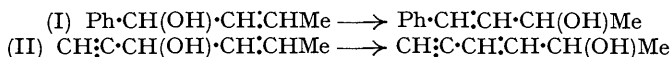


### 403. The Kinetics of Anionotropic Rearrangement. Part VIII. Medium Composition, Acidity Function, and Reaction Rate.

By ERNEST A. BRAUDE and E. S. STERN.

The rates of acid-catalysed rearrangement of phenylpropenyl- and ethynylpropenyl-carbinol in water-dioxan, water-ethanol, and water-acetone mixtures have been determined over the entire range of medium composition at hydrochloric acid concentrations of 0.1 and 1M. The proportionality between rate constants and acidity function, previously noted when the acid concentration is varied at constant solvent composition (Part I, *J.*, 1944, 436), also holds when the solvent composition is varied at constant acid concentration. This relationship confirms a reaction mechanism involving a fast reversible proton-transfer followed by a slow rearrangement of the oxonium ion formed. Variations in the rate constants with medium composition are mainly due to variations in the proton-transfer equilibrium  $\text{ROH} + \text{SH}^+ \rightleftharpoons \text{ROH}_2^+ + \text{S}$ , where  $\text{SH}^+$  represents the solvated proton.

THE influence of medium composition on the rate of acid-catalysed anionotropic rearrangement has been investigated in earlier papers (cf. Parts II and V, *J.*, 1944, 443; 1946, 496). It was found that in water-ethanol- and water-dioxan-hydrochloric acid media the rate constants for a constant acid concentration vary strongly with solvent composition, passing through a minimum in the region of 80% by volume of organic solvent. These measurements have now been extended to cover the whole range of water-dioxan, water-ethanol, and water-acetone mixtures for the rearrangements of phenylpropenylcarbinol (I) in 0.1M-, and ethynylpropenyl-carbinol (II) in 1M-hydrochloric acid. The main object of the study was to test whether the



correlation between the rate of rearrangement and the acidity function of the medium, previously established for the variation of acid concentration at constant solvent composition (Part I, *J.*, 1944, 336), also holds when the solvent composition is varied at constant acid concentration. The relevant acidity functions have now been determined (preceding paper).

The data are collected in Tables I and II. In all three solvent mixtures, the rate constants ( $k$ ) initially decrease with increasing proportions of organic solvent, pass through a minimum when the concentration ( $c_s$ ) of organic solvent reaches about 80% by volume, and finally increase again. The variations in  $k$  run parallel to those in the acidity function  $H$ , and the quantity  $\log k - H$  is approximately constant.

TABLE I.

Rearrangements of phenylpropenylcarbinol (I) in 0.1M-hydrochloric acid at 30.0°:  $k$  = first-order rate constants  $\times 10^4 \text{ min.}^{-1}$  (see Experimental);  $H$  = acidity functions of the medium (see preceding paper).

Vol. % of organic solvent.	Dioxan.		Ethanol.		Acetone.	
	$k$ .	$\log k - H$ .	$k$ .	$\log k - H$ .	$k$ .	$\log k - H$ .
20	21,000	5.59	—	—	—	—
40	7,500	5.55	8,700	5.46	10,700	5.70
60	2,100	5.55	2,400	5.41	3,500	5.71
70	1,230	5.48	1,350	5.30	2,100	5.57
80	690	5.23	890	5.20	1,680	5.66
90	620	4.88	740	5.10	1,360	5.52
100	5,700	5.11	25,000	5.01	42,000	5.35

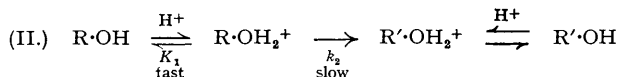
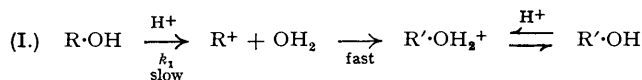
TABLE II.

Rearrangements of ethynylpropenylcarbinol (II) in 1M-hydrochloric acid at 30.0°:  $k$  = first-order rate constants,  $H$  = acidity functions.

Vol. % of organic solvent.	Dioxan.		Ethanol.		Acetone.	
	$k$ .	$\log k - H$ .	$k$ .	$\log k - H$ .	$k$ .	$\log k - H$ .
20	103	2.18	111	2.08	98	2.17
40	30.5	2.37	43	2.16	35.5	2.08
60	11.7	2.31	15.3	2.03	13.3	2.04
70	10.2	2.02	7.7	1.83	10.4	1.97
80	*	*	5.1	1.65	15.3	1.88
90	*	*	4.9	1.53	150	1.91
100	75	2.28	77	1.50	14,900	1.93

\* Medium components form a two-phase system.

The relation between  $H$  and  $\log k$  affords a criterion of the reaction mechanism (cf. Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 830; 1936, **58**, 2182; Hammett and Zucker, *ibid.*, 1939, **61**, 2791). The two most likely mechanisms of rearrangement are (cf. Part VII, this vol., p. 794):



In (I) a slow formation of the carbonium ion by the reaction between the carbinol and a solvated proton (represented simply by  $H^+$ ) is followed by a fast rearrangement of the carbonium ion. In (II) a fast formation of the oxonium ion by the reversible proton transfer from the solvent to the carbinol is followed by a slow unimolecular rearrangement of the oxonium ion. The overall rate constants will be given, respectively, by

$$(I) \quad k = k_1[H^+] \frac{f_{ROH} f_{H^+}}{f_X} \dots \dots \dots (1)$$

$$(II) \quad k = K_1 k_2[H^+] \frac{f_{ROH} f_{H^+}}{f_Y} \dots \dots \dots (2)$$

where  $k$ 's represent rate constants,  $K$ 's equilibrium constants, and  $f$ 's activity coefficients, and where X and Y refer to the transition states of the slow steps. Since no changes in charge-type are involved, the activity coefficient terms are likely to be constant and not very different from unity, so that  $k = k_1[H^+]$  in (1) and  $k = K_1 k_2[H^+]$  in (2). Since both  $k_1$  and  $k_2$  should be largely independent of the solvent, variations of  $k$  with solvent composition at constant acid concentration can only be accounted for either by changes in the degree of dissociation of the acid, or by variations in the equilibrium constant  $K_1$ . Recent conductivity measurements (Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330) show that the dissociation of hydrogen chloride in aqueous ethanol remains practically complete up to 90% ethanol concentration and then decreases. An earlier suggestion (Part II, *loc. cit.*) that the over twenty-fold decrease in  $k$  between 20% and 80% ethanol is due to a decrease in the dissociation of the acid is thus incorrect, and the fact that  $\log k$  can be expressed as a linear function of the dielectric constant must have a different significance. In aqueous dioxan the degree of dissociation does initially decrease with increasing dioxan concentration (Owen and Waters, *J. Amer. Chem. Soc.*, 1938, **60**, 2371) but much less rapidly than the corresponding fall in the rate constants. The large variations of  $k$  with solvent composition are thus not readily accounted for in terms of the carbonium-ion mechanism (I). They are to be expected, however, for the oxonium-ion mechanism (II), since the rate equation now involves the equilibrium constant  $K_1$  of the proton-transfer reaction  $R \cdot OH + H^+ \rightleftharpoons R \cdot OH_2^+$  and since it has been shown (preceding paper) that the corresponding equilibrium constants for the conversion of other neutral bases into their conjugate acids also vary with solvent composition, in a similar manner to  $k$ . Since  $H = \log \{([H^+]K_B^s/K_B^{s,0})\}$ , where  $H$  is the acidity function and  $K_B^s$  and  $K_B^{s,0}$  are the equilibrium constants of the reaction  $B + H^+ \rightleftharpoons BH^+$  in a solvent S and in water respectively, it is readily deduced from (2) that

$$\log k = H + \log (k_2/K_{ROH}^{H_3O^+}) \dots \dots \dots (3)$$

where  $K_{ROH}^{H_3O^+}$  is the equilibrium constant of the reaction  $H_3O^+ + ROH \rightleftharpoons ROH_2^+ + H_2O$  in water, *i.e.*,  $\log k - H = \text{constant}$ . The relatively small deviations from the relationship apparent in Tables I and II are not surprising, since the acidity function is strictly independent of the indicator base (B) only for compounds closely related in structure (Braude, this vol., p. 1972), whereas the nitroanilines used in the determinations of  $H$ , because of their suitable physical properties, are quite different in type from the carbinols involved in the anionotropic rearrangements. The conclusion that the latter proceed by the oxonium-ion mechanism (II) is in agreement with independent evidence (cf. Part VII, *loc. cit.*).

The variations in  $k$  with solvent composition at constant acid concentration are thus to be ascribed primarily to changes in the equilibrium  $R \cdot OH + SH^+ \rightleftharpoons R \cdot OH_2^+ + S$  and in the ratios  $[R \cdot OH_2^+]/[R \cdot OH]$  due to changes in the proton affinity of the solvent.

## EXPERIMENTAL.

The technique of kinetic measurements was that previously described (Parts I and V, *loc. cit.*);  $x\%$  by volume of organic solvent stands for a medium obtained by mixing  $x$  ml. of organic solvent and  $(100 - x)$  ml. of water containing the appropriate amount of hydrochloric acid to give a 0.1M- or 1M-solution. In practice, aqueous solutions were prepared by mixing  $x$  ml. of organic solvent,  $(90 - x)$  ml. of water, and 10 ml. of 1M- or 10M-hydrochloric acid, and making up to 100 ml. with a mixture of  $x$  ml. of organic solvent and  $(100 - x)$  ml. of water. The molar concentration of organic solvent is then given by  $1800xd/[18xd + (100 - x)M]$ , where  $d$  and  $M$  are its density and molecular weight, respectively. Anhydrous solutions were prepared immediately before use (Braude, this vol., p. 1975). In view of the considerable ultra-violet light absorption of acetone, the choices of the carbinol concentration and of the dilution ratio for the spectrometric assay were rather more critical than with the other solvents. Four typical runs are given below.

*Rearrangements of phenylpropenylcarbinol in 0.1M-hydrochloric acid at 30.0°.* [Carbinol concentration, 0.2% w/v. Acetone concentration, (a) 80%, (b) 100%.]

(a) Time, mins. ....	0	1	2	3	4	$\infty$	
$E_{1\text{cm.}}^{1\%}$ (2510 A.) .....	30	220	410	520	600	1260	
$10^4k$ (min. <sup>-1</sup> ) .....	—	1650	1660	1690	1710	—	(Mean) 1680
(b) Time, mins. ....	0	0.25	0.40	0.55	$\infty$		
$E_{1\text{cm.}}^{1\%}$ (2510 A.) .....	30	850	1020	1120	1260		
$10^4k$ (min. <sup>-1</sup> ) .....	—	44,000	41,000	40,000	—		(Mean) 42,000

*Rearrangements of ethynylpropenylcarbinol in 1M-hydrochloric acid at 30.0°.* [Carbinol concentration, 0.5%. Acetone concentration, (a) 80%, (b) 100%.]

(a) Time, mins. ....	0	650	820	1000	1160	$\infty$	
$E_{1\text{cm.}}^{1\%}$ (2230 A.) .....	—	830	940	1000	1080	1300	
$10^4k$ (min. <sup>-1</sup> ) .....	—	15.6	15.8	14.8	15.0	—	(Mean) 15.3
(b) Time, mins. ....	0	0.20	0.40	0.60	$\infty$		
$E_{1\text{cm.}}^{1\%}$ (2230 A.) .....	—	340	590	760	1300		
$10^4k$ (min. <sup>-1</sup> ) .....	—	15,300	15,000	14,500	—		(Mean) 14,900

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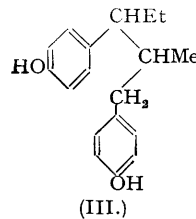
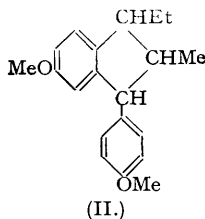
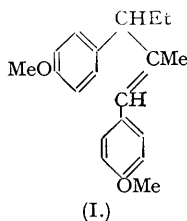
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## 404. Dimerides of Anethole.

By WILSON BAKER and G. F. FLEMONS.

*iso*Anethole (I), previously known only as an oil, is shown to be a mixture consisting mainly of crystalline (m. p. 40—40.5°) *trans*(?)-*iso*anethole and a smaller amount of liquid *cis*(?)-*iso*anethole. The claim that metanethole (II) exists in two forms, sublimable and non-sublimable, is incorrect.

ANETHOLE undergoes dimerisation under the influence of hydrogen chloride to give *iso*anethole, which has been shown by Goodall and Haworth (*J.*, 1930, 2482) to possess the structure (I). These authors oxidised the liquid *iso*anethole to anisic acid and methyl 1-*p*-methoxyphenyl-*n*-propyl ketone, but this experiment leaves in doubt the question, not previously raised, as to whether *iso*anethole is the *cis*- or *trans*- isomeride or a mixture of the two. Formula (I) represents what may be termed the *trans*-form, attention being focussed on the main Ar-C-C-C-Ar chain of the molecule. Optically active forms of *iso*anethole are possible.



Baker and Enderby (*J.*, 1940, 1094) showed that anethole could be dimerised by refluxing in 43% sulphuric acid, giving a mixture of the saturated, crystalline dimeride metanethole (II)