Ionization Constants of 3-Substituted Propiolic Acids in Water

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The pK_a of ten 3-substituted propiolic acids $XC{\equiv}CCO_2H$ with X = OPh, Me, Ph, $SiMe_3$, SPh, H, I, Cl, Br, and CO_2Et have been measured at 25 °C in water by a conductance method. The effect of substituents has been compared in the propiolic, acrylic, and benzoic series by means of linear free energy relationships. It is found that the Hammett and the DSP equations are less precisely obeyed in the propiolic series. Significant deviations occur for hydrogen and iodine which confirm the positive character of these groups when bound to an ethynyl group.

PREVIOUS experimental determinations of ionization constants for 3-substituted propiolic acids $XC{\equiv}CCO_2H$ are rare. These have dealt only with the unsubstituted compound,[1] with alkyl,[1-5] vinyl,[1] ethynyl,[1] and phenyl [1,2] substituents, and with acetylenedicarboxylic acid in water.†,[11,12] A preliminary study [13] in our laboratory has also reported data for bromo- and chloro-propiolic acids. More generally the lack of data for substituted ethynyl compounds has already been mentioned in a review of substituent effect in nonaromatic unsaturated systems.[14]

Since the equilibria of ionization processes still represent the most important experimental basis for evaluating substituent effects, we decided to measure new ionization constants for 3-substituted propiolic acids in water as part of a study on the effects of substituents in acetylene systems.

A correlation analysis of the data is reported. It shows that substituents may act quite differently according to whether they are linked to an *sp* or an sp^2 hybridized carbon atom.

EXPERIMENTAL AND RESULTS

Methods.—The ionization constants were determined at 25 °C by conductance measurements on aqueous solutions of the acid only, according to the method of Ives.[15,16] Calculations of thermodynamic ionization constants K_a and of limiting equivalent conductances Λ_o were carried out using equation (1), a linear equation of the form $y = \Lambda_o - x/K_a$, where a is the limiting Onsager slope, A the Debye–Hückel coefficient, and the other symbols have the following significance: C = molar concentration of acid, $C_i{=}\alpha C$ = ionic concentration, $\alpha{=}\Lambda/\Lambda_i$ = degree of ionization, Λ = equivalent conductance of acid at concentration C, Λ_i = equivalent conductance of a hypothetical fully ionized solution of acid at a concentration αC.

$$\Lambda + \frac{aC_i{}^{1/2}}{1 + C_i{}^{1/2}} = \Lambda_o - \frac{1}{K_a}\frac{\Lambda^2 C}{\Lambda_o - aC_i{}^{1/2}/(1 + C_i{}^{1/2})}\,10^{-2AC_i{}^{1/2}/(1+C_i{}^{1/2})} \quad (1)$$

The method consists in finding by successive approximations the value of Λ_o which, when incorporated into the quantity x, gives, on linear extrapolation to zero concentration, a limiting value of y which is identical to the value of Λ_o. Equation (1) is like the Ives' equation but, due to the large ionization constants and therefore the higher ionic concentrations expected in this work, the extended equations (2) and (3) were used for expressing the variation of Λ_i and of the mean activity coefficient γ with the ionic concentration.

$$\Lambda_i = \Lambda_o - aC_i{}^{1/2}/(1 + C_i{}^{1/2}) \quad (2)$$

$$\log\gamma = -AC_i{}^{1/2}/(1 + C_i{}^{1/2}) \quad (3)$$

Apparatus.—The conductances were measured at 2 000 Hz on a Philips PW 9501 conductivity meter equipped with a PW 9512 conductivity cell. The cell containing the solution of acid was immersed in a transformer oil-bath in which a temperature of 25 °C was maintained to ±0.02 °.

Solutions.—A stock solution (500 cm^3) made up by weight. This was diluted to obtain twelve solutions of concentrations in the range 5×10^{-4}—5×10^{-3}M. The specific conductance of the doubly distilled water used as solvent was less than $10^{-6}\ \Omega^{-1}\ cm^{-1}$.

Materials.—Propiolic, tetrolic, and phenylpropiolic acids are purified commercial products. Other acids were synthesized as follows. $ClC{\equiv}CCO_2H$ and $BrC{\equiv}CCO_2H$ were prepared from propiolic acid by the hypohalogenite method of Strauss,[17] m.p. 70 and 84 °C, respectively. $IC{\equiv}CCO_2H$ was obtained by reacting $BrC{\equiv}CCO_2H$ with NaI in acetone (yield 75%), m.p. 142 °C.[18] $Me_3SiC{\equiv}CCO_2H$ was synthesized by reacting propiolic acid dianion with $ClSiMe_3$, followed by hydrolysis (yield 70%), b.p. 62 ° at 0.2 mmHg.[18] $EtO_2CC{\equiv}CCO_2H$ was prepared by carbonation of the lithium derivative of ethyl propiolate followed by acid hydrolysis (yield 87%), b.p. 68° at 0.02 mmHg.[18] $PhOC{\equiv}CCO_2H$ and $PhSC{\equiv}CCO_2H$ were prepared by carbonation of the lithium derivatives of $PhOC{\equiv}CH$ and $PhSC{\equiv}CH$. The lithium carboxylates were then reacted with $ClSiMe_3$ and the silicon compounds hydrolysed (yields 55 and 72% respectively), m.p. 88 and 68 °C.[18]

Thermodynamic pK_a values are given in Table 1, the error shown being calculated from the confidence interval of the regression coefficient of y on x [equation (1)] at the 95% confidence level. The validity of our experimental procedure and of the treatment of data has been ascertained by comparison with the very precise Λ_o 392.01 ohm^{-1} $equiv.^{-1}$ cm^2 and pK_a 2.8677 values of Ives [16] for chloroacetic acid: here we found Λ_o 393.6 and pK_a 2.857 at 25 °C. Our preliminary measurements [12] on tetrolic, propiolic, bromo-, and chloro-propiolic acids have been repeated with the better

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† In other solvents results refer to substituted phenylpropiolic acids in aqueous ethanol [6,7] and in aqueous dioxan,[7,8] to the substituents Me, Ph, $SiMe_3$, H, and Br in methanol,[9] and to acetylenedicarboxylic acid in aqueous alcohols.[10]

TABLE 1

Thermodynamic pK_a values of 3-substituted propiolic acids $XC{\equiv}CCO_2H$ in aqueous solution at 25 °C

X	pK_a	X	pK_a
OPh	3.09 ± 0.02	I	2.002 ± 0.013
Me	2.656 ± 0.009	H	1.940 ± 0.010
Ph	2.253 ± 0.008	Br	1.903 ± 0.010
$SiMe_3$	2.205 ± 0.015	Cl	1.889 ± 0.010
SPh	2.11 ± 0.03	CO_2Et	1.05

experimental procedure and treatment of data of this work and led to the more precise values given in Table 1. Data in Table 1 cannot be easily compared with literature values available for propiolic, tetrolic, and phenylpropiolic acids[1-4] because these are generally not thermodynamic constants, except the pK_a 2.652 value of German *et al.*[4] for tetrolic acid which is in good agreement with the pK_a 2.655 value in this work. Our conductimetric results in water are equally in good qualitative agreement with the potentiometric results of Golovanova *et al.*[9] in methanol for Br–, Me_3Si–, Ph–, Me–, and $H{-}C{\equiv}CCO_2H$ as shown by the least-square results of equation (4).

$$\text{p}K_a\ (\text{methanol}) = 0.93\ \text{p}K_a\ (H_2O) + 5.09\quad r\ 0.94\quad n\ 5 \qquad (4)$$

The conductivity of acetylenedicarboxylic acid monoethyl ester decreases with time. This was attributed to autocatalytic[19] acid-catalysed hydrolysis of this ester or a decarboxylation reaction.[12] However the mean of repeated measurements on solutions of freshly synthesized samples of $HO_2CC{\equiv}CCO_2Et$ agrees with the first ionization constant of $HO_2CC{\equiv}CCO_2H$ recently reported by Schwartz *et al.*[12] In the following discussion this led us to retain the pK_{a_1} and pK_{a_2} values of Schwartz for $HO_2CC{\equiv}CCO_2H$ in preference to the less reliable values of Bottei and Joern.[11]

Aqueous solutions of trimethysilyl-, phenoxy-, and thiophenoxy-propiolic acids seem to be unstable.

DISCUSSION

On the pK_a scale of strength of carboxylic acids,[20] the 3-substituted propiolic acids range between dihalogeno- and monohalogeno-acetic acids. They are *ca.* 200 times stronger in water than the corresponding *trans*-3-substituted acrylic acids and 4-substituted benzoic acids. Obviously the increased acidity of propiolic acids is related to the greater electronegativity of the *sp* hybridized carbon of the ethynyl group than that of the sp^2 hybridized carbon of the vinyl and phenyl groups.

The substituent effects in propiolic (acetylenic) acids can be most meaningfully examined by comparison with corresponding acrylic (ethylenic), and benzoic acids on the basis of linear free energy relationships (l.f.e.r.s). Such relationships can be drawn from the data in Table 2 and the least-squares equations are (5) and (6).

$$\text{p}K_a\ (XC{\equiv}CCO_2H) = 2.45\ \text{p}K_a\ (XC_6H_4CO_2H) - 8.05 \qquad (5)$$
$$r\ 0.93,\ n\ 11$$

$$\text{p}K_a\ (XC{\equiv}CCO_2H) = 1.06\ \text{p}K_a\ (XCH{=}CHCO_2H) - 2.34 \qquad (6)$$
$$r\ 0.90,\ n\ 12$$

The slopes of the l.f.e.r. lines show that substituent effects are propagated by the triple bond as efficiently as by the double bond but much more efficiently than by the benzene ring. This can be partly explained by the shorter distance between the substituent and the function in the acetylenic and ethylenic systems than in the benzoic system. The correlation coefficients give the impression that substituent effects are correlated in the three systems. This led Charton[21] to conclude that the σ_p substituent constant defined from the pK_a of benzoic acids and successfully applied to aromatic systems,[22] also applies to acetylenic acids. However a careful detection of outliers based on normalized residuals[23] shows that hydrogen and iodine deviate significantly in both equations (5) and (6) [although this does not necessarily confirm the values of Dippy[24] for the pK_a of *p*-phenoxybenzoic acid in water nor the unrealistic[25] $\sigma_{p\text{-OPh}}$ −0.32 derived from it;[26] note that the OPh is not revealed as an outlier in equation (5)]. Other experimental evidence confirms the peculiar behaviour of hydrogen and iodine when linked to an *sp* hybridized carbon atom. They have an unusual positive character as shown from dipole moment measurements[27] and from the ability of $HC{\equiv}CX$[28] and $IC{\equiv}CX$[29] molecules to form complexes with electron donors.

TABLE 2

pK_a Values of 3-substituted propiolic acids, *trans*-3-substituted acrylic acids, and 4-substituted benzoic acids in water at 25 °C and inductive and resonance substituent constants

Substituent X	pK_a propiolic	pK_a acrylic	pK_a benzoic	σ_I [i]	σ_R [i]
OPh	3.09	*c*	4.52 [f]	0.40	−0.48
trans-MeCH=CH	2.665 [a]	4.505 [a]	*c*	0.07	−0.16
Me	2.656	4.693 [e]	4.366 [g]	−0.01	−0.16
Bu^t	2.655 [a]	*c*	4.389 [g]	−0.01	−0.18
Et	2.605 [a]	4.695 [e]	4.353 [g]	−0.01	−0.14
Ph	2.253	4.438 [d]	*c*	0.12	−0.11
CO_2^-	2.035 [b]	4.301 [e]	4.145 [h]	−0.19	0.23
$SiMe_3$	2.205	*c*	4.192 [g]	−0.11	0.12
SPh	2.11	*c*	*c*	0.31	−0.24
I	2.002	3.74 [e]	3.961 [g]	0.40	−0.16
H	1.940	4.255 [e]	4.202 [g]	0	0
$MeC{\equiv}C$	1.94 [a]	4.20 [a]	*c*	0.30	−0.27
Br	1.903	3.71 [e]	3.988 [g]	0.47	−0.25
Cl	1.889	3.79 [e]	3.986 [g]	0.47	−0.25
CO_2H	0.957 [b]	3.396 [e]	3.839 [h]	0.30	0.11
CO_2Et	1.05	3.396 [e]	*c*	0.30	0.11

[a] Ref. 1. [b] Statistically corrected from data of ref. 12. [c] Not available. [d] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1937, 1008. [e] Ref. 14. [f] Ref. 24. [g] Average of the reliable values compiled in M. Charton, *Prog. Phys. Org. Chem.*, 1981, **13**, 119. [h] Ref. 20. [i] Reference of footnote *g*.

Deviations may originate from different inductive and/or different resonance effects in the acetylenic systems. The CNDO/2 study by Brownlee and Taft[30] of substituent effects on σ- and π-electronic distributions of substituted fluorobenzenes, fluoroethylenes, and fluoroacetylenes as well as on substituted benzenes, ethylenes, and acetylenes has shown that to a first approximation π-electronic (resonance) effects are independent of the hydrocarbon cavity. This conclusion is supported by the work of Katritzky and Topsom[31] who have detected resonance interactions by i.r. intensity measurements in substituted acetylenes, ethylenes, and benzenes.* In contrast to the π-effects, the electronic (inductive) effects are not simply related. An inductive scale peculiar to the acetylenic system is not unexpected since inductive effects originate from the difference in electronegativity between the substituents and the carbon to which they are bonded, and since hybridized *sp* carbons are more electronegative than hybridized sp^2 carbons. The influence of changed hybridization on inductive effects has been noticed in other systems [32,33] and was suspected by a referee of Charton's work.[21]

The dual substituent parameter (DSP) equation [34] $pK_a = \rho_I\sigma_I + \rho_R\sigma_R + pK_a^\circ$ which uses inductive σ_I and resonance σ_R substituent constants defined from aliphatic and aromatic systems (substituents bonded to sp^3 or sp^2 carbons) fails also to put hydrogen and iodine on the regression plane. However the DSP analysis gives estimates of ρ_I and ρ_R [the regression coefficients of equations (7)—(9)] which can be compared by means of

$$pK_a\ (XC{\equiv}CCO_2H) = 2.11 - 2.29\ \sigma_I - 3.44\ \sigma_R \qquad r\ 0.95,\ n\ 15\ \dagger\ \text{(this work)} \quad (7)$$

$$pK_a\ (XCH{=}CHCO_2H) = 4.35 - 2.26\ \sigma_I - 2.09\ \sigma_R \qquad r\ 0.997,\ n\ 16\ \text{(ref. 14)} \quad (8)$$

$$pK_a\ (XC_6H_4CO_2H) = 4.20 - \sigma_I - \sigma_R \qquad r\ 1.000\ \text{(by definition)} \quad (9)$$

the percentage resonance effect [14] $P_R = 100\rho_R/(\rho_I + \rho_R)$. In the acetylenic system $P_R \approx 60$ while $P_R = 50$ in the benzoic system. The difference in P_R being statistically significant at the 95% confidence level, this result shows that π-delocalization is probably more important for groups bonded to a triple bond than it is for groups bonded to a benzene ring. This is not unexpected since the X–C^{sp} bond length which is always shorter than X–C^{sp^2} should result in better overlap of *p* or π orbitals on the X substituent with the π orbitals of the triple bond.[35]

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* An additional feature in substituted acetylenes is the presence of two orthogonal orbitals for the substituent to interact with. However, taking account of this does not improve the i.r. correlations.

† The σ_I and σ_R values of the COO^- substituent are unreliable, so this group was not used in establishing the correlation equation.

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