The Kinetics and Mechanism of the Acid-Catalyzed Hydration of Phenylbenzoylacetylene[1,2]

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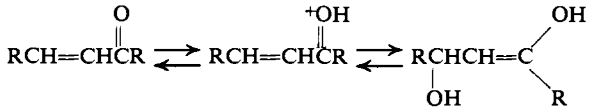
Abstract: Phenylbenzoylacetylene acts as a weak base in sulfuric acid, being one-half protonated in 73.7% sulfuric acid, $H_0 = -6.51$. The rate of hydration of phenylbenzoylacetylene, corrected for protonation, correlates with the acidity of the medium, a plot of log k *vs.* H_0 having nearly unit slope. The rate of hydration is very sensitive to the electron-donating ability of substituents in the phenyl ring, with ρ being -4.2 (*vs.* σ^+ substituent constants). As the rate of hydration is reduced in deuterated medium, k_{H_2O}/k_{D_2O} being approximately 2, it is concluded that the mechanism of hydration involves rate-determining proton transfer to carbon to give a vinylic carbonium ion. The possible intervention of an allenediol as an intermediate has been excluded by the study of appropriately substituted compounds.

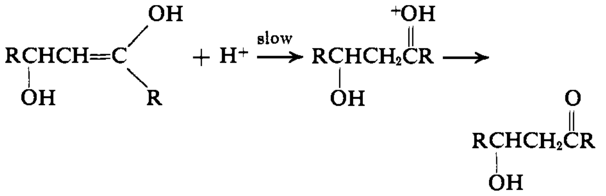
Studies of the acid-catalyzed hydration of unsaturated acids[4] and of unsaturated ketones[5–7] have revealed very interesting differences in the reaction pathways accessible for these two classes of compounds. For unsaturated acids, hydration involves the rate-limiting addition of a proton to the olefinic carbon to give a carbonium ion, which is rapidly converted to the hydroxy acid (eq 1). With the possible exception of the hydration of acrylic acid studied by Pressman and Lucas,[8] this mechanism accommodates the data for all conjugated unsaturated acids.

$$\mathrm{ArCH{=}CHCOOH + H^+ \xrightarrow{slow} Ar\overset{+}{C}HCH_2COOH \xrightarrow{fast} ArCHOHCH_2COOH} \quad (1)$$

In contrast, the hydration of unsaturated ketones generally involves a 1,4-addition mechanism in which the oxonium salt of the ketone is attacked by water at the β-carbon atom to give the hydroxy enol. The hydroxy enol is then protonated in the rate-limiting step (eq 2 and 3) as shown by the elegant study of Bell, Preston, and Whitney.[7]



$$\mathrm{RCH{=}CH\overset{\overset{O}{\|}}{C}R \rightleftarrows RCH{=}CH\overset{\overset{^+OH}{\|}}{C}R \rightleftarrows \underset{\underset{OH}{|}}{RCH}CH{=}C(OH)R} \quad (2)$$



$$\mathrm{\underset{\underset{OH}{|}}{RCH}CH{=}C(OH)R + H^+ \xrightarrow{slow} \underset{\underset{OH}{|}}{RCH}CH_2\overset{\overset{^+OH}{\|}}{C}R \longrightarrow \underset{\underset{OH}{|}}{RCH}CH_2\overset{\overset{O}{\|}}{C}R} \quad (3)$$

The hydration of arylpropiolic acids[1] shows very close similarities to the hydration of cinnamic acids, and it is therefore most interesting to make comparisons between acetylenic ketones and α,β-unsaturated ketones. Such is the purpose of the present report.

Experimental Section[9]

Preparation of Materials. Phenylbenzoylacetylene (1) was prepared by the method of Dufraisse,[10] from ethynylbenzene and benzoyl chloride, mp 47.0–47.5° (lit.[10] 49°). **Phenyl-*p*-methylbenzoylacetylene (2)** was prepared similarly from ethynylbenzene and *p*-methylbenzoyl chloride, mp 70.5–71.0° (lit.[11] 72°), and in a similar fashion from ethynylbenzene and *p*-nitrobenzoyl chloride, **phenyl-*p*-nitrobenzoylacetylene (3)** was prepared, mp 162.5–163.0° (lit.[11] mp 161–162°). ***p*-Methylphenylbenzoylacetylene (4)** was prepared from 4-methylethynylbenzene (from *p*-methylacetophenone[12]) and benzoyl chloride, mp 58.5–59.0° (lit.[13] mp 57°), in similar fashion.

From *p*-methoxycinnamic acid, 2-bromo-1-(4-methoxyphenyl)-ethylene was obtained following the procedure of Allen and Cook[14] and converted to 4-methoxyethynylbenzene by the method of Smissman, *et al.*[15] The 4-methoxyethynylbenzene was converted to its sodium salt in tetrahydrofuran and allowed to react with benzoyl chloride to afford ***p*-methoxyphenylbenzoylacetylene (5)**, mp 25.0–26.0° (lit.[16] 29°).

The diaroylmethanes were prepared by condensing the substituted benzaldehyde with acetophenone to give the corresponding benzalacetophenone. The unsaturated ketone was treated with bromine to yield the dibromide, which was in turn treated with sodium ethoxide to yield the enol ethyl ether of the corresponding aroylacetophenone. Treatment with dilute acid afforded the aroylacetophenone. In this fashion were prepared **benzoylacetophenone**, mp 77.0–77.4°, in 69% yield from benzaldehyde; **4-methylbenzoylacetophenone**, mp 83.0–84.0° (lit.[17] 84°), in 58% yield; **4-methoxybenzoylacetophenone**, mp 130.5–131.0° (lit.[18] 130–131°), in 69% yield; **4-nitrobenzoylacetophenone**, mp 161.0–162.0° (lit.[19] 162–163°), in 55% yield.

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[1] Previous paper: D. S. Noyce, M. A. Matesich, and P. E. Peterson, *J. Am. Chem. Soc.*, **89**, 6625 (1967).

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[3] National Science Foundation Predoctoral Fellow, 1964–1966; National Institutes of Health Predoctoral Fellow, 1966–1967.

[4] D. S. Noyce, H. S. Avarbock, and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1647 (1952), and immediately preceding papers.

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[9] Melting points were determined using a Büchi melting point apparatus. Boiling points and melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 237 spectrophotometer; ultraviolet spectra were scanned with a Cary Model 14 spectrophotometer.

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Product Isolation. A. From Phenylbenzoylacetylene. To 200 ml of 80% sulfuric acid was added 1.16 g of phenylbenzoylacetylene dissolved in 10 ml of dioxane. This mixture was stirred at 25° for 4 hr and then poured onto 500 g of ice. The aqueous mixture was extracted three times with ether, and the combined ether extracts were extracted once with saturated aqueous sodium bicarbonate, dried with magnesium sulfate, and concentrated on a rotary evaporator. The residue was recrystallized from ethanol to afford 1.15 g of benzoylacetophenone (92% yield), mp 75.5–77.0°. A mixture melting point with an authentic sample was not depressed and an infrared spectrum of the product was identical with that of an authentic sample.

B. From Phenyl-4-nitrobenzoylacetylene. To 300 ml of 80% sulfuric acid was added 0.98 g of phenyl-4-nitrobenzoylacetylene dissolved in 50 ml of dioxane. A higher concentration of dioxane was necessary in this instance in order to ensure complete solution. After stirring the solution for 2 hr, it was added to 500 ml of ice–water, and the aqueous mixture was extracted three times with ether. The combined ether extracts were extracted with sodium bicarbonate, dried with magnesium sulfate, and concentrated on a rotary evaporator. The residue consisted of 1.01 g (96% yield) of 4-nitrobenzoylacetophenone, mp 160.0–162.0°. A mixture melting point with an authentic sample was not depressed.

Product Stability Studies. In order to establish the stability of the product of hydration of the acetylenes, the following large-scale experiment was carried out.

To 300 ml of 50% sulfuric acid was added 1.0 g of 4-methoxybenzoylacetophenone dissolved in 30 ml of dioxane. The solution was stirred for 20 hr after which time it was extracted directly with ether. The ether extracts were extracted with sodium bicarbonate, dried with magnesium sulfate, and condensed on a rotary evaporator. The residue consisted of 0.94 g of a faintly yellow solid (94% recovery), mp 129.0–131.0°. A mixture melting point with an authentic sample was not depressed.

The stability in sulfuric acid of the substituted benzoylacetophenones obtained from the hydration was also examined by preparing a 10^{-5} *M* solution of each diketone in 40, 60, and 80% sulfuric acid. The ultraviolet spectra of these solutions were observed; only the more acidic solutions were found to change slightly over a period of 3 to 4 days. This change in absorbance is presumably due to an acid-catalyzed decomposition of the benzoylacetophenones to the corresponding benzoic acids and acetophenones.[20] However, in all cases, this decomposition of the benzoylacetophenones was sufficiently slower than the hydration of the acetylenic ketones to the diketone that good first-order kinetics could be observed over more than 95% reaction.

Kinetic Procedure. Stock solutions (1.2×10^{-3} *M*) of the substituted phenylbenzoylacetylenes were prepared in dioxane.

The kinetic solutions were prepared by pipetting 1.25 ml of the stock solution into a 25-ml volumetric flask and diluting to 25 ml with the appropriate aqueous sulfuric acid solution. This kinetic solution was placed directly into a 1-cm quartz cell in a thermostated cell compartment of a Beckman DU spectrophotometer. The final substrate concentration was *ca.* 6×10^{-5} *M* with the solvent consisting of 5% aqueous dioxane (vol %). For 4-methoxyphenylbenzoylacetylene, 10-cm quartz cells were used; therefore, the stock solution was diluted by a factor of ten before the kinetic solution was prepared.

Several absorbing species were present in any kinetic run: the acetylenic ketone, the acetylenic ketone protonated on oxygen, the benzoylacetophenone and its tautomers, and protonated benzoylacetophenone. The spectra of these species vary with acidity due to equilibrium protonation of the ketone and to other general medium effects.[21,22] However, in all cases, it was possible to observe a sufficient change in the ultraviolet spectrum to follow the rate of hydration spectroscopically.

The kinetics were followed by observing a decrease in absorbance of the acetylenic ketone at a given wavelength as a function of time. The absorbance readings were taken for ten half-lives (99.9% reaction).

The wavelength chosen for the kinetic runs corresponded to the wavelength where the greatest difference in absorbance between the acetylenic ketone and the benzoylacetophenone occurred. In every case, this wavelength was approximately at a λ_{max} for the acetylenic ketone above 280 mμ. Thus, the reaction proceeded with a decrease in absorption. The data were plotted as $\log(A_t - A_\infty)/(A_0 - A_\infty)$ *vs.* time.

Table I contains a summary of the conditions used for studying the rate of hydration of the various compounds.

Table I. Conditions Used for Kinetic Studies

$XC_6H_4C{\equiv}CC{=}OC_6H_4Y$

X	Y	Temp, °C	Acid	λ, mμ	Concn, × 10^5	l^a, cm
(5) *p*-CH_3O	H	24.85	H_2SO_4	340	0.580	10.0
		24.85	D_2SO_4	340	0.580	10.0
		44.65	H_2SO_4	340	5.80	1.0
(4) *p*-CH_3	H	25.00	H_2SO_4	320	6.02	1.0
		25.00	D_2SO_4	320	6.20	1.0
		44.11	H_2SO_4	320	6.02	1.0
(1) H	H	25.00	H_2SO_4	314	5.75	1.0
		25.00	D_2SO_4	314	5.75	1.0
		44.60	H_2SO_4	314	6.80	1.0
(2) H	*p*-CH_3	25.00	H_2SO_4	325	6.34	1.0
(3) H	*p*-NO_2	25.00	H_2SO_4	285	5.32	1.0

[a] l = length of uv cell.

Acid concentrations were determined by duplicate titrations of the kinetic solution with standard sodium hydroxide solutions to the phenolphthalein end point. The value of H_0 for a given acidity was taken from the data of Noyce and Jorgenson for the 5% dioxane–aqueous sulfuric acid system.[5,21]

For the kinetics studied at elevated temperatures, it was assumed that the temperature corrections for H_0 were the same as the corrections for the purely inorganic water–sulfuric acid solutions at the same H_0.[23,24] For kinetic measurements carried out in deuteriosulfuric acid solutions, values of the corresponding acidity function, D_0, were determined in the following fashion. Hogfeldt and Bigeleisen[25] have shown that the indicator acidities in H_2O–H_2SO_4 and D_2O–D_2SO_4 are the same at any given molarity above 0.1 *M*. Comparison on the basis of the mole fraction sulfate in the medium is essentially equivalent.[1,4] Comparisons were therefore made on the basis of the mole fraction of acid in the acid–water mixture which was used to dilute the dioxane. Thus, D_0 is defined for a kinetic solution prepared by diluting 1.25 ml of dioxane to 25 ml with a D_2O–D_2SO_4 mixture containing a mole fraction X_D of acid *as equal to* H_0 for a similar solution prepared by diluting 1.25 ml of dioxane to 25 ml with a H_2O–H_2SO_4 mixture containing a mole fraction X_H of acid if and only if $X_D = X_H$.

Kinetic Data. Least-squares calculation of the observed rate constants were carried out using an IBM 7094 computer at the University of California Computing Center and a nonlinear least-squares program.[26] Correlation of the rates with the acidity function was examined; correlation coefficients "*r*" were greater than 0.997; the standard deviation in log *k* was generally less than 0.03.

Results and Discussion

The conversion of phenylbenzoylacetylene (**1**) to dibenzoylmethane is smoothly and quantitatively accomplished by aqueous sulfuric acid. In 60% sulfuric acid the conversion is fairly slow; in 80% sulfuric acid the conversion is very rapid. Between these two extremes, the rate–acidity profile shows a blend of two different behaviors. At high acidity (above 75% sulfuric acid) the rate appears to be approaching a limiting value; near 60% sulfuric acid the rate is proportional to the acidity of the medium.

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(26) This program was adapted from that of DeTar by Mr. Howell Hammond. We wish to thank Mr. Hammond for his assistance at this point.

Table II. Rate of Hydration of Phenylbenzoylacetylene in Sulfuric Acid

% H_2SO_4	$-H_0$	10^5k_{obsd}, sec^{-1}	10^5k_{cor}, sec^{-1}	$\log k_{cor} + H_0$	A_0[a]	Fraction[b] protonated
			At 25.00°			
59.98	4.65	1.66	1.67	−9.43	1.140	0.01
61.53	4.84	2.42	2.47	−9.45	1.116	0.02
63.73	5.10	4.57	4.76	−9.42	1.115	0.04
65.48	5.35	7.23	7.69	−9.46	1.046	0.06
67.71	5.65	12.4	14.1	−9.50	0.995	0.12
69.40	5.89	18.4	22.7	−9.51	0.944	0.19
71.52	6.18	29.0	42.7	−9.55	0.869	0.32
73.63	6.52	40.8	82.3	−9.60	0.785	0.51
75.51	6.81	53.0	158.0	−9.61	0.750	0.66
77.67	7.16	59.8	332.0	−9.64	0.700	0.82
79.17	7.41	67.7	617.0	−9.62	0.665	0.89
81.04	7.72	75.0	1250.0	−9.62	0.581	0.94
			At 44.60°			
58.00	4.47	11.2	11.3	−8.42		0.01
59.71	4.67	17.4	17.9	−8.42		0.03
61.48	4.89	27.0	28.4	−8.44		0.05
63.55	5.15	44.7	48.5	−8.46		0.08
65.34	5.39	70.9	84.3	−8.46		0.16
67.54	5.69	117.0	154.0	−8.50		0.24

[a] Initial absorbance at 314 mμ of a solution 5.75×10^{-5} M in phenylbenzoylacetylene, extrapolated to zero time. [b] Fraction protonated = $BH^+/(B + BH^+)$.

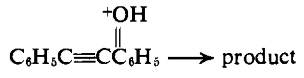
Importantly, it is also observed that the initial spectrum of phenylbenzoylacetylene changes as the acidity is altered. Plotting the initial absorbance at 314 mμ *vs.* H_0 gives a sigmoid titration-like curve, from which the pK_{BH^+} for phenylbenzoylacetylene may be estimated as −6.5.

This then provides an explanation for the curvature in the rate–acidity profile mentioned above.

Table II presents the data obtained for the hydration of phenylbenzoylacetylene. Column 3 gives the observed pseudo-first-order rate as a function of acidity, and column 7 gives the fraction of phenylbenzoylacetylene converted to the oxonium salt at various acidities.

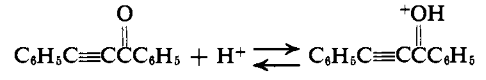
If one now corrects the observed rates for partial conversion to the oxonium salt, the corrected rates, k_{cor}, given in column 4 are obtained. It is to be noted that now $\log k + H_0$ is sensibly constant (as presented in column 5). A plot of the logarithms of the corrected rates *vs.* H_0 is linear with a slope of 0.927 ± 0.01.

Two general mechanistic schemes may be presented, and cannot be distinguished on the basis of this information alone. On the one hand, these features of the data may simply mean that the rate-limiting process involves a further transformation of the oxonium salt of phenylbenzoylacetylene (eq 4). Alternatively the

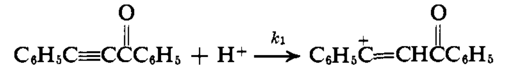


$$C_6H_5C{\equiv}C\overset{{}^{+}OH}{\overset{\|}{C}}C_6H_5 \longrightarrow \text{product} \qquad (4)$$

reaction may involve the rate-limiting reaction of phenylbenzoylacetylene itself with a proton (eq 5 and 6), and oxonium salt formation is simply a diversionary



$$C_6H_5C{\equiv}C\overset{O}{\overset{\|}{C}}C_6H_5 + H^+ \rightleftharpoons C_6H_5C{\equiv}C\overset{{}^{+}OH}{\overset{\|}{C}}C_6H_5 \qquad (5)$$



$$C_6H_5C{\equiv}C\overset{O}{\overset{\|}{C}}C_6H_5 + H^+ \xrightarrow{k_1} C_6H_5\overset{+}{C}{=}CH\overset{O}{\overset{\|}{C}}C_6H_5 \qquad (6)$$

side reaction.

As will be shown in a later section of this discussion, the latter possibility is correct, and the former possibility (eq 4) is inconsistent with other information.

Effect of Substituents on Basicity. In order to examine the effects of substituents on the rate of hydration of substituted phenylbenzoylacetylenes, a selected group of substituted compounds have been examined. In each case, of course, it is necessary to determine the basicity of the acetylenic ketone, and, where necessary, to make the appropriate corrections. It may be noted that as the general reaction scheme emerges, it is also possible to determine the pK_{BH^+} from the variation in rate with acidity as well as from the initial spectrum of the acetylenic ketone in solutions of different acidities. The interrelation between rate and pK has been thoroughly discussed by Long and Paul[27] and need not be repeated here.

In Table III are collected all of the pK's which have been determined either spectrally or kinetically.

Table III. Equilibrium Acidity Constants for Substituted Phenylbenzoylacetylenes

			pK_{BH^+}[a]			
Compd	Temp, °C	Acid	Method A[b]	Method B[c]	Method C[d]	Best value
1	25.00	H_2SO_4	−6.5	−6.45	−6.51	−6.51
	45.00	H_2SO_4		−6.30	−6.20	−6.20
	25.00	D_2SO_4	−6.30		(−5.9)[e]	−6.30
4	25.00	H_2SO_4		−6.20	−6.18	−6.18
	25.00	D_2SO_4	−5.90	−6.00	−6.02	−6.02
2	25.00	H_2SO_4	−6.00		(6.1)[e]	−6.00
3	25.00	H_2SO_4		−7.60	−7.77	−7.77

[a] pK_{BH^+} is more properly the acidity value, H_0 (or D_0), at which the ketone is 50% converted to the oxonium salt. [b] Method A. Determination of pK_{BH^+} from a plot of initial absorbance *vs.* H_0. [c] Method B. Determination of pK_{BH^+} from a plot of $\log k_{obsd}$ *vs.* H_0, and extrapolating the linear portion of such a plot from lower acidities to the acidity at which $k_{extrapolated}/k_{obsd} = 2$. [d] Method C. Fitting of kinetic data to the equation $\log k_{obsd} = \log [K_{BH^+}/(K_{BH^+} + h_0)] + \alpha \log h_0 + \beta$. [e] These values are subject to very large uncertainties due to the specific range of acidity over which rate data were available. The "best values" were accordingly chosen as those determined by method A.

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Table IV. Rates of Hydration of Substituted Phenylbenzoylacetylenes in H_2SO_4

Compd	% H_2SO_4	$-H_0$	10^5k_{obsd}, sec^{-1}	10^5k_{cor}, sec^{-1}	log $k_{cor} + H_0$	A_0[a]	Fraction[b] protonated
At 25.00°							
2	61.48	4.84	3.10	3.29	−9.32	1.160	0.06
	63.69	5.11	4.96	5.57	−9.36	1.190	0.11
	65.61	5.36	7.39	9.12	−9.40	1.180	0.19
	67.61	5.63	10.1	14.4	−9.47	1.070	0.30
	69.33	5.87	13.5	23.7	−9.50	0.980	0.43
	71.37	6.16	15.7	38.3	−9.58	0.890	0.59
	73.10	6.42	19.5	72.2	−9.56	0.810	0.73
	75.25	6.76	23.1	151.0	−9.57	0.730	0.85
	77.08	7.06	22.5	282.0	−9.61	0.710	0.92
3	65.60	5.36	4.42	4.42	−9.71		0.00
	67.52	5.61	7.93	7.93	−9.71		0.00
	69.22	5.86	13.8	13.9	−9.72		0.01
	71.32	6.15	24.8	25.3	−9.75		0.02
	73.31	6.45	47.0	49.4	−9.76		0.05
	75.48	6.79	87.8	95.5	−9.80		0.10
	77.02	7.05	159.0	189.0	−9.77		0.16
	78.85	7.38	258.0	423.0	−9.75		0.39
4	51.63	3.73	3.65	3.65	−8.17		0.00
	53.80	3.97	4.83	4.83	−8.08		0.00
	56.13	4.22	13.8	13.9	−8.08		0.01
	58.00	4.43	22.2	22.4	−8.08		0.02
	59.80	4.63	34.0	35.1	−8.09		0.03
	61.45	4.83	50.8	52.9	−8.11		0.04
	63.11	5.11	93.8	102.0	−8.10		0.08
	65.66	5.39	148.0	172.0	−8.15		0.14
	67.56	5.63	240.0	308.0	−8.14		0.22
	69.34	5.88	351.0	532.0	−8.15		0.34
	71.42	6.17	487.0	955.0	−8.19		0.49
	73.51	6.50	636.0	1930.0	−8.22		0.67
	73.57	6.50	652.0	1970.0	−8.21		0.67
	75.50	6.81	828.0	4360.0	−8.17		0.81
	77.49	7.13	1120.0	11290.0	−8.08		0.90
5[c]	26.78	1.37	2.24	2.24	−6.02		0.00
	30.54	1.63	4.25	4.25	−6.00		
	34.37	1.92	7.81	7.81	−6.03		
	38.55	2.27	17.7	17.7	−6.02		
	43.80	2.79	55.8	55.8	−6.04		<0.01
At Elevated Temperatures[d]							
5[e]	21.68	1.08	7.91		−5.18		
	27.04	1.40	17.8		−5.15		
	30.66	1.65	32.0		−5.14		
	34.52	1.97	64.3		−5.16		
	37.34	2.16	105.0		−5.14		
4[f]	42.57	2.67	3.38		−7.14		
	47.67	3.26	9.41		−7.29		
	49.71	3.48	16.7		−7.26		
	53.92	3.95	41.8		−7.33		
	56.18	4.25	73.0		−7.39		

[a] Initial absorbance. [b] Fraction protonated = $BH^+/(B + BH^+)$. [c] T = 24.85°. [d] H_0 corrected for temperature. [e] At 44.65°. [f] At 44.11°.

The data on the basicity of ketones **1** and **4** show that the effect of substituents in the phenyl ring is much as expected. The transmission of the influence of the substituent through the acetylenic group appears to be somewhat less effective than through the olefinic moiety. For the acetylenic ketones, ρ is about 1.0, whereas, for substituted chalcones,[28] ρ is 1.26.

The basicity of the acetylenic ketones is more sharply affected by substituents in the benzoyl ring. From compounds **1**, **2**, and **3**, ρ is about 1.7. This is very similar to the effect of substituents on the basicity of benzophenones,[29] though the correlation for benzophenones is not of particularly high quality, as discussed by Stewart, *et al.*[30] Placing the p*K*'s of benzophenones on the Jorgenson and Hartter H_0 scale,[31] ρ is 1.6. The related series of acetophenones[32] and of benzaldehydes[33] give substantially larger ρ values.[34] These relative ρ values are consistent with the interpretation that the presence of a group in the side chain which can conjugate with the carbonyl group contributes to the stability of the protonated species, decreasing the effect of substituents in the neighboring phenyl ring.

Relative Reactivity. For the substituted compounds, the measured rates of hydration are presented in Table IV. It is to be noted that the reaction rate is extremely

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Table V. Rates of Hydration of Phenylbenzoylacetylenes in Deuteriosulfuric Acid at 25.00°

Compd	Wt % D_2SO_4	$-D_0$[a]	10^5k_{obsd}, sec^{-1}	10^5k_{cor}, sec^{-1}	$\log k + D_0$	A_0[b]	Fraction[c] protonated
1	64.16	5.46	4.06	4.67	−9.79	1.070	0.13
	65.82	5.68	5.56	6.86	−9.84	1.069	0.19
	65.83[d]	5.68	5.96	7.42	−9.81		0.19
	70.15[d]	6.30	11.9	23.8	−9.92		0.50
	70.55	6.35	11.6	24.7	−9.96	0.860	0.53
	72.10	6.59	13.9	40.9	−9.98	0.845	0.66
	74.64	6.97	16.9	93.9	−10.00	0.758	0.82
	77.83	7.48	18.4	307.0	−9.99	0.725	0.94
	77.91	7.50	17.8	297.0	−10.03	0.694	0.95
4	52.84	4.12	4.56	4.61	−8.46	1.030	0.01
	56.72	4.56	11.5	11.9	−8.48	0.985	0.03
	60.20	4.97	25.4	27.6	−8.53	0.970	0.08
	66.30	5.75	87.1	134.0	−8.62	0.826	0.35
	69.96	6.27	146.0	406.5	−8.65	0.720	0.64
	73.82	6.84	169.0	1300.0	−8.73	0.600	0.87
5[e]	34.20	2.08	4.50	4.50	−6.43		
	37.47	2.40	10.1	10.1	−6.40		
	41.07	2.75	23.2	23.2	−6.38		
	42.79	2.96	33.6	33.6	−6.44		
	44.05	3.08	42.8	42.8	−6.46		
	46.73	3.38	77.9	77.9	−6.47		<0.01

[a] For definition see Experimental Section. [b] Initial absorbance extrapolated to time 0. [c] $BH^+/(B + BH^+)$. [d] Kinetics followed at 330 mμ. [e] $T = 24.85°$.

sensitive to the effect of substituents in the phenyl ring. This observation first of all serves to support the conclusion that the reaction path does not proceed from the oxonium salt. Were this the case, reaction rates compared in 60% sulfuric acid would be expected to show a direct one-to-one relationship to the relative basicities of ketones **1** and **4**. This is not observed. Further, the sensitivity to the effect of substituents serves to support the critical role of a step like eq 6 in the reaction pathway. The generation of a positive charge at the benzylic position would be expected to respond sharply to the electron-donating ability of substituents in the phenyl ring, as observed. This conclusion is, of course, entirely analogous to that drawn earlier in studies from these laboratories on the hydration of phenylpropiolic acids.[1] Comparing rates at $H_0 = -4.00$ for **1**, **4**, and **5** (conditions under which none are appreciably protonated) and extrapolating to this acidity as necessary give a ρ for this set of substituents of -4.21. This may be compared with the ρ of -4.77 observed for the hydration of substituted phenylpropiolic acids.

Quite in contrast, the hydration rate is relatively insensitive to the electronic nature of the substituent in the benzoyl ring. The rate difference between **2** and **3** is only a factor of 2 (compare rates in 65.6% acid).

Solvent Isotope Effects. As more definitive support for the conclusion that the rate-limiting step for the hydration of phenylbenzoylacetylene involves a proton transfer to carbon from the acidic medium, we have measured the solvent isotope effect on the rate. The rate data are presented in Table V and are compared in Table VI.

The rate of hydration of phenylbenzoylacetylene is less in deuteriosulfuric acid media. In 60% sulfuric acid, where **1** is almost completely unprotonated, k_{H_2O}/k_{D_2O} may be estimated as 1.95, by a short extrapolation of the data in D_2SO_4. As an interesting sidelight, the measured basicity of phenylbenzoylacetylene is greater in the deuterated medium (*cf.* Table III). This information provides a useful extension of the studies summarized by Hogfeldt and Bigeleisen[25] on the basicities of a variety of functional classes in deuterated media.

Table VI. Solvent Isotope Effect on Observed Rate of Hydration[a]

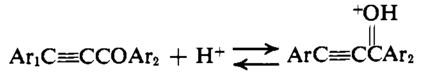
Compd	N_{SO_4}	$-H_0$	$10^5k_{obsd}^{H_2O}$	$10^5k_{obsd}^{D_2O}$	k_H/k_D
1	0.3133	5.5	9.34	4.27	2.18
	0.3516	6.0	21.9	8.13	2.69
	0.3875	6.5	39.8	13.2	3.02
	0.4551	7.0	57.2	17.0	3.31
	0.4827	7.5	67.6	17.8	3.80
4	0.2076	4.0	8.52	3.55	2.40
	0.2401	4.5	25.7	10.0	2.57
	0.2758	5.0	72.5	26.3	2.78
	0.3133	5.5	182.0	60.3	3.02
	0.3516	6.0	407.0	115.0	3.55
	0.3875	6.5	631.0	162.0	3.89
5	0.1063	2.0	9.55	3.98	2.40
	0.1317	2.5	29.5	12.0	2.46
	0.1557	3.0	91.3	36.3	2.51

[a] Interpolated from Tables II, IV, and V.

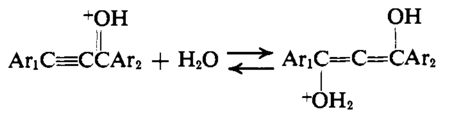
These two factors combine to give an observed rate of hydration of phenylbenzoylacetylene in 80% sulfuric acid which is now fourfold smaller in the corresponding deuterated sulfuric acid medium.

These data serve to establish without question that the rate-limiting step involves proton transfer to carbon. Equation 6 represents such a step. However, one further reaction sequence may be written for which there is also a rate-determining proton transfer, but in the later stages of the over-all process.

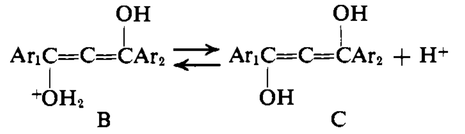
The Possibility of an Allenediol Intermediate. A reaction scheme such as that presented in eq 7–10

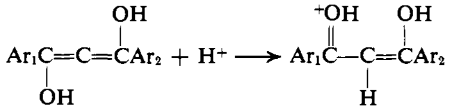


$$Ar_1C{\equiv}CCOAr_2 + H^+ \rightleftarrows ArC{\equiv}C\overset{\overset{+}{O}H}{\overset{\|}{C}}Ar_2 \qquad (7)$$



$$Ar_1C{\equiv}C\overset{\overset{+}{O}H}{\overset{\|}{C}}Ar_2 + H_2O \rightleftarrows Ar_1\underset{\underset{+OH_2}{|}}{C}{=}C{=}\overset{OH}{\overset{|}{C}}Ar_2 \qquad (8)$$


$$\underset{B}{\underset{\substack{|\\ {}^{+}OH_2}}{Ar_1C}{=}C{=}\overset{\substack{OH\\|}}{C}Ar_2} \rightleftharpoons \underset{C}{\underset{\substack{|\\ OH}}{Ar_1C}{=}C{=}\overset{\substack{OH\\|}}{C}Ar_2} + H^+ \qquad (9)$$


$$\underset{\substack{|\\ OH}}{Ar_1C}{=}C{=}\overset{\substack{OH\\|}}{C}Ar_2 + H^+ \longrightarrow Ar_1\overset{\substack{{}^{+}OH\\ \|}}{C}{-}\underset{\substack{|\\ H}}{C}{=}\overset{\substack{OH\\|}}{C}Ar_2 \qquad (10)$$

represents a possible reaction path which must be considered.

If now eq 10 represents the rate-limiting process, a solvent isotope effect of the magnitude observed would be expected with the following restrictions. Equations 7, 8, and 9 must be rapid and reversible in order to give the observed solvent isotope effect. Furthermore, there can be no substantial accumulation of either of the intermediate species represented in eq 9 in order that the excellent pseudo-first-order kinetics observed would be obtained.

The postulation of an allenediol (C) as an intermediate in the sequence finds analogy in the studies we have carried out on chalcones[5] and the studies of the hydration of mesityl oxide by Bell, Preston, and Whitney.[7] The related allenetriol was considered as an intermediate in the hydration of phenylpropiolic acid,[1] but discarded as unlikely. Similar arguments can be presented to render C as unlikely intermediate. In the present instance a further and much more definitive argument may be presented regarding C.

As indicated above, the steps leading to C must be reversible and C must be present at only low concentration levels in order for the observed kinetic behavior to be obtained. This then means that two different unsymmetrical acetylenic ketones such as **2** and **4** must rapidly interconvert in sulfuric acid and then give the same rate of formation of *p*-methylbenzoylacetophenone, *or* that one or the other of the ketones, **2** or **4**, would not exhibit simple first-order behavior. Neither of these required phenomena is observed. Hence, the possibility of the allenediol as an intermediate can be definitely excluded, and eq 6 therefore represents the rate-limiting process.

Two additional features of the data should be mentioned which are in complete accord with this conclusion. The activated complex for eq 10 contains an additional molecule of water, and in the very high sulfuric acid region, one would therefore be led to anticipate a decreased rate of reaction (as the activity of water in the medium drops). This is not observed. Finally, the sensitivity of the measured rates of substituents is not that to be expected for eq 10.

Activation Parameters. The rate data at 45° allow the determination of the energy of activation for the reaction. From the rate data at relatively low acidities the energies of activation given in Table VII can be calculated. Extrapolated rates at $H_0 = 0$ allow calculation of $\Delta S^{\ddagger}$.

Table VII. Activation Parameters for the Hydration of Phenylacetylenes

Compd	Δ log k_{obsd}	E_a, kcal	$\Delta H^{\ddagger}$	k_0,[d] sec^{-1}	$\Delta S^{\ddagger}$
1	1.00[a]	22.1	21.5	8.13×10^{-10}	−28.0
4	0.81[b]	18.4	17.7	1.35×10^{-8}	−35.0
5	0.82[c]	18.1	17.5	1.05×10^{-6}	−27.3

[a] At $H_0 = -5.00$. [b] At $H_0 = -3.00$. [c] At $H_0 = -1.00$. [d] Extrapolated rate at $H_0 = 0$ at 25°.

The very negative entropy of activation falls in line with the value observed for other rate-limiting transfers as recently correlated by Matesich.[35]

Comparison of Acetylenic Ketones and α,β-Unsaturated Ketones. The hydration of phenylbenzoylacetylene shows several marked differences from the hydration of α,β-unsaturated ketones. The hydration of mesityl oxide[7] is much more facile than the hydration of the analogous acid, dimethylacrylic acid.[36] The rate of hydration of phenylbenzoylacetylene, however, is of the same magnitude as the hydration of phenylpropiolic acid. Furthermore, the rate profiles *vs.* H_0 for these classes of compounds show interesting differences, which are smoothly accommodated by the mechanisms deduced.

These comparisons serve to show that the vinylic cation is an intermediate readily accessible from acetylenic systems.

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