (see below). The "spontaneous" rate is zero, no measurable rearrangement occurs in the absence of acid, and the k–c_A plot (Fig. 1) passes through the origin.

FIG. 1.



At higher acid concentrations (both of hydrochloric and sulphuric acid) the rate becomes proportional to Hammett's acidity function (H_0), which is a measure of the tendency of the medium to donate a proton to a neutral base (Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 827; Hammett, "Physical Organic Chemistry," McGraw Hill, 1941). The H_0 values actually apply to purely aqueous solution whereas the rate constants were determined in aqueous alcohol. The plot is nevertheless justified because experiments in media of varying alcohol content show (forthcoming paper) that the relative values of the k's for different concentrations of acid are only inappreciably affected by extrapolating to zero alcohol content of the medium.

The above results appear to indicate specific hydrogen-ion * catalysis. However, the interpretation of the variation of rate with catalyst concentration and catalyst activity respectively is still a matter of controversy and it seemed imperative to apply a more generally accepted criterion to confirm the absence of general acid catalysis at low acidities. Such a criterion is provided by the dependence of the reaction rate on the total concentration of a true buffer. The range of available standard buffer mixtures conforming to the conditions

* We shall employ the term "hydrogen-ion" to denote the mixture of lyonium ions present in the solution.

already enumerated for the choice of solvent is very restricted; *e.g.*, appreciable ethyl acetate formation takes place in sodium acetate–hydrochloric acid buffers containing 20% by volume of alcohol. Recourse was finally had to sodium acetate–acetic acid buffers in which the speed of reaction is very low and only the first 10% of the course of the reaction could conveniently be followed, but ester formation as measured by the alkalimetrically-determined decrease in acidity of the solution was practically absent. The velocity constants obtained under these conditions may not be trustworthy to more than ± 5%, but they suffice to show (Table II) that the rate is independent of the acetate concentration in a series of solutions of almost constant hydrogen-ion concentration (the hydrogen-ion concentration of a true buffer at constant ionic strength being almost independent of the dilution), thus confirming specific hydrogen-ion catalysis. This conclusion is further illustrated by the fact that in contrast to the results obtained with "strong" electrolytes (hydrochloric and sulphuric acid), in the case of "weak" electrolytes (phosphoric and acetic acid), k increases more slowly than c above $c_A = 0{\cdot}1$M because the weak acids exert their own buffer action at high concentrations (see below). In anhydrous acetic acid, which contains practically no hydrogen ion, the rate of rearrangement is immeasurably slow.

In a series of eight weak acids of different charge types, the rate constants can be expressed by

$$\log k = 0{\cdot}58 \log K_A + 2{\cdot}05 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

where k is the first-order constant (min.$^{-1}$) in a 20% alcoholic solution of acid (1M) at 30° and K_A is the thermodynamic dissociation constant of the acid in water (taken from Landolt–Börnstein, "Tabellen") (Table III, Fig. 2). The investigation could not be extended to certain other aliphatic, and to aromatic acids, because of the ease of esterification of the former and the high-intensity light absorption of the latter. Second and third dissociation constants of the polybasic acids could be neglected since the error thus introduced is much smaller than the average deviation. Equation (1) is identical in form with the Brönsted relation for general acid catalysis, but no statistical corrections have been applied in the present case. Theoretically, since

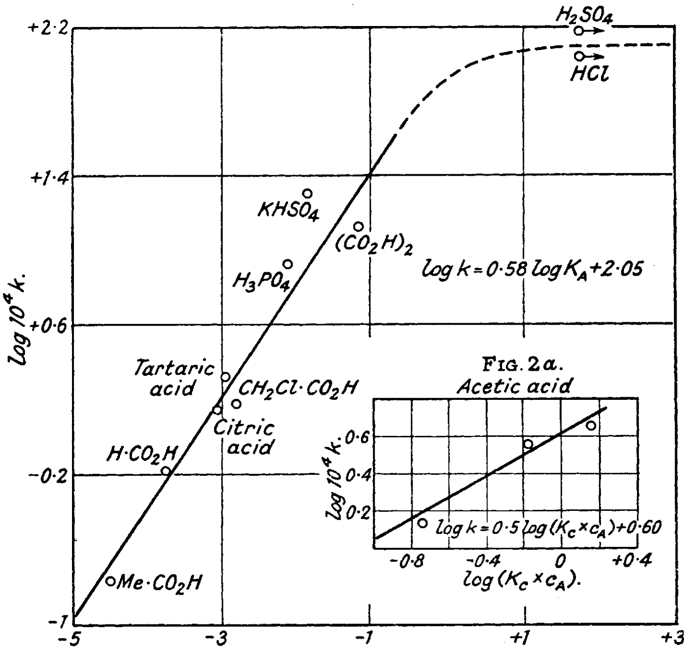
TABLE III.

Reaction medium, 20% aqueous EtOH; $c = 0{\cdot}0729$ mol./l.; catalyst concentration = 1M; $t = 30{\cdot}0°$; k = first-order rate constant; K_A = acid dissociation constant; $\log k_{\text{calc.}} = 2{\cdot}05 + 0{\cdot}58 \log K_A$.

Catalyst.	K_A.	$k_{\text{obs.}} \times 10^4$ (min.$^{-1}$).	$k_{\text{calc.}} \times 10^4$ (min.$^{-1}$).	Catalyst.	K_A.	$k_{\text{obs.}} \times 10^4$ (min.$^{-1}$).	$k_{\text{calc.}} \times 10^4$ (min.$^{-1}$).
$KHSO_4$	$1{\cdot}2 \times 10^{-2}$	20 *	8·6	Tartaric acid	$1{\cdot}0 \times 10^{-3}$ †	2·08	2·0
$(CO_2H)_2$	$6{\cdot}5 \times 10^{-2}$ †	13·4	23	Citric acid	$8{\cdot}3 \times 10^{-4}$ †	1·41	1·8
H_3PO_4	$7{\cdot}5 \times 10^{-3}$ †	8·60	6·5	$H{\cdot}CO_2H$	$1{\cdot}8 \times 10^{-4}$	0·665	0·76
$CH_2Cl{\cdot}CO_2H$	$1{\cdot}4 \times 10^{-3}$	1·48	2·4	AcOH	$1{\cdot}8 \times 10^{-5}$	0·170	0·20

* Extrapolated value. † First ionisation.

FIG. 2.



$$K_A = [H^+][A^-]/[HA] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

(activity coefficients being neglected) and $[H^+] = [A^-]$ in the absence of salts, then

$$\log [H^+] = 0{\cdot}5 \log K_A + 0{\cdot}5 \log [HA] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

At constant acid concentration [HA] can be regarded as constant in a series of weak acids where $K_A < 10^{-2}$, and in a reaction specifically catalysed by H^+, $k = [H^+] \times$ constant, hence

$$\log k = 0{\cdot}5 \log K_A + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The slight discrepancy between the theoretical exponent of 0·5 and the observed one of 0·58, and the deviations from linearity in the plot are not surprising, since dissociation constants in water were used whereas the reaction medium actually contained 20% of alcohol, and the relative strengths of aliphatic acids vary in different solvents (Hammett, *Trans. Faraday Soc.*, 1938, **34**, 156). For stronger acids when $K_A > 10^{-2}$, the slope of the log k–log K_A curve will decrease (since [HA] is decreasing), until for strong acids when $[HA] \rightarrow 0$ and $K_A \rightarrow \infty$ it becomes almost parallel to the x axis.

The high acid concentration (1M) was chosen for comparing the catalytic activity of different acids because, at lower concentrations within the range of applicability of the Debye–Hückel theory, the reaction rates are too slow for convenient measurement at moderate temperatures. The relation (4) thus holds even at high ionic strengths at which both k/c_A (the so-called catalytic constant) and the concentration dissociation constant (K_c) of the acid are no longer constants and vary to a different extent with the concentration (c_A) for different acids. The condition for this follows from (2), which becomes

$$\log k = 0{\cdot}5 \log (K_A c_A) + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

when $c_A \approx [HA]$. Equation (5) is satisfied in the case of acetic acid (Fig. 2*a*) where the relevant K_c values are available (Falkenhagen, "Elektrolyte," 1932, p. 32).

The accuracy of the kinetic measurements does not at present warrant an investigation of salt effects at low salt concentrations. At high ionic strengths the primary salt effect is positive (Table IV), and again proportional to Hammett's acidity function H_0. It decreases with increasing acid concentration in the case of hydrochloric acid. The effects produced by different salts at constant ionic strength show a rough parallelism to the activity coefficients of the salts in aqueous solution divided by the molar concentrations in which they are present, but bear no relation to their co-ordinating powers, thus illustrating once more that hydrogen ion is the only effective catalyst (cf. Bodendorf and Böhme, *Annalen*, 1935, **516**, 1). The salt effect is much higher in the case of the weak acids owing to the simultaneous operation of the secondary salt effect.

TABLE IV

Reaction medium, 20% aqueous EtOH; $t = 30{\cdot}0°$; $c = 0{\cdot}0729$ mol./l.; k_A = first-order rate constant in presence of acid only; k_S = first-order rate constant in presence of salt; r = % increase in k due to added salt = $100 (k_S - k_A)/k_A$.

Catalyst.	$k_A \times 10^4$ (min.$^{-1}$).	$k_S \times 10^4$ (min.$^{-1}$).	r.	Catalyst.	$k_A \times 10^4$ (min.$^{-1}$).	$k_S \times 10^4$ (min.$^{-1}$).	r.
0·4M-HCl + 0·4M-KCl	32·9	36·3	10·3	0·4M-HCl + 0·5M-$BaCl_2$	32·9	56·0	70·0
,, 0·6 ,,	,,	40·2	22·5	,, 1M-KBr	,,	55·5	68·8
,, 0·8 ,,	,,	49·9	51·7	,, 1M-LiCl	,,	55·3	68·0
,, 1·0 ,,	,,	52·9	60·8	,, 1M-NaCl	,,	55·3	68·0
,, 1·2 ,,	,,	60·8	84·8	,, 0·5M-$ZnCl_2$	,,	53·0	61·1
,, 1·6 ,,	,,	62·5	90·0	,, 1M-KCl	,,	52·9	60·8
,, 1·8 ,,	,,	65·3	98·3	,, 1M-NH_4Cl	,,	49·0	48·9
,, 2·0 ,,	,,	76·8	134	,, 0·33M-$AlCl_3$	,,	45·4	38·0
0·1M-HCl + 1M-KCl	6·25	11·0	76·0	,, 1M-$AlCl_3$	,,	134	307
0·4M ,, ,,	32·9	52·9	60·8	1M-H_3PO_4 + 1M-KCl	8·6	17·8	107
1·0M ,, ,,	111	164	47·8	1M-AcOH ,,	0·170	0·370	118

Rate constants were measured over the temperature range from 0° to 60°, and obey an Arrhenius equation (Table V). The deviations from linearity of the log k–$1/T$ plots only slightly exceed those to be expected from the probable error in k. The experimental energies of activation deduced vary from 19 to 24 (± 0·3) kg.-cals. over a very wide range of acidities, but in calculating experimental energies of activation from the overall temperature coefficients of the reaction, no allowance is made for the temperature-dependence of acid strength.

TABLE V

Reaction medium: 20% aqueous EtOH; $c = 0{\cdot}0729$ mol./l. throughout; E = Arrhenius energy of activation.

t.	Catalyst.	$k \times 10^4$ (min.$^{-1}$).	E (kg.-cals.).	t.	Catalyst.	$k \times 10^4$ (min.$^{-1}$).	E (kg.-cals.).	t.	Catalyst.	$k \times 10^4$ (min.$^{-1}$).	E (kg.-cals.).
30°	0·1M-HCl	6·25	23·2	0°	1M-HCl	1·73	24·2	30°	0·2M-H_2SO_4	15·2	23·8
40	,,	21·0		30	,,	111		40	,,	52·9	
50	,,	64·4		40	,,	415		50	,,	159	
60	,,	220		50	,,	1230		60	,,	550	
30	0·4M-HCl	32·9	23·5	0	4M-HCl	106	19·4	30	1M-H_3PO_4	8·60	21·6
40	,,	122		30	,,	3700		60	,,	225	
50	,,	330						30	1M-AcOH	0·170	22·2
								40	,,	0·521	
								50	,,	1·60	
								60	,,	4·49	

In 0·4M-hydrochloric acid the rate of racemisation of (+)propenylethynylcarbinol ($[\alpha]_D^{20°} = +45°$) as determined by the change in optical rotation is almost the same as the rate of rearrangement as measured by the change in ultra-violet light absorption, the two values of *k* being 27·5 ± 1·5 and 30·8 ± 0·6 × 10^4 min.$^{-1}$ respectively. Under the experimental conditions employed, complete racemisation was observed.

EXPERIMENTAL.

Kinetic Measurements.—The reactions were carried out in 50 ml. of reaction medium contained in 150-ml. Pyrex three-necked flasks. The centre neck carried a glass-joint double-surface condenser, one side neck was fitted with an inlet tube for passing a slow stream of nitrogen through the solution, and the second side neck carried a glass stopper and was used for the withdrawal of samples. The precaution of carrying out the reaction in nitrogen was later found to be unnecessary, propenylethynylcarbinol and its isomer being quite stable in aqueous-alcoholic solution for periods exceeding the duration of the experiments (the stability depends on the acidity of the solution and the temperature, ranging from 1 to 2 days in 4M-hydrochloric acid at 30° to periods exceeding 2 weeks in 0·01M-hydrochloric acid before any detectable decomposition occurs).

Four reaction flasks were kept in a rectangular water tank of 20 l. capacity, kept at constant temperature by means of a large bulb toluene–mercury thermoregulator, electronic valve relay, and a 250-watt carbon-filament lamp, and an electric stirrer. For experiments above 50°, an 800-watt resistance heating element was substituted for the lamp, and a thin layer of paraffin oil was spread over the water surface to reduce evaporation. Temperatures were checked against an N.P.L. certificated thermometer and were constant within $< \pm 0{\cdot}05°$. Runs at 0° were carried out in a tightly stoppered 150-ml. flask immersed in a large volume of a mixture of ice and water, the whole being kept in a refrigerator at 0°.

To start a run, a sample of propenylethynylcarbinol previously weighed out into a short sample tube was dropped into the reaction flask already containing the reaction medium at the temperature of the run, the stopper replaced, and the flask vigorously shaken until the contents were homogeneous, the whole operation requiring less than 5 secs. Samples of the reaction mixture were then withdrawn at appropriate intervals by means of a fast-delivery, narrow-stem 1-ml. pipette and run into a graduated flask (25—100 ml.) containing sufficient dilute alcoholic potassium hydroxide to neutralise the 1 ml. of reaction medium, and the volume made up to the mark. The use of a small-capacity pipette has the twofold advantage of (i) allowing the withdrawal and discharge of the sample to be completed within 10 seconds (with an error of within ± 0·5%)—this was essential as the half-time of reaction of the fastest runs was only 4 minutes—and (ii) permitting a high and variable dilution ratio which makes it possible to combine in one operation the stopping of the reaction and the dilution to a suitably low concentration for spectrographic examination.

The spectrophotometric assay was carried out by standard methods on a Hilger medium quartz spectrograph (E488) fitted with a Spekker photometer using a condensed spark between tungsten-steel electrodes as light source. Freshly distilled propenylethynylcarbinol has an intensity of light absorption at 2235 A. of $E^{1\%}_{1\,\mathrm{cm.}} < 2$, whereas its rearranged isomer hex-3-en-5-yn-2-ol has a maximum at 2235 A. of $E^{1\%}_{1\,\mathrm{cm.}} = 1300$. For readings above $E^{1\%}_{1\,\mathrm{cm.}} = 100$ the amount of rearrangement is therefore directly proportional to the $E^{1\%}_{1\,\mathrm{cm.}}$ value of the solution (using the reaction medium at the same dilution in the comparison cell). The accuracy of the determination of extinction coefficients by this method is not better than ± 2—5% for general work in this wave-length region, but by employing standard conditions, accurate blank determinations, and interpolation to 0·01*E*, it is possible to obtain results within ± 1%. Together with errors arising from pipetting, etc., the total traceable error should not exceed ± 2%. This corresponds to a maximum error of ± 0·5—3% in the first-order velocity constants calculated by $k = (2{\cdot}3/\tau)\log_{10}a/(a - x)$ for $x = (0{\cdot}15\text{—}0{\cdot}85)a$ within one run. Runs in which variations in *k* exceeded ± 5% were rejected. Consistency between averaged *k* values for different runs is greatly dependent on the accuracy of the value for *a* (the $E^{1\%}_{1\,\mathrm{cm.}}$ value of the fully rearranged carbinol); this was averaged from a large number of determinations as $E^{1\%}_{1\,\mathrm{cm.}}$ (2235 A.) $= 1300 + 0{\cdot}5(t - 30)$ for the pipette employed, where *t* is the temperature of the run. The slight variation in this value with *t* is mainly due to thermal expansion of the pipette, but since the absolute values are immaterial in the calculation of first-order constants, the pipette was not recalibrated in absolute units for sampling at different temperatures. Averaged *k* values should thus be within ± 2—3%; agreement between duplicate runs was generally better than this. A few typical runs are given below:

Reaction medium: 20% (vol.) EtOH, 80% (vol.) H_2O throughout; $E^{1\%}_{1\,\mathrm{cm.}}$ at 2235 A.; time in mins., and *k* in min.$^{-1}$ throughout.

(i) Catalyst: 0·4M-HCl; $c = 0{\cdot}0822$ mol./l.; $t = 30{\cdot}0°$.

	Time.	$E^{1\%}_{1\,\mathrm{cm.}}$	$k \times 10^4$.
(a)	60	232	32·7
	120	431	33·7
	240	715	33·2
	360	885	31·6
	480	1010	31·3
	∞	1300	——
			Mean 32·5
(b)	60	234	33·0
	120	436	33·9
	240	728	34·1
	360	905	32·9
	480	1030	32·8
	∞	1300	——
			Mean 33·3

(ii) Catalyst: 1M-HCl; $c = 0{\cdot}0729$ mol./l.; $t = 30{\cdot}0°$.

Time.	$E^{1\%}_{1\,\mathrm{cm.}}$	$k \times 10^4$.
40	468	111
72	715	111
137	1015	110
∞	1300	——
		Mean 111

(iii) Catalyst: 4M-HCl; $c = 0{\cdot}0729$ mol./l.; $t = 30{\cdot}0°$.

2	700	3860
4	985	3550
6	1160	3700
∞	1300	——
		Mean 3700

(iv) Catalyst: 1M-HCl; $c = 0{\cdot}0729$ mol./l.; $t = 40{\cdot}0°$.

Time.	$E^{1\%}_{1\,\mathrm{cm.}}$	$k \times 10^4$.
16·5	642	415
22·5	788	413
29·0	914	417
∞	1305	——
		Mean 415

(v) Catalyst: 1M-AcOH; $c = 0{\cdot}0729$ mol./l.; $t = 50{\cdot}0°$.

1500	280	1·62
2940	500	1·65
4320	660	1·64
6960	845	1·51
∞	1310	——
		Mean 1·60

Three to five individual values of *k* were determined in each run, as far as possible in the region $x = (0{\cdot}30\text{—}0{\cdot}70)a$ where the relation between the error in $E^{1\%}_{1\,\mathrm{cm.}}$ and *k* is most favourable. End values (*a*), when determined, were taken after not less than ten times the time of half-change, corresponding to more than 99·9% rearrangement. In slow runs, *a* was determined, where possible, by warming for the appropriate period to complete the reaction. In all cases the value of *a* taken for the calculation of *k* was the averaged value, $1300 + 0{\cdot}5(t - 30)$. The smallest velocity constant measured was $0{\cdot}08 \times 10^{-4}$ min.$^{-1}$, the largest 3700×10^{-4} min.$^{-1}$, corresponding to times of half-change of 50 days and 2 minutes respectively.

A few runs were carried out with resolved (+)propenylethynylcarbinol, and the rearrangement followed by observing the change in optical rotatory power as well as in light absorption. 1-Ml. samples of the reaction mixture were run into an equal volume of alcoholic potassium hydroxide, and the rotation determined in a semi-micro 1-dcm. cell, a sodiumvapour lamp being used as light source. The low rotations measured did not permit of great accuracy, but the results suffice to establish the essential identity of the velocity constants determined by the two methods and the fact that complete racemisation accompanies the rearrangement under the conditions of the experiment.

Medium, 20% (vol.) EtOH, 80% (vol.) H_2O; catalyst, 0·4M-HCl; c = 0·208 mol./l.; t = 30·0°.

Time (mins.)	16	136	197	254	331	∞	
$a_D^{20°}$	0·53°	0·39°	0·34°	0·25°	0·215°	0·00°	
$k \times 10^4$ (min.$^{-1}$)	—	25·5	24·5	31·0	28·5	—	Mean 27·5

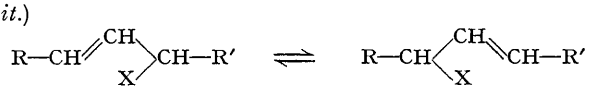
Analysis of Reaction Products.—In view of the wide range of conditions employed, it was necessary to confirm that the reaction product in every case was in fact the rearranged carbinol, as established by Jones and McCombie (*loc. cit.*) for the heterogeneous rearrangement, and not the corresponding ester, ether, etc. Some guidance is provided by the $E^{1\%}_{1\,\mathrm{cm.}}$ end value a which is somewhat different for the carbinol and its various derivatives, but in a number of representative runs the final reaction product was isolated and examined by means of refractive index, Zerewitinoff, Zeisel, and chloride determinations. Evidence of ester formation was sought for, especially in the case of acetic acid runs, by titration of the reaction mixture with standard sodium hydroxide. No products other than the rearranged carbinol were detected in appreciable quantities under any of the conditions investigated except in hydrochloric acid media of acid concentration exceeding 1M where 2-chlorohex-3-en-5-yne is formed in increasing amounts as primary reaction product, but this is hydrolysed to the carbinol at a rate comparable to that of the rearrangement. Small amounts of ethyl acetate and ethyl chloroacetate (corresponding to $< 10\%$ of the acid present) were formed in acetic acid and chloroacetic acid runs, and small amounts of diethyl ether were produced when phosphoric acid was used as catalyst.

pH *Determinations.*—These were carried out by measuring the E.M.F.'s of cells H_2(Pt)|HCl–KCl soln.|satd.KCl bridge| 1·0N-KCl–$HgCl_2$, the pH of the solution being given by pH = (E.M.F. − 0·283)/0·0058, liquid junction potentials being neglected. The hydrogen electrode was of the enclosed vessel type. E.M.F.'s were determined with a Hinsley potentiometer and moving-coil galvanometer to ± 1 mv. corresponding to about ± 0·02 pH unit. Steady conditions were attained after 30—60 minutes. Checking against a standard acetate buffer and hydrochloric acid–potassium chloride mixture gave agreement within 0·02 pH. The values obtained for the 20% alcoholic hydrochloric acid–potassium chloride mixtures differ considerably from Clark and Lubs's values for purely aqueous solutions.

Materials.—The propenylethynylcarbinol (for which we thank Mr. B. C. L. Weedon) had b. p. 82°/46 mm., $n_D^{20°}$ = 1·4647, $E^{1\%}_{1\,\mathrm{cm.}}$ at 2235 A. < 2, this value being unchanged after 3 months at 0°. We are indebted to Dr. J. Kenyon, F.R.S., for a sample of resolved propenylethynylcarbinol ($[\alpha]_D^{20°}$ + 45°). Burnett's absolute alcohol was used throughout the investigation. All other materials were "AnalaR" reagents or were purified by standard methods. A. R. Borax, dried and kept in a desiccator over anhydrous silica gel, was used as primary volumetric standard.

DISCUSSION.

Previous discussion of anionotropic rearrangements * has centred about two types of mechanism: an intermolecular, ionic mechanism (Burton and Ingold, *loc. cit.*), $\mathrm{CHR{:}CH{\cdot}CHXR^1 \rightleftharpoons CHR{:}CH{\cdot}\overset{+}{C}HR^1 + X^- \rightleftharpoons \overset{+}{C}HR{\cdot}CH{:}CHR^1 + X^- \rightleftharpoons CHRX{\cdot}CH{:}CHR^1}$, and an intramolecular homopolar mechanism (Kenyon, Partidge, and Phillips, *loc. cit.*)



These mechanisms were originally proposed in connection with anionotropic rearrangements in the arylallyl alcohol series, evidence for the former being derived mainly from qualitative data on the dependence of the ease of rearrangement on the electronic properties of R, R^1, and X, the ionising power of the solvent, and the exchange of X for other anions during rearrangement. Evidence for the intramolecular mechanism was obtained mainly from investigations of the stereochemical changes accompanying rearrangement. It has been suggested that the partial racemisation observed during the rearrangement of α-phenyl-γ-methylallyl alcohol in solvents of low ionising power is due to the simultaneous operation of both mechanisms (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 601).

The salient experimental facts relating to the oxotropic rearrangement of propenylethynylcarbinol and our interpretations of them are as follows:

(i) In 20% aqueous alcohol the rearrangement is of the first order, the rate constant being independent of the concentration of carbinol and directly proportional to the hydrogen-ion concentration at low acidities. At high concentrations of strong acids and in the presence of salts, the rate becomes proportional to Hammett's acidity function, which is a measure of the tendency of the medium to donate a proton to a neutral base. The rate constants in solutions of different acids at constant concentration can be expressed by $k = K_A^x$ + a constant, where the exponent x has a value close to the theoretical one of 0·5 for specific hydrogen-ion catalysis.

Hydrogen-ion is the effective catalyst. The transition state of the reaction does not involve a solvent molecule (cf. Hammett, *loc. cit.*).

(ii) No products other than the rearranged carbinol are formed at acid concentrations as high as 1M-hydrochloric or acetic acid.

If the hydroxyl group separates as a charged anion, the rearrangement must be intramolecular with respect to other anions present.

(iii) Under the particular conditions examined, the isomerisation of the optically active carbinol is accompanied by complete racemisation proceeding at the same rate.

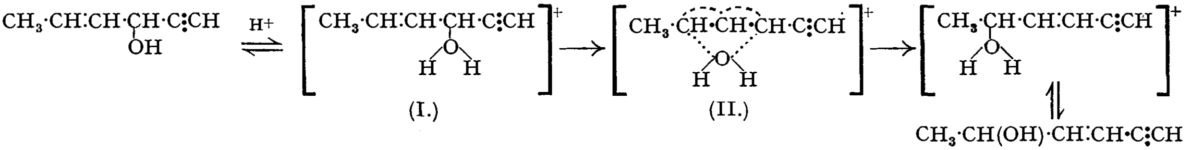
---

* We propose the name "oxotropy" for anionotropic changes where X = OH, corresponding to the term "prototropy" for cationotropic changes where X = H.

Two possibilities have to be considered. Either the carbonium ion produced by the fission of the carbon–oxygen bond is optically stable and the racemisation is brought about by the actual electronic rearrangement, or the reaction involves the production of an optically unstable carbonium ion and the fission of the carbon–oxygen bond proceeds simultaneously with the electron migration. The optical instability of *positive* carbonium ions now appears to be generally accepted (Waters, " Physical Aspects of Organic Chemistry," Routledge, 1942, p. 340), and the second interpretation must be regarded as correct.

(iv) The experimental energy of activation varies from 19 to 24 kg.-cals. over a wide range of acidities. Unless the true energy of activation is very much higher than the experimental value, the rate-determining step of the reaction can involve neither the normal covalent nor the normal ionic fission of the carbon–oxygen bond.

Clearly the above conclusions are not wholly in accord with either of the two types of mechanism referred to above. They can be explained, however, in terms of the following mechanism which includes elements of both :



The first step is the reversible formation of the oxonium ion (I), the existence of which in acid solution would be postulated quite independently of the reaction it subsequently undergoes, as has been emphasised already by Young and Lane (*loc. cit.*) in their discussion of anionotropic rearrangements accompanying replacement halogenations. The second step is the *simultaneous* migration of the double-bond electron pair and the hydroxyl group as a neutral water molecule. The transition state in which both migrations are half completed is represented by (II). The essential rôle of the hydrogen-ion catalyst is thus to lower the energy of activation by converting the rate-determining step from a fission of the carbon–oxygen bond into two ions, into the fission of the carbon–oxygen bond into a carbonium ion and a neutral molecule. Such a mechanism brings this case of acid catalysis into line with the general principle that the main function of a catalyst is to provide an alternative reaction path with a lower energy of activation. On this basis the reaction is clearly intramolecular with respect to other anions present in the solution; it is probably intramolecular with respect to the solvent also, but the latter point requires confirmation, *e.g.*, by carrying out the reaction in a medium enriched with ^{18}O.

The further discussion of the mechanism proposed above and its implications is deferred until data are available as to the effect of solvents and substituents on the reaction rate and the energy of activation.

The authors thank Professor I. M. Heilbron, D.S.O., F.R.S., for his interest and encouragement, Dr. D. J. G. Ives for helpful discussions, and the Rockefeller Foundation for financial assistance.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, March 27th,* 1944.]