of acetone and alcohol, forming large white needles, which melted to a deep red liquid at 158.1–158.6° cor. The yield was 11 g. or 53.5% of the theoretical.

Anal. Calcd. for $C_{30}H_{34}O_3S_2$: C, 71.2; H, 6.72; S, 12.6. Found: C, 71.8; H, 6.41; S, 12.75.

Reaction of "Anhydro-*p*-methoxypropiophenone Disulfide" with Copper Chromite.—Two grams of the sulfur compound was dissolved in 40 ml. of dry xylene and 10 g. of finely ground copper chromite was added. The mixture was stirred and refluxed for two and one-half hours. After cooling, the mixture was filtered and the xylene removed by vacuum distillation. The residue of brown oil was dissolved in about 10 volumes of hot methanol and cooled, giving yellowish crystals which were recrystallized from methanol in yellow needles, m. p. 112.3–112.8° cor. The yield was 0.85 g., or 66% of the theoretical.

Anal. Calcd. for $C_{20}H_{20}O_2S$: C, 74.1; H, 6.18; S, 9.87. Found: C, 74.5; H, 6.19; S, 9.71.

Demethylation.—The procedure given by Kharasch[9] for demethylation of stilbestrols was used: 1.07 g. of the dianisylthiophene was dissolved in 25 ml. of ethylene glycol, 2.5 g. of potassium hydroxide added, and the mixture sealed in a glass bomb under a pressure of 0.5 mm. of mercury. It was kept at 225° for eighteen hours. When cool it was opened, and the contents diluted with 2 volumes of water and filtered. When 8 ml. of concentrated hydrochloric acid was added, the solution set to a gel immediately. It was digested on a steam-bath, filtered and washed with water and dried. It was recrystallized with difficulty from benzene or toluene. After two recrystallizations from benzene, the gray material darkened at 185°, melted at 194–196°. The yield was 0.61 g., 61% of the theoretical. The compound is a phenol, as the deep yellow color with ferric chloride and the solubility in base indicate.

Anal. Calcd. for $C_{18}H_{16}O_2S$: C, 73.0; H, 5.41; S, 10.81. Found: C, 72.5; H, 5.37; S, 10.83.

Acetylation.—The 2,4-di-*p*-hydroxyphenyl-3,5-dimethylthiophene was readily acetylated by heating 0.1 g.

with 0.1 g. of fused sodium acetate in 2.5 ml. of acetic anhydride on a steam-bath for one hour. The mixture was then poured over ice and stirred until the oil had solidified. The amorphous solid was centrifuged out and recrystallized three times from ethyl alcohol, giving fine white needles of the diacetate, which softened at 121°, but melted at 125.9–126.9° cor.

Anal. Calcd. for $C_{22}H_{20}O_4S$: C, 69.5; H, 5.26; S, 8.42. Found: C, 69.7; H, 5.29; S, 8.25.

Formation of the Thiophene in Two Steps.—Approximately 2 g. of "Anhydro-*p*-methoxypropiophenone disulfide" was refluxed in 30 ml. of xylene for three hours. The solution became deep purple in color. The xylene was distilled off under vacuum, and the residual brown oil was taken up in ethanol and stored in the refrigerator. No crystals were obtained in twenty-four hours, although both 2,4-di-*p*-anisyl-3,5-dimethylthiophene and "anhydro-*p*-methoxypropiophenone disulfide" are readily crystallized from alcohol. A few drops of the alcohol solution decolorized an acetone solution of potassium permanganate, indicating unsaturation. The alcohol solution was refluxed for two hours with copper chromite. Upon cooling the filtered alcohol solution, yellow needles were obtained, m. p. 112–113.5°. Mixed with 2,4-di-*p*-anisyl-3,5-dimethylthiophene, the melting point was 112–113°.

Summary

A new method for the synthesis of 2,4-diarylthiophenes, in yields of 65 to 85% based on the reaction of "anhydroketone disulfides" with copper chromite, is described.

The mechanism of this reaction is discussed.

Four new compounds, "Anhydro-*p*-methoxypropiophenone disulfide," 2,4-di-*p*-hydroxyphenyl-3,5-dimethylthiophene, and its dimethyl ether and diacetate, are characterized.

BLOOMINGTON, INDIANA   RECEIVED JANUARY 31, 1944

(9) Kharasch and Kleiman, THIS JOURNAL, **65**, 11 (1943).

Acetylenic Ethers. IV.[1] Hydration

BY THOMAS L. JACOBS AND SCOTT SEARLES, JR.

It has been shown[2] that acetylenic ethers add water more rapidly than vinyl ethers but less rapidly than ketene acetals. The hydration is acid catalyzed and the rate has been followed quantitatively for several vinyl ethers.[3,4,5] It was of interest to carry out similar experiments with several acetylenic ethers for comparison.

Experimental

A dilatometric method was used to follow the hydration because it has been employed successfully to study the vinyl ethers[3,4,5] and because methods of analysis for acetylenic hydrogen or for the unsaturation of the triple bond are relatively inexact and have not been applied with success to acetylenic ethers. Butyl acetate was isolated[2] in 67% yield by heating butoxyacetylene with

distilled water. In dilute solutions containing traces of acid this hydration is the only significant reaction; both the polymerization of the acetylenic ether and the hydrolysis of the ester are slow enough to be neglected. In aqueous alcohol the reaction is accompanied by marked volume contraction. The concentrations of the solutions studied were 0.025 to 0.03 molar.

The acetylenic ethers used in this work were carefully refractionated samples.[2,6] The ethoxyacetylene may have contained a little water and traces of water may have been introduced into all the ethers when samples were being sealed in small bulbs since for this operation the bulbs were embedded in dry-ice and open to the air.

The dilatometer was similar to that described by Leutner[7] and used to study the hydration of vinyl ethers.[3,4,5] The measuring bulb had a volume of 110 ml. and the capillary was 25 cm. long, had a diameter of 0.36 mm. and was uniform within 1% over the calibrated portion.

The acetylenic ethers are not very soluble in water and

(1) For the third paper of this series see Jacobs and Whitcher, THIS JOURNAL, **64**, 2635 (1942).

(2) Jacobs, Cramer and Hanson, *ibid.*, **64**, 223 (1942).

(3) A. Skrabal and R. Skrabal, *Z. physik. Chem.*, **181A**, 449 (1938).

(4) R. Skrabal, *ibid.*, **185A**, 81 (1939).

(5) Zahorka and Wiemann, *Monatsh.*, **71**, 229 (1938).

(6) Jacobs, Cramer and Weiss, THIS JOURNAL, **62**, 1849 (1940). The ethoxyacetylene was prepared by Mr. John E. Hanson and Mr. Elbert Davis. The phenoxyacetylene was prepared by Mr. William Penn Tuttle, Jr.

(7) Leutner, *Monatsh.*, **66**, 222 (1935).

measurements were made in 12.5 and 42.7% by weight alcohol and water.[8] The rate of hydration of ethoxyacetylene and butoxyacetylene was followed most accurately and conveniently at pH 6 to 7. The solutions were weakly buffered and the acetylenic ethers were dissolved by crushing the bulbs containing the samples under a known amount of the solvent containing the basic portion of the buffer. This solution was transferred to the mixing chamber of the dilatometer in the thermostat and stirred until the temperature was constant. A dilute, thermostated solution of the acidic portion of the buffer was then transferred to the mixing chamber and the solution stirred and forced several times into the measuring chamber and back. The measuring chamber was finally filled to the desired capillary height using mercury to seal the stopcock as described by Leutner[7] and readings were taken at regular intervals.

The hydration of phenoxyacetylene was followed conveniently at pH 2; hydrochloric acid was used and the solution was not buffered.

It was necessary to allow considerable time for thermostatting after the sample bulbs were broken because the heats of solution of acetylenic ethers in aqueous alcohol are rather large. When a bulb containing 0.151 g. of ethoxyacetylene was broken in 140 ml. of 12.5% alcohol (pH 7.4) at 24.8° in a Dewar flask the temperature drop was 0.120°. Using a value of 1.026 cal. per g. degree as the specific heat of the solvent[9] and neglecting the heat capacity of the Dewar flask, the heat of solution of one mole of ethoxyacetylene in 64.9 liters of 12.5% alcohol is −7.9 kcal.

Measurements were carried out at 25.0° in a thermostat controlled by a large mercury regulator. The maximum temperature variation during a run was 0.003° and in some experiments it was as little as 0.001°. It was not possible to correct the capillary reading accurately for temperature variations since the changes were not synchronous. A preferable procedure is to use the readings of a second dilatometer containing only the solvent to correct the measurements.[10] Due to the 'war, it was not possible to obtain more of the capillary tubing of the correct size to construct another dilatometer. In 12.5% alcohol when the temperature changes were random and fairly rapid a variation of 0.001° altered the capillary height 0.05 to 0.1 mm. and the maximum effect on the capillary reading lagged behind the temperature change by 0.1 to 0.8 minute. Any sustained shift in the temperature altered the reading 3 or 4 times as much. In 42.7% alcohol the capillary reading varied 4 or 5 times as much as in 12.5% alcohol and the rate constants are correspondingly less reliable. However, the volume changes which occur with acetylenic ethers during hydration are larger than with vinyl ethers. The dilatometer capillary in work with the latter[3,4,5] had a diameter of only 0.05 mm.

The pH's of the solution were measured with a Model G Beckmann pH meter which makes use of a glass electrode. Dole[11] reported that in dilute alcohol there is practically no error in the voltage of the glass electrode and this was found to be true for 12.5% alcohol solutions. In solutions containing more alcohol there is an error depending upon the amount of alcohol present[11] and in addition the electrode is somewhat erratic.[12] The readings were found to

(8) Dilute alcohol was chosen as the solvent because it was used by Skrabal[s] in his studies of the vinyl ethers. The 12.5% by weight ethanol was prepared conveniently by mixing 800 ml. of distilled water and 150 ml. of the azeotropic mixture of water and ethanol which is 95.57% by weight ethanol. The ethanol was a carefully refractionated sample. The 42.7% by weight ethanol was prepared by mixing equal volumes of water and 95.57% ethanol. Only ethoxyacetylene was sufficiently soluble to be studied in the more dilute alcohol.

(9) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1929, Vol. 5, p. 116.

(10) Palomaa, Salmi and Suoja, Ber., 72, 313 (1939).

(11) Dole, THIS JOURNAL, 54, 3095 (1932).

(12) Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.

be unreliable if the instrument was used in alcohol solution continuously for fifteen minutes or longer, but such treatment did no damage to the electrode, for correct values were obtained on standard aqueous buffers immediately after such erratic behavior in alcohol. Figure 1 gives the relationship between pH readings of hydrochloric acid solutions in 42.7% ethanol and the log $1/H_3O^+$ of identical concentrations of the same acid in water. The graphical mean of the deviations is 0.16 pH unit with a possible variation of 0.05 pH unit. Such a variation corresponds to an uncertainty in the hydrogen ion concentration of ±12%. This is present only in the rate determinations on ethoxy- and butoxyacetylene in 42.7% alcohol, since with phenoxyacetylene the hydrochloric acid concentrations were known accurately.
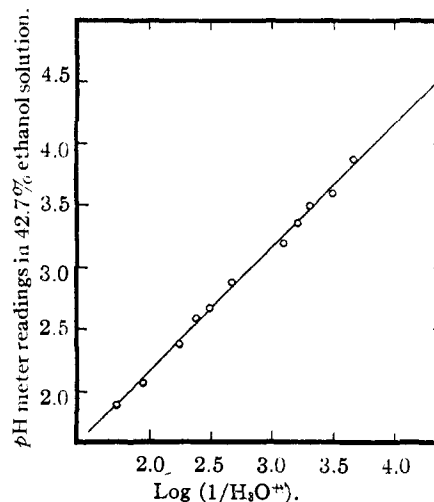

Fig. 1.—The relationship between pH readings in 42.7% ethanol solutions and log $(1/H_3O^+)$ in water solutions of identical concentration.

Either phosphate or acetate buffers were used with the alkoxyacetylenes and the exact concentrations of the salts were not known. In the phosphate buffers the concentration of disodium acid phosphate was approximately 1×10^{-4} M and of monosodium acid phosphate 1 to 2.5×10^{-3} M. This corresponds to an ionic strength of 1.3 to 2.8×10^{-3} M. The concentration of sodium acetate in the acetate buffer was approximately 4.5×10^{-3} M and of acetic acid 1.5 to 3×10^{-3} M.

Calculations, Results and Discussion

The hydration was found to be first order with respect to acetylenic ether and to hydronium ion. Since the latter acts as a catalyst only, the rate law at any given pH was $-dc/dt = kc$. The equation may, therefore, be written in its integrated form as

$$\log \frac{(h_\infty - h)}{(h_\infty - h_0)} = -\frac{kt}{2.3}$$

where h_0, h_∞ and h are the capillary readings at the beginning and end of the reaction and at time t. The specific rate constant, k, was evaluated graphically by plotting log $(h_\infty - h)$ against t in minutes and determining the slope of the curve. Accurate experimental values of h_∞ were not obtained due to the difficulty of maintaining a constant temperature for a sufficiently long period of time, but by a trial and error method an empirical h_∞ was chosen which gave most nearly a straight

line. The method of Guggenheim[13] which eliminates h_∞ was also applied to the data. The points did not fall as accurately on a straight line as in the first method since random errors in the individual readings are magnified. However, the rate constants as determined by the two methods always agreed within 2%. Table I summarizes the results and Fig. 2 gives the experimental curves from which the values of k were obtained for runs C, E, H, and K. The other runs give equally good lines.

TABLE I

Acetylenic ether	Experiment	pH	$k \times 10^4$	k_a
Ethoxyacetylene[a]	B	6.47	3.12	8.91×10^3
	C	6.03	8.42	8.91×10^3
	D	5.10	63.1	7.93×10^3
	E	5.85	6.20	4.39×10^3
	F	5.95	4.50	4.01×10^3
Butoxyacetylene	G	6.27	3.89	7.24×10^3
	H	5.96	7.39	6.74×10^3
Phenoxyacetylene	J	2.470	1.91	0.564
	K	2.470	1.85	.546
	L	2.255	3.03	.545

[a] Experiments B, C and D were carried out in 12.5% alcohol and k_a was calculated from the equation $k_a = (k - k_w)/(H_3O^+)$. Experiments E and F were carried out in 42.7% alcohol.

To show that the direct reaction of water with these esters contributes very little to the total reaction rate one experiment was carried out on
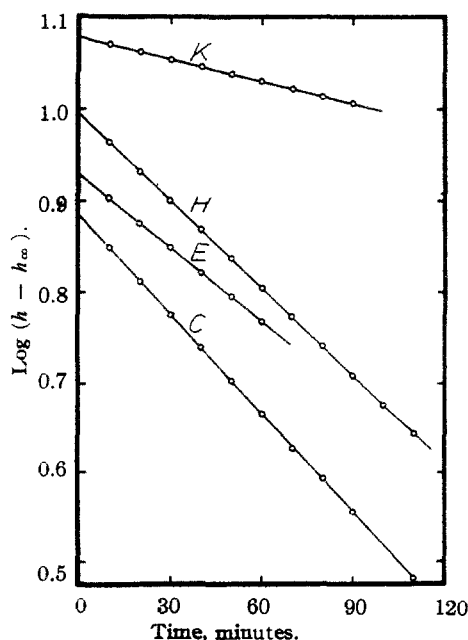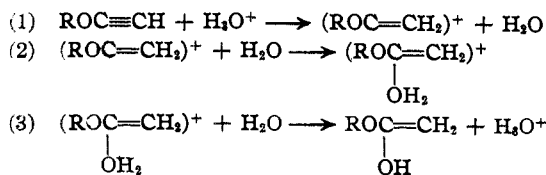

Fig. 2.—Hydration of acetylenic ethers at 25°: C, ethoxyacetylene in 12.5% ethanol; E, ethoxyacetylene in 42.7% ethanol; H, butoxyacetylene in 42.7% ethanol; K, phenoxyacetylene in 42.7% ethanol.

(13) Guggenheim, Phil. Mag., [7] 2, 538 (1926).

ethoxyacetylene in 12.5% alcohol at pH 8.97. The reaction was less than a third complete in sixty hours and the determination was much less accurate than experiments in acid solution. From the slope of the curve, k was found to be 1.1 $\times 10^{-4}$. This represents the sum of the rate constant of acid catalyzed hydration, $k_a(H_3O^+)$ and the rate constant of hydration by water, k_w. Since $k_a = 9 \times 10^3$ and $(H_3O^+) = 1.1 \times 10^{-9}$, $k_w = 1.0 \times 10^{-4}$. The hydration by water should be independent of the acid concentration and k_w was therefore subtracted from k in the calculation of k_a for experiments in 12.5% ethanol (Experiments B, C, and D). The value of k_w in 42.7% alcohol was not determined because it was less than in 12.5% alcohol and the variations of capillary reading with temperature were so large.

The hydrolysis of saturated ethers is believed to proceed through an oxonium intermediate of the type $[RO(H)R]^+$ and cleavage of one of the alkyl-oxygen bonds.[14,15] A. Skrabal[16] and R. Skrabal[4] have formulated the reaction mathematically to permit calculation of the rates of hydrolysis of unsymmetrical ethers from the rates of symmetrical ones. This treatment does not hold for vinyl ethers and R. Skrabal[4] believed that this was due to a different mechanism of hydrolysis, probably the addition of water to the double bond of the vinyl group as Paul[17] suggested earlier. No direct evidence for this addition could be obtained because the hemiacetal produced is hydrolyzed more rapidly than the vinyl compound.[16] The hydrolysis of ethynyl ethers appears to be similar to that of vinyl ethers, but in this case the compound obtained by the addition of water to the triple bond is the enol form of an ester. This rearranges to the ester which hydrolyzes very much less rapidly than the acetylenic ether.[18] A mechanism which is consistent with the observed kinetics may be formulated as follows

(1) $ROC{\equiv}CH + H_3O^+ \longrightarrow (ROC{=}CH_2)^+ + H_2O$

(2) $(ROC{=}CH_2)^+ + H_2O \longrightarrow (ROC{=}CH_2)^+$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad OH_2$

(3) $(ROC{=}CH_2)^+ + H_2O \longrightarrow ROC{=}CH_2 + H_3O^+$
$\quad\quad |\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$
$\quad OH_2 \qquad\qquad\qquad\qquad\qquad\qquad OH$

(14) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 299.

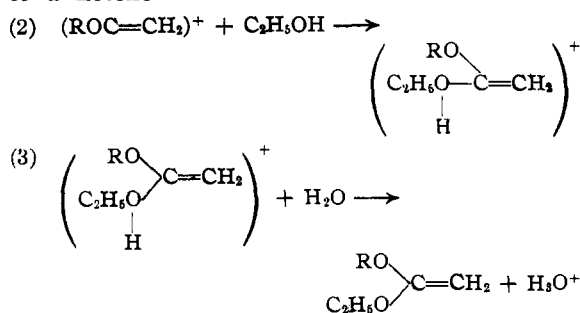(15) Bonhoeffer and Reitz, Z. physik. Chem., 179A, 135 (1937).

(16) A. Skrabal, Ber., 72, 446 (1939).

(17) Paul, Bull. soc. chim., [5] 1, 971 (1934).

(18) The rate constant, k_a, for the acid catalyzed hydrolysis of ethyl acetate in water at 25° is 6.5 $\times 10^{-5}$ min.$^{-1}$ moles^{-1} liters [Dawson and Lowson, J. Chem. Soc., 2146 (1928)] and the constant for the reaction with base in water at 25° is 6.76 min.$^{-1}$ moles^{-1} liter [Terry and Stieglitz, THIS JOURNAL, 49, 2216 (1927)]. It has been shown by Caudri [Rec. trav. chim., 48, 422 (1929)] that in aqueous alcohol the rate constant for the reaction with base decreases as the amount of alcohol increases (in 10% and 20% alcohol by volume k has values of 6.23 and 5.70, respectively, compared with a value of 6.54 which he obtained in water). At a pH of 6 the pseudo first order rate constant for the over-all hydrolysis in water is 7.4 $\times 10^{-8}$ min.$^{-1}$. This is negligible compared with the pseudo first order rate constant of 8.7 $\times 10^{-4}$ for ethoxyacetylene at pH 6 in 12.5% alcohol at 25°.

(4) $ROC{\equiv}CH_2 \longrightarrow ROC{-}CH_3$
        | ‖
        OH   O
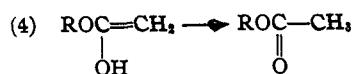
The first step involves the transfer of a proton to the β-carbon atom and is probably the same as the first step in the acid catalyzed hydration of an ordinary ethylenic bond,[19] a reaction which shows the same kinetics and for which hydronium ion appears to be the only acid with an appreciable effect on the rate. This specific acid catalysis seems to hold for the acetylenic ethers as well since the values of k_a obtained from different runs on the same compound by dividing k by the hydronium ion concentration are the same even when the concentration of other acids such as dihydrogen phosphate ion or acetic acid are varied severalfold. The question of the rate determining step remains open. An alternative mechanism which may be important in 42.7% alcohol involves the formation of a ketene acetal. This would be converted

(2) $(ROC{\equiv}CH_2)^+ + C_2H_5OH \longrightarrow$

$$\left(\begin{array}{c} RO \\ \diagdown \\ C_2H_5O{-}C{=}CH_3 \\ | \\ H \end{array}\right)^+$$

(3) $$\left(\begin{array}{c} RO \\ \diagdown \\ C_2H_5O \diagup C{=}CH_2 \\ | \\ H \end{array}\right)^+ + H_2O \longrightarrow$$

$$\begin{array}{c} RO \\ \diagdown \\ C_2H_5O \diagup C{=}CH_2 + H_3O^+ \end{array}$$

rapidly to the ester, possibly to some extent through the ortho ester.

Table II lists the average values of k_a for vinyl and ethynyl ethers, for diethyl ether and for two olefins.

TABLE II

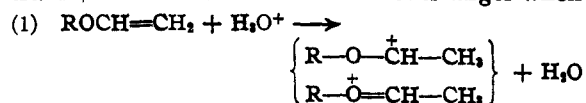RATE CONSTANTS FOR ACID CATALYZED HYDRATIONS OR HYDROLYSES AT 25°

Compound	k_a (min.$^{-1}$, moles^{-1} l.)	Solvent
Diethyl ether[3]	1.46×10^{-11}	Water
Ethyl vinyl ether[5]	1.73×10^2	Water
Isopropyl vinyl ether[4]	5.20×10^2	Water
Divinyl ether[3]	5.0×10^{-1}	Water
	2.9×10^{-1}	25% alc. (by vol.)
Ethoxyacetylene	8.6×10^3	12.5% alc. (by wt.)
	4.2×10^5	42.7% alc. (by wt.)
Butoxyacetylene	7.0×10^3	42.7% alc. (by wt.)
Phenoxyacetylene	5.5×10^{-1}	42.7% alc. (by wt.)
Isobutylene[19]	2.3×10^{-2} [a]	Water
Trimethylethylene[19]	1.3×10^{-2} [a]	Water

[a] These are the values for k_a at an ionic strength of 0.05 N. For isobutylene the extrapolated value at zero ionic strength is 2.2×10^{-2} (min.$^{-1}$, moles^{-1}, l.).

All of the differences in rate constants are in the directions expected if step (1) is rate determining. Vinyl ethers hydrate more rapidly than alkenes because of the extra stabilization due to resonance

(19) Lucas and Eberz, THIS JOURNAL, **56**, 460 (1934); Lucas and Liu, *ibid.*, **56**, 2138 (1934); Hammett, ref. 14, p. 292.

in the intermediate onium ion and hence in the transition state as well. The effect is larger when

(1) $ROCH{=}CH_2 + H_3O^+ \longrightarrow$

$$\left\{\begin{array}{c} R{-}O{-}\overset{+}{C}H{-}CH_3 \\ R{-}\overset{+}{O}{=}CH{-}CH_3 \end{array}\right\} + H_2O$$

the double bond is replaced by a triple bond since the ability of the latter to take part in such resonance is greater.[20] This does not permit a direct prediction of the relative rates of hydration of ethynyl and vinyl ethers, but only of the former relative to alkynes; however it is not surprising that acetylenic ethers hydrate more readily than vinyl ethers. No measurements have been made of the rates of the acid-catalyzed hydration of alkynes. When the ability of oxygen to enter such conjugation is decreased by its attachment to another group such as vinyl or phenyl which permits crossed conjugation, the transition state would be less readily achieved. Thus divinyl ether hydrates more slowly than ethyl vinyl and phenoxyacetylene more slowly than alkoxyacetylenes. In this connection it is interesting that the dipole moment of phenoxyacetylene[21] is not greatly different from that of phenetole or diphenyl ether while the alkoxyacetylenes have higher dipole moments.[21]

Acknowledgments.—Thanks are due to Dr. S. Winstein and Dr. J. B. Ramsay of the Department of Chemistry of the University of California at Los Angeles for many helpful suggestions throughout the course of this work. Part of the preliminary work on the problem was done by Mr. L. R. Pollack. We also wish to thank Mr. Harry L. Masser of the Southern California Gas Company for a scholarship granted to the junior author.

Summary

The rates of the acid catalyzed hydration of ethoxy-, butoxy- and phenoxy-acetylene have been measured at 25° in dilute alcoholic solutions by a dilatometric method. The reaction is first order with respect to ether and hydronium ion concentration and consists in the addition of water to the triple bond yielding an ester. The hydration is very similar to that of vinyl ethers, but proceeds more rapidly. A mechanism consistent with the kinetics is proposed.

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(20) This is most clearly shown by the greater shortening of the carbon–halogen bond distances in halogenoacetylenes such as bromoacetylene as compared with halogenoethylenes. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 1940, p. 216; Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935); de Laszlo, *Nature*, **135**, 474 (1935); Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938). The lower dipole moments of halogenated acetylenes relative to halogenated olefins is further evidence. Pflaum and Wenzke, THIS JOURNAL, **56**, 1106 (1934); Wilson and Wenzke, *ibid.*, **56**, 2025 (1934).

(21) Jacobs, Roberts and MacMillan, THIS JOURNAL, **66**, 656 (1944). The dipole moments of the acetylenic ethers were calculated by the Onsager equation [THIS JOURNAL, **58**, 1486 (1936)] from measurements of the dielectric constants of the pure liquids and are not directly comparable with the accurate values for the aryl ethers.