929. *Researches on Acetylenic Compounds. Part LIII.* The Relative Strengths of Some Unsaturated Carboxylic Acids.*

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Values for the dissociation constants at 25° in aqueous 0·1M-sodium chloride solution are reported for a number of acetylenic, allenic, and conjugated dienoic acids. The results permit some generalisations regarding the electronic influences of these unsaturated systems.

IT has been known for some time that αβ-acetylenic acids (I) are more acidic than their ethylenic and saturated analogues, and that the acetylenic bond exerts, generally, a powerful electron-attracting influence.[1]

$$\underset{\text{(I)}}{R{\cdot}C{\equiv}C{\cdot}CO_2H} \qquad \underset{\text{(II)}}{R{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}CO_2H} \qquad \underset{\text{(III)}}{H{\cdot}C{\equiv}C{\cdot}[CH_2]_n{\cdot}CO_2H}$$

Variations already reported in the dissociation constants of acids (I) are considerable; where R = H,[2] Me,[3] Bu^n,[4] and Ph,[2] pK_a values of 1·85, 2·61, 2·85, and 2·33 have been

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* Part LII, *J.*, 1956, 4073.

[1] Dippy, *Chem. Rev.*, 1939, **25**, 179; Walsh, *Trans. Faraday Soc.*, 1947, **2**, 18; Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 70.

[2] Wilson and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 1266.

[3] Jeffery, German, and Vogel, *J.*, 1937, 1604.

[4] Braude and Jones, *J.*, **1946**, 128.

published. It appeared that a much wider range of data, obtained under comparable conditions, might throw light on the relative magnitude of conjugative, hyperconjugative, and inductive effects in these systems. We now report results, obtained potentiometrically at 25° in 0·10M-sodium chloride solution, for a group of acetylenic acids of the types (I—III), and for some other unsaturated acids; with a few exceptions the pK_a values are believed to be accurate to ±0·05.

Several of the acids were obtained by a modification of published procedures, an acetylenic hydrocarbon being prepared by dehydrohalogenation with sodamide in liquid ammonia and converted *in situ* into its sodium derivative, which was then treated with carbon dioxide in ethereal suspension. Although yields were sometimes inferior to those obtained by a two-stage process, the method is convenient for the preparation of small quantities. 4-Phenylbut-3-ynoic and hex-5-en-3-ynoic acid were prepared by condensation of the bromomagnesium derivatives of phenylacetylene and vinylacetylene, respectively, with ethylene oxide, and oxidation of the resultant primary alcohols with chromic acid.[5]

Dissociation constants of αβ-*acetylenic acids* (I).

R	pK_a	Lit. value	R	pK_a	Lit. value
H	1·84, 1·84	1·85 [a]	$C{\vdots}CMe$	1·94, 1·94	—
Me	2·60, 2·58	2·61 [b]	$C{\vdots}CEt$ [g]	1·89, 1·91	—
Et [d]	2·61, 2·60	—	$C{\vdots}CBu^n$ [g]	1·89, 1·89	—
Bu^n [e]	2·59, 2·61	2·85 [c]	$[C{\vdots}C]_2{\cdot}Et$ [g]	1·67 *	—
Bu^t [f]	2·66, 2·65	—	$CH\overset{t}{:}CHMe$ [h]	2·66, 2·67	—
$CH_2{\cdot}CMe_3$ [f]	2·52, 2·54	—	Ph [i]	2·23, 2·23	2·23 [a]

Dissociation constants of βγ-*acetylenic acids* (II).

R	H [j]	Me [k]	$C{\vdots}CMe$ [g]	$CH{:}CH_2$ [f]	Ph [f]
pK_a	3·31, 3·33	3·60, 3·58	3·23, 3·23	3·37, 3·41	3·44, 3·43

Dissociation constants of ω-*acetylenic acids* (III).

n	2 [l]	3 [l]	4 [l]
pK_a	4·20, 4·21	4·59, 4·60	4·57, 4·58

Dissociation constants of various acids.

Acid	pK_a	Acid	pK_a
$H_2C{:}C{:}CH{\cdot}CO_2H$ [j]	3·69, 3·68	$Me{\cdot}C{\vdots}C{\cdot}CH\overset{t}{:}CH{\cdot}CO_2H$ [h]	4·20 *
$Ph{\cdot}CH{:}C{:}CH{\cdot}CO_2H$ [f]	3·68 *, 3·71 *	$Me{\cdot}CH\overset{t}{:}CH{\cdot}CH\overset{t}{:}CH{\cdot}CO_2H$	4·48 *, 4·53 *
$HC{\vdots}C{\cdot}CH\overset{t}{:}CH{\cdot}CO_2H$ [m]	3·74, 3·76	$Me{\cdot}CH\overset{c}{:}CH{\cdot}CH\overset{c}{:}CH{\cdot}CO_2H$ [h]	4·51 *, 4·48 *

[a] Ref. 2. [b] Ref. 3. [c] Ref. 4. [d] Zoss and Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 1151. [e] Haynes and Jones, *J.*, 1946, 504. [f] This paper. [g] Jones, Thompson, and Whiting, unpublished work. [h] Ref. 17. [i] Gilman and Young, *J. Org. Chem.*, 1936, **1**, 315. [j] Ref. 6. [k] Jones, Whitham, and Whiting, *J.*, 1954, 3201. [l] Eglinton and Whiting, *J.*, 1953, 3052. [m] Ref. 5.

N.B. References are to the actual method of preparation used, rather than to the first synthesis.

When 4-phenylbut-3-ynoic acid was heated to 40° with 18% potassium carbonate solution, the corresponding allenic acid could be isolated in 52% yield. The ultraviolet spectra of solutions of 4-phenylbuta-2 : 3-dienoic and of 4-phenylbut-3-ynoic acids, in potassium carbonate solution after equilibration at 40°, were virtually identical, and corresponded to a 3 : 2-concentration-ratio of the two anions. This contrasts with the virtually complete conversion of but-3-ynoic into buta-2 : 3-dienoic anions under similar conditions.[6] Under more drastic conditions 4-phenylbuta-2 : 3-dienoic acid underwent hydration and fission to benzyl methyl ketone, rather than rearrangement to the αβ-acetylenic acid.[6] 4-Phenylbuta-2 : 3-dienoic acid was first obtained by the action of nickel carbonyl on 3-chloro-3-phenylprop-1-yne,[7] and its spectrographic properties will be discussed later.

[5] Heilbron, Jones, and Sondheimer, *J.*, 1947, 1589.
[6] Eglinton, Jones, Mansfield, and Whiting, *J.*, 1954, 3197.
[7] Jones, Whitham, and Whiting, *J.*, to be published.

DISCUSSION

In the simple αβ-acetylenic acids (I), the unique position of propiolic acid (I; R = H) is at once obvious. Replacement of the terminal hydrogen atom by any alkyl group, a phenyl or a propenyl group, increases the pK_a value by 0·6—0·9.[1] The small differences among the various alkyl substituents indicate that C–H hyperconjugation is not of predominant importance in reducing the dissociation constant; the slightly increasing effect from methyl to *tert.*-butyl is reminiscent of the trend of dipole moments of the alkyl cyanides, reported by Ingold.[8] A second acetylenic bond, on the other hand, increases the dissociation constant fivefold relative to the corresponding monoacetylenic acid, but the effect of further increase in the polyacetylenic chain is much smaller.

When a methylene group is interposed between the acetylenic linkage and the carboxyl group, the effects observed when R is varied in the structure (II) are analogous, but all ΔpK_a values are smaller by a factor of 2—2·5, as is usual when a methylene group is inserted (cf. the chloro- and iodo-acids, $X\cdot[CH_2]_n\cdot CO_2H$).[9] Increasing the separation of the ethynyl and carboxyl groups produces the expected progressive weakening as *n* increases from 0 to 3, but hept-6-ynoic acid (III; *n* = 4) is unexpectedly strong. Conceivably this may be due to some weak cyclic interaction between the triple bond and the $\cdot CO_2^-$ grouping. The results imply that the ethynyl group approximates in electron-attracting power to an iodine atom.

In contrast to the acetylenic acids, the two stereoisomeric hexadienoic acids show almost identical dissociation constants differing little from those of monoethylenic and saturated acids. The absence of an increase in dissociation constant on passing from the 2-*trans* to the 2-*cis* isomer suggests that there is little hindrance to coplanarity in the latter. This contrasts with the cases of *o*- and *p*-toluic acid and of tiglic and angelic acid, where steric hindrance in one isomer, by inhibiting the acid-weakening effect of conjugative interaction, enables the intrinsic electron-attracting tendencies of unsaturated systems to assert themselves.[10]

Evidently the allene grouping shows net electron-attracting powers intermediate between those of ethylenic and acetylenic linkages.

Diagnostic use has already been made of the results recorded above.[11]

EXPERIMENTAL

The acids were dissolved in 0·10M-sodium chloride solution, 20 c.c. of a 0·01M-solution being employed when the solubility and the quantity of material permitted. In the titrations 0·1M-sodium hydroxide solution was added from a burette which could be read to 0·01 c.c., pH values being measured with a glass electrode, calomel electrode directly immersed, and a Cambridge pH meter, calibrated before and after with 0·05M-potassium hydrogen phthalate solution. The temperature was maintained at 25° ± 0·5°. Readings from the first and the last quarter of the titration were ignored; 10—15 values of the pK_a were calculated from the central portion of the titration, and the mean was determined. The standard deviation from the mean value was about 0·03, but accuracy greater than ±0·05 unit is not claimed because of systematic errors. The conditions used maintained constant ionic strength; no activity corrections were made. Each determination was carried out in duplicate when possible.

Because of shortage of material or low solubility it was necessary to work in more dilute solution, down to 0·005M, in some cases which are marked with an asterisk in the Table. Here precision was lower, and results should be taken as ±0·10 unit. Occasionally a systematic drift to lower acidity was evident as the titration proceeded, remedied by further purification of the acid involved.

4 : 4-*Dimethylpent-2-ynoic Acid*.—3 : 3-Dichloro-2 : 2-dimethylbutane[12] (31·0 g.) in ether (100 c.c.) was added to a suspension of sodamide, prepared from sodium (15 g.) in liquid ammonia (1 l.), during 40 min., and the mixture stirred for 4 hr. Ether (250 c.c.) was then added, and the

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[8] Ingold, *op. cit.*, pp. 100 and 115.

[9] Derick, *J. Amer. Chem. Soc.*, 1911, **33**, 1152.

[10] Ingold, *op. cit.*, p. 744.

[11] Bu'lock, Jones, Mansfield, Thompson, and Whiting, *Chem. and Ind.*, 1954, 990.

[12] Favorski, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 425.

mixture transferred from the vacuum flask to a beaker; most of the ammonia evaporated during 12 hr. A further 250 c.c. of ether were added, and the mixture was warmed to 30° in a slow stream of dry nitrogen to remove the remainder of the ammonia; then a large excess of solid carbon dioxide was added. After 14 hr. water (25 c.c.) was added cautiously, followed by dilute sulphuric acid. Isolation of the acidic fraction and distillation gave the acetylenic acid (8·3 g., 33%), m. p. 48—49° (uncorr.) [Moureu and Delange [13] give b. p. 110°/10 mm., m. p. 47—48° (uncorr.)]. Its infrared spectrum showed a strong band at 2222 cm.$^{-1}$, and the equivalent weight found agreed with the theoretical value.

5 : 5-*Dimethylhex*-2-*ynoic Acid* (with J. L. H. ALLAN).—1 : 2-Dibromo-4 : 4-dimethylpentane [14] (40 g.) in ether (100 c.c.) was added to a suspension of sodamide, prepared from sodium (14 g.) in liquid ammonia (500 c.c.), during 90 min. After 16 hours' stirring 250 c.c. of ether were added and the mixture was heated in a stream of nitrogen for 4 hr. Ether (500 c.c.) was added, the mixture was cooled externally to −60°, and roughly powdered solid carbon dioxide was added until the 3 l.-flask was full. After 3 days dilute sulphuric acid was added, and the acidic fraction was isolated with ether, giving a residue (9·0 g.) which was sublimed at up to 120° (bath temp.)/10^{-4} mm., yielding 7·7 g. (37%) of material, m. p. 42—46°, raised with some difficulty to 46·5° by crystallisation from light petroleum at −6° (Favorski and Opel [15] give m. p. 48—49·5°).

Hexa-2 : 4-*diynoic Acid*.—1 : 4-Dichlorobut-2-yne [16] (61 g.) was added to a suspension of sodamide, prepared from sodium (38 g.) in liquid ammonia (500 c.c.). After 5 min. methyl iodide (71 g.) was added dropwise. After a further 2 hr., a suspension of sodamide, prepared from sodium (3 g.) in liquid ammonia (500 c.c.) was added. The mixture was stirred for 1½ hr., ether (250 c.c.) was added, and the mixture was set aside in a beaker while most of the ammonia evaporated, during 12 hr., then transferred to an autoclave containing an excess of crushed carbon dioxide. After 48 hr. the complex was decomposed with dilute sulphuric acid, and the diacetylenic acid (2·65 g., 5%) was isolated; it had m. p. 118° (Allan *et al.*[17] give m. p. 118°).

Hex-5-*en*-3-*ynoic Acid*.—A solution of chromic acid (25·5 c.c.; 6N in 12N-sulphuric acid) was added dropwise to a solution of hex-5-en-3-yn-1-ol [18] (3·4 g.) in acetone (100 c.c.), the temperature being kept near 20°. After 17 hr. water was added and the acidic fraction was isolated giving *hex*-5-*en*-3-*ynoic acid* (750 mg., 19%), m. p. 60—61° (Found: C, 65·45; H, 5·6. $C_6H_6O_2$ requires C, 65·45; H, 5·5%). Light absorption in 95% ethanol: maximum, 2230 Å, inflexion, 2320 Å; ε = 12,200 and 10,400, respectively.

4-*Phenylbut*-3-*ynoic Acid*.—4-Phenylbut-3-yn-1-ol [19] (8·0 g.) was dissolved in acetone (200 c.c.) and treated at 15—20° with a solution of chromic acid (36 c.c.; as above). After 3 hr. water was added and the acidic product isolated. Crystallisation from light petroleum gave the *acid* (4·1 g., 47%), m. p. 71° (Found: C, 75·1; H, 5·2. $C_{10}H_8O_2$ requires C, 75·0; H, 5·05%).

4-*Phenylbuta*-2 : 3-*dienoic Acid*.—The above acid (11·0 g.) was heated at 40° with potassium carbonate solution (100 c.c.; 18%) for 1 hr. Isolation of the acidic material and crystallisation from light petroleum gave the allenic acid (0·5 g.), m. p., and mixed m. p. with an authentic [7] specimen, 92° (Found: C, 75·25; H, 5·3. $C_{10}H_8O_2$ requires C, 75·0; H, 5·05%). When heated with potassium hydroxide solution (75 c.c.; 9%) at 90° for 2 hr., 4-phenylbut-3-ynoic acid (0·5 g.) gave benzyl methyl ketone (0·25 g., 60%), b. p. 106° (bath temp.)/9 mm., n_D^{19} 1·5160 (Danilov and Venus-Danilova [19] give b. p. 100—101°/14 mm., n_D^{20} 1·5168). The 2 : 4-dinitrophenylhydrazone had m. p. 155—156°, undepressed with an authentic specimen.

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[13] Moureu and Delange, *Bull. Soc. chim. France*, 1903, **29**, 648.

[14] Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4555.

[15] Favorski and Opel, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 74.

[16] Nazarov and Elizarova, *Bull. acad. Sci. U.R.S.S.*, 1940, 189.

[17] Allan, Jones, and Whiting, *J.*, 1955, 1862.

[18] Murray and Cleveland, *J. Amer. Chem. Soc.*, 1938, **60**, 2664.

[19] Danilov and Venus-Danilova, *Ber.*, 1927, **60**, 1067.