57. *Substituent Effects in the Acid-catalysed Hydration of Phenylacetylenes.*

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The relative rates, $k_{\text{rel.}}$, of hydration of $X{\cdot}C_6H_4{\cdot}C{\equiv}CH$ compounds by a mixture of acetic acid (2 vol.) and 1—11M-aqueous sulphuric acid (1 vol.) have been measured. For *meta*- and *para*-substituents the rates fit a Yukawa–Tsuno relation, *viz.*, $\log k_{\text{rel.}} = -4{\cdot}3\ [\sigma + 0{\cdot}81(\sigma^+ - \sigma)]$. Low rates for *ortho*-substituted compounds are believed to originate in steric hindrance to solvation.

WE recently described the effects of substituents, X, on the rates of cleavage of phenylethynyltriethylgermanes, $X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}GeEt_3$, by aqueous methanolic perchloric acid.[1] We have now obtained similar information for a closely related reaction, hydration of phenylacetylenes, $X{\cdot}C_6H_4{\cdot}C{\equiv}CH$, in a mixture of acetic acid and aqueous sulphuric acid at 50·2°. Rates were determined spectrophotometrically, and the results are shown in Table 1 as first-order rate constants, k, at the sulphuric acid concentration specified, and as rates, $k_{\text{rel.}}$, relative to that of the parent compound, phenylacetylene, calculated on the assumption that relative rates are independent of the acid concentration, which can be seen to be true at least for fairly small changes in the concentration.

TABLE 1.

Hydration of substituted phenylacetylenes in acetic acid–water–sulphuric acid at 50·2°.

Subst.	$[H_2SO_4]$ (M) *	10^3k (min.$^{-1}$)	$k_{\text{rel.}}$	Subst.	$[H_2SO_4]$ (M) *	10^3k (min.$^{-1}$)	$k_{\text{rel.}}$
p-MeO	1·25	199	950	*m*-MeO	9·60	105	0·52
2,4,6-Me$_3$	1·25	65·7	—	*o*-MeO	9·60	104	0·52
	2·53	220	310	*p*-Cl	8·46	24·0	0·28
p-Me	2·53	10·9	—		9·60	56·2	0·28
	5·68	123	15·5	*p*-I	9·60	47·6	0·24
	6·05	190	15·6	*p*-Br	9·60	43·6	0·22
2,3-Me$_2$	6·05	146	12·0	*o*-F	9·60	11·9	0·059
p-Bu^t	6·05	128	10·5	*o*-I	9·60	11·3	0·056
o-Me	6·05	60·8	5·0	*o*-Cl	9·60	7·55	0·038
m-Me	6·05	23·3	1·91	*o*-Br	9·60	6·92	0·034
	7·10	55·4	1·92		10·9	20·7	—
	8·46	161	1·89	*m*-Cl	10·9	12·4	0·021
p-F	6·05	17·8	1·46	*m*-Br	10·9	11·0	0·018
H	5·68	7·94	1·00	*m*-CF$_3$	10·9	2·83	0·0047
	6·05	12·2	1·00				
	7·10	28·8	1·00				
	8·46	85	1·00				
	9·60	201	1·00				

* Concn. of aqueous acid, 1 vol. of which was added to 2 vol. of acetic acid.

We also submitted 1-tritio-2-phenylacetylene to hydration under conditions similar to those used for the rate studies, and after about 50% of the reaction had occurred we recovered the unchanged phenylacetylene and found that it had not lost any of its tritium.

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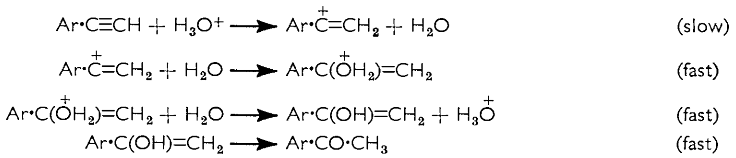
[1] Bott, Eaborn, and Walton, *J. Organometallic. Chem.*, 1964, **1**, 420.

The mechanism of the hydration is thus the same as that established for hydration of alkynylalkyl ethers and sulphides in aqueous acids,[2] a rate-determining proton transfer being followed by a rapid reaction of the formed carbonium ion with the solvent to give a hydroxy-ethene which rapidly rearranges to a ketone:



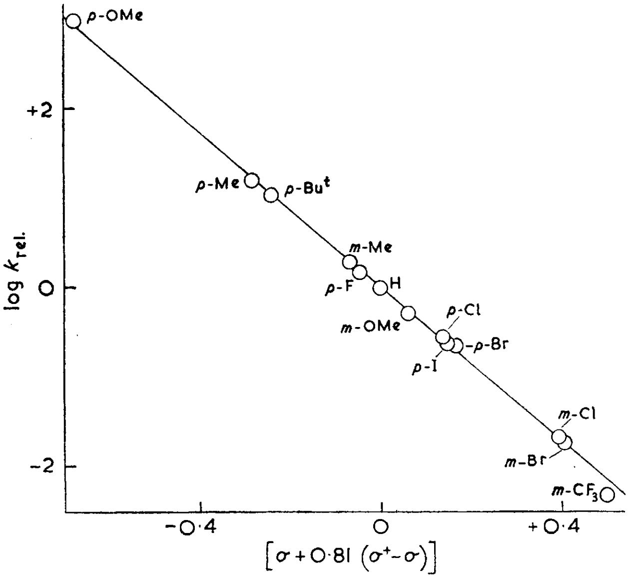
$$\mathrm{Ar{\cdot}C{\equiv}CH + H_3O^+ \longrightarrow Ar{\cdot}\overset{+}{C}{=}CH_2 + H_2O} \qquad \text{(slow)}$$

$$\mathrm{Ar{\cdot}\overset{+}{C}{=}CH_2 + H_2O \longrightarrow Ar{\cdot}C(\overset{+}{O}H_2){=}CH_2} \qquad \text{(fast)}$$

$$\mathrm{Ar{\cdot}C(\overset{+}{O}H_2){=}CH_2 + H_2O \longrightarrow Ar{\cdot}C(OH){=}CH_2 + H_3\overset{+}{O}} \qquad \text{(fast)}$$

$$\mathrm{Ar{\cdot}C(OH){=}CH_2 \longrightarrow Ar{\cdot}CO{\cdot}CH_3} \qquad \text{(fast)}$$

The effects of substituents on the rate of the reaction are thus their effects on the rate of formation of the carbonium ion (I), and the influence of *m*- and *p*-substituents might be expected to correlate with their electrophilic σ^+-constants.[3] A plot of log $k_{\text{rel.}}$ against σ^+ is, in fact, reasonably linear, but a better plot is obtained (see Figure) by use of the Yukawa-Tsuno relation, log $k_{\text{rel.}} = \rho[\sigma + r(\sigma^+ - \sigma)]$, with $\rho = -4{\cdot}3$ [derived from the line through the points for (X =) *m*-Me, H, *m*-Cl, and *m*-Br (cf. ref. 1)] and $r = 0{\cdot}81$. Table 2 lists calculated values of *r*, corresponding with $\rho = -4{\cdot}3$, for each substituent, and reveals that there is not a large spread of values; the mean value of *r* for the *para*-substituents is 0·81.



Plot of log $k_{\text{rel.}}$ against $[\sigma + 0{\cdot}81\ (\sigma^+ - \sigma)]$.

TABLE 2.

Values of *r* for *p*-X·C_6H_4·C≡CH compounds.

X	OMe	Me	Bu^t	F	Cl	Br	I
r	0·83	0·76	0·68	0·74	0·87	0·96	0·82

The Yukawa-Tsuno relation applies also to the cleavage of X·C_6H_4·C≡C·GeEt$_3$ compounds, with $\rho = -3{\cdot}3$, and a mean value for *r* of 0·46. (In a diagram in ref. 1, a value of 0·64 was used for *r*, for reasons stated; the values of *r* calculated for each substituent

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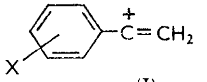
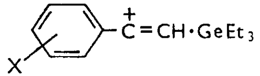
[2] Jacobs and Searles, *J. Amer. Chem. Soc.*, 1944, **66**, 686; Drenth and Hogeveen, *Rec. Trav. chim.*, 1960, **79**, 1002; Hogeveen and Drenth, *ibid.*, 1963, **82**, 375, 410, and references therein.

[3] (*a*) Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913; 1958, **80**, 4979; (*b*) Okamoto and Brown, *ibid.*, 1957, **79**, 1909; (*c*) Brown, Okamoto, and Ham, *ibid.*, 1957, **79**, 1906.

separately show a spread, but for all the *para*-substituents are smaller than in the hydration.) In closely related reactions, it is common for a smaller value of r to be associated with a smaller value of ρ.[4] The smaller value of ρ in the cleavage can be attributed to stabilization


(I)


(II)

of the carbonium ion (II) by electron-release from the triethylgermyl group; this causes the transition state for the formation of the ion to be less removed from the initial state than is the case in hydration, so that in the transition state less charge is present on the carbon atom next to the ring.

As in the cleavage of the $X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}GeEt_3$ compounds, *ortho*-substituted compounds are markedly less reactive than would be expected by comparison with their *meta*- and *para*-isomers. The most obvious example of this is the *o*-methoxy-compound, which is *less* reactive than the unsubstituted compound although its *para*-isomer is almost 1000 times more reactive than the latter. These *ortho*-effects are presumably associated with steric hindrance to solvation of the carbonium ion centres in the ions (I) and (II). Similar, though smaller, *ortho*-effects occur in solvolysis of $X{\cdot}C_6H_4{\cdot}CMe_2Cl$ compounds in 90% aqueous-acetone,[3] in which the rate-determining step also involves formation of a carbonium ion centre adjacent to the ring; for example, although the *o*-methoxy-compound is more reactive than the unsubstituted compound by a factor of 105, it is much less reactive than its *para*-isomer, which is 3360 times more reactive than the unsubstituted compound,[3b] while the *o*-chloro-compound is less reactive than its *meta*-isomer,[3c] contrary to what would be expected from electronic effects alone. The carbonium ion centre in each of the ions (I) and (II) is probably more exposed to solvent molecules than is that in the ion $Ph{\cdot}CMe_2^+$, and thus solvation is likely to play an even bigger part with the ions derived from the acetylenes, and steric hindrance to such solvation will hence have a larger effect. It is noteworthy that there are no such *ortho*-effects in the gas-phase thermal decomposition of 1-phenylethyl acetates in which solvent effects are absent.[5] (In this reaction a partial positive charge is present next to the ring in the transition state, and substituent effects fit the Yukawa-Tsuno relation, with a value of r similar to that in the hydration.) For example,[5b] the *o*-methoxy-group activates 1·82 times compared with the *p*-methoxy-group's 3·16 times, and the *o*-methyl group activates slightly more than the *p*-methyl group. It is also noteworthy that electrostatic interactions between the *ortho*-substituents and the carbonium ion centre seem not to be very important in the hydration, since such effects would lead to an enhanced reactivity with the *o*-halogeno-compounds.

For 2,3-dimethyl- and 2,4,6-trimethyl-phenylacetylene, the observed rates are not very different from those calculated by assuming additivity of effects of the separate methyl groups; for the 2,3-Me_2- and 2,4,6-Me_3-compounds, $k_{obs.}/k_{calc.} = 1{\cdot}3$ and 0·79, respectively. The latter figure is in contrast with the puzzlingly high value for $k_{obs.}/k_{calc.}$ of 1·7 in cleavage of the compound 2,4,6-$Me_3{\cdot}C_6H_2{\cdot}C{\equiv}C{\cdot}GeEt_3$.[1]

Products of Hydration.—It has long been known that only moderate yields of ketones can be obtained from mineral-acid catalysed hydration of acetylenes on a preparative scale,[6] and in several experiments with phenylacetylene we were unable to isolate acetophenone in more than 64% yield. However, careful examination of the ultraviolet spectrum of the products from hydration under the conditions used for the rate measurements showed that acetophenone had been formed quantitatively. It is likely that polymerization occurs at the higher concentrations used for preparative work, presumably by attack of a carbonium ion of type (I) on another acetylene molecule.

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[4] Norman and Radda, *Tetrahedron Letters*, 1962, 125; Bott and Eaborn, *J.*, 1963, 2139.

[5] (*a*) Taylor and Smith, *Tetrahedron*, 1963, **19**, 937; (*b*) Taylor, Smith, and Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

[6] Michael, *Ber.*, 1906, **39**, 2143; Grignard and Perrichon, *Ann. Chim.* (*France*), 1926, **5**, 5.

A Note on the Ease of Electrophilic Substitution at Aromatic and Phenylacetylenic Carbon Atoms.—Because hydration of acetylenes is faster than hydrogen-exchange, the latter reaction cannot be used to give a measure of the relative ease of electrophilic substitution at aromatic and acetylenic carbon atoms, and the ease of addition to the triple bond prevents such a comparison being made directly with most electrophilic reagents. However, from the rates of cleavage of the C–Ge bonds in $X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}GeEt_3$ and $X{\cdot}C_6H_4{\cdot}GeEt_3$ compounds[7] it can be deduced that the electrophilic substitution occurs some 3500 times as readily at the β-acetylenic carbon atom of phenylacetylene as at a carbon atom of benzene.

EXPERIMENTAL

Preparation of Arylacetylenes.—o-*Methoxyphenylacetylene.* *o*-Hydroxyphenylacetylene (8·7 g.),[8] was refluxed with dimethyl sulphate (9·4 g.), water (30 ml.), and potassium hydroxide (4·3 g.) for 2 hr., and the mixture was then added to water. Ether extraction, followed by washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave *o*-methoxyphenylacetylene (8·1 g., 84%), b. p. 93°/11 mm., n_D^{25} 1·5660 (lit.,[9] b. p. 92°/13 mm.).

p-*Methoxyphenylacetylene.* Ethyl *p*-hydroxycinnamate was treated with bromine in carbon tetrachloride to give the dibromo-derivative, which was treated with ethanolic potassium hydroxide to give *p*-methoxyphenylpropiolic acid.[10] Steam-distillation of the copper salt of this acid in presence of sodium carbonate gave *p*-methoxyphenylacetylene, which was extracted with ether; the ethereal solution was washed, dried (Na_2SO_4), and fractionated to give material of b. p. 90°/10 mm., m. p. 29° (lit.,[9] b. p. 86°/9 mm., m. p. 29°).

Other arylacetylenes. Other arylacetylenes were made by the conventional route, involving dehydrochlorination of the mixture of chlorostyrenes obtained from the appropriate ketone and phosphorus pentachloride. Potassium hydroxide in refluxing ethanol was used for the dehydrochlorination, except for the mesityl compound, for which sodamide in liquid ammonia was used.[11] The acetylenes so made, and also commercially available phenylacetylene, were purified through their silver derivatives.[12]

The following new $R{\cdot}C{\equiv}C{\cdot}H$ *compounds* were obtained: (R =) *p*-$Bu^t{\cdot}C_6H_4$, b. p. 67°/1·7 mm., n_D^{25} 1·5286 (Found: C, 90·8; H, 8·8. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%); *o*-$I{\cdot}C_6H_4$, b. p. 75°/1·0 mm., n_D^{25} 1·6362 (Found: C, 42·7; H, 2·5. C_8H_5I requires C, 42·2; H, 2·2%); *p*-$I{\cdot}C_6H_4$, m. p. 70·5° (Found: C, 42·3; H, 2·2%); 2,3-$Me_2{\cdot}C_6H_3$, b. p. 69°/8·5 mm., n_D^{25} 1·5284 (Found: C, 92·1; H, 7·6. $C_{10}H_{10}$ requires C, 92·2; H, 7·8%).

Mesitylacetylene had b. p. 97°/14 mm., n_D^{25} 1·5440, and the other previously reported $X{\cdot}C_6H_4{\cdot}C{\equiv}CH$ compounds[9,13] had the following properties: (X =) H, b. p. 144°/760 mm., n_D^{25} 1·5472; *o*-Me, b. p. 59°/16 mm., n_D^{25} 1·5444; *m*-Me, b. p. 60°/16 mm., n_D^{20} 1·5405; *p*-Me, b. p. 60°/16 mm., n_D^{25} 1·5450; *m*-OMe, b. p. 84°/12 mm., n_D^{25} 1·5560; *o*-Br, b. p. 92°/16 mm., n_D^{25} 1·5898; *m*-Br, b. p. 89°/15 mm., n_D^{25} 1·5963; *p*-Br, m. p. 64—64·5°; *o*-Cl, b. p. 76°/19 mm., n_D^{25} 1·5686; *m*-Cl, b. p. 71°/15 mm., n_D^{25} 1·5610; *p*-Cl, b. p. 68°/15 mm., m. p. 43·5—44°; *o*-F, b. p. 60°/32 mm., n_D^{25} 1·5200; *p*-F, b. p. 73°/19 mm., m. p. 26—27°; *m*-CF_3, b. p. 53°/26 mm., n_D^{25} 1·4628.

Hydration Products.—A mixture of phenylacetylene (18 g.), glacial acetic acid (250 ml.), and 6M-sulphuric acid (125 ml.), was kept at 50° for 10 hr., with occasional shaking, during which time it went bright yellow. It was then diluted with water and neutralized with sodium carbonate. Ether extraction, followed by washing (saturated NaCl), drying (Na_2SO_4), and fractionation of the extract gave acetophenone (14·3 g., 64%), b. p. 202°, n_D^{25} 1·5312. A syrupy residue (6 g.) remained in the still pot.

For all the acetylenes under the conditions of the kinetic studies (see below), the ultraviolet spectra at the end of the runs were identical in shape with those of the expected ketones. With phenylacetylene, the spectrum agreed quantitatively (to within ±1% in optical density) with

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[7] Eaborn and Pande, *J.*, 1961, 297.
[8] Prey and Pieh, *Monatsh.*, 1949, **80**, 790.
[9] Cook and Danyluk, *Tetrahedron*, 1963, **19**, 177.
[10] Abbott, *Org. Synth.*, Coll. Vol. II, 515.
[11] Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120.
[12] Jacobs, *Org. Reactions*, 1949, **5**, 1.
[13] Otto, *J. Amer. Chem. Soc.*, 1934, **56**, 1393; Solomon and Filler, *ibid.*, 1963, **85**, 3492.

that determined for a solution of acetophenone of appropriate concentration in the reaction medium.

Rate Measurements.—A solution (2 vol.) of the arylacetylene in glacial acid, of concn. C, shown in Table 3, was mixed with aqueous sulphuric acid (1 vol.) of concn. shown in Table 1, and a sample was transferred to a 1 cm. stoppered quartz cell which was placed in a thermostatted holder at 50·2 ± 0·03° in a Unicam S.P. 500 Spectrophotometer. After about 8 min., optical densities, D_t, were recorded at suitable times, t, at a wave-length, λ (Table 3), pre-determined after comparison of the spectra of the acetylene and the expected ketone. First-order rate constants were determined graphically by use of the equation $kt = \ln [(D_\infty - D_0)/(D_\infty - D_t)]$, where D_0 is the optical density at the (arbitrary) zero time and D_∞ that after 10 half-lives.

In the following typical runs, rate constants are calculated for individual points. Concentrations shown are those of solutions before mixing.

(i) [$C_6H_5\cdot C\equiv CH$], 6·1 × 10^{-4}M; [H_2SO_4], 6·05M; λ, 273 mμ.

t (min.)	0	10	30	50	70	90	100	∞
10^3D	194	246	333	401	454	499	512	648
10^3k (min.$^{-1}$)	—	12·2	12·2	12·2	12·1	12·2	11·8	—

(ii) [p-$Bu^t\cdot C_6H_4\cdot C\equiv CH$], 1·7 × 10^{-4}M; [H_2SO_4], 6·05M; λ, 279 mμ.

t (min.)	0	1	2	3	4	5	6	7	∞
10^3D	253	285	314	340	361	382	401	414	527
10^3k (min.$^{-1}$)	—	125	127	127	128	128	130	127	—

(iii) [m-$Br\cdot C_6H_4\cdot C\equiv CH$], 5·3 × 10^{-4}M; [H_2SO_4], 10·9M; λ, 286 mμ.

Time (min.)	0	24	50	73	80	107	121	140	∞
10^3D	306	422	521	586	604	655	678	703	812
10^3k (min.$^{-1}$)	—	10·8	11·1	11·0	11·1	10·9	11·0	11·0	—

Rate constants could be duplicated to within ±1·5%.

TABLE 3.

Concentration of $X\cdot C_6H_4\cdot C\equiv CH$, and wavelength used.*

X	10^4C (M)	λ (mμ)	X	10^4C (M)	λ (mμ)	X	10^4C (M)	λ (mμ)
p-OMe	1·5	290	H	6	273	o-I	6	292
p-Me	8	281	o-F	11	291	p-Cl	3	281·5
m-Fe	5	283	m-OMe	3	310	p-Br	2	282
p-Bu^t	1·5	279	o-OMe	11	310	p-I	1·2	278
o-Me	11	283·5	o-Cl	3	287·5	m-Br	5	286
p-F	8	281	o-Br	8	287·5	m-Cl	5	287·5
						m-CF_3	11	282

* For 2,3-$Me_2\cdot C_6H_3\cdot C\equiv CH$, C = 9M, λ = 285·5; for 2,4,6-$Me_3\cdot C_6H_2\cdot C\equiv CH$, C = 11M, λ = 272.

Hydration of 1-*phenyl*-2-*tritioacetylene.*—A mixture of 6M-sulphuric acid (100 ml.) and ice-cold glacial acetic acid (200 ml.) containing 1-phenyl-2-tritioacetylene (16·0 g.) was kept at 50 ± 0·1° for 1 hr. (approx. one half-life), then cooled and poured on to crushed ice. The mixture was neutralized with sodium hydrogen carbonate, and ether extraction, followed by washing, drying (Na_2SO_4), and fractionation of the extract gave recovered phenyltritioacetylene, b. p. 143°, n_D^{25} 1·5470 (5·2 g.). By liquid scintillation counting the relative activities of the starting and recovered tritiophenylacetylenes were shown to be 100/98 ± 2.

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