In order to determine stability to reaction conditions, the experiments compiled in Table IV were performed. In each case the compounds in question were dissolved in sufficient solvent to reproduce solvolysis concentrations. Each tube was maintained at 117° for ten half-lives (approximately 150 hr). The amount of alcohol produced in each case was obtained by adding a weighed amount of cyclohexanol and determining from vpc traces the relative area of a given alcohol to that of the cyclohexanol standard.

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The Acid-Catalyzed Hydration of Phenylacetylene. Evidence for the Vinyl Cation Intermediate[1,2]

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Abstract: The acid-catalyzed hydration of phenylacetylene parallels the acidity function, a plot of log k_{obsd} against $-H_0$ having a slope of 1.24. The reaction involves a rate-determining proton transfer as shown by the solvent isotope effect, k_{H_2O}/k_{D_2O} being 2.5. The rate of hydration of substituted phenylacetylenes is extremely sensitive to the nature of substituents in the ring, and correlation with σ^+ constants gives a ρ value of -3.84. Examination of the rate of hydration of *p*-methoxyphenylacetylene in aqueous buffers reveals that the reaction is subject to general acid catalysis. Evidence to demonstrate that the first intermediate in the hydration reaction is a vinyl cation is presented. A small amount of exchange of the acetylenic hydrogen of phenylacetylene in strongly acidic media is observed.

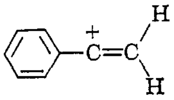
In a continuation of our studies of the mechanisms of the reactions of unsaturated systems with acid, we have examined the acid-catalyzed hydration of phenylacetylene. These studies represent a natural supplement of previously reported studies on phenylpropiolic acid[4] and phenylbenzoylacetylene.[5]

As these studies were in progress Bott, *et al.*,[6] reported the relative rates of hydration of several substituted phenylacetylenes in acetic acid–water–sulfuric acid mixtures and noted the strong sensitivity of the reaction to the electron demands of the substituent. Bott, *et al.*,[6] concluded that the reaction rates as measured were best fit by the Yukawa–Tsuno equation.[7]

We have examined this reaction under a variety of different circumstances in order to gain more mechanistic insight into the nature of the intermediates involved. The hydration of phenylacetylene (**1**), *p*-methoxyphenylacetylene (**2**), *p*-methylphenylacetylene (**3**), and *p*-chlorophenylacetylene (**4**) has been studied in aqueous sulfuric acid. The reaction is smooth and quantitative when the concentration of organic substrate is kept low. Bott, *et al.*,[6] have commented upon the difficulty of reproducing on a preparative scale the quantitative conversion of phenylacetylene to acetophenone as shown by spectral changes at 10^{-5} *M* levels. The suggestion that subsequent bimolecular aldol condensation destroys some acetophenone is in complete accord with our observations as well.

The hydration reaction shows strong acid catalysis, plots of the logarithm of the observed rate constants *vs.* H_0 being linear. Such a plot for **1** has a slope of -1.24 at 25°. Measured rate data for phenylacetylene and three substituted phenylacetylenes is given in Table I; Tables II and III contain derived information.

The activation energies and entropies of activation accord with those to be expected for a rate-limiting proton transfer. As we reported briefly earlier,[2] the evidence including the solvent isotope effect[8] supports the rate-limiting formation of a vinyl cation intermediate of structure **A**.



A

General Acid Catalysis. A rate-determining proton transfer to phenylacetylene (eq 1) implies general acid catalysis.

$$C_6H_5C{\equiv}CH + H^+ \xrightarrow{\text{slow}} A \qquad (1)$$

catalysis. To examine whether general acid catalysis is, in fact, operative, it is only necessary to examine the behavior of a sufficiently reactive substituted phenylacetylene; *p*-methoxyphenylacetylene (**2**) is satisfactory.

At 45° the rate of hydration of **2** may be followed in formic acid–formate buffers; the data are given in Table IV.

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Table I. Rate of Hydration of Substituted Phenylacetylenes in Sulfuric Acid

Compd	Temp, °C	% H_2SO_4	$-H_0$	10^4k, sec^{-1}
1	24.92	5.98	−0.02	0.00276
		32.43	1.82	0.570
		33.98	1.93	0.667
		38.48	2.27	2.06
		39.64	2.36	2.84
		40.27[a]	2.42	2.98
		41.93	2.57	4.74
		42.08	2.58	5.10
		44.04	2.78	8.15
		45.19	2.90	11.7
		48.42	3.24	28.8
		5.28[b]	2.38	2.56
		6.12[b]	2.93	11.2
		6.72[b]	3.38	39.9
1	44.11	21.66	1.05	0.488
		23.28	1.17	0.665
		26.44	1.38	1.18
		32.59	1.83	4.01
		33.96	1.93	5.42
		34.08	1.94	5.55
2	24.88	0.49	−1.11	0.192
		1.55	−0.65	0.621
		3.04	−0.34	1.38
		3.95	−0.21	1.97
		3.95[c]	−0.21	2.00
		3.96	−0.21	2.01
		3.96[c]	−0.21	1.97
		6.00	−0.02	3.49
		6.06	−0.01	3.59
		9.60	0.25	7.80
		9.72	0.26	8.04
		14.14	0.60	19.1
2	44.93	0.12	−1.74	0.357
		0.34	−1.34	0.975
		0.47	−1.19	1.34
		1.48	−0.70	4.15

[a] Cu(II) added, 2×10^{-5} *M*. [b] Molarity of $HClO_4$. [c] Followed at 240 mμ rather than at 296 mμ.

Table II. Least-Squares Treatment of Acidity Dependence Data for Arylacetylenes

Compd	Temp, °C	$-d \log k/dH_0$	*r*
1	24.92	1.24 ± 0.01	0.9995
	44.11	1.189 ± 0.006	0.9999
2	24.88	1.185 ± 0.015	0.9995
	44.93	1.005 ± 0.008	0.9998
3	24.88	1.26 ± 0.03	0.9986
	44.93	1.149 ± 0.001	>0.9999
4	24.86	1.17 ± 0.01	0.9998
	44.63	1.195 ± 0.006	0.9999

Table III. Activation Parameters for Hydration of Phenylacetylenes

Compd	Temp, °C	$-\text{Log } k_0$[a]	E_a, kcal	$\Delta H^\ddagger$	$\Delta S^\ddagger$
1	24.92	6.52	21.5	20.9	−18.2
	44.11	5.56			
2	24.88	3.425	16.3	15.7	−21.6
	44.93	3.682			
3	24.88	5.30	22.2	21.6	−10.4
	44.93	4.28			
4	24.86	6.80	17.3	16.7	(−33.6)
	44.63	6.01			

[a] Extrapolated rate at $H_0 = 0$.

For formic acid, the data are best represented by eq 2.

$$k_{obsd} = k_{H^+}C_{H_3O^+} + k_{HFm}C_{HFm} = (2.23 \times 10^{-3}\ M^{-1}\ sec^{-1})C_{H_3O^+} + (4.31 \times 10^{-6}\ M^{-1}\ sec^{-1})C_{HFm} \quad (2)$$

The hydration of phenylacetylene thus is an example of the growing number of reaction types which exhibit both general acid catalysis for the more reactive members of the series, and also good linear correlations with the acidity function H_0. These include the study of aromatic hydrogen exchange reactions.[9,10]

Table IV. Hydration of *p*-Methoxyphenylacetylene in Buffer Solutions at 44.85 ± 0.05°[a]

HA, *M*	$NaClO_4$, *M*	k_{obsd}, sec^{-1}	pH
0.050	0.075	1.18×10^{-6}	3.36
0.100	0.050	1.42×10^{-6}	3.36
0.141	0.0294	1.57×10^{-6}	3.36

[a] Formic acid–sodium buffer, ratio 2:1, ionic strength 0.1.

More recently Schubert, Lamm, and Keefe have demonstrated general acid catalysis in the hydration of an appropriately substituted styrene.[11] The hydrolysis of vinyl ethyl ether shows general acid catalysis[12] and the hydrolysis of 2,5-dimethylfuran is linearly related to H_0.[13] Drenth and Hogeveen[14,15] have shown that the hydration of ethynyl thio ethers is subject to general acid catalysis and also that the rate of hydration is linearly related to the acidity function for less reactive compounds.

Exchange Experiments. A further facet of the role of a vinyl cation intermediate such as A is the possibility of two branching pathways for the subsequent reaction of A. Grob and Cseh[16] have observed that the solvolysis of α-bromostyrene in 80% ethanol at 200° gives phenylacetylene as well as acetophenone. Ionization to a vinyl cation followed by reaction with solvent or by proton loss would explain these observations. Fahey and Lee[17] have observed that the addition of HCl to 1-phenylpropyne gives both *cis* and *trans* products and have interpreted these results in terms of partitioning of a vinylic cation intermediate.

We have carried out a study of the possibility of exchange of the acetylenic hydrogen of **1** under the strongly acidic conditions of the hydration. Using a 40% sulfuric acid solution which was tritium labeled the hydration of **1** was allowed to proceed to 50% completion, and unreacted **1** was then carefully reisolated. A sample purified by vapor phase chromatography showed 0.6% exchange.

Furthermore, a similar experiment carried out using deuteriosulfuric acid gave completely concordant results.

It is easily established that these facts represent acid-catalyzed exchange of the acetylenic hydrogen. Base-catalyzed exchange can be excluded by considera-

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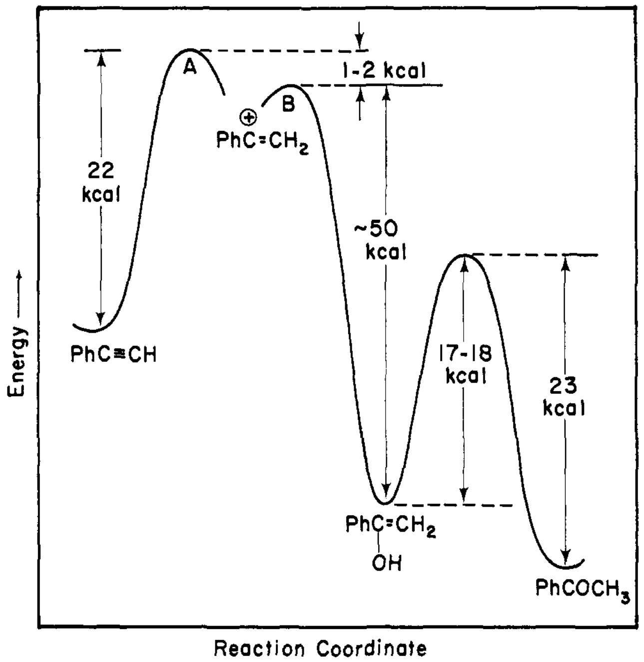

Figure 1. Energy–reaction coordinate diagram for the acid-catalyzed hydration of phenylacetylene. The ordinate is not to scale.

tion of the data of Ballinger and Long[18] and of Eaborn, *et al.*[19] The extrapolated rate of base-catalyzed exchange is at least four powers of ten less than the rate of incorporation of deuterium into phenylacetylene. Further, Ballinger and Long[18] report that there is no evidence for a water-catalyzed reaction. Similarly, extraneous exchange of aromatic hydrogens can be ruled out by consideration of the rate of aromatic exchange of benzene[20] and the general electronic influence which the ethynyl group would exert. Eaborn[6] has also presented an additional argument which likewise effectively excludes exchange of aromatic hydrogens from consideration under our conditions.

Thus, these experiments shows that the vinyl cation represents an intermediate in the hydration of phenylacetylene which may either collapse with solvent to give the enol of acetophenone or lose a proton to regenerate phenylacetylene. This information is best presented in capsule form by construction of an energy–reaction coordinate diagram (Figure 1).

Moureu and Andre[21] have reported that equilibrium 3 lies 37 kcal/mole in favor of the ketone based on the

$$C_6H_5C{\equiv}CH + H_2O \rightleftharpoons C_6H_5COCH_3 \qquad (3)$$

heats of combustion of these compounds. Combined with the data of Zucker and Hammett[22] on the rate of enolization of acetophenone and an estimate of the enol content of acetophenone (0.001%),[23] this information allows construction of a relatively complete energy–reaction coordinate diagram, given in Figure 1.

Experimental Section

Materials Commercial **phenylacetylene** was redistilled and further purified by preparative vapor phase chromatography. ***p*-Methoxyphenylacetylene (2)**[24] was purified by sublimation, mp 25.5–26.0° (lit.[25] 29°). ***p*-Methylphenylacetylene (3)** was purified by distillation and ***p*-chlorophenylacetylene (4)** was purified by sublimation, mp 45–46° (lit.[26] 43–44°).

Kinetic Procedures. A stock solution of the alkyne (about 1×10^{-3} *M*) was prepared in 95% ethanol. One milliliter of this solution was diluted to 20 ml with sulfuric acid of the desired concentration to prepare the kinetic solutions. Kinetics were followed using a Beckman DU spectrophotometer by observing the appearance of the absorption band characteristics of the ketone. The ultimate spectrum was identical with that of a solution of the corresponding ketone. The final spectrum was stable for periods corresponding to ten half-lives or longer.

The kinetic solutions were titrated in duplicate, and the value of the acidity function corresponding to this per cent by weight acid was determined by reference to the data of Hartter for sulfuric acid solutions containing 5% ethanol.[27] As Hartter noted, below 20% sulfuric acid the 5% ethanol media and purely aqueous media are indistinguishable. The data of Bascombe and Bell[28] have been used in the more dilute range. For the general acid catalysis studies, formic acid–sodium formate buffers were prepared from reagent grade materials with addition of sufficient sodium perchlorate to bring the ionic strength to 0.1. The measured pH of these solutions was 3.36.

The rates were followed at 45° by observing the appearance of the ketone band at 296 mμ.

Exchange Experiments. Twenty-five milligrams of ethynylbenzene was placed in 5 ml of 95% ethanol, and this solution was diluted to 100 ml with 40% D_2SO_4 in D_2O. The final concentration of acid was 39.99% by weight as determined titrimetrically.

After 85 min at 25° (57% reaction), the reaction solution was cooled, diluted with ice water, and extracted with five 2-ml portions of pentane. The pentane extracts were combined, dried over anhydrous magnesium sulfate for 20 min, filtered, and concentrated to a volume of about 100 μl. Phenylacetylene was isolated by vpc using a 0.25 in. × 5 ft 20% SF-96 on Firebrick column at 120°. A control experiment with deuteriophenylacetylene prepared by base exchange showed that no loss of deuterium was observed during vpc. The recovered phenylacetylene contained 1.13 ± 0.10% ethynyl-*d*-benzene (average of five determinations on three separate fractions using a CEC 130 mass spectrometer).

In another experiment, 50 mg of $^{3}H_{1}$-enriched water (1 Ci/g) was added to 100 ml of 36% by weight aqueous sulfuric acid. Nine milligrams of ethynylbenzene was added to 50 ml of this radioactive solution. After 93 min at 25° (50% reaction) the reaction was poured into 25 ml of ice-cold distilled water to effectively quench the reaction. An additional 45 μl (41.8 mg) of ethynylbenzene was then added to facilitate the isolation. The solution was extracted with four 5-ml portions of pentane and the alkyne was isolated by gas chromatography as described above.

In order to ensure that neither the quenching nor the isolation procedure was the source of any incorporation, a sample of ethynylbenzene was allowed to react in an acid solution identical with the one above except for the presence of tritiated water. This reaction solution was quenched in 25 ml of ice-cold distilled water to which had been added 12.5 mg of 1-Ci/g tritiated water and 45 μl of ethynylbenzene. Thus, after both solutions were quenched, they were essentially identical. The isolation was performed under the same conditions.

A weighed portion (14.2 mg) of the recovered acetylene was counted using 15 ml of a scintillation solution prepared using 0.2 g of *p*-bis[2-(5-phenyloxazolyl)]benzene, 8.0 g of 2,5-diphenyloxazole, and 2000 ml of Baker and Adamson reagent grade toluene using a Nuclear Chicago Mark I scintillation counter at 4°.

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